Objective Questions I (Only one correct option)

1. An organic compound X showing the following solubility profile is (2019 Main, 8 April I)



- **2.** When metal 'M' is treated with NaOH, a white gelatinous precipitate 'X' is obtained, which is soluble in excess of NaOH. Compound 'X' when heated strongly gives an oxide which is used in chromatography as an adsorbent. The metal *'M'* is (2018 Main) (a) Zn (b) Ca (c) Al (d) Fe
- 3. In the following reaction sequence in aqueous solution, the species X, Y and Z, respectively, are (2016 Adv.)

$$\begin{split} & \operatorname{S_2O_3^{2-}} \xrightarrow{\operatorname{Ag}^+} \underbrace{X}_{(\operatorname{Clear solution})} \xrightarrow{\operatorname{Ag}^+} \underbrace{Y}_{(\operatorname{White ppt.})} \xrightarrow{\operatorname{With time}} \underbrace{Z}_{(\operatorname{Black ppt.})} \\ & (a) \left[\operatorname{Ag}(\operatorname{S_2O_3})_2\right]^{3-}, \operatorname{Ag}_2\operatorname{S_2O}_3, \operatorname{Ag}_2\operatorname{S} \\ & (b) \left[\operatorname{Ag}(\operatorname{S_2O}_3)_3\right]^{5-}, \operatorname{Ag}_2\operatorname{SO}_3, \operatorname{Ag}_2\operatorname{S} \\ & (c) \left[\operatorname{Ag}(\operatorname{SO}_3)_2\right]^{3-}, \operatorname{Ag}_2\operatorname{S_2O}_3, \operatorname{Ag} \\ & (d) \left[\operatorname{Ag}(\operatorname{SO}_3)_3\right]^{3-}, \operatorname{Ag}_2\operatorname{SO}_4, \operatorname{Ag} \end{split}$$

4. In Carius method of estimation of halogens 250 mg of an organic compound gave 141 mg of AgBr. The percentage of bromine in the compound is (atomic mass Ag = 108, Br = 80) (2015 Main) (d) 60

- **5.** Upon treatment with ammoniacal H_2S , the metal ion that precipitates as a sulphide is (2013 Adv.) (a) Fe (III) (b) Al (III) (d) Zn(II) (c) Mg (II)
- **6.** Passing H_2S gas into a mixture of Mn^{2+} , Ni^{2+} , Cu^{2+} and $H\sigma^{2+}$ ions in an acidified aqueous solution precipitates

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(a) Cu	uS and HgS		(b)	MnS and	CuS	(2011)

- 7. 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, 3M) (a) Pb^{2+} (b) Hg^{2+} (c) Cu^{2+} (d) Co^{2+}
- 8. MgSO₄ on reaction with NH₄OH and Na₂HPO₄ forms a white crystalline precipitate. What is its formula? (2006) (a) $Mg(NH_4)PO_4$ (b) $Mg_3(PO_4)_2$ (c) MgCl₂ · MgSO₄ (d) MgSO₄
- **9.** $CuSO_4$ decolourises on addition of KCN, the product is (a) $[Cu(CN)_4]^{2-}$ (2006, 3M) (b) Cu^{2+} get reduced to form $[Cu(CN)_4]^{3-}$ (c) Cu(CN)₂ (d) CuCN
- **10.** A solution when diluted with H_2O and boiled, it gives a white precipitate. On addition of excess NH₄Cl/NH₄OH, the volume of precipitate decreases leaving behind a white gelatinous precipitate. Identify the precipitate which dissolves in NH₄OH / NH₄Cl. (2006, 3M) (a) Zn(OH)₂ (b) Al(OH)₃ (c) Mg(OH)₂ (d) Ca(OH)₂
- **11.** A metal nitrate reacts with KI to give a black precipitate which on addition of excess of KI convert into orange colour solution. The cation of metal nitrate is (2005, 1M) (a) Hg^{2+} (b) Bi^{3+} (c) Sn^{2+} (d) Pb^{2+}
- **12.** $(NH_4)_2 Cr_2 O_7$ on heating gives a gas which is also given by

	(2004, 1M)
(a) Heating NH ₄ NO ₂	(b) Heating NH ₄ NO ₃
(c) $Mg_3N_2 + H_2O$	(d) Na(comp.) + H_2O_2

13. A sodium salt of an unknown anion when treated with MgCl₂ gives white precipitate only on boiling. The anion is (2004, 1M) (d) NO_3^-

(a) SO_4^{2-} (b) HCO_3^- (c) CO_3^{2-}

14. $[X] + H_2SO_4 \rightarrow [Y]$ a colourless gas with irritating smell

 $[Y] + K_2Cr_2O_7 + H_2SO_4 \longrightarrow$ green solution

[X] and $[Y]$ are		(2003, 1M)
(a) SO_3^{2-} , SO_2	(b) Cl ⁻ , HCl	
(c) S ²⁻ , H ₂ S	(d) CO_3^{2-} , CO_2	

(2015 Adv.)

- **15.** 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*. (2002, 3M) (a) $X = CO_2$, $Y = CI_2$ (b) $X = CI_2$, $Y = CO_2$ (c) $X = CI_2$, $Y = H_2$ (d) $X = H_2$, $Y = CI_2$
- 16. An aqueous solution of a substance gives a white precipitate on treatment with dilute hydrochloric acid, which dissolves on heating. When hydrogen sulphide is passed through the hot acidic solution, a black precipitate is obtained. The substance is a (2000, 1M) (a) Hg₂²⁺ salt (b) Cr²⁺ salt (c) Ag⁺ salt (d) Pb²⁺ salt
- 17. In nitroprusside ion the iron and NO exist as Fe (II) and NO⁺ rather than Fe (III) and NO. These forms can be differentiated by (1998, 2M) (a) estimating the concentration of iron (b) measuring the concentration of CN (c) measuring the solid state magnetic moment (d) thermally decomposing the compound
- 18. An aqueous solution FeSO₄ · Al₂(SO₄)₃ and chrome alum is heated with excess of Na₂O₂ and filtered. The materials obtained are (1996, 1M)
 (a) a colourless filtrate and a green residue
 (b) a yellow filtrate and a green residue
 (c) a yellow filtrate and a brown residue
 (d) a green filtrate and brown residue
- **19.** The brown ring complex compound is formulated as $[Fe(H_2O)_5(NO)^+] SO_4$. The oxidation state of iron is

- **20.** Which one amongst the following pairs of ions cannot be separated by H_2S in dilute HCl? (1986, 1M) (a) Bi^{3^+} , Sn^{4^+} (b) Al^{3^+} , Hg^{2^+} (c) Zn^{2^+} , Cu^{2^+} (d) Ni^{2^+} , Cu^{2^+}
- **21.** The compound insoluble in acetic acid is
(a) calcium oxide
(b) calcium carbonate
(c) calcium oxalate(1986, 1M)
(d) calcium hydroxide
- **23.** For the equilibrium, $2H_2O \longrightarrow H_3O^+ + OH^-$, the value of ΔG° at 298 K is approximately (2019 Main 11 Jan II) (a) -80 kJ mol^{-1} (b) 100 kJ mol $^{-1}$ (c) 80 kJ mol^{-1} (d) -100 kJ mol^{-1}

Objective Questions II

(One or more than one correct option)

24. The correct option(s) to distinguish nitrate salts to Mn^{2+} and Cu^{2+} taken separately is (are) (2018 Adv.)

- (a) Mn²⁺ shows the characteristic green colour in the flame test
- (b) Only Cu^{2+} shows the formation of precipitate by passing H_2S in acidic medium
- (c) Only Mn²⁺ shows the formation of precipitate by passing H₂S in faintly basic medium
- (d) Cu²⁺ / Cu has higher reduction potential than Mn²⁺ / Mn (measured under similar conditions)
- **25.** The reagent(s) that can selectively precipitate S^{2-} from a mixture of S^{2-} and SO_4^{2-} in aqueous solution is (are)

(a)
$$CuCl_2$$
 (b) $BaCl_2$
(c) $Pb(OOCCH_3)_2$ (d) $Na_2[Fe(CN)_5NO]$

26. The pair(s) of ions where both the ions are precipitated upon passing H_2S gas in presence of dilute HCl, is (are)

(a)
$$Ba^{2+}$$
, Zn^{2+} (b) Bi^{3+} , Fe^{3+}
(c) Cu^{2+} , Pb^{2+} (d) Hg^{2+} , Bi^{3+}

