PRINCIPLES RELATED TO PHYSICAL CHEMISTRY
[JEE ADVANCED PREVIOUS YEAR SOLVED PAPERS]

JEE ADVANCED

Single Correct Answer Type

1. The ion that cannot be precipitated by both HCl and H_2S is

a. Pb^{2+} **b.** Cu^{+} **c.** Ag^{+} **d.** Sn^{2+}

(IIT-JEE 1982)

2. The pair of compounds which cannot exist together in solution is

a. $NaHCO_3$ and NaOH **b.** Na_2CO_3 and $NaHCO_3$
c. Na_2CO_3 and NaOH **d.** $NaHCO_3$ and NaCl

(IIT-JEE 1986)

3. The compound insoluble in acetic acid is

a. calcium oxide **b.** calcium carbonate
c. calcium oxalate **d.** calcium hydroxide

(IIT-JEE 1986)

4. Which one among the following pairs of ions cannot be separated by H_2S in dilute hydrochloric acid?

a. Bi^{3+}, Sn^{4+} **b.** Al^{3+}, Hg^{2+}
c. Zn^{2+}, Cu^{2+} **d.** Ni^{2+}, Cu^{2+}

(IIT-JEE 1986)

5. Which compound is formed when excess of KCN is added to an aqueous solution of copper sulphate?

a. $Cu(CN)_2$ **b.** $K_2[Cu(CN)_4]$
c. $K[Cu(CN)_2]$ **d.** $K_3[Cu(CN)_4]$

(IIT-JEE 1995)

6. An aqueous solution contains Hg^{2+}, Hg_2^{2+}, Pb^{2+} and Cd^{2+}. The addition of HCl (6N) will precipitate:

a. Hg_2Cl_2 only **b.** $PbCl_2$ only
c. $PbCl_2$ and Hg_2Cl_2 **d.** $PbCl_2$ and $HgCl_2$

(IIT-JEE 1995)

7. An aqueous solution of $FeSO_4 \cdot Al_2(SO_4)_3$ and chrome alum is heated with excess of Na_2O_2 and filtered. The materials obtained are

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 a brown residue.

(IIT-JEE 1996)

8. The only cations present in a slightly acidic solution are Fe^{3+}, Zn^{2+} and Cu^{2+}. The reagent that when added in excess to this solution would identify to separate Fe^{3+} in one step is

a. 2 M HCl **b.** 6 M NH_3
c. 6 M NaOH **d.** H_2S gas

(IIT-JEE 1997)

9. 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

a. Hg_2^{2+} salt **b.** Cu^{2+} salt

c. Ag^{+} salt **d.** Pb^{2+} salt

(IIT-JEE 2002)

10. 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'.

a. $X = CO_2, Y = Cl_2$ **b.** $X = Cl_2, Y = CO_2$

c. $X = Cl_2, Y = H_2$ **d.** $X = H_2, Y = Cl_2$

(IIT-JEE 2002)

11. $[X] + H_2SO_4 \rightarrow [Y]$ a colourless gas with irritating smell, $[Y] + K_2Cr_2O_7 + H_2SO_4 \rightarrow$ green solution. [X] and [Y] are:

a. SO_3^{2-}, SO_2 **b.** Cl^{-}, HCl

c. S^{2-}, H_2S **d.** CO_3^{2-}, CO_2

(IIT-JEE 2003)

12. 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?

a. FeS **b.** MgS **c.** HgS **d.** ZnS

(IIT-JEE 2003)

13. A sodium salt of an unknown anion when treated with $MgCl_2$ gives white precipitate only on boiling. The anion is

a. SO_4^{2-} **b.** $HCO_3^{\ominus}$ **c.** CO_3^{2-} **d.** $NO_3^{\ominus}$

(IIT-JEE 2004)

14. 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

a. Hg^{2+} **b.** Bi^{3+} **c.** Pb^{2+} **d.** Cu^{+}

(IIT-JEE 2005)

15. $CuSO_4$ decolourises on addition of KCN; the product is

a. $[Cu(CN)_4]^{2-}$

b. Cu^{2+} get reduced to form $[Cu(CN)_4]^{3-}$

c. $Cu(CN)_2$

d. CuCN **(IIT-JEE 2006)**

16. The species present in the solution when CO_2 is dissolved in water are

a. $CO_2, H_2CO_3, HCO_3^{\ominus}, CO_3^{2-}$

b. H_2CO_3, CO_3^{2-}

c. $CO_3^{2-}, HCO_3^{\ominus}$

d. CO_2, H_2CO_3 **(IIT-JEE 2006)**

17. 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 dissolves in NH_4OH/NH_4Cl

a. $Al(OH)_3$ **b.** $Zn(OH)_2$

c. $Ca(OH)_2$ **d.** $Mg(OH)_2$

(IIT-JEE 2006)

18. 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

a. Pb^{2+} **b.** Hg^{2+} **c.** Cu^{2+} **d.** Co^{2+}

(IIT-JEE 2007)

19. Passing H_2S gas into a mixture of Mn^{2+}, Ni^{2+}, Cu^{2+} and Hg^{2+} ions in an acidified aqueous solution precipitates.

a. CuS and HgS **b.** MnS and CuS

c. MnS and NiS **d.** NiS and HgS

(IIT-JEE 2011)

20. Sulphide ores are common for the metals

a. Ag, Cu and Pb **b.** Ag, Cu and Sn

c. Ag, Mg and Pb **d.** Al, Cu and Pb

(IIT-JEE 2013)

