

DAY THIRTY SIX

Analytical Chemistry

Learning & Revision for the Day

- Qualitative Inorganic Analysis
- Detection of Functional Group
- Chemistry Involved in Titrimetric Exercises
- Some Important Experiment

Analytical chemistry deals with qualitative and quantitative analysis of the substances.

Qualitative Inorganic Analysis

The qualitative analysis deals with the detection and identification of various constituents present in inorganic salt or a mixture of salts.

1. Inorganic Salts

These are the products of neutralisation reaction of an acid and a base. Therefore, they contain an anion and a cation. By identifying these cations and anions, the salt can be identified.

2. Anions or acid Radicals

These are divided into three groups depending upon their reactions with dilute and concentrated sulphuric acid.

Group I Anions (react with dilute sulphuric acid)

Group I anions	Gases evolved with dil. H_2SO_4
Carbonate (CO_3^{2-})	Brisk effervescence of CO_2
Sulphite (SO_3^{2-})	Colourless gas with odour of burning sulphur (SO_2)
Sulphide (S^{2-})	Colourless gas with smell of rotten eggs (H_2S)
Nitrite (NO_2^-)	Brown fumes with pungent odour (NO_2)

Group II Anions (react with conc. H_2SO_4)

Group II anions	Gases evolved with conc. H_2SO_4
Chloride (Cl^-)	Colourless gas with pungent smell (HCl)
Bromide (Br^-)	Brown fumes (Br_2)
Iodide (I^-)	Violet fumes of (I_2)
Nitrate (NO_3^-)	Pungent, light brown (NO_2) gas

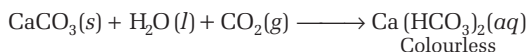
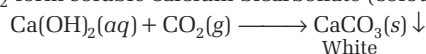
Group III Anions (not affected by both dil. and conc. H_2SO_4)

Sulphate and phosphate are present in group III anions.

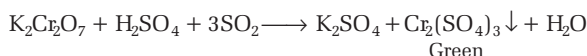
Confirmatory Tests for Group I Anions

Following anions decomposes on reaction with dil. H_2SO_4 to give gases. These gases indicate the nature of acid radical present in the salt.

- (i) **Carbonate** (CO_3^{2-}) The evolved gas is carbon dioxide (CO_2) gas. It is recognised by passing it through lime water which turns milky due to formation of CaCO_3 and excess of CO_2 form soluble calcium bicarbonate (colourless).

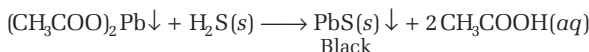


- (ii) **Sulphite** (SO_3^{2-}) The evolved gas is SO_2 . This gas turns acidified $\text{K}_2\text{Cr}_2\text{O}_7$, paper green due to reduction of Cr (VI) to Cr (III).



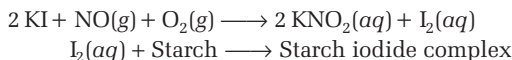
Like SO_2 , H_2S also turns potassium dichromate paper green. So, before testing SO_3^{2-} , S^{2-} must be tested and if present, it should be removed.

- (iii) **Sulphide** (S^{2-}) The evolved gas is $\text{H}_2\text{S}(g)$. It is tested with lead acetate paper which turns black due to the formation of black lead sulphide.



H_2S gives violet colour with sodium nitroprusside, $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]$ due to the formation of sodium thio nitroprusside, $\text{Na}_4[\text{Fe}(\text{CN})_5\text{NOS}]$.

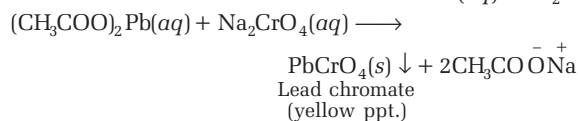
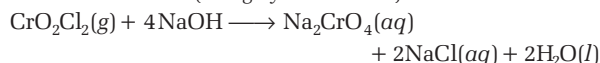
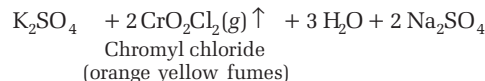
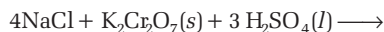
- (iv) **Nitrite** (NO_2^-) The evolved gas oxidises I^- to I_2 which gives blue colour with starch.



Confirmatory Tests for Group II Anions

Following anions decomposes on reaction with conc. H_2SO_4 to give gases.

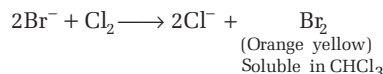
- (i) **Chlorides** (Cl^-) The evolved gas is HCl . It is identified by bringing a rod dipped in ammonium hydroxide near the mouth of the test tube when dense white fumes (NH_4Cl) are produced.
- (ii) **Chromyl chloride test** is the confirmatory test for chloride. On heating with solid $\text{K}_2\text{Cr}_2\text{O}_7$ and conc. H_2SO_4 , chloride gives orange yellow vapours of chromyl chloride (CrO_2Cl_2) which on passing over NaOH and then on treating with lead acetate forms yellow ppt. of lead chromate.



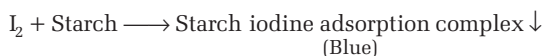
Chlorides, on treating with $\text{HNO}_3 + \text{AgNO}_3$ solution, form white precipitate (AgCl) which is soluble in NH_4OH . Chromyl chloride test is not given by chlorides of Hg, Sn, Ag, Pb and Sb.

- (iii) **Bromide** (Br^-) The evolved gas is HBr . On treating bromides with HNO_3 and AgNO_3 solution, pale yellow precipitate of AgBr is formed which is partially soluble in excess of NH_4OH .

On shaking bromides with chlorine water and chloroform, the chloroform layer turns yellow (or brownish yellow). This is known as **layer test**.

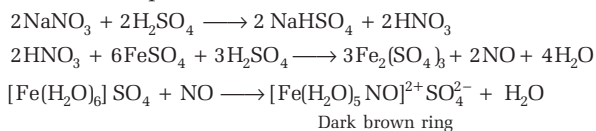


- (iv) **Iodide** (I^-) The evolved gas is HI along with violet iodine vapours. The obtained I_2 gas is recognised by treating it with starch solution which turns blue.



If layer test is performed for iodide, the CHCl_3 layer turns violet.

- (v) **Nitrate** (NO_3^-) On reaction with conc. H_2SO_4 first form colourless HNO_3 which decomposes to give brown fumes of nitrogen dioxide. Presence of nitrate is confirmed by performing ring test. In ring test, the water extract of nitrate salt is treated with freshly prepared FeSO_4 solution and then conc. H_2SO_4 is added. Formation of dark brown ring between two layers confirms the presence of nitrate radical.



Confirmatory Tests for Group III Anions

The following are the steps involved in the confirmatory tests for group III anions.

Sulphate (SO_4^{2-}) BaCl_2 test is the confirmatory test for sulphate. The white precipitate of BaSO_4 is insoluble in conc. HNO_3 .

3. Cations or Basic Radicals

Following dry test methods are used to identify cations.

- (i) **Flame test** is used to identify the cations by developing different colours. These are as follows:

Name of radicals	Colour obtained
Sodium (Na^+)	Golden yellow
Lithium (Li^+)	Carmine red
Potassium (K^+)	Violet
Copper (Cu^{2+})	Bluish green
Calcium (Ca^{2+})	Brick red or dull red
Strontium (Sr^{2+})	Crimson red
Barium (Ba^{2+})	Apple green

- (ii) **Borax bead test** is used to identify the cation by developing different colour in different flame.

Basic radicals	Oxidising flame (Non-luminous)	Reducing flame (Luminous)
Nickel (Ni)	Light brown	Black
Gold (Au)	Rose-violet	Violet
Chromium (Cr)	Green	Green
Iron (Fe)	Yellow	Bottle green
Copper (Cu)	Light blue or green	Colourless or red

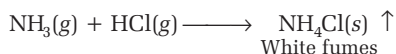
Borax bead test is performed only for coloured substances.

- (iii) **Wet Tests** On the basis of solubility product and reagents used, the basic radicals are classified into following six groups.

