# QUALITATIVE ANALYSIS

**Analysis of substance is carried out in order to establish its qualitative and quantitative chemical composition.** Qualitative analysis deals with identifying the components of a substance. Inorganic salts are formed due to neutralization of acids and bases. So a salt comprises of two parts a cation or basic radical contributed by the base and an anion or acidic radical contributed by an acid.
A charged atom or groups of atoms which participates in chemical reactions.

$$\underset{\text{Base}}{Cu(OH)_2} + \underset{\text{Acid}}{H_2SO_4} \longrightarrow \underset{\text{salt}}{CuSO_4} + H_2O$$

$Cu^{2+}$ $SO_4^{2-}$

**(1) Basic radical** **(2) Acidic radical**

* Positive radical – Basic radical
* Negative radical – Acid radical

**(1)** **Basic radical or cation :** It is the radical having positive charge. The magnitude of charge depends upon the base in which it is in combination with $OH^-$ ions or formally of the basic oxide. $Pb^{+2}$, $Cu^{+2}$, $Al^{+3}$, $Fe^{+3}$, $Zn^{+2}$, $Ni^{+2}$, $Ca^{+2}$, $Ba^{+2}$, $Mg^{+2}$, $NH_4^+$

**(2)** **Acid radical or Anion :** It is the radical having negative charge. The magnitude of charge depends upon the acid in which it is in combination with hydrogen. $CO_3^{2-}$, $S^{-2}$, $SO_4^{2-}$, $NO_2^-$, $NO_3^-$, $Cl^-$, $Br^-$, $I^-$

**Qualitative analysis :** Involves the detection and identification of these radicals in salts whether single slats or double salts, or detection of radicals in mixture of salts or even radicals present in common fertilizers. Qualitative analysis is a valuable tool in industries. However in laboratories semi Micro analysis is performed.

There are separate 'procedures for detecting cations and anions, therefore qualitative analysis is studied under cation analysis and anion analysis.

Qualitative analysis deals with the identification of various constituents present in a chemical mixture. The systematic procedure involves:

**1. Preliminary tests**

a. Physical appearance b. Dry heating test
c. Charcoal cavity test d. Flame test e. Borax bead test

**2. Indicatory tests**

a. Dilute acid tests b. Concentrated acid test

**3. Confirmatory tests**

a. Physical examination b.Gas evolved on heating or by adding any reagent
c. Analysis of acid radicals d. Analysis of basic radicals

**1. Preliminary tests**

**(a) Physical appearance :** The physical examination of the unknown mixture involves the study of solubility colour, smell and density.

**Following salts are soluble in water:**

| | Soluble | Insoluble |
|---|---|---|
| (i) | All the halides ($X^- = Cl, Br, I$) are soluble in water Except Ag, Cu, Hg, Pb, | All the $CO_3^-$, $C_2O_4^{2-}$, $S^{-2}$, $SO_3^{2-}$ are insoluble in water. Except alkyl metal |
| (ii) | All nitrates | **Note :** $FeC_2O_4$ is soluble in water |
| (iii) | All nitrites except $AgNO_2$ | |
| (iv) | All sulphate are soluble in water Except Ag, Sr, Ba, Pb, Hg, Ca, Sn | |
| (v) | All the acitates ($CH_3COO^-$) are soluble in water. Except Ag, Hg | |

| | Experiment | Observation | Inference |
|---|---|---|---|
| (a) | Smell<br>Take a pinch of the salt between your fingers and rub with a drop of water | Ammonical smell<br>Vinegar like smell<br>Smell like that of rotten eggs | $NH_4^+$<br>$CH_3COO^-$<br>$S^{2-}$ |
| (b) | Density | (i) Heavy<br>(ii) Light fluffy powder | Salt of $Pb^{2+}$ or $Ba^{2+}$<br>Carbonate salts |
| (c) | Deliquescence | Salt absorbs moisture and becomes paste like | (i) If coloured may be $Cu(NO_3)_2$, $FeCl_3$<br>(ii) If colourless, may be $Zn(NO_3)_2$, chlorides of $Zn^{2+}$, $Mg^{2+}$ etc. |
| (d) | Colour | Blue or Bluish green<br>Greenish<br>Light Green<br>Dark brown<br>Pink, Violet<br>Light pink, flesh colour<br><br>White | $Cu^{2+}$ or $Ni^{2+}$<br>$Ni^{2+}$<br>$Fe^{2+}$<br>$Fe^{3+}$<br>$Co^{2+}$<br>$Mn^{2+}$<br><br>Shows the absence of $Cu^{2+}$, $Ni^{2+}$, $Fe^{2+}$, $Fe^{3+}$, $Mn^{2+}$, $Co^{2+}$ |

**(b) Dry heating test:**

On heating a small amount of mixture in a dry test tube, quite valuable information can be generated by carefully performing and noting the observations here. On heating some salts undergo decomposition thus evolving the gases or may undergo characteristic changes in the colour of residue.

| Observation | Inference |
|---|---|
| **(1) Gas evolved** | |
| (a) **Colourless and odourless gas** | |
| $CO_2$ gas - turns lime water milky | $CO_3^{2-}$ |
| (b) **Colourless gas with odour** | |
| (i) $H_2S$ gas-Smells like rotten eggs, turns lead acetate paper black. | Hydrated $S^{2-}$ |
| (ii) $SO_2$ gas-Characteristic suffocating smell, turns acidified potassium dichromate solution or paper green. | $SO_3^{2-}$ |
| (iii) HCl gas- Pungent smell, white fumes with ammonia, white precipitate with silver nitrate solution. | $Cl^-$ |
| (iv) Acetic acid vapours-Characteristic vinegar like smell. | $CH_3COO^-$ |
| (v) $NH_3$ gas- Characteristic smell, turns Nessler's solution brown. | $NH_4^+$ |
| (c) **Coloured gases-Pungent smell** | |
| (i) $NO_2$ gas-Reddish brown, turns ferrous sulphate solution black. | $NO_2^-$ or $NO_3^-$ |
| (ii) $Cl_2$ gas - Greenish yellow, turns starch iodide paper blue. | $Cl^-$ |
| (iii) $Br_2$ vapours- Reddish brown, turns starch paper orange red. | $Br^-$ |
| (iv) $I_2$ vapour- Dark violet, turns starch paper blue. | $I^-$ |
| **(2) Sublimate formed** | |
| (a) White sublimate | $NH_4^+$ |
| (b) Black sublimate accompanied by violet vapours | $I^-$ |
| (c) Steel grey, garlic odour | As |
| (d) Grey sublimate | Hg |
| (e) Yellow sublimate | S,$As_2S_3$ |
| **(3) Fusion test** | |
| The mixture swells up into voluminous mass. | Alkali metals salts or salts containing waterof crystallisation |
| **(4) Swelling** | |
| The mixture swells up into voluminous mass. | $PO_4^{3-}$, $BO_3^{3-}$ indicated |
| **(5) Residue** | |
| (i) Yellow when hot, white when cold. | $Zn^{2+}$ |
| (ii) Brown when hot and yellow when cold | $Pb^{2+}$ |
| (iii) Original salt blue becomes white on heating | Hydrated $CuSO_4$ |
| (iv) Coloured salt becomes brown or black on heating | indicated $Co^{2+}$, $Fe^{2+}$, $Fe^{3+}$, $Cr^{3+}$, $Cu^{2+}$, $Ni^{2+}$, $Mn^{2+}$ indicated. |

