CHAPTER

23 Analytical Chemistry

Section-A JEE Advanced/ IIT-JEE

A Fill in the Blanks

1. If metal ions of group III are precipitated by NH_4Cl and NH_4OH without prior oxidation by conc. HNO_3 ..... is not completely precipitated. *(1984 - 1 Mark)*
2. The formula of the deep red liquid formed on warming dichromate with KCl in concentrated sulphuric acid is ..... . *(1993 - 1 Mark)*

B True / False

1. Addition of ammonium chloride to a solution containing ferric and magnesium ions is essential for selective precipitation of ferric hydroxide by aqueous ammonia. *(1985 - ½ Mark)*
2. From the acidic solution containing copper (+2) and zinc (+2) ions, copper can be selectively precipitated using sodium sulphide. *(1987 - 1 Mark)*

C MCQs with One Correct Answer

1. The ion that cannot be precipitated by both HCl and H_2S is *(1982 - 1 Mark)*
   (a) Pb^{2+} (b) Cu^{+}
   (c) Ag^{+} (d) Sn^{2+}
2. Which one among the following pairs of ions cannot be separated by H_2S in dilute hydrochloric acid? *(1986 - 1 Mark)*
   (a) Bi^{3+}, Sn^{4+} (b) Al^{3+}, Hg^{2+}
   (c) Zn^{2+}, Cu^{2+} (d) Ni^{2+}, Cu^{2+}
3. An aqueous solution contains Hg^{2+}, Hg_2^{2+}, Pb^{2+} and Cd^{2+}. The addition of HCl (6N) will precipitate : *(1995S)*
   (a) Hg_2Cl_2 only (b) $PbCl_2$ only
   (c) $PbCl_2$ and Hg_2Cl_2 (d) $PbCl_2$ and $HgCl_2$
4. Identify the correct order of solubility of Na_2S, CuS and ZnS in aqueous medium *(2002S)*
   (a) $CuS > ZnS > Na_2S$ (b) $ZnS > Na_2S > CuS$
   (c) $Na_2S > CuS > ZnS$ (d) $Na_2S > ZnS > CuS$
5. An aqueous solution of a substance gives a white precipitate on treatment with dilute hydrochloric acid, which dissolves on heating. When hydrogen sulfide is passed through the hot acidic solution, a black precipitate is obtained. The substance is a *(2002S)*
   (a) Hg_2^{2+} salt (b) Cu^{2+} salt
   (c) Ag^{+} salt (d) Pb^{2+} salt
6. A gas 'X' is passed through water to form a saturated solution. The aqueous solution on treatment with silver nitrate gives a white precipitate. The saturated aqueous solution also dissolves magnesium ribbon with evolution of a colourless gas 'Y'. Identify 'X' and 'Y'. *(2002S)*
   (a) $X = CO_2, Y = Cl_2$ (b) $X = Cl_2, Y = CO_2$
   (c) $X = Cl_2, Y = H_2$ (d) $X = H_2, Y = Cl_2$
7. $[X] + H_2SO_4 \longrightarrow$ [Y] a colourless gas with irritating smell, $[Y] + K_2Cr_2O_7 + H_2SO_4 \longrightarrow$ green solution. [X] and [Y] are: *(2003S)*
   (a) SO_3^{2-}, SO_2 (b) Cl^{-},HCl
   (c) S^{2-}, H_2S (d) CO_3^{2-}, CO_2
8. 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} of MnS, FeS, ZnS and HgS are 10^{-15}, 10^{-23}, 10^{-20} and 10^{-54} respectively, which one will precipitate first? *(2003S)*
   (a) FeS (b) MgS (c) HgS (d) ZnS
9. A metal nitrate reacts with KI to give a black precipitate which on addition of excess of KI is converted into orange colour solution. The cation of the metal nitrate is *(2005S)*
   (a) Hg^{2+} (b) Bi^{3+} (c) Pb^{2+} (d) Cu^{+}
10. A solution when diluted with H_2O and boiled, gives a white precipitate. On addition of excess NH_4Cl/NH_4OH, the volume of precipitate decreases leaving behind a white gelatinous precipitate. Identify the precipitate which disolves in NH_4OH/NH_4Cl *(2006 - 3M, –1)*
    (a) $Al(OH)_3$ (b) $Zn(OH)_2$
    (c) $Ca(OH)_2$ (d) $Mg(OH)_2$
11. A solution of a metal ion when treated with KI gives a red precipitate which dissolves in excess KI to give a colourless solution. Moreover, the solution of metal ion on treatment with a solution of cobalt (II) thiocyanate gives rise to a deep blue crystalline precipitate. The metal ion is *(2007)*
    (a) Pb^{2+} (b) Hg^{2+} (c) Cu^{2+} (d) Co^{2+}
12. Passing H_2S gas into a mixture of Mn^{2+}, Ni^{2+}, Cu^{2+} and Hg^{2+} ions in an acidified aqueous solution precipitates *(2011)*
    (a) CuS and HgS (b) MnS and CuS
    (c) MnS and NiS (d) NiS and HgS
13. Upon treatment with ammoniacal H_2S, the metal ion that precipitates as a sulfide is *(JEE Adv. 2013)*
    (a) Fe(III) (b) Al(III) (c) Mg(II) (d) Zn(II)

D MCQs with One or More Than One Correct

1. The reagents, NH_4Cl and aqueous NH_3 will precipitate
   (a) Ca^{2+} (b) Al^{3+} *(1991 - 1 Mark)*
   (c) Bi^{3+} (d) Mg^{2+}
   (e) Zn^{2+}
2. Which of the following statement(s) is (are) correct when a mixture of NaCl and $K_2Cr_2O_7$ is gently warmed with conc. H_2SO_4? *(1998 - 2 Marks)*
   (a) A deep red vapour is evolved
   (b) The vapours when passed into NaOH solution gives a yellow solution of Na_2CrO_4
   (c) Chlorine gas is evolved
   (d) Chromyl chloride is formed
3. Which of the following statement(s) is (are) correct with reference to the ferrous and ferric ions? *(1998 - 2 Marks)*
   (a) Fe^{3+} gives brown colour with potassium ferricyanide.
   (b) Fe^{2+} gives blue precipitate with potassium ferricyanide.
   (c) Fe^{3+} gives red colour with potassium thiocyanate.
   (d) Fe^{2+} gives brown colour with ammonium thiocyanate.
4. The pair(s) of ions where BOTH the ions are precipitated upon passing H_2S gas in presence of dilute HCl, is(are) *(JEE Adv. 2015)*
   (a) Ba^{2+}, Zn^{2+} (b) Bi^{3+}, Fe^{3+}
   (c) Cu^{2+}, Pb^{2+} (d) Hg^{2+}, Bi^{3+}
5. The reagent(s) that can selectively precipitate S^{2-} from a mixture of S^{2-} and SO_4^{2-} in aqueous solution is(are) *(JEE Adv. 2016)*
   (a) $CuCl_2$ (b) $BaCl_2$
   (c) $Pb(OOCCH_3)_2$ (d) $Na_2[Fe(CN)_5NO]$