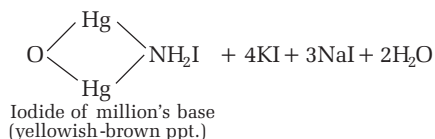
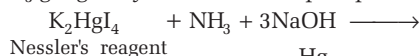
Group number (with radicals)	Group reagent
0 (NH_4^+)	NaOH
I (Pb^{2+} , Ag^+ , Hg_2^{2+})	Dil. HCl
II (Pb^{2+} , Cu^{2+} , Bi^{3+} , Cd^{2+} , Sn^{2+})	H_2S in presence of dil. HCl
III (Fe^{3+} , Al^{3+} , Cr^{3+})	NH_4Cl + NH_4OH
IV (Ni^{2+} , Zn^{2+} , Mn^{2+} , Co^{2+})	H_2S in presence of NH_4OH
V (Ba^{2+} , Ca^{2+} , Sr^{2+})	$(\text{NH}_4)_2\text{CO}_3$ in presence of NH_4Cl and NH_4OH
VI (Mg^{2+})	Na_2HPO_4

Confirmatory Tests for Zero Group (NH_4^+)

Ammonium ion on heating with NaOH gives NH_3 gas which is recognised by taking a glass rod dipped in HCl above the mouth of test tube.

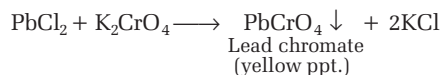
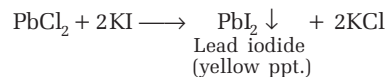


NH_3 gas gives yellowish-brown precipitate with Nessler's reagent.

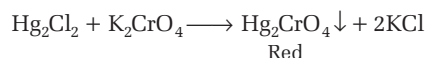


Confirmatory Tests for First Group Radicals (Pb^{2+} , Ag^+ , Hg_2^{2+})

Lead chloride (PbCl_2) is soluble in hot water and gives yellow precipitate with KI and with K_2CrO_4 .



Hg_2Cl_2 is blackened by NH_3 and with K_2CrO_4 , it gives red precipitate.



AgCl gives red precipitate with K_2CrO_4 which is soluble in NH_4OH .



For testing sulphate, if Ag and Pb cations are present then $\text{Ba}(\text{NO}_3)_2$ must be used in place of BaCl_2 otherwise chlorides of Ag or Pb may get precipitated.

Confirmatory Tests for Second Group Radicals (Pb^{2+} , Cu^{2+})

On passing H_2S gas, the cations of group II forms precipitates and can be put into two groups on the basis of the colour of their sulphides.

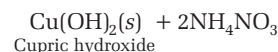
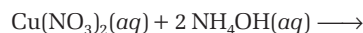
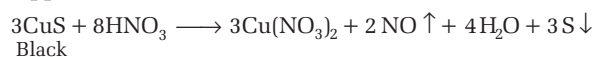
Second Group Radicals

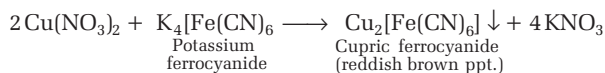
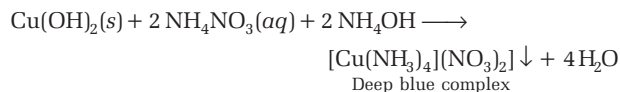
Cu^{2+}	Pb^{2+}
(i) Cu^{2+} with HNO_3 and excess of conc. NH_4OH gives blue colour or ppt.	(i) Pb^{2+} with alcohol and conc. H_2SO_4 gives white ppt.
(ii) Cu^{2+} with potassium ferrocyanide solution, forms a reddish brown ppt.	(ii) Pb^{2+} with potassium chromate solution gives yellow ppt.

For IIInd group cations, H_2S must be passed in hot solution slowly to get more granular and easily filterable precipitates.

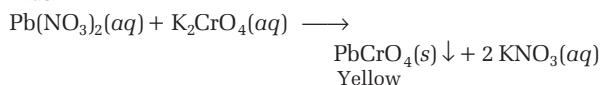
The following are some chemical equations which play an important role while confirmation of Cu^{2+} and Pb^{2+} given as:

1. Copper (Cu^{2+})





2. Lead (Pb^{2+})



Confirmatory Tests for Third Group Radicals (Fe^{3+} , Al^{3+})

Both are precipitated as hydroxides. These are precipitated by addition of NH_4Cl and NH_4OH .

Third group radicals

Fe^{3+}
Red Brown ppt. $\text{Fe}(\text{OH})_3$

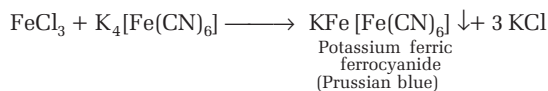
- (i) The brown ppt is soluble in dil. HCl.
- (ii) With $\text{K}_4[\text{Fe}(\text{CN})_6]$ solution, Fe^{3+} gives a blue colour or ppt.
- (iii) With KCNS solution, Fe^{3+} gives a blood red colouration.

Al^{3+}
White gelatinous ppt. $\text{Al}(\text{OH})_3$

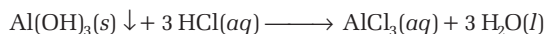
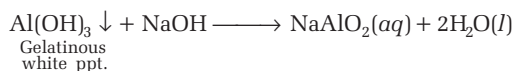
- (i) **Lake test** The white ppt is soluble in NaOH. The obtained solution on treatment with HCl and a few drops of blue litmus solution followed by excess of NH_4OH solution gives a blue lake.
- (ii) In charcoal cavity cobalt nitrate test Al^{3+} gives a blue mass.

The following are some chemical equations which play an important role while confirmation of Fe^{3+} and Al^{3+} given as :

(i) Iron (Fe^{3+})



(ii) Aluminium (Al^{3+})



Addition of ammonium hydroxide precipitates Al as aluminium hydroxide. $\text{Al}(\text{OH})_3$ gets adsorbed on the blue colouring matter of litmus to form a complex that floats as blue lake over a colourless solution.

Confirmatory Tests for Fourth Group Radicals (Zn^{2+} , Ni^{2+})

These are precipitated as sulphides in ammoniacal medium.

Fourth group radicals

Zn^{2+}

(i) Dirty white ppt. (ZnS)

In cobalt nitrate test, Zn^{2+} gives green mass.

- (ii) The precipitate is soluble in dil. HCl. The obtained solution on treatment with NaOH solution gives white ppt which dissolves in excess of NaOH.

- (iii) With potassium ferrocyanide solution, Zn^{2+} gives white ppt.

Ni^{2+}

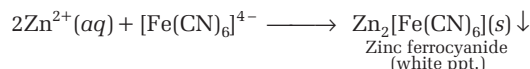
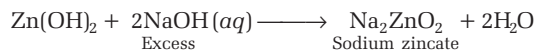
(i) Black ppt. (NiS)

The black ppt is soluble in *aqua-regia*.

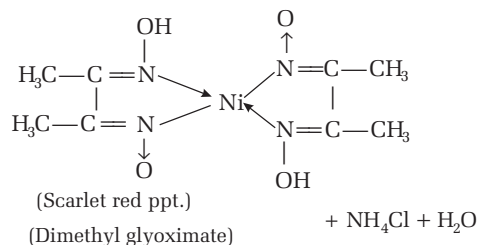
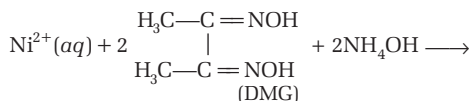
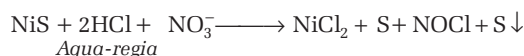
- (ii) Ni^{2+} with dimethyl glyoxime and excess of NH_4OH gives scarlet red ppt.

In IVth group, H_2S should not be passed continuously, otherwise NiS turns in colloidal state. The following are the some chemical equations which play an important role while confirmation of Zn^{2+} and Ni^{2+} given as:

(i) Zinc (Zn^{2+})



(ii) Nickel (Ni^{2+})



Confirmatory Tests for Fifth Group Radicals

(Ba²⁺, Ca²⁺, Sr²⁺) First boil off H₂S and then add (NH₄)₂CO₃ and NH₄OH.

Fifth group radicals

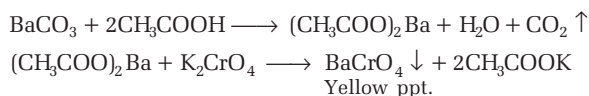
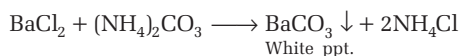


The obtained ppt is soluble in acetic acid.

- | | |
|---|--|
| (i) With K ₂ CrO ₄ (in excess) solution, Ba ²⁺ gives yellow ppt. | (i) With ammonium oxalate solution, Ca ²⁺ gives white ppt. |
| (ii) Ba ²⁺ imparts green colour to the flame in flame test. | (ii) Ca ²⁺ imparts brick red colour to the flame in flame test. |

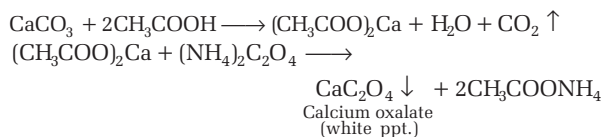
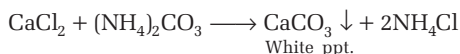
The following are the some chemical equations which play an important role while confirmation of Ba²⁺ and Ca²⁺ given as:

1. Barium (Ba²⁺)

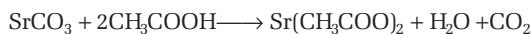
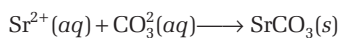


BaCl₂ is volatile and provides apple green colour to the flame.