**(c) Charcoal Cavity Test**

The mixture is mixed with double of its amount of anhydrous sodium carbonate and placed in a charcoal block having a small cavity. The mass is moistened with a drop of water and heated in a reducing flame with a blow pipe. Metal salt is converted into metal via carbonate and oxide. E.g.,

$CuCl_2 + Na_2CO_3 \rightarrow CuCO_3 + 2NaCl$

$CuCO_3 \rightarrow CuO + CO_2$

$CuO + \rightarrow Cu + CO$

The colour in the cavity bead or incrustation is observed.

| S.No. | Observation | Inference |
|---|---|---|
| 1. | Formation of metallic bead | |
| | (i) Lustrous white, malleable | Ag |
| | (ii) Greyish white, marks paper | Pb |
| | (iii) White, does not mark paper | Sn |
| | (iv) Red | Cu |
| 2. | Incrustation with metal | |
| | (i) White incrustation, brittle metal | Sb |
| | (ii) Yellow incrustation, brittle metal | Bi |
| | (iii) Yellow incrustation, malleable metal | Pb |
| 3. | Incrustation without metal | |
| | (i) White and yellow when hot | ZnO, SnO |
| | (ii) Yellow and orange when hot | BiO |
| | (iii) Brown | CdO |
| | (iv) White (volatile, garlic odour) | $As_2O_3$ |

**(d) Flame Test**

A paste of salts and concentrated HCl is taken into the lower oxidising zone and colour imparted to the flame by salts is observed. The salts of group V ($Ba^{2+}$, $Ca^{2+}$, $Sr^{2+}$) are identified by colours of the flame.

| Colour of the flame | Inference |
|---|---|
| Greenish blue | Cu salt and $BO_3^{-3}$ |
| Apple-green | Ba |
| Crimson-red | Sr |
| Brick-red | Ca |
| Golden-yellow | Na |
| Violet | K |
| Carmine-red | Li |

**Important note**

(1) Be & Mg don't give flame test due to high ionization potential.

(2) Colourless white salt dont' possess Cu, Ni, Co, Fe, Mn, Cr etc.

(3) White substances which swells are alum, borate and phosphate.

**Sublimation Action of a Substance and Colour**

| | |
|---|---|
| White | $HgCl_2$, $Hg_2Cl_2$, $As_2O_3$, $Sb_2O_3$ |
| Yellow | $AlCl_3$ and $NH_3$ halides |
| Brown | $HgO$, $Hg(NO_3)_2$ |
| Blue, Black and Voilet | Iodides |
| Black | As, Sb, Hg sulphides and iodides. |

**(e) Borax Bead Test**

On heating borax the colourless glass bead formed consists of sodium metaborate and boric anhydride.

$$Na_2B_4O_7.\,10H_2O \xrightarrow{Heat} Na_2B_4O_7 \xrightarrow{Heat} \underbrace{2NaBO_2 + B_2O_3}_{\text{Glassy bead (mass)}}$$

On heating with a coloured salt, the glassy bead forms a coloured metaborate in oxidising flame.

$$CuSO_4 \rightarrow CuO + SO_3$$

$$CuO + B_2O_3 \rightarrow Cu(BO_2)_2$$

Copper metaborate
(Blue)

| Metal | Oxidising - flame | | Reducing - flame | |
|---|---|---|---|---|
| | **Hot** | **Cold** | **Hot** | **Cold** |
| Copper | Green | Blue | Colourless | Brown-red |
| Iron | Brown-yellow | Pale-yellow | Bottle green | Bottle green |
| Chromium | Green | Green | Green | Green |
| Cobalt | Blue | Blue | Blue | Blue |
| Nickel | Violet | Brown | Grey | Grey |

**(f) Cobalt Nitrate Charcoal Test**

The mixture is mixed with double of its amount with sodium carbonate, placed in the charcoal cavity, and moistened with a drop of water and heated in an oxidising flame with the help of a blow pipe. After cooling, one or two drops of cobalt nitrate solution are added and the mass is again heated in the oxidising flame. Metal oxide combines with cobalt oxide (from cobalt nitrate) forming mixed oxide of characteristic colour.

$$ZnCl_2 + Na_2CO_3 \rightarrow ZnCO_3 + 2NaCl$$

$$ZnCO_3 \rightarrow ZnO + CO_2$$

$$2\,Co(NO_3)_2 \rightarrow 2CoO + 4NO_2 + O_2$$

$$ZnO + CoO \rightarrow \underset{\substack{\text{Cobalt zincate}\\(\text{green})}}{CoZnO_2}$$

| Colour | Inference |
|---|---|
| Blue mass | Al |
| Green residue | Zn |
| Pink residue | Mg |
| Bluish green | Sn |

## IDENTIFICATION OF ACIDIC RADICALS

**Group I :** This group consists of radical which are detected by dilute $H_2SO_4$ or dilute HCl.
These are (i) Carbonate, (ii) Sulphite, (iii) Sulphide, (iv) Acetate and (v) Nitrite

**Group II :** This group consists of radicals which are detected by concentrated $H_2SO_4$.
These are (i) Chloride, (ii) Bromide, (iii) Iodide, (iv) Nitrate and (v) Oxalate

**Group III :** The radicals which do not give any characteristic gas with dilute and concentrated $H_2SO_4$.
These are (i) Sulphate, (ii) Phosphate, (iii) Borate and (iv) Fluoride.

**(A) Observation of Dil. HCl / $H_2SO_4$ + little amount of substance on slow heating.**

**(1) $CO_3^{-2}$ (Carbonate)**

**Test/Observation/Analysis**

(i) Sharp bubbling of colourless gas ($CO_2$)
(ii) Gas truns milky to lime water.
(iii) On passing excess gas through lime water, milky colour disappears.

**Reaction :**

$CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + H_2O + CO_2\uparrow$
$CO_2 + Ca(OH)_2 \rightarrow CaCO_3\downarrow$ (Milky) $+ H_2O$
$CaCO_3 + CO_2 + H_2O \rightarrow Ca(HCO_3)_2$
(soluble)

**(2) $SO_3^{-2}$ (Sulphite)**

**Test/Observation/Analysis**

(i) Colourless gas ($SO_2$) in which very unpleasant smell of burnt sulphur
(ii) Gas turns green to moist acidic $K_2Cr_2O_7$ paper $K_2SO_4 + Cr(SO_4)_3$ (green) $+ H_2O$
(iii) Sulphite gives white ppt. with $BaCl_2$, which is soluble in dil. HCl

**Reaction :**

$CaSO_3 + H_2SO_4 \rightarrow CaSO_4 + H_2O + SO_2\uparrow$
$K_2Cr_2O_7 + H_2SO_4 + 3SO_2 \rightarrow$
$Na_2SO_3 + BaCl_2 \rightarrow 2NaCl + BaSO_3\downarrow$

**(3) $S^{-2}$ (Sulphide)**

**Test/Observation/Analysis**

(i) Colourless gas with rotten egg smell ($H_2S$)

(ii) Gas turns black to lead-acetate paper

(iii) Sulphide turns violet colour to Sodium nitroprusside solution

**Reaction :**

$CaS + H_2SO_4 \rightarrow CaSO_4 + H_2S\uparrow$

$(CH_3COO)_2Pb + H_2S \rightarrow PbS\text{-(black)} + 2CH_3COOH$

$Na_2S + Na_2[FeNO(CN)_5] \rightarrow Na_4[Fe(NOS)(CN)_5]$

(violet)