E Subjective Problems

1. Account for the following. Limit your answer to two sentences:
   The precipitation of second group sulphides in qualitative analysis is carried out with hydrogen sulphide in presence of hydrochloric acid and not nitric acid. *(1979)*
2. Compound A is a light green crystalline solid. It gives the following tests: *(1980)*
   (i) It dissolves in dilute sulphuric acid. No gas is produced.
   (ii) A drop of $KMnO_4$ is added to the above solution. The pink colour disappears.
   (iii) Compound A is heated strongly. Gases B and C, with pungent smell, come out. A brown residue D is left behind.
   (iv) The gas mixture (B) and (C) is passed into a dichromate solution. The solution turns green.
   (v) The green solution from step (iv) gives a white precipitate E with a solution of barium nitrate.
   (vi) Residue D from step (iii) is heated on charcoal in a reducing flame. It gives a magnetic substance.
   Name the compounds A, B, C, D and E
3. When 16.8 g of white solid X were heated, 4.4 g of acid gas A that turned lime water milky was driven off together with 1.8 g of a gas B which condensed to a colourless liquid. The solid that remained, Y, dissolved in water to give an alkaline solution, which with excess barium chloride solution gave a white precipitate Z. The precipitate effervesced with acid giving off carbon dioxide. Identify A, B and Y and write down the equation for the thermal decomposition of X. *(1984 - 4 Marks)*
4. A mixture of two salts was treated as follows : *(1987 - 5 Marks)*
   (*i*) The mixture was heated with manganese dioxide and concentrated sulphuric acid when yellowish green gas was liberated.
   (*ii*) The mixture on heating with sodium hydroxide solution gave a gas which turned red litmus blue.
   (*iii*) Its solution in water gave blue precipitate with potassium ferricyanide and red colouration with ammonium thiocyanate.
   (*iv*) The mixture was boiled with potassium hydroxide and the liberated gas was bubbled through an alkaline solution of K_2HgI_4 to give brown precipitate.
   Identify the two salts. Give ionic equations for reactions involved in the tests (*i*), (*ii*) and (*iii*).
5. A hydrated metallic salt A, light green in colour, on careful heating gives a white anhydrous residue B. B is soluble in water and its aqueous solution reacts with NO to give a dark brown compound C. B on strong heating gives a brown residue D and a mixture of two gases E and F. The gaseous mixture when passed through acidified permanganate, discharges the pink colour and when passed through acidified $BaCl_2$ solution gave a white precipitate. Identify A, B, C, D, E and F. *(1988 - 3 Marks)*
6. When 20.02 g of a white solid X is heated 4.4 g of an acid gas A and 1.8 g of a neutral gas B are evolved, leaving behind a solid residue Y of weight 13.8 g. A turns lime water milky and B condenses into a liquid which changes anhydrous copper sulphate blue. The aqueous solution of Y is alkaline to litmus and gives 19.7 g of white precipitate Z with barium chloride solution. Z gives carbon dioxide with an acid. Identify A, B, X, Y and Z. *(1989 - 5 Marks)*
7. The gas liberated on heating a mixture of two salts with NaOH, gives a reddish brown precipitate with an alkaline solution of $K_2[HgI_4]$. The aqueous solution of the mixture on treatment with $BaCl_2$ gives a white precipitate which is sparingly soluble in conc. HCl. On heating the mixture with $K_2Cr_2O_7$ and conc. H_2SO_4, red vapours of A are produced. The aqueous solution of the mixture gives a deep blue colouration B with potassium ferricyanide solution. Identify the radicals in the given mixture and write the balanced equations for the formation of A and B. *(1991 - 4 Marks)*
8. A light bluish green crystalline compound responds to the following tests :
   (*i*) Its aqueous solution gives a brown precipitate or colour with alkaline $K_2[HgI_4]$ solution.
   (*ii*) Its aqueous solution gives a blue colour with $K_3[Fe(CN)_6]$ solution.
   (*iii*) Its solution in hydrochloric acid gives a white precipitate with $BaCl_2$ solution.
   Identify the ions present and suggest the formula of the compound. *(1992 - 4 Marks)*

9. An orange solid (A) on heating gave a green residuce (B), a colourless gas (C) and water vapour. The dry gas (C) on passing over heated Mg gave a white solid (D). (D) on reaction with water gave a gas (E) which formed dense white fumes with HCl. Identify (A) to (E) and give reactions involved. *(1993 - 3 Marks)*
10. A is a binary compound of a univalent metal, 1.422 g of A reacts completely with 0.321 g of sulphur in an evaccuated and sealed tube to give 1.743 g of a white crystalline solid B, that forms a hydrated double salt, C with $Al_2(SO_4)_3$. Identify A, B and C *(1994 - 5 Marks)*
11. A scarlet compound A is treated with conc. HNO_3 to give a chocolate brown precipitate B. The precipitate is filtered and the filtrate is neutralised with NaOH. Addition of KI to the resulting solution gives a yellow precipitate C. The precipitate B on warming with conc. HNO_3 in the precence of $Mn(NO_3)_2$ produces a pink-coloured solution due to the formation of D. Identify A, B, C and D. Write the reaction sequence. *(1995 - 4 Marks)*
12. Calcium burns in nitrogen to produce a white powder which dissolves in sufficient water to produce a gas (A) and an alkaline solution. The solution on exposure to air produces a thin solid layer of (B) on the surface. Identify the compounds A and B. *(1996 - 2 Marks)*
13. A colourless inorganic salt (A) decomposes completely at about 250°C to give only two products, (B) and (C), leaving no residue. The oxide (C) is a liquid at room temperature and neutral to moist litmus paper while the gas (B) is a neutral oxide. White phosphorus burns in excess of (B) to produce a strong white dehydrating agent. Write balanced equations for the reactions involved in the above process. *(1996 - 3 Marks)*
14. During the qualitative analysis of a mixture containing Cu^{2+} and Zn^{2+} ions, H_2S gas is passed through an acidified solution containing these ions in order to test Cu^{2+} alone. Explain briefly. *(1998 - 2 Marks)*
15. A white solid is either Na_2O or Na_2O_2. A piece of red litmus paper turns white when it is dipped into a freshly made aqueous solution of the white solid. *(1999 - 4 Marks)*
    (i) Identify the substance and explain with balanced equation.
    (ii) Explain what would happen to the red litmus if the white solid were the other compound.
16. An aqueous solution containing one mole of HgI_2 and two moles of NaI is orange in colour. On addition of excess NaI the solution becomes colouress. The orange colour reappears on subsequent addition of NaOCl. Explain with equations. *(1999 - 3 Marks)*
17. An aqueous blue coloured solution of a transition metal sulphate reacts with H_2S in acidic medium to give a black precipitate **A,** which is insoluble in warm aqueous solution of KOH. The blue solution on treatment with KI in weakly acidic medium, turns yellow and produces a white precipitate **B**. Identify the transition metal ion. Write the chemical reactions involved in the formation of **A** and **B**. *(2000 - 4 Marks)*
18. Write the chemical reactions associated with the 'borax bead test' of cobalt (II) oxide. *(2000 - 3 Marks)*
19. A white substance (A) reacts with dilute H_2SO_4 to produce a colourless gas (B) and a colourless solution (C). The reaction between (B) and acidified $K_2Cr_2O_7$ solution produces a green solution and a slightly coloured precipitate (D). The substance (D) burns in air to produce a gas (E) which reacts with (B) to yield (D) and a colourless liquid. Anhydrous copper sulphate is turned blue on addition of this colourless liquid. Addition of aqueous NH_3 or NaOH to (C) produces first a precipitate, which dissolves in the excess of the respective reagent to produce a clear solution in each case. Identify (A), (B), (C), (D) and (E). Write the equations of the reactions involved. *(2001 - 10 Marks)*
20. When a white crystalline compound **X** is heated with $K_2Cr_2O_7$ and concentrated H_2SO_4, a reddish brown gas **A** is evolved. On passing **A** into caustic soda solution, a yellow coloured solution of **B** is obtained. Neutralizing the solution **B** with acetic acid and on subsequent addition of lead acetate, a yellow precipitate **C** is obtained. When **X** is heated with NaOH solution, a colourless gas is evolved and on passing this gas into K_2HgI_4 solution, a reddish brown precipitate **D** is formed. Identify **A, B, C, D** and **X**. Write the equations of reactions involved. *(2002 - 5 Marks)*
21. A mixture consists of A (yellow solid) and B (colourless solid) which gives lilac colour in flame.
    (a) Mixture gives black precipitate C on passing $H_2S_{(g)}$ through its aqueous solution.
    (b) C is soluble in aqua-regia and on evaporation of aqua-regia and adding $SnCl_2$ gives greyish black precipitate D.

    The salt solution with NH_4OH gives a brown precipitate.
    (i) The sodium carbonate extract of the salt with $CCl_4/FeCl_3$ gives a violet layer.
    (ii) The sodium carbonate extract gives yellow precipitate with $AgNO_3$ solution which is insoluble in NH_3.