2. Calcium (Ca²⁺)



3. Strontium (Sr²⁺)

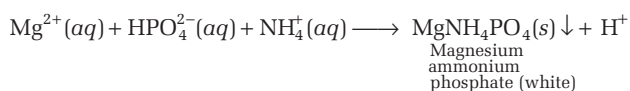


Confirmatory Tests for Sixth Group Radicals (Mg²⁺)

- Mg²⁺ with little NH₄Cl, excess of NH₄OH and sodium phosphate solution, forms white crystalline ppt.
- Mg²⁺ with dil. HCl and a few drops of magneson reagent forms blue colour or ppt.

Chemical Equation Involved in the Confirmation of Mg²⁺

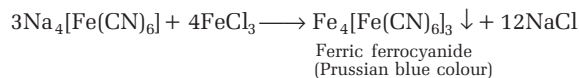
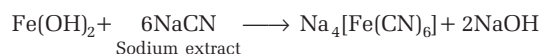
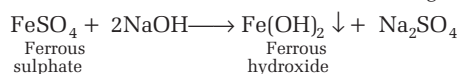
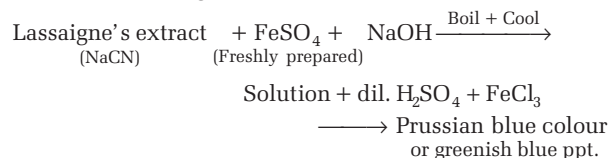
The following is the chemical equation which plays an important role while confirmation of Mg²⁺ given as:



Detection of Extra Element in Organic Compounds

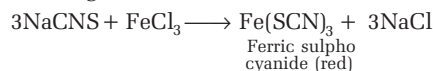
Presence of extra elements (i.e. N, S and X) in an organic compound is identified by **Lassaigne's test**, in which the Lassaigne's extract is prepared by fusing the compound with sodium metal. The reason of fusion is to convert covalent compounds into inorganic (ionisable) compounds.

1. Detection of Nitrogen

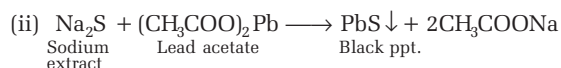
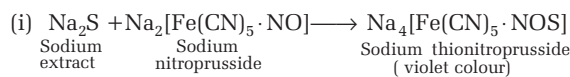


If S is also present alongwith N.

In the test of nitrogen, blood red colour is obtained instead of blue or green.



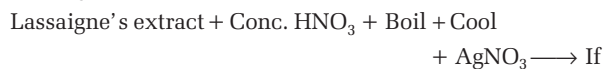
2. Detection of Sulphur



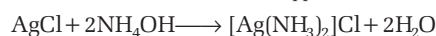
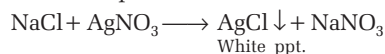
3. Detection of Halogens

There are two tests involved during the detection of halogens, i.e. AgNO₃ test and Beilstein's test.

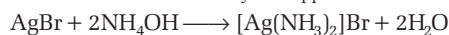
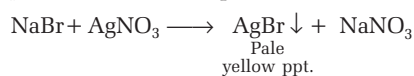
(i) AgNO₃ Test



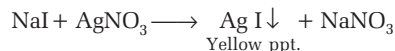
- (a) white curdy ppt. is formed which is soluble in NH₄OH, it indicates the presence of Cl⁻ ion.



- (b) pale yellow ppt. is obtained which is partially soluble in NH₄OH, it indicates the presence of Br⁻ ion.



- (c) Yellow ppt. is formed which is insoluble in NH_4OH , it indicates the presence of Γ^- ion.



(ii) **Beilstein's Test**

If a copper wire, dipped in organic compound, on heating gives green or bluish green flame, it shows the presence of halogens.

Several halogen free compounds such as pyridine, purines, urea, thiourea etc., also impart green colour to the flame, so this test is not very reliable. However, production of no green or blue colour confirms the absence of halogen.

Therefore, this test is a confirmative one to show the absence of halogens rather than to show its presence.

Beilstein's test is not given by fluorine because copper fluoride is not volatile.

Detection of Functional Groups

Following methods can be used to detect the functional groups.

- 1. Tests for Carboxylic Acid ($-\text{COOH}$)** Carboxylic acids give brisk effervescence of CO_2 with sodium bicarbonate. They react with ethyl alcohol and conc. H_2SO_4 to give fruity smell due to formation of ester.
- 2. Tests for Alcoholic ($-\text{OH}$) Group** Alcohols give red colour with ceric ammonium nitrate. Primary, secondary and tertiary alcohols are distinguished by using Lucas reagent. With Lucas reagent (anhy. ZnCl_2 + conc. HCl),
 - (i) tertiary alcohols give turbidity immediately.
 - (ii) secondary alcohols give turbidity after 5 minutes.
 - (iii) primary alcohols do not produce turbidity at room temperature.
- 3. Tests for Phenolic ($\text{Ph}-\text{OH}$) Group** Phenols give characteristic colours (green, blue and violet) with FeCl_3 solution due to formation of $[\text{Fe}(\text{OC}_6\text{H}_5)_6]^{3-}$ complex ion. In **Liebermann's nitroso reaction**, phenol gives blue colour (indophenol ion) which turns red (indophenol) on adding NaOH . Nitrophenols do not give the above two tests.
- 4. Tests for Aldehyde ($-\text{CHO}$) Group** Aldehydes give silver mirror with Tollen's reagent, red ppt with Fehling solution, violet colour with Schiff's reagent and red-yellow ppt with Benedict's solution. Except Benedict's solution test, all other are also given by aromatic aldehydes. Therefore, this test is used to differentiate between aliphatic and aromatic aldehydes.

5. Tests for Ketone Group $\left(\begin{array}{c} R \\ \diagdown \\ C \\ \diagup \\ R \end{array} = O \right)$

Ketones give white ppt with sodium bisulphite. With sodium nitroprusside, ketones give red or purple colour.

- 6. Tests for Primary Amines ($R-\text{NH}_2$)** On adding acetone and a few drops of sodium nitroprusside to the aliphatic primary amines, violet red colour is obtained.

Aliphatic primary amines give brisk effervescence with HNO_2 while aromatic primary amines give red dye on treating with HNO_2 and alkaline solution of β -naphthol.

Tests for Secondary Amines ($\overset{R}{\underset{|}{R}-\text{NH}}$) Secondary amines give positive Liebermann's nitroso test. It gives blue colour on heating the mixture with nitrous acids and 1-2 drops of phenol and H_2SO_4 . With HNO_2 , secondary amines give oily dark coloured liquid.

Chemistry Involved in the Titrimetric Exercises

In titrimetric or volumetric analysis, the amount of a chemical species present in the given unknown solution is determined by measuring the volumes of the solution taking part in the given chemical reactions.

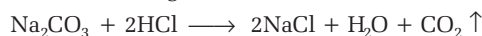
The chemical species react in the ratio of their chemical equivalent masses. The main purpose of this analysis is called titration.

Some important terms used in titrimetric exercises are as follows

- (i) Analyte and Titrant** The substance being analysed is called analyte and that which is added to analyte in a titration is called titrant.
- (ii) Equivalence Point or End Point** It is point at which the reaction between two solutions is just complete. It is generally represented by change in colour, pH, conductivity etc.
- (iii) Standard Solution** Solution of known concentration is called standard solution.
- (iv) Primary Standard Substance** The substance, standard solution of which can be prepared directly by dissolving its definite weight in definite volume of solvent is called primary standard substance, e.g. crystalline oxalic acid, anhydrous Na_2CO_3 , Mohr's salt etc. The substance, which occur in pure state, are non-hygroscopic, non-deliquescent, generally behave as primary standard substance.
- (v) Secondary Standard Substance** Their standard solution cannot be prepared directly. e.g. KMnO_4 , NaOH , KOH etc.
- (vi) Indicator** It shows the end point of a titration.

Titration of Na₂CO₃ vs HCl (Acid and Base)

The titration of Na₂CO₃ vs HCl is a neutralisation titration (acidimetry and alkalimetry) which involve the neutralisation of an acid with a base e.g.



