IONIC EQUILIBRIUM-III

Exercise-1

✍ **Marked questions are recommended for Revision.**

PART - I : SUBJECTIVE QUESTIONS

Section (A) : Solubility, Solubility product and Simple solubility calculations

Commit to memory :

Solubility (s; in mol/L) of a sparingly soluble salt A_xB_y : $K_{sp} = x^x.y^y.(s)^{x+y}$

A-1. Although it is a violent poison if swallowed, Mercury(II) cyanide $Hg(CN)_2$, has been used as a typical skin antiseptic. (K_{sp} of $Hg(CN)_2 = 1.35 \times 10^{-23}$, Atomic mass of Hg = 200 u). Assume no ion to be undergoing hydrolysis.

(a) What is the molar solubility of this salt in pure water ?

(b) How many milligrams of $Hg(CN)_2$ dissolve per litre of pure water ?

(c) How many milliliters of water are required to dissolve 1.134 g of the salt ?

A-2. How many milligrams of gold(III) ion are there per litre of solution in a saturated aqueous solution of gold (III) iodide ? $AuI_3(s) \rightleftharpoons Au^{3+}(aq) + 3I^-(aq)$. K_{sp} of $AuI_3 = 2.7 \times 10^{-47}$, atomic mass of Au = 197 u. Assume no hydrolysis of Au^{3+} ion.

Section (B) : Condition for precipitation, Common ion effect on solubility

Commit to memory :

Condition for precipitation of A_xB_y : Ionic product or $K_{IP} > K_{sp}$; $[A^{y+}]^x\,[B^{x-}]^y > K_{sp}$ of A_xB_y

Common ion effect on solubility : Solubility (s') of A_xB_y (sparingly soluble ; K_{sp}) in a solution of 'c' M A_pD_q/E_rB_p (both readily soluble) : $(pc)^x(ys')^y = K_{sp}$; s' = **.....**

B-1. What can be the maximum concentration of equimolar solutions of ferrous sulphate ($FeSO_4$) and sodium sulphide (Na_2S), so that when mixed in equal volumes, there is no precipitation of iron sulphide (FeS) ? (For iron sulphide, $K_{sp} = 6.25 \times 10^{-18}$) Assume no ion to be undergoing hydrolysis.

B-2.✍ Calculate the solubility of silver phosphate (Ag_3PO_4) in mg/mL (a) in pure water and (b) in a solution that is 0.03 M in $AgNO_3$. [$K_{sp}(Ag_3PO_4) = 2.7 \times 10^{-23}$]. Assume no ion to be undergoing hydrolysis. Atomic mass of Ag = 108 u.

Section (C) : Simultaneous Solubility, Complex Formation

Commit to memory :

Simultaneous solubility (s_1 & s_2) of A_xB_y & A_xC_y (both sparingly soluble) :

$$\frac{K_{sp}(A_xB_y)}{K_{sp}(A_xC_y)} = \frac{[B^{x-}]^y}{[C^{x-}]^y} = \frac{(ys_1)^y}{(ys_2)^y} = \left(\frac{s_1}{s_2}\right)^y$$

Further, $(xs_1 + xs_2)^x\,(ys_1)^y = K_{sp}(A_xB_y)$ & $(xs_2 + xs_1)^x\,(ys_2)^y = K_{sp}(A_xC_y)$. Put s_1 in terms of s_2 from eq.1 in eq.2 or eq.3 to obtain s_2 & then obtain s_1.

Complex formation : Upon mixing M^{n+} & L and analyzing the reaction $M^{n+} + xL \rightleftharpoons [ML_x]^{n+}$ through chemical equilibrium (assuming M^{n+} to be completely consumed), concentrations of L and $[ML_x]^{n+}$ can be obtained. When they are put in expression of K_c, $[M^{n+}]_{eq}$ can be obtained.

C-1.✍ Calculate the simultaneous solubility of AgCl and AgI. Assume no hydrolysis of Ag^+ ion.
K_{sp} (AgCl) = 1×10^{-10}, K_{sp} (AgI) = 8.5×10^{-17}

C-2. On passing 1 mole NH_3 gas through 1 L of 0.2 M $CuSO_4$ solution, determine $[Cu^{2+}]$ in the resulting solution. Given : K_f of $[Cu(NH_3)_4]^{2+} = 2 \times 10^{13}$. Assume no hydrolysis of Cu^{2+} ion.

