

Experimental Chemistry

QUALITATIVE ORGANIC ANALYSIS

Experiment 1

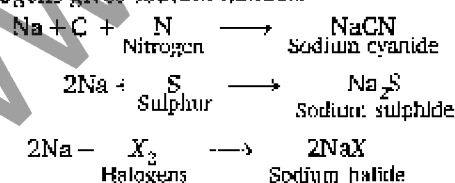
Detection of Elements

Object

To detect the elements (N, S and X) present in organic compound by Lassaigne's test.

Principle

As organic compounds are covalent compounds, so they do not ionise. For testing ions, the elements present in organic compounds have to be converted into ionic compounds. For this, the organic compound is heated with sodium, so that the element present in organic compound is converted into sodium compound i.e., ionic compound eg. with Na, nitrogen forms sodium cyanide, sulphur forms sodium sulphide and halogens gives sodium halides.



Procedure

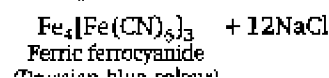
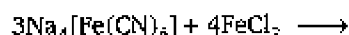
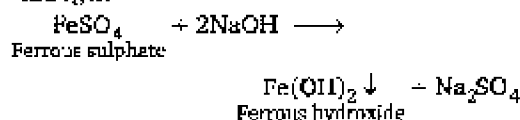
A small piece of freshly cut sodium is dried between folds of a filter paper. It is taken in a clean ignition tube and then covered with the organic substance. The tube is gently heated in the flame

filtrate which should be clear, colourless and transparent, is known as Sodium Extract (Lassaigne's extract) if filtrate is not clear, colourless and transparent, then repeat the process by using a large piece of sodium.

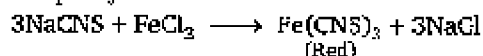
Sodium extract so obtained is used for the detection of elements (N, S and X) by following methods.

Detection of Nitrogen

- (i) Treat 1 mL of sodium extract with 1 or 2 drops of freshly prepared saturated solution of FeSO_4 followed by 2 drops of NaOH . Boil the contents for 1–2 minutes. Cool it and add dil H_2SO_4 drop by drop with shaking till a clear solution is obtained. Then, add 2 drops of FeCl_3 . (If hydrochloric acid is used in place of sulphuric acid, then addition of ferric chloride is not required). Formation of a prussian blue colour or greenish blue ppt indicates the presence of nitrogen.

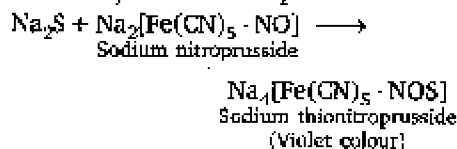


test of nitrogen a red colour is obtained instead of green or blue due to formation of ferric sulphocyanide.

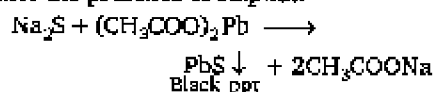


Detection of Sulphur

- (i) Add 2–3 mL of freshly prepared sodium nitroprusside (colourless) to 1 mL of sodium extract. Formation of violet or purple colour indicates the presence of sulphur.



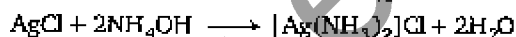
- (ii) Add acetic acid to acidified the sodium extract. Now a small quantity of lead acetate is added to this acidic solution. Formation of a black ppt indicates the presence of sulphur.



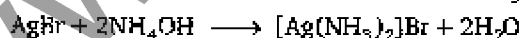
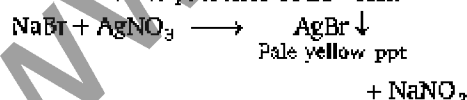
Detection of Halogens

- (i) Boil 1 mL of sodium extract with 2 or 3 drops of conc. HNO_3 , cool and then, add AgNO_3 . After adding AgNO_3 if

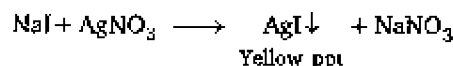
- (a) White curdy ppt is formed which is soluble in NH_4OH , then it indicates the presence of Cl^- ion.



- (b) Pale yellow ppt is obtained which is partially soluble in NH_4OH , then it indicates the presence of Br^- ion.

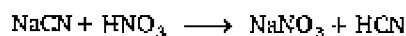


- (c) Yellow ppt is formed which is insoluble in NH_4OH , then it indicates the presence of I^- ion.

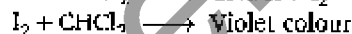
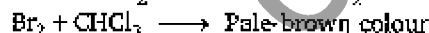
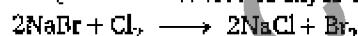


Note: During the test for halogens, sodium extract is boiled with few drops of conc. HNO_3 in order to

decompose NaCN and Na_2S , so that they may not interfere in this test.



- (ii) Acidify the sodium extract with dil HNO_3 , add 2 drops of chloroform or carbon tetrachloride and shake vigorously with chlorine water. If chloroform layer turns pale brown—Bromine is present but if turns violet, then Iodine is present (chloroform test or layer test).



Experiment 2

Object

To detect the presence of halogens by Beilstein's test.

Procedure

Take copper wire and heat its one end in a non-luminous flame till it ceases to impart green colour to the flame. Dip the hot wire in the organic compound to be tested. Again heat, formation of a green or bluish green flame identifies the presence of halogens.

Several halogen free compounds such as pyridine, purines, urea, thiourea etc also impart green colour to the flame, so the test is not very reliable. However, production of no green or blue colour confirms the absence of halogen. Therefore, the test is a confirmative one to show the absence of halogens rather than to show its presence.

Experiment 3

Detection of Functional Groups

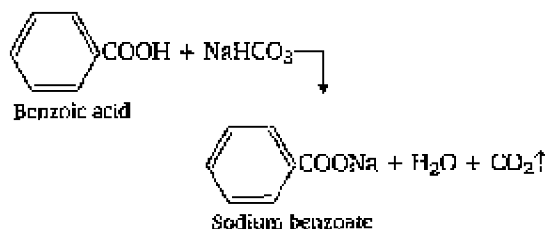
Object

To detect various functional groups present in organic compounds.

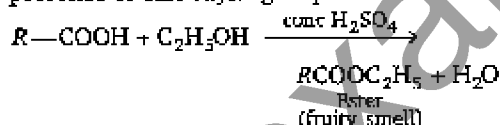
Tests for Carboxylic ($-\text{COOH}$) Group

- (i) **Litmus paper test** : Dip blue litmus paper in the aqueous solution or suspension of the compound. It turns red.
- (ii) **Sodium bicarbonate test** : In a test tube take a little quantity of the compound and then

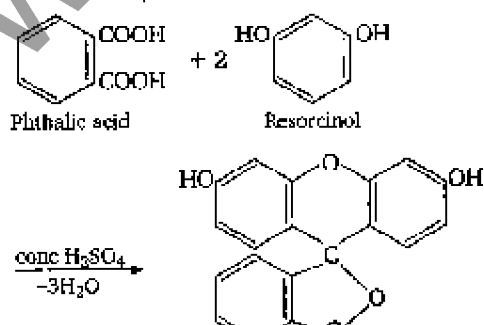
add a saturated solution of sodium bicarbonate. Formation of brisk effervescence shows the presence of $-\text{COOH}$ group.



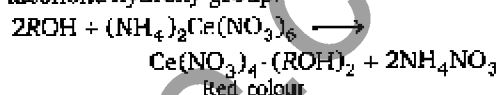
- (iii) **Ester formation** : Heat a small quantity of organic compound with ethyl alcohol and a little conc H_2SO_4 . Cool the solution and pour in a tube containing water. A fruity smell, due to formation of an ester, indicates the presence of carboxylic group.



- (iv) **Fluorescence test** : Heat gently a little amount of organic compound with resorcinol and a few drops of conc H_2SO_4 in a hard glass test tube for about two minutes. Cool and pour the contents into a beaker containing NaOH diluted largely with water. Formation of intense green orange fluorescence indicates the presence of 1,2 or ortho-dicarboxylic groups.

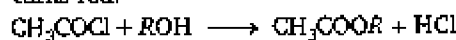


nitrate. A red colour indicates the presence of alcoholic hydroxy group.



- (ii) **Evolution of HCl and H_2** : In a dry test tube take some organic compound and add a small amount of anhyd. CaSO_4 . Filter the solution in another dry test tube and divide the filtrate into two parts.

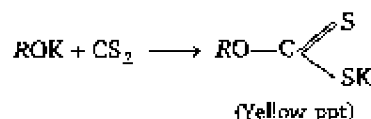
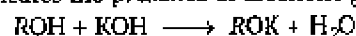
- (a) To first part, add 2 drops of acetyl chloride very carefully and expose a moist blue litmus paper at the mouth of the test tube. If the compound contains an alcohol group, then the litmus paper turns red.



- (b) To second part, add a small piece of dry sodium. Effervescence indicates the presence of alcoholic group.



- (iii) **Xanthate test** : To 1 mL of the conc aqueous solution of organic compound add pelletes of KOH . Heat and cool. Then, add 1 mL of ether followed by the addition of 2-3 drops of carbon disulphide. Formation of a yellow ppt indicates the presence of alcoholic group.



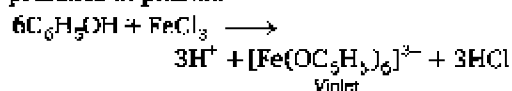
Filter the above solution and to 1 mL of the filtrate add 0.5 mL of ammonium molybdate solution and excess of dil HCl . Production of a red or blue colour confirms the presence of alcoholic group.

- (iv) **Lucas test** : This test is used to distinguish between primary, secondary and tertiary

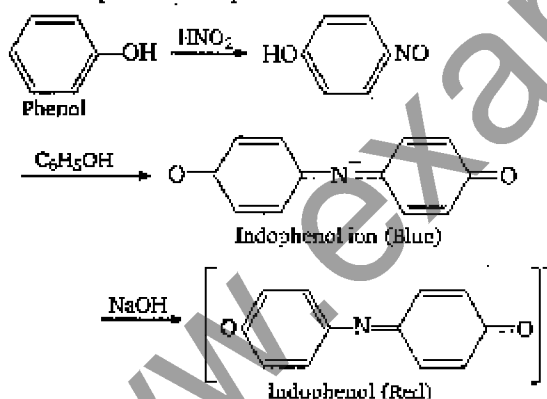
- (b) Formation of turbidity after 4-5 min shows the presence of **secondary alcohols**.
- (c) If solution remains clear, then **primary alcohol** is present.

Tests for Phenolic (Ph—OH) Group

- (i) **Ferric chloride test** : To aqueous or alcoholic solution of compound, add few drops of ferric chloride (FeCl_3). Formation of green, blue or violet colour shows the presence of phenol.

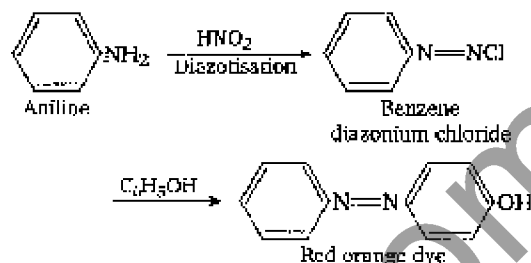


- (ii) **Liebermann's nitroso reaction** : Fuse a little amount of compound with a crystal of NaNO_2 in a test tube. Cool the mixture and add 1 mL conc H_2SO_4 . A deep green to blue solution is formed which turns red when poured in a large excess of water. The red aqueous solution becomes again deep green or blue if made alkaline with NaOH . It shows the presence of phenol.

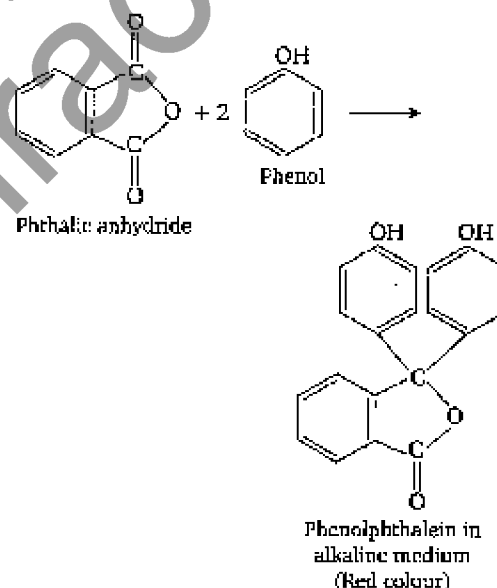


Note : ~~Phenol~~ ~~in not respond to~~ FeCl_3 test as well as ~~Liebermann's nitroso reaction~~.