    Identify A and B, and the precipitates C and D. *(2003 - 4 Marks)*

G Comprehension Based Questions

PASSAGE-1

p-Amino-*N*, *N*-dimethylaniline is added to a strongly acidic solution of **X**. The resulting solution is treated with a few drops of aqueous solution of **Y** to yield blue coloration due to the formation of methylene blue. Treatment of the aqueous solution of **Y** with the reagent potassium hexacyanoferrate(II) leads to the formation of an intense blue precipitate. The precipitate dissolves on excess addition of the reagent. Similarly, treatment of the solution of **Y** with the solution of potassium hexacyanoferrate (III) leads to a brown coloration due to the formation of **Z**. *(2009)*

1. The compound **X** is
   (a) $NaNO_3$ (b) NaCl
   (c) Na_2SO_4 (d) Na_2S
2. The compound **Y** is
   (a) $MgCl_2$ (b) $FeCl_2$
   (c) $FeCl_3$ (d) $ZnCl_2$
3. The compound **Z** is
   (a) $Mg_2[Fe(CN)_6]$ (b) $Fe[Fe(CN)_6]$
   (c) $Fe_4[Fe(CN)_6]_3$ (d) $K_2Zn_3[Fe(CN)_6]_2$

PASSAGE-2

An aqueous solution of a mixture of two inorganic salts, when treated with dilute HCl, gave a precipitate (P) and a filtrate (Q). The precipitate P was found to dissolve in hot water. The filtrate (Q) remained unchanged, when treated with H_2S in a dilute mineral acid medium. However, it gave a precipitate (R) with H_2S in an ammoniacal medium. The precipitate R gave a coloured solution (S), when treated with H_2O_2 in an aqueous NaOH medium.

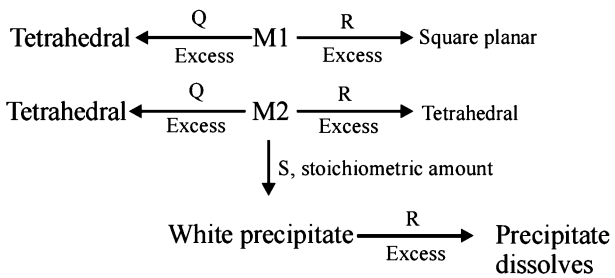
(JEE Adv. 2013-II)

4. The precipitate P contains
   (a) Pb^{2+} (b) Hg_2^{2+}
   (c) Ag^+ (d) Hg^{2+}
5. The coloured solution S contains
   (a) $Fe_2(SO_4)_3$ (b) $CuSO_4$
   (c) $ZnSO_4$ (d) Na_2CrO_4

PASSAGE-3

An aqueous solution of metal ion *M*1 reacts separately with reagents *Q* and *R* in excess to give tetrahedral and square planar complexes, respectively. An aqueous solution of another metal ion *M*2 always forms tetrahedral complexes with these reagents. Aqueous solution of *M*2 on reaction with reagent *S* gives white precipitate which dissolves in excess of *S*. The reactions are summarized in the scheme given below:

Scheme:



6. *M*1, *Q* and *R*, respectively are *(JEE Adv. 2014)*
   (a) Zn^{2+}, KCN and HCl (b) Ni^{2+}, HCl and KCN
   (c) Cd^{2+}, KCN and HCl (d) Co^{2+}, HCl and KCN
7. Reagent *S* is *(JEE Adv. 2014)*
   (a) $K_4[Fe(CN)_6]$ (b) Na_2HPO_4
   (c) K_2CrO_4 (d) KOH

H Assertion & Reason Type Questions

1. Read the following statement and explanation and answer as per the options given below : *(1989 - 2 Marks)*
   Assertion : A very dilute acidic solution of Cd^{2+} and Ni^{2+} gives yellow precipitate of CdS on passing hydrogen sulphide.
   Statement : Solubility product of CdS is more than that of NiS.
   (a) If both assertion and statement are correct and statement is an explanation of assertion.
   (b) If assertion is correct and statement is wrong, statement is not an explanation of assertion.
   (c) If assertion is wrong and statement is correct, statement is not an explanation of assertion.
   (d) If both assertion and statement are wrong and statement is not explanation of assertion.
2. Read the following statement and explanation and answer as per the options given below : *(1998 - 2 Marks)*
   Assertion : Sulphate is estimated as $BaSO_4$ and not as $MgSO_4$.
   Reason : Ionic radius of Mg^{2+} is smaller than that of Ba^{2+}
   (a) If both *assertion* and *reason* are correct, and *reason* is the correct explanation of the *assertion*.
   (b) If both *assertion* and *reason* are correct, but *reason* is not the correct explanation of the *assertion*.
   (c) If *assertion* is correct but *reason* is incorrect.
   (d) If *assertion* is incorrect but *reason* is correct.

I Integer Value Correct Type

1. Among PbS, CuS, HgS, MnS, Ag_2S, NiS, CoS, Bi_2S_3 and SnS_2, the total number of **BLACK** coloured sulphides is *(JEE Adv. 2014)*

Section-B JEE Main / AIEEE

1. When H_2S is passed through Hg_2S we get [2002]
   (a) HgS (b) $HgS + Hg_2S$
   (c) $Hg_2S + Hg$ (d) None of these.
2. How do we differentiate between Fe^{3+} and Cr^{3+} in group III?
   (a) by taking excess of NH_4OH solution [2002]
   (b) by increasing NH_4^+ ion concentration
   (c) by decreasing OH^- ion concentration
   (d) both (b) and (c)
3. Which one of the following statements is correct ?
   (a) From a mixed precipitate of AgCl and AgI, ammonia solution dissolves only AgCl [2003]
   (b) Ferric ions give a deep green precipitate on adding potassium ferrocyanide solution
   (c) On boiling a solution having K^+, Ca^{2+} and HCO_3^- ions we get a precipitate of $K_2Ca(CO_3)_2$
   (d) Manganese salts give a violet borax bead test in the reducing flame
4. The compound formed in the positive test for nitrogen with the Lassaigne solution of an organic compound is [2004]
   (a) $Fe_4[Fe(CN)_6]_3$ (b) $Na_3[Fe(CN)_6]$
   (c) $Fe(CN)_3$ (d) $Na_4[Fe(CN)_5NOS]$
5. The equation which is balanced and represents the correct product(s) is: [JEE M 2014]
   (a) $Li_2O + 2KCl \rightarrow 2LiCl + K_2O$
   (b) $\left[CoCl(NH_3)_5\right]^+ + 5H^+ \rightarrow Co^{2+} + 5NH_4^+ + Cl^-$
   (c) $\left[Mg(H_2O)_6\right]^{2+} + (EDTA)^{4-} \xrightarrow{\text{excess NaOH}} \left[Mg(EDTA)\right]^{2+} + 6H_2O$
   (d) $CuSO_4 + 4KCN \rightarrow K_2\left[Cu(CN)_4\right] + K_2SO_4$

23 Analytical Chemistry

Section-A : JEE Advanced/ IIT-JEE

A **1.** Fe^{3+} **2.** CrO_2Cl_2

B **1.** T **2.** T

C **1.** (d) **2.** (a) **3.** (c) **4.** (d) **5.** (d) **6.** (c) **7.** (a)
8. (c) **9.** (b) **10.** (b) **11.** (b) **12.** (a) **13.** (d)

D **1.** (a, b) **2.** (a, b, d) **3.** (b, c) **4.** (c, d) **5.** (a or a, c)

E **3.** CO_2, H_2O, $NaHCO_3$, Na_2CO_3, $BaCO_3$
A B X Y Z

4. $FeCl_2$, NH_4Cl

5. $FeSO_4.7H_2O$, $FeSO_4$, $FeSO_4.NO$, Fe_2O_3, SO_2, SO_3
A B C D E F

6. CO_2, H_2O, $KHCO_3$, K_2CO_3, $BaCO_3$
A B X Y Z

7. NH_4^+, Fe^{2+}, SO_4^{2-}, Cl^-.

8. NH_4^+, Fe^{2+}, SO_4^{2-}, $FeSO_4(NH_4)_2SO_4.6H_2O$

9. $(NH_4)_2Cr_2O_7$, Cr_2O_3, N_2, Mg_3N_2, NH_3
A B C D E

10. KO_2, K_2SO_4, $Al_2(SO_4)_3$, $24\,H_2O$
A B C D

11. Pb_3O_4, PbO_2, PbI_2
A B C

12. NH_3, $CaCO_3$
A B

15. (i) Na_2O_2, (ii) turns red litmus blue

17. Cu^{2+}

19. ZnS, H_2S, $ZnSO_4$, S, SO_2
A B C D E

20. CrO_2Cl_2, Na_2CrO_4, $PbCrO_4$, iodide of Millon's base, NH_4Cl
A B C D

21. HgI_2, KI, HgS, Hg
A B C D

G **1.** (d) **2.** (c) **3.** (b) **4.** (a) **5.** (d) **6.** (b) **7.** (d)

H **1.** (b) **2.** (b)

I **1.** 7

Section-B : JEE Main/ AIEEE

1. (c) **2.** (b) **3.** (a) **4.** (a) **5.** (b)

Section-A JEE Advanced/ IIT-JEE

A. Fill in the Blanks

1. Fe^{3+}; Without oxidation with HNO_3, the Fe^{2+} ions present would not be converted into Fe^{3+}. So $Fe(OH)_2$ will not be precipitated as its solubility product is higher than that of $Fe(OH)_3$ and as NH_4Cl suppresses the ionisation of NH_4OH, this solubility product is not reached.

