

M.Sc CHEMISTRY (Previous)

Syllabus

INORGANIC CHEMISTRY PRACTICAL MANUAL (QUALITATIVE AND QUANTITATIVE ANALYSIS)

1. Semi-Micro Qualitative Analysis of Inorganic salts Mixture
2. Determination of Chromium
3. Determination of Copper
4. Determination of Total Hardness of water
5. Determination of Nickel
6. Determination of Zinc

M.Sc CHEMISTRY (Previous)
(DISTANCE EDUCATION CENTRE – ACHARYA NAGARJUNA UNIVERSITY)

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(QUALITATIVE AND QUANTITATIVE ANALYSIS)

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QUALITATIVE ANALYSIS

INTRODUCTION

Macro Analysis: The quantity of the substance employed is 0.1 to 0.5 g and the volume taken for analysis is about 20 ml.

Semi micro Analysis: In this, the quantities are reduced to 10 to 20 times when compared with macro analysis i.e. about 0.05 g and 1 ml solution.

Micro Analysis: In this, the quantities are reduced to 100 to 200 times when compared with macro analysis.

Note: The given unknown substance is a mixture of salts containing cations and anion. It is very essential on the part of the student to record all observations as and when they are made. It is found to be best recorded in three columns, experimental, observation and inference. The first column is a list of all tests to be made and may be kept filled in advance. Negative reactions should not be ignored and should be recorded.

General instructions and clues:

1. The apparatus used must be clean.
2. Add solutions in drop wise.
3. Whenever a reagent is added, shake the test tube gently and thoroughly.
4. The conditions prescribed for precipitation must be followed scrupulously. When a precipitate is obtained, digest the precipitate for coagulation and then centrifuge. Ensure complete precipitation of the ion concerned. The precipitate must be washed to remove the adhering metal ions of other groups. The first washings must be added to the centrifuge from which the precipitate was obtained.
5. If the volume of the solution at any stage becomes too large, it should be reduced by evaporation.
6. If original solution of the mixture is made in HCl, I groups is absent.
7. (a) For analysis from II group onwards, adjust the acidity as follows: Take the centrifugate of I group or in the absence of I group, take 2 ml of the original solution and add it to 2 ml of water.
(b) If the original solution is made in water or in 6N HNO₃, after dilution add 6 drops of 6N HCl.
8. While testing II and IV groups: Before passing H₂S through the entire solution, pass H₂S through a small portion of it separately. If a precipitate forms, pass H₂S through the bulk of the solution. If no precipitate forms, pass on to the next group with the bulk solution.
9. The centrifugate obtained after precipitation II and IV group metals by passing H₂S must be made free of dissolved H₂S before using it for further group.
10. (a) If III group is absent, take small portions of this solution (having NH₄Cl and NH₄OH) to find out the presence of IV, V and VI group cations.
(b) If IV group is absent, take another portion of the solution and add (NH₄)₂CO₃ solution.
(c) If V group is also absent, take the other portion and test for VI group.

SYSTEMATIC PROCEDURE FOR THE SEMI-MICRO ANALYSIS

Experiment	Observation	Inference
I. Physical tests:		
a. Nature of the substance	Crystalline or amorphous	
b. <u>Odour</u> : Smell of the mixture is noticed.	Smell of vinegar Smell of ammonia Smell of H ₂ S	May be acetate ion May be ammonium May be sulphides
c. <u>Colour of the substance</u> *:	Colour less	Absence of salts like Fe, Co, Ni, Cr, Mn etc.
	Blue	Hydrated Cu ⁺² salts, anhydrous
	Brown	PbO ₂ , Fe ⁺³ salts, chromium, Nickel salts etc.
	Green	Hydrated Fe ⁺² salts, Ni ⁺² salts, some cr ⁺³ salts and some cu ⁺² salts.
	Pink	Salts of cobalt.
	Yellow colour	Salts of Col, Hg, As, Sb
	Black	Sulphides of Ag, Pb, Hg, Cu, Sb, Ni, Cu, Fe or oxides of Mn etc
d. Action of heat : The substance is taken in a small ignition tube and heated gently first and then more strongly in a Bunsen flame.	A) Sublimation: On the upper walls of the test tube (i) White sublimated is observed (ii) Yellow sublimate is observed. (iii) Black sublimate is observed.	May be ammonium salts, Hg(I) or Hg(II) chlorides, As(III), Sb(III), Se(IV) Oxides. May be Sulphur, As(III) sulphide and Hg(I) or Hg(II) iodides. May be Hg(I) or Hg(II) sulphides.

* It may not reflect in the mixture

Experiment	Observation	Inference
	<p>B) Evolution of gases:</p> <p>(i) Colourless and odourless CO₂ is observed which turns limewater to milky.</p> <p>(ii) Light greenish Chlorine gas is evolved which turns starch-iodide paper blue.</p> <p>(iii) Reddish brown bromine vapours or violet iodine vapours are observed.</p> <p>(iv) SO₂ is evolved.</p> <p>(v) NO₂ is evolved.</p> <p>(vi) Colourless, pungent ammonia is evolved.</p> <p>(vii) Oxygen is evolved.</p> <p>C. Substance chars with</p> <p>(i) smell of burnt sugar.</p> <p>(ii) loss of carbon</p> <p>D. Change in colour</p> <p>Yellow when hot white when cold</p>	<p>May be carbonates and organic compounds like oxalates.</p> <p>May be chlorides.</p> <p>May be bromides or iodides.</p> <p>May be sulphites, thiosulphates, sulphides.</p> <p>May be nitrates.</p> <p>May be ammonium salts.</p> <p>May be chlorates, perchlorates, bromates, iodates etc.</p> <p>May be tartarates.</p> <p>May be oxalates.</p> <p>Zinc salts</p>
(e) Flame test: Mix a small amount of the solid with two drops of Conc.HCl. Stir into paste with a platinum wire and introduce a little of the paste on the wire into the oxidizing region of the Bunsen flame.	<p>Violet</p> <p>Golden yellow</p> <p>Brick red</p> <p>Crimson red</p> <p>Apple green</p> <p>Bluish green</p> <p>Flashes of green</p>	<p>Potassium</p> <p>May be Na⁺</p> <p>Calcium</p> <p>Strontium</p> <p>Barium</p> <p>Copper</p> <p>May be Zn⁺², Mn⁺²</p>
f) Solubility: The solubility of the given compound is tested in water or dil HCl or dilHNO ₃	<p>Solubility is tested in water, dil HCl, dilHNO₃etc. aquaregia.</p> <p>Soluble completely in water and the soluble portion will not give precipitation with Na₂CO₃.</p> <p>Soluble in dil HCl.</p>	<p>Presence of NH₄⁺, K⁺ or Na⁺</p> <p>Absence of I group cations.</p>

Experiment	Observation	Inference
<p>g) Charcoal bead test: Mix the substance with twice its bulk of anhydrous Na_2CO_3 of fusion mixture ($\text{Na}_2\text{CO}_3 + \text{K}_2\text{CO}_3$) and place it in a cavity of charcoal. Moisture is with a drop of water and heat it on the reducing flame with the help of blowpipe. The formation of bead incrustation dirt colour while hot and cold.</p>	<p>A) A metallic bead is formed.</p> <ol style="list-style-type: none"> 1. White metallic 2. Red flame 3. Grey metallic particles <p>B) Incrustation with metal</p> <ol style="list-style-type: none"> 1. White brittle method 2. Yellow, brittle metal <p>C) Incrustation without metal:</p> <ol style="list-style-type: none"> 1. White yellow when hot 2. White Garlic odour 3. Brown 	<p>Ag^+ Cu Fe, Co, Ni</p> <p>Antimony Bismuth</p> <p>Zinc Arsenic Cadmium</p>

h. Borax bead test: A platinum wire is used for borax bead test. The free end of the platinum wire is coiled into a small loop. The loop is heated in the Bunsen flame until it is red hot and then quickly dipped into powdered borax. $[\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}]$, and heated until colourless and transparent. A minute quantity of substance is brought in contact with the hot bead and heated in the oxidizing flame. The colour is observed when the bead is hot and cold. The bead is heated in inner and outer flame and the colour is observed in hot and cold state.

Oxidising flame	Reducing flame	Metal
1. Green when hot, blue when cold	Colourless when hot and red when cold	Copper
2. Red when hot, yellows when cold	Colourless when hot and cold	Iron
3. Dark yellow when hot, green when cold.	When hot and cold green	Chromium
4. Violet when hot and cold	Colourless when hot and cold	Magnesium
5. Blue when hot and cold	Blue when hot and cold	Cobalt
6. Reddish brown when cold.	Blue when hot and cold	Nickel

II. Examination of volatile production on reaction with acid.

Experiment	Observation	Inference	
<p>1.Reaction with dil.HCl: The mixture is heated with dil HCl in a dry test tube</p>	a) Brisk effervesence, with evolution of colour less, colourless gas.	CO ₃ ⁻² (Carbonate) Or Bicarbonate(Hco ₃)	
	b) Colourless gas with penetrating smell of burning sulphur.	SO ₃ ⁻² (Sulphite)	
	c) Evolution of colourless gas with rotten egg smell and turns colour of lead acetate paper black.	Sulphide (S ⁻²)	
	d) Evolution of brown fumes with pungent colour	Nitrate (NO ₃ ⁻)	
	e) Evolution of colourless gas with suffocating smell burning sulphur and yellowish precipitate of sulphur is deposited at the bottom of the test tube.	Thiosulphate(S ₂ O ₃ ⁻²)	
	f) Pale blue liquid is closed and brown fumes are evolved	Nitrite(NO ₂ ⁻)	
	<p>2.Reaction with conc H₂SO₄: The mixture is heated with conc.H₂SO₄</p>	a) Colourless fuming gas sides of the test tube appear oily.	Fluoride(F ⁻)
		b) Colourless pungent gas	Chloride(Cl ⁻) Bromide(Br ⁻)
		c) Colourless pungent gas is evolved, some brown fumes are also evolved	
		d) Dark violet fumes are evolved	Iodide(I ⁻)
e) Pungent colourless (OR) light brown gas is evolved		Nitrate(NO ₃ ⁻)	
f) Colourless and odourless gas is evolved which burns with a blue flame at the month of the test tube.		Oxalate(C ₂ O ₄ ⁻²)	
g) White fumes of boric acid on heating.		Borate (BO ₃ ⁻³)	
h) Smell of vinegar		Acetate	
i) Charring occurs immediately and smell of burnt sugar's observed. CO+CO ₂ is evolved.		Tartrate(C ₄ H ₄ O ₆ ⁻²)	

III. Confirmatory Tests:

Experiment	Observation	Inference
1. Heat the mixture with dil.HCl or dil.H ₂ SO ₄ in dry test tube	Colourless gas is evolved which when passed into limewater turns milky.	Carbonate(CO ₃ ⁻²)
2. To the excess solution of salt mixture, add a solution of MgSO ₄ . boil the solution.	A white precipitate is formed.	Bicarbonate (HCO ₃ ⁻)
3. Heat the mixture with dil.HCl or dil.H ₂ SO ₄ in a dry test tube.	Evolution of colourless gas with suffocating odour of burning sulphur. The evolved gas turns potassium dichromate paper green.	Sulphite (SO ₃ ⁻²)
4. To the neutral or acid solution, AgNO ₃ solution is added. (OR) To the given mixture lead acetate solution is added.	Black precipitate is formed. Black precipitate is formed.	Sulphide (S ²⁻) Sulphide (S ²⁻)
5. To the solution of the mixture, a saturated solution of FeSO ₄ acidified with dil. acetic acid or with dil.H ₂ SO ₄ is added. (OR) To the mixture AgNO ₃ solution is added.	A brown ring is formed. FeSO ₄ .NO White crystalline precipitate of silver nitrite is formed.	Nitrite (NO ₂ ⁻) Nitrite (NO ₂ ⁻)
6. A small amount of the substance is rubbed with oxalic acid with a few drops of water between fingers. (OR) To the solution of mixture, Conc.H ₂ SO ₄ and CH ₃ OH are added and heated. It is then poured into water.	Smell of vinegar. Fruity odour is obtained.	Acetate (CH ₃ COO ⁻) Acetate (CH ₃ COO ⁻)
7. To the solution of mixture, lead acetate solution is added. (OR) To the mixture, FeCl ₃ solution is added.	At first no change is observed, but on further addition of the reagent a white ppt. is formed. A dark violet colour appears.	Thiosulphate (S ₂ O ₃ ²⁻) Thiosulphate (S ₂ O ₃ ²⁻)

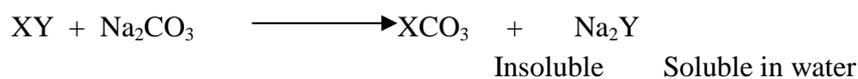
Experiment	Observation	Inference
8. To the given mixture conc.H ₂ SO ₄ is added and heated. (OR) The given mixture is heated with conc.H ₂ SO ₄ and MnO ₂ .	Colourless pungent gas evolved. A glass rod dipped in NH ₃ is brought near the test tube mouth. White dense fumes are observed.	Chloride (Cl ⁻)
9. Heat the mixture with K ₂ Cr ₂ O ₇ and conc.H ₂ SO ₄ .	Greenish yellow gas is evolved.	Chloride (Cl ⁻)
10. The given mixture is heated with Conc.H ₂ SO ₄ and MnO ₂ .	Reddish brown (CrO ₂ Cl ₂) vapours are evolved. These vapours when passed into the test tube containing NaOH and lead acetate solution a yellow ppt is formed.	Chloride (Cl ⁻)
11. The given mixture is heated with Conc.H ₂ SO ₄ and MnO ₂ .	Brown vapours of bromine are evolved.	Bromide (Br ⁻)
12. To the given mixture copper turnings and conc.H ₂ SO ₄ are added and heated.	Dark violet fumes are evolved. These violet vapours turns starch paper blue.	Iodide (I ⁻)
13. To the given mixture copper turnings and conc.H ₂ SO ₄ are added and heated.	Deep brown fumes are evolved.	Nitrate(NO ₃ ⁻)
13. To the mixture diphenylamine is added and heated gently. Cooled it and three drops of alcohol are added. (OR) To the solution of mixture dil.CH ₃ COOH and CaCl ₂ solution are added.	Blue colour chain is observed.	Oxalate (C ₂ O ₄ ²⁻)
14. To a little mixture in a porcelain dish a little conc.H ₂ SO ₄ and C ₂ H ₅ OH are added and burned. (OR) A small amount of mixture is taken and made paste with CaF ₂ and little conc.H ₂ SO ₄ . The paste is taken on a glass rod and brought to the edge of the flame.	A white ppt. which decolourises KMnO ₄ is observed.	Oxalate (C ₂ O ₄ ²⁻)
	These vapours burned with green edged flame.	Borate (BO ₃ ³⁻)
	Green flame is observed.	Borate (BO ₃ ³⁻)

Experiment	Observation	Inference
15. To the mixture lead acetate is added.	Yellow ppt soluble in HNO_3 and insoluble in CH_3COOH is formed.	Chromate ($\text{Cr}_2\text{O}_4^{2-}$)
16. The substance is neutralized with ammonia sol. And 1 ml of CH_3COOH is added. Then AgNO_3 solution is added.	Brown ppt. is formed.	Chromate (CrO_4^{2-})
17. To the solution of mixture, dil. CH_3COOH and CaCl_2 solution are added.	A white ppt. is formed.	Fluoride (F^-)
18. The mixture is boiled with conc. HNO_3 .	A canary yellow ppt. is formed. The ppt. is soluble in NH_4OH and alkaline hydroxide solution.	Phosphate (PO_4^{3-})
19. To the solution of mixture dil. HCl or HNO_3 and BaCl_2 solution are added.	A curdy white ppt. is formed. The ppt. is insoluble in conc. acid.	Sulphate (SO_4^{2-})
20. To the solution of mixture, equal amounts of saturated manganese(II) sulphate solution and 1M H_2SO_4 are added.	A red colour is observed. On concentration the solution brown MnO_2 (hydrated) separates.	Bromate (BrO_3^-)
21. To the solution of mixture barium chloride solution is added.	White ppt is observed. The ppt is sparingly soluble in hot water and in dil. HNO_3 , but insoluble in alcohol. The ppt is washed well and treated with sulphurous acid sol and 1 to 2 ml of chloroform. Violet colouration is observed.	Iodate (IO_3^-) Iodate (IO_3^-)
22. To the solution of mixture, Mercuric(II) nitrate solution is added.	White ppt. is observed.	Iodate (IO_3^-)
23. To the neutral solution of the mixture, a solution of cadmium sulphate in conc. ammonia solution is added.	A white crystalline ppt is formed.	Perchlorate (ClO_4^-)

Experiment	Observation	Inference
24. To the solution of mixture, potassium chloride or ammonium chloride solution is added.	A white ppt. is formed. The ppt. is insoluble in alcohol.	Perchlorate (ClO_4^-)
25. To the solution of mixture, lead nitrate or lead acetate solution is added and boiled.	Brown coloured ppt is observed.	Hypochlorite (OCl^-)
26. To the solution mixture, silver nitrate solution is added.	A white ppt is formed and the ppt is soluble in excess of the cyanide solution.	Cyanide (CN^-)
27. To the solution of mixture cobalt acetate is added.	Blue colouration observed due to the formation of a complex. The colour is intensified by the addition of ethanol.	Cyanate (OCN^-)
28. <u>Thiocyanates</u> : To the solution of mixture, silver nitrate solution is added.	A curdy white ppt. is formed. The ppt. is soluble in ammonia and insoluble in nitric acid.	Thiocyanate (SCN^-)
29. To the solution of mixture, cadmium acetate solution is added.	A white gelatinous ppt. is formed. The ppt is insoluble in boiling water but readily soluble in warm acetic acid. (Tartarates give no ppt.)	Citrate ($\text{C}_6\text{H}_5\text{O}_7^{3-}$)

Confirmatory tests for anions with sod. Carbonate extract:

One part of the given substance is mixed with 2 to 3 parts by weight of sodium carbonate and 15 ml of distilled water is added and boiled for about 10 to 15 minutes in a beaker. Now filtered it, the filtrate is called sodium carbonate extract.



