# Fill Ups of Analytical Chemistry, Past year Questions

**Q.1. If metal ions of group III are precipitated by $NH_4Cl$ and $NH_4OH$ without prior oxidation by conc. $HNO_3$ ..... is not completely precipitated. (1984 - 1 Mark)**

**Ans.** $Fe^{3+}$

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

**Q.2. The formula of the deep red liquid formed on warming dichromate with KCl in concentrated sulphuric acid is..... (1993 - 1 Mark)**

**Ans.** $CrO_2Cl_2$

**Sol.** Chromyl chloride ($CrO_2Cl_2$).

# True False of Analytical Chemistry, Past year Questions

**Q.1. Addition of ammonium chloride to a solution containing ferric and magnesium ions is essential for selective precipitation of ferric hydroxide by aqueous ammonia. (1985 - ½ Mark)**

**Ans. T**

**Sol. True:** Function of ammonium chloride is to suppress the Ionisation of $NH_4OH$ and thus check the precipitation of $Mg(OH)_2$ because the solubility product of $Mg(OH)_2$ is high.

This is used in salt analysis when 3rd group radicals are precipitated. The group reagent are $NH_4OH$ in presence of $NH_4Cl$.

**Q.2. From the acidic solution containing copper (+2) and zinc (+2) ions, copper can be selectively precipitated using sodium sulphide. (1987 - 1 Mark)**

**Ans. T**

**Sol. 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 questions of Analytical Chemistry (Part -1)

**Q.1. Account for the following. Limit your answer to two sentences: The precipitation of second group sulphides in qualitative analysis is carried out with hydrogen sulphide in presence of hydrochloric acid and not nitric acid. (1979)**

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

**Q.2. Compound A is a light green crystalline solid. It gives the following tests: (1980)**
**(i) It dissolves in dilute sulphuric acid. No gas is produced. (ii) A drop of $KMnO_4$ is added to the above solution. The pink colour disappears. (iii) Compound A is heated strongly. Gases B and C, with pungent smell, come out. A brown residue D is left behind. (iv) The gas mixture (B) and (C) is passed into a dichromate solution. The solution turns green. (v) The green solution from step (iv) gives a white precipitate E with a solution of barium nitrate. (vi) Residue D from step (iii) is heated on charcoal in a reducing flame. It gives a magnetic substance.**
**Name the compounds A, B, C, D and E**

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

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

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

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

**Q.3. When 16.8 g of white solid X were heated, 4.4 g of acid gas A that turned lime water milky was driven off together with 1.8 g of a gas B which condensed to a colourless liquid. The solid that remained, Y, dissolved in water to give an alkaline solution, which with excess barium chloride solution gave a white precipitate Z. The precipitate effervesced with acid giving off carbon dioxide. Identify A, B and Y and write down the equation for the thermal decomposition of X. (1984 - 4 Marks)**

**Ans. Sol.** Representing the given facts in the form of equation.

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

The above equation leads to the following facts: (i) Since the gas A turned lime water milky, it must be $CO_2$.

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

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

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

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

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

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

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

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

Calculation of atomic weight of metal M $MHCO_3$ = 84; M + 1 + 12 + 48 = 84
M + 61 = 84; M = 84 – 61 = 23

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

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

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

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

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

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

**Q.4. A mixture of two salts was treated as follows : (1987 - 5 Marks)**
**(i) The mixture was heated with manganese dioxide and concentrated sulphuric acid when yellowish green gas was liberated.**
**(ii) The mixture on heating with sodium hydroxide solution gave a gas which turned red litmus blue.**
**(iii) Its solution in water gave blue precipitate with potassium ferricyanide and red colouration with ammonium thiocyanate.**
**(iv) The mixture was boiled with potassium hydroxide and the liberated gas was bubbled through an alkaline solution of $K_2HgI_4$ to give brown precipitate.**
**Identify the two salts. Give ionic equations for reactions involved in the tests (i), (ii) and (iii).**

**Ans. Sol.** (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 NH4Cl.

Ionic reactions :

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

(Yellowish green)

(ii) $NH_4^+ + OH^- \xrightarrow{\text{heat}} NH_3\uparrow + H_2O$

turns red litmus blue

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

(blue ppt.)