2. Chromyl chloride (CrO_2Cl_2).

B. True/ False

1. **True :** Function of ammonium chloride is to suppress the ionisation of NH_4OH and thus check the precipitation of $Mg(OH)_2$ because the solubility product of $Mg(OH)_2$ is high.
This is used in salt analysis when 3rd group radicals are precipitated. The group reagent are NH_4OH in presence of NH_4Cl.

2. **True :** K_{sp} of CuS is less than K_{sp} of ZnS. On passing H_2S in acidic medium, the dissociation of H_2S is suppressed due to common ion effect and it provides $[S^{2-}]$ which is just sufficient to cross over K_{sp} of CuS and not K_{sp} of ZnS. Thus only CuS gets precipitated.

C. MCQs with ONE Correct Answer

1. **(d)** Sn^{2+} can be precipitated by H_2S but not by HCl.

2. **(a)** **NOTE :** The ions of group II of salt analysis are precipitated by HCl and H_2S whereas members of group IV are precipitated by H_2S in alkaline medium.
$\because$ Bi^{3+} and Sn^{4+} both belong to group II
$\therefore$ They will be precipitated by HCl in presence of H_2S.
Both Bi^{3+} and Sn^{4+} belong to group II of qualitative inorganic analysis and will get precipitated by H_2S.

3. (c) **NOTE:**
Only group I cations are precipitated by dil. HCl

$$\underset{(X)}{SO_3^{2-}} + H_2SO_4 \longrightarrow \underset{(Y)}{SO_2} + H_2O + SO_4^{2-}$$

$$3SO_2 + K_2Cr_2O_7 + H_2SO_4$$

$$\longrightarrow K_2SO_4 + \underset{\text{(green colour solution)}}{Cr_2(SO_4)_3} + H_2O$$

Only $PbCl_2$ and Hg_2Cl_2 will precipitate as Pb^{2+} and Hg_2^{2+} as first group basic radicals and their solubility product is less than the other radicals.

NOTE : dil. HCl is the first group reagent.

4. (d) Sodium salts are highly soluble. Cu^{2+} belongs to the II[nd] group in salt analysis and is precipitated as CuS, whereas Zn^{2+} belongs to the IV group and is precipitated as ZnS after CuS because of higher K_{sp} of ZnS.

5. (d) $$Pb^{+2} + 2HCl \longrightarrow \underset{\substack{\text{White ppt}\\ \text{dissolves on boiling}\\ \text{[Soluble in hot water]}}}{PbCl_2\downarrow} \xrightarrow{H_2S} \underset{\text{B lack ppt.}}{PbS\downarrow}$$

6. (c) Since the saturated aqueous solution of (X) give white ppt with $AgNO_3$, so (X) may be Cl_2. Hence

$$\underset{(X)}{Cl_2} + H_2O \rightarrow HOCl + HCl$$

$$HCl + AgNO_3 \longrightarrow \underset{\text{white}}{AgCl\downarrow} + HNO_3$$

$$2HCl + Mg \rightarrow \underset{(Y)}{MgCl_2} + H_2\uparrow$$

7. (a) SO_2 and H_2S, both being reducing agents, can turn acidified dichromate solution green. SO_2 can be obtained by the action of acid upon sulphite, while H_2S is evolved by the action of acid upon sulphide. However, SO_2 has a burning sulphur smell which is irritating. H_2S has rotten egg like smell.

8. (c) **TIPS/Formulae :** For precipitation,
Ionic product > solubility product
HgS having the lowest K_{sp} among the given compounds will precipitate first.

9. (b) $$Bi(NO_3)_3(aq) + 3KI(aq) \longrightarrow \underset{\text{Black}}{BiI_3(s)} + 3KNO_3(aq)$$

$$BiI_3(s) + KI(aq) \longrightarrow \underset{\text{Orange}}{K[BiI_4]}$$

The metal ion is Bi^{3+}.

10. (b) Precipitate of $Zn(OH)_2$ formed at initial stage dissolves in excess of NH_4OH due to the formation of tetrammine Zn (II) complex.

$$Zn^{2+} + 2NH_4OH \longrightarrow Zn(OH)_2\downarrow + 2NH_4^+$$

$$Zn(OH)_2 + 4NH_4^+ \longrightarrow [Zn(NH_3)_4]^{2+} + 2H_2O + 2H^+$$

11. (b) $$Hg^{2+} + 2KI \longrightarrow \underset{\text{(red ppt)}}{HgI_2\downarrow} + 2K^+$$

$$HgI_2 + 2KI \longrightarrow K_2[HgI_4]$$

$$Hg^{2+} + Co^{2+} + 4SCN^- \longrightarrow \underset{\text{(deep blue crystalline)}}{Co[Hg(SCN)_4]\downarrow}$$

12. (a) In presence of acid, ionisation of H_2S is supressed, so less number of S^{2-} are furnished. Hence only those sulphides are precipitated which has low solubility product (K_{sp}); thus only CuS and HgS are precipitated.

13. (d) The group reagent of fourth group is ammoniacal H_2S by which Zn^{2+} ion will be precipitated as ZnS, whereas Fe^{3+} ion and Al^{3+} ions will be precipitated as hydroxides.

D. MCQs with ONE or More Than One Correct

1. (a, b) Al^{3+} (third group radical) and Ca^{2+} (fifth group radical) precipitate out as their hydroxide with NH_4Cl and aq. NH_3 (NH_4OH) which are the group reagents.

2. (a,b,d) The reactions are

$$4NaCl + K_2Cr_2O_7 + 6H_2SO_4 \rightarrow \underset{\text{(Red vapours)}}{2CrO_2Cl_2} + 4NaHSO_4 + 2KHSO_4 + 3H_2O$$

$$\underset{\substack{\text{chromyl}\\ \text{chloride}}}{CrO_2Cl_2} + 4NaOH \rightarrow \underset{\substack{\text{yellow}\\ \text{solution}}}{Na_2CrO_4} + 2NaCl + 2H_2O$$

3. (b, c) The blue precipitate of Fe^{2+} ions with potassium ferricyanide is due to formation of Turnbull's blue $KFe^{II}[Fe^{III}(CN)_6]$

$$Fe^{2+} + K_3[Fe(CN)_6] \rightarrow \underset{\text{Potassium ferro ferricyanide}}{K.Fe^{II}[Fe^{III}(CN)_6]} + 2K^+$$

The red colouration of Fe^{3+} ions with potassium thiocyanate is due to the formation of $[Fe(CNS)_3]$

$$Fe^{2+} + 3KCNS \longrightarrow \underset{\substack{\text{(Ferric thiocyanate}\\ \text{red colour)}}}{[Fe(CNS)_3]} + 3K^+$$

4. (c, d) Only group II cations precipitate as sulphide with H_2S in acidic medium that is (Cu^{2+}, Pb^{2+}) and (Hg^{2+}, Bi^{3+})

5. (a or a, c)

	S^{2-}	SO_4^{2-}
Cu^{2+}	CuS (ppt)	$CuSO_4$ (Soluble)
Ba^{2+}	BaS (Soluble)	$BaSO_4$ (ppt)
$Pb(OAc)_2$	PbS (ppt)	$PbSO_4$ (ppt)
$Na_2[Fe(CN)_5NO]$	$Na_4[Fe(CN)_5(NOS)]$ Colour (not a ppt)	____

E. Subjective Problems

1. HNO_3 is strong oxidising agent and it oxidises H_2S to S. So HNO_3 cannot be used to precipitate second group elements.