21. Roasting of sulphides gives the gas X as a by product. This is a colourless gas with choking smell of burnt sulphur and causes great damage to respiratory organs as a result of acid rain. Its aqueous solution is acidic, acts as a reducing agent and its acid has never been isolated. The gas X is

a. CO_2 **b.** SO_3 **c.** H_2S **d.** SO_2

(IIT-JEE 2013)

22. Identify the correct order of solubility in aqueous medium:

a. $Na_2S > CuS > ZnS$ **b.** $Na_2S > ZnS > CuS$

c. $CuS > ZnS > Na_2S$ **d.** $ZnS > Na_2S > CuS$

(IIT-JEE 2013)

23. Upon treatment with ammonical H_2S, the metal ion that precipitates as a sulphide is

a. Fe(III) **b.** Al(III) **c.** Mg(II) **d.** Zn(II)

(JEE Advanced 2013)

Multiple Correct Answers Type

1. The reagents, NH_4Cl and aqueous NH_3 will precipitate

a. Ca^{2+} **b.** Al^{3+} **c.** Bi^{3+} **d.** Mg^{2+}

e. Zn^{2+} **(IIT-JEE 1991)**

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?

a. A deep red vapour is evolved

b. The vapours when passed into NaOH solution gives a yellow solution of Na_2CrO_4

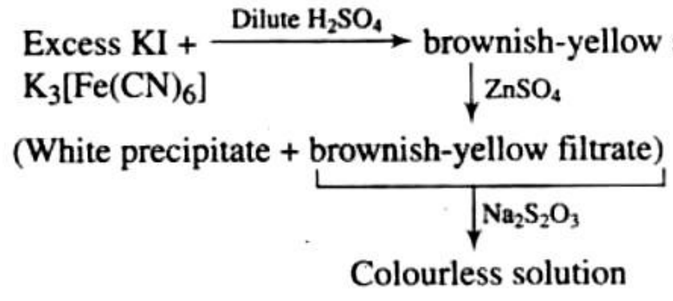
c. Chlorine gas is evolved

d. Chromyl chloride is formed **(IIT-JEE 1998)**

3. Which of the following statement(s) is (are) correct with reference to the ferrous and ferric ions?
   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.
   (IIT-JEE 1998)

4. 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
   a. NH_4NO_3 **b.** NH_4NO_2
   c. NH_4Cl **d.** $(NH_4)_2SO_4$
   (IIT-JEE 2008)

5. For the given aqueous reaction, which of the statement(s) is(are) true?



   a. The first reaction is a redox reaction.
   b. White precipitate is $Zn_3[Fe(CN)_6]_2$.
   c. Addition of filtrate to starch solution gives blue colour.
   d. White precipitate is soluble in NaOH solution.
   (IIT-JEE 2012)

6. 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+}
   (JEE Advanced 2015)

Linked Comprehension Type

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. **(IIT-JEE 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 Advanced 2013)**

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

Integet Answer 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 Advanced 2014)

Assertion-Reasoning Type

1. Read the following statement and explanation and answer as per the options given below:
   Assertion: A very dilute acidic solution of Cd^{2+} and Ni^{2+} gives yellow precipitate of CdS on passing hydrogen sulphide.
   Reason: Solubility product of CdS is more than that of NiS.
   a. If both assertion and reason are correct and reason is the explanation of assertion.
   b. If assertion is correct and reason is wrong, reason is not the explanation of assertion.
   c. If assertion is wrong and reason is correct, reason is not the explanation of assertion.
   d. If both assertion and reason are wrong and reason is not the explanation of assertion. **(IIT-JEE 1989)**
2. Read the following statement and explanation and answer as per the options given below:
   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.
   (IIT-JEE 1998)

Fill in the Blanks Type

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. **(IIT-JEE 1984)**

2. The formula of the deep red liquid formed on warming dichromate with KCl in concentrated sulphuric acid is _____ **(IIT-JEE 1993)**

True/False Type

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

Subjective Type

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. **(IIT-JEE 1979)**
2. Suggest a simple qualitative test to distinguish between each of the following pairs:
   i. $PbCO_3$ and $PbSO_4$
   ii. $CaCl_2$ and $MgCl_2$
   iii. Na_2SO_3 and $Na_2S_2O_3$ **(IIT-JEE 1979)**
3. A white amorphous powder A on heating yields a colourless, non-combustible gas B and a solid C. The latter 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 dilute HCl with the evolution of gas, which is identical in all respect 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 gas obtained above gives a white precipitate D on the addition of excess of NH_4OH and passing H_2S. Another portion of the solution gives initially a white precipitate E on the addition of NaOH solution, which dissolves on further addition of base. Identify the compounds A, B, C, D and E. **(IIT-JEE 1979)**
4. Explain the following in not more than two sentences:
   "A solution of $FeCl_3$ in water gives a brown precipitate on standing". **(IIT-JEE 1980)**
5. 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 $KMnO_4$ 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 **(IIT-JEE 1980)**
6. 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. **(IIT-JEE 1984)**
7. What happens when
   i. Hydrogen sulphide is bubbled through an aqueous solution of sulphur dioxide.
   ii. Aqueous ammonia is added dropwide to a solution of copper sulphate till it is in excess.
   iii. Tin is treated with concentrated nitric acid.
   iv. $CrCl_3$ solution is treated with sodium hydroxide and then with hydrogen peroxide.
   v. Pb_3O_4 is treated with nitric acid. **(IIT-JEE, 1985)**
8. Write the balanced equations for the reactions, when "a mixture of potassium chlorate, oxalic acid, and sulphuric acid is heated." **(IIT-JEE 1985)**
9. 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. **(IIT-JEE 1986)**
10. Write the balanced equation for the following. "Potassium permanganate is reacted with warm solution of oxalic acid in the presence of sulphuric acid." **(IIT-JEE 1987)**
11. A mixture of two salts was treated as follows:
    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 ammonoium 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). **(IIT-JEE 1987)**

12. 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. **(IIT-JEE 1988)**

13. 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 an alkaline medium.

ii. Cobalt (II) solution reacts with KNO_2 in acetic acid medium. **(IIT-JEE 1989)**

14. When 20.02 g of a white solid X is heated 4.4g of an acid gas A and 1.8 g of a natural gas B are evolved, leaving behind a solid residue Y of weight 13.8g. 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 19.7g of white precipitate Z with barium chloride solution. Z gives carbon dioxide with an acid. Identify A, B, X, Y and Z.