(b) $Fe^{3+} + 3CNS^- \rightarrow Fe(CNS)_3$

Ferric thiocyanate
(blood red colour)

**Q.5. A hydrated metallic salt A, light green in colour, on careful heating gives a white anhydrous residue B. B is soluble in water and its aqueous solution reacts with NO to give a dark brown compound C. B on strong heating gives a brown residue D and a mixture of two gases E and F. The gaseous mixture when passed through acidified permanganate, discharges the pink colour and when passed through acidified $BaCl_2$ solution gave a white precipitate. Identify A, B, C, D, E and F. (1988 - 3 Marks)**

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

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

$FeSO_4.7H_2O$

$FeSO_4.7H_2O \xrightarrow{\Delta} FeSO_4 + 7H_2O$

(A) (B)

$2FeSO_4 \xrightarrow{\Delta} Fe_2O_3 + SO_2\uparrow + SO_3\uparrow$ (s)

(B) (D) (E) (F)

Brown

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

$FeSO_4(aq) + NO \rightarrow FeSO_4.NO$

Brown ring (C)

(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 $BaSO_4$.

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

**Q.6. When 20.02 g of a white solid X is heated 4.4 g of an acid gas A and 1.8 g of a neutral gas B are evolved, leaving behind a solid residue Y of weight 13.8 g. A turns lime water milky and B condenses into a liquid which changes anhydrous copper sulphate blue. The aqueous solution of Y is alkaline to litmus and gives 19.7 g of white precipitate Z with barium chloride solution. Z gives carbon dioxide with an acid. Identify A, B, X, Y and Z. (1989 - 5 Marks)**

**Ans. Sol.** Representing the given facts in the form of equation, we get

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

The above equation leads to the following facts: (i) Since the gas A turned lime water milky, it must be $CO_2$.

(ii) **NOTE :** The compound Y is alkaline to litmus and when treated with BaCl2 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:

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

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.

$$\underset{X}{2KHCO_3} \xrightarrow{heat} \underset{A}{CO_2} + \underset{B}{H_2O} + \underset{Y}{K_2CO_3}$$

$$K_2CO_3 + BaCl_2 \rightarrow \underset{(white)}{BaCO_3} + 2KCl$$

Hence, we have

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

**Q. 7. The gas liberated on heating a mixture of two salts with NaOH, gives a reddish brown precipitate with an alkaline solution of $K_2[HgI_4]$. The aqueous solution of the mixture on treatment with $BaCl_2$ gives a white precipitate which is sparingly soluble in conc. HCl. On heating the mixture with $K_2Cr_2O_7$ and conc. $H_2SO_4$, red vapours of A are produced.**
**The aqueous solution of the mixture gives a deep blue colouration B with potassium ferricyanide solution. Identify the radicals in the given mixture and write the balanced equations for the formation of A and B. (1991 - 4 Marks)**

**Ans. Sol.** Let us summarise the given facts of the question.

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

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

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

The given reactions lead to the following conclusions.

(i) Formation of reddish brown precipitate on treatment with alk. $K_2[HgI_4]$ indicates the evolution of $NH_3$ gas and hence the presence of $NH^{4+}$ in the mixture of salts.

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

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

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

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

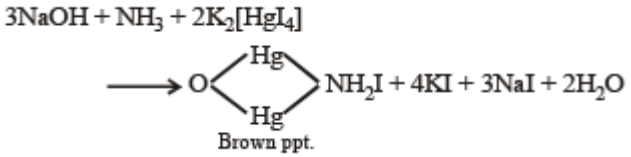
Equations for the formation of A and B.

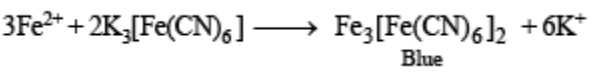
$$4NaCl + K_2Cr_2O_7 + 3H_2SO_4 \xrightarrow{\text{Heat}} K_2SO_4 + 2Na_2SO_4 + \underset{\text{Chromyl chloride}}{2CrO_2Cl_2\uparrow} + 3H_2O$$

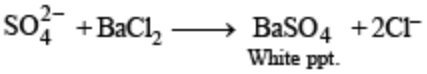
$$3Fe^{2+} + 2K_3[Fe(CN)_6] \rightarrow \underset{\text{(Blue ppt.) (B)}}{\overset{\text{(orange)(A)}}{Fe_3[Fe(CN)_6]_2}} + 6K^+$$