- (iii) **Dye test** : Take a drop of aniline in a test tube and add 0.5 mL conc HCl solution, dilute it with water, cool in a freezing bath and add dilute NaNO_2 solution while shaking. In a second test tube take the organic compound and add excess of 2N NaOH solution. Now add the content of both the test tubes. Formation of a dye of orange or red colour indicates the presence of phenolic group.



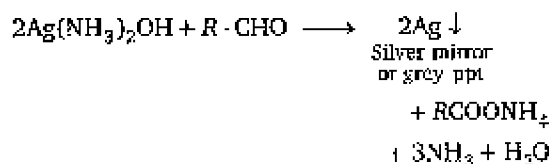
- (iv) **Phthalein test** : Heat a small amount of organic compound with double amount of phthalic anhydride and a drop of conc H_2SO_4 for one minute. Cool and make it alkaline with dil NaOH . Pour a few drops of the alkaline liquid in 20 mL of water. Formation of characteristic colour shows the presence of phenol.



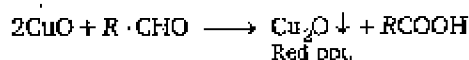
Red colour	—	Phenol, o-cresol
Blue colour	—	Catechol
Fluorescent green	—	Resorcinol
Green	—	α -naphthol
Light green	—	β -naphthol

Tests for Aldehyde (—CHO) Group

- (i) **Tollen's reagent test** : Take a little quantity of the compound in a test tube and add 2 mL of freshly prepared reagent. Shake, warm and allow the contents to stand for 2-3 minutes. Formation of silver mirror or a grey ppt indicates the presence of an aldehydic group.

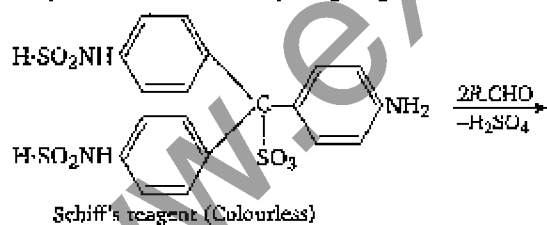


- (ii) **Fehling's solution test** : Take a mixture of equal amounts of Fehling's solution A and B, and a few drops of organic compound and boil the contents. Formation of a red ppt shows the presence of an aldehyde.

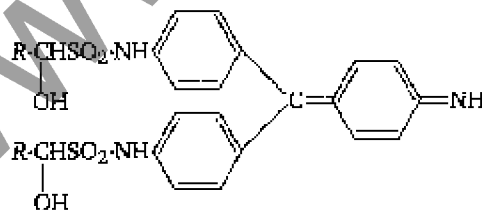


Note : Both the above test are also given by reducing sugars.

- (iii) **Schiff's reagent test** : Add 5-6 drops of organic compound to 2 mL of the reagent. Shake vigorously. After some time formation of a deep red or violet colour indicates the presence of an aldehydic group.



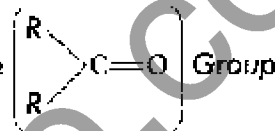
Schiff's reagent (Colourless)



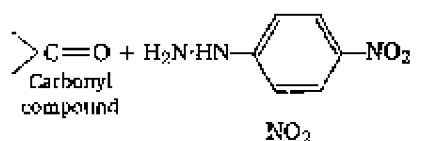
Violet colour

- (iv) **Benedict's solution test** : Boil the compound with 2-3 mL of Benedict's solution for few minutes. Appearance of a red-yellow ppt confirms the presence of aliphatic

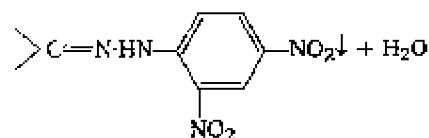
Tests for Ketone



- (i) **2,4-dinitro phenyl hydrazine test** : In a dry test tube add few drops of the organic compound (if liquid) or its alcoholic solution (if solid) to about 2 mL of the reagent and one drop of conc H_2SO_4 . Shake vigorously, heat (if necessary) and allow to stand for about 5 minutes. A yellow or orange ppt separates out in case of a compound containing carbonyl group due to formation of respective hydrazones.

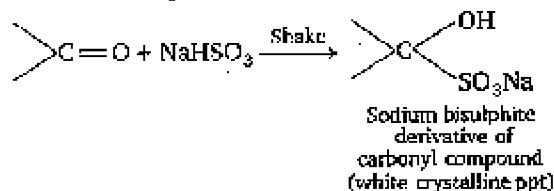


2 : 4 Dinitro phenyl hydrazine



Yellow or orange red coloured crystalline derivative of 2 : 4 dinitrophenyl hydrazine of carbonyl compound

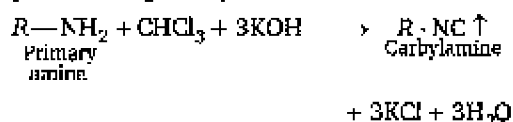
- (ii) **Sodium bisulphite test** : Add a very small quantity of organic compound to 1 mL of saturated solution of sodium bisulphite and shake vigorously. Formation of white ppt shows the presence of carbonyl group.



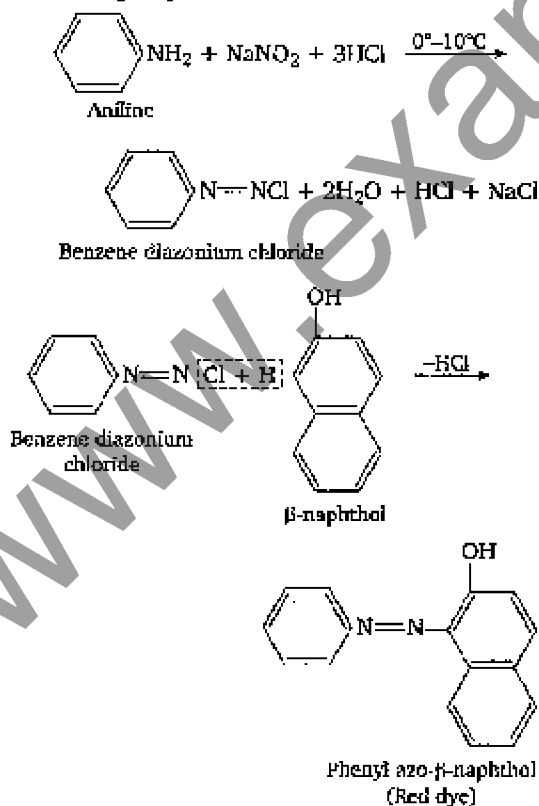
Note: The first two tests are given by aldehydes also. Therefore, no differentiation between aldehydes and ketones is should be known that ketone do not give any test with Tollens' reagent, Schiff's solution, Fehling's solution and Benedict's solution.

Tests for Primary Amine ($-\text{NH}_2$) Group

- (i) **Carbylamine test** : Boil a little quantity of the compound with 2 drops of chloroform and 2 mL of alcoholic caustic potash. An intolerable offensive odour of carbylamine indicates the presence of primary amine.



- (ii) **Dye test :** Dissolve about 0.2 g of the compound in dil HCl and cool. Now, add 10% aq NaNO_2 solution. Pour all this content into a beaker containing alkaline β -naphthol solution. Formation of a red or orange dye indicates the presence of aromatic primary amino group.



- (iii) **Rimini test :** To about 0.3 g of the compound taken in a test tube add 5 mL of water, 1 mL acetone and few drops of sodium nitroprusside. Allow to stand for 2 min. Formation of a violet red colour shows the presence of aliphatic primary amine.

Test for Secondary Amine (NH) Group

Libermann's nitroso test : To about 0.2 g of organic compound, add freshly prepared solution of nitrous acid and then add 1-2 drops each of phenol and conc H_2SO_4 . On heating a blue colouration which changes to red on dilution with water and black with aq alkali confirms the presence of secondary amine.

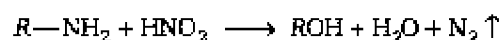
Test for Tertiary Amine (\rightarrow N) Group

Ohkuma test : Add about 5-6 drops of the citric acid-acetic anhydride reagent to the alcoholic solution of the compound, shake and heat in a boiling water bath. Development of a red or purple colour within 2-3 minutes, indicates the presence of tertiary amine.

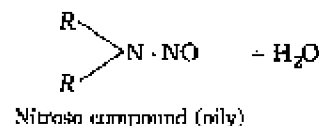
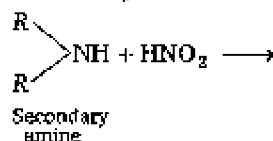
Tests to Distinguish between Primary, Secondary and Tertiary Amines

- (i) **Nitrous acid test :** Prepare a solution of nitrous acid by adding ice cold dil HCl to a solution of 1% aq NaNO_2 . Add gradually this solution to 0.2 g of the organic compound in 10 mL dil HCl.

(a) Formation of brisk effervescence shows the presence of **aliphatic primary amine**.



(b) Formation of an oily dark coloured liquid indicates the presence of **secondary amine**.



(c) No reaction indicates the presence of **aliphatic tertiary amine** while production of green or brown colour indicates the presence of **aromatic tertiary amines**.

(ii) **Hinsberg's test** : To about 0.2 g of the compound, add 1 mL of 5% NaOH and 3 mL pyridine. Shake well and add few drops of benzene sulphonyl chloride with continuous shaking.

- (a) Formation of yellow colour indicates the presence of **primary amine**.
- (b) Formation of orange colour shows the presence of **secondary amine**.
- (c) Formation of a red or purple colour shows the presence of **tertiary amines**.

PREPARATION OF SOME INORGANIC COMPOUNDS

Experiment 4

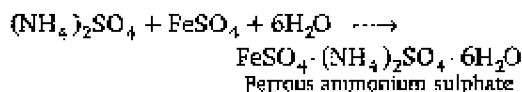
Mohr's Salt

Object

To prepare Mohr's salt or ferrous ammonium sulphate $[\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}]$.

Principle

When solutions of ferrous sulphate and ammonium sulphate are mixed together, evaporated and cooled, very light green coloured crystals of ferrous ammonium sulphate are obtained.



reason for adding dil H_2SO_4 is to prevent the hydrolysis of ferrous sulphate i.e. to prevent the conversion of ferrous sulphate into ferrous hydroxide $[\text{Fe}(\text{OH})_2]$. Now, add 13 g of ammonium sulphate solution in water to the above solution, concentrate and crystallise by cooling. Separate the crystals and dry between the folds of filter papers.

Result

Yield : 30 g

Appearance : Light green crystals.

PREPARATION OF ORGANIC COMPOUNDS

Experiment 5

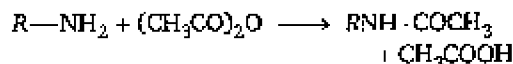
Acetanilide

Object

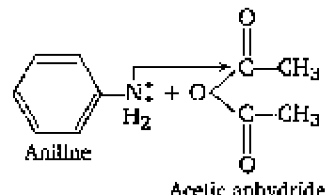
To prepare acetanilide from aniline.

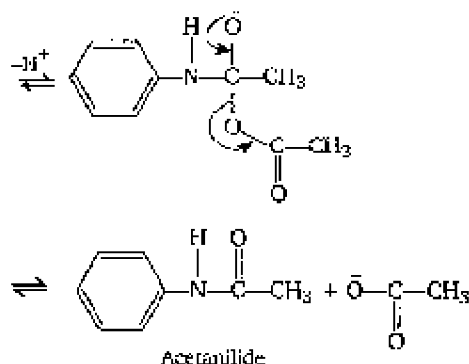
Principle

Amines containing $-\text{NH}_2$ and $>\text{NH}$ groups respectively can be directly acetylated. Their reactive hydrogen atoms get replaced by the acetyl group ($-\text{COCH}_3$) to give acetyl derivatives of the type $\text{RNH} \cdot \text{COCH}_3$ and $\text{R}_2\text{N} \cdot \text{COCH}_3$ respectively which may be regarded as mono and di-alkyl substituted acetamide.



The mechanism of this reaction is as follows:





(i) First method

Reagents

Aniline	—	5 mL
Acetic anhydride	—	5 mL
Acetic acid	—	5 mL
Zinc dust	—	0.025 g

Procedure

Take 5 mL of aniline in a 150 mL conical flask and add 10 mL of a mixture of equal volumes of 5 mL acetic anhydride and 5 mL acetic acid followed by 0.025 g zinc. Now fit a reflux water condenser and boil the contents gently for about 12–15 minutes. Now pour the hot mixture in 200 mL of ice cold water with continuous stirring. Acetanilide rapidly crystallises. Filter at the pump and wash with cold water.

Recrystallise 1 g of it from 50 mL dilute acetic acid. Filter at the pump and wash thoroughly with water and dry.