In it, first the standard solution of Na₂CO₃ $\left(\frac{N}{10} \text{ Na}_2\text{CO}_3\right)$ is

prepared and then titrated its 20 mL with HCl solution by adding a few drops of methyl orange indicator. Change in colour shows the end point.

Calculations involved in the titration are as follows:

(i) Weight of Na₂CO₃ dissolved in 250 mL measuring flask
= z = g

$$\text{Weight of Na}_2\text{CO}_3 \text{ in } 100 \text{ mL} = \dots \times 4 \\ = \dots \text{ g / L}$$

$$\text{Normality of Na}_2\text{CO}_3 \text{ (prepared)} \\ = \frac{\text{strength (g / L)}}{\text{eq. wt. of oxalic acid}} = \frac{\dots}{63} \text{ N}$$

(ii) For the titration using standard Na₂CO₃ solution

$$\begin{array}{ccc} N_1 V_1 & = & N_2 V_2 \\ \text{Na}_2\text{CO}_3 & & \text{HCl} \\ \text{(known)} & & \\ N_2 & = & \dots \text{ N} \end{array}$$

(iii) For the titration using supplied Na₂CO₃ solution

$$\begin{array}{ccc} N_3 V_3 & = & N_4 V_4 \\ \text{Na}_2\text{CO}_3 & & \text{HCl} \\ \text{(unknown)} & & \\ N_3 & = & \dots \end{array} \quad [\because N_4 = N_2]$$

$$\text{Strength of Na}_2\text{CO}_3 \text{ in g / L} = N_3 \times \text{eq. wt. of Na}_2\text{CO}_3 = \dots$$

- In acidimetry and alkalimetry, the choice of indicators mainly depends upon the nature of the acids and alkalies used. Methyl orange, phenolphthalein are some of the important indicators used in these titrations.
- As no indicator gives correct results in the titration of weak acids against weak bases, such titrations are to be avoided.

Use of Indicators

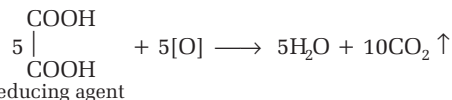
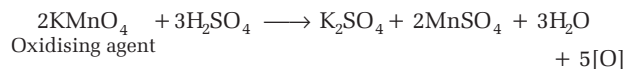
The indicators used in various acid-base titrations are shown below:

Indicators in Acid-base Titrations

Acid-base titrations	Indicators
Strong acid vs strong base	Bromothymol blue, phenolphthalein, methyl orange, thymolphthalein
Strong base acid vs weak base	Methyl orange, methyl red, bromocresol green
Weak acid vs strong base	Phenolphthalein, thymolphthalein
Weak acid vs weak base	Phenol red

Titration of Oxalic Acid vs KMnO₄

- This is an example of redox titrations, in which a reducing agent (oxalic acid) is estimated by titrating it with a standard solution of oxidising agent (KMnO₄). Such reactions are accompanied by the change in valency of ions. In these titrations oxidation and reduction takes place simultaneously, i.e. while one substance is being oxidised, the other one is being reduced.



The last drop of KMnO₄ itself acts as an indicator.

- In this titration, first the standard solution of oxalic acid is prepared which is then titrated with KMnO₄ solution in the presence of dil. H₂SO₄. The procedure is repeated to obtain a set of concurrent readings.

Calculations involved in the titration are as follows:

(i) Weight of oxalic acid dissolved in 250 mL measuring flask = z = g

$$\text{Weight of oxalic acid in } 1000 \text{ mL} = \frac{\dots \times 1000}{250} = \dots \text{ g/L}$$

$$\text{Normality of oxalic acid (prepared)} \\ = \frac{\text{Strength (g/L)}}{\text{Eq. wt. of oxalic acid}} = \frac{\dots}{63.04} \text{ N}$$

(ii) For the titrations using standard oxalic acid solution

$$\begin{array}{ccc} N_1 V_1 & = & N_2 V_2 \\ \text{(Oxalic acid)} & & \text{(KMnO}_4\text{)} \\ \text{(Known)} & & \\ \dots \text{ N} \times 20 \text{ mL} & = & N_2 \times \dots \end{array}$$

(iii) For the titration using supplied oxalic acid solution

$$\begin{array}{ccc} N_3 V_3 & = & N_4 V_4 \\ \text{Oxalic acid} & & \\ \text{(unknown)} & & \\ N_3 & = & \dots \text{ N} \end{array} \quad [\because N_4 = N_2]$$

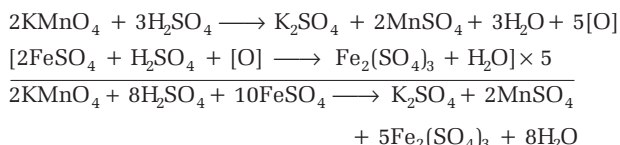
$$\text{Strength of oxalic acid in g / L} = N_3 \times \text{eq. wt. of oxalic acid} = \dots \text{ g/L}$$

- In oxalic acid vs H₂SO₄ titration mixture is heated to near about 70°–80°C. Sulphuric acid should be in excess otherwise a brown ppt. due to formation of MnO₂ will be formed. This titration cannot be carried out in the presence of acid like HNO₃ and HCl, because HNO₃ itself is an oxidising agent, so it will interfere with the oxidising action of KMnO₄ and HCl reacts chemically with KMnO₄ solution.

Titration of Mohr's Salt vs KMnO₄

This is also an example of redox titrations and work on the same principle as oxalic acid vs KMnO₄ titration. In this titration, the active constituent of ferrous ammonium sulphate

(Mohr's salt) is ferrous sulphate, which is oxidised to ferric sulphate by acidified potassium permanganate as follows:



Calculations involved in the titration are as follows:

- (i) Weight of ferrous ammonium sulphate dissolved in 250 mL measuring flask = $z = \dots$ g

Weight of ferrous ammonium sulphate in 1000 mL

$$= \frac{\dots \times 1000}{250} = \dots \text{ g/L}$$

Normality of ferrous ammonium sulphate (prepared)

$$= \frac{\text{strength (g/L)}}{\text{eq. wt. of ferrous ammonium sulphate}} = \frac{\dots}{63.04} \text{ N}$$

- (ii) For the titrations using standard ferrous ammonium sulphate solution

$$\begin{array}{ccc} N_1 V_1 & = & N_2 V_2 \\ \text{Mohr's salt} & & \text{KMnO}_4 \\ (\text{Known}) & & \end{array}$$

$$\frac{\dots}{63.04} \times 20 \text{ mL} = N_2 \times \dots$$

$$N_2 = \dots \text{ N}$$

- (iii) For the titration using supplied ferrous ammonium sulphate solution $N_3 V_3 = N_4 V_4$

$$\begin{array}{ccc} \text{Ferrous ammonium sulphate} & \text{KMnO}_4 & [\because N_4 = N_2] \\ & (\text{unknown}) & \end{array}$$

$$N_3 = \dots \text{ N}$$

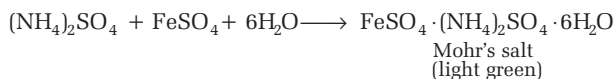
$$\begin{array}{l} \text{Strength of ferrous ammonium sulphate in g/L} = N_3 \times \text{eq. wt. of ferrous ammonium sulphate} = \dots \text{ g/L} \end{array}$$

Chemistry Involved in the Preparation of Compounds

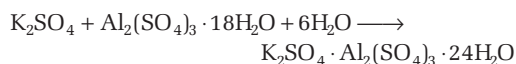
Chemistry involved in the preparation of inorganic and organic compounds are as follows:

Preparation of Inorganic Compounds

- The contents used for the **preparation of Mohr's salt**, i.e. ferrous ammonium sulphate $[\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}]$.

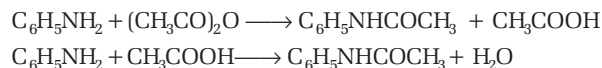


- Potash alum** is a double salt having composition $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$. It is prepared by concentrating a solution containing equimolar quantities of K_2SO_4 and $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$.

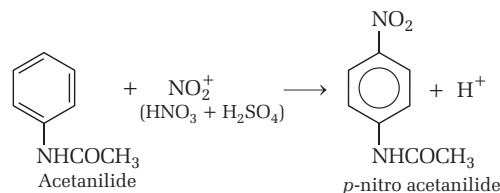


Preparation of Organic Compounds

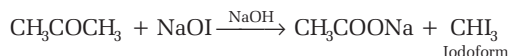
- Acetanilide** ($\text{C}_6\text{H}_5\text{NHCOCH}_3$) is obtained from aniline by treating it with acetic anhydride. Since, acetic anhydride is quite costly, it is not used now a days, instead it glacial acetic acid is used.