**Q.8. A light bluish green crystalline compound responds to the following tests :**
**(i) Its aqueous solution gives a brown precipitate or colour with alkaline $K_2[HgI_4]$ solution.**
**(ii) Its aqueous solution gives a blue colour with $K_3[Fe(CN)_6]$ solution.**
**(iii) Its solution in hydrochloric acid gives a white precipitate with $BaCl_2$ solution.**
**Identify the ions present and suggest the formula of the compound.**
**(1992 - 4 Marks)**

**Ans. Sol.** 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 $^{2-}$ $SO_4$ suggests that it is Mohr's salt i.e.' $FeSO_4(NH_4)_2SO_4.6H_2O$ Reactions :

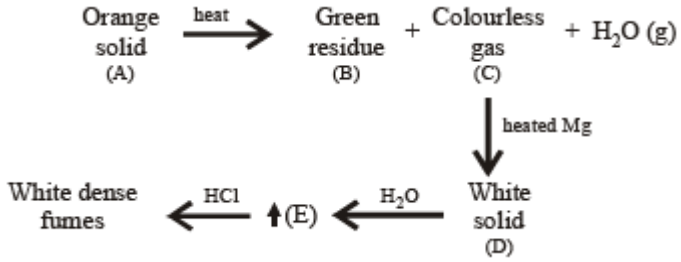



**Q.9. An orange solid (A) on heating gave a green residuce (B), a colourless gas (C) and water vapour. The dry gas (C) on passing over heated Mg gave a white solid (D). (D) on reaction with water gave a gas (E) which formed dense white fumes with HCl. Identify (A) to (E) and give reactions involved. (1993 - 3 Marks)**

**Ans. Sol.** Let us summaries the given facts




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

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

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

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

**Reactions:**

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

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

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

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

**Q.10. A is a binary compound of a univalent metal, 1.422 g of A reacts completely with 0.321 g of sulphur in an evaccuated and sealed tube to give 1.743 g of a white crystalline solid B, that forms a hydrated double salt, C with $Al_2(SO_4)_3$. Identify A, B and C (1994 - 5 Marks)**

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

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

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

32.1g of S reacts with 142.2g of $KO_2$ 0.321g of S reacts with = $\frac{142.2}{32.1} \times 0.321$ = 1.422 g

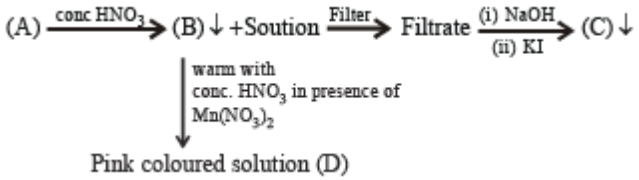
Similarly, 32.1 g of S gives 174.3 g of K2SO4

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

Both these data's are also given in the problem. Thus A is $KO_2$.

**Q.11. A scarlet compound A is treated with conc. $HNO_3$ to give a chocolate brown precipitate B. The precipitate is filtered and the filtrate is neutralised with NaOH. Addition of KI to the resulting solution gives a yellow precipitate C. The precipitate B on warming with conc. $HNO_3$ in the precence of $Mn(NO_3)_2$ produces a pink-coloured solution due to the formation of D. Identify A, B, C and D. Write the reaction sequence. (1995 - 4 Marks)**

**Ans. Sol.** Summary of the given facts.




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

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

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

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

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

# Subjective questions of Analytical Chemistry (Part -2)

**Q.12. Calcium burns in nitrogen to produce a white powder which dissolves in sufficient water to produce a gas (A) and an alkaline solution. The solution on exposure to air produces a thin solid layer of (B) on the surface. Identify the compounds A and B. (1996 - 2 Marks)**

**Ans. Sol.** The reactions are given as follows:

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

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

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

**Q.13. A colourless inorganic salt (A) decomposes completely at about 250°C to give only two products, (B) and (C), leaving no residue. The oxide (C) is a liquid at room temperature and neutral to moist litmus paper while the gas (B) is a neutral oxide. White phosphorus burns in excess of (B) to produce a strong white dehydrating agent. Write balanced equations for the reactions involved in the above process. (1996 - 3 Marks)**

**Ans. Sol.** Let us summaries the given facts.

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

$\xrightarrow{P}$ 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.