27. For the given aqueous reaction which of the statement(s) is

(are) true? Excess KI + K₃[Fe(CN)₆] $\xrightarrow{\text{Dilute H}_2\text{SO}_4}$ Brownish-yellow solution $\downarrow \text{ZnSO}_4$ (White precipitate + Brownish-yellow filtrate) $\downarrow \text{Na}_2\text{S}_2\text{O}_3$ Colourless solution (2012) (a) The first reaction is a redox reaction

- (b) White precipitate is $Zn_{2}[Fe(CN)_{6}]_{2}$
- (c) Addition of filtrate to starch solution gives blue colour
- (d) White precipitate is soluble in NaOH solution
- **28.** A solution of colourless salt *H* on boiling with excess NaOH produces a non-flammable gas. The gas evolution ceases after sometime. Upon addition of Zn dust to the same solution, the gas evolution restarts. The colourless salt(s) *H* is (are) (2008, 4M) (a) NH_4NO_3 (b) NH_4NO_2 (c) NH_4Cl (d) $(NH_4)_2SO_4$
- 29. Which of the following statement(s) is(are) correct when a mixture of NaCl and K₂Cr₂O₇ is gently warmed with conc. H₂SO₄? (1998, 2M)
 (a) A deep red vapour is evolved
 (b) The vapour when passed into NaOH solution gives a yellow solution of Na₂CrO₄

(c) Chlorine gas is evolved

- (d) Chromyl chloride is formed
- 30. Which of the following statement(s) is (are) correct with reference to the ferrous and ferric ions ? (1998, 2M) (a) Fe³⁺ gives brown colour with potassium ferricyanide (b) Fe²⁺ gives blue precipitate with potassium ferricyanide
 - (c) Fe³⁺ gives red colour with potassium thiocyanate
 - (d) Fe^{2+} gives brown colour with ammonium thiocyanate

31. The reagents, NH_4Cl and aqueous NH_3 will precipitate

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			(1991, 1M)
(a) Ca ²⁺	(b) Al ³⁺	(c) Bi ³⁺	(d) Mg ²⁺
(e) Zn^{2+}			

Assertion and Reason

Read the following questions and answer as per the direction given below :

- (a) Statement I is correct Statement II is correct Statement II is a correct; explanation of Statement I
- (b) Statement I is correct; Statement II is correct Statement II is not the correct explanation of Statement I.
- (c) Statement I is correct; Statement II is incorrect.
- (d) Statement I is incorrect; Statement II is correct.
- **32.** Statement I Sulphate is estimated as BaSO₄, not as MgSO₄.

Statement II Ionic radius of Mg^{2+} is smaller than that of Ba^{2+} . (1998, 2M)

33. Statement I A very dilute acidic solution of Cd²⁺ and Ni²⁺ gives yellow precipitate of CdS on passing H₂S.

Statement II Solubility product of CdS is more than that of NiS. (1989, 2M)

Passage Based Questions

Passage 1

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 summarised in the scheme given below

Tetrahedral
$$\leftarrow \frac{Q}{\text{excess}} = M_1 \xrightarrow{R} \text{Square planar}$$

Tetrahedral $\leftarrow \frac{Q}{\text{excess}} = M_2 \xrightarrow{R} \text{Tetrahedral}$

S, stoichiometric amount

White precipitate \xrightarrow{S} Precipitate dissolves

34. M_1 , Q and R, respectively are

(a) Zn^{2+} , KCN and HCl	(b) Ni^{2+} , HCl and KCN
(c) Cd^{2+} , KCN and HCl	(d) Co^{2+} , HCl and KCN

35. Reagent S is (a) $K_4[Fe(CN)_6]$ (b) Na_2HPO_4 (c) K_2CrO_4 (d) KOH

Passage 2

An aqueous solution of a mixture of two inorganic salts, when treated with dilute HCl, gave a precipitate (P) and filtrate (Q). The precipitate (P) was found to dissolve in hot water. The filtrate (Q) remained unchanged, when treated with H₂S in a dilute mineral acid

medium. However, it gave a precipitate (R) with H₂S in an ammoniacal medium. The precipitate R gave a coloured solution (S), when treated with H₂O₂ in an aqueous NaOH medium.

36. The precipitate P contains (2013 Adv.) (a) Pb^{2+} (b) Hg_2^{2+} (c) Ag^+ (d) Hg^{2+}

37. The coloured solution S contains
(a)
$$Fe_2(SO_4)_3$$
 (b) $CuSO_4$ (c) $ZnSO_4$ (d) Na_2CrO_4

Passage 3

When a metal rod M is dipped into an aqueous colourless concentrated solution of compound N, the solution turns light blue. Addition of aqueous NaCl to the blue solution gives a white precipitate O. Addition of aqueous NH₃ dissolves O and gives an intense blue solution. (2011)

- **38.** The metal rod M is
(a) Fe(b) Cu(c) Ni(d) Co**39.** The compound N is
(a) AgNO3
(c) Al(NO3)3(b) Zn(NO3)2
(d) Pb(NO3)2
- 40. The final solution contains

 (a) [Pb(NH₃)₄]²⁺ and [CoCl₄]²⁻
 (b) [Al(NH₃)₄]³⁺ and [Cu(NH₃)₄]²⁺
 (c) [Ag(NH₃)₂]⁺ and [Cu(NH₃)₄]²⁺
 (d) [Ag(NH₃)₂]⁺ and [Ni(NH₃)₆]²⁺

Passage 4

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 colouration 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 colouration due to the formation of *Z*.

(2009, 1M)
) NaCl
) Na ₂ S
(2009, 1M)
) FeCl ₂
) $ZnCl_2$
(2009, 1M)
) $Fe[Fe(CN)_6]$
) $K_2 Zn_3 [Fe(CN)_6]_2$

Fill in the Blanks

- The formula of the deep red liquid formed on warming dichromate with KCl in concentrated sulphuric acid is... (1993, 1M)
- 45. If metal ions of group III are precipitated by NH₄Cl and NH₄OH without prior oxidation by conc. HNO₃..... is not completely precipitated. (1984, 1M)

True/False

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

Integer Answer Type Question

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

Subjective Questions

49.
$$B \xrightarrow{\text{moist air}} MCl_4 \xrightarrow{\text{Zn}} A$$

(White fumes $M = (\text{Transition} \text{element colourless}) \xrightarrow{\text{Colour}} A$

Identify the metal M and hence MCl_4 . Explain the difference in colours of MCl_4 and A. (2005, 4M)

50.
$$\operatorname{Fe}^{3+} \xrightarrow{\operatorname{SCN}^{-} (\operatorname{excess})} \operatorname{Blood} \operatorname{red} (A) \xrightarrow{\operatorname{F}^{-} (\operatorname{excess})} \operatorname{Colourless} (B)$$

Identify A and B.

- (i) Write IUPAC name of A and B.
- (ii) Find out spin only magnetic moment of *B*. (2005)
- **51.** A_1 and A_2 are two ores of metal *M*. A_1 on calcination gives black precipitate, CO₂ and water.

$$A_{1} \xrightarrow{\text{Calcination}} \text{Black solid} + \text{CO}_{2} + \text{OH}_{2}$$

$$\xrightarrow{\text{dil. HCl}} I_{2} + \text{ppt}$$

$$A_{2} \xrightarrow{\text{Roasting}} \text{Metal} + \text{Gas}$$

$$\downarrow K_{2}\text{Cr}_{2}\text{O}_{7} + \text{H}_{2}\text{SO}_{4}$$
Green colour

Identify A_1 and A_2 .

(2004)

- **52.** A salt mixture consists of a yellow solid (*A*) and a colourless solid (*B*). The aqueous solution of the mixture
 - (i) On passing H₂S, we get a black precipitate of (C), which dissolves only in aqua-regia. On extraction and reaction with SnCl₂ a greyish white precipitate is obtained.
 - (ii) On treatment with ammonium hydroxide a reddish brown precipitate (*D*) is obtained.

The sodium extract of the solution gives the following tests:

- (i) On reaction with AgNO₃ it gives a yellow precipitate which is insoluble in NH₃.
- (ii) On shaking with FeCl₃ and CCl₄ a violet colouration in CCl₄ layer is obtained.

Mixture on performing flame test gives lilac colour. Identify the compounds (A), (B), (C) and (D). (2003)

53. 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 B is obtained. Neutralising the solution of B with acetic acid and on subsequent addition of lead acetate a yellow precipitate C is obtained.