2. (i) (A) is $FeSO_4.7H_2O$ because it is light green crystalline solid. Which dissolves in water containing H_2SO_4

(ii) On strong heating $FeSO_4$ both SO_2 **(B)** and SO_3 **(C)** are evolved. The colour of $KMnO_4$ disappears due to the formation of $MnSO_4$.

(iii) SO_2 being a reducing agent turns a dichromate solution green and forms H_2SO_4 in the solution. SO_3 dissolves in water to give H_2SO_4. Therefore, white ppt of $BaSO_4$ is formed with a solution of $Ba(NO_3)_2$

(iv) The brown residue left behind **(D)** is Fe_2O_3 which is reduced to Fe on heating in charcoal cavity. Fe is magnetic substance.

3. Representing the given facts in the form of equation.

$$\underset{16.8g}{(X)(g)} \xrightarrow{heat} \underset{4.4g}{A(g)} + \underset{1.8g}{B(g)} + Y(s)$$

The above equation leads to the following facts :

(i) Since the gas A turned lime water milky, it must be CO_2.

(ii) **NOTE :** The compound Y gives alkaline solution in water which when treated with $BaCl_2$ forms a white precipitate of Z. Since the compound Z when treated with acid gives effervescenes of CO_2, Z and hence Y must be metal carbonate, CO_3^{2-}. Hence Y may be written as metal carbonate MCO_3 or M_2CO_3.

(iii) When X is heated, it yields a carbonate (Y) along with the evolution of CO_2 (A) and another gas (B), it must be a bicarbonate.

(iv) The above facts point out that B may be water vapour Thus the above reaction can be written as below.

$$\underset{16.8\ g}{2MHCO_3} \xrightarrow{heat} \underset{4.4g}{CO_2} + \underset{1.8g}{H_2O} + M_2CO_3$$

Calculation of molecular weight of $MHCO_3$

4.4.g of CO_2 is given by 16.8 g of $MHCO_3$

$$\therefore 44g \text{ of } CO_2 \text{ is given by} = \frac{16.8}{4.4} \times 44 = 168\ g$$

Since two molecules of $MHCO_3$ are taking part in the reaction, the molecular weight of

$$MHCO_3(X) = \frac{168}{2} = 84$$

Calculation of atomic weight of metal M

$MHCO_3 = 84; M + 1 + 12 + 48 = 84$

$M + 61 = 84; M = 84 - 61 = 23$

Thus the metal must be Na and hence the given salt X is $NaHCO_3$. The above facts coincide with the given thermal decomposition.

$$2NaHCO_3 \xrightarrow{heat} CO_2 + H_2O + Na_2CO_3$$

(X) (A) (B) (Y)

$$Na_2CO_3 + BaCl_2 \rightarrow \underset{\text{white}}{\underset{(Z)}{BaCO_3}} + 2NaCl$$

$$BaCO_3 + HCl \longrightarrow BaCl_2 + H_2O + CO_2\uparrow$$

Thus A is CO_2, B is H_2O, Y is Na_2CO_3

4. (A) Test (i) of the problem indicates that the mixture contains Cl^- ion which is liberated as Cl_2 (yellowish green gas) when heated with MnO_2 and conc. H_2SO_4.

(B) Test (ii) indicates the presence of NH_4^+ ion in the mixture which gives ammonia when heated with NaOH solution. Since ammonia is basic in nature, it turns red litmus blue. Presence of NH_4^+ in the mixture is further confirmed by the given test (iv) according to which the gas (NH_3) gives brown precipitate with Nessler's reagent (alkaline solution of $K_2[HgI_4]$.

(C) Test (iii) indicates Fe^{2+} ion in the mixture which gives blue precipitate with potassium ferricyanide (note that potassium ferricyanide gives brown ppt. with Fe^{3+} ions).

(D) Red colouration with ammonium thiocynate indicates that the mixture also contains Fe^{3+} ions which are believed to be formed by the oxidation of Fe^{2+} ions by air.

$$2Fe^{2+} + 2H^+ + (O) \rightarrow 2Fe^{3+} + H_2O$$

Thus the mixture contains **$FeCl_2$ and NH_4Cl**.

Ionic reactions :

(i) $2Cl^- + MnO_2 + H_2SO_4 + 2H^+ \rightarrow Mn^{2+} + SO_4^{2-} + 2H_2O + \underset{\text{(Yellowishgreen)}}{Cl_2\uparrow}$

(ii) $NH_4^+ + OH^- \xrightarrow{heat} \underset{\text{turns red litmus blue}}{NH_3\uparrow} + H_2O$

(iii) (a) $3Fe^{2+} + 2[Fe(CN)_6]^{3-} \rightarrow \underset{\text{(blue ppt.)}}{Fe_3[Fe(CN)_6]_2}$

(b) $Fe^{3+} + 3CNS^- \rightarrow \underset{\substack{\text{Ferric thiocyanate}\\ \text{(blood red colour)}}}{Fe(CNS)_3}$

5. (i) (A) on heating loses water of crystallization and thus it is a hydrated salt.

(ii) Anhydrous salt (B) on heating gives two gases and brown residue and so (B) is $FeSO_4$. Thus (A) is $FeSO_4.7H_2O$

$$\underset{(A)}{FeSO_4.7H_2O} \xrightarrow{\Delta} \underset{(B)}{FeSO_4} + 7H_2O$$

$$\underset{(B)}{2FeSO_4} \xrightarrow{\Delta} \underset{\substack{(D)\\ \text{Brown}}}{Fe_2O_3} + \underset{(E)}{SO_2\uparrow} + \underset{(F)}{SO_3\uparrow}(s)$$

(iii) (B) is soluble in water and reacts with NO to give brown compound.

$$FeSO_4(aq) + NO \rightarrow \underset{\text{Brown ring (C)}}{FeSO_4.NO}$$

(iv) Gaseous mixture decolorizes acidified $KMnO_4$.

$$5SO_2 + 2KMnO_4 + 2H_2O \rightarrow K_2SO_4 + 2MnSO_4 + 2H_2SO_4$$

(v) Gaseous mixture on passing through $BaCl_2$, gives white ppt. of $BaSO_4$.

$$SO_3 + H_2O \rightarrow H_2SO_4$$
$$BaCl_2 + H_2SO_4 \rightarrow \underset{\text{white ppt.}}{BaSO_4} + 2HCl$$

6. Representing the given facts in the form of equation, we get

$$\underset{20.02\text{ g}}{(X)(g)} \xrightarrow{\text{heat}} \underset{4.4\text{ g}}{A(g)} + \underset{1.8\text{ g}}{B(g)} + \underset{13.8\text{ g}}{Y(s)}$$

The above equation leads to the following facts :

(i) Since the gas A turned lime water milky, it must be CO_2.

(ii) **NOTE :** The compound Y is alkaline to litmus and when treated with $BaCl_2$ forms a white precipitate of Z. Since the compound Z when treated with acid gives effervescenes of CO_2, Z and hence Y must contain carbonate, CO_3^{2-}. Hence Y may be written as metal carbonate MCO_3 or M_2CO_3.

(iii) When X is heated, it yields a carbonate (Y) along with the evolution of CO_2 (A) and a neutral gas (B), it must be a bicarbonate.

(iv) B changes anhydrous $CuSO_4$ blue, which point out that B is water.

Thus the above reaction can be written as below :

$$\underset{20.02\text{ g}}{2MHCO_3} \xrightarrow{\text{heat}} \underset{4.4\text{ g}}{CO_2} + \underset{1.8\text{ g}}{H_2O} + M_2CO_3$$

Calculation of molecular weight of $MHCO_3$

4.4 g of CO_2 is given by 20.02 g of $MHCO_3$

$$44\text{ g of } CO_2 \text{ is given by} = \frac{20.02}{4.4} \times 44 = 200.2\text{ g}$$

Since two molecules of $MHCO_3$ are taking part in the reaction, the molecular weight of

$$MHCO_3(X) = \frac{200.2}{2} = 100$$

Calculation of atomic weight of Metal M

$MHCO_3 = 100$; $M + 1 + 12 + 48 = 100$

$M + 61 = 100$; $M = 100 - 61 = 39$

Thus the metal must be K and hence the given salt X is $KHCO_3$. The above facts coincide with the given thermal decomposition.

$$\underset{X}{2KHCO_3} \xrightarrow{\text{heat}} \underset{A}{CO_2} + \underset{B}{H_2O} + \underset{Y}{K_2CO_3}$$
$$K_2CO_3 + BaCl_2 \rightarrow \underset{\text{(white)}}{BaCO_3} + 2KCl$$

Hence, we have

$X = KHCO_3$, $Y = K_2CO_3$, $Z = BaCO_3$, $A = CO_2$, $B = H_2O$

7. Let us summarise the given facts of the question.

$$\text{Red vapours of (A)} \xleftarrow[\text{conc. } H_2SO_4,\text{ heat}]{K_2Cr_2O_7} \textbf{Mixture of two salts}$$

$$\text{Mixture of two salts} \xrightarrow[\text{NaOH}]{\text{Heat with}} \text{Gas} \xrightarrow{\text{Alk. } K_2[HgI_4]} \underset{\text{brown ppt.}}{\text{Reddish}}$$

$$\text{Deep blue colour, (B)} \xleftarrow{K_3[Fe(CN)_6]} \textbf{Aq. solution of the mixture} \xrightarrow{BaCl_2} \text{White ppt.sparingly soluble in conc. HCl.}$$

The given reactions lead to the following conclusions.