**(4) $CH_3COO^-$ (Acetate)**

**Test/Observation/Analysis**

(i) Vinegar smell, acetate may be

(ii) Acetate gives blood red colour with neutral $FeCl_3$ solution

**Reaction :**

$(CH_3COO)_2Ca + H_2SO_4 \rightarrow 2CH_3COOH + CaSO_4$

(Vinegar smell)

$3(CH_3COO)_2Ca + 2FeCl_3 \rightarrow 2Fe(CH_3COO)_3 + 3CaCl_2$

**(5) $NO_2^-$ (Nitrite)**

**Test/Observation/Analysis**

(i) Red, brown $NO_2$ vapour comes out. Nitrite may be

(ii) Gas turns blue to acidic KI starch paper

**Reaction :**

$2KNO_2 + H_2SO_4 \rightarrow K_2SO_4 + 2HNO_2$

$3HNO_2 \rightarrow HNO_3 + 2NO\uparrow + H_2O$

$2NO + O_2 \rightarrow 2NO_2\uparrow$

$2KI + 2NO_2 \rightarrow 2KNO_2 + I_2\uparrow$

$Starch + I_2 \rightarrow$ blue colour

**(B) Observation of Conc. $H_2SO_4$ + little amount of substance of slow heating**

**(6) $Cl^-$ (Chloride)**

**Test/ observation/ Analysis**

(i) Colourless fuming gas (HCl) with fast smell

(ii) Chloride gives white ppt. with $AgNO_3$, which is soluble in $NH_4OH$

(iii) Chromyl chloride test **(v.imp.)**

(a) Sodium chloride when heated with $K_2Cr_2O_7$ & conc. $H_2SO_4$ then orange red vapour of chromyl chloride $CrO_2Cl_2$ comes out $Hg_2Cl_2$, $PbCl_2$, AgCl does not give the positive chromyl chloride test.

(b) This vapour when passed with NaOH gives yellow solution ($Na_2CrO_4$)

(c) Acidic solution of $Na_2CrO_4$ gives yellow ppt. with $(CH_3COO)_2Pb$

**Reaction :**

$2NaCl + H_2SO_4 \rightarrow Na_2SO_4 + 2HCl\uparrow$

$NaCl + AgNO_3 \rightarrow AgCl\downarrow + NaNO_3$

(white)

$AgCl + 2NH_4OH \rightarrow Ag(NH_3)_2Cl + 2H_2O$

(Soluble)

$4NaCl + K_2Cr_2O_7 + 3H_2SO_4 \rightarrow 2CrO_2Cl_2 + 2Na_2SO_4 + K_2SO_4 + 3H_2O$

(orange red)

$CrO_2Cl_2 + 4NaOH \rightarrow Na_2CrO_4 + 2NaCl + 2H_2O$

$Na_2CrO_4 + (CH_3COO)_2Pb \rightarrow 2CH_3COONa + PbCrO_4\downarrow$ (yellow ppt)

**(7) $Br^-$ (Bromide)**

**Test/ observation/ Analysis**

(i) Brown vapour comes out of $(Br_2)Br^-$ or $NO_3^-$ may be

(ii) Bromides gives light yellow ppt. with $AgNO_3$ which is partially soluble in $NH_4OH$.

(iii) Brown vapour of $Br_2$ when passed with $H_2O$ gives brown colouration whereas $NO_2$ vapour don't give any colour with $H_2O$

**Reaction :**

$2NaBr + H_2SO_4 \rightarrow Na_2SO_4 + 2HBr$

$2HBr + H_2SO_4 \rightarrow Br_2\uparrow + 2H_2O + SO_2\uparrow$

$NaBr + AgNO_3 \rightarrow AgBr\downarrow + NaNO_3$

(light yellow)

**(8) $I^-$ (Iodide)**

**Test/ observation/ Analysis**

(i) Dark violet fume of $I_2$ comes out.

(ii) Gives blue colouration with starch .

(iii) Iodides gives yellow ppt. with $AgNO_3$ which is insoluble in $NH_4OH$

(iv) Iodine with chloroform gives violet coloured chloroform

**Reaction :**

$2NaI + H_2SO_4 \rightarrow Na_2SO_4 + 2HI$

$2HI + H_2SO_4 \rightarrow I_2 \uparrow + 2H_2O + SO_2 \uparrow$

(violet)

$I_2$ + starch → Blue colour (complex)

$NaI + AgNO_3 \rightarrow AgI + NaNO_3$

(yellow)

$2KI + Cl_2$ (water) $\rightarrow 2KCl + I_2$

$I_2$ + chloroform → violet coloured chloroform

**(9) $NO_3^-$ (Nitrate)**

**Test/ observation/ Analysis**

(i) Brown smoke comes out ($NO_2$)

(ii) Ring test **(v. imp.)** aq. solution of salt is mixed in fresh $FeSO_4$ and conc. $H_2SO_4$ is passed through corners of test tube, brown ring is formed. (brown ring of nitrosoferrous sulphate)

**Reaction :**

$NaNO_3 + H_2SO_4 \rightarrow NaHSO_4 + HNO_3$

$4HNO_3 \rightarrow 2H_2O + O_2 + 4NO_2 \downarrow$

$NaNO_3 + H_2SO_4 \rightarrow NaHSO_4 + HNO_3$

$6FeSO_4 + 2HNO_3 + 3H_2SO_4 \rightarrow 3Fe_2(SO_4)_3 + 2NO + 4H_2O$

$FeSO_4 + 5H_2O + NO \rightarrow [Fe(H_2O)_5(NO)]\ SO_4$

Solution brown ring

**(10) $SO_4^{-2}$ (Sulphate)**

**Test/ observation/ Analysis**

Small amount of substance + conc. $HNO_3$ mixtures is heated & now adding $BaCl_2$ white ppt comes which is insoluble in acid or base sulphate confirmed

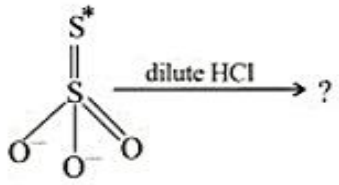
**Reaction :**

$Na_2SO_4 + 2HNO_3 \rightarrow 2NaNO_3 + H_2SO_4$

$H_2SO_4 + BaCl_2 \rightarrow BaSO_4 \downarrow + 2HCl$

(white)

***Illustration***

**Q.1** 


The products obtained are :

(A) $\overset{*}{S} + SO_2$ (B) $S + \overset{*}{S}O_2$ (C) $\overset{*}{S} + \overset{*}{S}O_2$ (D) None of these

**Ans.** (A)

[**Sol.** $\overset{*}{S}SO_3^{-2} + 2dil\ HCl(dil.) \rightarrow \overset{*}{S} + SO_2 + H_2O + 2Cl^-$ ]

**Q.2** $Na_2C_2O_4 + H_2SO_4 \longrightarrow$ **(A)** $+ Na_2SO_4$

$\downarrow \Delta$

$H_2O$ + **(X)** + **(Y)**

↓ (Burns with blue flame) ↓ (Turns lime water milky)

Which of the following reactions will give both gases **(X)** and **(Y)**?