(ii) Second method

Reagents

Aniline	—	5 mL
Conc HCl	—	4.5 mL
Acetic anhydride	—	6.4 mL (6.95 g)
Sodium acetate	—	8.5 g

Procedure

In a 400 mL beaker containing 250 mL of water, take 1 mL of conc HCl and 5 mL of aniline. Stir the solution and now to it add redistilled acetic anhydride (6.4 mL) and stir again and immediately

pour it into a solution of sodium acetate (prepared by dissolving 8.5 g of crystallised CH_3COONa in 25 mL of water). Place the beaker in ice bath and stir vigorously. Colourless crystals of almost pure acetanilide separate out. Filter at pump and wash with cold water. Dry on a porous plate or filter paper in air and weigh.

On recrystallisation from about 250 mL of boiling water (containing 5 mL of methylated spirit), snow white leaflets are obtained.

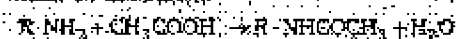
Result

- Weight of the crude acetanilide = g
- Weight of the recrystallised acetanilide = g
- Yield : 5 g
- MP : 114°C
- Appearance : Snow white leaflets

Precautions

- Zinc dust reduces the coloured impurities present in aniline and also helps to prevent oxidation of aniline during the reaction.
- A large amount of acetic anhydride and continued heating is however, avoided otherwise amounts of the diacetyl derivatives are formed.
- The solution of aniline in conc HCl should not be coloured. If it is so, then it should be heated with carbon for 5–10 minutes and filtered.

Note : Since acetic anhydride is quite costly, it is not used here. A days, instead glacial acetic acid is used which depends upon the displacement of the reversible equilibrium to the right by the removal of water on distillation.



It is always not feasible to remove water in such a way. That's why in laboratory a mixture of acetic acid and acetic anhydride is employed.

Experiment 6

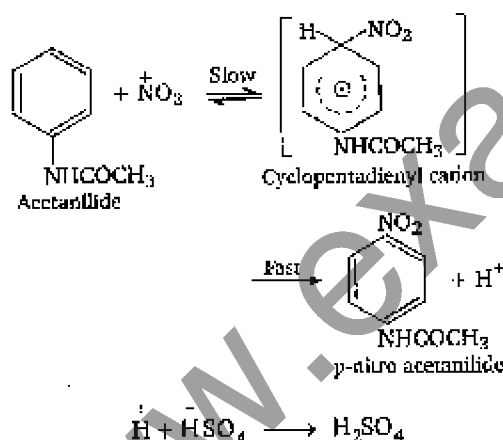
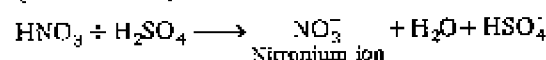
p-Nitro Acetanilide

Object

To prepare p-nitro acetanilide from

Principle

When acetanilide is treated with a mixture of conc HNO_3 and conc H_2SO_4 , it gives *p*-nitro acetanilide alongwith a little amount of *o*-isomer. In this process fuming HNO_3 in the presence of conc H_2SO_4 gives nitronium ion (NO_2^+) which attack on acetanilide to form *p*-nitro acetanilide through the cyclopentadienyl cation (intermediate) formation.



Reagents

Acetanilide	—	10 g
Gl. CH_3COOH	—	10.4 mL
Fuming HNO_3	—	4.4 mL
Conc H_2SO_4	—	20 mL
Ice		

Procedure

Dissolve 10.0 g of acetanilide in 10.4 mL of glacial acetic acid, taken in 100 mL beaker (warm

100 g of crushed ice, whereby the crude nitro acetanilide is precipitated. The product is diluted with 100 mL of cold water and allowed to stand for 10 min, *o*-nitro acetanilide (a little amount formed) goes into the solution while *p*-isomer remains insoluble. Filter it at pump, wash thoroughly with cold water and drain well. Recrystallise 1 g of it from alcohol.

Result

- (i) Weight of the crude *p*-nitroacetanilide = g
- (ii) Weight of recrystallised *p*-nitroacetanilide = g
- (iii) Yield : 8 g
- (iv) MP : 212°C
- (v) Appearance : Colourless crystals

Precautions

- (i) The temperature of the flask containing reaction mixture should be maintained below 10°C .
- (ii) To get good yield, reagents should be of pure quality.
- (iii) All the reagents are concentrated, so used very carefully.

Experiment 7

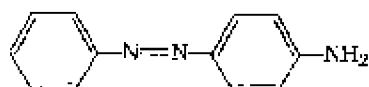
Aniline Yellow

Object

To prepare aniline yellow (*p*-amino azo benzene) from diazo amino benzene.

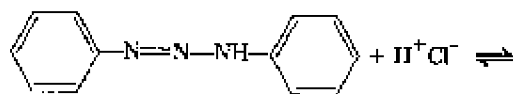
Principle

When diazo amino benzene is heated with aniline and a little amount of aniline hydrochloride at about 40°C for a short time. It gives *p*-amino azo

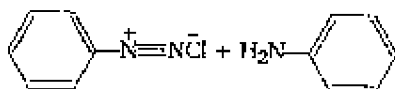


p amino azo benzene

The mechanism of the reaction is based on the equilibrium involving the diazo amino compound, phenyl diazonium chloride and aniline.



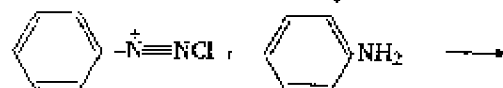
Diazo amino benzene



Phenyl diazonium chloride

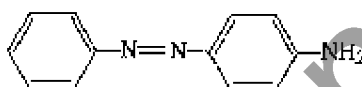
Aniline

The reaction takes place between the two latter compounds under weakly acidic conditions.



Benzene diazonium chloride

Aniline



Aniline yellow

Reagents

Diazo amino benzene	... 5 g
Aniline	... 14 mL
Aniline hydrochloride	... 2.5 g
Gl. acetic acid	... 15 mL

Procedure

In a 150 mL conical flask, dissolve 5 g of diazo amino benzene in 14 mL of aniline and to it add 2.5 g of finely powdered aniline hydrochloride, warm the contents with occasional shaking on a water bath at 40–45°C for about one hour. Now allow the mixture to stand at room temperature for next 14 min and add 15 mL of gl acetic acid which has been previously diluted with an equal volume of water (ie, 30 mL dil acetic acid). Shake the contents vigorously and allow again to stand for another 15 min. Filter the crude product at pump, wash with water and dry. Recrystallise 1 g from CCl_4 or dil alcohol.

Result

- (i) Weight of crude aniline yellow = g

- (ii) Weight of recrystallised aniline yellow = g
 (iii) Yield : 3.5 g
 (iv) M.P. : 125°C
 (v) Colour : Yellow crystals.

Precautions

- (i) After the addition of acetic acid to the reaction mixture, it should be shaken for sufficient time in order to convert excess of aniline in the form of its soluble acetate.
 (ii) To get good yield, reagent used should be of pure quality.

Experiment 8

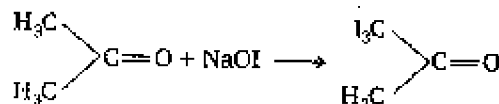
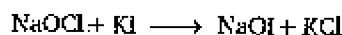
Iodoform

Object

To prepare iodoform from acetone.

Principle

Acetone when treated with potassium iodide and sodium hypochlorite (NaOCl), gives iodoform.



Reagents

Acetone	2.5 mL
KI	7.5 g
NaOCl (5%)	70–80 mL

Procedure

Take the solution of 7.5 g of potassium iodide (in 125 mL of water) in a 200 mL round bottom flask. Now add 2.5 mL acetone to it. Now stir the content and add slowly 5% NaOCl solution with frequent shaking, till the complete precipitation of iodoform (about 70–80 mL are required) occurs. Allow the contents to stand for 15 minutes and filter the product at pump, wash with cold water and recrystallise 1 g of it from alcohol.

Result

(i) Weight of crude iodoform = g

- (ii) Weight of recrystallised iodoform = g
 (iii) Yield : 4 g
 (iv) M.P. : 119°C
 (v) Colour : Yellow crystals

Precautions

To get good yield reagents should be of pure quality preferably of B.D.H.

TITRIMETRIC EXERCISES

Experiment 9

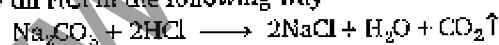
Na_2CO_3 vs HCl Titration

Object

To prepare $\frac{N}{10}$ Na_2CO_3 standard solution and find out the strength of the supplied Na_2CO_3 solution using hydrochloric acid as an intermediate solution.

Principle

The titration of Na_2CO_3 vs HCl is a neutralisation titration (acidimetry and alkalimetry) which involve the neutralisation of an acid with a base. eg. sodium carbonate is attacked by dil HCl in the following way



Indicator

Methyl orange (Dissolve 1 g of methyl orange in 1 L water).

End Point

Appearance of light pink colour.

Intermediate Solution

Intermediate solution (HCl) can be prepared by diluting concentrated hydrochloric acid one

Procedure

Rinse the burette with intermediate HCl solution and fill with it. Remove the air bubbles, if there, by opening the stopcock. Now pipette out 20 ml. of this sodium carbonate solution in a conical flask and add 2-3 drops of methyl orange indicator. Then, gradually add HCl solution from the burette into the solution of conical flask with continuous shaking till a light pink colour just appears. Light pink colour will indicate the end-point. Repeat the process till concurrent readings are obtained.

Now, wash the pipette with water and rinse it with supplied Na_2CO_3 solution. Pipette out 20 mL of this solution in a clean conical flask. Repeat the titration, using the same HCl solution in the burette, as usual.

Observations

- (i) Weight of empty weighing tube (x) = g
 (ii) Weight of weighing tube + Na_2CO_3 (y) = g
 (iii) Weight of sodium carbonate (Na_2CO_3) (z) = $y - x = \dots\dots$ g
 (iv) Volume of HCl used with 20 mL of known (prepared) Na_2CO_3 solution

	Volume of known Na_2CO_3 solution	Initial reading of burette	Final reading of burette	Volume of HCl used	Conc. of Na_2CO_3
1.	20 ml.	0 ml.			
2.	20 ml.	0 ml.			
3.	20 ml.	0 ml.			

- (v) Volume of HCl used with 20 mL of unknown (supplied) Na_2CO_3 solution.

	Volume of unknown Na_2CO_3	Initial reading of burette	Final reading of burette	Volume of HCl used	Concurrent reading
1.					
2.					
3.					

$$\begin{aligned}
 &= \dots\dots\dots \text{g} \\
 \text{Weight of Na}_2\text{CO}_3 \text{ in 100 ml, } &= \dots\dots\dots \times 4 \\
 &= \dots\dots\dots \text{g/L} \\
 \text{Normality of Na}_2\text{CO}_3 \text{ (prepared)} \\
 &= \frac{\text{strength (g/L)}}{\text{Eq. wt. of oxalic acid}} \\
 &= \frac{\dots\dots\dots}{53} \text{ N}
 \end{aligned}$$

(ii) For the titration using standard Na_2CO_3 solution

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

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

(iii) For the titration using supplied Na_2CO_3 solution

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

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

Result

The strength of supplied sodium carbonate solution is ... g/l.

Note: (i) In acidimetry and alkalimetry, the choice of indicators mainly depends upon the nature of the acids and alkalis used. Methyl orange, phenolphthalein are some of the important indicators used in these titrations.

(ii) As no indicator gives correct results in the titration of weak acids against weak bases, such titrations are to be avoided.

Experiment 10

Oxalic Acid vs KMnO_4 Titration

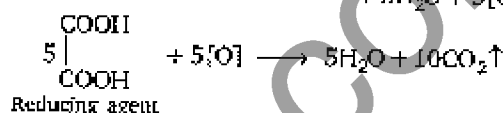
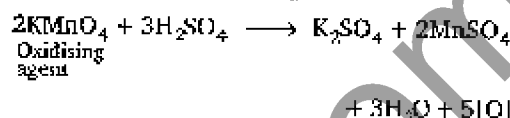
Object

To prepare $\frac{\text{N}}{30}$ oxalic acid standard solution and find out the strength of the supplied oxalic acid solution using potassium permanganate as an intermediate solution.

Principle

This is an example of Redox titrations, in which a reducing agent (as oxalic acid) is estimated by titrating it with a standard solution of oxidising agent (as KMnO_4). 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.



Indicator

The last drop of KMnO_4 itself acts as an indicator (self indicator).

End Point

Appearance of light pink colour.

Intermediate Solution

Dissolve 0.2107 g of KMnO_4 (potassium permanganate) in 200 ml, measuring flask with distilled water to prepare $\frac{\text{N}}{30}$ solution of KMnO_4 . $\frac{\text{N}}{30}$ solution of KMnO_4 is an intermediate solution.