When X is heated with NaOH solution, 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)

- **54.** 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 NH₃ 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, 10M)
- **55.** Write the chemical reactions associated with the 'borax bead test' of cobalt (II) oxide. (2000, 3M)
- **56.** 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, 4M)
- **57.** Write the chemical reactions associated with the 'brown ring test'. (2000, 1M)
- 58. An aqueous solution containing one mole of HgI₂ and two moles of NaI is orange in colour. On addition of excess NaI the solution becomes colourless. The orange colour reappears on subsequent addition of NaOCl. Explain with equations. (1999, 3M)
- **59.** 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, 2M)
- **60.** Aluminium sulphide gives a foul odour when it becomes damp. Write a balanced chemical equation for the reaction. (1997)
- **61.** A soluble compound of a poisonous element M, when heated with Zn/H_2SO_4 gives a colourless and extremely poisonous gaseous compound N, which on passing through a heated tube gives a silvery mirror of element M. Identify M and N. (1997)

62. 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, 3M)

- **63.** Gradual addition of KI solution of $Bi(NO_3)_3$ solution initially produces a dark brown precipitate which dissolves in excess of KI to give a clear yellow solution. Write chemical equations for the above reactions. (1996, 2M)
- **64.** 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 ppt *C*. The brown ppt *B* on warming with conc. HNO_3 in the presence 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, 4M)

65. An orange solid *A* on heating gave a green residue *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 the reaction involved.

(1993, 3M)

66. The acidic aqueous solution of ferrous ion forms a brown complex in the presence of NO_3^- , by the following two steps :

$$[\operatorname{Fe}(\operatorname{H}_2\operatorname{O})_6]^{2^+} + \operatorname{NO}_3^- + \operatorname{H}^+ \longrightarrow \dots + [\operatorname{Fe}(\operatorname{H}_2\operatorname{O})_6]^{3^+}$$
$$[\operatorname{Fe}(\operatorname{H}_2\operatorname{O})_6]^{2^+} + \dots \longrightarrow \dots \dots + \operatorname{H}_2\operatorname{O}$$

Complete and balance the equation. (1993, 2M)

- **67.** A light bluish green crystalline compound responds to the following tests
 - (i) Its aqueous solution gives a brown precipitate or colouration with $K_2[HgI_4]$.
 - (ii) Its aqueous solution gives a blue colour with $K_3[Fe(CN)_6]$.
 - (iii) Its solution in hydrochloric acid gives a white precipitate with BaCl₂.

Identify the ions present and suggest the formula of the compound. (1992, 4M)

68. In the following reaction, identify the compounds/reaction conditions represented by the alphabets *A* and *B*.

$$PbS \xrightarrow{\text{Heat in}} A + PbS \xrightarrow{B} Pb + SO_2$$
(1991, 1M)

- **69.** Give reason in one or two sentences for the following "The hydroxides of aluminium and iron are insoluble in water. However, NaOH is used to separate one from other. (1991, 2M)
- **70.** The gas liberated, on heating a mixture of two salts with NaOH, gives a reddish brown precipitate with an alkaline

solution of K_2 HgI₄. The aqueous solution of the mixture on treatment with BaCl₂ 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 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, 4M)

- **71.** Write the balanced chemical equations for the following
 - (i) Silver chloride is treated with aqueous sodium cyanide and the product thus formed is allowed to react with zinc in alkaline medium.
 - (ii) Cobalt (II) solution reacts with KNO₂ in acetic acid medium. (1989, 2M)
- **72.** Give reasons for, "The colour of mercurous chloride, Hg_2Cl_2 , changes from white to black when treated with ammonia." (1988, 1M)
- 73. A mixture of two salts was treated as follows :
 - (i) The mixture was heated with maganese 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 K₂HgI₄ to give brown precipitate.

Identify the two salts. Give ionic equations for reactions involved in the tests (i), (ii) and (iii). (1987, 5M)

- 74. Write balanced equation for the following "potassium permanganate is reacted with warm solution of oxalic acid in the presence of sulphuric acid." (1987, 1M)
- **75.** Mention the products formed in the following:
 - (i) Zinc oxide is treated with excess of sodium hydroxide solution.
 - (ii) Iodine is added to a solution of stannous chloride.
 - (iii) Sulphur dioxide gas, water vapour and air are passed over heated sodium chloride. (1986, 3M)
- 76. What happen when
 - (i) hydrogen sulphide is bubbled through an aqueous solution of sulphur dioxide.
 - (ii) aqueous ammonia is added dropwise to a solution of copper sulphate till it is in excess.
 - (iii) tin is treated with concentrated nitric acid.
 - (iv) CrCl₃ solution is treated with sodium hydroxide and then with hydrogen peroxide.
 - (v) Pb_3O_4 is treated with nitric acid. (1985, 5M)
- 77. Write down the balanced equations for the reactions, when, 'a mixture of potassium chlorate, oxalic acid and sulphuric acid is heated. (1985, 1M)

78. 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 effervesces with acid giving of carbon dioxide. Identify A, B and Y and write down the equation for the thermal decomposition of X. (1984, 4M)

- **79.** Compound *A* is a light green crystalline solid. It gives the following tests
 - (i) It dissolves in dilute sulphuric acid. No gas is produced.
 - (ii) A drop of KMnO₄ 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 compound A, B, C, D and E. (1980, 4M)

- 80. Explain the following in not more than two sentences. A solution of FeCl₃ in water gives a brown precipitate on standing. (1980, 1M)
- **81.** The precipitation of second group sulphides in qualitative analysis is carried out with hydrogen sulphide in the presence of hydrochloric acid but not in nitric acid. Explain. (1979, 2M)
- 82. A white amorphous powder A on heating yields a colourless, non-combustible gas B and a solid C. The later compound assumes a yellow colour on heating and changes to white on cooling. C dissolves in dilute hydrochloric acid and the resulting solution gives a white precipitate with $K_4Fe(CN)_6$ solution. A dissolves in dil. HCl with the evolution of gas, which is identical in all respect with B.

The gas B turns lime water milky, but the milkiness disappears with the continuous passage of gas. The solution of A as obtained above, gives a white ppt E on addition of NaOH solution, which dissolves on further addition of base. Identify the compounds A, B, C, D and E. (1979, 4M)

Answers

1. (c)	2. (c)	3. (a)	4. (a)	29. (a, b, c, d)	30. (b, c)	31. (b, c)	32. (b)
5. (d)	6. (a)	7. (b)	8. (a)	33. (c)	34. (b)	35. (d)	36. (d)
9. (b)	10. (a)	11. (b)	12. (a)	37 . (d)	38 . (b)	39 . (a)	40 . (c)
13. (b)	14. (a)	15. (c)	16. (d)	41 (J)	40 (a)	42 (h)	10. (c) 14. CrO Cl
17. (c)	18. (c)	19. (a)	20. (a)	41. (d)	42. (C)	43. (b)	44. CIO_2CI_2
21. (c)	22. (c)	23. (c)	24. (b,d)	45. Fe^{3+}	46. True	47. True	48. (6 or 7)
25. (a)	26. (c, d)	27. (a, c, d)	28. (a, b)	50. (5.92 BM)			

Hints & Solutions

1. *m*-cresol is the organic compound that shows the following solubility profile.



m-cresol on reaction with 10% NaOH forms 3-methyl sodiumphenoxide ion.



It does not react with H_2O , 5% HCl and 10% NaHCO₃. **Oleic acid** ($C_{18}H_{34}O_2$) is soluble in 10% NaOH and 10% NaHCO₃ due to the presence of COOH group. **Benzamide** $(C_6H_5CNH_2)$ is insoluble in 5% HCl, 10% NaOH and 10% NaHCO₃ due to the presence —CONH₂ group. *o*-toluidine is soluble in 5%. HCl due to presence of basic group (—NH₂) attached to ring.

2. Among the given metals Al forms white gelatinous ppt. with NaOH.

0

Hence, the probable metal can be Al. This ppt. is dissolved in excess of NaOH due to the formation of sodium metal Aluminate. Both the reactions are shown below.

$$\begin{array}{c|c} Al^{3+} & \underline{\operatorname{NaOH}} & Al(OH)_3 & \underbrace{\operatorname{Excess of NaOH}}_{\begin{array}{c} \text{blue} \\ \end{array}} \\ \begin{array}{c} \text{NaAlO}_2 \\ \text{Solium} \\ \text{metaaluminate} \\ \text{soluble} \\ \text{soluble} \\ \end{array}$$

Aluminium hydroxide on strong heating gives alumina (Al_2O_3) which is used as an adsorbent in chromatography. This reaction can be seen as :

$$2Al(OH)_3 \xrightarrow{\Delta} Al_2O_3 + 3H_2O_3$$

Thus, metal M is Al.