(A) $H_2C_2O_4 \xrightarrow{\Delta}$ (B) $FeC_2O_4 \xrightarrow{\Delta}$

(C) $HCOONa \xrightarrow[350°C]{\Delta}$ (D) $HCOOAg \xrightarrow{\Delta}$

**Ans.** **(A, B)**

[**Sol.** $Na_2C_2O_4 + H_2SO_4 \rightarrow H_2C_2O_4 + Na_2SO_4$

$H_2C_2O_4 \xrightarrow{\Delta} H_2O + X = CO + Y = CO_2$

$FeC_2O_4 \xrightarrow{\Delta} FeO + CO + CO_2$

$2HCOONa \xrightarrow{\Delta} Na_2C_2O_4 + H_2$

$2HCOOAg \xrightarrow{\Delta} Ag + HCOOH + CO_2$ ]

**Q.3** Which of the following would give yellow turbidity with dilute HCl?

(A) $S^{2-}$ (B) $S_2O_3^{2-}$ (C) $CO_3^{2-}$ (D) $NO_2^-$

**Ans.** **(B)**

[**Sol.** $S_2O_3^{2-} + 2HCl \xrightarrow{\Delta} SO_2\uparrow + 2Cl^- + S\downarrow + H_2O$

Suffocating smell of burning sulphur — Yellow turbidity or white turbidity ]

**Q.4** Salt A water soluble gives pink colour with phenolphthalene and salt B will not give pink colour with phenopthelene but both salt give colourless or odourless gas (X) on heating, gas (X) gives white turbidity with Baryta water which disappear on passing excess of gas (X). Salt A and B are.

(A) $CO_3^{2-}$ (B) $HCO_3^-$ (C) $HSO_3^-$ (C) $SO_3^{2-}$

**Ans.** **(A, B)**

**[Sol.** Salt A + HPh $\longrightarrow$ Pink colour

$CO_3^{2-}$

Salt B + HPh $\longrightarrow$ Hot pink colour

$HCO_3^{\ominus}$

$$CO_3^{2-} \mid HCO_3^{\ominus} \xrightarrow{\Delta} \underset{[X]}{CO_2} \uparrow$$

$$[X] + Ba(OH)_2 \longrightarrow \underset{\text{white turbidity}}{BaCO_3}$$

$$\downarrow \text{excess } CO_2$$

$Ba(HCO_3)_2$ soluble ]

## *Exercise*

**Q.1** Borax bead test of salt (M) is performed, violet colour of the bead is obtained under oxidising flame. What is the oxidation state of the cation present in salt (M)?

(A) +7 (B) + 4 (C) + 2 (D) can't be predicted.

**Ans.** **(D)**

**Q.2** Which of the following reaction(s) is / are not redox reaction.

(A) $CrO_4^{2-} + H^+ + H_2O_2 \xrightarrow{Et_2O}$

(B) $[Cr(OH)_4]^- + H_2O_2 + OH^- \longrightarrow$

(C) $MnO_4^- + H^+ + H_2O_2 \longrightarrow$

(D) $K_2Cr_2O_7$ (solid) + NaCl + $H_2SO_4$ (conc.) $\xrightarrow{\Delta}$

**Ans.** **(A, D)**

**Q.4** $SO_2$ gas is passed through starch iodate solution in acidic medium and the resulting solution is

(A) Salmon red coloured precipitate

(B) Red compound of unknwon composition

(C) Brown colour

(D) Deep blue solution

**Ans.** **(D)**

# TEST OF BASIC RADICALS

## I–Group

This group includes $Ag^+$, $Pb^{2+}$, and $Hg_2^{2+}$ (ous). The group reagent is dilute hydrochloric acid. The radicals are precipitated as their chlorides because the solubility product of these chlorides (AgCl, $PbCl_2$ and $Hg_2Cl_2$) is less than the solubility of all other chlorides which thus remain in solution.

| Radical | Test/ observation/ Analysis | Reaction |
|---|---|---|
| $Pb^{+2}$ | $Pb^{+2}$ ion gives yellow ppt. with $K_2CrO_4$ & KI soln. separately. | $PbCl_2 + K_2CrO_4 \rightarrow PbCrO_4$(yellow)$\downarrow + 2KCl$<br>$PbCl_2 + 2KI \rightarrow PbI_2 \downarrow$(yellow) $+ 2KCl$ |
| $Hg_2^{+2}$ | $Hg_2^{+2}$ gives black ppt. with $NH_3$ | $Hg_2Cl_2 + 2NH_4OH \rightarrow Hg(NH_2)Cl + Hg\downarrow$<br>$+ NH_4Cl + 2H_2O$ |
| $Ag^+$ | (i) AgCl is soluble in $NH_4OH$<br>(ii) $Ag^+$ ion gives yellow ppt. with KI | $AgCl + 2NH_4OH \rightarrow [Ag(NH_3)_2]Cl + 2H_2O$<br>$Ag^+ + I^- \rightarrow AgI \downarrow$ (yellow) |

**Note:** $PbCl_2$ is soluble in hot water (but insoluble in cold water) Whereas insoluble in both AgCl & $HgCl_2$

## II–Group

This group includes $Hg^{2+}$, $Pb^{2+}$, $Bi^{3+}$, $Cu^{2+}$, $Cd^{2+}$ (all in IIA), $As^{3+}$, $Sb^{3+}$, $Sn^{2+}$ and $Sn^{4+}$(all in IIB).

The group reagent is hydrogen sulphide in presence of HCl. These radicals are precipitated as their sulphides, whereas the sulphides of other metals remain in solution because of their high solubility product.

HgS, PbS, $Bi_2S_3$ and CuS are black, CdS, $As_2S_3$ and $SnS_2$ yellow, SnS brown, and $Sb_2S_3$ is orange.

The function of HCl is to decrease ionisation of $H_2S$ (due to common ion effect) so that only the solubility product of sulphides of II group radical is exceeded and not that of III, IV and V group. Hence III, IV and V group radicals are not precipitated by $H_2S$ in the presence of HCl.
Pbs and CdS are precipitated only on dilution due to higher $K_{sp}$.

IIA and IIB group sulphides are separated by yellow ammonium sulphide $(NH_4)_2S_x$ in which IIA group sulphides are insoluble whereas that of IIB are soluble forming thiosalts.