Standard Solution

Dissolve 0.525 g of oxalic acid (AR) in a 250 ml, measuring flask with distilled water to prepare a standard solution of oxalic acid (approx. $\frac{\text{N}}{30}$)

Procedure

Rinse the burette with intermediate solution of KMnO_4 and fill the burette with it. If there is any air bubbles in burette, then remove them by opening the stopcock. Rinse the pipette with oxalic acid solution and draw out 20 ml of it in a clean conical flask. Add one full test tube of dil H_2SO_4 in it and heat the flask to $70^\circ\text{--}80^\circ\text{C}$. Gradually add KMnO_4 solution from the burette into this warm solution with continuous shaking till a light pink colour just appears. Repeat this process until concurrent readings are obtained.

Now wash the pipette with water and rinse it with supplied (unknown) oxalic acid solution. Now pipette out 20 mL of this solution in a clean conical flask. Repeat the titration, using the same KMnO_4 solution in the burette, as usual.

Observations

- Weight of empty weighing tube (x) = g
- Weight of weighing tube + oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$) (y) = g
- Weight of oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$) (z) = y - x = g
- Volume of KMnO_4 used with 20 mL of known (prepared) oxalic acid solution

S.No.	Volume of oxalic acid (known) taken	Volume of KMnO_4 solution used	Weight of oxalic acid (g)	Conc. of KMnO_4 solution
1	20 mL	0 mL
2	20 mL	0 mL
3	20 mL	0 mL

- Volume of KMnO_4 used with 20 mL of unknown (supplied) oxalic acid solution.

S.No.	Volume of oxalic acid (unknown) taken	Volume of KMnO_4 solution used	Weight of oxalic acid (g)	Conc. of KMnO_4 solution
1	20 mL	0 mL
2	20 mL	0 mL
3	20 mL	0 mL

Calculations

- Weight of oxalic acid dissolved in 250 mL measuring flask = z = g
 Weight of oxalic acid in 1000 mL

$$= \frac{z \times 1000}{250} = \dots \text{ g/L}$$
 Normality of oxalic acid (prepared)

$$= \frac{\text{Strength (g) l.}}{\text{Eq. wt. of oxalic acid}}$$

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

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

- For the titration using supplied oxalic acid solution

$$N_3 V_3 = N_4 V_4$$

Oxalic acid (unknown) KMnO_4 [$\because N_3 = N_4$]

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

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

$$= \dots\dots\dots \text{ g/L}$$

Result

The strength of supplied oxalic acid solution is g/L.

Precautions

- The oxalic acid solution with dil H_2SO_4 is heated to near about $70^\circ - 80^\circ\text{C}$.
- Sulphuric acid should be in excess otherwise a brown ppt due to formation of MnO_2 will be formed.
- This titration cannot be carried out in presence of acid like HNO_3 and HCl because HNO_3 itself is an oxidising agent, so it will interfere with the oxidising action of KMnO_4 and HCl reacts chemically with KMnO_4 solution.

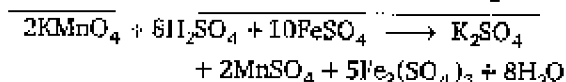
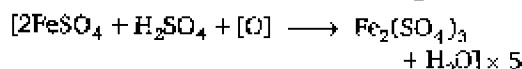
Experiment 11

$\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ (Mohr's salt) vs KMnO_4 Titration

Object

Prepare $\frac{\text{N}}{30}$ ferrous ammonium sulphate (Mohr's salt) standard solution and find out the

salt) is ferrous sulphate, which is oxidised to ferric sulphate by acidified potassium permanganate as follows.



Indicator

The last drop of KMnO_4 itself acts as an indicator (self indicator).

End Point

Appearance of light pink colour

Intermediate Solution

Dissolve 0.2107 g of KMnO_4 (potassium permanganate) in 200 mL measuring flask with distilled water to prepare $\frac{\text{N}}{30}$ solution of KMnO_4 .

$\frac{\text{N}}{30}$ solution of KMnO_4 is an intermediate solution.

Standard Solution

Dissolve 3.2666 g ferrous ammonium sulphate (Mohr's salt) (AR) in 250 mL measuring flask with distilled water to prepare a standard solution of nearly $\frac{\text{N}}{30}$ ferrous ammonium sulphate.

Procedure

Rinse the burette with intermediate solution of KMnO_4 and fill with it. If burette contains any air bubble, then remove it by opening the stopcock. Now, rinse the pipette with standard ferrous ammonium sulphate solution and draw out 20 mL of it in a clean conical flask. Add one small test tube of dil H_2SO_4 and titrate with KMnO_4 taken in burette. In the beginning KMnO_4 should be added in drops with constant shaking. At the end point when all the ferrous salt has been oxidised, the slight excess of KMnO_4 will make the solution light pink. The titration is repeated till concurrent readings are obtained.

Now wash the pipette with water and rinse it with supplied unknown ferrous ammonium sulphate solution and pipette out 20 mL of this

solution in a clean conical flask. Repeat the titration, using the same KMnO_4 solution in the burette, as usual.

Observations

- Weight of empty weighing tube (x) = ... g
- Weight of weighing tube + ferrous ammonium sulphate (y) = ... g
- Weight of ferrous ammonium sulphate (z) = y - x = ... g
- Volume of KMnO_4 used with 20 mL of known (prepared) ferrous ammonium sulphate

Sl. No.	Volume of ferrous ammonium sulphate taken in flask (mL)	Volume of KMnO_4 solution used (mL)	Weight of ferrous ammonium sulphate (g)
1	20 mL	0 mL	
2	20 mL	0 mL	
3	20 mL	0 mL	

- Volume of KMnO_4 used with 20 mL of unknown (supplied) ferrous ammonium sulphate

Sl. No.	Volume of ferrous ammonium sulphate taken in flask (mL)	Volume of KMnO_4 solution used (mL)	Weight of ferrous ammonium sulphate (g)
1	20 mL	0 mL	
2	20 mL	0 mL	
3	20 mL	0 mL	

Calculations

- Weight of ferrous ammonium sulphate dissolved in 250 mL measuring flask = z = ... 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

$$N_1 V_1 = N_2 V_2$$

Mohr's salt KMnO_4
(Known)

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

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

(iii) For the titration using supplied ferrous ammonium sulphate solution

$$N_3 V_3 = N_4 V_4$$

ferrous ammonium sulphate KMnO_4
(unknown)

$$[\because N_4 = N_2]$$

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

Strength of ferrous ammonium sulphate in g/L $= N_3 \times \text{Eq. wt. of ferrous ammonium sulphate}$
 $= \dots \text{ g/L}$

Result

The strength of supplied Mohr's salt solution is ... g/L

Precautions

- This titration is carried out at laboratory temperature.
- Sulphuric acid should be present in excess otherwise a brown ppt due to formation of MnO_2 will be formed.

QUALITATIVE INORGANIC ANALYSIS

Experiment 12

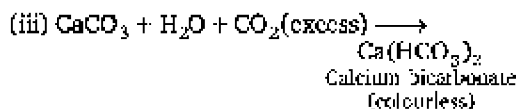
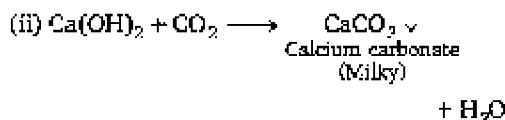
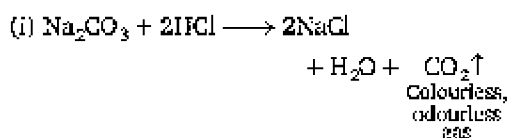
Principle

Acidic radicals or anions of first group, when treated with dil H_2SO_4 , evolve gases with characteristic colour and smell. On the basis of action of these gases, anions are identified.

Tests for the anions of group I radicals

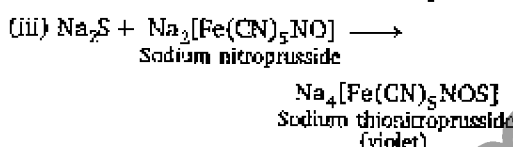
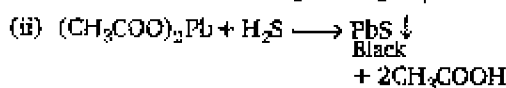
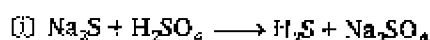
Carbonate (CO_3^{2-})	1.	Take mixture in a dry test tube and add dil. HCl or H_2SO_4 . Warm gently.	Test: effervescent with the evolution of colourless and odourless gas (CO_2).	CO_2 may be
	2.	Pass the evolved gas into lime water.	Test: water turns milky.	CO_2 confirmed.
	3.	If on long heating the gas is passed in excess.	Milkiness disappears.	CO_3^{2-} confirmed.

Reactions involved in the test of carbonate (CO_3^{2-})



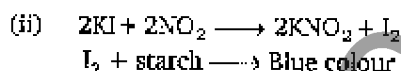
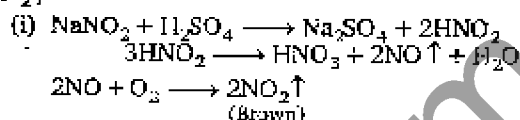
2.	Take filter paper dipped in lead acetate on the mouth of test tube	Filter paper turns black due to formation of PbS	S ²⁻ is confirmed
3.	Take a filter paper dipped in alkaline sodium nitroprusside on the mouth of test tube	The evolved gas turns the filter paper violet	S ²⁻ confirmed

Reactions involved in the test of sulphide (S²⁻)



Radical	Test	Observation	Inference
Nitrite (NO ₂ ⁻)	1. Take mixture in a dry test tube and add dil HCl. Warm gently.	Evolved gas (NO ₂) turns moist paper blue.	NO ₂ may be evolved.
	2. Take filter paper dipped in (Starch + KI) solution on the mouth of test tube.	The evolved gas turns filter paper blue.	NO ₂ confirmed.
	3. Add 2-3 drops of KI and starch solution in the test tube.	Deep blue or violet colour appears.	NO ₂ confirmed.

Reactions involved in the test of nitrite (NO₂⁻)



Experiment 13

Analysis of Second Group Anions

Object

To identify the acidic radicals or anions of group second [ie, Cl⁻, Br⁻, I⁻, NO₃⁻].

Principle

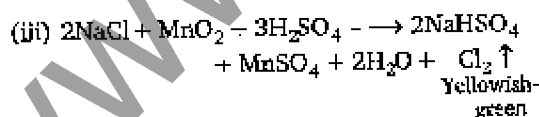
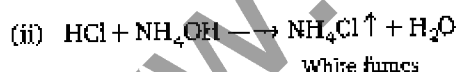
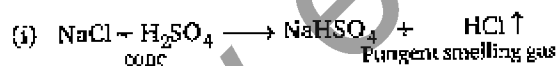
Acidic radicals or anions of second group give no response with dil acids but with conc acids, they evolve gases with characteristic colour and smell, thus can be identified by using conc acids.

Tests for the anions of group II radicals

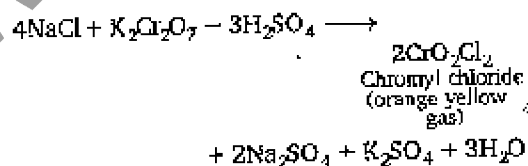
Radical	Test	Observation	Inference
Chloride (Cl ⁻)	1. Heat the mixture with 1-2 ml conc H ₂ SO ₄ in a dry test tube.	A colourless, pungent gas (HCl) is evolved.	Cl ⁻ may be confirmed.
	2. Bring a glass rod dipped in NH ₄ OH near the mouth of test tube.	White dense fumes are formed.	Cl ⁻ confirmed.
	3. Heat the mixture with conc H ₂ SO ₄ and MnO ₂ in a dry test tube.	Greenish-yellow (Cl ₂) pungent gas is evolved.	Cl ⁻ confirmed.
	4. Chromyl chloride test.		

Heat the mixture with solid $K_2Cr_2O_7$ and conc H_2SO_4 .	Orange yellow vapours of chromyl chloride (CrO_2Cl_2) are evolved.	Cl ⁻ confirmed
Now collect these vapours in a test tube containing NaOH. Acidified it with acetic acid and add lead acetate solution.	A yellow ppt of lead chromate is formed.	