Where X and Y are cations and anions respectively.

Experiment	Observation	Inference
<p>1. <u>Tests for Halogens:</u> The sod. Carbonate extract is neutralized with dil.HNO₃ and 3 ml of AgNO₃ solution is added.</p>	<p>a. A white ppt of AgCl is formed which is soluble in ammonia solution. b. A pale yellow ppt. of AgBr is formed and is hardly soluble in ammonia solution. c. Yellow ppt. is obtained which is insoluble in ammonia solution.</p>	<p>Chloride (Cl⁻) Bromide (Br⁻) Iodide (I⁻)</p>
<p>2. The sod. Carbonate extract is neutralized with dil.H₂SO₄ and freshly prepared FeSO₄ solution is added. Then keeping the test tube in an inclined position, conc.H₂SO₄ is added from the walls of the test tube.</p>	<p>Brown ring of FeSO₄.NO is formed at the junction of two liquids.</p>	<p>Nitrate (NO₃⁻)</p>
<p>3. The sod. carbonate extract is acidified with CH₃COOH and CaCl₂ solution is added. The ppt is dissolved in dil.H₂SO₄ and warmed. To it few drops of acidified KMnO₄ is added.</p>	<p>A whit ppt of CaC₂O₄ is formed. The colour of KMnO₄ is discharged.</p>	<p>Oxalate (C₂O₄²⁻)</p>
<p>4. About 10 ml of extract is heated with 0.5 ml of C₂H₅OH and H₂SO₄ in a boiling test tube. The expelled vapours are brought near the flame.</p>	<p>The vapours burn with green edged flame.</p>	<p>Borate (BO₃³⁻)</p>
<p>5. The sod. Carbonate extract is neutralized with dil.HCl and neutral FeCl₃ solution is added.</p>	<p>Deep colouration is formed. On boiling it becomes brownish red ppt.</p>	<p>Acetate (CH₃COO⁻)</p>
<p>6. The sod. carbonate is neutralized with dil.HNO₃. Then Conc.HNO₃ and ammonium molybdate are added and heated.</p>	<p>A canary yellow ppt is formed.</p>	<p>Phosphate (PO₄³⁻)</p>
<p>7. To the sod. carbonate dil HCl is added to neutralize and then BaCl₂ solution is added.</p>	<p>White ppt. is formed. The ppt is insoluble in Conc. HCl</p>	<p>Sulphate (SO₄²⁻)</p>

Experiment	Observation	Inference
8. The sod. carbonate extract is acidified with dil.HNO ₃ and AgNO ₃ solution is added in excess. This is heated in a boiling water bath.	A brilliant silver mirror is formed.	Tartarate (C ₄ H ₄ O ₆ ²⁻)
9. The sod. carbonate extract is neutralized with HNO ₃ . Now it is heated with NaNO ₂ is added.	Whit ppt. of AgCl is formed	Chlorate (ClO ₃ ⁻)

(C) Special ions:

Experiment	Observation	Inference
1. To the neutral solution of mixture, AgNO ₃ solution is added.	Yellow colour ppt. Brown colour ppt	Arsenite(AsO ₃ ³⁻) Arsenate(AsO ₄ ³⁻)
2. To the solution of mixture, ferrous sulphate and sulphuric acid are added.	The solution becomes yellow.	Permanganate (MnO ₄ ⁴⁻)
3. To the solution of mixture, lead acetate solution is added.	Yellow ppt is formed. The ppt turns white or pale yellow on standing	Vanadate (VO ₃ ⁻)
4. To the solution of mixture, potassium hexacyanoferrate(II) solution is added.	A reddish brown ppt is formed. The ppt is insoluble in dilute mineral acids but soluble in solutions of caustic alkalis and ammonia.	Molybdate (MoO ₄ ⁴⁻)
5. To a solution of mixture, ferric chloride solution and acid are added.	Prussian blue ppt is formed.	Ferrocyanide ion [Fe(CN) ₆] ⁴⁻
6. To a solution of mixture, ferric chloride solution is added.	Brown colouration is observed.	Ferricyanide ion [Fe(CN) ₆] ³⁻

Removal of interfering radicals: Oxalate, Borate, Fluoride, Phosphate, tartarate, chromate, Citrate in are known as interfering radicals. Their presence in the mixture stands in the usual way of analysis of basic radicals after second group. Actually salts of these radicals are soluble in acid medium but are insoluble in neutral or alkaline medium. Upto II group the medium remains acidic, hence they are not precipitated and thus they do not interfere. But in and after III group the medium is made alkaline by the addition of NH_4OH in which majority of the salts of these interfering radicals are insoluble. So in the III group oxalates, Phosphates, fluorides, borates etc of metals of III group and subsequent groups get precipitated. The hydroxides of the III group metals are also precipitated. In this way the normal procedure of analysis will be disturbed. Therefore it is essential to remove the interfering radicals before adding NH_4OH for the test of IIIrd group and subsequent group radicals.

Removal of oxalate: Take 2gm of the mixture in a porcelain dish and heat it strongly for 5-10 minutes. Now add 2-4 ml of con. HNO_3 and evaporate to dryness. Repeat the process four to five times when all oxalic acid gets oxidized to CO_2 . Oxalate can also be removed from III group precipitate in the same manner described above.

Removal of Tartrate: Take 2gm of the mixture in a porcelain dish and heat strongly for 5-10 minutes. Now add 2-4 ml of Con. HNO_3 and evaporate to dryness. Repeat the process four or five times till all the tartarate is removed.

Removal of Borate: Take 2g of the mixture in a porcelain dish and add 2-4ml of con HCl. Evaporate the solution to almost dryness. Repeat this operation five to six times. The residue is dissolution little con HCl, diluted with water and can be used as the original solution. It can be removed form the IIIrd group precipitate in the manner described above.

Removal of fluoride: Fluoride is also removed by the same method as borate forming hydrofluoric acid which volatilizes. It can be removed from the III group precipitate in the manner described above.

Removal of chromate: Chromate can also be removed by the same above method.

Removal of Phosphate: The filtrate of III group is boiled to remove H_2S . Two drops of conc HNO_3 are added to convert ferrous salt into ferric one. Now NH_4Cl and NH_4OH (excess) are added till a clear smell of ammonia is obtained. If no ppt is obtained, then there is no need of removing phosphate. Now in this solutions containing ppt, sodium acetate and acetic acid are added in excess till the smell of acetic acid is noticed. If whole of the ppt dissolves then III group is supposed to be absent, if not then proceed as follows:

<u>Residue:</u> III groups is present. Test as usual. If no residue is left behind III group is usually absent.	<u>Filtrate:</u> Now the filtrate or the total solution in a beaker is taken and neutral FeCl_3 solution is added slowly without shaking until tea colour is obtained. Boiled for 5 to 10 minutes and filter.	
	<u>Filtrate:</u> NH_4Cl and NH_4OH (excess) is added till lit smells of ammonia and filtered.	<u>Residue:</u> It is rejected. FePO_4 , $\text{Fe}(\text{OH})_2\text{CH}_3\text{COO}$ Basic ferric acetate
	<u>Filtrate:</u> Test the 4 th and subsequent group radicals as usual.	<u>Residue:</u> Reject it.

Treatment of Insolubles

Substances which are not soluble in conc. HCl (or HCl + HNO_3) are termed as insolubles. The insoluble materials met with commonly in mixtures are sulphates of Sr, Ba, Pb, some sulphides, particularly SnS_2 (mosaic gold), ignited oxides like Al_2O_3 , Cr_2O_3 , Fe_2O_3 and phosphates of some tetravalent metals like Zr.

On treating the unknown with HCl to prepare the solution for cation analysis, only the soluble dissolve. Insolubles and any chlorides of cations of group I remain in the residue. The residue is examined ;for group I ;using the following reagents in order- hot water, aq. NH_3 , HCl, HNO_3 . Any residue left over has to be analysed by the special procedure for insolubles.

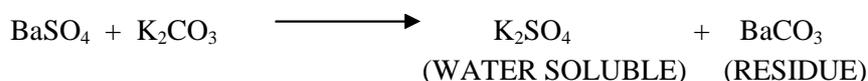
Procedure for analysis of an insoluble

The insoluble residue is dried and fused on a nickel foil with small bit of solid NaOH and a crystal of KNO_3 and cooled. Placed the foil in a crucible or beaker and added 2 cc of 5% Na_2CO_3 and boiled, filtered.

<u>Residue:</u> Warmed with a little dil. HNO_3 and filtered. Rejected any residue. The solution tested for groups III and IV.	<u>Filtrate:</u> Neutralised with HCl and evaporated to dryness. Digested with HCl, filtered.	
	<u>Residue:</u> SiO_2	<u>Filtrate:</u> Tested for cations of group II and III.

Notes:

1. Fusion with NaOH opens epoxides, sulphides, sulphates and phosphates. On boiling with Na_2CO_3 group V metals are precipitated as carbonates. The weakly negative amphoteric metals eg. Zr are precipitated as hydroxides. Hydroxides and carbonates are found in the residue. The solution contains anions of the amphoteric metals and anions like silicate and phosphate.
2. In the case of insoluble residue containing only barium or strontium sulphate fusion with fusion mixture ($\text{Na}_2\text{CO}_3 + \text{K}_2\text{CO}_3$) is enough. Fusion may be done in a broken bit of porcelain. The mass is leached with water and the residual carbonate is dissolved in dil. HCl and tested for the metal ion.



Classification of cations into groups:

Group	Group Reagent	Cations included	Precipitate with colour
I	Cold dil.HCl	Hg_2^{2+} , Ag^+ , Pb^{2+} , Tl^+ , W^{6+}	Hg_2Cl_2 , AgCl , PbCl_2 , TlCl (All white) H_2WO_4 (light yellow)
IA	Hydrazine hydrochloride	Se^{4+} , Se^{6+} , Te^{4+}	Metallic Se (Red), Metallic Te (Blue black)
II	Dil. HCl + H_2S	Hg^{2+} , Cu^{2+} , Pb^{2+} , Cd^{2+} , Bi^{3+}	HgS , CuS , PbS (All black), CdS (Yellow), Bi_2S_3 (Brownish black)
	KOH	As^{3+} , As^{5+} , Sb^{3+} , Sb^{5+} , Sn^{2+} , Sn^{4+} , Mo^{6+}	As_2S_3 , As_2S_5 (yellow), Sb_2S_3 , Sb_2S_5 (orange red) SnS (brown) SnS_2 (yellow), MoS_3 (Brown)
III	Solid NH_4Cl + NH_4OH	Fe^{3+} , Al^{3+} , Cr^{3+} , Ce^{4+} , Zr^{4+} , Ti^{4+} , V^{5+} (VO_3^-), U^{6+} (UO_2^{2+})	$\text{Fe}(\text{OH})_3$ (Red brown), $\text{Al}(\text{OH})_3$ (Gelatinous white) $\text{Cr}(\text{OH})_3$ (Bluish green) $\text{Zr}(\text{OH})_4$, $\text{Ti}(\text{OH})_4$ (Both white), $\text{Ce}(\text{OH})_4$, $(\text{NH}_4)_2\text{U}_2\text{O}_7$ (both yellow), NH_4VO_3 (pale blue)
IV	Solid NH_4Cl + NH_4OH + H_2S	Co^{2+} , Ni^{2+} , Mn^{2+} , Zn^{2+} , Tl^+ (traces)	CoS , NiS , Tl_2S (All black), ZnS (dirty white), MnS (Flesh coloured)
V	Solid NH_4Cl + NH_4OH + $(\text{NH})_2\text{CO}_3$	Ba^{2+} , Sr^{2+} , Ca^{2+}	BaCO_3 , SrCO_3 , CaCO_3 (All white)
VI	–	NH_4^+ , Mg^{2+} , Li^+ , Na^+ , K^+	Flame test: Li (Crimson red), Na (Golden yellow), K (Lilac)

Test for NH_4^+ :

Since many ammonium salts are added during the course of analysis, the ion has to be tested in the given mixture before proceeding to the systematic cation analysis.

- (i) NaOH Test: To 0.5 ml of the original solution, 0.5 ml of NaOH solution is added in a test tube and heated. The evolved gas is smelled. Ammonia gas smell indicates NH_4^+ .
- (ii) Nessler's reagent Test: To a few drops of the original solution in a test tube, a few drops of Nessler's reagent are added. Brick red precipitate indicates NH_4^+ .

Preparation of original solution:

Prepare original solution of the mixture trying its solubility in the following solvents in the order given:

1. Distilled water
2. Dil. HNO_3
3. Conc. HNO_3
4. Conc. HCl
5. Aquaregia (1:3 conc. HNO_3 : Conc. HCl)

Separation of cations into groups

To 4 ml of original solution in a centrifuge tube, dil.HCl is added drop wise. If a precipitate is formed, dil. HCl is added till precipitation is completed, cooled and centrifuged. To the residue 6 drops of water are added, shaken, cooled and centrifuged again. This centrifuge is added to the one already obtained.