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

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

**Q.14. During the qualitative analysis of a mixture containing $Cu^{2+}$ and $Zn^{2+}$ ions, $H_2S$ gas is passed through an acidified solution containing these ions in order to test $Cu^{2+}$ alone.**

**Explain briefly. (1998 - 2 Marks)**

**Ans. Sol.** 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.

**Q.15. A white solid is either $Na_2O$ or $Na_2O_2$. A piece of red litmus paper turns white when it is dipped into a freshly made aqueous solution of the white solid. (1999 - 4 Marks) (i) Iden tify the substance and explain with balan ced equation. (ii) Explain what would happen to the red litmus if the white solid were the other compound.**

**Ans. Sol.** (i) The substance is $Na_2O_2$. When dissolved in water, the solution becomes alkaline with the liberation of $H_2O_2$ $Na_2O^{2+}$ $2H_2O \rightarrow 2NaOH + H_2O_2$

**NOTE:** Due to the alkaline solution, the red litmus paper will turn into blue, which subsequently changes into white due to oxidation caused by $H_2O_2$. (ii) The substance $Na_2O$ merely produces alkaline solution and thus the red litmus paper will turn into blue.

$Na_2O + H_2O \rightarrow 2NaOH$

**Q.16. An aqueous solution containing one mole of $HgI_2$ and two moles of NaI is orange in colour. On addition of excess NaI the solution becomes colouress. The orange colour reappears on subsequent addition of NaOCl. Explain with equation s. (1999 - 3 Marks)**

**Ans. Sol.** Sodiumiodide on reaction with $HgI_2$ gives colour less complex salt, $Na_2[HgI_4]$

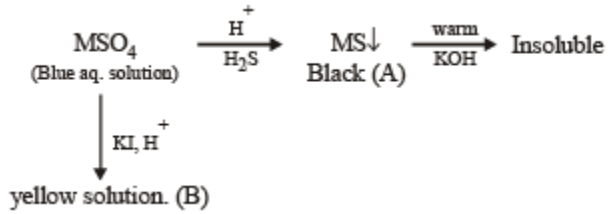
$$HgI_2 + 2NaI \rightleftharpoons Na_2[HgI_4]$$

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 $Na_2[HgI_4]$ $HgI_2 + 2NaI$ (excess) → $Na_2[HgI_4]$ (colourless) The orange colour of $HgI_2$ reappears due to conversion of $Na_2[HgI_4]$ into $HgI_2$ by means of NaOCl

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

**Q. 17. An aqueous blue coloured solution of a transition metal sulphate reacts with H2S in acidic medium to give a black precipitate A, which is insoluble in warm aqueous solution of KOH. The blue solution on treatment with KI in weakly acidic medium, turns yellow and produces a white precipitate B. Identify the transition metal ion. Write the chemical reactions involved in the formation of A and B. (2000 - 4 Marks)**

**Ans. Sol.** Summary of the given facts




The reaction corresponds to copper sulphate.

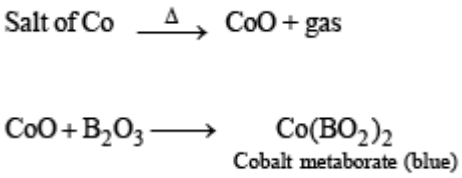
$$2CuSO_4 + 2KI \xrightarrow{H^+} \underset{\text{White (B)}}{Cu_2I_2}\downarrow + I_2 + K_2SO_4$$

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

**Q.18. Write the chemical reactions associated with the 'borax bead test' of cobalt (II) oxide. (2000 - 3 Marks)**

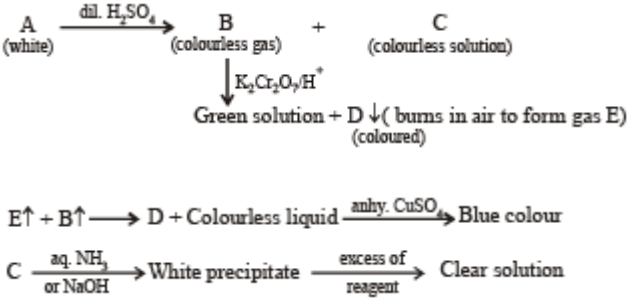
**Ans. Sol.**

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



**Q.19. A white substance (A) reacts with dilute $H_2SO_4$ to produce a colourless gas (B) and a colourless solution (C). The reaction between (B) and acidified $K_2Cr_2O_7$ solution produces a green solution and a slightly coloured precipitate (D). The substance (D) burns in air to produce a gas (E) which reacts with (B) to yield (D) and a colourless liquid.**
**Anhydrous copper sulphate is turned blue on addition of this colourless liquid. Addition of aqueous $NH_3$ or NaOH to (C) produces first a precipitate, which dissolves in the excess of the respective reagent to produce a clear solution in each case. Identify (A), (B), (C), (D) and (E). Write the equations of the reactions involved. (2001 - 10 Marks)**

**Ans. Sol.**



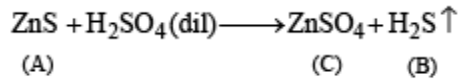
The above set leads to following conclusions.