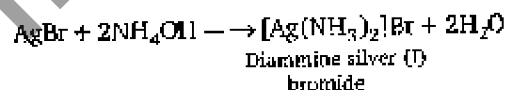
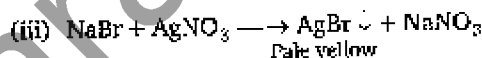
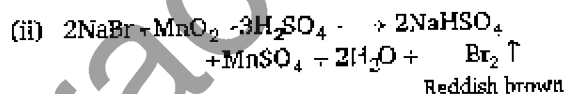
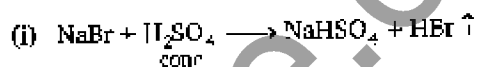
Reactions involved in the test of chloride (Cl^-)



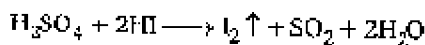
(iv) Chromyl chloride test



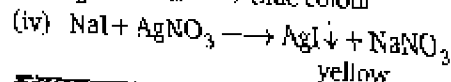
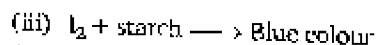
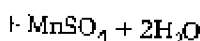
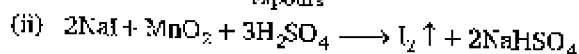
Reactions involved in the test of bromide (Br^-)



Radical or anion	S.N.	Experiment	Observation	Inference
Bromide (Br^-)	1	Heat the mixture with 1-2 ml conc H_2SO_4 in a dry test tube.	Dark violet fumes (Br_2) are evolved.	F may be
	2	Heat the mixture with MnO_2 and conc H_2SO_4 .	Violet vapours in excess are evolved.	F may be
	3	Take a paper dipped in starch solution on the mouth of test tube.	Paper turns blue.	F confirmed
	4	To the	A yellow	F confirmed



Violet
vapours

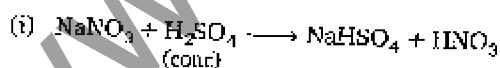


yellow

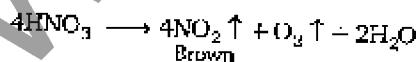
Radical	Test	Observation	Inference
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Nitrate (NO ₃)	1. Heat the mixture with 1-2 mL conc. H ₂ SO ₄ in a dry test tube.	Pungent light brown gas (NO ₂) is evolved.	NO ₃ may be
	2. Heat the mixture with copper turnings and conc. H ₂ SO ₄ .	Dark brown fumes (NO ₂) are evolved.	NO ₃ may be
	3. Ring test: To the solution add freshly prepared solution of FeSO ₄ . Shake well gradually and add conc. H ₂ SO ₄ by the sides of test tube.	A brown ring of FeSO ₄ .NO is formed at the junction of two liquids.	NO ₃ is confirmed.

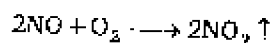
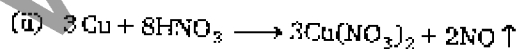
Reactions involved in the test of nitrate (NO₃)



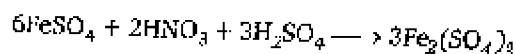
(conc)



Brown



(iii) Ring test



Ferrous nitroso
sulphate
(Brown ring)

Experiment 14

Analysis of Third Group Anions

Object

To identify the anions of group third [SO₄²⁻].

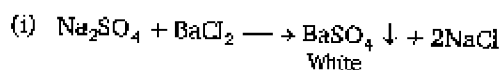
Principle

Third group radicals are identified on the basis of precipitate obtained.

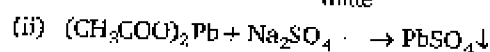
Tests for group III radicals

Radical	Test	Observation
Sulphate (SO ₄ ²⁻)	1. In the solution of mixture, add dil. HCl, then add conc. BaCl ₂ solution.	A white ppt. of BaSO ₄ is formed (insoluble in all conc. acids).
	2. In the solution of mixture, add lead acetate solution.	The white ppt. of PbSO ₄ is formed.

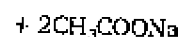
Reactions involved in the test of sulphate (SO₄²⁻)



White



white



Experiment-15

Analysis of Basic Radicals by Dry Tests

Object

To identify basic radicals or cations in a mixture by dry tests.

Flame Test

Principle : This test is based upon the fact that in a state of high ionisation of chloride some of the cations impart characteristic colour to the flame, as the cation absorbs energy from the flame and transmit the same as light of characteristic colour.

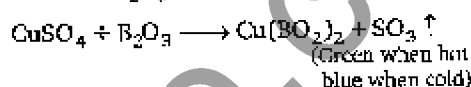
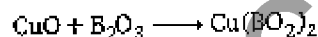
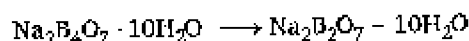
Procedure : Make a loop at the tip of platinum wire round the point of pencil and clean it by conc HCl. Now take some of the paste of substance (substance + 2-3 drops conc HCl) on it and introduce it into the edge of a non-luminous bunsen flame. Observe the colour of flame.

Observation

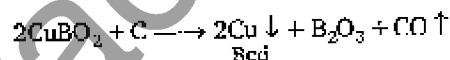
Name of Radicals	Colour when heated in flame	Colour in cool flame
Sodium (Na ⁺)	Golden yellow	Nil
Lithium (Li ⁺)	Carmine red	Nil
Potassium (K ⁺)	Violet	Pink or purple
Copper (Cu ²⁺)	Brisk green	Nil
Calcium (Ca ²⁺)	Brick red or dull red	Light green
Strontium (Sr ²⁺)	Crimson red	Crimson red
Barium (Ba ²⁺)	Apple green	Brisk green

Borax Bead Test

Principle : Borax (Na₂B₄O₇ · 10H₂O) on strong heating, first loses its water of crystallisation and then shrinks to form a transparent glassy bead of sodium metaborate (NaBO₂) and boric anhydride (B₂O₃).



(b) Reducing flame



Procedure : Make a loop at the tip of the wire, heat in the flame and dip it into borax powder. Heat it strongly when borax loses its water of crystallisation, swells up and is finally converted into a transparent glassy bead. Now this bead is touched with mixture under examination. Heat the bead strongly in non-luminous flame and then in luminous flame.

Observation

Bead colour	Oxidizing flame (Non-luminous)	Reducing flame (Luminous)
Nickel (Ni)	Light brown	Black
Gold (Au)	Pale violet	Violet
Chromium (Cr)	Green	Green
Iron (Fe)	Yellow	Brisk green
Copper (Cu)	Light blue or green	Colourless or red

Experiment 16

Analysis of Basic Radicals by Wet Tests

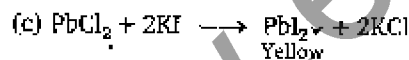
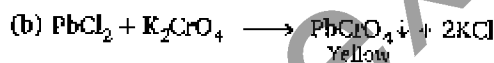
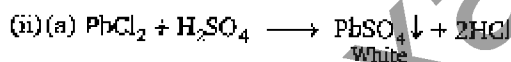
Object

To identify basic radicals or cation by wet tests.

Tests for the cations of various groups

Group	SN	Experiment	Observation	Inference
I	1	To the original solution of mixture add dil. HCl	White ppt is obtained	1st group present
	2	Filter the ppt and keep the filtrate for 11th group.		
	3	Dissolve ppt in hot water and divide into three parts		
	3(a)	Cool 1st part under tap water	White shining crystals are formed	1st group (Pb ²⁺) may be
	3(b)	In 11th part add acetic acid and K ₂ CrO ₄	Yellow ppt of PbCrO ₄ (PbCrO ₄)	1st group confirmed
	3(c)	In 11th part add KO solution	Yellow ppt of Pb ₂ O ₃ Ag ⁺	confirmed

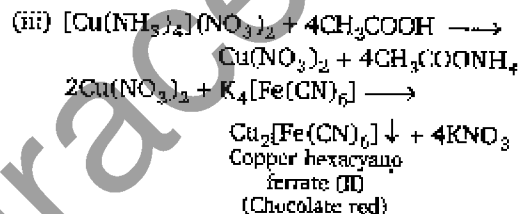
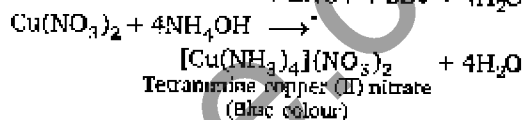
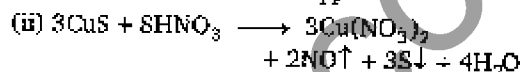
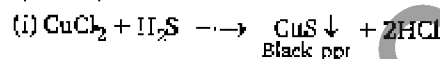
Reactions involved in the test of lead (Pb²⁺)



Group	SN	Experiment	Observation	Inference
II	1	In 1st group filtrate pass H ₂ S gas	Black ppt	2nd group present
	2	Filter the ppt and keep the filtrate for 11th group		
	3	Dissolve the ppt in 50% HNO ₃ , then boil, cool and filter. Now add NH ₄ OH solution	Blue solution	11th group (Cu ²⁺) may be

4	To the solution add acetic acid (in excess) and K ₄ [Fe(CN) ₆]	Brown colour of ppt	11th group (Cu ²⁺) confirmed
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Reactions involved in the test of copper (Cu²⁺)

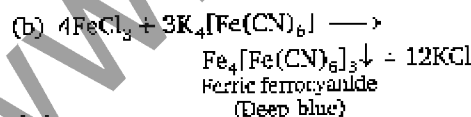
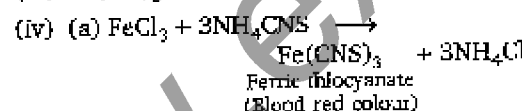
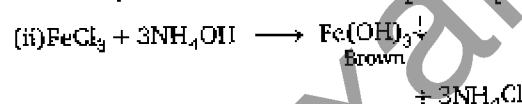
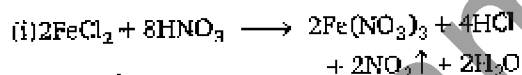


Group	SN	Experiment	Observation	Inference
III	1	In 2nd group filtrate + HNO ₃ (cool and boil) and add NH ₄ Cl and NH ₄ OH (in excess)	If brown ppt (white ppt)	3rd group (Fe ³⁺) may be
	2	Filter the ppt and keep the filtrate for 11th group		
	3	Dissolve ppt in HCl and NoCl solution and filter		
	4	Divide the ppt obtained after filtration into two parts		
	4(a)	To 1st part add dil. HNO ₃ and K ₄ [Fe(CN) ₆]	Deep blue colour	11th group (Fe ³⁺) confirmed

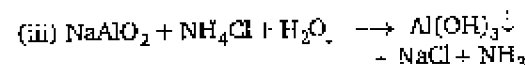
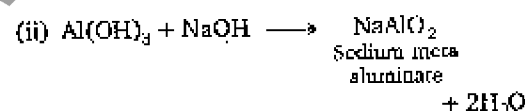
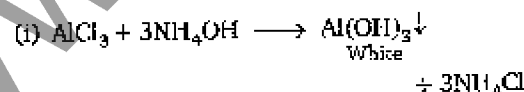
4	To second part add dil. H_2O_2 solution and potassium thiocyanide.	Blood red Fe^{3+} confirmed.
5	In the filtrate obtained in step 3 add NH_4Cl and boil.	All groups confirmed.

Reactions involved in the test of iron (Fe^{3+}) and aluminium (Al^{3+})

For iron



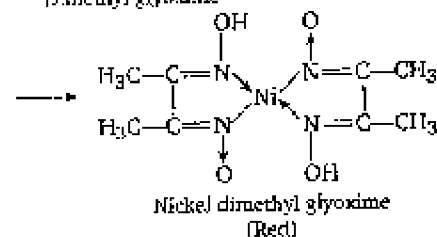
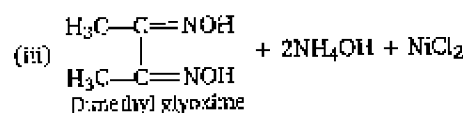
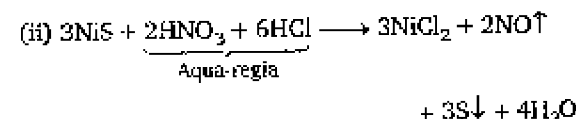
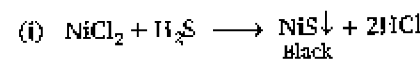
For aluminium

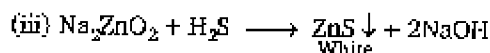


2	Filter the ppt and keep the filtrate for V group. Add dissolve ppt in dil. HCl and anne. tests.	
3	To one part add NH_4OH in excess and dimethyl glyoxime.	IV group (Ni^{2+}) confirmed.
4	To second part add H_2S ppt.	IV group (Zn^{2+}) confirmed.