- During the preparation of acetanilide, some zinc dust is added to reduce the coloured impurities and also to prevent the oxidation of aniline.
- p-nitro acetanilide** is prepared by the nitration of acetanilide, by using fuming HNO_3 + conc. H_2SO_4 .



- During the preparation of p-nitro acetanilide from acetanilide, the temperature of the flask should be maintained below 10°C .
- Iodoform** (CHI_3) is obtained by treating acetone with KI and sodium hypochlorite (NaOCl). The colour of crystals of iodoform is yellow.



- Aniline yellow**, also called p-amino azobenzene, is obtained from diazoamino benzene. It is carcinogenic and basic dye.

Some Important Experiments

- Enthalpy of Solution of CuSO_4** It is the amount of heat absorbed or evolved on dissolving one mole of it in excess of the solvent at a given temperature and pressure. It is positive when heat is absorbed and negative when heat is given out during dissolution. It can be determined by putting a known volume of water in a thermally insulated vessel and then finding out its change in temperature on adding a known weight of the substance into it. From the change in temperature, heat absorbed or evolved can be calculated.

$$\text{Heat evolved or absorbed} = \text{Heat gained or lost}$$

$$= m \times s \times t$$

$$= 100 \times 4.2 \times (t_2 - t_1) \text{ J}$$

$$\text{Number of moles of } \text{CuSO}_4 \text{ dissolved} = \frac{W}{M} \left(\frac{10}{249} \right)$$

Heat of solution of

$$\text{CuSO}_4 \cdot \text{H}_2\text{O} = 100 + 4.2 \times (t_2 - t_1) \times \frac{249}{10}$$

2. Enthalpy of neutralisation of strong acid and strong base

It is defined as the heat evolved when one mole of H^+ ions is completely neutralised by a base.

To find this, whole procedure is divided into two step. First step is the determination of water equivalent of the beaker. The second step is the determination of heat of neutralisation by using same beaker.

$$\text{Water equivalent of beaker (W)} = \left[\frac{50 \times 4.2(t_2 - t_3)}{(t_3 - t_1)} \right] - (50 \times 4.2)^\circ\text{C}$$

t_1 = Initial temperature of cold water

t_2 = Temperature of hot water

t_3 = Temperature of the mixture

$$Q (\text{heat evolved}) = (100 \times 4.2 + W)(t_5 - t_4)$$

t_5 = Temperature of $\text{HCl} + \text{NaOH}$

t_4 = Temperature of HCl

3. Preparation of lyophilic and lyophobic sols

Two methods are employed for preparation of sol. These are as follows

(i) **Condensation method** that involves the increase in size of the solute particle in solution upto the colloidal size. It may be effected by hydrolysis, oxidation, reduction or double decomposition.

(ii) **Dispersion method** that involves crushing of bigger particles in a suspension to the colloidal size. Generally mechanical method is involved to reduce the size of particle.

4. Kinetic study of reaction of iodide ion with hydrogen peroxide at room temperature.

Here, the rate of reaction is determined by reaction with thiosulphate ions and starch solution.

- The iodine produced in the reaction of iodide and H_2O_2 reacts with thiosulphate and cannot colour starch blue.
- This continues till the whole of thiosulphate has been consumed. After that the solution turns blue.

DAY PRACTICE SESSION 1

FOUNDATION QUESTIONS EXERCISE

1 A substance on treatment with dil. H_2SO_4 liberates a colourless gas which produces (i) turbidity with baryta water and (ii) turns acidified dichromate solution green. The reaction indicates the presence of

- (a) CO_3^{2-} (b) S^{2-} (c) SO_3^{2-} (d) NO_2^-

2 The brown ring test for NO_2^- and NO_3^- is due to the formation of complex ion with formula

- (a) $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ (b) $[\text{Fe}(\text{NO})(\text{CN})_5]^{2-}$
(c) $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]^{2+}$ (d) $[\text{Fe}(\text{H}_2\text{O})(\text{NO})_5]^{2+}$

3 The acidic solution of a salt produced a deep blue colour with starch iodide solution. The salt may be

- (a) chloride (b) nitrite
(c) acetate (d) bromide

4 Borax when heated on platinum wire forms a glass like bead which is made up of

- (a) sodium tetraborate
(b) sodium metaborate
(c) sodium metaborate and boric anhydride
(d) boric anhydride and sodium tetraborate

5 In the borax bead test of Co^{2+} , the blue colour of bead is due to the formation of

- (a) B_2O_3 (b) Co_3B_2
(c) $\text{Co}(\text{BO}_2)_2$ (d) CoO

6 A solution of 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

→ AIEEE 2010

- (a) Pb^{2+} (b) Hg^{2+} (c) Cu^{2+} (d) Co^{2+}

7 If Fe^{3+} and Cr^{3+} both are present in group III of qualitative analysis, then distinction can be made by

- (a) addition of NH_4OH in the presence of NH_4Cl when only $\text{Fe}(\text{OH})_3$ is precipitated
(b) addition of NH_4OH in the presence of NH_4Cl when $\text{Cr}(\text{OH})_3$ and $\text{Fe}(\text{OH})_3$ both are precipitated and on adding Br_2 water and NaOH , $\text{Cr}(\text{OH})_3$ dissolves
(c) precipitate of $\text{Cr}(\text{OH})_3$ and $\text{Fe}(\text{OH})_3$ as obtained in (b) are treated with conc. HCl when only $\text{Fe}(\text{OH})_3$ dissolves
(d) Both (b) and (c)

8 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) Zn^{2+} , Ni^{2+}

9 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 and separate Fe^{3+} in one step is

- (a) 2 M HCl (b) 6 M NH_3
(c) 6 M NaOH (d) H_2S gas

10 Which one of the following statement is correct?

- (a) Fe^{2+} gives brown colour with ammonium thiocyanate
 (b) Fe^{2+} gives blue precipitate with potassium ferricyanide
 (c) Fe^{3+} gives brown colour with potassium ferricyanide
 (d) Fe^{3+} gives red colour with potassium ferrocyanide

11 A metal nitrate reacts with KI to give a black precipitate which on addition of excess of KI convert into orange colour solution. The cation of metal nitrate is

- (a) Hg^{2+} (b) Bi^{3+} (c) Pb^{2+} (d) Cu^{+}

12 Sodium carbonate cannot be used in place of $(\text{NH}_4)_2\text{CO}_3$ for the identification of Ca^{2+} , Ba^{2+} and Sr^{2+} ions (in group V) during mixture analysis because → JEE Main (Online) 2013

- (a) Mg^{2+} ions will be precipitated
 (b) concentration of CO_3^{2-} ions is very low
 (c) sodium ions will react with acid radicals
 (d) Na^{+} ions will interfere with the detection of Ca^{2+} , Ba^{2+} , Sr^{2+} ions

13 Match the following and choose the correct option.

Ion + Reagent		Colour	
A.	$\text{Fe}^{3+} + [\text{Fe}(\text{CN})_6]^{4-}$	1.	Cherry red
B.	$\text{Fe}^{3+} + \text{CNS}^-$	2.	Pink
C.	$\text{Ni}^{2+} + \text{DMG}$	3.	Blood red
D.	$\text{Mn}^{2+} + \text{PbO}_2 + \text{H}^+$	4.	Blue

Codes

- | | | | | | | | | | |
|-----|---|---|---|---|-----|---|---|---|---|
| A | B | C | D | A | B | C | D | | |
| (a) | 1 | 4 | 2 | 3 | (b) | 4 | 3 | 1 | 2 |
| (c) | 3 | 4 | 2 | 1 | (d) | 3 | 1 | 4 | 3 |

14 When metal 'M' is treated with NaOH, a white gelatinous precipitate 'X' is obtained, which is soluble in excess of NaOH. Compound 'X' when heated strongly gives an oxide which is used in chromatography as an adsorbent. The metal 'M' is → JEE Main 2018

- (a) Zn (b) Ca (c) Al (d) Fe

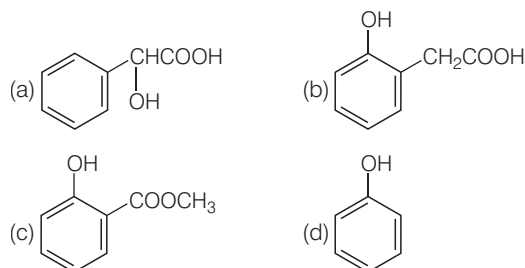
15 Which of the following gives blood red colour with KCNS?