Ca, being below sodium in electrochemical reactivity series, cannot displaces Na from its aqueous solution.

Zn reacts with NaOH to form sodium zincate which is a soluble compound.

Fe reacts with sodium hydroxide to form tetrahydroferrate (II) sodium which is again a soluble complex.

3.
$$2S_2O_3^{2-} + Ag^+ \longrightarrow [Ag(S_2O_3)_2]^{3-}$$

(Clear solution)

$$[Ag(S_2O_3)_2]^{3-} + 3Ag^+ \longrightarrow 2Ag_2S_2O_3$$
(White ppt.)

 $Ag_2S_2O_3 + H_2O \longrightarrow Ag_2S + H_2SO_4$ (Black ppt.)

4. Given, Weight of organic compound = 250 mg

Weight of AgBr = 141 mg

 \therefore According to formula of % of bromine by Carius method

% of Br =
$$\frac{\text{Atomic weight of Br}}{\text{Molecular weight of AgB}}$$

$$\frac{\text{Weight of AgBr}}{\text{Weight of organic bromide}} \times 100$$

:. % of Br =
$$\frac{80}{188} \times \frac{141}{250} \times 100 = \frac{1128000}{47000} = 24\%$$

5. PLAN K_{sp} (ZnS) is very high and Zn²⁺ is precipitated as ZnS by high concentration of S²⁻ formed when H₂S is passed in ammoniacal solution.

$$H_2S \rightleftharpoons Zn^+ + S^{2-}$$
 (I
H⁺ + OH⁻ \rightleftharpoons H_2O (II)

Reaction (I) is favoured in forward side if H^+ is removed immediately by OH^- (NH₄OH).

$$Zn^{2+} + S^{2-} \longrightarrow ZnS \downarrow$$

White pp

Fe³⁺ and Al³⁺ are precipitated as hydroxide.

- **6.** In acidic medium, H₂S is very feebly ionised giving very small concentration of sulphide ion for precipitation. Therefore, the most insoluble salts CuS and HgS are precipitated only.
- 7. $\operatorname{Hg}^{2+} + 2I^{-} \longrightarrow \operatorname{HgI}_{2} (\operatorname{red})$

$$Hgl_{2} + 2KI \longrightarrow K_{2}[Hgl_{4}]$$

Soluble
$$Hg^{2+} + Co(SCN)_{2} \longrightarrow Co[Hg(SCN)_{4}]$$

- 8. $MgSO_4 + NH_4OH + Na_2HPO_4 \longrightarrow Mg(NH_4)PO_4 \downarrow$ White $+ Na_2SO_4 + H_2O$
- 9. $CuSO_4^+ 2KCN \longrightarrow Cu(CN)_2 + K_2SO_4$ $2Cu(CN)_2 \longrightarrow 2Cu(CN) + \begin{vmatrix} CN \\ CN \\ CN \end{vmatrix}$ (Cyanogen) $CuCN + 3KCN \longrightarrow 3K^+ + [Cu(CN)_4]^{3-}$ 10. $Zn^{2+} + 2H_2O \longrightarrow Zn(OH)_2 \downarrow + 2H^+$ White

11.
$$\operatorname{Bi}^{3+} + 3\operatorname{I}^{-} \longrightarrow \operatorname{Bi}_{3} \downarrow \xrightarrow{\operatorname{I}^{-}}_{\operatorname{excess}} \operatorname{[Bi}_{4}]_{\operatorname{Orange}}_{\operatorname{Solution}}$$

- 12. Both $(NH_4)_2 Cr_2 O_7$ and $NH_4 NO_2$ on heating gives nitrogen gas.
- **13.** A sodium salt of an unknown anion when treated with MgCl gives white precipitate (MgCO₃) only on boiling. Hence, the action must be HCO_3^- ion.

$$MgCl_2 + 2NaHCO_3 \xrightarrow{\Delta} MgCO_3 + 2NaCl + H_2O + CO_2$$

 $+ H_2O$

14.
$$SO_3^{2-} + H_2SO_4 \longrightarrow SO_2^{\uparrow} + H_2O + SO_4^{2-}$$

 SO_2 is a colourless gas with irritating odour.
 $3SO_2 + K_2Cr_2O_7 + H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3$
 Y
Green
solution

15. $\operatorname{Cl}_2 + \operatorname{H}_2 O \longrightarrow \operatorname{HCl} + \operatorname{HOCl} X$

$$HCl + AgNO_3 \longrightarrow AgCl \downarrow (white) + HNO_3$$

$$2\text{HCl} + \text{Mg} \longrightarrow \text{MgCl}_2 + \text{H}_2(g) \uparrow$$

- **16.** $PbCl_2$ is soluble in hot water and PbS (black) is formed on passing $H_2S(g)$ through acidic solution.
- **17.** Fe(II) and Fe(III) will have different values of magnetic moment due to different number of unpaired electrons in their *d*-orbitals.
- **18.** Yellow filtrate contains CrO_5 and brown residue contain Fe_2O_3 .
- **19.** The total positive valency is +2 (because the only anion is SO_4^{2-}). Therefore, oxidation state of Fe must be +1.
- **20.** Both Bi^{3+} and Sn^{4+} belongs to same analytical group II.
- **21.** CaC_2O_4 is insoluble in acetic acid. This distinguishes Ca^{2+} from Ba^{2+} ion.
- **22.** Ag^+ is precipitated by HCl only while all others are precipitated by passing H_2S in the presence of HCl.
- **23.** We know that,

 $\Delta G^{\circ} = -2.303 RT \log K$

$$2H_2O \longrightarrow H_3O^+ + \bar{O}H$$

$$[H^+][OH^-] = 10^{-14}$$
 or $K = 10^{-14}$

$$\Delta G^{\circ} = -2.303 \times 8.314 \, \mathrm{JK}^{-1} \mathrm{mol}^{-1} \times 298 \mathrm{K} \times \mathrm{log} 10^{-14}$$

$$= 79881.8 \text{J} \text{ mol}^{-1} = 79.8 \text{kJ} \approx 80 \text{ kJ} \text{ mol}^{-1}$$

24. Statement wise explanation is

Statement (a) Mn^{2+} produces yellow-green colour in flame test while Cu²⁺ produces bluish-green colour in flame test. Thus, due to the presence of green colour in both the cases, flame test is not the suitable method to distinguish between nitrate salts of Cu²⁺ and Mn²⁺. Hence this statement is wrong. **Statement (b)** Cu²⁺ belong to group II of cationic or basic radicals. It gives black ppt. of CuS if H₂S is passed through it in the presence of acid (e.g HCl). Mn²⁺ does not show this

property hence this can be considered as a suitable method to distinguish between ${Mn}^{2+}$ and ${Cu}^{2+}$.

Hence, this statement is correct.

Statement (c) In faintly basic medium when H_2S is passed both Cu^{2+} and Mn^{2+} forms precipitates. Thus, it is not suitable method to distinguish between them.

Hence, this statement is incorrect

Statement (d) The standard reduction potential of Cu^{2+}/Cu is +0.34 V while that of Mn²⁺/Mn is -1.18V. This can be used to distinguish between Cu^{2+} and Mn^{2+} . In general less electropositive metals have higher SRP.

Hence, this statement is correct.

25.
$$S^{2-} + CuCl_2 \longrightarrow CuS \downarrow (black ppt.)$$

 $SO_4^{2-} + CuCl_2 \longrightarrow$ Soluble, Thus

- (a) $CuCl_2$ selectively precipitates S^{2-} .
- (b) $S^{2-} + BaCl_2 \longrightarrow BaS \downarrow$ (soluble)

$$SO_4^{2-} + BaCl_2 \longrightarrow BaSO_4 \downarrow \text{(white ppt.)}$$

(b) precipitates SO_4^{2-} and not S^{2-} .

(c)
$$S^{2^-} + Pb^{2^+} \longrightarrow PbS \downarrow$$
 (black ppt.)
 $SO_4^{2^-} + Pb^{2^+} \longrightarrow PbSO_4 \downarrow$ (white ppt.)
 S^{2^-} and $SO_4^{2^-}$, both are precipitated.