| Radical | Test/ observation/ Analysis | Reaction |
|---|---|---|
| $Hg^{+2}$ | Adding $Hg^{+2}$ ion white ppt. obtained which turns black | $2Hg^{+2} + SnCl_2 \rightarrow Sn^{+4} + Hg_2Cl_2\downarrow$ (white)<br>$HgCl_2 + SnCl_2 \rightarrow SnCl_4 + 2Hg\downarrow$ (black) |
| $Pb^{+2}$ | (i) In solution, $Pb^{+2}$ gives white ppt. with $H_2SO_4$ | $Pb^{+2} + H_2SO_4 \rightarrow PbSO_4\downarrow + 2H^+$ (white) |
| | (ii) In solution $Pb^{+2}$ ion gives yellow ppt. with $K_2CrO_4$ & KI | $Pb^{+2} + Cr_2O_4^{-2} \rightarrow PbCrO_4\downarrow$ (yellow)<br>$Pb^{+2} + 2I^- \rightarrow PbI_2\downarrow$ (yellow) |
| $Cu^{+2}$ | (i) These ion gives dark blue colour with excess $NH_4OH$ | $Cu^{+2} + NH_4OH \rightarrow [Cu(NH_3)_4]^{+2} + H_2O$ (dark blue colour) |
| | (ii) $Cu^{+2}$ ion gives chocolate colour with $K_4Fe(CN)_6$ | $2Cu^{+2} + K_4Fe(CN)_6 \rightarrow Cu_2[Fe(CN)_6]\downarrow + 4k$ (chocolate or red brown ppt.) |
| $Bi^{+3}$ | $Bi^{+3}$ ion gives white ppt. while adding water In HCl soln. | $BiCl_3 + H_2O \rightarrow BiOCl\downarrow + 2HCl$ (white bismuth oxychloride)<br>$BiCl_3 + 3Na_2SnO_2 + 6NaOH \rightarrow$ (sodium stanite)<br>$2Bi\downarrow + 3Na_2SnO_3 + 6NaCl + 3H_2O$ (black sodium stanate) |
| $Cd^{+2}$ | (i) The yellow precipitate is dissolved in 50% $HNO_3$. To the resulting solution, $NH_4OH$ is added slowly. A white ppt. appears which dissolve in excess of $NH_4OH$. | $3Cds + 8HNO_3 \rightarrow 3Cd(NO_3)_2 +$ (50%) $4H_2O + 2NO + 3S$<br>$Cd(NO_3)_2 + 2NH_4OH \rightarrow 2NH_4NO_3 + Cd(OH)_2\downarrow$ white ppt.<br>$Cd(OH)_2 + 2NH_4OH + 2NH_4NO_3 \rightarrow [Cd(NH_3)_4](NO_3)_2 aq. + 4H_2O$ |
| | (ii) When $H_2S$ gas is passed in this solution a yellow ppt. appears | $[Cd(NH_3)_4](NO_3)_2 + H_2S \rightarrow CdS\downarrow 2NH_4NO_3 + 2NH_3$ (yellow ppt.) |

## III group

This group includes $Fe^{3+}$, $Al^{3+}$, and $Cr^{3+}$. The group reagent is $NH_4OH$ and in presence of $NH_4Cl$, the radicals are precipitated as their hydroxides. The function of $NH_4Cl$ is to suppress the ionisation of $NH_4OH$ so that only the III$^{rd}$ group radicals are precipitated, because the solubility product of III$^{rd}$ group hydroxides is less than that of IV and VI group hydroxides.

Excess of $NH_4Cl$ should be added, or else managanese will be precipitated in III group.

| Radical | Test/ observation/ Analysis | Reaction |
|---|---|---|
| $Fe^{+3}$, $Cr^{+3}$ & $Al^{+3}$ | These ion precipts in the form of hydroxide on adding $NH_4Cl$ & $NH_4OH$ | $Fe^{+3} + 3OH^- \rightarrow Fe(OH)_3$ (red ppt.)<br>$Cr^{+3} + 3OH^- \rightarrow Cr(OH)_3$ (green ppt.)<br>$Al^{+3} + 3OH^- \rightarrow Al(OH)_3$ (white ppt.) |

**Note : In the analysis of III group, some drops of conc. $HNO_3$ are also added before oxidising $Fe^{+2}$ to $Fe^{+3}$.**

| | | |
|---|---|---|
| $Al^{+3}$ | White ppt. of $Al(OH)_3$ is soluble in NaOH | **Imp.** $Al(OH)_3 + NaOH \rightarrow NaAlO_2 + 2H_2O$ (sodium metaaluminate) |
| $Cr^{+3}$ | ppt. of $Cr(OH)_3$ is soluble in NaOH + $Br_2$ water soln. in this soln. when $BaCl_2$ is added yellow | $Br_2 + H_2O \rightarrow 2HBr + O$<br>$2Cr(OH)_3 + 4NaOH + 3O \rightarrow 2Na_2CrO_4 + 5H_2O$<br>ppt. is obtained $Na_2CrO_4 + BaCl_2 \rightarrow BaCrO_4\downarrow$ (yellow ppt.) $+ 2NaCl$ |
| $Fe^{+3}$ | (i) (a) Brown ppt. of $Fe(OH)_3$ is soluble in HCl<br>(b) When KCNS is added in this soln. soln. blood red colouration is obtained<br>(ii) In this soln., on adding $K_4[Fe(CN)_6]$, prussian blue colour is obtained | $Fe(OH)_3 + 3HCl \rightarrow FeCl_3 + 3H_2O$<br>$FeCl_3 + 3KCNS \rightarrow Fe(CNS)_3 + 3KCl$ (ferric thiocyanate) (blood red)<br>$4FeCl_3 + 3K_4[Fe(CN)_6 \rightarrow Fe_4[Fe(CN)_6]_3 + 12KCl$ (ferric ferrocyanide prussian blue) |

## IV group

This group includes $Co^{2+}$, $Ni^{2+}$, $Zn^{2+}$ and $Mn^{2+}$. The group reagent is hydrogen sulphide in ammonical solution. Radicals are precipitated as sulphides which are insoluble in $NH_4OH$.

CoS, NiS - Black MnS - Buff ZnS-White

The function of ammonium hydroxide is to increase the ionisation of $H_2S$.

Thus, an excess of sulphide ions will be available and hence the ionic product of IV group sulphides exceeds their solubility product and precipitates will be obtained.

| Radical | Test/ observation/ Analysis | Reaction |
|---|---|---|
| $Zn^{+2}$, $Mn^{+2}$<br>$Co^{+2}$, $Ni^{+2}$<br>$Co^{+2}$, $Ni^{+2}$<br>$Zn^{+2}$<br>$Mn^2$ | These ions in presence of $NH_4OH$ precipititate on passing $H_2S$.<br>Black (CoS, NiS)<br>ppt., (soluble in aqua–ragia)<br>White (ZnS) (soluble in HCl)<br>Pink or buff (MnS), soluble in HCl | $MCl_2 + H_2S \rightarrow MS\downarrow + 2HCl$ |
| $Ni^{+2}$ | In presence of $NH_4OH$, Ni salt on reaction with dimethyl glyoxime (DMG) turns red ppt. of nickel dimethyl glyxoime → Nickel dimethyl glyoxime (red ppt) | **V. Imp.** $CH_3-C(=NOH)-C(=NOH)-CH_3 + NiCl_2 + 2NH_4OH \rightarrow (C_4H_7N_2O_2)2Ni\downarrow + 2NH_4Cl + 2H_2O$ |
| $Co^{+2}$ | Cobalt salt turns blue colouration with $NH_4CNS$ | $CoCl_2 + 4NH_4CNS \rightarrow (NH_4)_2[Co(CNS)_4] + 2NH_4Cl$ (ammonium cobalt thiocyanate) (blue colour) |
| $Zn^{+2}$ | In solution, $Zn^{+2}$ ion turns white ppt. with NaOH which is soluble in excess NaOH | **V. Imp**<br>$Zn^{+2} + 2NaOH \rightarrow Zn(OH)_2\downarrow$ (white) $+ 2Na$<br>$Zn(OH)_2 + 2NaOH \rightarrow Na_2ZnO_2 + 2H_2O$ |
| $Mn^{+2}$ | (a) $Mn^{+2}$ ion gives pink ppt. with NaOH<br>(b) On heating turns black or brown | **V. Imp**<br>$Mn^{+2} + 2NaOH \rightarrow Mn(OH)_2\downarrow + 2Na$ (Pink)<br>$Mn(OH)_2 + O \xrightarrow{\Delta} MnO_2 + H_2O$ (brown and black) |

## V group

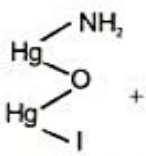
This includes $Ba^{2+}$, $Sr^{2+}$ and $Ca^{2+}$. The group reagent is ammonium carbonate in the presence of $NH_4Cl$ and $NH_4OH$. These are precipitated as carbonates which are insoluble in $NH_4OH$.