(IIT-JEE 1989)

15. 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."

(IIT-JEE 1991)

16. In the following reaction, identify the compounds/reaction conditions represented by A and B.

$$PbS \xrightarrow{\text{Heat in air}} A + PbS \xrightarrow{B} Pb + SO_2$$

(IIT-JEE 1991)

17. 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. **(IIT-JEE 1991)**

18. 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. **(IIT-JEE 1992)**

19. The acidic aqueous solution of ferrous ion forms a brown complex in the presence of $NO_3^{\ominus}$ by the following two steps:

$$[Fe(H_2O)_6]^{2+} + NO_3^{\ominus} + H^{\oplus} \rightarrow ... + [Fe(H_2O)_6]^{3+} + H_2O$$

$$[Fe(H_2O)_6]^{2+} + ... \rightarrow ... + H_2O$$

Complete and balance the equations. **(IIT-JEE 1993)**

20. 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 reactions involved. **(IIT-JEE 1993)**

21. 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 **(IIT-JEE 1994)**

22. 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 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. **(IIT-JEE 1995)**

23. The gradual addition of KI solution to $Bi(NO_3)_3$ solution initially produces a dark brown precipitate which dissolves in excess of KI to give a yellow solution. Write the chemical equations for the above reactions.

(IIT-JEE 1996)

24. 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. **(IIT-JEE 1996)**

25. 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. **(IIT-JEE 1996)**

26. Element A burns in nitrogen to give an ionic compound B. Compound B reacts with water to give C and D. A solution of C becomes "milky" on bubbling carbon dioxide. Identify A, B, C and D. **(IIT-JEE 1997)**

27. 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. **(IIT-JEE 1998)**

28. 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.

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.

(IIT-JEE 1999)

29. 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 colourless. The orange colour reappears on subsequent addition of NaOCl. Explain with equations. **(IIT-JEE 1999)**

30. Write the chemical reactions associated with the "brown ring test." **(IIT-JEE 2000)**

31. 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. **(IIT-JEE 2000)**

32. Write the chemical reactions associated with the 'borax bead test' of cobalt (II) oxide. **(IIT-JEE 2000)**

33. 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. **(IIT-JEE 2001)**

34. 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. **(IIT-JEE 2002)**

35. Identify the following:

$$Na_2CO_3 \xrightarrow{SO_2} A \xrightarrow{Na_2CO_3} B \xrightarrow{\text{Element S}} C \xrightarrow{I_2} D$$

Also, mention the oxidation state of S in all the compounds. **(IIT-JEE 2003)**

36. 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. **(IIT-JEE 2003)**

37. AlF_3 is insoluble in anhydrous HF but when little KF is added to the compound it becomes soluble. On addition of BF_3, AlF_3 is precipitated. Write the balanced chemical equations. **(IIT-JEE 2004)**

38.

$$\underset{\substack{\text{(White fumes}\\ \text{having smell)}}}{B} \xleftarrow{\text{Molar air}} \underset{\substack{\text{M = (Transition}\\ \text{element colourless)}}}{MCl_4} \xrightarrow{Zn} \underset{\substack{\text{(Purple}\\ \text{colour)}}}{A}$$

Identify the metal M and hence MCl_4. Explain the difference in colours of MCl_4 and A. **(IIT-JEE 2005)**

Answer Key

JEE Advanced

Single Correct Answer Type

1. d.	**2.** a.	**3.** c.	**4.** a.	**5.** d.
6. c.	**7.** c.	**8.** b.	**9.** d.	**10.** c.
11. a.	**12.** c.	**13.** b.	**14.** b.	**15.** d.
16. a.	**17.** b.	**18.** b.	**19.** a.	**20.** a.
21. d.	**22.** b.	**23.** d.		

Multiple Correct Answers Type

1. a., b.	**2.** a., b., d.	**3.** b., c.
4. a., b.	**5.** a., c., d.	**6.** c., d.

Linked Comprehension Type

1. d.	**2.** c.	**3.** b.	**4.** a.	**5.** d.

Integer Answer Type

1. (7)

Assertion–Reasoning Type

1. d. **2.** b.

Fill in the Blanks Type

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

True/False Type

1. True. **2.** True.

Hints and Solutions

JEE ADVANCE

Single Correct Answer Type

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

2. a. $NaHCO_3$ and NaOH cannot coexist in solution because $NaHCO_3$ is an acid salt. It reacts with the base NaOH as follows:

$$NaHCO_3 + NaOH \rightarrow Na_2CO_3 + H_2O$$

3. c. Acetic acid, being an acid, reacts with calcium oxide, hydroxide and calcium carbonate. No reaction with calcium oxalate.

4. a. 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.

5. d. $2CuSO_4 + 10KCN \rightarrow 2K_3[Cu(CN)_4] + 2K_2SO_4 + (CN)_2$
First, $Cu(CN)_2$ is formed which decomposes to form $(CN)_2$ and $Cu_2(CN)_2 \cdot Cu_2(CN)_2$ then combines with KCN to form $K_3[Cu(CN)_4]$.