- (d) $S^{2^-} + Na_2[Fe(CN)]_5NO \longrightarrow Na_4[Fe(CN)]_5NOS]$ Sodium nitroprusside (Purple colour) But no colour with $SO_4^{2^-}$.
- **26.** Only radicals of I and II group of qualitative analysis get precipitated with H_2S in the presence of dilute HCl.

(c)
$$\operatorname{Cu}^{2^{+}} + \operatorname{H}_{2}S \xrightarrow{\operatorname{H}^{+}} \operatorname{Cu}S \downarrow_{\operatorname{Black}}$$

 $\operatorname{Pb}^{2^{+}} + \operatorname{H}_{2}S \xrightarrow{\operatorname{H}^{+}} \operatorname{Pb}S \downarrow_{\operatorname{Black}}$
(d) $\operatorname{Hg}^{2^{+}} + \operatorname{H}_{2}S \xrightarrow{\operatorname{H}^{+}} \operatorname{Hg}S \downarrow_{\operatorname{Black}}$
 $\operatorname{Bi}^{3^{+}} + \operatorname{H}_{2}S \xrightarrow{\operatorname{H}^{+}} \operatorname{Bi}_{2}S_{3} \downarrow_{\operatorname{Brown ppt}}$

 Ba^{2+} , Zn^{2+} and Fe^{3+} are not precipitated as sulphide.

27.
$$K_3$$
 [Fe(CN)₆] + KI (excess) \longrightarrow

 $K_{4}[Fe(CN)_{6}] + KI_{3}(redox)$ Brownish yellow solution

$$K_4[Fe(CN)_6] + ZnSO_4 \rightarrow K_2Zn_3[Fe(CN)_6]_2$$

K. Zn[Fe(CN)_1]

or K₂Zn[Fe(CN)₆] White ppt

 $\begin{array}{ccc} I_3^- & + 2Na_2S_2O_3 \longrightarrow Na_2S_4O_6 + 2NaI + & I_2 \\ Brownish & Clear & (Turns starch \\ yellow & solution & solution \\ filtrate & & blue \end{array}$

K₂Zn[Fe(CN)₆]reacts with NaOH as

$$K_2Zn[Fe(CN)_6] + NaOH \longrightarrow [Zn(OH)_4]^2 + [Fe(CN)_6]^4$$

- **28.** $NH_4NO_3 + NaOH \longrightarrow NaNO_3 + NH_3 + H_2O$ $NH_4NO_2 + NaOH \longrightarrow NaNO_2 + NH_3 + H_2O$
- **29.** When mixture of NaCl is heated with $K_2Cr_2O_7$ in concentrated H_2SO_4 , red vapour of chromyl chloride (CrO_2Cl_2) is produced. Vapours of chromyl chloride when passed through NaOH, solution turns yellow due to formation of Na₂CrO₄. Some chlorine gas is also evolved owing to the following side reaction :

$$6\text{Cl}^- + \text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ \longrightarrow 3\text{Cl}_2(g) \uparrow + 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$$

30. The blue precipitate of Fe^{2+} ion with potassium ferricyanide is due to formation of Turnbull's blue KFe[Fe(CN)₆].

$$Fe^{2+} + K_3[Fe(CN)_6] \longrightarrow KFe[Fe(CN)_6] + 2K^2$$

The red colour of Fe^{3+} ion with potassium thiocyanate is due to formation of $[Fe(SCN)_3]$.

$$Fe^{3+} + 3KSCN \longrightarrow [Fe(SCN)_3] + 3K^+$$

Red coloured

- **31.** Both Al^{3+} and Bi^{3+} are precipitated as their hydroxides.
- **32.** As MgSO₄ is soluble in water, so not used for estimation of SO_4^{2-1} ion.
- **33.** Cation Cd^{2+} belongs to group II while Ni²⁺ belongs to group III of analytical group. Group II radicals are precipitated by passing $H_2S(g)$ through acidic solution of salt but radicals of group III are precipitated by passing $H_2S(g)$ in NH₃/NH₄Cl buffer solution of salt due to greater solubility products of later salts.
- **34. PLAN** This problem can be solved by using concept of chemical reactions of transition metal ions (,) colour and structure of transition metal compounds.

Here, among given four option Ni^{2+} and Zn^{2+} has ability to form tetrahedral as well as square planar complex depending upon types of reagent used.

 Ni^{2+} on reaction with KCN forms square planar complex $[Ni(CN)_4]^{2-}$ due to strong field strength of CN.

$$Ni^{2+} + KCN \longrightarrow [Ni(CN)_4]^{2-}$$

Square planar

While on reaction with HCl, Ni^{2+} forms stable tetrahedral complex $[Ni(Cl)_4]^{2-}$.

 Zn^{2+} , on the other hand, on reaction with KCN as well as HCl produces tetrahedral complex because of its d^{10} electronic configuration.

$$Zn^{2+} \xrightarrow[excess]{HCl} [ZnCl_4]^{2-} \\ KCN \\ [Zn(CN)_4]^{2-} \\ \hline KOH \\ excess} [Zn(OH)_4]^{2-} \\ White ppt$$

Complete reaction sequence can be shown as

$$\begin{bmatrix} \text{NiCl}_{4} \end{bmatrix}^{2-} & \xleftarrow{\text{HCl}(\underline{Q})}_{\text{excess}} & \text{Ni}^{2+} & \underbrace{\text{KCN}(R)}_{\text{excess}} \in \begin{bmatrix} \text{Ni}(\text{CN})_{4} \end{bmatrix}^{2-}_{\text{Square planar}} \\ \begin{bmatrix} \text{ZnCl}_{4} \end{bmatrix}^{2-} & \xleftarrow{\text{HCl}(\underline{Q})}_{\text{excess}} & Zn^{2+} & \underbrace{\text{KCN}(R)}_{\text{excess}} \in \begin{bmatrix} \text{Zn}(\text{CN})_{4} \end{bmatrix}^{2-}_{\text{Tetrahedral}} \\ & \downarrow \text{KOH}(s) \\ & Zn(\text{OH})_{2} & \underbrace{\text{KOH}}_{\text{excess}} \in \begin{bmatrix} \text{Zn}(\text{OH})_{4} \end{bmatrix}^{2-}_{\text{Soluble}} \end{bmatrix}$$

35. Zn^{2+} on treatment with excess of KOH produces $[Zn(OH)_4]^{2-}$.

36, 37. PLAN PbCl₂ is soluble in hot water.

In ammoniacal medium, cations of group III and IV may be precipitated as hydroxide or sulphide and dissolved in H_2O_2 due to oxidation.

Mixture of two inorganic salts
$$(i)$$
 HCl
 (ii) Filter

$$\underbrace{\operatorname{CrO}_{4}^{2^{-}} \xleftarrow{\operatorname{H_2O_2}}_{\operatorname{NaOH}} \operatorname{Cr(OH)_3} \xleftarrow{\operatorname{NH_4OH/H_2S}}_{\operatorname{ppt}} \operatorname{Filtrate} \operatorname{ppt}}_{\text{filtrate}}$$

Thus, **Q. 35.** P is Pb²⁺. **Q. 36.** S is Na₂CrO₄.

- **38.** Appearance of blue colour on addition of the metal rod M to the solution of N is an indication that metal may be Cu. Later formation of white precipitate on addition of NaCl and dissolution of this precipitate in aqueous ammonia confirm that while precipitate is of AgCl. This implies that the solution N is of AgNO₃. This confirm that the metal M is only Cu.
- **39.** The compound N is AgNO₃, explained above.
- **40.** Since, in the beginning, concentrated AgNO₃ solution was taken, some AgNO₃ remain in solution which gives white precipitate of AgCl on addition of NaCl. The precipitate finally dissolve in ammonia and Cu²⁺ present in solution also forms complex with ammonia as

The comprehension describing methylene-blue test.



Therefore,

41. *X* is Na_2S .

- **42.** *Y* is FeCl₃.
- **43.** Compound Z is $Fe[Fe(CN)_6]$.
- **44.** Heating chloride salt with K₂Cr₂O₇ in conc. H₂SO₄ gives off a deep vapour of chromyl chloride (CrO₂Cl₂).
- **45.** Because $Fe(OH)_2$ is soluble.
- 46. ZnS is soluble in dil. HCl but CuS does not dissolve in dil. HCl.
- **47.** In absence of NH₄Cl, both Fe(OH)₃ and Mg(OH)₂ will be precipitated.
- **48.** From qualitative analysis of the different metal ions it is found that PbS, CuS, HgS, Ag₂S, NiS, CoS are black coloured.