Section (D) : Selective Precipitation, Solubility exchange

Commit to memory :

Selective precipitation: On gradually adding A_pB_q(s ; readily soluble) to a solution containing C_1M X^{w-} & C_2M Y^{z-}

$[A^{q+}]$ req. for A_wX_q pptn = $\sqrt[w]{\frac{K_{sp}(A_wX_q)}{(C_1)^q}}$; $[A^{q+}]$ req. for A_zY_q pptn = $\sqrt[z]{\frac{K_{sp}(A_zY_q)}{(C_2)^q}}$

Minimum value of $[A^{q+}]$ req. will tell which salt will precipitate first.

Solubility exchange: Upon treating a solution of C_pD_q / C_pD_q(s) (readily soluble) with A_xB_y(s) / saturated solution of A_xB_y (sparingly soluble) such that some A_xB_y gets converted to A_pD_y(sparingly soluble), then :

$$\sqrt[x]{\frac{K_{sp}(A_xB_y)}{[B^{x-}]_f^y}} = \sqrt[p]{\frac{K_{sp}(A_pD_y)}{[D^{p-}]_f^y}}$$

D-1. A solution which is 0.1 M in NaI and also 0.1 M in Na_2SO_4 is treated with solid $Pb(NO_3)_2$. Which compound, PbI_2 or $PbSO_4$, will precipitate first ? What is the concentration of anion of the least soluble compound when the more soluble one starts precipitating ? $K_{sp}(PbI_2) = 9 \times 10^{-9}$, $K_{sp}(PbSO_4) = 1.8 \times 10^{-8}$. Assume no hydrolysis of Pb^{2+} ion.

D-2. 0.1 mole AgCl(s) is added to 1 litre H_2O. Next, crystals of NaBr are added until 75% of the AgCl is converted to AgBr(s), the less soluble silver halide. What is $[Br^-]$ in the resulting solution ? K_{sp} of AgCl is 1.75×10^{-10} and K_{sp} of AgBr is 5.25×10^{-13}. Assume no hydrolysis of Ag^+ ion.

PART - II : ONLY ONE OPTION CORRECT TYPE

Section (A) : Condition for precipitation, Common ion effect on solubility

Commit to memory :

Condition for precipitation of A_xB_y : Ionic product or $K_{IP} > K_{sp}$; $[A^{y+}]^x [B^{x-}]^y > K_{sp}$ of A_xB_y

Common ion effect on solubility : Solubility (s') of A_xB_y (sparingly soluble; K_{sp}) in a solution of 'c' M A_pD_q/E_rB_p (both readily soluble) : $(pc)^x(ys')^y = K_{sp}$; s' = **.....**

A-1. What is the minimum pH at which $Mg(OH)_2$ starts precipitating from a solution containing 0.02 M $MgCl_2$? K_{sp} of $Mg(OH)_2 = 1.8 \times 10^{-11}$.

(A) 4.52 (B) 9.04 (C) 9.48 (D) 8.48

Section (B) : Simultaneous solubility and Complex formation

Commit to memory :

Simultaneous solubility (s_1 & s_2) of A_xB_y & A_xC_y (both sparingly soluble) :

$$\frac{K_{sp}(A_xB_y)}{K_{sp}(A_xC_y)} = \frac{[B^{x-}]^y}{[C^{x-}]^y} = \frac{(ys_1)^y}{(ys_2)^y} = \left(\frac{s_1}{s_2}\right)^y$$

Further, $(xs_1 + xs_2)^x (ys_1)^y = K_{sp}(A_xB_y)$ & $(xs_2 + xs_1)^x (ys_2)^y = K_{sp}(A_xC_y)$. Put s_1 in terms of s_2 from eq.1 in eq.2 or

eq.3 to obtain s_2 & then obtain s_1.

Complex formation : Upon mixing M^{n+} & L and analyzing the reaction $M^{n+} + xL \rightleftharpoons [ML_x]^{n+}$ through chemical equilibrium (assuming M^{n+} to be completely consumed), concentrations of L and $[ML_x]^{n+}$ can be obtained. When they are put in expression of K_c, $[M^{n+}]_{eq}$ can be obtained.

B-1. Simultaneous solubility of two sparingly soluble salts A & B having some common ion :
(A) is greater than their respective solubilities in separate solutions.
(B) lies in between their solubilities in separate solutions.
(C) is less than its solubility in separate solutions for more soluble salt, but is greater than its solubility in separate solution for less soluble salt.
(D) is less than their respective solubilities in separate solutions.