<i>Residue:</i> I groups cations are present. Analysed by I group table.	<i>Centrifugate:</i> A few crystals of hydrazine hydrochloride are added, heated on water bath and centrifuged.						
	<i>Residue:</i> IA groups cations are present. Analysed by IA group table.	<i>Centrifugate:</i> 2 drops of 6% H ₂ O ₂ are added, heated, diluted with 2 ml water and H ₂ S is passed and centrifuged.				<i>Centrifugate:</i> H ₂ S is boiled off and 3 to 4 drops of Conc.HNO ₃ is added. Boiled it again. (Test for the presence of Fe ³⁺ by taking 1 drop of the solution and adding 2 drops of NH ₄ SCN solution. Deep red colouration indicates Fe). To the bulk of solution, 2 drops of FeCl ₃ and 5 drops of saturated NH ₄ Cl are added. The solution is heated without boiling. To the hot solution 1:1 NH ₄ OH (excess) is added and centrifuged.	
		<i>Residue:</i> IIA & IIB groups cations. Boiled with 1ml of 2N KOH and centrifuged.					
	<i>Residue:</i> IIA group cations. Analysed by IIA group table.	<i>Centrifugate:</i> IIB group cations. Analysed by IIB table.	<i>Residue:</i> III group cations. Analysed by III group table.	<i>Centrifugate:</i> 4 drops of NH ₄ OH is added, H ₂ S gas is passed till precipitation is completed and centrifuged.			
		<i>Centrifugate:</i> H ₂ S is boiled off and concentrated to 2 ml. A few drops of NH ₄ OH and 10 to 15 drops of saturated (NH ₄) ₂ CO ₃ are added. (If a precipitate is formed, a few more drops of (NH ₄) ₂ CO ₃ are added so that precipitation is completed). Heated in water bath and centrifuged.					
<i>Residue:</i> IV group cations. Analysed by IV group table.		<i>Residue:</i> V group cations. Analysed by V group table.		<i>Centrifugate:</i> Analysed for VI group cations.			

Analysis of cations including the less familiar elementsANALYSIS OF GROUP -I

To 4ml of the original solution, 2ml of dil HCl is added. Boiled and cooled. Centrifuge the cold solution. Washed the precipitate with cold water. Combine washings and centrifugate and save it for analysis of further groups.

<i>Residue:</i> Chlorides of Pb^{+2} , Hg_2^{2+} , Ag^+ , Tl^+ and WO_2 . The residue is boiled with 3 ml water, centrifuged the hot solution rapidly and the clear solution is removed immediately. (If the residue is completely soluble in water Hg_2^{2+} , W^{6+} and Ag^+ are absent.)			
<i>Residue:</i> Hg_2Cl_2 , $AgCl$, WO_2 ; :Washed twice with hot water to remove any Pb^{+2} , Tl^+ chlorides. Washings are rejected. $\frac{1}{2}$ c.c. of dil.aq. NH_3 is added, warmed and centrifuged.		<i>Centrifugate:</i> $PbCl_2$ and $TlCl$. 2 drops of conc. H_2SO_4 are added and heated to fumes. Then 1 c.c. of water is added cautiously, stirred and centrifuged	
<i>Residue:</i> Black Three drops of conc. HCl and a drop of conc. HNO_3 are added, heated and centrifuged. To the clear centrifugate, 3 drops of $SnCl_2$ are added. White or grey ppt. Mercury	<i>Centrifugate:</i> $[Ag(NH_3)_2]Cl$ and ammonium tungstate Dil. HCl was added drop wise till a ppt begins to form. It is redissolved with drops of aq. NH_3 . Two drops of KI are added and centrifuged.	<i>Residue:</i> Whit $PbSO_4$ 5 drops of NH_4Oac are added and warmed. 2 drops of dil HOAc and 2 drops of K_2CrO_4 are added. A yellow ppt is observed. Lead	<i>Centrifugate:</i> Tl_2SO_4 Just neutralized with aq. NH_3 and 2 drops of KI solution and 2 drops of $Na_2S_2O_3$ are added. Yellow ppt. TlI indicates Thallium Flame colour - green
	<i>Residue:</i> Yellow AgI insoluble in aq. NH_3 indicates Silver		<i>Centrifugate:</i> Evaporated to half the bulk and 2 drops of $SnCl_2$ and 2 drops of conc. HCl are added and warmed. Blue ppt. shows Tungsten

Spot tests for Tl:

- To one drop of the solution, one drop of $Na_3[Co(NO_2)_6]$ solution is added. A light red precipitate of $Tl_3[Co(NO_2)_6]$ forms.
- To one drop of the solution, one drop of $K_2Cr_2O_7$ solution is added. Yellow precipitate of Tl_2CrO_4 insoluble in dil. HNO_3 is formed.

Analysis of Group - I_A

To the centrifugate from I group, a few crystals of hydrazine hydrochloride are added and heated on water bath. Centrifuged, washed the residue with water and combine washings with centrifugate.

<i>Residue:</i> Add two drops of conc. HCl and equal amount of bromine water. Boiled and 5 drops of saturated NH ₄ Cl is added and centrifuged.		<i>Centrifugate:</i> Examined for further groups.	
<i>Residue:</i> Orange yellow crystals (NH ₄) ₂ [PtCl ₆] Platinum	<i>Centrifugate:</i> Add 2-3 crystals of oxalic acid, boiled and centrifuged.		
	<i>Residue:</i> Brown ppt. Gold	<i>Centrifugate:</i> Add aq.NH ₃ . Red ppt is formed. Pd is present. Add a slight excess of NH ₃ and then dil. HCl and centrifuge.	
		<i>Residue:</i> Yellow crystals of [Pd(NH ₃) ₃ Cl ₂]. Boiled with 5 drops of conc. HCl and one drop of conc.HNO ₃ . Extracted with minimum 1N HCl and 2 drops of dimethyl glyoxime reagent. Yellow ppt Palladium,	<i>Centrifugate:</i> A few crystals of NH ₂ OH.HCl are added , warmed and centrifuged.
		<i>Residue:</i> Red Crystalline powder shows Selenium	<i>Centrifugate:</i> A crystal of N ₂ H ₄ . 2HCl was added and boiled. A blue-black colour crystalline ppt shows Tellurium

ANALYSIS OF GROUP II [A and B- Copper and tin groups]
Separation of copper and Tin groups

To the centrifugate from group I, one drop of 6% H_2O_2 is added. Heated and dilute to about 3 c.c. Transferred to a small conical flask, neutralized with aq NH_3 (litmus) and 1 to 2 c.c. of dil.HCl is added. Heated and saturated with H_2S . It is preferable to close the flask with a one-holed stopper and introduce the H_2S delivery tube through it so that the tip is above the solution level. This enables to build up a slight pressure of H_2S . The flask should be well shaken. The precipitate is removed by centrifugation, diluted the centrifugate to 5 c.c. Warmed, saturated with H_2S again and centrifuged. Washed the residue with 1 c.c. water and added washings to centrifugate.

<i>Residue:</i> Contains sulphides of copper and tin groups. Boiled with 1 to 2 c.c. of 2N NaOH, heated and centrifugated. Washed residue with water and combined the centrifugate and washings.		<i>Centrifugate:</i> Examined for group group III and subsequent groups.
<i>Residue:</i> copper group sulphides. This residue is used for the analysis of II_A group.	<i>Centrifugate:</i> Neutralised with dil.HCl (litmus), heated and centrifuged. Washed the precipitate. The centrifugate and washings are discarded. The precipitate is used for the analysis of II_B group.	

Analysis of group - II_A

The ppt is washed once with 1 c.c. of water to remove alkali. Washings are discarded. 1.5 c.c. of dil. HNO₃ is added to residue. Boiled the solution, 2 drops of dil. H₂SO₄ are added and centrifuged.

<i>Residue:</i> HgS and PbSO ₄ . Washed with 1 c.c. of water. Centrifuged and washings are discarded. 5 drops of saturated NH ₄ OAc, heated and centrifuged.		<i>Centrifugate:</i> Nitrates of Cu ²⁺ , Cd ²⁺ and Bi ³⁺ . Slight excess of ammonia (smell) is added in drop wise. Heated and centrifuged.	
<i>Residue:</i> 3 drops of conc. HCl are added and heated. Diluted to ½ c.c. with water and 2 drops of SnCl ₂ are added. White or grey ppt. indicates Mercury	<i>Centrifugate:</i> 1 drop of dil. HOAc and 2 drops of K ₂ CrO ₄ . Yellow ppt. shows Lead	<i>Residue:</i> Dil. HCl is added drop wise till the residue is dissolved and 3 drops of stannite solution is added. Black and white ppt shows Bismuth	<i>Centrifugate:</i> Deep blue if Cu is present. Divided into two portions. (i) Dil. HOAc is added drop wise till pale blue and then 2 drops of K ₄ [Fe(CN) ₆] are added. Reddish brown ppt indicates Copper (ii) To another part, drops of KCN are added till the solution become colourless. Diluted with equal volume of water. H ₂ S is passed. Yellow ppt indicates Cadmium

Sodium stannite solution: Sodium hydroxide solution is added drop wise to 0.5 ml of SnCl₂ solution. A white precipitate is formed and continued the addition of NaOH till the precipitate is dissolved.

Analysis of group II_B

The ppt is washed with NH_4Cl solution. 10 drops of conc. HCl are added, stirred and heated for a minute. 10 drops of water are added. Stirred and centrifuged.

<i>Residue:</i> As_2S_3 and MoS_3 . 5 drops of saturated $(\text{NH}_4)_2\text{CO}_3$ solution is added. Stirred well and centrifuged.		<i>Centrifugate:</i> Contains Tin and Antimony
<i>Residue:</i> Dark brown MoS_3 . 3 drops of conc. HCl and 2 drops of bromine water are added. The solution is boiled to expel the excess bromide. The solution is then diluted and 5 drops of 10% KCNS , 3 drops of SnCl_2 , 10 drops of amyl alcohol were added and shaken. Formation of red alcohol layer indicates Molybdenum	<i>Centrifugate:</i> The centrifugate is acidified. (i) To one portion, 5 drops of saturated solution of $(\text{NH}_4)_2\text{CO}_3$ are added and shaken. Acidified the centrifugate carefully with dil HCl . Yellow ppt is formed indicating As. (ii) To another portion, 3 drops of AgNO_3 are added and then aq NH_3 drop by drop. Reddish brown precipitate is formed indicating As. (iii) To another portion a piece of Zn and 5 drops of dil H_2SO_4 are added. The test tube plugged loosely with cotton and placed HgCl_2 paper over it. Yellow or reddish stains indicates Arsenic	Divide centrifugate into several portions. i) To 5 drops of the centrifugate, a small quantity of iron filings or Zn dust is added. Warmed to dissolve the metal and 3 drops of HgCl_2 is added. White Hg_2Cl_2 or grey Hg indicates Tin ii) To 5 drops of the centrifugate, a few crystals of NaNO_2 are added and shaken. 5 drops of Rhodamine B reagent is added. Lavender colour indicates Antimony iii) To 5 drops of centrifugate, crystals of oxalic acid are added to saturation. The solution is diluted and H_2S is passed. Orange precipitate indicates Antimony

Spot test for Molybdenum: To a drop of molybdate solution, a drop of 10% KSCN is added. Then a drop of Conc. HCl and a drop of SnCl_2 are added. Red spot indicates Mo.

Before proceeding to the analysis of III group cations, the interfering radicals should be removed.

Analysis of group III [iron group]

H₂S is boiled off from the centrifugate from group II. 2 drops of conc. HNO₃ are added and boiled. A drop of the solution is tested for the presence of Fe⁺³ with KSCN. Two drops of FeCl⁺³ are added to the bulk of the solution and then five drops of saturated NH₄Cl solution. Heated without boiling. To the hot solution, aq.NH₃ is added to very slight excess. Centrifuged, washed the residue with small amounts of NH₄Cl solution and washings are added to centrifuge. The centrifugate is examined for groups IV and on.

<u>Residue:</u> Hydrated oxides of various metals of the group. Dissolved in minimum amount of dil HCl, about 50 mg of oxalic acid crystals are added, digested to hot and centrifuged.	
<u>Residue:</u> Oxalates of Th and Ce 1 c.c. of saturated (NH ₄) ₂ C ₂ O ₄ are added, boiled and centrifuged.	<u>Centrifugate:</u> Neutralised with aq.NH ₃ and digested to hot for a few minutes. Centrifuged and discarded the sol. The residue is washed with dil NH ₄ Cl solution and washings are discarded. Suspended in 1 c.c. of water in a boiling tube and about 50 mg Na ₂ O ₂ are added. Boiled till effervescence ceases, centrifuged, washed the residue with water and combined washings with centrifugate.
<u>Residue:</u> 1	<u>Centrifugate:</u> 2
	<u>Residue:</u> Hydrated oxides of Tl, Fe, Ti, Zr and Mn. Redissolved in dil HCl, boiled and divided into several test portions. i. To the first portion, 2 drops of KI and then Na ₂ S ₂ O ₃ (in drops) are added. Yellow ppt of TlI indicates Thallium ii. To the second portion, syrupy phosphoric acid is added in dropwise just to decolourise the iron. 2 drops of 6% H ₂ O ₂ and 2 drops of dil H ₂ SO ₄ are added. Orange colour indicates Titanium Ppt indicates Zirconium . Centrifuged.
	<u>Centrifugate:</u> Chromate, aluminate, uranate, vanadate and beryllate. Acidified with dil HNO ₃ , 5 drops of Pb(NO ₃) ₂ are added and then about 200 mg of NH ₄ OAc crystals are added, stirred well and centrifuged.
	<u>Residue:</u> PbCrO ₄ and Pb(VO ₃) ₄ Dissolve in 10 drops of dil.HNO ₃ and cooled. 10ml of amyl alcohol & 3 drops of 6% H ₂ O ₂ , shaken. Blue alcohol layer indicates Chromium Reddish brown aq. Layer shows vanadium. The aq.
	<u>Centrifugate:</u> Nitrates of Pb ⁺² , Al ³⁺ , Be ²⁺ , UO ₂ ⁺² 3 drops of dil. HCl are added and H ₂ S is passed. Centrifuged and precipitated PbS is rejected. The centrifugate is boiled to expel H ₂ S. Cooled and saturated [(NH ₄) ₂]CO ₃ is added drop wise carefully. Boiled for a minute and centrifuged.
	<u>Residue:</u> Basic carbonates & hydroxides of Al and Be. Dissolved in the minimum volume of dil.HCl, 2 drops of Na ₂ S ₂ O ₃ are added. Warmed and centrifuged.
	<u>Centrifugate:</u> Complex of uranyl carbonate Evaporated to a small volume, acidified with dil.HCl (to remove any ppt) and 2 drops of K ₄ [Fe(CN) ₆] are added. Brown ppt turns yellow on adding NaOH indicates Uranium
	<u>Residue:</u> Al(OH) ₃ Confirmed by Thenard's blue test Aluminium
	<u>Centrifugate:</u> Beryllium Confirmed by Quinalizarin test Beryllium

		<p><u>Residue:</u> White Zirconium phosphate</p> <p>Zirconium</p> <p><u>Centrifugate:</u> 20 mg of $\text{Na}_2\text{S}_2\text{O}_3$ is added and heated. White ppt of $\text{Ti}(\text{OH})(\text{PO}_4)$</p> <p>Titanium</p> <p>iii. To the third portion, a drop of conc. H_2SO_4 is added to remove HCl. 5 drops of dil. HNO_3 & 50mg of NaBiO_3 are added and shaken. Purple colour of HMnO_4 indicates</p> <p>Manganese.</p>	<p>solution is boiled, 3 drops of dil. HCl is added and cooled. 2 drops of 2% aq. soln. of tannin and aq. NH_3 are added. Deep blue colour .</p> <p>To another portion, 3 drops of aq. NH_3 is added and H_2S is passed. Red colour indicates</p> <p>Vanadium</p>			
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1. Residue: Cerium oxalate. 3 drops of 2N NaOH are added and boiled. Centrifuged and the residue is dissolved in dil. HNO_3 . 3 drops of dil. aq. NH_3 and 2 drops of 6% H_2O_2 are added to 2 drops of the solution and heated. Yellowish brown CeO_2 indicates **Cerium**.
A drop of conc. HNO_3 is added to the 2 drops of the solution and boiled. It is evaporated to dryness and the residue is extracted with three drops of water and one drop of 5% alcoholic solution of anthranilic acid. Dark blue ppt is formed which rapidly dissolves to a brown solution. This indicates **Cerium**.
2. Centrifugate: Oxalato complex of thorium. 5 drops of dil HCl are added to the solution. White ppt of $\text{Th}(\text{C}_2\text{O}_4)_2$ is formed. 5 drops of 2N NaOH are added, boiled and centrifuged. So formed, residue $\text{Th}(\text{OH})_4$ is dissolved in dil. HCl. Just neutralized with aq. NH_3 and 5 droops of m-nitrobenzoic acid reagent is added. Heated to 80°C . White ppt indicates **Thorium**.