MnS — dirty pink/buff coloured, SnS₂—yellow coloured.

 Bi_2S_3 — brown/black (brownish black) coloured.

Hence, correct integer is (6 or 7).

49. $MCl_4 \xrightarrow{Zn}$ Purple coloured compound (A) Colourless

$$M \xrightarrow{\text{Transition metal}} B \text{ (white fumes)}$$

$$\Rightarrow M = \text{Ti}, \quad A = [\text{Ti}(\text{H}_2\text{O})_6]^{3+}; \quad B = \text{TiO}_2$$

Ti (IV) contains no *d*-electron, while *d*-*d* transition of single electron of Ti (III) will cause colour change.

50. (i)
$$\operatorname{Fe}^{3^+} + 3\operatorname{SCN}^- \longrightarrow \operatorname{Fe}(\operatorname{SCN})_3$$
 (blood red colouration)
Iron (III)
thiocyanate
 A
 $\operatorname{Fe}(\operatorname{SCN})_3 + \operatorname{F}^-$ (excess) \longrightarrow $[\operatorname{FeF}_6]^{3^-} + 3\operatorname{SCN}^-$

(ii) Magnetic moment (
$$\mu_s$$
) = $\sqrt{n(n+2)}$ BM

$$= \sqrt{35} \text{ BM} = 5.92 \text{ BM}$$

51.
$$A_1 = \text{Cu(OH)}_2 \cdot \text{CuCO}_3 \text{ and } A_2 = \text{Cu}_2\text{S}$$

 $A_1 \xrightarrow{\text{Calcination}} 2\text{CuO} + \text{CO}_2 + \text{H}_2\text{O}$
Black
 $A_1 \xrightarrow{\text{Dil. HCl}} \text{CuCl}_2 + \text{CO}_2 + \text{H}_2\text{O}$

$$\begin{array}{c} 2\mathrm{CuCl}_{2}+4\mathrm{KI} \longrightarrow 2\mathrm{CuI}+\mathrm{I}_{2}+4\mathrm{KCl}\\ 2\mathrm{Cu}_{2}\mathrm{S}\left(A_{2}\right)+3\mathrm{O}_{2} \longrightarrow 2\mathrm{Cu}_{2}\mathrm{O}+2\mathrm{SO}_{2} \end{array}$$

$$Cu_2S + 2Cu_2O \xrightarrow{\Delta} 6Cu + SO_2$$

52. $A + B \longrightarrow$ lilac colour in flame

(i)
$$\underbrace{A + B}_{\text{Mixture}} \xrightarrow{\text{H}_2\text{S}} C \downarrow_{\text{Black}}$$

 $C \xrightarrow{\text{Soluble}}_{\text{in aqua-regia}} \text{Soluble} \xrightarrow{\text{Evaporation}} \text{Residue}$
 $\xrightarrow{\text{SnCl}_2} \text{Greyish black} \downarrow (D)$

$$\Rightarrow$$
 C is HgS.

(ii)
$$\underbrace{A + B}_{\text{Solution of}} \xrightarrow{\text{NH}_4\text{OH}} \text{Brown ppt.}$$

Solution of mixture
Sodium extract $\underbrace{\text{AgNO}_3}_{\text{Mixture}}$ Yellow ppt. $\underbrace{\text{NH}_3}_{\text{Mixture}}$ Insoluble
Sodium extract of salt $\underbrace{\text{CCl}_4/\text{FeCl}_3}_{\text{Cl}_4/\text{FeCl}_3}$ Violet layer
 $\Rightarrow A = \text{KI}$ and $B = \text{HgI}_2$.
53. $X = \text{NH}_4\text{Cl}; A = \text{CrO}_2\text{Cl}_2; B = \text{Na}_2\text{CrO}_4; C = \text{PbCrO}_4;$
 $D = \text{H}_2\text{N}(\text{HgO})\text{HgI}.$
Reactions involved :
(i) $4\text{NH}_4\text{Cl}(X) + \text{K}_2\text{Cr}_2\text{O}_7 + 6\text{H}_2\text{SO}_4 \longrightarrow 2\text{CrO}_2\text{Cl}_2(A)$
 $+ 4\text{NH}_4\text{HSO}_4 + 2\text{KHSO}_4 + 3\text{H}_2\text{O}$
(ii) $\text{CrO}_2\text{Cl}_2(A) + 2\text{NaOH} \longrightarrow \text{Na}_2\text{CrO}_4(B) + 2\text{HCl}$
(iii) $\text{Na}_2\text{CrO}_4(B) + (\text{CH}_3\text{COO})_2\text{Pb} \longrightarrow \text{PbCrO}_4 \downarrow (C)$
 $+ 2\text{CH}_3\text{COONa}$
(iv) $\text{NH}_4\text{Cl}(X) + \text{NaOH} \longrightarrow \text{NaCl} + \text{H}_2\text{O} + \text{NH}_3$
(v) $2\text{K}_2\text{HgI}_4 + \text{NH}_3 + 3\text{KOH} \longrightarrow \text{H}_2\text{N}(\text{HgO})\text{HgI}(D)$
 $+ 7\text{KI} + 2\text{H}_2\text{O}$

54. Since, the white substance *A* gives a colourless gas *B* with dil. H_2SO_4 , such gas may be H_2S So, the substance *A* may be a metal sulphide (Na/K/Zn, etc.)

When H_2S gas reacts with acidified $K_2Cr_2O_7$, it gives green coloured solution of $Cr_2(SO_4)_3$ alongwith slightly yellow ppt of *D* as sulphur.

$$\begin{array}{c} \mathrm{K_2Cr_2O_7} + 4\mathrm{H_2SO_4} + 3\mathrm{H_2S} \longrightarrow \mathrm{K_2SO_4} + \mathrm{Cr_2(SO_4)_3} \\ \mathrm{Green} \\ + 3\mathrm{S} + 7\mathrm{H_2} \\ D \end{array}$$

S on burning in air gives SO₂ (*E*). Substance *E* on reaction with B (H₂S) produces D (s) :

$$\begin{array}{ccc} 2\mathrm{H}_{2}\mathrm{S} + \mathrm{SO}_{2} & \longrightarrow 2\mathrm{H}_{2}\mathrm{O} & (l) + 3\mathrm{S} \downarrow \\ B & E & D \end{array}$$

Anhydrous CuSO₄ produces blue colour in water.

Solution C produces ppt first with $NH_3/NaOH$ which dissolve in excess $NH_3/NaOH$. Hence, A must be ZnS.

$$ZnS + dil. H_2SO_4 \longrightarrow ZnSO_4(aq) + H_2S(g)$$

$$ZnSO_4 + 2NaOH \longrightarrow Zn(OH)_2 \downarrow + Na_2SO_4$$

$$C$$

$$Zn(OH)_2 + 2NaOH \longrightarrow [Zn(OH)_4]^{2-} + 2Na^+$$

55.
$$\operatorname{Na}_{2}\operatorname{B}_{4}\operatorname{O}_{7} \xrightarrow{\Delta} 2\operatorname{Na}\operatorname{BO}_{2} + \operatorname{B}_{2}\operatorname{O}_{3}$$

 $\operatorname{CoO} + \operatorname{B}_{2}\operatorname{O}_{3} \xrightarrow{\Delta} \operatorname{Co}(\operatorname{BO}_{2})_{2}$
Blue

56. The transition metal is Cu^{2+} . The compound is $CuSO_4 \cdot 5H_2O$. It dissolves in water to give blue coloured solution due to presence of Cu^{2+} . On passing $H_2S(g)$ in acid medium of salt solution black precipitate of CuS is obtained which is not soluble in aqueous KOH solution.

$$CuSO_4 + H_2S \xrightarrow{H^+} CuS \downarrow + H_2SO_4$$

black

On adding KI solution to aqueous solution of $CuSO_4$, yellow solution of CuI_2 is formed in the beginning which decompose into white ppt of CuI.

$$\begin{array}{ccc} \text{CuSO}_4 + 2\text{KI} & \longrightarrow & \text{CuI}_2 + \text{K}_2\text{SO}_4 \\ 2\text{CuI}_2 & \longrightarrow & 2\text{CuI} \downarrow + \text{I}_2 \\ & \text{White} \end{array}$$

57. $NaNO_3 + H_2SO_4 \longrightarrow NaHSO_4 + HNO_3$

$$2HNO_3 + 6FeSO_4 + 3H_2SO_4 \longrightarrow 3Fe_2(SO_4)_3 + 2NO + 2H_2O$$

$$FeSO_4 + NO \longrightarrow [Fe(NO)SO_4]$$
Brown ring
(nitrosoferrous subpate)

58. NaI on reaction with HgI_2 gives a complex salt :

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

The orange colour is due to residual HgI₂. On addition of excess NaI, whole HgI₂ is converted to complex Na₂[HgI₄] as colour disappear. The orange colour of HgI₂ reappear due to conversion of Na₂[HgI₄] into HgI₂ on treatment with NaOCl.