(i) Formation of reddish brown precipitate on treatment with alk. $K_2[HgI_4]$ indicates the evolution of NH_3 gas and hence the presence of NH_4^+ in the mixture of salts.

(ii) Heating of mixture with $K_2Cr_2O_7$ and conc. H_2SO_4 to give red vapours (of chromyl chloride) indicates the presence of Cl^- ion in the mixture.

(iii) Reaction of aqueous solution of the mixture with barium chloride solution to give white ppt. (of $BaSO_4$) sparingly soluble in conc. HCl indicates the presence of SO_4^{2-} ions in the mixture.

(iv) **NOTE :** Reaction of aqueous solution of the mixture with potassium ferricyanide solution to give deep blue colour indicates the presence of Fe^{2+} ions in the mixture.

Hence the mixture contains following four ions :

NH_4^+, Fe^{2+}, SO_4^{2-} and Cl^-.

Equations for the formation of A and B.

$$4NaCl + K_2Cr_2O_7 + 3H_2SO_4 \xrightarrow{\text{Heat}} K_2SO_4 + 2Na_2SO_4 + \underset{\text{Chromyl chloride (orange)(A)}}{2CrO_2Cl_2\uparrow} + 3H_2O$$

$$3Fe^{2+} + 2K_3[Fe(CN)_6] \rightarrow \underset{\text{(Blue ppt.) (B)}}{Fe_3[Fe(CN)_6]_2} + 6K^+$$

8. 'Compound gives brown ppt. with alkaline $K_2[HgI_4]$ and so contain NH_4^+ ions.'

'Compound gives blue colour with $K_3[Fe(CN)_6]$ and so contains Fe^{2+} ions.'

'Solution of compound in HCl gives white ppt. with $BaCl_2$ and so it contains SO_4^{2-} ions.'

'Bluish green compound with NH_4^+, Fe^{2+} and SO_4^{2-} suggests that it is Mohr's salt i.e.'

$$FeSO_4(NH_4)_2SO_4.6H_2O$$

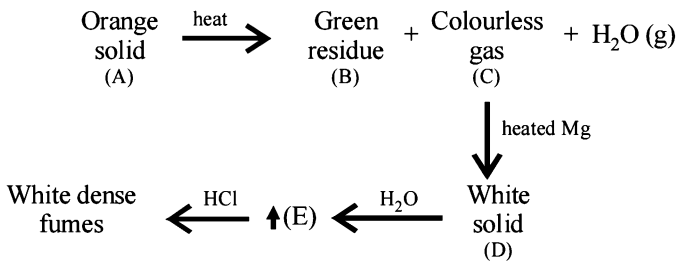
Reactions :

$$3NaOH + NH_3 + 2K_2[HgI_4] \rightarrow \underset{\text{Brown ppt.}}{O\langle^{Hg}_{Hg}\rangle} NH_2I + 4KI + 3NaI + 2H_2O$$

$$3Fe^{2+} + 2K_3[Fe(CN)_6] \longrightarrow \underset{\text{Blue}}{Fe_3[Fe(CN)_6]_2} + 6K^+$$

$$SO_4^{2-} + BaCl_2 \longrightarrow \underset{\text{White ppt.}}{BaSO_4} + 2Cl^-$$

9. Let us summarise the given facts



(i) Formation of white dense fumes by gas (E) with HCl indicates that the gas (E) is ammonia (NH_3).

(ii) Formation of ammonia (E) by the hydrolysis of white solid (D) indicates that (D) should be magnesium nitride, Mg_3N_2.

(iii) Since compound (D) is formed by reaction of gas (C) with magnesium, the colourless gas (C) must be nitrogen.

(iv) Orange colour of the original compound (A) and green colour of the residue (B) indicates that compound (A) is ammonium dichromate, $(NH_4)_2Cr_2O_7$.

Reactions :

$$\underset{\substack{\text{Ammoniumdichromate}\\ \text{Orange Solid (A)}}}{(NH_4)_2Cr_2O_7} \xrightarrow{\Delta} \underset{\text{(C)}}{N_2\uparrow} + \underset{\substack{\text{(B)}\\ \text{Cromium Oxide}\\ \text{green residue}}}{Cr_2O_3} + 4H_2O$$

$$\underset{\text{(C)}}{N_2} + 3Mg \xrightarrow{\Delta} \underset{\text{(D)}}{Mg_3N_2}$$

$$\underset{\text{(D)}}{Mg_3N_2} + 6H_2O \rightarrow 3Mg(OH)_2 + \underset{\text{(E)}}{2NH_3}\uparrow$$

$$\underset{\text{(E)}}{NH_3} + HCl \rightarrow \underset{\text{(White fumes)}}{NH_4Cl}$$

10. As the solid B forms a hydrated salt C with $Al_2(SO_4)_3$; B should be sulphate of a monovalent cation, *i.e.* M_2SO_4.

Now since sulphate of a monovalent cation contains one sulphur atom per mol, weight of metal sulphate obtained by 32.1 g (at. wt. of S) should be the molecular weight of the metal sulphate. Thus, – 0.321 g of sulphur is present in 1.743 g of B

$$\therefore \text{ 32.1 g of sulphur is present in} = \frac{1.743}{0.321} \times 32.1 = 174.3 \text{ g}$$

Thus mol. wt. of B (M_2SO_4) = 174.3 g mol^{-1}

$2x + 32.1 + 64 = 174.3$ (at wt. of $M = x$]

$2x = 78.2 \Rightarrow x = 39.1$

Atomic weight 39.1 corresponds to metal potassium, K.

Thus B is K_2SO_4, and C is $K_2SO_4 . Al_2(SO_4)_3 . 24H_2O$

Nature of compound A : Since A is a binary compound of potassium and it reacts with sulphur to form K_2SO_4, it must be oxide of potassium, probably potassium superoxide (KO_2) which is supported by the given data.

$$\underset{\text{(A)}}{2KO_2} + S \rightarrow \underset{\text{(B)}}{K_2SO_4}$$

$2(39.1 + 32) = 142.2$

32.1 g of S reacts with 142.2 g of KO_2

$$0.321 \text{ g of S reacts with} = \frac{142.2}{32.1} \times 0.321 = 1.422 \text{ g}$$

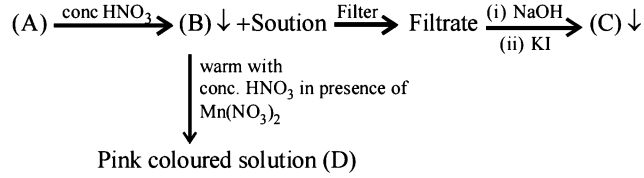
Similarly,

32.1 g of S gives 174.3 g of K_2SO_4

$$0.321 \text{ g of S gives} = \frac{174.3}{32.1} \times 0.321 = 1.743 \text{ g}$$

Both these datas are also given in the problem. Thus A is KO_2.