Thenard's blue test: Al^{+3} is best confirmed by the Thenard's blue test since Be^{+2} interferes in the aluminon and alizarins tests. The residue of $\text{Al}(\text{OH})_3$ is shaken with a little water and poured on a piece of filter paper. Two drops of $\text{Co}(\text{NO}_3)_2$ solution are then added and the paper is burnt. Blue tinted ash (Thenard's blue) shows aluminium.

Quinalizarin test for Be^{+2} : Quinalizarin (1:2:5:8 – tetrahydroxy anthraquinone gives a blue colour with Be^{+2} in faintly alkaline medium. The reagent is 0.05% solutionj in 0.1N NaOH. Al^{+3} , Mg^{+2} ions interfere in this test. Al^{+3} gives a red-violet colour while Mg^{+2} gives a similar blue colour. In alkaline solutions Al^{+3} does not interfere if present in small quantities. The interference from Mg^{+2} is overcome by adding as drop of bromine water.

Analysis of Group IV

To the centrifugate from III group cations, aq. NH_3 is added if necessary and H_2S is passed till the completion precipitation. Heated for a few minutes and centrifuged. The residue washed with 1 c.c. water and washings are added to centrifugate.

<i>Residue:</i> Stirred with 1 c.c. water and 5 drops of dil. HCl are added and centrifuged.			
<i>Residue:</i> CoS and NiS. 5 to 10 drops of conc. HCl is added and transferred to a beaker. A small crystal of KClO_3 is added, boiled and evaporated just to dryness. Dissolved in 1 c.c. water and divided into two portions.		<i>Centrifugate:</i> Zn^{2+} , Mn^{2+} . NaOH is added in slight excess and centrifuged.	
To 5 drops of solution, a few crystals of NH_4CNS and 10 drops of amyl alcohol are added and shaken. Blue alcohol layer shows Cobalt.	To 5 drops of solution, 3 drops of dimethylglyoxime reagent and aq. NH_3 are added. Scarlet ppt indicates Nickel	<i>Residue:</i> $\text{Mn}(\text{OH})_2$ It turns brown in air. 10ml of dil. HNO_3 and about 50mg NaBiO_3 are added. Stirred well and centrifuged. Pink coloured centrifugate shows Manganese	<i>Centrifugate:</i> Divided into two portions. (i) H_2S is passed through a portion of the solution. White or dry white ppt (ii) A part of the solution is acidified with HOAc and $[\text{K}_4\text{Fe}(\text{CN})_6]$ is added. White ppt indicates Zinc

Analysis of group V

The centrifugate from zinc group is neutralized with dil.HNO₃ and evaporated to dryness. Heated continuously to remove ammonia salts by volatilisation and cooled. The ppt is dissolved in the minimum quantity of dil. HCl and 3 drops in excess are added. Neutralised with aq.NH₃ and 2 drops are added in excess. Saturated (NH₄)₂CO₃ solution is added dropwise to precipitate cations completely. The precipitate is digested and centrifuged. Washed with 1 c.c. water and washings are added to the centrifugate.

<i>Residue:</i> Dissolved in the minimum amount of dil HOAc, then 3 drops of K ₂ CrO ₄ solution are added and centrifuged.		<i>Centrifugate:</i>
<i>Residue:</i> Yellow BaCrO ₄ Dissolved in conc.HCl and examined flame colour. Transient green colour indicates Barium	<i>Centrifugate:</i> Ca ⁺² , Sr ⁺² Neutralised with aq.NH ₃ . Reprecipitated as carbonates, centrifuged and the centrifugate is rejected. Residue is redissolved in dil HOAc and tested as described below: (i) <u>Test for Sr⁺²</u> : To 3 drops of solution, 3 drops of CaSO ₄ solution is added, boiled and let to stand. White ppt of SrSO ₄ is formed. Centrifuged and the centrifugate is discarded, stirred with 5 drops of water and poured on a small piece of filter paper. The paper is charred, moistened the product with conc. HCl, the flame colour is examined. Flashes of crimson indicates Strontium (ii) <u>Test for Ca⁺²</u> : To 5 drops of the solution, 5 drops of saturated (NH ₄) ₂ SO ₄ solution is added, boiled, cooled and centrifuged. (a) To one half of the centrifugate, 3 drops of 3% ammonium oxalate solution followed by aq.NH ₃ are added. Formation of white ppt indicates Ca ²⁺ . It is confirmed by flame test to give brick red colour. (b) To other half of centrifugate, 3 drops of saturated NH ₄ Cl and 3 drops of [K ₄ Fe(CN) ₆] are added and allowed to stand. Pale yellow ppt indicates Calcium	Examined for group VI cations.

ANALYSIS OF GROUP VI

This group includes Mg^{+2} , NH_4^+ and the alkali metals (Li^+ , Na^+ and K^+). NH_4^+ is tested out in the beginning of cation analysis itself.

Evaporate the centrifugate from group V to dryness, add 5 drops of conc. HNO_3 and evaporate cautiously till there are no more fumes. Extract residue with water. Divide into several portions,

Test for Mg^{2+} :

- To 3 drops of the solution 2 drops of NH_4Cl , 2 drops of aqueous ammonia and three drops of Na_2HPO_4 are added. The sides of the tube are scratched with a glass rod. White crystalline precipitate of MgNH_4PO_4 shows magnesium.
- To 3 drops of the test solution 5 drops dil. HCl are added. Stirred and one drop of magneson reagent and then NaOH solution is added drop wise. Blue precipitate confirms Mg .

Magneson reagent: 10 mg of magneson (p-nitrobenzoresorcinol) is dissolved in 100 ml of 1 N NaOH solution.

Test for Na^+ :

- To 5 drops of the solution an equal quantity of-zinc uranyl acetate and 10 drops of ethanol are added. Shaken and allowed to stand. Yellow crystalline precipitate shows sodium.
- To 5 drops of the solution, 5 drops of uranyl magnesium acetate solution and a few drops of methanol are added. Yellow crystalline precipitate of sodium magnesium acetate confirms sodium.
- A few drops of the solution are mixed with 2 drops of conc. HCl and performed flame test. Golden yellow colour shows sodium.

Test for K^+ :

- To 3 drops of the solution, 3 drops sodium hexanitritocobaltate (III) [cobalt nitrite] solution and then 6 drops of ethanol are added. Shaken and allowed to stand. Yellow precipitate shows potassium.
- To 3 drops of the solution, 3 drops of a freshly prepared saturated solution of tartaric acid are added. To it 5 drops alcohol and are added and shaken vigorously. White precipitate show potassium.
- A few drops of the solution are mixed with 2 drops of conc. HCl and performed flame test. Pale violet (lilac) colour shows potassium.

Test for Li⁺:

- a) To 5 drops of the solution, a few drops of ammonium hydroxide are added till ammoniacal and NH_4F solution is added. Slow formation of a white gelatinous precipitate indicates lithium.
- b) To 5 drops of the solution, an equal quantity of zinc uranyl acetate and 10 drops of methanol are added. Shaken and allowed to stand. Like in sodium test, yellow crystalline precipitate forms. The precipitate is $\text{LiZn}[(\text{UO}_2)_3(\text{Oac})_9] \cdot 6\text{H}_2\text{O}$.
- c) To 3 drops of the solution, 2 drops of conc.HCl are added. Flame test is done. Scarlet red colour indicates lithium.

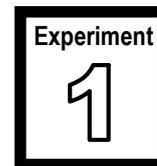
Test for Cs⁺:

Cesium imparts a blue colour to the flame and Cs^+ forms a bright red precipitate with KBiI_4 .

Feric periodate reagent: Dissolve 2g KIO_4 in 10cc of freshly prepared 2 N KOH solution. Dilute to 50cc with water add 3 cc of 10% FeCl_3 solution and dilute to 100cc with 2N KOH.



DETERMINATION OF CHROMIUM



AIM:

To determine the amount of chromium (VI) present in the given solution by volumetry.

APPARATUS:

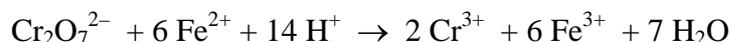
Burette (50ml), pipette (20ml), volumetric flask (250ml), measuring cylinder (10ml), conical flask (250ml).

CHEMICALS REQUIRED:

Potassium dichromate, ammonium ferrous sulphate, sulphuric acid, phosphoric acid, diphenylamine indicator.

PRINCIPLE:

Potassium dichromate is an excellent primary standard due to its availability in pure form and its stability is upto its fusion point. Potassium dichromate reacts with iron(II) in acidic medium.



From the equation it follows that equivalent weight of potassium dichromate is equal to $1/6^{\text{th}}$ of its formula weight = 49.03gm.

$$0.05\text{N dichromate solution in 250 ml requires } \frac{49.03 \times 0.05}{4} = 0.6129 \text{ g}$$

The green colour due to the Cr^{3+} ions formed by the reduction of potassium dichromate makes it impossible to ascertain the end point of a dichromate titration which is not possible for visual inspection. So, a red-ox indicator like diphenylamine is employed which gives a strong and unmistakable colour change. Since, the ferric ion interferes in the detection of end point, they are complexed by the addition of phosphoric acid.

PREPARATION OF REAGENTS:

Preparation of standard potassium dichromate solution (0.05N):

About 2g of A.R. potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) is powdered finely and heated for 30–60 minutes in an air oven at $140 - 150^\circ\text{C}$ and allowed to cool in a desiccator. About 0.613 g of substance is weighed accurately and quantitatively transferred into a 250 ml volumetric flask with the aid of a small funnel. The transferred potassium dichromate is dissolved in small amount of distilled water and then made upto the mark. The normality is calculated.

Preparation of iron(II) solution (0.05N):

Approximately 0.05N Mohr's salt (Ferrous ammonium sulphate) is prepared by dissolving about 5 g of the salt in 250 ml of 2N sulphuric acid solution.

Preparation of diphenylamine (DPA) indicator:

About 1.0 g of diphenylamine is dissolved in 100 ml of conc. sulphuric acid.

PROCEDURE:**(a) Standardisation of iron(II) solution:**

The burette is filled with standard potassium dichromate solution and initial reading is noted. 20.0 ml. of iron(II) solution is pipetted out into a 250 ml conical flask. To it 10 ml of 10N sulphuric acid is added and the solution is diluted to 50 ml by adding distilled water. To the solution 5ml syrupy phosphoric acid and two or three drops of diphenylamine indicator are added. Then titrated against standard potassium dichromate taken in a burette. The end point is colourless to blue via green. The titrations are repeated until concurrent values are obtained.

Knowing the normality and volume of potassium dichromate solution run down and the volume of iron(II) solution taken, the normality of iron(II) can be calculated using the formula $V_1N_1 = V_2N_2$.

The given unknown solution of dichromate is made up to the mark in 100 ML volumetric flask and the amount of chromium present is determined.

ESTIMATION OF CHROMIUM:

The burette is filled with unknown potassium dichromate solution and initial reading is noted. 20.0 ml. of the standardized iron(II) solution is pipetted out into a 250 ml conical flask. To it 10 ml of 10N sulphuric acid is added and the solution is diluted to 50 ml by adding distilled water. To the solution 5ml syrupy phosphoric acid and two or three drops of diphenylamine indicator are added. Then titrated against unknown potassium dichromate taken in a burette. The end point is colourless to blue via green. The titrations are repeated until concurrent values are obtained.

From the normality and volume of iron(II) taken and the volume of the unknown dichromate solution run down, the normality of dichromate in the given solution can be calculated using the formula $V_2N_2 = V_3N_3$. Thus, from the normality of the given dichromate solution, the amount of chromium present in the given solution can be calculated.

Report: The amount of chromium present in the given 100 ml solution is _____ g

OBSERVATIONS AND CALCULATIONS**Preparation of standard potassium dichromate solution:**

Weight of the bottle + $K_2Cr_2O_7$ = W_1 = _____ g

Weight of weighing bottle = W_2 = _____ g

W_3 = Weight of $K_2Cr_2O_7$ transferred into 250ml volumetric flask = $(W_1 - W_2)$ = _____ g

N_1 = Normality of standard dichromate solution

$$= \frac{\text{Weight of potassium dichromate taken} \times 1000}{\text{Eq. wt. of potassium dichromate} \times \text{volume of dichromate solution}}$$

$$= \frac{W_3 \times 1000}{49.03 \times 250} = \text{_____ N}$$

Standardisation of iron(II) solution:

S.No.	Vol. of iron(II) sol. transferred (V_1 ml)	Burette Readings		Volume of dichromate rundown (V_2 ml)
		Initial	Final	
1	20.0			
2	20.0			
3	20.0			

We know that $V_1N_1 = V_2N_2$

Where V_1 = Volume of standard dichromate solution = _____ ml

N_1 = Normality of standard dichromate solution = _____ N

V_2 = Volume of iron(II) solution = 20ml

N_2 = Normality of iron(II) = ?

Therefore, $N_2 = \frac{V_1N_1}{V_2} = \text{_____ N}$

Determination of chromium(VI) in the given Solution:

S.No.	Vol. of unknown iron(II) transferred (V_3 ml)	Burette Readings		Volume of chromium sol. rundown (V_2 ml)
		Initial	Final	
1	20.0			
2	20.0			
3	20.0			

We know that $V_2N_2 = V_3N_3$

Where $V_2 =$ Volume of iron(II) solution = 20ml

$N_2 =$ Normality of iron(II) solution = _____N

$V_3 =$ Volume of given chromium solution = _____ ml

$N_3 =$ Normality of given chromium solution = _?

Therefore, $N_3 = \frac{V_2N_2}{V_3} =$ _____ N

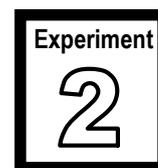
Amount of chromium present in the given 100 ml solution =

$\frac{\text{Normality of the given dichromate solution} \times \text{Eq. wt. of chromium} \times \text{Volume of the given solution}}{1000}$

$$= \frac{N_3 \times 17.3366 \times 100}{1000} = \text{_____ g}$$



DETERMINATION OF COPPER



AIM:

To determine the amount of copper (II) present in the given solution by iodometry.

APPARATUS:

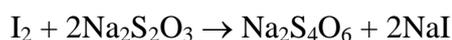
Burette (50ml), pipette (20ml), volumetric flask (250ml), measuring cylinder (10ml), conical flask (250ml).

CHEMICALS REQUIRED:

Analytical reagent grade copper sulphate penta hydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$), sulphuric acid, sodium carbonate, glacial acetic acid, sodium thiosulphate, potassium iodide, ammonium thiocyanate, starch.

PRINCIPLE:

When a solution of potassium iodide is added to a slightly acidic solution of copper sulphate, iodine is liberated and the liberated iodine is titrated against standard solution of sodium thiosulphate (hypo). Potassium iodide reacts with copper sulphate as follows.



From the equation it follows that equivalent weight of copper sulphate pentahydrate is equal to its formula weight = 249.68gm.

$$0.05\text{N copper sulphate pentahydrate in 100 ml requires } \frac{249.68 \times 0.05}{10} = 1.2484 \text{ g}$$

PREPARATION OF REAGENTS:

Preparation of standard copper sulphate solution (0.05N):

About 1.25 g of A.R. copper sulphate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) is weighed accurately and quantitatively transferred into a 100 ml volumetric flask with the aid of a small funnel. The transferred copper sulphate is dissolved in small amount of distilled water and 3 or 4 drops of dil. H_2SO_4 are added to prevent hydrolysis. The solution is made upto the mark and the normality is calculated.

Preparation of hypo (0.05N):

About 3.2 g of sodium thiosulphate is weighed and dissolved in 250 ml of distilled water.

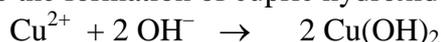
Preparation of starch solution:

About one gram of soluble starch is made a paste with a little amount of distilled water and is poured in about 100 ml of boiling distilled water. The solution is boiled for two minutes and cooled.