Reactions involved in the test of nickel (Ni^{2+}) and zinc (Zn^{2+})

For nickel

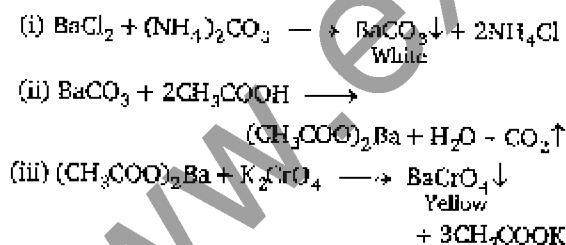




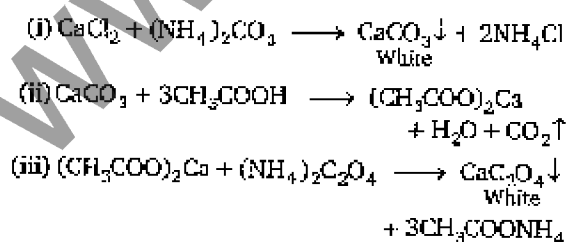
Group	Test	Observation	Inference
V	1. In IV group, filtrate add NH_4OH and $(NH_4)_2CO_3$	White ppt	V group may be
	2. Filter the ppt and wash the filtrate for VI group. Now dissolve ppt in acetic acid and boil		
	3. Divide the solution in two parts		
3(a)	For first part, yellow ppt of add $CaCO_3$, $BaCrO_4$ is obtained		V group (Pb^{2+}) confirmed
3(b)	In second white ppt of add calcium $(NH_4)_2C_2O_4$ co-precipitate solution		V group (Ca^{2+}) confirmed

Reactions involved in the test of barium (Ba^{2+}) and calcium (Ca^{2+})

For barium

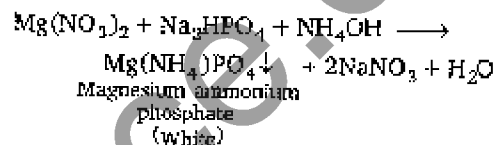


For calcium



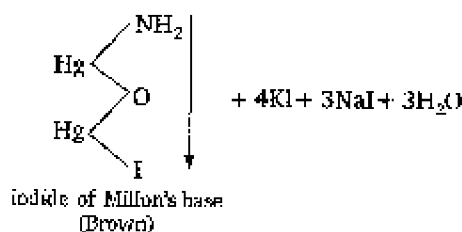
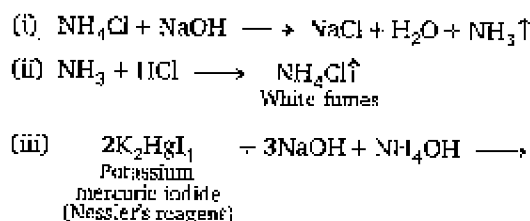
Group	Test	Observation	Inference
VI	1. In fifth group, add NH_4OH excess and disodium hydroxide phosphate (Na_2HPO_4) and shake	Crystalline ppt	W Group (Mg^{2+}) confirmed

Reactions involved in the test of magnesium (Mg^{2+})



Group	Test	Observation	Inference
7 (Zero)	1. Heat a little Smell of ammonia with ammonium $NaOH$ is dry obtained test tube		NH_4^+ may be
	2. Take a glass White lamp and dipped in conc. NH_4Cl and conc. HCl and obtained the mouth of test tube		NH_4^+ may be
	3. In the solution Brown colour of mixture add on ppt Nessler's reagent		NH_4^+ confirmed

Reactions involved in the test of ammonium ion (NH_4^+)



■ Practical Based Questions ■

- Phenolphthalein is an indicator for acid-base titration, it exists as
 - benzenoid form in acid and quinonoid form in basic solution
 - quinonoid form in acid and benzenoid form in basic solution
 - quinonoid form in both
 - benzenoid form in both
- Which statement is correct?
 - Fe^{2+} gives brown colour with ammonium thiocyanate
 - Fe^{2+} gives blue precipitate with potassium ferricyanide
 - Fe^{3+} gives brown colour with potassium ferricyanide
 - Fe^{3+} gives red colour with potassium ferrocyanide
- Four samples of acids and bases are taken for an experiment
 - 100 mL of 1 M NaOH and 100 mL of 1 M HCl
 - 100 mL of 2 M KOH and 100 mL of 1 M H_2SO_4
 - 100 mL of 1 M CH_3COOH and 100 mL of 1 M NaOH
 - 100 mL of 0.5 M KOH and 100 mL of 0.5 M HNO_3

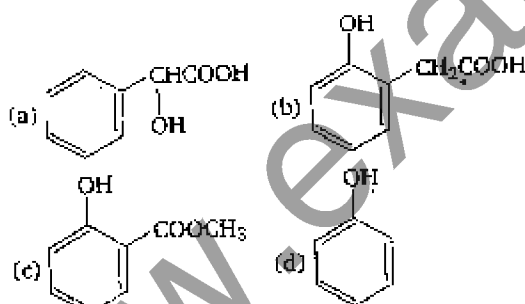
Now for each sample enthalpy of neutralisation is calculated. Now the result shows that

 - enthalpy of neutralisation calculated in each case is found same
 - in case (1) and (4), the value of enthalpy of neutralisation is same
 - in case (1), (2) and (4) the value of enthalpy calculated is same
 - the value of enthalpy calculated is different for each sample
- Which of the following will not give Lassaigne's
 - benzenoid form in acid and quinonoid form in basic solution
 - quinonoid form in acid and benzenoid form in basic solution
 - quinonoid form in both
 - benzenoid form in both
- During the preparation of acetanilide from aniline a small amount of zinc is added to the reaction mixture because
 - zinc induces the precipitation
 - zinc prevents the reduction of aniline during the reaction
 - zinc reduces the coloured impurities in the aniline and also prevents its oxidation during the reaction
 - zinc form a white crystalline complex with aniline
- An aqueous solution of colourless metal sulphate M gives a white precipitate with NH_4OH . This was soluble in excess of NH_4OH . On passing H_2S through this solution a white ppt is formed. The metal M in the salt is

(a) Ca	(b) Ba
(c) Al	(d) Zn
- In the titration of oxalic acid vs potassium permanganate, potassium permanganate acts as
 - external indicator
 - self indicator
 - reductant
 - both (b) and (c)
- In the preparation of *p*-nitro acetanilide from aniline, nitration is not done by nitrating mixture (a mixture of conc H_2SO_4 and conc HNO_3) because
 - on nitration it gives *o*-nitro acetanilide
 - it gives a mixture of *o*- and *p*-nitro aniline
 - $-\text{NH}_2$ group gets oxidised
 - it forms a mixture of *o*- and *p*-nitro acetanilide
- In the reaction of KMnO_4 with an oxalate in acidic medium, MnO_4^- is reduced to Mn^{2+} and $\text{C}_2\text{O}_4^{2-}$ is oxidised to CO_2 . Hence, 50 mL of 0.04 M KMnO_4 is equivalent to
 - 100 mL of 0.1 M $\text{H}_2\text{C}_2\text{O}_4$
 - 50 mL of 0.2 M $\text{H}_2\text{C}_2\text{O}_4$

- (c) in cold water egg albumin mix well whereas yolk get separated
(d) cold water is purest form of water
12. Which of the following compounds cannot be used in preparation of iodoform?
(a) CH_3CHO (b) CH_3COCH_3
(c) HCHO (d) 2-propanol
13. In Lassaigne's test, the organic compound is fused with a piece of sodium metal in order to
(a) increase the ionisation of the compound
(b) decrease the melting point of the compound
(c) convert the ionic compound into a mixture of covalent compounds
(d) convert the covalent compound into a mixture of ionic compounds
14. In the kinetic study of reaction of iodide ion with hydrogen peroxide, a known volume of sodium rhiosulphate 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
15. A white sodium salt dissolves readily in water to give a solution which is neutral to litmus. When silver nitrate solution is added to the solution, a white precipitate is obtained which does not dissolve in dil HNO_3 . The anion could be
(a) CO_3^{2-} (b) Cl^-
(c) SO_4^{2-} (d) S^{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) Aldehyde (d) Amines
17. Which of the following pairs has heat of neutralisation equal to 13.7 kcal?
(a) HCl , NH_4OH (b) HNO_3 , KOH
(c) NaOH , CH_3COOH (d) H_2SO_4 , NH_4OH
18. For preparing 250 mL of N/20 solution of Mohr's salt, the amount of Mohr's salt needed is
(a) 9.8 g (b) 4.9 g
(c) 19.6 g (d) 3.2 g
19. 0.5 g mixture of $\text{K}_2\text{Cr}_2\text{O}_7$ and KMnO_4 was treated with excess of KI in acidic medium. I_2 liberated required 100 cm^3 of 0.15 N $\text{Na}_2\text{S}_2\text{O}_3$ solution for titration. The percentage amount of $\text{K}_2\text{Cr}_2\text{O}_7$ in the mixture is
(a) 85.36% (b) 14.64%
(c) 58.63% (d) 26.14%
20. An unknown inorganic compound (A) gave the following reactions
(1) The compound (A) on heating gave a residue, oxygen and an oxide of nitrogen.
(2) An aqueous solution of compound (A), on addition of tap water gave a turbidity which is insoluble in nitric acid.
(3) The turbidity dissolved in NH_4OH solution.
Thus, the compound (A) is
(a) NaCl (b) AgCl
(c) NaNO_3 (d) AgNO_3
21. An organic compound gave positive iodoform and Tollen's tests. The organic compound is
(a) $\text{CH}_3\text{CH}_2\text{OH}$ (b) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$
(c) CH_3CHO (d) CH_3COCH_3
22. One desires to prepare a positively charged sol of silver iodide. This can be achieved by
(a) adding a little AgNO_3 solution to KI solution in slight excess
(b) adding a little KI solution to AgNO_3 solution in slight excess
(c) mixing equal volumes of equimolar solutions of AgNO_3 and KI
(d) None of the above
23. During the test for halogens, sodium extract is heated with conc HNO_3 . The reason for this is
(a) to decompose NaCN and Na_2S
(b) Na_2S is soluble in HNO_3
(c) NaCN is soluble in HNO_3
(d) silver halides are insoluble in HNO_3 .
24. Which of the following will oxidise 126 g of oxalic acid ($\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) in acidic medium?
(a) $1/3$ mole of $\text{K}_2\text{Cr}_2\text{O}_7$
(b) 2 mole of $\text{K}_2\text{Cr}_2\text{O}_7$
(c) $1/3$ mole of KMnO_4
(d) $5/2$ mole of KMnO_4
25. A laboratory reagent imparts green colours to the flame. On heating with solid $\text{K}_2\text{Cr}_2\text{O}_7$ and conc H_2SO_4 it evolves a orange red gas. Identify the reagent.
(a) CaCl_2 (b) BaCl_2
(c) CuCl_2 (d) None of these
26. Which reagent can be used to identify nickel ion?
(a) Resorcinol
(b) Dimethyl glyoxime
(c) Diphenyl benzidine
(d) Potassium ferrocyanide
27. The titration of Mohr's salt vs KMnO_4 is an example of redox titration. In this titration

- KMnO_4 oxidises only ferrous salt to the ferric salt (no effect on other ions) but we can not use ferrous sulphate in place of Mohr's salt because
- it is less stable than Mohr's salt
 - in air it oxidised to ferric sulphate
 - in air it loses water of crystallisation
 - All of the above
28. 3.92 g of ferrous ammonium sulphate (Mohr's salt) react completely with 50 mL $\frac{N}{10}$ KMnO_4 solution. The percentage purity of the sample is
- 50
 - 76.4
 - 80
 - 39.2
29. A compound liberates CO_2 with NaHCO_3 and also gives colour with neutral FeCl_3 solution. The compound can be



30. Positive Beilstein's test for halogens shows that
- a halogen is definitely present
 - a halogen may be present
 - a halogen is absent
 - None of the above
31. Which of the following statement is wrong about aniline yellow?
- It is carcinogenic
 - It is also called *p*-amino azobenzene
 - It is an acid dye
 - It is also called 4-phenyl azoaniline
32. Leveling bulb is used during experiment to study kinetics of the dissociation of hydrogen peroxide