11. Summary of the given facts.



From the colour of the known compound and reaction involved, it is clear that (A) is red lead (Pb_3O_4) and its various reactions can be represented as below.

$$\underset{\text{(A) Scarlet}}{Pb_3O_4} + 4HNO_3 \longrightarrow \underset{\text{(B) brown}}{PbO_2} + 2Pb(NO_3)_2 + 2H_2O$$

$$\underset{\text{Filtrate}}{Pb(NO_3)_2} + 2KI \longrightarrow \underset{\text{(C)}}{PbI_2}\downarrow + 2KNO_3$$

$$\underset{\text{Ppt. (B)}}{5\ PbO_2} + 2Mn(NO_3)_2 + 4HNO_3$$

$$\longrightarrow \underset{\substack{\text{(D)}\\ \text{Pink colouration}}}{Pb(MnO_4)_2} + 4Pb(NO_3)_2 + 2H_2O$$

12. The reactions are given as follows :

$$3Ca + N_2 \longrightarrow \underset{\substack{\text{Calcium nitride}\\ \text{(white powder)}}}{Ca_3N_2}$$

$$Ca_3N_2 + 6H_2O \longrightarrow 3\,Ca(OH)_2 + \underset{\text{(A)}}{2NH_3}$$

$$Ca(OH)_2 + \underset{\text{from air}}{CO_2} \longrightarrow \underset{\text{Solid layer (B)}}{CaCO_3} + H_2O$$

13. Let us summaries the given facts.

$$\underset{\text{(colourless salt)}}{A} \xrightarrow{250^\circ C} \underset{\substack{\text{(liquid at room}\\ \text{temp, neutral)}}}{C} + \underset{\text{(neutral oxide)}}{B}$$

$$\xrightarrow{P} \text{Strong white dehydrating agent}$$

(i) Since the resulting dehydrating agent is derived from P, it is likely to be P_4O_{10}.

(ii) P_4O_{10} is produced by burning phosphorus in excess of neutral oxide (B) which is likely to be NO_2.

(iii) Thus the salt A should be NH_4NO_3 which explains all given reactions.

$$\underset{(A)}{NH_4NO_3} \xrightarrow{250°C} \underset{(B)}{N_2O} + \underset{(C)}{H_2O}$$

$$P_4 + 10N_2O \longrightarrow P_4O_{10} + 10N_2$$

14. The solubility products of CuS and ZnS are

$K_{sp}(CuS) \approx 10^{-38}$ and $K_{sp}(ZnS) \approx 10^{-22}$

Since $K_{sp}(CuS) << K_{sp}(ZnS)$, very small concentration of S^{2-} is sufficient to cause the precipitation of Cu^{2+} ions. In order to have very small concentration of S^{2-} ions, acidic medium is used. Due to the common ion H^+, the ionisation of H_2S is suppressed:

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

The available concentration of S^{2-} ions in acidic medium causes only the precipitation of CuS and not that of ZnS.

15. (i) The substance is Na_2O_2. When dissolved in water, the solution becomes alkaline with the liberation of H_2O_2

$$Na_2O_2 + 2H_2O \rightarrow 2NaOH + H_2O_2$$

NOTE : Due to the alkaline solution, the red litmus paper will turn into blue, which subsequently changes into white due to oxidation caused by H_2O_2.

(ii) The substance Na_2O merely produces alkaline solution and thus the red litmus paper will turn into blue.

$$Na_2O + H_2O \rightarrow 2NaOH$$

16. Sodium iodide on reaction with HgI_2 gives colourless complex salt, $Na_2[HgI_4]$

$$HgI_2 + 2NaI \rightleftharpoons Na_2[HgI_4]$$

Colour is due to presence of residual HgI_2

But on addition of excess NaI, it becomes colourless due to change of residual HgI_2 into $Na_2[HgI_4]$

$$HgI_2 + 2NaI \text{ (excess)} \rightarrow Na_2[HgI_4] \text{ (colourless)}$$

The orange colour of HgI_2 reappears due to conversion of $Na_2[HgI_4]$ into HgI_2 by means of NaOCl

$$3Na_2HgI_4 + 2NaOCl + 2H_2O \longrightarrow \underset{\text{Orange colour}}{3HgI_2} + 2NaCl + 4NaOH + 2NaI_3$$

17. Summary of the given facts

$$\underset{\text{(Blue aq. solution)}}{MSO_4} \xrightarrow[H_2S]{H^+} \underset{\text{Black (A)}}{MS\downarrow} \xrightarrow[KOH]{warm} \text{Insoluble}$$

$$MSO_4 \xrightarrow{KI,\ H^+} \text{yellow solution. (B)}$$

The reaction corresponds to copper sulphate.

$$CuSO_4 + H_2S \xrightarrow{H^+} \underset{\text{Black(A)}}{CuS\downarrow} + H_2SO_4$$

$$2CuSO_4 + 2KI \xrightarrow{H^+} \underset{\text{White (B)}}{Cu_2I_2\downarrow} + I_2 + K_2SO_4$$

$$I_2 + I^- \longrightarrow I_3^- \text{ (Yellow solution)}$$

18. $$\underset{\text{Borax}}{Na_2B_4O_7.10H_2O} \xrightarrow{\Delta} Na_2B_4O_7 \xrightarrow{740°C} 2NaBO_2 + \underset{\text{Transparent}}{B_2O_3}$$

$$\text{Salt of Co} \xrightarrow{\Delta} CoO + \text{gas}$$

$$CoO + B_2O_3 \longrightarrow \underset{\text{Cobalt metaborate (blue)}}{Co(BO_2)_2}$$

19. $$\underset{\text{(white)}}{A} \xrightarrow{\text{dil. } H_2SO_4} \underset{\text{(colourless gas)}}{B} + \underset{\text{(colourless solution)}}{C}$$

$$B \xrightarrow{K_2Cr_2O_7/H^+} \text{Green solution} + \underset{\text{(coloured)}}{D\downarrow} (\text{ burns in air to form gas E})$$

$$E\uparrow + B\uparrow \longrightarrow D + \text{Colourless liquid} \xrightarrow{\text{anhy. } CuSO_4} \text{Blue colour}$$

$$C \xrightarrow[\text{or NaOH}]{\text{aq. } NH_3} \text{White precipitate} \xrightarrow[\text{reagent}]{\text{excess of}} \text{Clear solution}$$

The above set leads to following conclusions.

(i) Since the gas (B) is colourless and turns acidified $K_2Cr_2O_7$ solution green, it should be H_2S.

(ii) Since H_2S gas is obtained by the reaction of dil. H_2SO_4 on A, the latter must be sulphide.

(iii) The white colour of the sulphide (A) points out towards ZnS.

Thus the various reactions can be written as given below.

$$\underset{(A)}{ZnS} + H_2SO_4(dil) \longrightarrow \underset{(C)}{ZnSO_4} + \underset{(B)}{H_2S}\uparrow$$

$$\underset{(B)}{3H_2S} + K_2Cr_2O_7 + 4H_2SO_4 \longrightarrow \underset{\text{(green)}}{K_2SO_4 + Cr_2(SO_4)_3} + 7H_2O + \underset{(D)}{3S}$$

$$\underset{(D)}{S} + O_2 \longrightarrow \underset{(E)}{SO_2}\uparrow \xrightarrow{2H_2S(B)} \underset{\text{(colourless liq)}}{2H_2O} + \underset{D}{3S}\downarrow$$

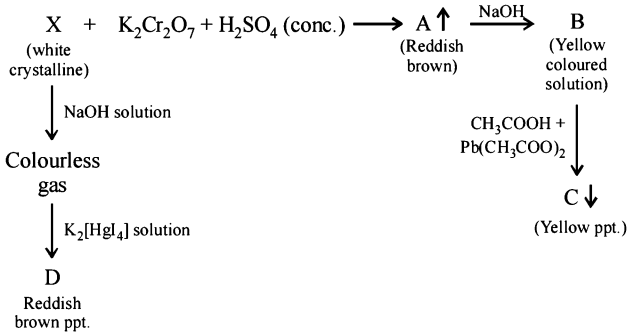
$$\underset{\text{(white)}}{CuSO_4} + \underset{\text{(colourless liquid)}}{5H_2O} \longrightarrow \underset{\text{(blue)}}{CuSO_4 . 5H_2O}$$

(Hydrated $CuSO_4$)

$$\underset{(C)}{ZnSO_4} + 2NaOH \longrightarrow \underset{\text{white. ppt}}{Zn(OH)_2}\downarrow$$

$$\xrightarrow[\text{(excess)}]{2NaOH} \underset{\text{(soluble)}}{Na_2ZnO_2} + 2H_2O$$