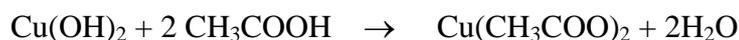
PROCEDURE:**(a) Standardisation of sodium thiosulphate:**

The burette is filled with hypo solution to be standardized and initial reading is noted.

20.0 ml. of standard solution of copper is transferred into a conical flask. To this sodium carbonate solution (1%) is added drop wise till the appearance of the slight turbidity. The formation of the turbidity is due the formation of cupric hydroxide.



Then about 5ml of acetic acid is added where upon turbidity disappears by the formation of cupric acetate.



10ml of 10% solution of potassium iodide are added and diluted to 100ml. The contents are allowed to stand for about 10 minutes, placing a watch glass on the top of the flask in order to arrest liberated iodine vapours. There after, vapours are condensed by flushing distilled water with the jet of the wash bottle. Hypo is rundown from the burette until the colour of the solution turns to straw yellow. To this 1-2ml of starch solution is added and again hypo is rundown until the solution turns to pale blue. To this about 2 g of ammonium thiocyanate salt is added. Then the solution turns deep blue. Again hypo is run down until the blue colour just disappears to give a fleshy white precipitate. The final reading of the burette is noted. The difference between initial and final readings of hypo gives the volume of hypo rundown. The titrations are repeated until concurrent values are obtained.

Knowing the normality and volume of copper solution taken and the volume of hypo run down, the normality of hypo can be calculated using the formula $V_1N_1 = V_2N_2$.

The given unknown solution of copper is made up to the mark in 100 ML volumetric flask and the amount of copper present determined.

ESTIMATION OF COPPER:

20.0 ml. of the given solution of copper is transferred into a conical flask. To this sodium carbonate solution (1%) is added drop wise till the appearance of the slight turbidity. Then about 5ml of acetic acid and 10ml of 10% solution of potassium iodide are added and diluted to 100ml. The contents are allowed to stand for about 10 minutes, placing a watch glass on the top of the flask in order to arrest liberated iodine vapours. There after, vapours are condensed by flushing distilled water with the jet of the wash bottle. Hypo is run down from the burette until the colour of the solution turns to straw yellow. To this 1-2ml of starch solution is added and again hypo is run down until the solution turns to pale blue. To this about 2 g of ammonium thiocyanate salt is added. Then the solution turns deep blue. Again hypo is run down until the blue colour just disappears to give a fleshy white precipitate. The final reading of the burette is noted. The difference between initial and final readings of hypo gives the volume of hypo run down. The titrations are repeated until concurrent values are obtained.

From the normality and volume of hypo run down and the volume of the given solution, the normality of copper in the given mixture can be calculated using the formula $V_2N_2 = V_3N_3$. Thus, from the normality of the given Cu^{+2} solution, the amount of copper present in the given solution can be calculated.

Report: The amount of copper present in the given 250 ml solution is _____ g

OBSERVATIONS AND CALCULATIONS**Preparation of standard copper sulphate solution:**

Weight of the bottle + $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ = W_1 = _____ g

Weight of weighing bottle = W_2 = _____ g

W_3 = Weight of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ transferred into 100ml volumetric flask = $(W_1 - W_2)$ = _____ g

N_1 = Normality of standard copper sulphate solution

$$= \frac{\text{Weight of copper sulphate taken} \times 1000}{\text{Equivalent weight of copper sulphate} \times \text{volume of copper solution}}$$

$$= \frac{W_3 \times 1000}{249.68 \times 100} = \text{_____ N}$$

Standardisation of Hypo:

S.No.	Vol. of standard copper sol. transferred (V_1 ml)	Burette Readings		Volume of hypo rundown (V_2 ml)
		Initial	Final	
1	20.0			
2	20.0			
3	20.0			

We know that $V_1N_1 = V_2N_2$

Where $V_1 =$ Volume of standard copper sulphate solution = 20ml

$N_1 =$ Normality of standard copper sulphate solution =

$V_2 =$ Volume of hypo = _____ ml

$N_2 =$ Normality of hypo = ?

Therefore, $N_2 = \frac{V_1N_1}{V_2} = \text{_____} N$

Determination of Cu^{2+} in the given Solution:

S.No.	Vol. of unknown copper sol. transferred (V_3 ml)	Burette Readings		Volume of hypo rundown (V_2 ml)
		Initial	Final	
1	20.0			
2	20.0			
3	20.0			

We know that $V_2N_2 = V_3N_3$

Where $V_2 =$ Volume of hypo = _____ ml

$N_2 =$ Normality of hypo = _____ N

$V_3 =$ Volume of given copper solution = 20ml

$N_3 =$ Normality of given copper solution = _?

$$\text{Therefore, } N_3 = \frac{V_2 N_2}{V_3} = \text{_____ N}$$

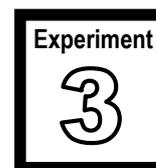
Amount of copper present in the given 100 ml solution =

$$\frac{\text{Normality of the given copper solution} \times \text{Atomic wt. of copper} \times \text{Volume of the given solution}}{1000}$$

$$= \frac{N_3 \times 63.54 \times 100}{1000} = \text{_____ g}$$



DETERMINATION OF TOTAL HARDNESS OF WATER



AIM: To determine the total hardness of the given water sample by complexometry.

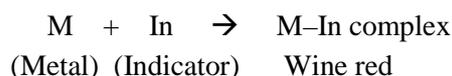
APPARATUS: Burette-50ml, conical flask-250ml, Measuring cylinder (5ml)

CHEMICALS REQUIRED:

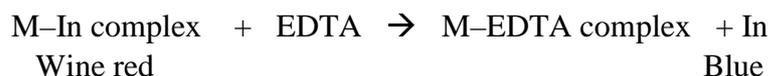
Disodium salt of EDTA, ammonium chloride, ammonium hydroxide, eriochrome black-T (EBT).

THEORY:

The hardness of the water is generally due to the presence of calcium and magnesium ions. Ions like Ca^{2+} and Mg^{2+} have a tendency to form complexes with EDTA. Certain dyestuffs which form weak coloured complexes with cations can serve as visual complexometric indicators. For titrimetric determination of such metal ions, first the metal - indicator complex is formed which is wine red in colour.



During titrations with EDTA, the metal ions are progressively complexed by EDTA. At final the indicator is displaced from metal-indicator (M-In) complex leaving free indicator. The colour change accompanying this progress gives the end point.



PREPARATION OF REAGENTS:

Preparation of standard EDTA solution:

Disodium salt of ethylene diamine tetra acetic acid is available commercially and can be used as primary standard. The commercial analytical reagent may contain a trace of moisture. So it is dried at 80°C . Then its composition agree exactly with the formula $\text{Na}_2\text{H}_2\text{C}_{10}\text{H}_{12}\cdot 2\text{H}_2\text{O}$ with molecular weight 372.5. About 0.9314 g of disodium salt of EDTA is weighted accurately and dissolved in 250 ml of distilled water in a volumetric flask.

Preparation of buffer solution (pH=10):

7 gm of ammonium chloride is dissolved in 56.8 ml of liquor ammonia (i.e., ammonium hydroxide) and diluted to 100 ml.

Preparation of eriochromeblack–T (EBT):

0.2 gm of eriochromeblack–T dyestuff is dissolved in 15 ml of triethanolamine and 5 ml of absolute alcohol is added to reduce viscosity. The indicator is stable for several months.

(or)

4.0 gm of eriochromeblack–T dyestuff is dissolved in 100 ml of methanol, which is stable for atleast one month.

PROCEDURE:

By the aid of a burette, a 50 ml of the given water sample is transferred in to a 250 ml conical flask. About 4 ml of buffer solution and two drops of EBT indicator are added. The wine red solution is titrated against standard EDTA solution taken in a burette. The end point is wine red to blue.

The experiment is repeated till two concurrent values are obtained and the total hardness is calculated in terms of calcium carbonate.

Method of calculation:

Total hardness of water is determined in terms of amount of CaCO_3 present in million parts of water. Calcium and magnesium forms a 1:1 complex with EDTA.

Report: The total hardness of the given water sample is _____ ppm.

Precautions:

1. The titration should be carried out slowly with the shaking after addition of each drop of EDTA solution, because of the slow formation of complexes.
2. Buffer solution should be freshly prepared.
3. Addition of excess indicator should be avoided.

OBSERVATIONS AND CALCULATIONS:

Weight of Disodium ethylene diamine tetra acetate (w) = _____ g in 250 ml

Molarity of Disodium ethylene diamine tetra acetate solution (M_1)

$$= \frac{\text{Wt. of EDTA salt} \times 1000}{\text{Eq. wt. of EDTA salt} \times \text{volume}}$$

$$= \frac{w \times 1000}{372.25 \times 250} = \text{_____ M}$$

Total hardness determination:

S.No.	Vol. of hard water transferred (V_2 ml)	Burette Readings		Volume of standard EDTA sol. rundown (V_1 ml)
		Initial	Final	
1	50.0			
2	50.0			
3	50.0			

We know that $V_1M_1 = V_2M_2$

Where V_1 = Volume of standard EDTA solution = _____ M

M_1 = Molarity of EDTA solution = _____ M

V_2 = Volume of hard water = 50 ml

M_2 = Molarity of hard water (in terms of CaCO_3) = ?

Therefore, $M_2 = \frac{V_1M_1}{V_2} = \text{_____ M}$

Total hardness of water (in terms of CaCO_3)

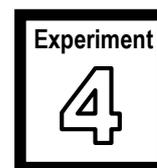
= Molarity of water sample w.r.t. $\text{CaCO}_3 \times \text{Mol. Wt. of } \text{CaCO}_3 \times 1000 \text{ mg/lit}$

= $M_2 \times 100.09 \times 1000 = \text{_____ mg/lit}$

Total hardness of water (in terms of CaCO_3) = _____ mg / lit



DETERMINATION OF NICKEL



AIM:

To determine the amount of nickel present in the given solution by gravimetry.

APPARATUS:

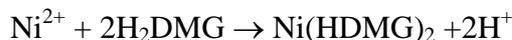
Burette (50ml), volumetric flask (250ml), measuring cylinder (10ml), beakers (500ml), sintered glass crucibles (SG₃).

CHEMICALS REQUIRED:

Nickel sulphate or nickel chloride (preferably nickel ammonium sulphate), hydrochloric acid, ethyl alcohol, dimethyl glyoxime, liquor ammonia (ammonium hydroxide).

PRINCIPLE:

Nickel is precipitated by the addition of the alcoholic solution of dimethyl glyoxime (DMG) (or by an aqueous solution of sodium salt of dimethyl glyoxime) to a hot solution of nickel and then slight excess of ammonia is added. The obtained bright red precipitate is washed with cold water, filtered through SG₃ crucible, weighed as nickel dimethyl glyoximate after drying in an oven at 100 to 110⁰C.



PROCEDURE:

50.0ml of the nickel solution is transferred into a 500ml beaker. To it 3 to 4ml of 1:1 dilute HCl and 50ml of water are added. To the hot nickel solution of 30 ml of 1% alcoholic solution of dimethylglyoxime is added and then slight excess of aqueous ammonia solution is added to precipitate nickel as nickel dimethylglyoximate. The beaker containing precipitate and contents are heated on a steam bath for about one hour to coagulate the precipitate so as to filter easily. Then the solution is transferred through a previously weighed sintered glass crucible dried at (100 to 120⁰C). The precipitate is washed with cold water until the washings do not give test for chloride. The precipitate is dried in an oven at 100–110⁰C, cooled in a desiccator and weighed. From the weight of nickel dimethyl glyoximate obtained, the amount of nickel is calculated.

The same experiment is repeated with another 50.0ml of the given mixture.

Report: The amount of nickel present in the given 250 ml solution is _____ g (original)

The amount of nickel present in the given 250 ml solution is _____ g (duplicate)

Precautions:

1. For the gravimetric determination of nickel, the experiment shall be conducted in duplicate.
2. The crucibles shall be preheated and weighed.

OBSERVATIONS AND CALCULATIONS**Crucible – I: (Original)**

W_1 = Weight of empty sintered Crucible = _____ g

W_2 = Weight of the crucible + nickel dimethyl glyoximate = _____ g

W_3 = Weight of nickel dimethyl glyoximate = $W_2 - W_1$ = _____ g

288.942g of nickel dimethyl glyoximate contains 58.71g of nickel.

Therefore, W_3 g of nickel dimethyl glyoximate (or 50 ml of the given solution) contains =

$$\frac{58.71}{288.942} \times W_3 \text{ g of nickel}$$

Amount of nickel present in the given 250 ml solution = $\frac{58.71}{288.942} \times W_3 \times \frac{250}{50}$ = _____ g

Crucible – II: (Duplicate)

W_4 = Weight of empty sintered Crucible = _____ g

W_5 = Weight of the crucible + nickel dimethyl glyoximate = _____ g

W_6 = Weight of nickel dimethyl glyoximate = $W_5 - W_4$ = _____ g

288.942g of nickel dimethyl glyoximate contains 58.71g of nickel.

Therefore, W_6 g of nickel dimethyl glyoximate (or 50 ml of the given solution) contains =

$$\frac{58.71}{288.942} \times W_6 \text{ g of nickel}$$

Amount of nickel present in the given 250 ml solution = $\frac{58.71}{288.942} \times W_6 \times \frac{250}{50}$ = _____ g



DETERMINATION OF ZINC



AIM:

To determine the amount of zinc present in the given solution by gravimetry.

APPARATUS:

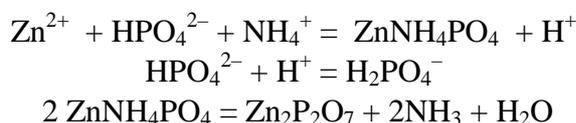
Burette (50ml), volumetric flask (250ml), measuring cylinder (10ml), beakers (500ml), sintered glass crucibles (SG₃).

CHEMICALS REQUIRED:

Conc.HCl, ammonium hydroxide, diammonium hydrogen phosphate, methyl red indicator.

PRINCIPLE:

The zinc can be precipitated as zinc ammonium phosphate ($\text{ZnNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$) and weighed as ZnNH_4PO_4 (after drying at 105°C) or as $\text{Zn}_2\text{P}_2\text{O}_7$ (after ignition at $800 - 900^\circ\text{C}$). The precipitant is diammonium hydrogen phosphate ($(\text{NH}_4)_2\text{HPO}_4$, which exerts an important buffering action (due to $\text{HPO}_4^{2-} / \text{H}_2\text{PO}_4^-$):



It has been shown that the most satisfactory results are obtained over the pH range 6.4 to 6.9 (optimum pH 6.6), and that when the pH exceeds 7.0 the precipitate is difficult to remove from beaker.

Considerable quantities of alkali salts should be absent, for in their presence the precipitate is contaminated with zinc sodium (or potassium) phosphate. These may be removed by double precipitation; the precipitate is dissolved in the minimum volume dilute hydrochloric acid and re-precipitated.

PROCEDURE:

The given solution is made up to the mark. 50 ml of the given solution is transferred into a 500ml beaker and one ml of conc.HCl is added. One or two drops of methyl red indicator are added and the solution is neutralized by the addition of 1:1 ammonium hydroxide solution. The solution is diluted with 100 ml of distilled water. The beaker is heated nearly boiling and treated

25 ml of 10% A.R. diammonium hydrogen phosphate is slowly added. A flocculent precipitate zinc phosphate is first formed. The contents are heated on a water bath for 30 – 60 minutes until the flocculent precipitate changes to crystalline zinc ammonium phosphate, which settled readily. The solution is allowed to stand until the solution is at room temperature. The precipitate is filtered through a weighed SG crucible. Then precipitate is washed with 1% diammonium hydrogen phosphate solution until the precipitate is free from chlorides. Finally the precipitate washed few times with neutral 50% ethanol to remove the phosphate solution. The crucibles are heated to constant weight at 100 – 105⁰C. The precipitate is weighed as zinc ammonium phosphate.

The same experiment is repeated with another 50.0ml of the given mixture.