- In acidic solution, dichromate ions are converted to chromate ions
 - $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ on heating undergo exothermic decomposition to give Cr_2O_3
 - Potassium dichromate is used as a titrant for estimation of Fe^{2+} ions
34. Which of the following reagents can be used to distinguish between sodium carbonate and sodium sulphite?
- Lime water
 - Baryta water
 - Acidified $\text{K}_2\text{Cr}_2\text{O}_7$ solution
 - H_2SO_4 solution
35. An aqueous solution of 6.3 g oxalic acid dihydrate is made up to 250 mL. The volume of 0.1 N NaOH required to completely neutralize 10 mL of this solution is
- 40 mL
 - 20 mL
 - 10 mL
 - 4 mL
36. In case of weak acid and strong base, the heat of neutralisation is less than 13.7 kcal because some part of heat is utilized in
- dissociation of base
 - association of base
 - dissociation of acid
 - association of acid
37. The methods used for the preparation of lyophilic and lyophobic sols are respectively
- oxidation and reduction
 - dissolution in water and peptisation
 - peptisation and oxidation
 - All of the above
38. Which of the following substances is not used in the preparation of Mohr's salt?
- Ferrous sulphate
 - Ammonium sulphate
 - Dil. sulphuric acid
 - All are used
39. The gas liberated on heating a mixture of two salts with NaOH , give a reddish brown precipitate with an alkaline solution of K_2HgI_4 . The aqueous solution of the mixture on treatment with BaCl_2

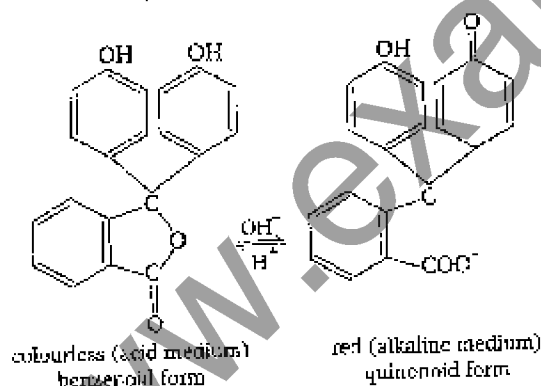
- (c) NH_4^+ , Fe^{3+} , SO_4^{2-} , Cl^-
 (d) NH_4^+ , Ca^{2+} , SO_4^{2-} , Cl^-
40. An organic compound does not reduce Tollen's reagent and Fehling's solution but gives red colour with ceric ammonium nitrate, then the organic compound is
 (a) an alcohol (b) an aldehyde
 (c) a phenol (d) a ketone
41. 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 conc of I⁻ ion increases
 (b) increases as conc of I⁻ ion increases
 (c) increases in the presence of UV light
 (d) both (b) and (c)
42. A solution of one mole of copper sulphate is prepared at infinite dilution. It is expressed as follows
 $\text{CuSO}_4(\text{s}) + (\text{aq}) \longrightarrow \text{CuSO}_4(\text{aq})$
 On adding some solvent to this solution, the enthalpy of solution
 (a) increases
 (b) decreases
 (c) remains the same
 (d) may be increased or decreased
43. If Cl_2 gas is passed into aqueous solution of KI containing some CCl_4 and the mixture is shaken, then
 (a) upper layer become violet
 (b) lower layer becomes violet
 (c) homogeneous violet layer is formed
 (d) None of the above
44. 1.5 g pyrolusite ore is treated with 50 mL of N-oxalic acid and dil H_2SO_4 . The remaining acid is transferred to 250 mL measuring flask. 25 mL of this solution requires 30 mL of $\frac{\text{N}}{10}$ KMnO_4 for titration. The percentage of MnO_2 in the sample of pyrolusite is
 (a) 58% (b) 65%
 (c) 45% (d) 35%
45. Experiment to study kinetics of the dissociation of hydrogen peroxide must be performed by group of two or three so that
 (a) when one is recording data other should be swirling flask at constant rate
 (b) experiment can be performed by one student only as outcomes are independent on rate of mixing of mixture 1 and 3
 (c) for safety purpose
 (d) None of the above
46. In III group precipitation, NH_4Cl is added before adding NH_4OH to
 (a) decrease conc of OH^-
 (b) prevent interference of PO_4^{3-}
 (c) increase conc of Cl^-
 (d) increase conc of OH^- ion
47. The enthalpy of neutralisation of a weak acid in 1 M solution with a strong base is $-56.1 \text{ kJ mol}^{-1}$. If the enthalpy of ionisation of acid is 1.5 kJ mol^{-1} and enthalpy of neutralisation of the strong acid with a strong base is -57.3 kJ eq^{-1} . What is the percentage ionisation of the weak acid in molar solution (assume the acid is monobasic)
 (a) 25 (b) 20
 (c) 15 (d) 10
48. During the preparation of acetanilide from aniline, the excess of acetic anhydride and prolonged heating should be avoided because
 (a) it is oxidised
 (b) it is reduced
 (c) diacetyl derivative is formed
 (d) triacetyl derivative is formed
49. At 298 K, the heat of solution of $\text{CuSO}_4(\text{s})$ is $-91.21 \text{ kJ mol}^{-1}$ and that of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}(\text{s})$ is $-20.18 \text{ kJ mol}^{-1}$. The heat of hydration of $\text{CuSO}_4(\text{s})$, i.e. ΔH for the reaction
 $\text{CuSO}_4(\text{s}) + 5\text{H}_2\text{O}(\text{l}) \longrightarrow \text{CuSO}_4 \cdot 5\text{H}_2\text{O}(\text{s})$
 (a) $-111.39 \text{ kJ mol}^{-1}$ (b) $-71.03 \text{ kJ mol}^{-1}$
 (c) $-105.02 \text{ kJ mol}^{-1}$ (d) $-75.05 \text{ kJ mol}^{-1}$
50. The gas liberated on treating a mixture of two salts with dil H_2SO_4 turns lime water milky and turbidity disappears with the passage of excess of gas. The aqueous solution of mixture gives white crystalline ppt with NaCl solution. The filtrate gives a black precipitate, when H_2S is passed into it. The aqueous solution of mixture on heating gives reddish brown gas and when treated with ammonium hydroxide and excess of disodium hydrogen phosphate gives a white crystalline precipitate. The mixture contains
 (a) CO_3^{2-} , Pb^{2+} , NO_3^- , Mg^{2+}
 (b) CO_3^{2-} , Pb^{2+} , NO_3^- , Ca^{2+}
 (c) CO_3^{2-} , Pb^{2+} , Cl^- , Mg^{2+}
 (d) CO_3^{2-} , Pb^{2+} , Cl^- , Ca^{2+}

ANSWERS

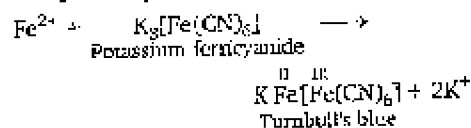
1. (a)	2. (b)	3. (c)	4. (a)	5. (b)	6. (c)	7. (d)	8. (b)	9. (c)	10. (c)
11. (b)	12. (c)	13. (d)	14. (b)	15. (b)	16. (c)	17. (b)	18. (b)	19. (b)	20. (d)
21. (c)	22. (b)	23. (a)	24. (a)	25. (b)	26. (b)	27. (d)	28. (a)	29. (b)	30. (b)
31. (c)	32. (b)	33. (b)	34. (c)	35. (a)	36. (c)	37. (b)	38. (d)	39. (c)	40. (a)
41. (d)	42. (c)	43. (b)	44. (a)	45. (a)	46. (a)	47. (c)	48. (c)	49. (c)	50. (a)

HINTS & SOLUTIONS

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



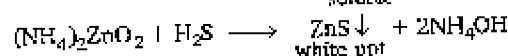
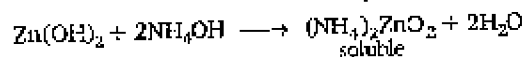
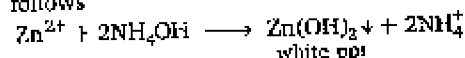
2. The blue precipitate of Fe²⁺ ions with potassium ferricyanide is due to the formation of Turnbull's blue K₃Fe[Fe(CN)₆].



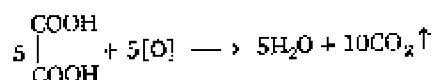
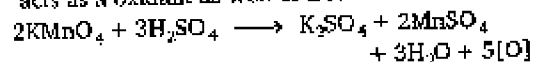
3. As in cases (1), (2) and (4), the acids and bases taken are strong and the enthalpy of neutralisation of all strong acids with strong

reaction. So, it is added to the reaction mixture during the preparation of acetanilide from aniline.

7. All the given metals form white ppt with NH₄OH but only ppt of Zn is soluble in excess of NH₄OH and on passing H₂S it gives white ppt of ZnS, so the metal is Zn and reactions takes place as follows



8. In the titration of oxalic acid vs KMnO₄, KMnO₄ acts as a oxidant as well as a self indicator.



9. The nitration of aniline is difficult to carry out with nitrating mixture, since —NH₂ group get oxidised which is not required. So, the amino group is first protected by acylation to form acetanilide which is then nitrated to give p-nitro acetanilide as a major product.

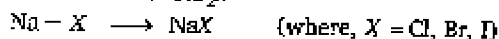
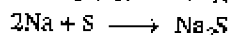
10. Equivalent mass of $\frac{\text{molar mass}}{\text{molar mass}}$

11. During the formation of egg albumin sol, hot water is not used because in hot water precipitation of egg albumin takes place whereas in cold water formation of precipitate does not occur.

12. Formaldehyde cannot produce iodoform, as only those compound which contains either $\text{CH}_3-\underset{\text{OH}}{\text{CH}}-$ group or $\text{CH}_3-\underset{\text{O}}{\text{CH}}-$ group on

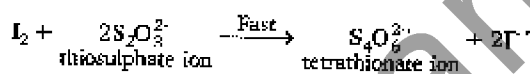
reaction with iodine and sodium hydroxide (alkali) yield iodoform.

13. In Lassaigue's test, the organic compound is fused with a piece of Na metal to convert covalent compounds into a mixture of ionic compounds such as

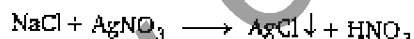


14. In the given experiment following reaction occurs
 $\text{I}_2\text{O}_2 + 2\text{I}^- + 2\text{H}^+ \longrightarrow 2\text{H}_2\text{O} + \text{I}_2$

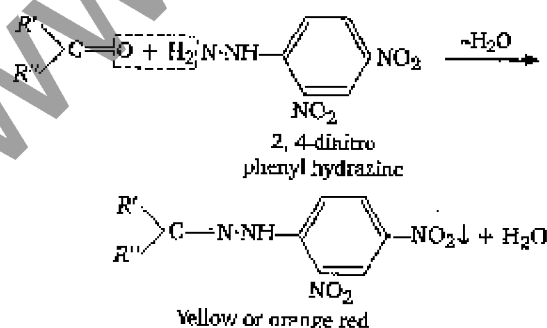
Iodine liberated in this reaction reacts with sodium thiosulphate solution and is reduced to iodide ions.



15. NaCl is a salt of strong acid and strong base, hence on dissolution will give neutral solution. As white ppt is obtained by the addition of AgNO_3 to the solution of Na salt, it can be of AgCl . Further AgCl is also insoluble in HNO_3 . Hence, the anion is Cl^- .



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. Heat of neutralisation of strong acid and strong base is always 13.7 kcal.

18. The ionic equation for oxidation of Mohr's salt is
 $\text{Fe}^{2+} \longrightarrow \text{Fe}^{3+} + e^-$

$$\text{Now, Eq. of Mohr's salt} = \frac{392}{1} = 392$$

$$\begin{aligned} \text{Strength} &= \text{Normality} \times \text{Eq. mass} \\ &= \frac{1}{20} \times 392 = 19.6 \text{ g/L} \end{aligned}$$

Thus, for preparing 250 mL of N/20 Mohr's salt solution, Mohr's salt needed

$$= \frac{19.6}{1000} \times 250 = 4.9 \text{ g}$$

19. Let the amount of the $\text{K}_2\text{Cr}_2\text{O}_7$ in the mixture be x g.

then, amount of KMnO_4 will be $(0.5 - x) \text{ g}$

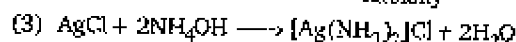
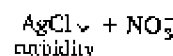
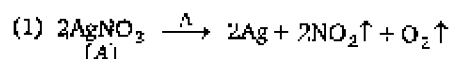
$$\therefore \left(\frac{x}{49} + \frac{0.5 - x}{31.6} \right) = \frac{100 \times 0.15}{1000}$$

where, 49 is Eq. wt. of $\text{K}_2\text{Cr}_2\text{O}_7$ and 31.6 is Eq. wt. of KMnO_4 .

On solving, we get $x = 0.0732 \text{ g}$

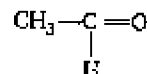
$$\text{percentage of } \text{K}_2\text{Cr}_2\text{O}_7 = \frac{0.0732 \times 100}{0.5} = 14.64\%$$

20. The solution of compound 'A' gives turbidity with tap water (which contains Cl^- ions) and the turbidity [due to formation of AgCl] is insoluble in nitric acid but soluble in NH_4OH . Hence, the compound 'A' is AgNO_3 . The reactions are as follows

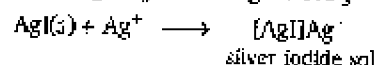
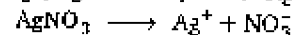


21. The compound which contains $-\text{CHO}$ group, gives positive Tollen's test and the compound with $\text{CH}_3-\underset{\text{O}}{\text{C}}-$ group gives positive iodoform test.