- (a) Cu^{2+} (b) Fe^{3+} (c) Al^{3+} (d) Zn^{2+}

16 In organic analysis, the reagent 2, 4-dinitro phenyl hydrazine is used for the detection of which of the following functional groups?

- (a) Alcohol (b) Acid (c) Ketone (d) Amines

17 A compound liberates CO_2 with NaHCO_3 and also gives colour with neutral FeCl_3 solution. The compound can be



18 Which of the following compounds is not expected to show 'Lassaigne's test for nitrogen'? → JEE Main (Online) 2013

- (a) Propanenitrile
 (b) Hydroxylamine hydrochloride
 (c) Nitromethane
 (d) Ethanamine

19 Which of the following will not give Lassaigne's test for nitrogen ?

- (a) NH_2-NH_2 (b) $\text{C}_6\text{H}_5-\text{N}=\text{N}-\text{C}_6\text{H}_5$
 (c) CH_3CONH_2 (d) $\text{CH}_3\text{C}\equiv\text{N}$

20 Phenolphthalein is an indicator for acid-base titration, it exists as

- (a) benzenoid form in acid and quinonoid form in basic solution
 (b) quinonoid form in acid and benzenoid form in basic solution
 (c) quinonoid form in both
 (d) benzenoid form in both

21 The compound formed in the positive test for nitrogen with the Lassaigne solution of an organic compound is

- (a) $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$
 (b) $\text{Na}_3[\text{Fe}(\text{CN})_6]$
 (c) $\text{Fe}(\text{CN})_3$
 (d) $\text{Na}_4[\text{Fe}(\text{CN})_5\text{NOS}]$

22 In the titration of oxalic acid vs potassium permanganate, potassium permanganate acts as

- (a) external indicator
 (b) self indicator
 (c) reductant
 (d) Both (b) and (c)

23 Sodium salt of an organic acid 'X' produces effervescence with conc. H_2SO_4 . 'X' reacts with the acidified aqueous CaCl_2 solution to give a white precipitate which decolourises acidic solution of KMnO_4 . 'X' is → JEE Main 2017

- (a) $\text{C}_6\text{H}_5\text{COONa}$ (b) HCOONa
 (c) CH_3COONa (d) $\text{Na}_2\text{C}_2\text{O}_4$

24 In the kinetic study of reaction of iodide ion with hydrogen peroxide, a known volume of sodium thiosulphate solution is added to

- (a) oxidise iodide ion to iodine
 (b) reduce iodine to iodide ion
 (c) form a soluble blue complex
 (d) induce the reaction rate

25 In the reaction, $2\text{H}_2\text{O}_2 \xrightarrow{\text{I}^-} 2\text{H}_2\text{O} + \text{O}_2$, the rate of reaction

- (a) decreases as concentration of I^- ion increases
 (b) increases as concentration of I^- ion increases
 (c) increases in the presence of UV light
 (d) Both (b) and (c)

Direction (Q. Nos. 26-28) *In the following questions, Assertion (A) followed by Reason (R) is given. Choose the correct answer out of the following choices.*

- (a) Assertion and Reason both are correct statements and Reason is the correct explanation of the Assertion
- (b) Assertion and Reason both are correct statements but Reason is not the correct explanation of the Assertion
- (c) Assertion is correct incorrect and Reason is incorrect
- (d) Both Assertion and Reason are incorrect

26 Assertion (A) NO_2^- is decomposed by urea in the mixture of NO_3^- and NO_2^- .

Reason (R) NO_3^- interfere in the ring test of NO_2^- .

27 Assertion (A) Borax bead test is not suitable for Al (III).

Reason (R) Borax bead test is given by cell inorganic salts.

28 Assertion (R) Addition of $(\text{NH}_4)_2\text{CO}_3$ to an aqueous solution of BaCl_2 in the presence of NH_4Cl and NH_4OH precipitates BaCO_3 .

Reason (R) $\text{Ba}(\text{OH})_2$ is soluble in water.

DAY PRACTICE SESSION 2

PROGRESSIVE QUESTIONS EXERCISE

- A metal X on heating strongly in the presence of O_2 gives an oxide which is also constituent of a white paint. Metal X on treatment with dil. H_2SO_4 evolves the lightest gas Y and the resultant solution on crystallisation gives Z . The metal is also used as a protective coating on iron. The metal is
 - (a) Al
 - (b) Cu
 - (c) Zn
 - (d) Pb
- A mixed oxide of iron and chromium, $\text{FeO} \cdot \text{Cr}_2\text{O}_3$ is fused with sodium carbonate in the presence of air to form a yellow compound A . On acidification, the compound A forms an orange compound B which is strong oxidising agent. Identify A and B .
 - (a) $\text{K}_2\text{Cr}_2\text{O}_7$, K_2CrO_4
 - (b) Na_2CrO_4 , $\text{Na}_2\text{Cr}_2\text{O}_7$
 - (c) K_2CrO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$
 - (d) $\text{Na}_2\text{Cr}_2\text{O}_7$, Na_2CrO_4
- A translucent white waxy solid A on heating in an inert atmosphere is converted to its allotropic form B . Allotrope A on reaction with very dilute aqueous KOH liberates a highly poisonous gas C having rotten fish smell. With excess of chlorine form D which hydrolysis to compound E . Identify compound A .
 - (a) White phosphorus
 - (b) Red phosphours
 - (c) Phosphine
 - (d) Phosphorus pentachloride
- When conc. H_2SO_4 was added to an unknown salt present in a test tube, a brown gas A was evolved. The gas intensified when copper turnings were also added into this test tube. On cooling the gas A changed into colourless B . Identify gases A and B .
 - (a) NO_2 , N_2O_4
 - (b) N_2O_4 , NO_2
 - (c) N_2O , NO_2
 - (d) NO , NO_2
- A blackish brown solid A when fused with alkali metal hydroxide in the presence of air, produces a dark green coloured compound B which on electrolytic oxidation in alkaline medium gives a dark purple coloured compound C . Identify A and C .
 - (a) MnO_2 , KMnO_4
 - (b) K_2MnO_4 , KMnO_4
 - (c) KMnO_4 , MnO_2
 - (d) KMnO_4 , K_2MnO_4
- In third group of qualitative analysis, the precipitate employed is a mixture of NH_4Cl and NH_4OH . If NH_4Cl is not available in the laboratory and the mixture does not contain Mn^{2+} , we can use
 - (a) $(\text{NH}_4)_2\text{SO}_4$
 - (b) $(\text{NH}_4)_2\text{CO}_3$
 - (c) NH_4NO_3
 - (d) All of these
- A metal X on heating in nitrogen gas gives $Y \cdot Y$ on treatment with H_2O gives a colourless gas which when passed through CuSO_4 solution gives a blue colour. Y is
 - (a) $\text{Mg}(\text{NO}_3)_2$
 - (b) Mg_3N_2
 - (c) NH_3
 - (d) MgO
- Consider the following statements.
 - (I) A black colour compound B is formed on passing H_2S through the solution of a compound A in NH_4OH
 - (II) B on treatment with HCl and KClO_3 gives A .
 - (III) A on treatment with KCN given a buff coloured precipitate which dissolves in excess of this reagent forming a compound C .
 - (IV) The compound C is changed into compound D when its aqueous solution is boiled.
 - (V) The solution of A was treated with excess of NaHCO_3 and Br_2 water. On cooling and shaking for sometime a green colour of compound E is formed. No change is observed on heating.