Report: The amount of zinc present in the given 250 ml solution is _____ g (original)

The amount of zinc present in the given 250 ml solution is _____ g (duplicate)

Precautions:

1. For the gravimetric determination of zinc, the experiment shall be conducted in duplicate.
2. The crucibles shall be preheated and weighed.

OBSERVATIONS AND CALCULATIONS

Crucible – I: (Original)

W_1 = Weight of empty sintered Crucible = _____ g

W_2 = Weight of the crucible + zinc ammonium phosphate = _____ g

W_3 = Weight of zinc ammonium phosphate = $W_2 - W_1$ = _____ g

178.395g of zinc ammonium phosphate contains 65.39g of zinc.

Therefore, W_3 g of zinc ammonium phosphate (or 50 ml of the given solution) contains =

$$\frac{65.39}{178.395} \times W_3 \text{ g of zinc}$$

Amount of zinc present in the given 250 ml solution = $\frac{65.39}{178.395} \times W_3 \times \frac{250}{50} =$ _____ g

Crucible – II: (Duplicate)

W_4 = Weight of empty sintered Crucible = _____ g

W_5 = Weight of the crucible + zinc ammonium phosphate = _____ g

W_6 = Weight of zinc ammonium phosphate = $W_5 - W_4$ = _____ g

178.395g of zinc ammonium phosphate contains 65.39g of nickel.

Therefore, W_6 g of zinc ammonium phosphate (or 50 ml of the given solution) contains =

$$\frac{65.39}{178.395} \times W_6 \text{ g of zinc}$$

Amount of zinc present in the given 250 ml solution = $\frac{65.39}{178.395} \times W_6 \times \frac{250}{50}$ = _____ g

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PRACTICAL - II :: ORGANIC CHEMISTRY

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EXPERIMENT - 1

PREPARATION OF ACETANILIDE

AIM : To Prepare Acetanilide from Aniline.

CHEMICALS REQUIRED:

1. Aniline – 10ml
2. Acetic Anhydride – 10ml
3. Glacial Acetic Acid – 10ml

PROCEDURE :

Take 10ml of Aniline into a 250ml round-bottomed flask equipped with reflux condenser. To this 10ml of acetic acid and 10ml of acetic anhydride are added. Then the mixture is refluxed for 30 to 60 minutes.

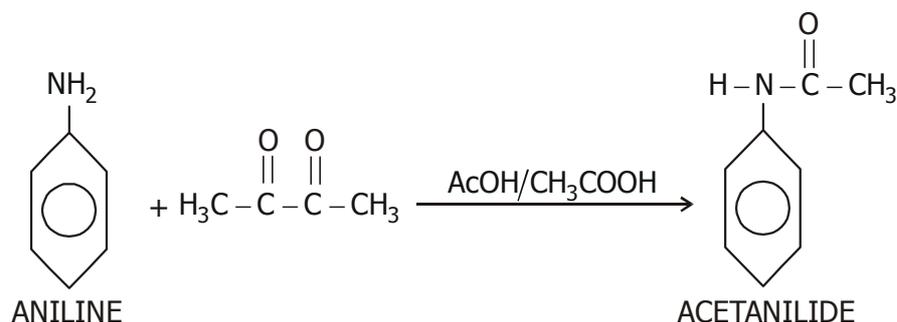
Transfer the contents of the flask into 250 ml ice-cold water. Filter the crude at the Pump. Yellow colored precipitate is formed on the filter paper.

Re-Crystallize the crude Acetanilide from Acetic Acid or from hot water. The crude product is boiled in water and saturated solution is prepared. The suspended impurities are removed by filtering the hot solution. After cooling the crystals of acetanilide separate.

REPORT :

The yield of Acetanilide is _____ Gms.

The melting point of Acetanilide is _____ °C



EXPERIMENT - 2**PREPARATION OF BENZOIC ACID**

AIM : To prepare Benzoic acid by the Oxidation of Benzyl Chloride.

CHEMICALS REQUIRED :

1. Benzyl Chloride - 3 ml
2. Potassium Permanganate - 7 gms
3. Sodium Carbonate (Na_2CO_3) - 1 gms

PROCEDURE :

Suspend in a 250 ml round bottomed flask, 3ml of Benzyl chloride in 125ml of boiling water to which about 1 gms of Sodium Carbonate is added. Introduce slowly 7 gms of finely powdered KMnO_4 .

Heat under reflux until the purple color of KMnO_4 disappears (1 to 4 hours).

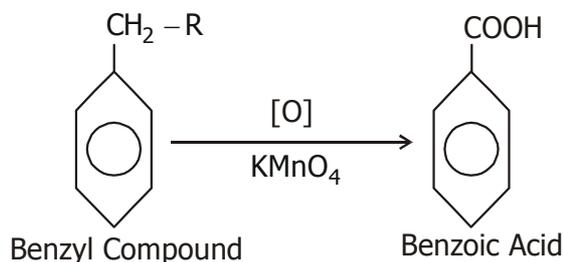
Allow the mixture to cool and filter. Carefully acidify the filtrate with Conc. HCl.

Filter the ppt of Benzoic acid and re-crystallize it from hot water.

REPORT :

The yield of Benzoic acid is _____.

The melting point of Benzoic acid is _____ °C

PRINCIPLE :

Where $\text{R} = -\text{H}, -\text{CH}_3, -\text{X}, -\text{NH}_2$

EXPERIMENT - 3

PREPARATION OF *meta* - DI NITRO BENZENE

AIM : To prepare m - Di-Nitro Benzene from Nitro Benzene by Nitration.

CHEMICALS REQUIRED :

1. Nitro Benzene - 3 ml
2. Conc.HNO₃ - 3.5 ml
3. Conc. H₂SO₄ - 5 ml

PROCEDURE :

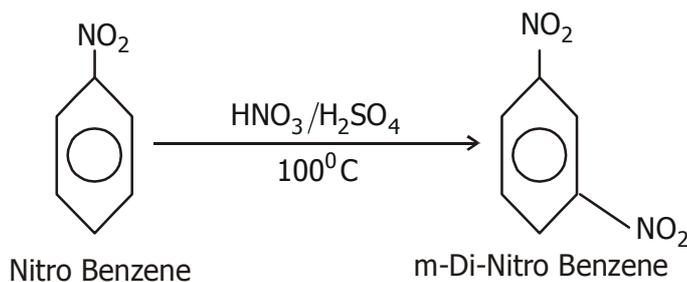
In 100 ml of round-bottomed flask, 3.5 ml of Conc.HNO₃ & 5 ml of Conc. H₂SO₄ are taken. 3ml of Nitro Benzene is added in small portions and shaken well. For each addition, reflux the addition on a water bath for about 30 minutes with a continuous shaking.

Transfer the reaction mixture into 250 ml of crushed ice. Filter, washed with cold water and dried. Re-crystallize the crude M-di Nitro Benzene from Ethanol.

REPORT :

The yield of M- Di-Nitro Benzene is ____.

The melting point of M- Di-Nitro Benzene is ____ °C.



EXPERIMENT- 4**PREPARATION OF ASPIRIN**

AIM : To Prepare Aspirin from Salicylic Acid.

CHEMICALS REQUIRED :

1. Salicylic Acid - 5 gms
2. Acetic Anhydride - 7.5 ml
3. 3M NaOH - 25 ml

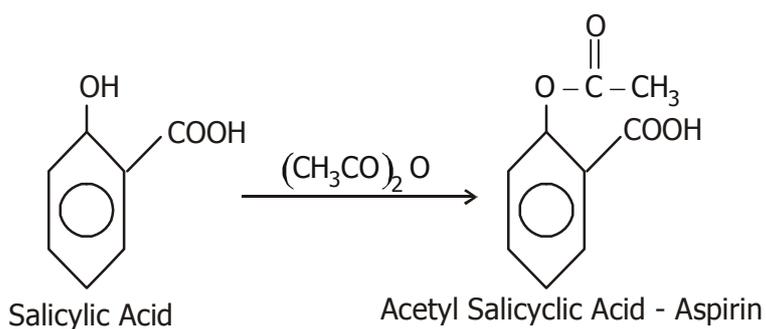
PROCEDURE :

Dissolve 5gms of Salicylic Acid in 25 ml of 3 M NaOH solution. Add 15 to 20 gms of crushed ice followed by Acetic Anhydride. Shake the mixture for about 30 to 60 seconds. The Aspirin separates in a practically pure condition either at once or after acidifying or by the addition of mineral acid (Conc. HCl). Collect the compound. Filter and Re-crystallize it from hot water.

REPORT :

The yield of Aspirin is _____.

The melting point of aspirin is _____ °C



Experiment - 5

PREPARATION OF *p*-BROMO ACETANILIDE

AIM : To prepare *p*-Bromo Acetanilide from Acetanilide.

CHEMICALS REQUIRED :

1. Acetanilide - 13.5 Gms
2. Glacial Acetic Acid - 45 ml
3. Bromine - 5.3 ml

PROCEDURE :

Dissolve 13.5 gms of Acetanilide in 25 ml of Glacial acetic acid in 250 ml Conical flask. To this add 30 ml of Bromine solution (5.3 ml of Bromine in 25 ml of Glacial Acetic acid) drop by drop from Separating funnel.

The process is to be continued for half an hour. The conical flask is to be shaken well till entire process is completed. During the process of addition, the flask should be placed in a water bath containing ice-cold water.

At one instance, a yellow precipitate is observed in the conical flask. Stop the process and transfer the entire mixture in the conical flask into the beaker, which is filled with ice blocks (or) Ice-cold water.

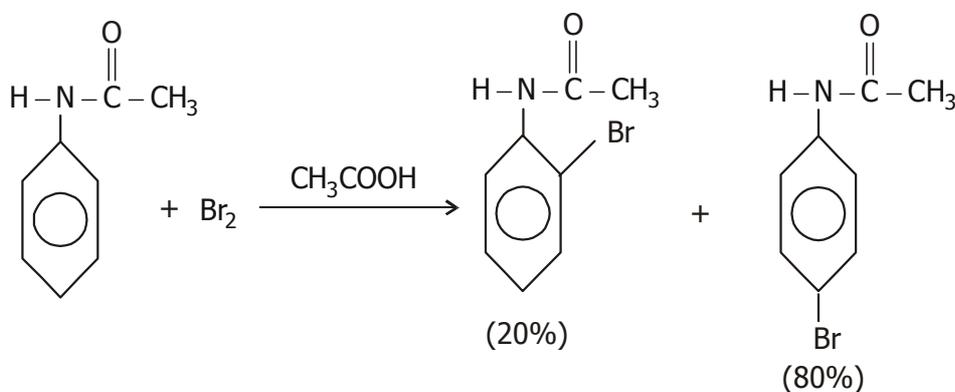
Filter the precipitate and see that no moisture is present and collect the entire mixture and stored it.

Take a small amount of the mixture and re crystallize with alcohol.

REPORT :

The yield of *p*-Bromo Acetanilide is _____.

The Melting point of *p*-Bromo Acetanilide is _____ °C.



QUALITATIVE ANALYSIS SYSTEMATIC PROCEDURE

BINARY MIXTURE ANALYSIS

PRELIMINARY TESTS :

EXPERIMENT	OBSERVATION	INFERENCE
1. Effect of NaHCO_3 : Take a little amount of mixture in a test tube, to this a saturated solution of NaHCO_3 is added.	The given mixture is soluble with quick effervescence and regenerated with conc. HCl.	May be Acidic Compound
2. Effect of dil. HCl: Take a little amount of mixture in a test tube, to this dil. HCl solution is added.	The given mixture is soluble in dil. HCl and regenerated with NaOH.	May be basic compound.
3. Effect of Dil. Alkali: Take a little amount of the mixture in a test tube, to this Dil. Alkali is added.	The given mixture is soluble in dil. Alkali and regenerated with conc. with HCl	May be Phenol compound
4. Ether Solubility: Take a little amount mixture in a test tube, to this ether is added.	The given mixture is insoluble in ether.	May be of the Carbohydrates.

SEPERATION OF MIXTURES

TYPE I :

The best way to confirm is to add a little NaHCO_3 to the mixture. If one of the mixtures is soluble, it is Acidic in nature. To check it add 2- 3 ml of Conc. HCl, then acid re-precipitates.

Take the whole mixture in a 250 ml beaker. Now add saturated solution of Bicarbonate slowly by stirring till all the CO_2 is liberated. Now transfer the whole mixture into a separating funnel and add ether about 30 to 40 ml. shake well. We get two layers, aqueous layer and ether layer (i.e. liquid form and precipitate form). The aqueous layer, which contains the sodium salt of carboxylic acid, is now worked up on by adding dil. HCl to neutralize sodium salt. When neutralization is complete filtered and dried.

The ether layer, which contains organic compound, is taken to an electrical water bath for expelling or evaporation of all the ether. Take the liquid from electrical water bath after a minute. Now, take the precipitate obtained after adding the ether is pressed with filter paper until the moisture is dried up and the melting point is calculated. Take the liquid from electrical water bath and add anhydrous MgSO_4 and decant the liquid. Then it is purified by distillation to get the boiling point. Thus, the compounds are separated.

TYPE II :

The best way to confirm is to add little acid to the mixture. If the one of the mixture is dissolved, it is basic in character. To check it the dissolution is confirmed by adding bicarbonate, and then the base re-precipitates. Now the mixture is taken in a beaker and adds about 10 to 20 ml of 5% acid. This is done in 2 lots of 10 ml each while stirring. The whole solution is taken in a separating funnel and about 40 ml of ether is added. After shaking some time, we get two layers.

The ether layer consists of Organic compound, and aqueous layer consists of basic compound.

- a) Taking in a beaker and expelling ether by an electrical water bath work up the ether layer on. After evaporation add anhydrous MgSO_4 , if is liquid distill it. If it is in solid state, dry the solid by means of filter paper till the moisture is dried out. Melting point is determined.
- b) The aqueous layer, which contains a base, is worked up on by neutralizing the acid with carbonate till CO_2 evolution stops. If the solid separates filter it. If it is liquid put it in a separating funnel. Once again add 40 ml ether. Now the ether layer will contain the base.
- c) The ether is expelled. If liquid aqueous layer add anhydrous MgSO_4 and distilled. The aqueous layer is rejected. Thus, the separation of the basic compound and neutral compound is done.

TYPE III :

After examining that it is neither cboxylic nor basic, look out for the phenol substances, by adding 5% Alkali. Check whether it re-precipitates by neutralizing with Acid. If so, it is confirmed that it is Phenol compound.

Take whole mixture in a beaker and add 5 % alkali at about 15 ml. Shake and stir it with glass rod. Dissolve the whole mixture completely in alkali.

Transfer the whole mixture in a separation funnel and add 40 ml of ether, shake it and there exists two layers. The ether layer containing organic compound and aqueous layer containing phenol compound as a sodium salt.

TYPE IV :

By doing all the preliminary tests, it is confirmed that the given compound is type is TYPE IV mixture. To separate TYPE IV mixture, 40 ml of ether is added to the given mixture and stirred with glass rod.

The ether soluble layer is decanted and insoluble solid is pressed by means of filter paper and is separated. The ether layer is worked up as used by heating on an electrical water bath till all the ether is evaporated. The solid thus formed is separated.