6. c. Only group I cations are precipitated by dil. HCl

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

$$3SO_2 + K_2Cr_2O_7 + H_2SO_4 \rightarrow K_2SO_4 + \underset{\text{(green colour solution)}}{Cr_2(SO_4)_3} + H_2O$$

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.

7. c. In the presence of peroxide, chromium ions are oxidized to chromate ions which give a yellow filtrate. Ferric ions form brown precipitate of $Fe(OH)_3$.

8. b. Fe^{3+} is a third group radical, whose reagent is NH_4OH in presence of NH_4Cl. So if 6M NH_3 is added in the slightly acidic (HCl) solution of ions it will lead to the precipitation of Fe^{3+} as $Fe(OH)_3$.

$$Fe^{3+} + Zn^{2+} + Cu^{2+} \xrightarrow{6M\ NH_3}$$

$$\underset{\text{Brown ppt}}{Fe(OH)_3} + \underset{\text{Soluble}}{[Zn(NH_3)_4]^{2+}} + \underset{\text{Soluble}}{[Cu(NH_3)_4]^{2+}}$$

9. d. $Pb^{+2} + 2HCl \rightarrow \underset{\substack{\text{White ppt.}\\ \text{dissolves on boiling}\\ \text{[Soluble in hot water]}}}{PbCl_2 \downarrow} \xrightarrow{H_2S} \underset{\text{Black ppt}}{PbS \downarrow}$

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

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

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

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

11. a. [X] $\rightarrow H_2SO_4 \rightarrow$ [Y] colourless gas with irritating smell
[Y] $\rightarrow H_2SO_4 + K_2Cr_2O_7 \rightarrow$ Green solution.
Sulphite ion give sulphur dioxide gas with sulphuric acid, which turns acidified potassium dichromate to green.

$$SO_3^{2-} + H_2SO_4 \rightarrow SO_2 + H_2O + SO_4^{2-}$$

$$3SO_2 + K_2Cr_2O_7 + H_2SO_4 \rightarrow K_2SO_4 + \underset{\text{(Green)}}{Cr_2(SO_4)_3} + H_2O$$

12. c. For precipitation,
Ionic product > Solubility product
HgS having the lowest K_{sp} among the given compounds will precipitate first.

13. b. It must be a bicarbonate ion because first magnesium bicarbonate is formed which is soluble, then on heating, magnesium carbonate is formed which is insoluble and forms a precipitate.

$$MgCl_2 + 2NaHCO_3 \rightarrow \underset{\text{Soluble}}{Mg(HCO_3)_2} + 2NaCl$$

$$Mg(HCO_3)_2 \xrightarrow{\Delta} \underset{\text{White}}{MgCO_3 \downarrow} + H_2O + CO_2$$

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

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

The metal ion is Bi^{3+}

15. d. $2CuSO_4 + 10KCN \rightarrow 2K_3[Cu(CN)_4] + 2K_2SO_4 + (CN)_2$
First, $Cu(CN)_2$ is formed which decomposes to form $(CN)_2$ and $Cu(CN)_2 \cdot Cu_2(CN)_2$ then combines with KCN to form $K_3[Cu(CN)_4]$.

16. a. $CO_2 + H_2O \rightleftharpoons H_2CO_3$

$H_2CO_3 \rightleftharpoons H^{\oplus} + HCO_3^{\ominus}$

$HCO_3^{\ominus} \rightleftharpoons H^{\oplus} + CO_3^{2-}$

17. 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.

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

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

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

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

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

19. a. In the presence of acid, ionization of H_2S is suppressed, 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.

20. a. Sulphide ore of Ag is Aregentite and of Pb is Galena (PbS) and of Cu is copper glance (Cu_2S).
Hence (a) is correct.

21. d. $S^{2-} + O_2 \xrightarrow{\text{Roasting}} SO_2 + 2e^{\ominus}$

i. Sulphides on roasting never form SO_3, since it is produced by reacting SO_2 with O_2 in the presence of a catalyst (Pt, or V_2O_5) and at optimum temperature (720 K) and high pressure (2 bar)
$SO_2 + O_2 \rightleftharpoons 2SO_3$
So X can be SO_2 not SO_3.

ii. SO_2 and SO_3 both are colourless gas but only SO_2 has a chocking smell of SO_2. NO_2 and SO_2 from atmosphere after oxidation and reaction with water are major contributor to acid rain.
$2SO_{2(g)} + O_{2(g)} + 2H_2O_{(l)} \rightarrow 2H_2SO_{4(aq)}$
$4NO_{2(g)} + O_{2(g)} + 2H_2O_{(l)} \rightarrow 4HNO_{3(aq)}$
So X can be SO_2 not SO_3.

iii. Aqueous solution of both SO_2 and SO_3 are acidic. SO_2 acts as reducing agent (undergo oxidation from +4 to +6 oxidation state) but SO_3 does not acts as reducing agent (i.e., it has maximum oxidation state of +6)
So X can be SO_2 not SO_3.

iv. SO_2 reacts with H_2O as given below, and H_2SO_3 is never isolated.
$SO_2 + x.H_2O \rightleftharpoons SO_2.xH_2O$.
Hence the answer is (d), i.e. SO_2.

22. b. Higher the K_{sp} of sulphide more is the solubility in aqueous medium.
In the salt analysis K_{sp} of sulphides increases from group I of salt analysis to group IV of salt analysis.
Cu^{+2} ion is in group II whereas Zn^{+2} is in group IV of salt alalysis.

$\therefore$ Solubility of ZnS > CuS

Since the K_{sp} of sulphides of sodium is the highest, therefore it is highly soluble.

Hence the answer is (b), i.e., solubilities of

$$Na_2S > ZnS > CuS$$

23. 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.