 $3Na_2[HgI_4] + 2NaOCl + 2H_2O \longrightarrow 3HgI_2 + 2NaCl$

+ 4NaOH + 2NaI

59. K_{sp} (solubility product) of CuS is less than K_{sp} of ZnS. On passing H₂S(g) in acidic solution, dissociation of H₂S is suppressed due to common ion effect and it provide small concentration of S²⁻, sufficient for precipitation of CuS but insufficient for precipitation of ZnS.

60.
$$Al_2S_3 + 6H_2O \longrightarrow 2Al(OH)_3 \downarrow + 3H_2S\uparrow$$

Foul dour

61. The poisonous element M may be As. On the basis of given information :

М

AsCl₃ + 6H
$$\xrightarrow{Zn}_{H_2SO_4}$$
 AsH₃ + 3HCl
2AsH₃ $\xrightarrow{\Delta}$ 2As + 3H₂ \uparrow

62.
$$A \xrightarrow{250^{\circ}C} B + C$$

Inorganic salt Neutral Neutral oxide (liquid)

Oxide C is liquid and neutral to litmus, so it is H_2O . White phosphorus burns in excess of B to give P_4O_{10} .

Therefore, *B* is N₂O.

$$NH_4NO_3(A) \xrightarrow{\Delta} N_2O + 2H_2O(l)$$

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

63. On addition of KI solution to a Bi(NO₃)₃ solution, firstly a dark brown precipitate of BiI₃ is formed that dissolve in excess of KI forming a clear yellow solution of BiI₄ :

$$Bi^{3+} + 3I^- \longrightarrow BiI_3 \downarrow \stackrel{I^-}{\longrightarrow} BiI_4^-$$

Dark Clear yellow
brown solution

64. $A(\operatorname{Pb}_3O_4) \xrightarrow{\operatorname{CHNO}_3} B(\operatorname{PbO}_2) \xrightarrow{\operatorname{Filtered}} \operatorname{Pb(NO}_3)_2$ Scarlet $B(\operatorname{PbO}_2) \xrightarrow{\operatorname{Filtered}} \operatorname{Pb(NO}_3)_2$

Filtrate is neutralised with NaOH and on reaction with KI, gives yellow ppt of PbI_2 .

$$Pb(NO_3)_2 + 2KI \longrightarrow PbI_2 \downarrow + 2KNO_3$$

Yellow

 PbO_2 on warming with conc. HNO_3 in presence of $Mn(NO_3)_2$ produced pink solution due to formation of $Pb(MnO_4)_2$ (I).

$$5PbO_2 + 2Mn(NO_3)_2 + 4HNO_3 \longrightarrow Pb(MnO_4)_2 + 4Pb(NO_3)_2 + 2H_2O$$
$$\Rightarrow A = Pb_3O_4, B = PbO_2, C = PbI_2 \text{ and } D = Pb(MnO_4)_2.$$

65.
$$A \xrightarrow{\Delta} B \downarrow + C \uparrow H_2 O(v) \uparrow$$

Orange solid Green Colourless

 $C + Mg \longrightarrow D$ (white solid) $D + H_2O \longrightarrow E(g) \xrightarrow{HCl}$ White fumes.

Hence, *E* must be ammonia gas so *D* must be Mg₃N₂ and *C* is N₂(g). This N₂ is obtained on strong heating of $(NH_4)_2Cr_2O_7$ because $(NH_4)_2Cr_2O_7$ is orange solid and produces green Cr_2O_3 residue on heating.

$$(\mathrm{NH}_{4})_{2}\mathrm{Cr}_{2}\mathrm{O}_{7} \xrightarrow{\Delta} \mathrm{Cr}_{2}\mathrm{O}_{3} + \mathrm{N}_{2} + 4\mathrm{H}_{2}\mathrm{O}$$

Orange (A) Green (B) C

$$\mathrm{N}_{2} + \mathrm{Mg} \xrightarrow{\Delta} \mathrm{Mg}_{3}\mathrm{N}_{2} \xrightarrow{\mathrm{H}_{2}\mathrm{O}} \mathrm{NH}_{3} + \mathrm{Mg}(\mathrm{OH})_{2}$$

$$D \xrightarrow{E} \mathrm{NH}_{3} + \mathrm{HCl} \longrightarrow \mathrm{NH}_{4}\mathrm{Cl} \text{ (white fumes)}$$

E

66.
$$3[Fe(H_2O)_6]^{2^+} + NO_3^- + 4H^+ \longrightarrow NO + 3[Fe(H_2O)_6]^{3^+} + 2H_2O$$

 $[Fe(H_2O)_6]^{2^+} + NO \longrightarrow [Fe(H_2O)_5NO]^{2^+} + H_2O$

- **67.** (i) Brown precipitate or colour with K_2HgI_4 , indicates the presence of NH_4^+ ion.
 - (ii) Aqueous Fe(II) solution gives a blue colour with $K_3[Fe(CN)_6]$ due to formation of $Fe[Fe(CN)_6]$ ion :

$$Fe^{2+} + Fe(CN)_6^{3-} \longrightarrow Fe[Fe(CN)_6]$$

Blue colouration

(iii) Aqueous solution of SO_4^{2-} ion in HCl gives white ppt with $BaCl_2$ solution.

$$SO_4^{2-} + BaCl_2 \longrightarrow BaSO_4 \downarrow + 2Cl^{-}$$

68. PbS
$$\xrightarrow{\text{Heat in}}_{\text{air}}$$
 PbO + PbS $\xrightarrow{\text{Heat in}}_{\text{absence of air}}$ Pb + SO₂

69. In excess of NaOH, Al(OH)₃ dissolves forming NaAlO₂ while Fe(OH)₃ remains insoluble.

70. Formation of a reddish-brown precipitate with alkaline K_2HgI_4 solution indicates the presence of NH_4^+ ion and the gas liberated is ammonia :

$$NH_{4}^{+} + OH^{-} \longrightarrow H_{2}O + NH_{3}(g)$$

$$2K_{2}HgI_{4} + 3NaOH + NH_{4}^{+} \longrightarrow Hg \bigvee_{I}^{O} \downarrow$$

$$Hg \bigvee_{I}^{I}$$

$$+ 4KI + 3NaI + 3OH^{-}$$

On treatment with $BaCl_2$, a white precipitate is formed which indicates the presence of SO_4^{2-} anion :

$$\text{SO}_4^{2-} + \text{BaCl}_2 \longrightarrow \text{BaSO}_4 \downarrow + 2\text{Cl}^-$$

White

With $K_2Cr_2O_7$ and conc. H_2SO_4 , red vapour of CrO_2Cl_2 is evolved. This indicates presence of Cl^- ion.

On treatment with potassium ferricyanide, formation of deep blue solution indicates presence of Fe (II) ion :

$$\operatorname{Fe}^{2^+} + \operatorname{Fe}(\operatorname{CN})_6^{3^-} \longrightarrow \operatorname{Fe}_4[\operatorname{Fe}(\operatorname{CN})_6]_3$$

Blue

71. (i)
$$AgCl + 2NaCN \longrightarrow NaCl + Na[Ag(CN)_2]$$

 $2Na[Ag(CN)_2] + Zn \longrightarrow Na_2[Zn(CN)_2] + 2Ag$

(ii)
$$\operatorname{Co}^{2+} + 3\operatorname{KNO}_3 + 4\operatorname{NO}_2^- + 2\operatorname{H}^+ \longrightarrow \operatorname{K}_3[\operatorname{Co}(\operatorname{NO}_2)_6]$$

 $+ H_2O + NO$

- **72.** Mercurous chloride changes from white to black when treated with ammonia due to formation of metallic Hg.
- 73. (i) Mixture + $MnO_2 + H_2SO_4 \longrightarrow Yellowish$ green gas. conc. The above reaction suggest that the mixture contain Cl⁻. $2Cl^- + MnO_2 + H_2SO_4 \longrightarrow MnSO_4$

$$+ Cl_2 \uparrow + H_2O$$

- (ii) Mixture + NaOH \longrightarrow Gas turning red litmus blue. The above reaction indicates that the gas is ammonia. NH₄⁺ + NaOH \longrightarrow NH₃ + H₂O + Na⁺
- (iii) Solution of mixture + K₃[Fe(CN)₆] → blue ppt. The above reaction suggest that mixture contain a Fe(II) salt. Fe(II) salt react with K₃[Fe(CN)₆] to give blue ppt of Prussian blue complex

$$3Fe^{2+} + 2Fe(CN)_6^{3-} \longrightarrow Fe_3[Fe(CN)_6]_2 \downarrow$$

Blue

Red colouration with NH_4SCN suggests that some Fe(III) is also present. It is likely that a part of Fe(II) is oxidised to Fe(III) by air :

$$Fe^{3+} + 3NH_4SCN \longrightarrow Fe(SCN)_3 + 3NH_4^+$$

Red colouration

(iv) Mixture + KOH \longrightarrow gas $\uparrow \xrightarrow{K_2HgI_4}$ brown ppt.