IDENTIFICATION OF FUNCTIONAL GROUPS IN THE COMPOUNDS

SYSTEMATIC PROCEDURE

EXPERIMENT	OBSERVATION	INFERENCE
PHYSICAL CHARACTERISTICS:		
a) Physical state	i) Liquid (or) Solid ii) Amorphous (or) crystalline	
b) Colour	i) Pale yellow ii) Reddish orange iii) Brownish yellow iv) Pale pink v) Colourless	Nitro compounds Nitro amines Aniline Phenol Carbohydrates, aldehydes, ketones, carboxylic acids, esters and some simple hydrocarbons.
c) Odour	i) Odourless ii) Bitteralmonds iii) Fishy smell iv) Mouse like smell v) Pungent smell vi) Pleasant fruites (Phenolic) Carbolic smell Vinegar like Cinamon like	Carbohydrates, aromatic acids Nitrobenzene, benzaldehyde are absent Aromatic amines Acetamide Formaldehyde, formic acid Esters Phenols Acetic acid Cinnamaldehyde
d) Melting point/ Boiling point		
II. Solubility: Take a small amount of compound in a test tube and add 3-ml of solvent		
a) Water	Soluble in cold water	i) Carbohydrates, glucose, Fructose ii) Amides, urea acetamide
b) 5% NaOH	Soluble in 5% NaOH and regenerated with HCl	May be weak acid like phenols
c) 5% NaHCO ₃	Soluble in 5% NaHCO ₃ and regenerated with HCl	May be strong acids, benzoic, salicylic acids.

d) 5% HCl	Soluble in 5% HCl regenerated with NaOH.	May be amines like aniline
e) Ether	Soluble in ether	May be neutral compounds like, Chlorobenzene, Aldehydes, Ketones, Nitrobenzene etc.

III. Ignition Test :

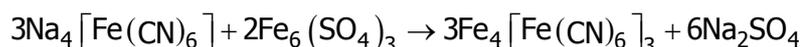
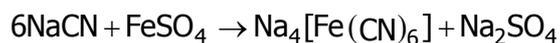
Heat a small amount of given compound on spatula	1) Burns with non-luminous and non-smoky flame.	Aliphatic compound
	2) Burns with Luminous and smokes flame	Aromatic compound
	3) Burns with sugar smell	Carbohydrates

IV Detection of Extra Elements

LASSAIGNE'S TEST: (Sodium fusion extract test): Preparation of sodium fusion extract: A small piece of sodium metal is placed in a clean, dry ignition tube. Heat the tube slowly to red heat. To tube add few drops/crystals of the given compound, heat tube to red-hot. Keep it in the red not condition for 1-2 minutes and then plunge into a mortar containing 10ml of distilled water in a mortar. The bottom part of the tube breaks away with the substance; grind the contents well with the pestle. Filter it, the filtrate is called "Sodium fusion extract". Use the filtrate for testing extra elements.

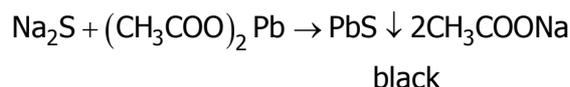
i) Test for Nitrogen :

Take 2ml of sodium Nitrogen is fusion extract add freshly prepared FeSO_4 and heated. Add conc H_2SO_4 slowly .	Prussian blue colour is observed	Nitrogen present observed
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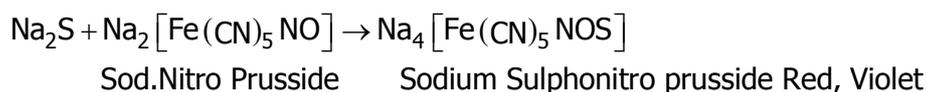


ii) Test for Sulphur :

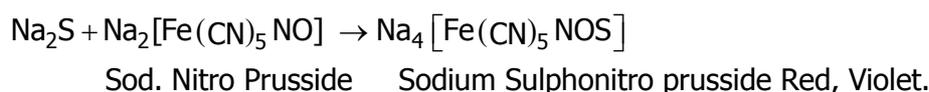
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|--|--|--------------------|
| a) Acidify the sodium extract (2ml) with dil. acetic acid (2ml) and add a few drops (4-5) of lead acetate solution | A black precipitate of Lead sulphide is formed | Sulphur is present |
|--|--|--------------------|

**b) Sodium nitro prusside test :**

- | | | |
|---|--|--------------------|
| To the sodium fusion extract (2ml) add a freshly prepared aqueous solution of sodium nitro prusside (1-2 drops) | A deep reddish violet colour is observed | Sulphur is present |
|---|--|--------------------|

**iii) Test for Halogens:**

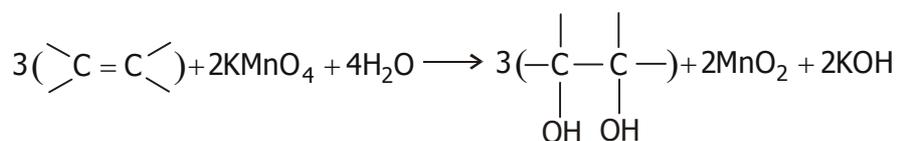
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| Acidify the sodium-fusion extract (2 ml) with dilute nitric acid (2-3 ml). Boil the solution gently for 1-2 minutes. Add silver nitrate solution (0.5 ml) to the above solution | i) A white ppt is formed which is soluble in NH_4OH | Presence of Chlorine |
| | ii) A pale yellow ppt is formed which is soluble in NH_4OH | Presence of bromide. |
| | iii) Yellow ppt is formed which is insoluble in NH_4OH | Presence of Iodine |



Test for unsaturation:

i) Bayer test:

- | | | |
|---|------------------------------------|----------------------|
| Dissolve the organic compound (0.2 ml) in water (2ml) (or) acetone Add (2%) potassium permanganate solution dropwise with shaking | Colour of bayer's reagent remained | Saturated compound |
| | Decolourisation takes place | Unsaturated Compound |

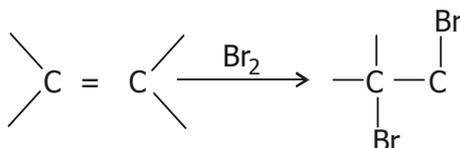


ii) Br₂ in CCl₄ :

Dissolve the organic compound (0.1g (or) 0.2 ml) in carbon tetrachloride (2 ml) and add drop wise with shaking a solution of (5%) Br₂ in CCl₄.

Decolourisation takes place
Decolourisation doesn't
takes place

Unsaturated compound
Saturated compound



DETECTION OF FUNCTIONAL GROUPS

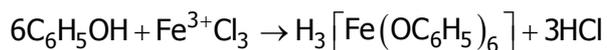
TEST FOR PHENOLS

i) With neutral FeCl₃ test :

The compound to be dissolved in alcohol and add 1 (or) 2 drops of 5% FeCl₃ Solution.

Violet (or) Blue
colour is observed

Phenol is present



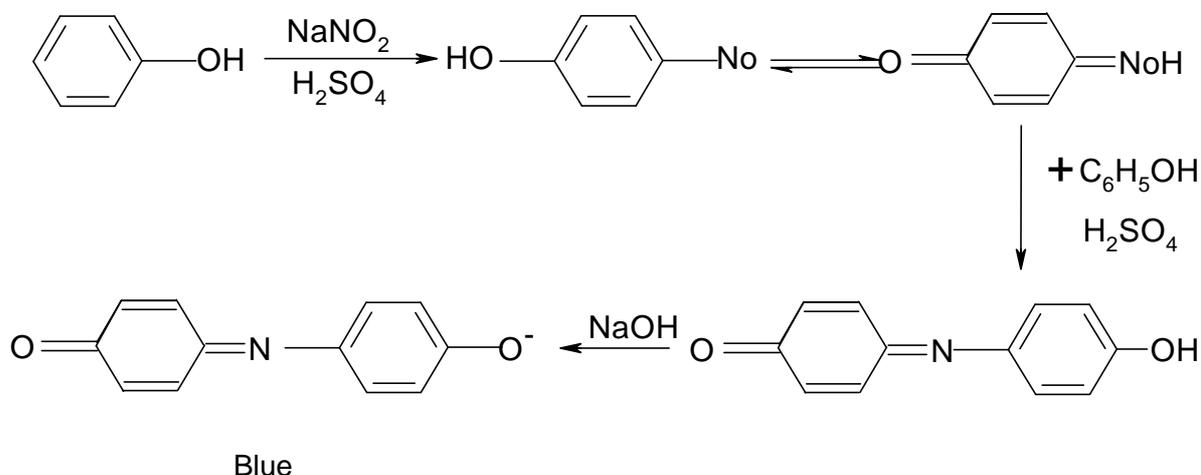
ii) Liebermann's nitroso

reaction:

Take the compound in a dry test tube add sodium nitrite and conc sulphuric acid (1 ml). Mix well and heat gently.

A blue colour is obtained.
The solution turns red on dilution with water and blue on basification with dil sol of NaOH

Phenol is present

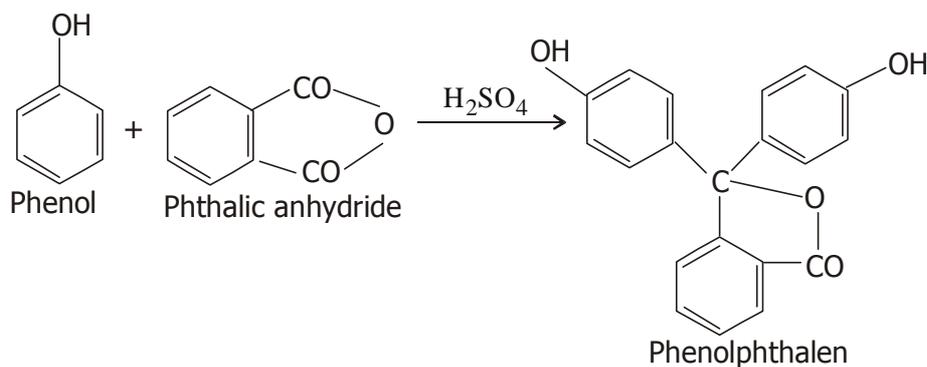


iii) Phthalein Test :

Take the given compound with an equal amount of phthalic anhydride and concentrated sulphuric acid (2-3 drops) for 1-2 minutes. Heat gently. Cool and pour into a beaker containing dilute solution of NaOH solution.

- i) Red colour is observed
- ii) Bluish purple
- iii) Blue colour
- iv) Red solution with strong yellow green fluorescence
- v) Green colour is observed
- vi) Faint green with some fluorescence

Phenol is present
 m-cresol
 catechol
 resorcinol
 α - Naphthol
 β - Naphthol



II. TEST FOR CARBOXYLIC ACIDS

i) NaHCO_3 Test :

To a saturated solution of sodium bicarbonate in water (1 ml) add the given compound

Brisk effervescence is observed

Carboxylic acid is present

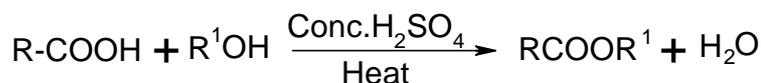


ii) Ester Test :

Heat the mixture of the acid, ethanol (1 ml) and concentrated sulphuric acid in a dry test-tube in a water bath. Pour the reaction mixture carefully into a beaker containing Na_2CO_3 solution

Fruity smell is observed

Carboxylic acid is present



iii) FeCl_3 Test:

Neutralise 0.5 gm of the acid with excess of ammonia in a boiling test tube. Boil the solution to remove excess of ammonia, cool and add a few drops of neutral ferric chloride solution.

(ii) A buff (or) brownish coloured ppt is obtained

Aromatic acids

(iii) An intense yellow colour is obtained

α - Hydroxy acids

(iv) A violet (or) fleshy colour is obtained

β - substituted aromatic hydroxy acids

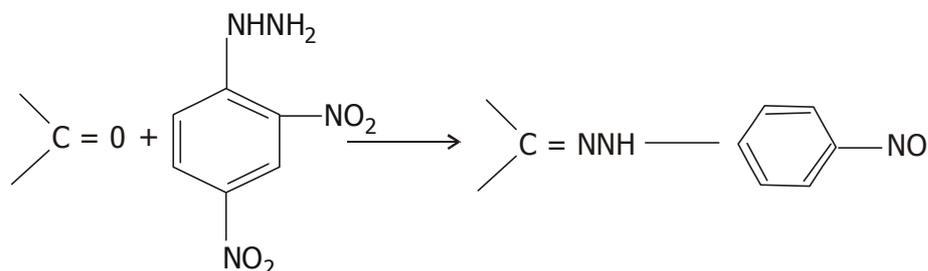
III. TEST FOR CARBONYL COMPOUNDS

i) Reaction with 2,4 DNP¹

Dissolve the carbonyl compound (100 mg (or) 1-2 drops) in ethanol (2-3 ml). To this add an alcoholic solution of 2,4-dinitro-phenyl hydrazine (2 ml) and shake the mixture well.

A yellow or orange colour ppt is formed

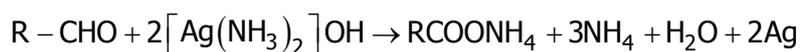
May be a carbonyl compound

**ii) Tollen's Test:**

To the Tollen's reagent (1 ml) add a solution of the aldehyde (2 drops (0.1) 50mg) dissolved in aldehyde free alcohol. (-2-3 ml) and warm the solution in a hot water bath.

A grey black ppt (or) silver mirror deposits on the inner walls of a test tube

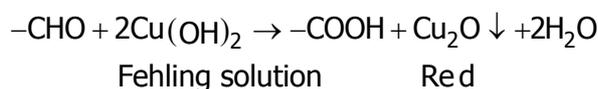
May be aldehyde is present

**iii) Fehling test :**

Add Fehling solution (2-3 ml) by mixing equal amounts of Fehling A + Fehling B) to the organic compound. And warm the mixture.

Red precipitate of cuprous oxide is formed

May be aldehyde is present

**iv) Schiff's Test:**

To a solution organic compound add Schiff's reagent (2-3 drops) and shake the contents

Violet (or) purple colour (pink) is observed

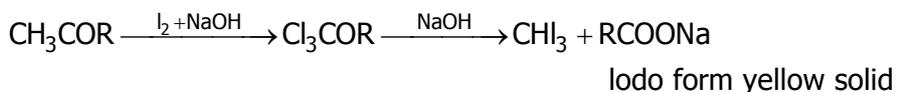
May be aldehyde is present

v) Iodo form test :

Dissolve the given compound (2-3 ml (or) 100 mg) in water (2-3 ml) in a test tube and add 2-3ml NaOH (10%). To this add a saturated solution of Iodine - inKI with stirring until the dark colour of Iodine persists. Heat the solution in a boiling water bath for 1-2 minutes.

A yellow ppt of Iodo form is observed

May be ketone



vi) Test for esters :

i) Phenol phthalin test (Hydrolysis) :

Add the given compound (0.1) to a dilute solution of NaOH (1% 12 ml). Add a drop of phenolphthalein. Add more NaOH to obtain pink colour. Now boil the solution for 5 minutes

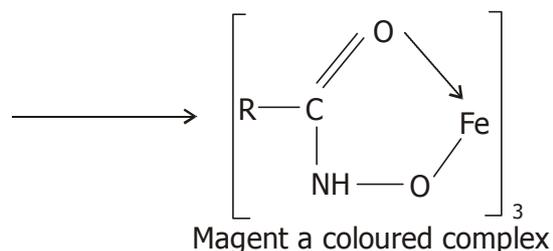
Pink colour disappears May be ester



ii) Hydroxylamine test :

Mix the compound with hydroxylamine hydro chloride (1 ml) and sodium hydroxide (0.2 ml) and heat the mixture to boiling. Cool and add HCl (2 ml) and then add ferric chloride solution (1-2 drops)

Magenta colour is formed Ester is present

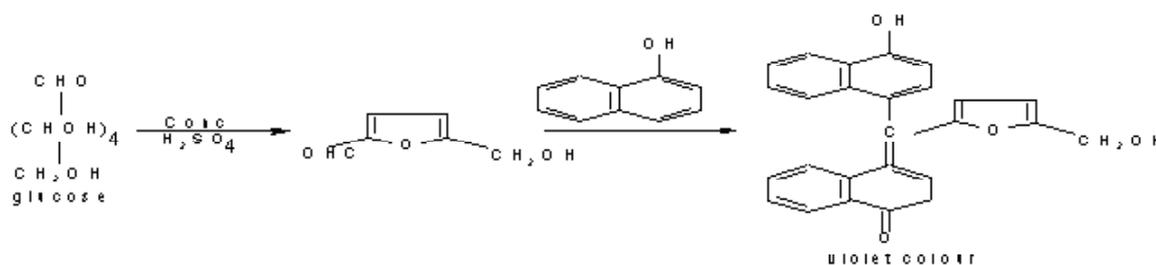


v) Test for carbohydrates :

i) Molisch's test :

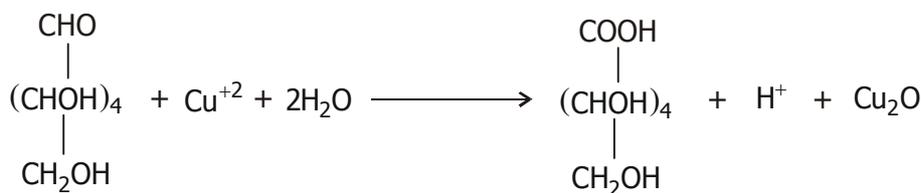
Add an alcoholic solution of α -NaPhthol (10%) to an aqueous solution of substance. Then add conc H₂SO₄ (1 ml) carefully along the sides of the test tube. Allow to stand for 2 minutes.