The function of ammonium chloride is to suppress the ionisation of $NH_4OH$ and $(NH_4)_2CO_3$ and thus check the precipitation of $Mg(OH)_2$ (along with V group carbonates) because the solubility product of $Mg(OH)_2$ and $MgCO_3$ is high. Further $NH_4Cl$ should also not be added in excess, as the high concentration of $NH_4^+$ ions will decrease the ionisation of $(NH_4)_2CO_3$ to such an extent that sufficient $CO_3^{2-}$ ions may not be present and carbonates of this group of metals may not precipitate.

| Radical | Test/ observation/ Analysis | Reaction |
|---|---|---|
| $Ba^{+2}$, $Sr^{+2}$, $Ca^{+2}$ | On adding $(NH_4)_2CO_3$, these precipitates in the form of carbonates. soluble in $CH_3COOH$ | $M^{+2} + (NH_4)_2CO_3 \rightarrow MCO_3 + 2NH_4^+$<br>$BaCO_3$, $CaCO_3$, $SrCO_3$ (white) |
| $Ba^{+2}$ | Gives $Ba^{+2}$ ion in solution<br>(i) Yellow ppt. with $K_2CrO_4$<br>(ii) white ppt. with $(NH_4)_2SO_4$<br>(iii) white ppt. with $(NH_4)_2C_2O_4$ | <br>$Ba^{+2} + K_2CrO_4 \rightarrow BaCrO_4\downarrow$ (yellow) $+ 2K$<br>$Ba^{+2} + (NH_4)_2SO_4 \rightarrow BaSO_4\downarrow$(white) $+ 2NH_4^+$<br>$Ba^{+2} + (NH_4)_2C_2O_4 \rightarrow BaC_2O_4\downarrow$(white) $+ 2NH_4^+$ |
| $Sr^{+2}$ | $Sr^{+2}$ ion with $(NH_4)_2SO_4$ gives white precipitate | $Sr^{+2}(NH_4)_2SO_4 \rightarrow SrSO_4\downarrow + 2NH_4^+$ (white ppt.) |
| $Ca^{+2}$ | $Ca^{+2}$ ion gives white ppt. only with $(NH_4)_2C_2O_4$ | $Ca^{+2} + (NH_4)_2C_2O_4 \rightarrow CaC_2O_4\downarrow + 2NH_4^+$ (white)<br>$Sr^{+2} + (NH_4)_2C_2O_4 \rightarrow SrC_2O_4\downarrow + 2NH_4^+$ (white ppt.) |

**Note : The order of that is same as above $Ba^{+2}$, $Sr^{+2}$, $Ca^{+2}$**

## VI Group

| Radical | Test/ observation/ Analysis | Reaction |
|---|---|---|
| $Mg^{+2}$<br>Zero group/<br>$NH_4^+$ | $Mg^{+2}$ ion gives white ppt. with $NH_4OH$ & $(NH_4)_2HPO_4$<br>(i) (a) All ammonium salts on reacting with base like (NaOH), gives smell of $NH_3$<br>(b) Gas evolved ($NH_3$) gives white fume with HCl<br>(c) On passing $NH_3$ in $Hg_2(NO_3)_2$, blake colour is obtained<br>(b) Brown ppt. is obtained with nesseler's reagent | $Mg^{+2} + (NH_4)_2HPO_4 + NH_4OH \rightarrow MgNH_4PO_4\downarrow$ (white) $+ 2NH_4^+ + H_2O$<br>(a) $NH_4Cl + NaOH \rightarrow NaCl + NH_3\uparrow + H_2O$<br>(b) $NH_3 + HCl \rightarrow NH_4Cl\uparrow$ (white fume)<br>(c) $Hg_2(NO_3)_2 + 2NH_3 \rightarrow Hg + Hg(NH_2)NO_3 + NH_4NO_3$ (black) $\rightarrow$<br>(d) $2K_2HgI_4 + 4KOH + NH_4Cl \rightarrow$ (Nesseler's reagent)<br>  $+ 7KI + KCl.3H_2O$<br>(Iodide solution black or brown ppt.) |

***Illustration***

**Q.1** During group analysis, reddish brown ppt. is observed in group-III. What is the oxidation state of the metal present in the above precipitate.

(A) +2 (B) +3 (C) both +2 and +3 (D) Can't be predicted

**Ans.** **(B)**

**[Sol.** +3

$Fe(OH)_3$

Reddish brown ]

**Q.2** Which of the following statement is correct.

(A) Using KCN solution $Cu^{2+}$ and $Cd^{2+}$ ion can not be distinguished

(B) $SO_2Cl_2$ on hydrolysis produces two molecules of HCl and Caro's acid.

(C) The oxidation state of Ag in AgO is +2.

(D) No indicator is required in the estimation of $KMnO_4$ using standard oxalic acid solution

**Ans.** **(D)**

**[Sol.** (A) $KCN \rightarrow Cu^{+2} \rightarrow Cu(CN)_2$ Yellow ppt.

$KCN \rightarrow Cd^{+2} \rightarrow Cd(CN)_2$ White ppt.

(B) $SO_2Cl_2 \xrightarrow{2H_2O} H_2SO_4 + 2HCl$

(C) AgO exist as $Ag^{+1}[Ag^{+3}O_2]$

(D) $KMnO_4$ act as self indicator. ]

**Q.3** KI is added in excess into $Hg(NO_3)_2$ solution. The observation is

(A) Yellow ppt. of $HgI_2$ (B) Scarlet red ppt. of $HgI_2$

(C) Colourless solution of $[HgI_4]^{2-}$ (D) None of these

**Ans.** **(C)**

**[Sol.** $Hg(NO_3)_2 + 2KI \longrightarrow HgI_2 + 2KNO_3$

$MgI_2 + 2KI \longrightarrow K_2[HgI_4]$

---

$Hg(NO_3)_2 + 4KI \longrightarrow K_2[HgI_4] + 2KNO_3$

--- ]

**Q.4** Unknown solution of salt 'A' $\xrightarrow{K_3[Fe(CN)_6]}$ green ppt is obtained.

Which of the following radicals will be confirmed.

(A) $Ni^{2+}$ (B) $Cu^{2+}$ (C) $S_2O_3^{2-}$ (D) $SO_3^{2-}$

**Ans.** **(B)**

**[Sol.** $Cu^{+2} + K_3[Fe(CN)_6] \rightarrow \underset{\text{green PPT}}{Cu_3[Fe(CN)_6]}$

*Exercise*

**Q.1** Select correct statement(s)

(I) When excess $FeCl_3$ solution is added to $K_4[Fe(CN)_6]$ solution in addition to $Fe^{III}[Fe^{II}(CN)_6]^-$, $Fe^{II}[Fe^{III}(CN)_6]^-$ is also formed due to side redox reaction

(II) When $FeCl_2$ is added to $K_3[Fe(CN)_6]$ solution, in addition to $Fe^{II}[Fe^{III}(CN)_6]^-$, $Fe^{III}[Fe^{II}(CN)_6]^-$ is also formed due to side redox reaction.