Multiple Correct Answer Type

1. a., b.

Al^{3+} (third group radical) and Ca^{2+} (fifth group radical) precipitated 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

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

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

3. b., c.

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

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

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

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

4. a., b.

The gas is ammonia and the salt can be nitrate or nitrite as suggested by the following reactions:

$$NH_4NO_3 + NaOH \rightarrow NaNO_3 + NH_3 + H_2O$$

$$NaNO_3 + 8[H] \rightarrow NaOH + NH_3 + 2H_2O$$

$$NH_4NO_2 + NaOH \rightarrow NaNO_2 + NH_3 + H_2O$$

$$NaNO_2 + 6[H] \rightarrow NaOH + NH_3 + H_2O$$

5. a., c:, d.

$$KI_{(aq)} + K_3[Fe(CN)_6]_{(aq)} \longrightarrow \underset{\text{Brownish yellow}}{KI_{3(aq)}} + [Fe(CN)_{6(aq)}]$$

$$\downarrow$$

$$[K_2Zn[FeCN)_6]\downarrow \quad \text{OR} \quad \underset{\text{White ppt.}}{K_2Zn_3[FeCN)_6]_2\downarrow} + KI_{3(aq)}$$

$$\downarrow Na_2S_2O_3$$

$$I^{\ominus}_{(aq)} + S_4O^{2-}_{6\,(aq)}$$

Colourless

6. 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+}).

Linked Comprehension Type

1. d.

2. c.

3. b. For 1-3

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

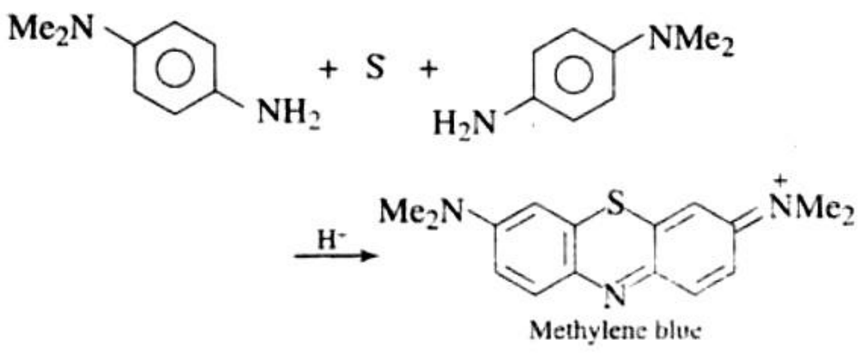
$$\underset{Y}{4Fe^{3+}} + 3[Fe(CN)_6]^{4-} \rightarrow \underset{\substack{\text{hexacyanoferrate (II)}\\ \text{or ferrocyanide}}}{Fe_4[Fe(CN)_6]_3}\downarrow \quad \underset{\text{Intense blue ppt. soluble in excess of ferrocyanide}}{}$$

$$\underset{Y}{Fe^{3+}} + \underset{\substack{\text{hexacyanoferrate (III)}\\ \text{or ferrocyanide}}}{[Fe(CN)_6]^{3-}} \rightarrow \underset{\substack{\text{Brown colour}\\ \text{(Z)}}}{Fe[Fe(CN)_6]}$$

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

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

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



4. a. Lead salts give white precipitate of $PbCl_2$ with dil. HCl which is soluble in hot water.

$Pb^{++} + 2Cl^- \rightarrow PbCl_2$ (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.

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

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

Integer Answer Type

1. (7) Black sulphide are

PbS, CuS, HgS, NiS, CoS, Bi_2S_3 and Ag_2S

MnS is buff

SnS_2 is yellow.

Bi_2S_3 in its crystalline form is dark brown but Bi_2S_3 precipitate obtained is black in colour.

Assertion-Reasoning Type

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.

Fill in the Blanks Type

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) and as NH_4Cl suppresses the ionization of NH_4OH, this solubility product is not reached.

2. Chromyl chloride (CrO_2Cl_2).

$$K_2Cr_2O_7 + 2H_2SO_4 \rightarrow 2KHSO_4 + 2CrO_3 + H_2O$$
$$KCl + H_2SO_4 \rightarrow KHSO_4 + HCl$$
$$CrO_3 + 2HCl \rightarrow \underset{\text{Orange red vapour}}{CrO_2Cl_2} + H_2O$$

True/False Type

1. **True:**
   Function of ammonium chloride is to suppress the ionization 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.

Subjective Type

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.

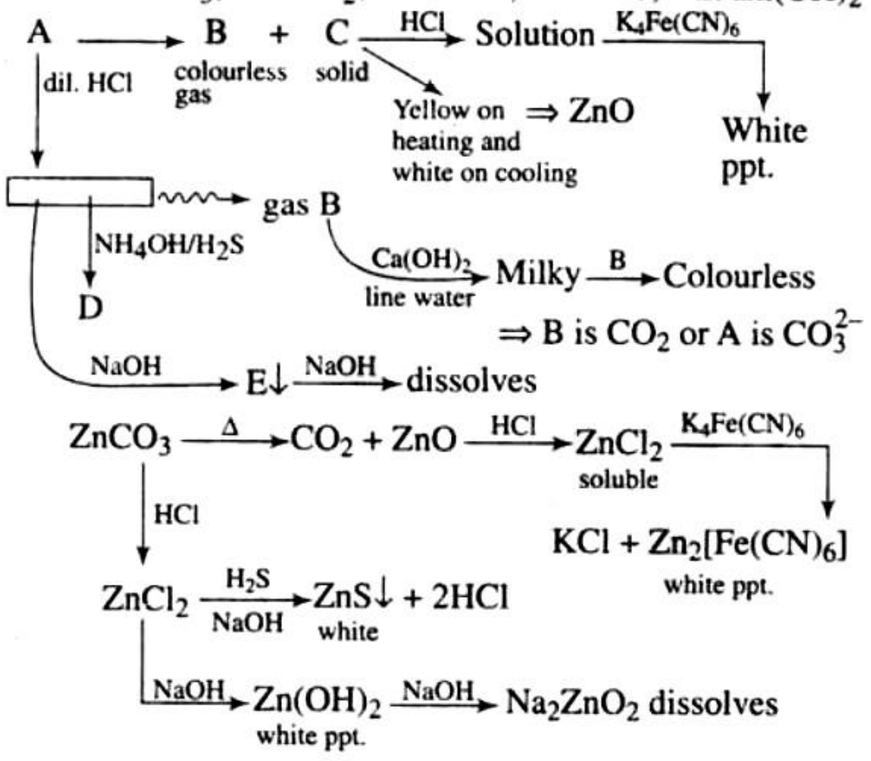
2. i. $PbCO_3 + HCl \xrightarrow{\Delta} CO_2\uparrow$