The compound E is

 - (a) $\text{Na}_4[\text{Fe}(\text{CN})_5\text{NOS}]$
 - (b) $\text{Na}_3[\text{Co}(\text{CO}_3)_3]$
 - (c) $[\text{Cu}(\text{NH}_3)_4](\text{NO}_3)_2$
 - (d) $\text{Fe}_3[\text{Fe}(\text{CN})_6]_2$

- 9 A gaseous mixture containing X, Y and Z gases, when passed into acidified $K_2Cr_2O_7$ solution, gas X was absorbed and the solution was turned green. The remainder gas mixture was then pass through lime water, which turns milky by absorbed gas Y. The residual gas when passed through alkaline pyrogallol solution, it turned black. The gases X, Y and Z are respectively
- (a) SO_2 , CO_2 , O_2 (b) O_2 , CO_2 , SO_2
 (c) SO_2 , O_2 , CO_2 (d) CO_2 , SO_2 , O_2

- 10 A reddish brown metal X when heated in presence of oxygen forms a black compound Y which is basic in nature when heated with hydrogen gas gives back X. Identify X and Y.
- (a) Zn, ZnO
 (b) Cu, CuO
 (c) Fe, FeO
 (d) Pb, PbO

ANSWERS

SESSION 1

- | | | | | | | | | | |
|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| 1 (c) | 2 (c) | 3 (b) | 4 (c) | 5 (c) | 6 (b) | 7 (d) | 8 (d) | 9 (b) | 10 (b) |
| 11 (b) | 12 (a) | 13 (b) | 14 (c) | 15 (b) | 16 (c) | 17 (b) | 18 (b) | 19 (a) | 20 (a) |
| 21 (a) | 22 (b) | 23 (d) | 24 (b) | 25 (d) | 26 (c) | 27 (d) | 28 (b) | | |

SESSION 2

- | | | | | | | | | | |
|-------|-------|-------|-------|-------|-------|-------|-------|-------|--------|
| 1 (c) | 2 (b) | 3 (a) | 4 (a) | 5 (a) | 6 (c) | 7 (b) | 8 (b) | 9 (a) | 10 (b) |
|-------|-------|-------|-------|-------|-------|-------|-------|-------|--------|

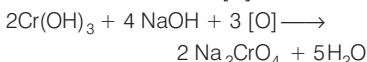
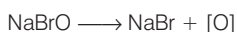
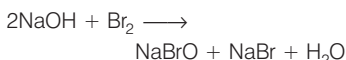
Hints and Explanations

SESSION 1

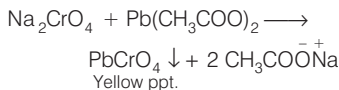
- 1 SO_3^{2-} gives SO_2 with dil. H_2SO_4 which gives turbidity with $Ba(OH)_2$ and turns acidified dichromate solution green due to its reduction to Cr^{3+} ions.
- 2 The brown ring test for nitrates and nitrites is due to the formation of $[Fe(H_2O)_5NO]^{2+}$ complex ion.
- 3 Starch iodide solution contains iodide which is oxidised by NO_2^- to I_2 which gives blue colour with starch.
- 4 Borax on strong heating, first loses its water of crystallisation and then shrinks to form a transparent glassy bead of sodium metaborate and boric anhydride.
- $$Na_2B_4O_7 \xrightarrow{\text{Borax}} 2NaBO_2 + B_2O_3 \xrightarrow{\text{Sodium meta Boric anhydride}} \text{transparent glassy bead}$$
- 5 $CoO + B_2O_3 \xrightarrow{\text{Blue bead}} Co(BO_2)_2$
- 6 $Hg^{2+} + 2I^- \longrightarrow HgI_2$
 $HgI_2 + 2I^- \xrightarrow{\text{Excess}} [HgI_4]^{2-}$
 $Hg^{2+} + Co(SCN)_2 \longrightarrow Hg(SCN)_2 \downarrow$
 Blue crystalline ppt
- 7 If Fe^{3+} and Cr^{3+} both are present, then very first solid ammonium

chloride and ammonium hydroxide is added slowly till the solution gives smell of ammonia. Fe^{3+} and Cr^{3+} precipitates in the hydroxide form.

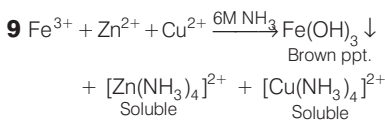
For identification, precipitate is treated with NaOH and Br_2 water, yellow colouration confirms Cr^{3+} ion.



Solution is acidified and treated with lead acetate solution.

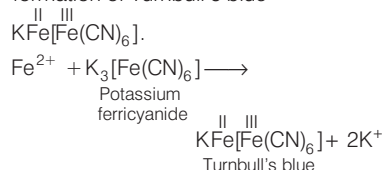


- 8 Both Zn^{2+} and Ni^{2+} belong to group IV of qualitative inorganic analysis and will not get precipitated by H_2S .

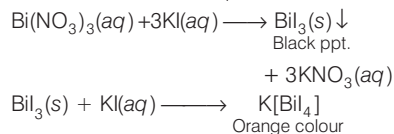


- 10 The blue precipitate of Fe^{2+} ions with potassium ferricyanide is due to the

formation of Turnbull's blue



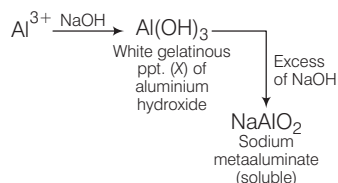
- 11 Bismuth nitrate, $Bi(NO_3)_3$ (having cation Bi^{3+}), reacts with KI to give a black precipitate of BiI_3 which on addition of excess of KI, dissolved to give orange colour solution of $K[BiI_4]$ complex salt.



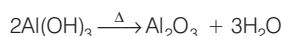
- 12 In fifth group, $(NH_4)_2CO_3$ is used in the presence of NH_4Cl . In presence of NH_4Cl , dissociation of $(NH_4)_2CO_3$ decreases and due to low concentration of CO_3^{2-} ions only V group radical are precipitated out. If Na_2CO_3 is used, concentration of CO_3^{2-} ions will increase and Mg^{2+} ions will also be precipitated.

- 13 A \longrightarrow 4; B \longrightarrow 3; C \longrightarrow 1; D \longrightarrow 2

- 14** Among the given metals, Al forms white gelatinous ppt. with NaOH. Hence, the probable metal can be Al. This ppt. is dissolved in excess of NaOH due to the formation of sodium metal aluminate. Both the reactions are shown below.



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



Thus, metal *M* is Al.

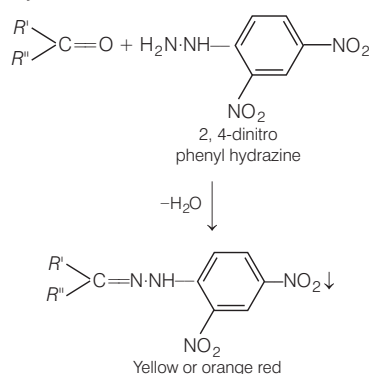
Ca, being below sodium in electrochemical reactivity series, cannot displace Na from its aqueous solution.

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

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

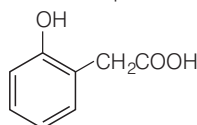
- 15** Fe^{3+} gives blood red colour with KCNS.

- 16** The reagent 2, 4-dinitro phenyl hydrazine is used for the detection of carbonyl group, i.e. aldehyde and ketone groups. With carbonyl group, this reagent gives red or yellow ppt due to the formation of respective hydrazones.



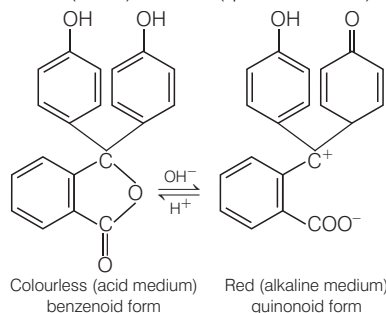
- 17** The compound liberates CO_2 with NaHCO_3 , so it contains $-\text{COOH}$ group and it also gives colour with neutral FeCl_3 solution, so it also contains a $-\text{OH}$ group directly attached to the

benzene ring (i.e. phenol). Hence, the structure of the compound is



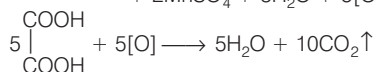
- 18** Hydroxylamine hydrochloride is not expected to show Lassaigne's test for nitrogen. This is because Lassaigne's test is positive for nitrogen only when the compound contains carbon alongwith nitrogen.
- 19** NH_2-NH_2 will not give Lassaigne's test for nitrogen due to absence carbon alongwith nitrogen.

- 20** Phenolphthalein is colourless in acid solution (benzenoid form) and pink in alkali (basic) solution (quinonoid form).

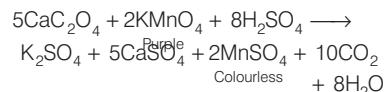


- 21** If nitrogen is present in organic compound, then sodium extract contains NaCN.
- $$\text{Na} + \text{C} + \text{N} \xrightarrow{\text{Fuse}} \text{NaCN}$$
- $$\text{FeSO}_4 + 6\text{NaCN} \longrightarrow \text{Na}_4[\text{Fe(CN)}_6] + \text{Na}_2\text{SO}_4$$
- A changes to Prussian blue $\text{Fe}_4[\text{Fe(CN)}_6]_3$ on reaction with FeCl_3 .
- $$4\text{FeCl}_3 + 3\text{Na}_4[\text{Fe(CN)}_6] \longrightarrow \text{Fe}_4[\text{Fe(CN)}_6]_3 + 12\text{NaCl}$$

- 22** In the titration of oxalic acid vs KMnO_4 , KMnO_4 acts as an oxidant as well as a self-indicator.
- $$2\text{KMnO}_4 + 3\text{H}_2\text{SO}_4 \longrightarrow \text{K}_2\text{SO}_4 + 2\text{MnSO}_4 + 3\text{H}_2\text{O} + 5[\text{O}]$$

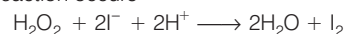


- 23** The reaction takes place as follows
- $$\text{Na}_2\text{C}_2\text{O}_4 + \text{H}_2\text{SO}_4 \longrightarrow \text{Na}_2\text{SO}_4 + \text{H}_2\text{O} + \text{CO} \uparrow + \text{CO}_2 \uparrow$$
- (X) (conc.) Effervescence
- $$\text{Na}_2\text{C}_2\text{O}_4 + \text{CaCl}_2 \longrightarrow \text{CaC}_2\text{O}_4 + 2\text{NaCl}$$
- (X) White ppt.