(III) $Fe^{III}[Fe^{II}(CN)_6]^-$ is paramagnetic while $Fe^{II}[Fe^{III}(CN)_6]^-$ is diamagnetic

(IV) $Fe^{III}[Fe^{II}(CN)_6]^-$ is diamagnetic while $Fe^{II}[Fe^{III}(CN)_6]^-$ is paramagnetic

(A) I, II (B) III, IV (C) All (D) None

**Ans.** **(A)**

**Q.2** Which of the following compound is/are partially soluble or insoluble in $NH_4OH$ solution

(1) $Fe(OH)_3$ (2) $Ag_2CrO_4$ (3) $Al(OH)_3$ (4) $Ag_2CO_3$ (5) $Ni(OH)_2$

(A) 1, 3, 5 (B) 2, 3, 4 (C) 1, 3 (D) 2, 3, 5

**Ans.** **(C)**

**Q.3** The sulphide which is insoluble in both ammonium sulphide and $HNO_3$ is

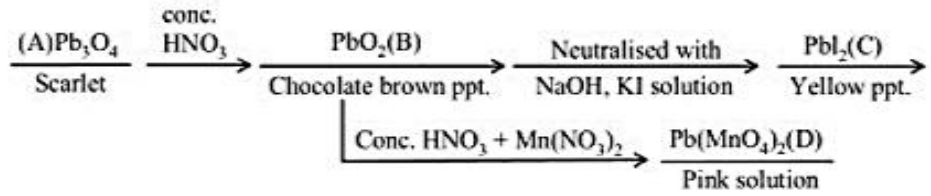
(A) $Bi_2S_3$ (B) CuS (C) FeS (D) HgS

**Ans.** **(D)**

## SOLVED EXAMPLE

**Q.1** A scarlet compound A is treated with concentrated $HNO_3$ to give a chocolate-brown precipitate B. The precipitate is filtered and the filterate 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. Also, write the reaction sequence.

**Sol.** Since yellow precipitate (C) is obtained with KI and the pink-coloured solution is formed with concentrated $HNO_3$ and $Mn(NO_3)_2$, the compound should be of Pb. We know that $Pb_3O_4$ is a scarlet compound.




The equations are as follows:

(i) $Pb_3O_4 + 4HNO_3 \longrightarrow PbO_2\downarrow + 2Pb(NO_3)_2 + 2H_2O$

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

(iii) $5PbO_2 + 4HNO_3 + 2Mn(NO_3)_2 \longrightarrow Pb(MnO_4)_2 + 4Pb(NO_3)_2 + 2H_2O$

**Q.2** A certain salt (X) gives the following tests:

(i) Its aqueous solution is alkaline to litmus.

(ii) On strong heating, it swells to give a glassy material.

(iii) When concentrated sulphuric acid is added to a hot concentrated solution of (X), white crystals of an acid separate out.

Identify (X) and write down the chemical equations for reactions at step (i), (ii), and (iii).

**Sol.** Since the aqueous solution of salt (X) is alkaline to litmus, it should be sodium or potassium salt. It swells to give a glassy material on heating, the salt (X) should be borax, that is, $Na_2B_4O_7$ or $Na_2B_4O_7.10H_2O$. It is further confirmed by the reaction of borax and concentrated $H_2SO_4$ as it gives boric acid which is a white crystalline compound. Boric acid is a weak acid.

The reactions are as follows:

(i) $Na_2B_4O_7 + 7H_2O \rightarrow \underset{\text{Highly ionisable}}{2NaOH} + \underset{\text{feebly ionisable}}{4H_3BO_3}$

Since NaOH is highly ionisable and $H_3BO_3$ is feebly ionisable, the solution is alkaline.

(ii) $Na_2B_4O_7 \xrightarrow{\text{heat}} \underset{\text{(glassy bead)}}{2NaBO_2 + B_2O_3}$

(iii) $Na_2B_4O_7 + H_2SO_4 + 5H_2O \longrightarrow Na_2SO_4 + 4H_3BO_3$.

We know that $H_3BO_3$ is a white crystalline compound and is a weak acid.

**Q.3**

(i) An inorganic compound (A) is formed on passing a gas (B) through a conc. liquor containing $Na_2S$ and sodium sulphite.

(ii) On adding (A) into a dilute solution of silver nitrate a white precipitate appears which quickly changes into a black coloured compound (C).

(iii) On adding two or three drops of $FeCl_3$ into the excess of solution (A) a violet coloured compound (D) is formed. This colour disappears quickly.

(iv) On adding a solution of (A) into the solution of cupric chloride, a white precipitate is first formed which dissolves on adding excess of (A) forming a compound (E).

Identify (A) to (E) and give chemical equations for the reactions at steps (i) to (iv).

**Sol.** The reactions indicate that the compound (A) is sodium thiosulphate. It is formed in step (i) by passing gas (B) which is either $I_2$.

(i) $Na_2S + \underset{\text{(B)}}{Na_2SO_3} + I_2 \longrightarrow Na_2S_2O_3 + 2NaI$

(ii) $2AgNO_3 + Na_2S_2O_3 \longrightarrow \underset{\text{(White ppt)}}{Ag_2S_2O_3} + 2NaNO_3$

$Ag_2S_2O_3 + H_2O \longrightarrow \underset{\text{(C) black}}{Ag_2S} + H_2SO_4$

(iii) $S_2O_3^{2-} + Fe^{3+} \longrightarrow \underset{\text{(D) violet}}{[Fe^{3+}(S_2O_3)_2]^-}$

$[Fe(S_2O_3)_2]^- + Fe^{3+} \longrightarrow 2Fe^{2+} + S_4O_6^{2-}$

(iv) $2Cu^{2+} + 3S_2O_3^{2-} \longrightarrow \underset{\text{white ppt.}}{Cu_2S_2O_3}\downarrow + S_4O_6^{2-}$

$3Cu_2S_2O_3\downarrow + 2Na_2S_2O_3 \longrightarrow \underset{\text{(E) soluble complex}}{Na_4[Cu_6(S_2O_3)_5]}$

white ppt. (excess)

**Q.4**

(i) A blue coloured compound (A) on heating gives two of the products (B) & (C).

(ii) A metal (D) is deposited on passing hydrogen through heated (B).

(iii) The solution of (B) in HCl on treatment with the $K_4[Fe(CN)_6]$ gives a chocolate brown coloured precipitate of compound (E).

(iv) (C) turns lime water milky which disappears on continuous passage of (C) forming a compound (F).

Identify (A) to (F) and give chemical equations for the reactions at step (i) to (iv).

**Sol.** $A = 2CuCO_3 \cdot Cu(OH)_2$, $B = CuO$, $C = CO_2$, $D = Cu$, $E = Cu_2[Fe(CN)_6]$, $F = Ca(HCO_3)_2$.

Azurite

**Q.5** A light bluish green crystalline compound responds to the following tests:

(i) Its aqueous solution gives a brown precipitate or colouration 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.

**Sol.** The brown colouration with alkaline $K_2HgI_4$ indicates the presence of $NH^+_4$ ions. The blue colouration with $K_3[Fe(CN)_6]$ indicates the presence of $Fe^{2+}$ ions. The white precipitate with $BaCl_2$ solution indicates the presence of $SO^{2-}_4$ ions. The formula of the compound is $FeSO_4(NH_4)_2SO_4.6H_2O$.