20. Let us summarise the given facts.



NOTE : Reaction of compound X with NaOH solution and subsequent treatments indicate that X has NH_4^+ radical. On the other hand, reaction of X with $K_2Cr_2O_7$ solution, conc. H_2SO_4 and subsequent treatments indicate that A has Cl^- radical. Thus compound X is NH_4Cl which explains all the above reactions.

$$4NH_4Cl + K_2Cr_2O_7 + 3H_2SO_4$$
(X)

$$\longrightarrow K_2SO_4 + 2(NH_4)_2SO_4 + \underset{\text{Chromyl chloride, (A)}\\\text{(reddish brown)}}{2CrO_2Cl_2\uparrow} + 3H_2O$$

$$CrO_2Cl_2 + 4NaOH \longrightarrow 2NaCl + \underset{\text{Sod.chromate,(B)}\\\text{(yellow coloured Solution)}}{Na_2CrO_4} + 2H_2O$$

$$\underset{B}{Na_2CrO_4} + (CH_3COO)_2Pb \longrightarrow 2CH_3COONa + \underset{\text{Lead chromate, (C)}\\\text{(yellow ppt.)}}{PbCrO_4\downarrow}$$

$$\underset{(X)}{NH_4Cl} + NaOH \longrightarrow NH_3\uparrow + NaCl + H_2O$$

$$NH_3 + 2K_2HgI_4 + 3KOH$$

$$\longrightarrow \left[\begin{array}{c} Hg \\ O \quad NH_2I \\ Hg \end{array}\right] + 7KI + 2H_2O$$

Iodide of Millon's base, (D)
(reddish brown ppt)

21. [A = HgI_2(yellow), B = KI(colourless)]

$$HgI_2 + H_2S \longrightarrow \underset{(C)}{HgS} + 2HI \;;\; HgI_2 \xrightarrow{\text{aqua regia}} HgCl_2 \;;$$

$$HgCl_2 + SnCl_2 \longrightarrow \underset{\text{(greyish black)}}{Hg\downarrow} + \underset{(D)}{SnCl_4}$$

$$2KI + HgI_2 \longrightarrow \underset{\text{(orange)}}{K_2[HgI_4]} \;;$$

$$2K_2[HgI_4] + NH_3 + 3KOH \longrightarrow \underset{\text{iodide of Milon's base (brown)}}{[HgOHgNH_2]I\downarrow} + 7KI + 2H_2O$$

$$HgI_2 + Na_2CO_3 \longrightarrow 2NaI \xrightarrow{CCl_4} \text{Violet layer}$$
$$\downarrow AgNO_3$$
$$AgI\downarrow \text{ (Yellow)}$$
(Insoluble in ammonia)

G. Comprehension Based Questions

For 1-3

Reaction of Y indicates that it is Fe^{3+} salt.

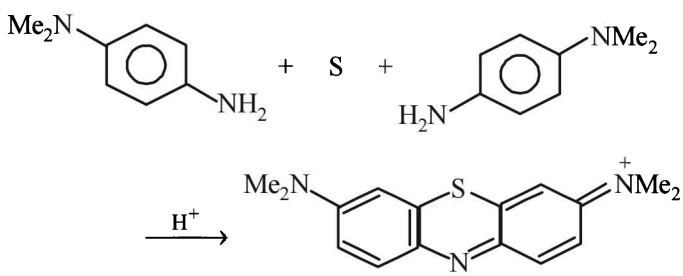
$$\underset{Y}{4Fe^{3+}} + \underset{\text{hexacyanoferrate (II) or ferrocyanide}}{3[Fe(CN)_6]^{4-}} \longrightarrow \underset{\text{Intense blue ppt. soluble in excess of ferrocyanide}}{Fe_4[Fe(CN)_6]_3\downarrow}$$

$$\underset{Y}{Fe^{3+}} + \underset{\text{hexacyanoferrate (III) or ferricyanide}}{[Fe(CN)_6]^{3-}} \longrightarrow \underset{\text{Brown colour}}{Fe[Fe(CN)_6]}$$

NOTE : since the product formed (methylene blue) has sulphur in its structure, it should be supplied by the compound X which is thus Na_2S.

$$Na_2S + 2H^+ \longrightarrow H_2S + 2Na^+$$

$$FeCl_3 + H_2S \longrightarrow FeCl_2 + 2HCl + S$$



Methylene blue

Thus

1. **(d)** **2.** **(c)** **3.** **(b)**

4. **(a)** Lead salts give white precipitate of $PbCl_2$ with dil. HCl which is soluble in hot water.
$Pb^{++} + 2Cl^- \longrightarrow PbCl_2$ (White ppt) soluble in hot water

5. **(d)** The filtrate on treatment with ammoniacal H_2S gives a precipitate which dissolves in aqueous NaOH containing H_2O_2 giving a coloured solution. It contains Cr^{3+} ion.

$$Cr^{+3} + 3NH_4OH \xrightarrow[\text{medium}]{H_2S \text{ in ammoniacal}} \underset{\text{(Green)}}{Cr(OH)_3\downarrow}$$

$$2Cr(OH)_3 + 3H_2O_2 + 4NaOH \rightarrow \underset{\text{(yellow colour)}}{2Na_2CrO_4} + 8H_2$$

6. **(b)** $\underset{(M1)}{Ni^{2+}} + \underset{(Q)}{4HCl} \longrightarrow \underset{\text{Tetrahedral}}{[NiCl_4]^{2-}}$

$$\underset{(M1)}{Ni^{2+}} + \underset{(R)}{4KCN} \longrightarrow \underset{\text{Square planar}}{[Ni(CN)_4]^{2-}}$$

[**Note:** $Co^{2+} + 6CN^- \longrightarrow \underset{\text{Octahedral}}{[Co(CN)_6]^{4-}}$]

7. (d)

$$\underset{(M2)}{Zn^{2+}} + \underset{(S)}{2OH^-} \longrightarrow \underset{\text{white ppt.}}{Zn(OH)_2\downarrow} \xrightarrow[\text{excess}]{OH^-} \underset{\text{soluble}}{[Zn(OH)_4]^{2-}}$$

H. Assertion & Reason Type Questions

1. (d) Cd^{2+} is a 2nd group radical and Ni^{2+} is a 4th group radical. So solubility product of NiS has to be more than CdS. Further Cd^{2+} gives yellow colour of CdS with H_2S, but Ni^{2+} gives black colour of NiS with H_2S. So both assertion and statement are wrong. (d) is correct choice.

2. (b) Sulphate is estimated as $BaSO_4$ because of its insolubility in water. $BaSO_4$ forms a white ppt. Therefore reason is correct but do not explain the assertion.

I. Integer Value Correct Type

1. (7) All except MnS (buff coloured) and SnS_2 (yellow) are black in colour.

Section-B JEE Main/ AIEEE

1. (c) When H_2S is passed through Hg_2S we get a mixture of mercurous sulphide and mercury ($Hg_2S + Hg$).

2. (b) When we add NH_4Cl, it suppresses the ionisation of NH_4OH and prevents the precipitation of higher group hydroxide in gp(III).

NOTE : Further ferric chloride and chromium chloride form different colour precipitates with NH_4OH.

$$FeCl_3 + 3NH_4OH \longrightarrow \underset{\text{reddish brown}}{Fe(OH)_3\downarrow} + 3NH_4Cl$$

$$CrCl_3 + 3NH_4OH \longrightarrow \underset{\text{Bluish green.}}{Cr(OH)_3} + 3NH_4Cl$$

3. (a) Between AgCl and AgI, AgI is less soluble, hence ammonia can dissolve ppt. of AgCl only due to formation of complex as given below:

$$AgCl + 2NH_3 \rightarrow [Ag(NH_3)_2]Cl$$

4. (a) Prussian blue $Fe_4[Fe(CN)_6]_3$ is formed in lassaigne test for nitrogen.

$$3Na_4[Fe(CN)_6 + 4Fe^{3+} \longrightarrow \underset{\text{Prussian blue}}{Fe_4[Fe(CN)_4]_6} + 12Na^+$$

5. (b) The complex $[CoCl(NH_3)_5]^+$ decomposes under acidic medium, so

$$[CoCl(NH_3)_5]^+ + 5H^+ \longrightarrow Co^{2+} + 5NH_4^+ + Cl^-$$