   $PbSO_4 + HCl \xrightarrow{\Delta}$ No reaction

   ii. $CaCl_2$ imparts brick red colouration to burner flame and $MgCl_2$ does not impart any colour to flame.

   iii. $Na_2S_2O_3$ shows colour with $AgNO_3$ solution but Na_2SO_3 does not.

3. A:$ZnCO_3$; B: CO_2; C: ZnO; D: ZnS; E: $Zn(OH)_2$



4. A brown precipitate of ferric hydroxide is formed due to hydrolysis.

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

5. A: $FeSO_4$; B: SO_2; C: SO_3; D: Fe_2O_3; E: $BaSO_4$
According to the question

$$(A) \xrightarrow{H_2SO_4} Fe^{2+} + \underset{\text{Pink}}{MnO_4^-} \longrightarrow \underset{\text{colourless}}{Mn^{2+}} + Fe^{3+}$$

$$(A) \xrightarrow{\Delta} \underset{(D)}{Fe_2O_3} \xrightarrow[\text{reducing flame}]{\text{charcoal (C)}} Fe \text{ (a magnetic substance)}$$

$$\underset{(B)}{SO_2} \text{ and } \underset{(C)}{SO_3} \xrightarrow{Cr_2O_7^{2-}} SO_4^{2-} + Cr^{3+} [Cr_2(SO_4)_3\text{: green}]$$
$$\downarrow BaNO_3$$
(reducing action of gases) $BaSO_4$(E)

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

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

The above equation leads to the following facts:

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

ii. 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.

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

Calculation of molecular weight of $MHCO_3$
4.4g of CO_2 is given by 16.8g of $MHCO_3$

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

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.

$$\underset{(X)}{2NaHCO_3} \xrightarrow{\text{heat}} \underset{(A)}{CO_2} + \underset{(B)}{H_2O} + \underset{(Y)}{Na_2CO_3}$$
$$Na_2CO_3 + BaCl_2 \rightarrow \underset{\text{White}}{\underset{(Z)}{BaCO_3}} + 2NaCl$$
$$BaCO_3 + HCl \rightarrow BaCl_2 + H_2O + CO_2\uparrow$$

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

7. i. Sulphur is precipitated.

$$SO_2 + 2H_2S \rightarrow 3S + 2H_2O$$

ii. Ammonia gives deep-blue colour with copper sulphate due to the formation of a complex.

$$CuSO_4 + 2NH_4OH \rightarrow Cu(OH)_2 + (NH_4)_2SO_4$$

$$Cu(OH)_2 + 2NH_4OH + (NH_4)_2SO_4 \rightarrow \underset{\text{Blue}}{[Cu(NH_3)_4]SO_4} + 4H_2O$$

iii. Metastannic acid is formed.

$$Sn + 3HNO_3 \text{ (conc.)} \rightarrow H_2SnO_3 + 4NO_2 + H_2O$$

iv. A yellow solution of sodium chromate is produced.

$$H_2O_2 \rightarrow H_2O + O$$

$$2CrCl_3 + 10NaOH + 3[O] \rightarrow 2NaCrO_4 + 6NaCl + 3H_2O$$

v. Lead dioxide is precipitated.

$$Pb_3O_4 + 4HNO_3 \rightarrow 2Pb(NO_3)_2 + 2H_2O + PbO_2$$

8. $3KClO_3 + 3H_2SO_4 \text{ (conc.)} \xrightarrow{\Delta} 3KHSO_4 + HClO_4 + 2ClO_2 + H_2O$

$$(COOH)_2 \xrightarrow{\text{conc. } H_2SO_4} CO + CO_2 + H_2O$$

9. i. Sodium zincate is formed.

$$ZnO + 2NaOH \rightarrow Na_2ZnO_2 + H_2O$$

ii. Stannous chloride is a good reducing agent.
It reduces iodine to iodide.

$$SnCl_2 + 2HCl + I_2 \rightarrow SnCl_4 + 2HI$$

iii. Sodium sulphate is formed.

$$SO_2 + H_2O + \underset{\text{Air}}{\frac{1}{2}O_2} + 2NaCl \rightarrow Na_2SO_4 + 2HCl$$

10. Ionic equation:

$$2MnO_4^{\ominus} + 5C_2O_4^{2-} + 16H^{\oplus} \rightarrow 2Mn^{2+} + 8H_2O + 10CO_2$$

11. 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. $2Cl^- + MnO_2 + H_2SO_4 + 2H^+ \rightarrow Mn^{2+} + SO_4^{2-} + 2H_2O + \underset{\text{(Yellowish green)}}{Cl_2\uparrow}$