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

$NH^+_4$ ions in the aqueous solution give brown colouration with alkaline $K_2HgI_4$.$Fe^{2+}$ ions in aqueous solution give blue colouration with $K_3[Fe(CN)_6]$.

$2SO^{2-}_4$ ions in aqueous solution (dilute HCl) give a white precipitate with $BaCl_2$ solution.

**Q.6**

(i) An ore (A) on roasting with sodium carbonate and lime in the presence of air gives two compounds, (B) and (C).

(ii) The solution of (B) in conc. HCl on treatment with potassium ferrocyanide gives a blue colour or precipitate of compound (D).

(iii) The aqueous solution of (C) on treatment with conc. $H_2SO_4$ gives a orange coloured compound (E).

(iv) Compound (E) when treated with KCl gives an orange red compound (F) which is used as an oxidising reagents.

(v) The solution of (F) on treatment with oxalic acid and then with an excess of potassium oxalate gives blue crystals of compound (G).

Identify (A) to (G) and give balanced chemical equations for reactions at step (i) to (v).

**Sol.** The ors is chromite $FeOCr_2O_3$.

(i) $4FeO.\ Cr_2O_3 + 8Na_2CO_3 + 7O_2 \xrightarrow{\text{Lime}} \underset{\text{(B)}}{2Fe_2O_3} + \underset{\text{(C)}}{8Na_2CrO_4}$

(ii) $\underset{\text{(B)}}{Fe_2O_3} + 6HCl \longrightarrow 2FeCl_3 + 3H_2O$

$4FeCl_3 + 3K_4Fe(CN)_6 \longrightarrow \underset{\text{(D) Prussian blue}}{Fe[Fe(CN)_6]_3} + 12\ KCl$

(iii) $2Na_2CrO_4 + H_2SO_4 \longrightarrow \underset{\text{(E)}}{Na_2Cr_2O_7} + Na_2SO_4 + H_2O$

(iv) $Na_2Cr_2O_7 + 2KCl \longrightarrow \underset{\text{(F) orange red}}{K_2Cr_2O_7} + 2NaCl$

(v) $K_2Cr_2O_7 + 4H_2SO_4 + 3H_2C_2O_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 6CO_2 + 7H_2O$

$Cr_2(SO_4)_3 + 6K_2C_2O_4 \longrightarrow \underset{\text{(G) Blue crystal}}{2K_3[Cr(C_2O_4)_3]} + 3K_2SO_4$

**Q.7** A white substance (A) on heating with excess of dilute HCl gave an offensive-smelling gas (B) and a solution (C). Solution (C) on treatment with aqueous ammonia did not give any precipitate but on treatment with NaOH solution gave a precipitate (D), which dissolves in excess of NaOH solution. (A) on strong heating in air gave a strong-smelling gas (E) and a solid (F). Solid (F) dissolved completely in HCl and the solution gave a precipitate with $BaCl_2$ in acid solution. Identify (A) to (F) and write the chemical equations for the various reactions involved.

**Sol.** Since solution C gives precipitate with NaOH solution which is soluble in excess of NaOH, the cation

should be an amphoteric metal like Zn or Al. Again, solid F is soluble in HCl and gives a white precipitate with $BaCl_2$. Therefore, the anion must be $SO^{2-}_4$ ion.

Substance A gives an offensive-smelling gas and, thus, the compound A may be ZnS or $Al_2S_3$. But, $Al_2S_3$ on heating in air does not form $Al_2(SO_4)_3$.

∴ It is concluded that the compound A is ZnS. The chemical reactions are as follows:

$$\underset{(A)}{ZnS} + 2HCl \rightarrow \underset{(C)}{ZnCl_2} + \underset{(B)}{H_2S}\uparrow$$

$$ZnCl_2 + 2NaOH \rightarrow \underset{(D)}{Zn(OH)_2} + 2NaCl$$

$$Zn(OH)_2 + 2NaOH \rightarrow Na_2ZnO_2 + 2H_2O$$

$$3ZnS + 5O_2 \rightarrow \underset{(F)}{ZnSO_4} + \underset{(E)}{2SO_2} + 2ZnO$$

$$ZnSO_4 + BaCl_2 \rightarrow BaSO_4\downarrow + ZnCl_2$$

Hence A = ZnS; B = $H_2S$; C = $ZnCl_2$

D = $Zn(OH)_2$; E = $SO_2$; F = $ZnSO_4$

**Q.8** Complete the following by identifying (A) to (F).

(i) $CuSO_4 5H_2O \xrightarrow{100°C} (A) \xrightarrow{230°C} (B) \xrightarrow{800°C} (C) + (D)$

(ii) $AgNO_3 \xrightarrow{\text{Red hot}} (E) + (F) + O_2$

**Sol.** A = $CuSO_4 . H_2O$ , B = $CuSO_4$, C = CuO, D = $SO_3$ , E = Ag , F = $NO_2$

**Q.9** An unknown solid mixture contains one or two of the following: $CaCO_3$, $BaCl_2$, $AgNO_3$, $Na_2SO_4$, $ZnSO_4$, and NaOH. The mixture is completely soluble in water and the solution gives pink colour with phenolphthalein. When 0.1 N HCl solution is gradually added to the above solution, a precipitate is produced which dissolves with further addition of the acid. What is /are present in the solid? Give equations to explain the appearance of the precipitate and its dissolution.

**Sol.** Since the mixture is completely soluble in water, the presence of $CaCO_3$ is ruled out. Further, the solution of the mixture gives pink colour with phenolphthalein; therefore, NaOH is present in the mixture. Again, the precipitate is dissolved by adding HCl. This rules out the possibility of $BaCl_2$, $AgNO_3$, or $Na_2SO_4$. It is because if $BaCl_2$ is there, the precipitate of $Ba(OH)_2$ should be formed in the presence of NaOH whereas the mixture is completely soluble. If $AgNO_3$ is there, the precipitate of AgCl should be formed with HCl. There is no possibility to form precipitate with $Na_2SO_4$.

Now $ZnSO_4$ may be the second compound of the mixture. Actually, NaOH is in excess in the mixture. Therefore, sodium zincate is formed in the solution which is soluble in water. On adding HCl in $Na_2ZnO_2$, a precipitate of $Zn(OH)_2$ forms which dissolves in HCl to form $ZnCl_2$.

The reactions are as follows:

$$ZnSO_4 + 4NaOH \rightarrow Na_2SO_4 + 2H_2O + Na_2\,ZnO_2$$

$$Na_2ZnO_2 + 2HCl \rightarrow Zn(OH)_2\downarrow + 2NaCl$$

$$Zn(OH)_2 + 2HCl \rightarrow ZnCl_2 + 2H_2O$$

Hence, the mixture contains NaOH and $ZnSO_4$.

**Q.10** 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.

**Sol.** Since the colourless inorganic salt 'A' on heating gives no reside hence it should be ammonium salt. One of the products is oxide which is liquid at room temperature and neutral. Therefore, this oxide may be water. The second product is also neutral oxide. On the basis of above discussion, the compound 'A' may be $NH_4NO_3$. Its reactions are given below:

$$\underset{(A)}{NH_4NO_3} \rightarrow \underset{(B)}{N_2O} + \underset{(C)}{H_2O}$$

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

$P_4O_{10}$ is strong dehydrating agent.