B-2.✍ The solubility product values of AgCl and AgCNS are 1.8×10^{-10} and 1.6×10^{-11} respectively. When a solution is saturated with both solids, calculate the ratio $[Cl^-]/[CNS^-]$ and also $[Ag^+]$ in the solution : Assume no reaction of cation/anion.
(A) 1.125, 4×10^{-6} M (B) 11.25, 1.4×10^{-5} M (C) 1.25, 4×10^{-5} M (D) 1.25, 4×10^{-6} M

B-3. Which of the following options is true for a solution saturated with AgCl and AgBr, if their solubilities in mole per litre in separate water samples are x and y respectively ? Given : x > y. Assume no hydrolysis of Ag^+ ion.
(A) $[Ag^+] < [Br^-] + [Cl^-]$ (B) $x > [Cl^-] > [Br^-]$ (C) $[Br^-] > y$ (D) $[Ag^+] = x + y$

B-4. Upon mixing equal volumes of 0.02 M $AgNO_3$ & 0.16 M KCN solutions : (Assume no hydrolysis of any ion). Given : $Ag^+ (aq.) + 2CN^- (aq) \rightleftharpoons [Ag(CN)_2]^- (aq)$; $K_C = 10^{18}$
(A) $[NO_3^-] = 0.01$ M ; $[K^+] = 0.08$ M (B) $[CN^-] = 0.06$ M
(C) $[Ag(CN)_2^-] = 0.01$ M (D) All of these

B-5. In the above question (B-4), $[Ag^+]$ is about :
(A) 2.78×10^{-18} M (B) 1.67×10^{-19} M
(C) No free Ag^+ ions will be left in the solution (D) Cannot be determined

Section (C) : Selective Precipitation, Solubility exchange

Commit to memory :

Selective Precipitation : On gradually adding A_pB_q(s ; readily soluble) to a solution containing C_1 M X^{w-} & C_2 M Y^{z-}

$[A^{q+}]$ req. for A_wX_q pptn = $\sqrt[w]{\dfrac{K_{sp}(A_wX_q)}{(C_1)^q}}$; $[A^{q+}]$ req. for A_zY_q pptn = $\sqrt[z]{\dfrac{K_{sp}(A_zY_q)}{(C_2)^q}}$

Minimum value of $[A^{q+}]$ req. will tell which salt will precipitate first.

Solubility exchange : Upon treating a solution of C_pD_q / C_pD_q(s) (readily soluble) with A_xB_y(s) / saturated solution of A_xB_y (sparingly soluble) such that some A_xB_y gets converted to A_pD_y(sparingly soluble), then :

$$\sqrt[x]{\frac{K_{sp}(A_xB_y)}{[B^{x-}]_f^y}} = \sqrt[p]{\frac{K_{sp}(A_pD_y)}{[D^{p-}]_f^y}}$$

C-1. In a solution containing equal concentrations of X^-, Y^- & Z^-, MCl(s) (a readily soluble salt) is gradually added. If K_{sp} (MX) > K_{sp} (MY) > K_{sp} (MZ), then : (Assume no hydrolysis of any ion).
(A) MX will precipitate first.
(B) MY will precipitate first.
(C) MZ will precipitate first.
(D) Nothing can be said about which salt will precipitate first, as numerical data is not given.

C-2.✍ In above question, If $[X^-]_i : [Y^-]_i : [Z^-]_i = 100 : 10 : 1$ & $K_{sp}[MX] : K_{sp}[MY] : K_{sp}[MZ] = 10 : 0.1 : 1$, order of precipitation will be :
(A) MZ, then MX & MY at last (B) MY, then MX & MZ at last
(C) MX, then MY & MZ at last (D) MY, then MZ & MX at last

Exercise-2

✍ **Marked questions are recommended for Revision.**

PART - I : ONLY ONE OPTION CORRECT TYPE

1. A solution contains [NaCl] = [Na_2CO_3] = C M. Upon gradually adding $AgNO_3$(s) : (Assume no hydrolysis of any ion).

(A) Out of AgCl & Ag_2CO_3, one having lesser K_{sp} will start precipitating first.

(B) Out of AgCl & Ag_2CO_3, one having greater K_{sp} will start precipitating first.

(C) If, $\sqrt{\dfrac{K_{sp}(Ag_2CO_3)}{C}} < \dfrac{K_{sp}(AgCl)}{C}$ then Ag_2CO_3 will start precipitating first.

(D) If, $\sqrt{\dfrac{K_{sp}(Ag_2CO_3)}{C}} < \dfrac{K_{sp}(AgCl)}{C}$ then AgCl will start precipitating first.