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

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

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

12. 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 $FeSO_4 \cdot 7H_2O$

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

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

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

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

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 $BaSO_4$.

$$SO_3 + H_2O \rightarrow H_2SO_4$$

$$BaCl_2 + H_2SO_4 \rightarrow \underset{\text{White ppt.}}{BaSO_4} + 2HCl$$

13. i. Silver goes into the complex and then it is displaced with zinc.

$$AgCl + 2NaCN \rightarrow NaCl + Na[Ag(CN)_2]$$

$$2Na[Ag(CN)]_2 + Zn \rightarrow Na_2[Zn(CN)_4] + 2Ag\downarrow$$

ii. A yellow precipitate is formed.

$$KNO_2 + CH_3COOH \rightarrow CH_3COOK + HNO_2$$

$$CoCl_2 + 2KNO_2 \rightarrow Co(NO_2)_2 + 2KCl$$

$$Co(NO_2)_2 + 2HNO_2 \rightarrow Co(NO_2)_3 + NO + H_2O$$

$$Co(NO_2)_3 + 3KNO_2 \rightarrow K_2[Co(NO_2)_6]$$

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

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

15. In NaOH, the hydroxide of Al becomes soluble due to the formation of sodium meta-aluminate

$$Al(OH)_3 + NaOH \rightarrow NaAlO_2 + 2H_2O$$

Hydroxide of iron does not dissolve in NaOH.

16. $PbS \xrightarrow{\text{Heat in air}} PbO + PbS$

$$PbO + PbS \xrightarrow[[B]]{\text{Heat in [A] absence of air}} Pb + SO_2$$

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

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

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

Deep blue colour, (B) $\xleftarrow{K_3[Fe(CN)_6]}$ Aq. solution of the mixture $\xrightarrow{BaCl_2}$ 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. 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.

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

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

18. '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.'

$FeSO_4 (NH_4)_2SO_4 \cdot 6H_2O$

Reactions:

$$3NaOH + NH_3 + 2K_2[HgI_4] \rightarrow O\begin{<}{Hg}{Hg}\underset{\text{Brown ppt}}{>} NH_2I + 4KI + 3NaI + 2H_2O$$

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

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

19. $3[Fe(H_2O)_6]^{2+} + NO_3^{\ominus} + 4H^{\oplus} \rightarrow NO + 3[Fe(H_2O)_6]^{3+} + 2H_2O$

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

20. Let us summarise the given facts

$$\underset{\text{(A)}}{\text{Orange solid}} \xrightarrow{\text{heat}} \underset{\text{(B)}}{\text{Green residue}} + \underset{\text{(C)}}{\text{Colourless gas}} + H_2O(g)$$

$$\text{Colourless gas (C)} \xrightarrow{\text{heated Mg}} \underset{\text{(D)}}{\text{White solid}} \xrightarrow{H_2O} \text{(E)} \xrightarrow{HCl} \text{White dense fumes}$$

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:

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

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

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

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

21. 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, –0.321g 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 $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$
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.

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

$2(39.1 + 32) = 142.2$

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.

22. According to question

$$(A) \xrightarrow{\text{conc. } HNO_3} (B)\downarrow + \text{Solution} \xrightarrow{\text{Filter}} \text{Filtrate} \xrightarrow[\text{(ii) KI}]{\text{(i) NaOH}} (C)\downarrow$$

$(B)\downarrow \xrightarrow[\text{conc. } HNO_3 \text{ in presence of } Mn(NO_3)_2]{\text{warm with}}$ Pink coloured solution (D)

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.

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

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

$$\underset{\text{ppt. (B)}}{5PbO_2} + 2Mn(NO_3)_2 + 4HNO_3 \rightarrow \underset{\text{Pink colouration (D)}}{Pb(MnO_4)_2} + 4Pb(NO_3)_2 + 2H_2O$$

23. The 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 yellow solution. Iodide is oxidized to iodine which dissolves in KI to give a yellow solution of KI_3.

$$Bi^{3+} + H_2O \rightleftharpoons Bi(OH)^{2+} + H^{\oplus}$$

$$[NO_3^{\ominus} + 4H^{\oplus} + 3e^{\ominus} \rightarrow NO + 2H_2O] \times 2$$

$$[2I^{\ominus} \rightarrow I_2 + 2e^{\ominus}] \times 3$$

$$2NO_3^{\ominus} + 8H^{\oplus} + 6I^{\ominus} \rightarrow 2NO + 4H_2O + 3I_2$$

$$KI + I_2 \rightarrow KI_3$$

24. The reactions are given as follows:

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

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

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

25. According to question

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

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.

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

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

26. The given data suggest the following reactions.

$$\underset{\text{(A)}}{3Ca} + N_2 \rightarrow \underset{\text{(B)}}{Ca_3N_2}$$

$$Ca_3N_2 + 6H_2O \rightarrow \underset{\text{(C)}}{3Ca(OH)_2} + \underset{\text{(D)}}{2NH_3}$$

$$\underset{\text{(C)}}{Ca(OH)_2} + CO_2 \rightarrow CaCO_3 + H_2O$$

It is given that a solution of C becomes 'milky' on bubbling carbon dioxide. Therefore, it must be calcium or barium hydroxide which is more soluble than magnesium hydroxide.

27. The solubility products of CuS and ZnS are

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

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.