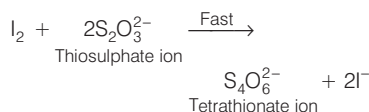


Hence, X is $\text{Na}_2\text{C}_2\text{O}_4$.

- 24** In the given experiment following reaction occurs



Iodine liberated in this reaction, reacts with sodium thiosulphate solution and is reduced to iodide ions.



- 25** The rate of the dissociation of hydrogen peroxide with I^- ion increases by increasing the concentration of I^- ion and also in presence of UV light.
- 26** Ring test is given by NO_3^- ion. While NO_2^- ion gives thiourea test and sulphanilic acid test.
- 27** Borax bead test is given by only coloured salts.
- 28** Barium comes under group V in cation analysis. Addition of $(\text{NH}_4)_2\text{CO}_3$ to an aqueous solution of BaCl_2 in the presence of NH_4Cl and NH_4OH precipitates BaCO_3 .

SESSION 2

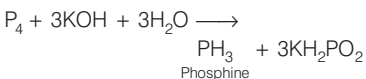
- 1** $\text{Zn} + \frac{1}{2}\text{O}_2 \longrightarrow \text{ZnO}$
- 'X' Zinc oxide (Y)
- $$\text{ZnO} + \text{H}_2\text{SO}_4 \longrightarrow \text{ZnSO}_4 + \text{H}_2\text{O}$$
- Zinc oxide is used as a constituent in white paint and it evolves H_2 gas on reacting with dilute H_2SO_4 .
- Zinc is widely used in galvanisation processes to protect steel and iron from rusting. This involves coating the surface of a metal with a thin layer of zinc to create corrosion resistant barrier.
- 2** $4\text{FeO} \cdot \text{Cr}_2\text{O}_3 + 8\text{Na}_2\text{CO}_3 + 7\text{O}_2 \longrightarrow 8\text{Na}_2\text{CrO}_4 + 2\text{Fe}_2\text{O}_3 + 8\text{CO}_2$
- (A) Sodium chromate (Yellow compound)
- $$2\text{Na}_2\text{CrO}_4 + \text{H}_2\text{SO}_4 \longrightarrow \text{Na}_2\text{Cr}_2\text{O}_7 + \text{Na}_2\text{SO}_4 + \text{H}_2\text{O}$$
- (A) (B) Orange

The compound (B) is strong oxidising agent.

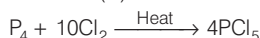
- 3** The white waxy solid (A) is white phosphorus. When white phosphorus is heated in an inert atmosphere at 573 K, it changes to red phosphorus.

(B) is red phosphorus.

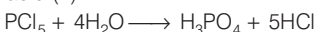
(A) on heating with KOH liberates phosphine (C) which is poisonous gas with rotten fish smell.



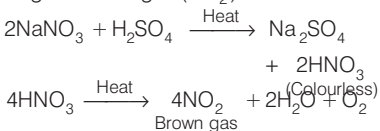
White phosphorus (P_4) burns with excess of Cl_2 to form phosphorus pentachloride (D).



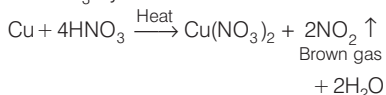
Hydrolysis of (D) gives phosphoric acid (E).



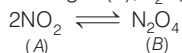
- 4** The given salt is a nitrate salt which on reaction with conc. H_2SO_4 gives first vapours of HNO_3 which decomposes to give brown gas (NO_2).



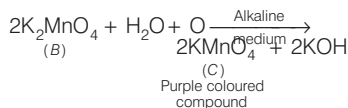
The gas intensified when copper turnings were added due to reduction of HNO_3 by Cu



On cooling the gas (A) changes into a colourless gas (B), N_2O_4 .



- 5** $2\text{MnO}_2 + 4\text{KOH} + \text{O}_2 \xrightarrow{\text{Fuse}}$
- (A)
Blackish brown compound
- $$2\text{K}_2\text{MnO}_4 + 2\text{H}_2\text{O}$$
- (B)
Potassium manganate
(Green coloured)



- 6** $(\text{NH}_4)_2\text{SO}_4$ will give white ppt. in presence of Ba^{2+} , Sr^{2+} , $(\text{NH}_4)_2\text{CO}_3$ will give white ppt. in presence of Ba^{2+} , Sr^{2+} and Ca^{2+} . To produce common ion (NH_4^+) and to suppress the ionisation of NH_4OH , NH_4NO_3 can be used in absence of Mn^{2+} .

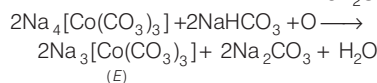
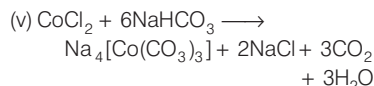
- 7** Y is Mg_3N_2 .

Magnesium react with nitrogen to form magnesium nitride. Magnesium nitride reacts with water to form ammonia and magnesium hydroxide. When ammonia gas is passed through CuSO_4 solution, it forms a blue precipitate.

- 8** The formation of black coloured compound (B) by passing H_2S through the alkaline solution of the compound indicate that (A) is a salt of the IV group radicals (Co^{2+} , Ni^{2+} or Zn^{2+}).

However, the given reactions especially reaction (iii) indicates that compound (A) is a cobalt salt (CoCl_2) which explains all the given reactions.

- (i) $\text{CoCl}_2 + 2\text{NH}_4\text{OH} + \text{H}_2\text{S} \longrightarrow$
- (A) $\text{CoS} + 2\text{NH}_4\text{Cl} + 2\text{H}_2\text{O}$
- (B)
- (ii) $\text{CoS} + 2\text{HCl} + \text{O} \xrightarrow{\text{(B)}}$
- (From KClO_3) $\text{CoCl}_2 + \text{H}_2\text{O} + \text{S}$
- $2\text{KClO}_3 \longrightarrow 2\text{KCl} + 3\text{O}_2$
- (iii) $\text{CoCl}_2 + 2\text{KCN} \longrightarrow$
- $\text{Co}(\text{CN})_2 \downarrow + 2\text{KCl}$
- Buff coloured
- $\text{Co}(\text{CN})_2 + 4\text{KCN} \longrightarrow \text{K}_4[\text{Co}(\text{CN})_6]$
- (iv) $2\text{K}_4[\text{Co}(\text{CN})_6] + \text{O} + \text{H}_2\text{O} \xrightarrow{\text{(C)}}$
- $2\text{K}_3[\text{Co}(\text{CN})_6] + 2\text{KOH}$
- (D)



- 9** (i) Gas (X) is absorbed in acidified $\text{K}_2\text{Cr}_2\text{O}_7$ and the solution turns green, so (X) is CO_2 .
- (ii) Gas (Y) is absorbed in lime water turning it white, so Y is CO_2 .
- (iii) Gas (Z) is absorbed in pyrogallol, so (Z) is O_2 .

Reactions

- (i) $3\text{SO}_2 + \text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4 \longrightarrow$
- (X) $\text{H}_2\text{SO}_4 + \text{Cr}_2(\text{SO}_4)_2 + \text{H}_2\text{O}$
- Green
- (ii) $\text{Ca}(\text{OH})_2 + \text{CO}_2 \longrightarrow$
- (Y) $\text{CaCO}_3 \downarrow + \text{H}_2\text{O}$
- White
- (iii) $\text{O}_2 + \text{Pyrogallol} \longrightarrow \text{Absorbed.}$
- (Z)

- 10** The metal X is copper. Copper on being heated in the presence of oxygen forms copper oxide which is basic in nature and black in colour. The chemical for the above reaction is as follows



If hydrogen gas is passed over this black coating that is CuO , the black coating turns brown as the reverse reaction takes place and copper is obtained black.

The chemical equation for this reaction is as follows



Thus, substance X is copper (Cu) and Y is copper oxide (CuO).