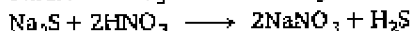
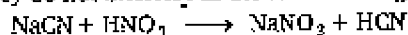
Thus, the structure of the compound should be



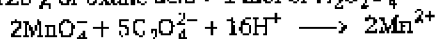
22. $\text{KI} + \text{AgNO}_3$ (slight excess) $\longrightarrow \text{AgI} + \text{KNO}_3$



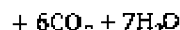
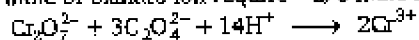
23. During the test for halogens, sodium extract is heated with conc. HNO_3 to decompose sodium cyanide or sodium sulphide present in it, so that they do not interfere in the test for halogens.



24. 126 g of oxalic acid = 1 mol of $\text{H}_2\text{C}_2\text{O}_4$



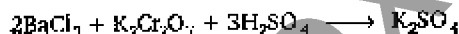
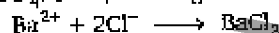
1 mole of oxalate ion require = $\frac{2}{5}$ mole KMnO_4



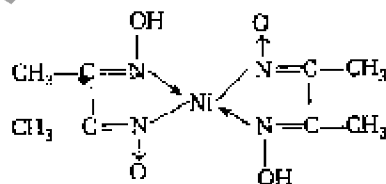
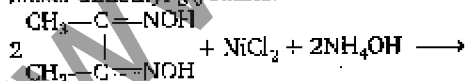
1 mole of oxalate ion require = $\frac{1}{3}$ mole



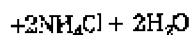
25. Ba^{2+} ion imparts green colour to the flame and Cl^- ion forms chromyl chloride (which is orange red in colour) when treated with $\text{K}_2\text{Cr}_2\text{O}_7$ and conc H_2SO_4 . Thus, the reagent is



26. Nickel salt reacts with dimethyl glyoxime in presence of NH_4OH to give scarlet red ppt of nickel dimethyl glyoxime.

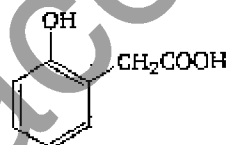


Nickel dimethylglyoxime
(scarlet red ppt)

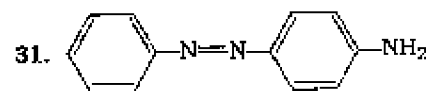


27. Due to all of the given reasons ferrous sulphate

29. The compound liberates CO_2 with NaHCO_3 , so it contains $-\text{COOH}$ group and it also give 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



30. A positive Beilstein's test for halogens does not always indicate the presence of halogen since some halogen free compounds viz urea, thiourea, amides etc also responds this test. The reason being the fact that these halogen free compounds form cuprous cyanide which is volatile and decomposes to copper which burns with green flame.



Aniline yellow

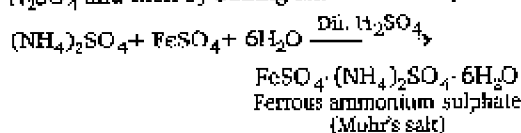
(p-amino azobenzene or 4-phenyl azoaniline)

It is a carcinogenic compound and a basic dye.

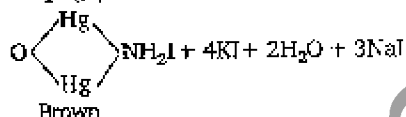
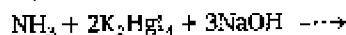
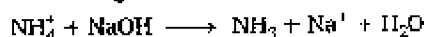
32. The main purpose of using levelling bulb is to assure that pressure within the reaction vessel is same as that in the room.
33. Acidic solution favours dichromate, whereas alkaline solution favours chromate.
34. On treatment with dilute HCl , Na_2CO_3 and Na_2SO_3 produce CO_2 and SO_2 respectively. SO_2 turns an acidified $\text{K}_2\text{Cr}_2\text{O}_7$ solution green whereas CO_2 does not change the colour of the solution.
- $$\text{Na}_2\text{CO}_3 + 2\text{HCl} \longrightarrow 2\text{NaCl} + \text{H}_2\text{O} + \text{CO}_2 \uparrow$$
- $$\text{Na}_2\text{SO}_3 + 2\text{HCl} \longrightarrow 2\text{NaCl} + \text{H}_2\text{O} + \text{SO}_2 \uparrow$$
- $$\underset{\text{orange yellow}}{\text{K}_2\text{Cr}_2\text{O}_7} + \text{H}_2\text{SO}_4 + 3\text{SO}_2 \longrightarrow \underset{\text{green}}{\text{K}_2\text{SO}_4} + \text{Cr}_2(\text{SO}_4)_3 + \text{H}_2\text{O}$$

7. Lyophilic sols are prepared by merely dissolving substances like gelatin, starch in water while lyophobic sols are prepared by special methods such as peptisation, oxidation, reduction etc.

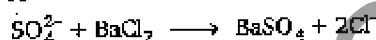
38. Ferrous ammonium sulphate (Mohr's salt) is prepared by dissolving ferrous sulphate in dil H_2SO_4 and then by adding ammonium sulphate.



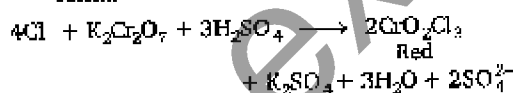
39. (i) The mixture on heating with NaOH liberate a gas which gives red ppt with alkaline K_2HgI_4 , so the gas is NH_3 and mixture contains NH_4^+ ion.



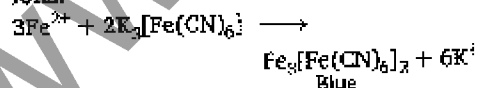
(ii) The aqueous solution of mixture gives white ppt with BaCl_2 , so it contains SO_4^{2-} ions.



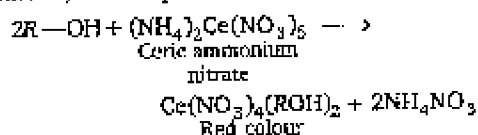
(iii) Mixture on heating with $\text{K}_2\text{Cr}_2\text{O}_7$ and conc. H_2SO_4 gives red vapours (CrO_2Cl_2), so contains Cl^- ions.



(iv) Aqueous solution of mixture gives blue colour with $\text{K}_3[\text{Fe}(\text{CN})_6]$, so mixture contains Fe^{2+} ions.



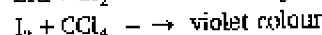
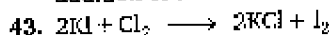
40. Alcohol gives red colour with ceric ammonium nitrate so, the compound is alcohol



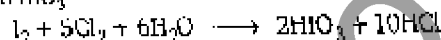
41. The rate of the dissociation of hydrogen peroxide with I^- ion increases by increasing the conc of I^- ion and also in presence of UV light.

42. The enthalpy change when one mole of a solute is

dilution, is called enthalpy of solution and further addition of solvent does not affect it.



Note: The excess of Cl_2 should be avoided otherwise the layer may become colourless due to conversion of I_2 to HIO_3 .



44. Normality equation

$$\frac{N_1 V_1}{\text{dil oxalic acid solution}} = \frac{N_2 V_2}{\text{KMnO}_4 \text{ solution}}$$

$$N_1 \times 25 = \frac{N}{10} \times 30$$

$$250 \text{ ml. of dil oxalic acid} = \frac{N}{10} \times \frac{30}{25} \times 250$$

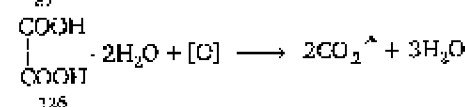
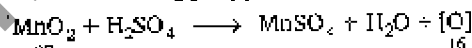
$$= 300 \text{ ml. of } \frac{N}{10} \text{ KMnO}_4$$

$$= 30 \text{ mL of N KMnO}_4 \text{ solution}$$

$$= 30 \text{ mL of N-oxalic acid}$$

Thus, the amount of acid used with pyrolusite

$$= 50 - 30 = 20 \text{ mL of N-oxalic acid}$$



$$63 \text{ g oxalic acid} = \frac{87}{2} \text{ g MnO}_2 = 8 \text{ g O}_2$$

$$\text{So, the amount of oxalic acid used} = 20 \times \frac{63}{1000} = 1.26 \text{ g}$$

$$\therefore 63 \text{ g oxalic acid} = \frac{87}{2} \text{ g MnO}_2$$

$$\therefore 1.26 \text{ g oxalic acid} = \frac{87 \times 1.26}{2 \times 63} = 0.87 \text{ g}$$

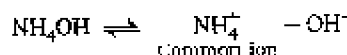
$$\therefore \text{The amount of MnO}_2 \text{ in 1.5 g pyrolusite} = 0.87 \text{ g}$$

$$\therefore \text{Amount of MnO}_2 \text{ in 100 g pyrolusite} = \frac{0.87}{1.5} \times 100 = 58\%$$

45. Because it is necessary to record data and swirl the flask (at constant rate) simultaneously.

46. In III group precipitation, NH_4Cl is added before adding NH_4OH to decrease the conc of OH^- , as NH_4Cl and NH_4OH dissociates as follows





Due to presence of common ion, conc of OH^- decreases and for III group precipitation lesser conc of OH^- is required.

47. The enthalpy of ionisation of weak acid is given by

$$\Delta H_{\text{ion (TBA)}} = \Delta H_{\text{N (weak acid/strong base)}} - \Delta H_{\text{N (strong acid/strong base)}}$$

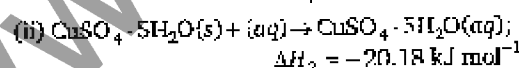
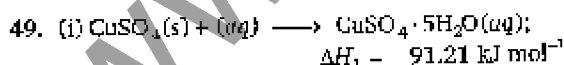
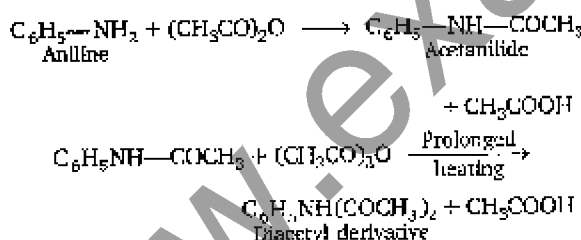
$$= -56.1 - (-57.3) = 1.2 \text{ kJ mol}^{-1}$$

$$\Delta H_{\text{(ionisation)}} = 1.5 \text{ kJ mol}^{-1}$$

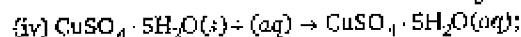
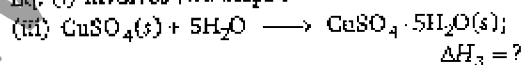
Hence, percentage ionisation in 1M solution

$$= \frac{(1.5 - 1.2)}{1.5} \times 100 = 20$$

48. During acetylation of aniline, the excess of acetic anhydride and prolonged heating results in the formation of diacetyl derivative.

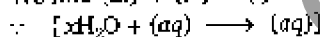


Eq. (i) involves two steps :



$$\Delta H_2 = -20.18 \text{ kJ/mol}$$

We find (iii) + (iv) = (i)



$$\Delta H_3 + \Delta H_2 = \Delta H_1$$

thus, for

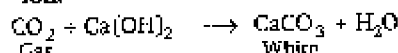


$$\Delta H_3 = \Delta H_1 - \Delta H_2$$

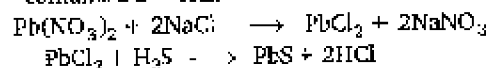
$$= -91.21 - (-20.18)$$

$$= -71.03 \text{ kJ mol}^{-1}$$

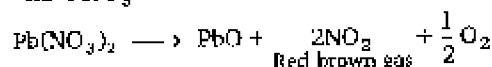
50. (i) The mixture with dil H_2SO_4 liberated a gas which turns lime water milky and turbidity disappears with the passage of excess of gas, so the gas is CO_2 and mixture contains CO_3^{2-} ion.



- (ii) The aqueous solution of mixture gives white ppt with NaCl solution and filtrate of this with H_2S gives black ppt thus, mixture contains Pb^{2+} ion.



- (iii) The aqueous solution of mixture on heating liberates reddish brown gas, so it should have NO_3^- ion.



- (iv) The aqueous solution with NH_4OH and excess of Na_2HPO_4 gives a white crystalline ppt, so mixture should have Mg^{2+} ions.