The above reaction indicates that the gas is NH_3 , i.e. mixture contain NH_4^+ ion. Hence, the mixture contains Fe^{2+} , NH_4^+ and Cl^- ions with some impurity of Fe^{3+} ion. The two salts are $FeCl_2$ and NH_4Cl .

- 74. $2KMnO_4 + 3H_2SO_4 + 5H_2C_2O_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 10CO_2$
- **75.** (i) $ZnO + 2NaOH \longrightarrow Na_2ZnO_2 + H_2O$ (ii) $Sn^{2+} + I_2 \longrightarrow Sn^{4+} + 2\Gamma$ (iii) $SO_2 + H_2O + \frac{1}{2}O_2 + 2NaCl \longrightarrow Na_2SO_4 + 2HCl$
- **76.** (i) $SO_2 + 2H_2S \longrightarrow 3S + 2H_2O$
 - (ii) $CuSO_4 + 4NH_3 \longrightarrow [Cu(NH_3)_4]SO_4$
 - (iii) $Sn + 3HNO_3 \longrightarrow H_2SnO_3 + 4NO_2 + H_2O$ Conc. Metastannic acid
 - (iv) $H_2O_2 + CrCl_3 + NaOH \longrightarrow Na_2CrO_4 + NaCl + H_2O$ Yellow
 - (v) $Pb_3O_4 \longrightarrow 2PbO + PbO_2$ $2PbO + PbO_2 + 4HNO_3 \longrightarrow 2Pb(NO_3)_2 + 2H_2O + PbO_2 \downarrow$
- 77. $3\text{KClO}_3 + 3\text{H}_2\text{SO}_4 \rightarrow 3\text{KHSO}_4 + \text{HClO}_4 + 2\text{ClO}_2 + \text{H}_2\text{O}$ (COOH)₂ + C · H₂SO₄ \longrightarrow CO + CO₂ + H₂O
- **78.** (X) is NaHCO₃ (M = 84). The reactions involved are :

$$2\text{NaHCO}_{3} \longrightarrow \text{Na}_{2}\text{CO}_{3}(s) + \text{CO}_{2}(g) + \text{H}_{2}\text{O}(g)$$

$$X \qquad Y \qquad A \qquad B$$

$$168 \text{ g} \qquad 106 \text{ g} \qquad 44 \text{ g} \qquad 18 \text{ g}$$

$$\Rightarrow \qquad 16.8 \text{ g} \qquad 10.6 \text{ g} \qquad 4.4 \text{ g} \qquad 1.8 \text{ g}$$

$$\text{CO}_{2} + \text{Ca}(\text{OH})_{2} \longrightarrow \text{CaCO}_{3} \downarrow + \text{H}_{2}\text{O}$$

 $H_2O(g)$ is condensed to liquid water.

$$\begin{array}{c} \operatorname{Na_2CO_3} + \operatorname{BaCl_2} \longrightarrow \operatorname{BaCO_3} + 2\operatorname{NaCl}_{Z} \\ \operatorname{BaCO_3} + 2\operatorname{HCl} \longrightarrow \operatorname{BaCl_2} + \operatorname{H_2O} + \operatorname{CO_2}_{Z} \\ \end{array}$$

- **79.** Compound A is a light green crystalline solid, so it may be $FeSO_4$.
 - (i) FeSO₄ is a salt of strong acid and weak base, so it hydrolyses in dil. H₂SO₄ but no gas is evolved.
 - (ii) $FeSO_4$ is a strong reducing agent, thus decolourises $KMnO_4$ solution :

$$5Fe^{2+} + MnO_4^- + 8H^+ \longrightarrow 5Fe^{3+} + Mn^{2+}_{Colourless} + 4H_2O$$

Purple

(iii) $FeSO_4$ on strong heating gives both $SO_2(B)$ and $SO_3(C)$ gases alongwith a residue of $Fe_2O_3(D)$.

$$2\text{FeSO}_4 \xrightarrow{\Delta} \text{Fe}_2\text{O}_3 + \frac{\text{SO}_2 + \text{SO}_3}{D} + \frac{\text{SO}_2 + \text{SO}_3}{B} + \frac{\text{SO}_2 + \text{SO}_3}{C}$$

(iv) The gaseous mixture reduced dichromate solution to green solution and also gives H_2SO_4 in solution :

$$\operatorname{Cr}_2\operatorname{O}_7^{2-} + 3\operatorname{SO}_2 + 2\operatorname{H}^+ \longrightarrow 3\operatorname{SO}_4^{2-} + \operatorname{H}_2\operatorname{O} + 2\operatorname{Cr}^{3+}_{\operatorname{Green}}$$

$$H_2O + SO_3 \longrightarrow H_2SO_4$$

(v) The sulphuric acid (formed in previous step) gives white ppt. with Ba(NO₃)₂ due to formation of BaSO₄ (*E*) :

$$H_2SO_4 + Ba(NO_3)_2 \longrightarrow BaSO_4 \downarrow + 2HNO_3$$

White (E)

- (vi) The residue D when heated on charcoal in a reducing flame reduces to iron (Fe) which is a magnetic substance.
 Hence, A = FeSO₄, B = SO₂, C = SO₃, D = Fe₂O₃ and E = BaSO₄.
- **80.** FeCl₃ is a salt of strong acid and weak base. In water, it hydrolyses slowly producing brown ppt of Fe(OH)₃.

$$FeCl_3 + 3H_2O \longrightarrow 3HCl + Fe(OH)_3 \downarrow$$

Brown

- **81.** Nitric acid is a strong oxidising agent, oxidises H_2S to S.
- **82.** (i) The compound *C* produced by heating *A* is white in colour and changes to yellow on heating, thus compound *C* may be ZnO. *C* with dil. HCl and $K_4[Fe(CN)_6]$ gives white ppt. This confirms that the compound *C* must be ZnO.

$$A \xrightarrow{\Delta} ZnO + B \text{ (gas)}$$

$$ZnO + 2HC1 \longrightarrow ZnCl_2 + H_2O$$

$$2ZnCl_2 + K_4[Fe(CN)_6] \longrightarrow 4KCl + Zn_2[Fe(CN)_6] \downarrow$$
White ppt

(ii) The gas *B* turns lime water milky and milkiness disappear with continuous passage of gas. Hence, the gas is CO_2 and compound *A* in ZnCO₃.

$$CO_{2} + Ca(OH)_{2} \longrightarrow H_{2}O + CaCO_{3} \downarrow$$

$$CaCO_{3} + CO_{2} + H_{2}O \longrightarrow Ca(HCO_{3})_{2}$$

$$ZnCO_3 \xrightarrow{\Delta} ZnO + CO_2$$

(iii) The solution of A gives white ppt of ZnS D with NH_4OH and excess of H_2S .

$$ZnCO_3 + HCl \longrightarrow CO_2\uparrow + ZnCl_2$$

 B
 $ZnCl_2 + H_2S \xrightarrow{NH_4OH} 2HCl + ZnS\downarrow (white)$

(iv) The solution of A also gives initially a white ppt E with NaOH, which dissolve in excess of reagent.

$$ZnCl_{2} + 2NaOH \longrightarrow Zn(OH)_{2} \downarrow + 2NaCl$$

$$E \text{ (white)}$$

$$Zn(OH)_{2} + 2NaOH \longrightarrow Na_{2}[Zn(OH)_{4}]$$

Soluble