2. For the reaction : $[Ag(CN)_2]^-(aq) \rightleftharpoons Ag^+(aq) + 2CN^-(aq)$, K_C at 25ºC is 4×10^{-19}. Calculate [Ag^+] in solution which was originally 0.1 M in KCN and 0.03 M in $AgNO_3$.

(A) 1.5×10^{-17} M (B) 7.5×10^{-18} M

(C) 4.6875×10^{-19} M (D) Value cannot be determined due to mathematical complications.

3.✍ A solution of Na_2CO_3 is added drop by drop to one litre of a solution containing 10^{-4} mole of Ba^{2+} and 10^{-5} mole of Ag^+. If K_{sp} for $BaCO_3$ is 8.1×10^{-9} and K_{sp} for Ag_2CO_3 is 6.9×10^{-12}, then which is not true? Assume no hydrolysis of CO_3^{2-} ion.

(A) No precipitate of $BaCO_3$ will appear until $[CO_3^{2-}]$ reaches 8.1×10^{-5} mol per litre.

(B) A precipitate of Ag_2CO_3 will appear when $[CO_3^{2-}]$ reaches 6.9×10^{-5} mol per litre.

(C) No precipitate of Ag_2CO_3 will appear until $[CO_3^{2-}]$ reaches 6.9×10^{-2} mole per litre.

(D) $BaCO_3$ will be precipitated first.

PART - II : SINGLE AND DOUBLE VALUE INTEGER TYPE

1.✍ When pure water is saturated with both $CaCO_3$ and CaC_2O_4, the concentration of calcium ion in the solution under equilibrium is 8×10^{-5} M. If the ratio of the solubility product of $CaCO_3$ to that of CaC_2O_4 is 3, what is the solubility product of $CaCO_3$ in pure water ? Report your answer after multiplying by 10^9 and rounding it off to nearest whole number.

2. On mixing equal volumes of 0.1 M $AgNO_3$ & 0.8 M KCN solutions, what % of original Ag^+ is in the form of free Ag^+ ions ? Given : K_d of $[Ag(CN)_2]^- = 10^{-18}$. Report your answer after multiplying it by 4.5×10^{16}. (Assume no hydrolysis of any ion)

PART - III : COMPREHENSION

Comprehension # 1

0.2 mole of $MgCl_2$(s) are added in 1 litre volume of a solution (S), already containing 0.2 mole of NaOH(s). Now answer the following questions :

1. Calculate pH of obtained solution. K_{sp} of $Mg(OH)_2$ is 1.6×10^{-12}.

(A) 8.6 (B) 8.5 (C) 8.65 (D) 8.56

2. What would be the new pH when 0.04 mole of NaOH(s) are added in the solution (S) ?

(A) 8.6 (B) 8.5 (C) 8.65 (D) 8.56

3.✍ Find the pH of the solution obtained after adding 0.04 mole of HCl(g) to the solution .

(A) 8.6 (B) 8.5 (C) 8.65 (D) 8.56

Comprehension # 2

Q.4, Q.5 and Q.6 by appropriately matching the information given in the three columns of the following table.

Following 3 columns contain informations regarding water solubility of some sparingly soluble salts and its relation with their solubility product constants (K_{sp}).
Take temperature as 25ºC.

Column-1		**Column-2**		**Column-3**	
(I)	Solubility > $\sqrt{K_{sp}}$	(i)	Solubility increases because of presence of common anion in solution	(P)	Solubility increases in acidic solution as pH decreases below 3
(II)	Solubility < $\left(\frac{K_{sp}}{27}\right)^{1/4}$	(ii)	Solubility decreases because of presence of common cation in solution	(Q)	Solubility increases in basic solution as pH increases above 11
(III)	Solubility = $\left(\frac{K_{sp}}{27}\right)^{1/4}$	(iii)	Solubility decreases because of presence of common anion in solution	(R)	Solubility is unaffected by pH of solution
(IV)	Solubility = $\sqrt{K_{sp}}$	(iv)	Solubility increases because of presence of common cation in solution	(S)	Anionic hydrolysis will make solubility in water greater than expected

4. For AgCN, the only correct combination is :
(A) (IV) (ii) (R) (B) (I) (iii) (S) (C) (I) (i) (P) (D) (I) (iii) (P)

5. For $Al(OH)_3$, the only correct combination is :
(A) (II) (iii) (S) (B) (II) (iv) (Q) (C) (III) (i) (P) (D) (II) (ii) (Q)