(i) Since the gas (B) is colourless and turns acidified $K_2Cr_2O_7$ solution green, it should be H2S.

(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) poin ts out towards ZnS.

Thus the various reactions can be written as given below.



$$3H_2S + K_2Cr_2O_7 + 4H_2SO_4$$
(B)

$$\longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3S$$
(green) (D)

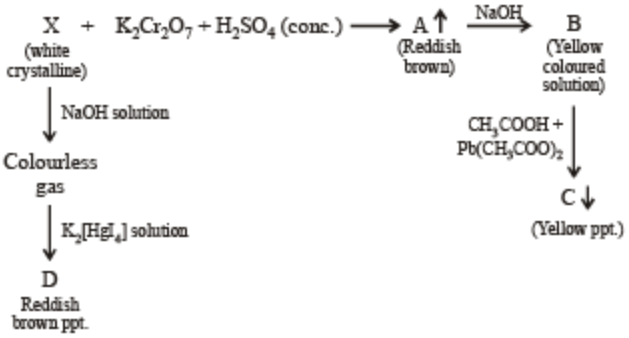
$$S + O_2 \longrightarrow SO_2\uparrow \xrightarrow{2H_2S(B)} 2H_2O + 3S\downarrow$$
(D) (E) (colourless liq) D

$$ZnSO_4 + 2NaOH \longrightarrow Zn(OH)_2\downarrow$$
(C) white ppt

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

**Q.20. When a white crystalline compound X is heated with $K_2Cr_2O_7$ and concentrated $H_2SO_4$, a reddish brown gas A is evolved. On passing A into caustic soda solution, a yellow coloured solution of B is obtained. Neutralizing the solution B with acetic acid and on subsequent addition of lead acetate, a yellow precipitate C is obtained. When X is heated with NaOH solution, a colourless gas is evolved and on passing this gas into $K_2HgI_4$solution, a reddish brown precipitate D is formed. Identify A, B, C, D and X. Write the equations of reactions involved. (2002 - 5 Marks)**

**Ans. Sol.** Let us summarise the given facts.




**NOTE:** Reaction of compound X with NaOH solution and subsequent treatments indicate that X has $NH^{4+}$ radical. On the other hand, reaction of X with $K_2Cr_2O_7$ solution, conc.

$H_2SO_4$ and subsequent treatments indicate that A has $Cl^-$ radical. Thus compound X is $NH_4Cl$ which explains all the above reactions.

$$\underset{(X)}{4NH_4Cl} + K_2Cr_2O_7 + 3H_2SO_4$$

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

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

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

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

$$NH_3 + 2K_2HgI_4 + 3KOH$$

$$\longrightarrow \underset{\substack{\text{Iodide of Millon's base, (D)}\\ \text{(reddish brown ppt)}}}{\left[\begin{array}{c} Hg \\ O \quad NH_2I \\ Hg \end{array}\right]} + 7KI + 2H_2O$$

**Q.21. A mixture consists of A (yellow solid) and B (colourless solid) which gives lilac colour in flame.**
**(a) Mixture gives black precipitate C on passing $H_2S$(g) through its aqueous solution.**
**(b) C is soluble in aqua-regia and on evaporation of aquaregia and adding $SnCl_2$ gives greyish black precipitate D.**
**The salt solution with NH4OH gives a brown precipitate.**
**(i) Th e sodium car bonate extract of th e salt with $CCl_4$/$FeCl_3$ gives a violet layer.**
**(ii) The sodium carbonate extract gives yellow precipitate with $AgNO_3$ solution which is insoluble in $NH_3$.**
**Identify A and B, and the precipitates C and D. (2003 - 4 Marks)**

**Ans. Sol.**

$$[A = HgI_2\,(\text{yellow}),\quad B = KI(\text{colourless})]$$

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

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

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

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

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

$$2NaI \xrightarrow{AgNO_3} \underset{\substack{\text{(Insoluble in ammonia)}}}{AgI\downarrow\ \text{(Yellow)}}$$