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

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

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.

$$Na_2O + H_2O \rightarrow 2NaOH$$

29. 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

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

30. Brown ring test is done for the detection of nitrates.
To a solution containing the salt and freshly prepared ferrous sulphate, concentrated sulphuric acid is added gradually along the sides of the tube. A brown ring appears at the junction of the two liquids.

$$NO_3^{\ominus} + 3Fe^{2+} \rightarrow NO + 3Fe^{3+} + 2H_2O$$

$$[Fe(H_2O)_6]^{2+} + NO \rightarrow \underset{\text{Brown}}{[Fe(H_2O)_5NO]^{2+}} + H_2O$$

31. According to question

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

$\downarrow$ KI, H^+

Yellow solution. (B)

The reaction corresponds to copper sulphate

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

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

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

32. $\underset{\text{Borax}}{Na_2B_4O_7 \cdot 10H_2O} \xrightarrow{\Delta}$

$$Na_2B_4O_7 \xrightarrow{740^\circ C} 2NaBO_2 + \underset{\text{Transparent}}{B_2O_3}$$

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

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

33. $\underset{\text{(White)}}{A} \xrightarrow{\text{dil.}H_2SO_4} \underset{\text{(colourless gas)}}{B} + \underset{\text{(Colourless solution)}}{C}$

$\downarrow K_2Cr_2O_7/H^+$

Green solution + $D\downarrow$ (burns in air to form gas E)

(coloured)

$$E\uparrow + B\uparrow \rightarrow D + \text{Colourless liquid} \xrightarrow{\text{anhyd. } CuSO_4} \text{Blue colour,}$$

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

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.

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

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

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

$$\underset{\text{(White)}}{CuSO_4} + \underset{\text{(colourless liquid)}}{5H_2O} \rightarrow \underset{\text{(blue)}}{CuSO_4 \cdot 5H_2O}$$

(Hydrated $CuSO_4$)

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

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

34. According to question

$\underset{\text{(White crystalline)}}{X} + K_2Cr_2O_7 + H_2SO_4 \text{ (conc.)} \rightarrow \underset{\text{(Reddish brown ppt.)}}{A} \xrightarrow{NaOH} \underset{\text{(Yellow coloured solution)}}{B}$

$\downarrow$ NaOH solution

Colourless gas

$\downarrow K_2(HgI_4)$ solution

D

Reddish brown ppt.

$\downarrow CH_3COOH + Pb(CH_3COO)_2$

$C\downarrow$

(Yellow ppt.)

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.

$$\underset{\text{(X)}}{4NH_4Cl} + K_2Cr_2O_7 + 3H_2SO_4 \rightarrow K_2SO_4 + 2(NH_4)_2SO_4 + \underset{\substack{\text{Chromyl chloride, (A)}\\\text{(reddish brown)}}}{2CrO_2Cl_2}\uparrow + 3H_2O$$

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

$$\underset{\text{(B)}}{Na_2CrO_4} + (CH_3COO)_2Pb \rightarrow 2CH_3COONa + \underset{\substack{\text{Leadchromate,}\\\text{(C)}\\\text{(yellow ppt.)}}}{PbCrO_4}\downarrow$$

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

$$NH_3 + 2K_2HgI_4 + 3KOH \rightarrow \left[\begin{array}{c} Hg \\ O \quad NH_2 \\ Hg \end{array}\right] I + 7KI + 2H_2O$$

Iodide of Million's base (D)

(reddish brown ppt)

35. $\underset{\text{[A]}}{2NaHSO_3} + Na_2CO_3 \rightarrow 2Na_2SO_3 + H_2O + CO_2$

$$\underset{\text{[A]}}{2NaHSO_3} + Na_2CO_3 \rightarrow \underset{\text{[B]}}{2Na_2SO_3} + H_2O + CO_2$$

$$\underset{\text{[B]}}{Na_2SO_3} + S \rightarrow \underset{\text{[C]}}{Na_2S_2O_3}$$

$$\underset{\text{[C]}}{2Na_2S_2O_3} + I_2 \xrightarrow{\Delta} \underset{\text{[D]}}{Na_2S_4O_6} + 2NaI$$

Oxidation states of sulphur:

$NaHSO_3$ (+6) $\quad$ Na_2SO_3 (+6)

$Na_2S_2O_3$ (+2) or (+5 and −1)

$Na_2S_4O_6$ (+2) or (+5 and 0)

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

$$HgI_2 + H_2S \rightarrow \underset{(C)}{HgS} + 2HI$$

$$HgI_2 \xrightarrow{\text{aqua regia}} HgCl_2;$$

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

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

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

$$HgI_2 + Na_2CO_3 \longrightarrow 2NaI \xrightarrow{CCl_4} \text{Violet layer}$$

$$\downarrow AgNO$$

$$AgI\downarrow \text{(Yellow)}$$

(Insoluble in ammonia)

37. Anhydrous HF is stabilized due to intermolecular H-bonding and is less dissociated. AlF_3 is soluble in HF in the presence of KF due to the formation of $[AlF_6]^{3-}$.

$$3KF + AlF_3 \rightarrow K_3[AlF_6]$$

BF_3 displaces out $F^{\ominus}$ from $[AlF_6]^{3-}$ because it is more acidic than AlF_3

$$K_3[AlF_6] + BF_3 \rightarrow AlF_3\downarrow 3KBF_4$$

38. $\underset{\substack{\text{(White fumes}\\ \text{having smell)}}}{B} \xleftarrow{\text{Molar air}} \underset{\substack{\text{M = (Transition}\\ \text{element colourless)}}}{MCl_4} \xrightarrow{Zn} \underset{\substack{\text{(Purple}\\ \text{colour)}}}{A}$

M = Ti, $MCl_4 = TiCl_4$

A = $[Ti(H_2O)_6]^{3+}$ B = TiO_2

Ti (IV) ion contains no d-electron, so it is colourless.

Ti (III) ion contains one d-electron, so it is coloured.