6. For PbS, the only correct combination is :
(A) (I) (iii) (P) (B) (IV) (iii) (S) (C) (I) (ii) (R) (D) (IV) (ii) (P)

Exercise-3

*** Marked questions may have more than one correct option.**

PART - I : JEE (ADVANCED) / IIT-JEE PROBLEMS (PREVIOUS YEARS)

1. For a sparingly soluble salt A_pB_q, the relationship of its solubility product (L_s) with its solubility (S) is : **[JEE-2001(S), 1/35]**
(A) $L_S = S^{p+q} . p^p . q^q$ (B) $L_S = S^{p+q} . p^q . q^p$ (C) $L_S = S^{pq} . p^p . q^q$ (D) $L_S = S^{pq} . (pq)^{p+q}$

2. A solution which is 10^{-3} M each in Mn^{2+}, Fe^{2+}, Zn^{2+} and Hg^{2+} is treated with 10^{-16} M sulphide ion. If K_{sp} values of MnS, FeS, ZnS and HgS are 10^{-15}, 10^{-23}, 10^{-20} and 10^{-54} respectively, which one will precipitate first ? **[JEE-2003, 3/84]**
(A) FeS (B) MgS (C) HgS (D) ZnS

3. Solubility product constant (K_{sp}) of salts of types MX, MX_2 and M_3X at temperature T are 4.0×10^{-8}, 3.2×10^{-14} and 2.7×10^{-15}, respectively. Solubilities (in mol dm^{-3}) of the salts at temperature T are in the order : **[JEE-2008, 3/163]**
(A) $MX > MX_2 > M_3X$ (B) $M_3X > MX_2 > MX$ (C) $MX_2 > M_3X > MX$ (D) $MX > M_3X > MX_2$

4. In 1 L saturated solution of AgCl [K_{sp}(AgCl) = 1.6×10^{-10}], 0.1 mole of CuCl [K_{sp}(CuCl) = 1.0×10^{-6}] is added. The resultant concentation of Ag^+ in the solution is 1.6×10^{-x}. The value of "x" is : **[JEE-2011, 4/180]**

5. The solubility of a salt of weak acid **(AB)** at pH 3 is **Y**$\times 10^{-3}$ mol L^{-1}. The value of Y is ____.
(Given that the value of solubility product of **AB** (K_{sp}) = 2×10^{-10} and the value of ionization constant of HB (K_a) = 1×10^{-8}) **[JEE(Advanced)-2018, 3/120]**

PART - II : JEE (MAIN) (PREVIOUS YEARS)

JEE(MAIN) ONLINE PROBLEMS

1. Zirconium phosphate [$Zr_3(PO_4)_4$] dissociates into three zirconium cations of charge +4 and four phosphate anions of charge –3. If molar solubility of ziroconium phosphate is denoted by S and its solubility product by K_{sp} then which of the following relationship between S and K_{sp} is correct ?

[JEE(Main) 2016 Online (19-04-14), 4/120]

(1) $S = \{K^{sp}/(6912)^{1/7}\}$ (2) $S = \{K^{sp}/144\}^{1/7}$

(3) $S = \{K^{sp}/6912\}^{1/7}$ (4) $S = \{K^{sp}/6912\}^{7}$

Answers

EXERCISE - 1

PART - I

A-1. (a) 1.5×10^{-8} M (b) 3.78×10^{-3} mg (c) 3×10^{8} mL **A-2.** 1.97×10^{-7} mg

B-1. 5×10^{-9} M **B-2.** (a) 4.19×10^{-4} mg/mL (b) 4.19×10^{-16} mg/mL

C-1. 10^{-5} M AgCl, 8.5×10^{-12} M AgI. **C-2.** 6.25×10^{-12} M

D-1. $PbSO_4$, 0.02 M **D-2.** 2.25×10^{-4} M

PART - II

A-1. (C) **B-1.** (D) **B-2.** (B) **B-3.** (B) **B-4.** (D)

B-5. (A) **C-1.** (C) **C-2.** (B).

EXERCISE - 2

PART - I

1. (C) **2.** (B) **3.** (B)

PART – II

1. 5 (actual answer = 4.8×10^{-9}) **2.** 50

PART - III

1. (A) **2.** (C) **3.** (D) **4.** (C) **5.** (D)

6. (A)

EXERCISE - 3

PART - I

1. (A) **2.** (C) **3.** (D) **4.** 7 **5.** 4.47

PART - II

JEE(MAIN) ONLINE PROBLEMS

1. (2)