A violet ring is observed at the junction of two layers. May be carbohydrate

**iii) Barfoed test :**

Heat the aqueous solution of the compound (1 ml) with Barfoed reagent (1 ml) in boiling water bath for 1-2 minutes.

i) red colour precipitate of Cu_2O is formed. Carbohydrate is present.

**iv) Test with Benedict solution :**

Add Benedict solution (2ml) to the aqueous solution of organic substance. (reducing sugar)

Red ppt is observed

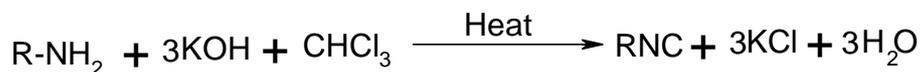
Carbohydrate is present

vi) TEST FOR 1°, 2°, 3° AMINES**i) Carbylamine test:**

To the compound add few ml of chloro form and then add 2 ml of Alcoholic KOH; mix well and gently warmed.

A foul smell is observed

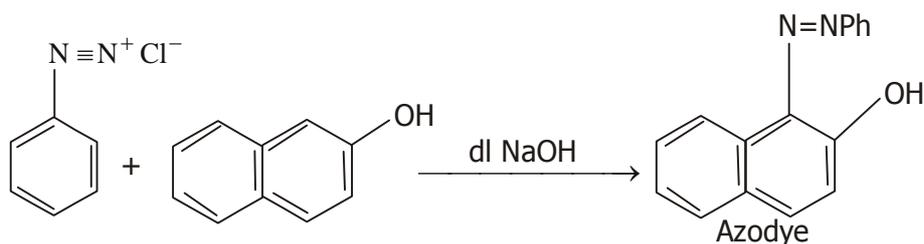
May be 1° amine.

**ii) Azodye test :**

Take 2 ml of compound, add 2 ml of HCl, cool in ice, and then add 2 ml of ice cold 10% Aq NaNO_2 solution. Add to it cold solution of 0.4 gms of 2-Naphthol in 4ml of 5% NaOH solution is added.

Orange-red dye is formed

Presence of 1° amine.

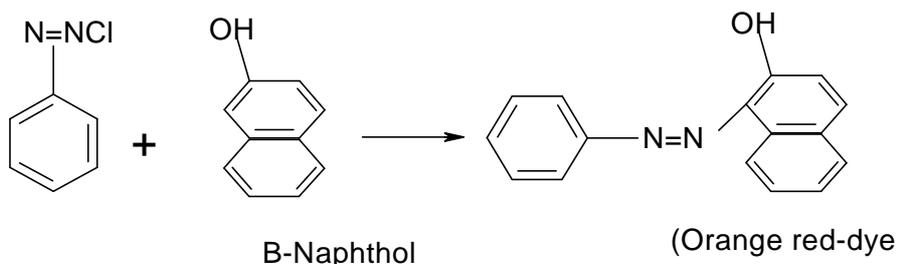
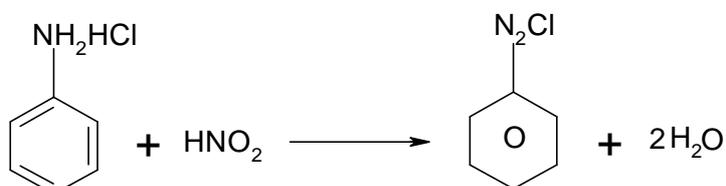


iii) Nitrous acid test :

Dissolve a pinch of compound in 5 ml of dil HCl, Cool it in ice and add 2 ml of ice cold 10% aqueous solution of NaNO_2 slowly by means of dropper. After completion of reaction add a sol of β -O Naphthol in 4 ml of 5% NaOH solution

- If an orange brilliant red coloured dye is formed.
- If yellow colour is observed
- If green colour is formed

May be 1° Amine
2° Amine
3° Amine

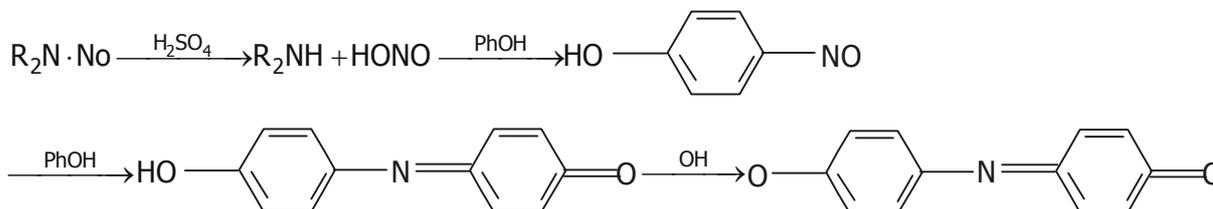


TEST FOR 2° AMINEi) Liber mannitroso test :

Dissolve the compound in dil HCl and cool in ice. Add few ml or 10% NaNO_2 solution. Cool and add 5 ml of water and extract with ether. Evaporate the ether. To tube add 5 drops of phenol and warm cool and

- An intense green colour is developed May be 2° Amine
- Which changes to pale red on pouring into watch
 - The colour changes to deep bluish green when NaOH is added to this solution.

add conc H_2SO_4 by the sides of test tube

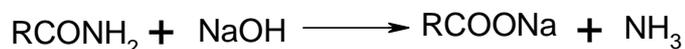


3) TEST FOR 3^o AMINES:

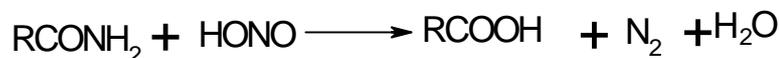
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|---|----------------------------|---------------------------------|
| i) Dissolve the compound in few ml of dil HCl and add 2 ml of 10% $\text{K}_4[\text{Fe}(\text{CN})_6]$ solution | White ppt is observed | 3 ^o Amine is present |
| ii) Add Nessler's reagent to the solution of organic compound in dil HCl | White colour ppt is formed | 3 ^o Amine is present |

VII. Test for Amides

- | | | |
|---|---------------------------|--------------|
| i) To the compound add few ml of 10% NaOH reflux (or) boil until NH_3 release. | Ammonia smell is observed | May be amide |
|---|---------------------------|--------------|



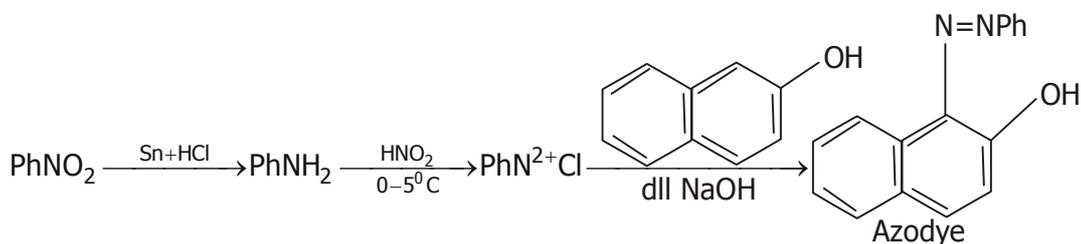
- | | | |
|---|---|--------------|
| ii) Nitrous acid test : Dissolve the pinch of organic compound in about 5 ml of dil HCl and few drops of 10% NaNO_2 solution | Brisk effervescence are obtained due to the evolution of N_2 | May be Amide |
|---|---|--------------|



Test for aromatic amides :

- | | | |
|--|-------------------------------|----------------|
| iii) To a little amount of compound, add hydroxylamine hydrochloride solution in ethylalcohol. Boil the contents for about five minutes. Cool and add about 4-5 drops of dilute 5% Ferric chloride solution. | Bluish red colour is observed | Aromatic amide |
|--|-------------------------------|----------------|



**TEST FOR HYDROCARBONS:**

i) Add conc H_2SO_4 to the organic compound	Soluble insoluble (two layers air for med)	Aromatic hydrocarbons Aliphatic
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Test with chloroform :

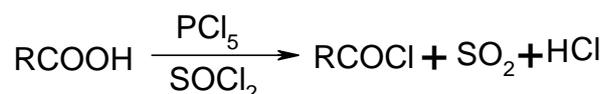
i) Heat anhydrous aluminium hydrochloride gently in a test tube and add organic compound and chloroform (2-3 drops)	Orange (or) red Blue Biphenyl (purple) Orange to red	Benzene Naphthalene Ar x
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PREPARATION OF DERIVATIVES FOR VARIOUS FUNCTIONAL GROUPS**Derivatives of carboxylic acids :**

The acid is first converted to acid chloride and the acid chloride is then converted to the amide, anilide derivatives.

Preparation of acid chloride by using thionyl chloride:

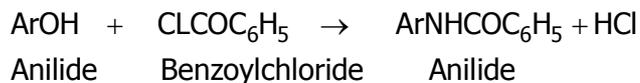
Place 1 gram of the acid into the round bottomed flask and add 5 ml of SOCl_2 and reflux the contents in a water bath for 30 minutes. Distill off excess of thionyl chloride and cool the residue. It is used for the preparation of acid derivatives.

**Amide derivative :**

Treat the acid chloride with 10ml of conc NH_3 solution and warm for few minutes and cool in an ice bath. Recrystallise the crude amide from water (or) dilute ethanol.

**Anilide derivative :**

Treat the acid chloride with aniline (1-2 ml) in C_6H_6 , warm on water bath, cool and filter if a solid separates out. If the solid aniline does not separate, wash the C_6H_6 layer with water, dil HCl, dil NaOH finally with water. Dry remaining C_6H_6 solution over anhydrous sodium sulphate (or) anhydrous CaCl_2 . Remove the solvent by distillation and recrystallise the residue from C_6H_6 (or) alcohol.



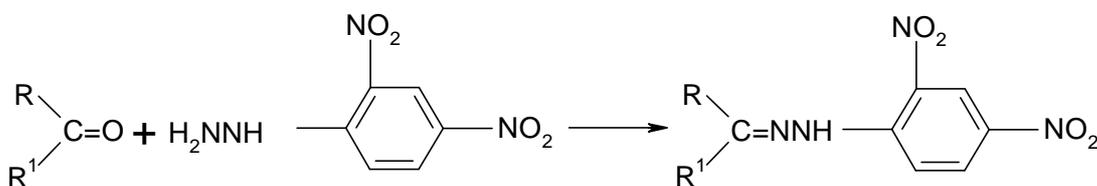
S-BENZYL THIO URANYL CHLORIDE

Dissolve the given acid in hot water and 5% aqueous NaOH solution is added till the solution is just alkaline to methyl orange. Add one drop of Dil. HCl; transfer the solution into benzyl Thio Uranium Chloride prepared in water. Cool the solution in Ice water. Filter out the substance formed and recrystallize from ethanol containing 10% of water. Melting point of the derivative is noted.

DERIVATIVES OF ALDEHYDES & KETONES

i). 2, 4 – DNP Test

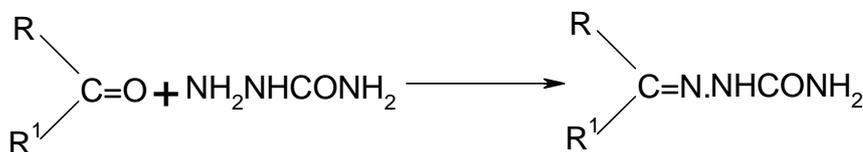
0.5 grams of substance or 2 ml of the given substance dissolved in 1 .c.c of methanol, to this 2 c.c of 2,4 –DNP solution is added and shake well. Then yellow precipitate is formed, it is recrystallised from alcohol.



2,4 - DNP

ii) Semi Carbazone :

Dissolve semi carbazide hydrochloride (2 gm) and sodium acetate (2g) in a minimum amount of water and add the carbonyl compound and shake well. Warm the contents on water bath for 10 minutes. Cool, filter and recrystallise from methanol.



iii) Iodo form test : Dissolve the given compound (2-3 ml (or) 100 mg) in water (2-3 ml) in a test tube and add 2-3ml NaOH (10%). To this add a saturated solution of Iodine – inKI with stirring until the dark colour of Iodine persists. Heat the solution in a boiling water bath for 1-2 minutes. A yellow ppt of Iodo form is observed.

Derivatives of Esters :

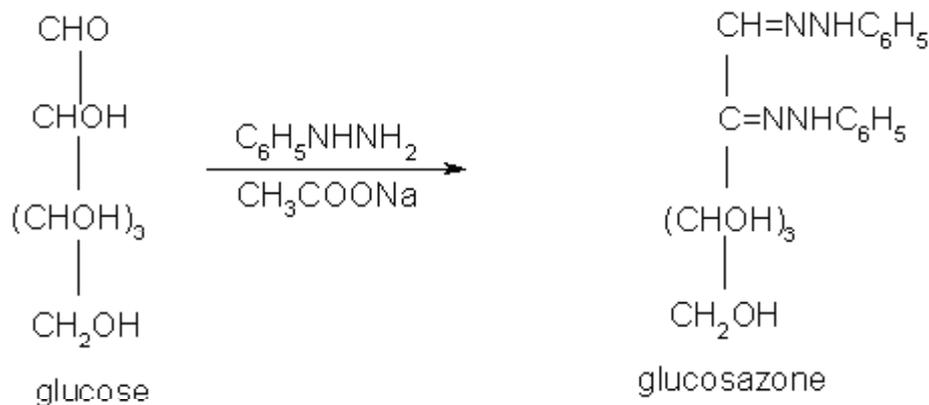
Hydrolysis of Ester: Place 1 gm of ester and sodium hydroxide (20 ml, 10%) in a round bottomed flask. Reflux the mixture gently for half an hour until the hydrolysis is complete. Cool, and acidify the solution with dil H_2SO_4 dil HCl. The acid separates out. Allow the mixture to stand in the ice water for five minutes then filter the solid. Recrystallise from hot water.



Derivatives of carbohydrates :

i) Osazone derivative :

Take 1 gm of carbohydrate in a clean test tube. In another test tube dissolve 0.4gm of phenyl hydrazine hydrochloride and 0.6 gms of crystalline sodium acetate in 4 ml of cold water and add this solution to sugar. Loosely cork the test tube, immerse it in a boiling water bath with periodical shaking and note the exact time required for the first appearance of turbidity (or) precipitate of the osazone which serves as a useful aid on the characterization of sugar, cool the solution, filter the osazone precipitate and recrystallise it from 50% alcohol.

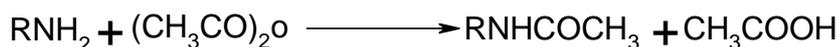


ii) Acetate derivative :

Take fused sodium acetate (1g), acetic anhydride (5 ml) and the carbohydrate (1g) in a dry boiling tube fitted with a condenser. Reflux the reaction mixture (30min to 2-hrs) pour the reaction mixture over ice cold water (50ml) with vigorous stirring to decompose the excess acetic anhydride. Filter the solid, wash with some cold water and recrystallise from ethanol.

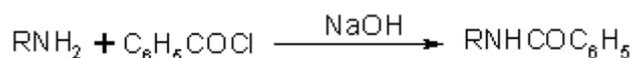
Derivatives of Amines :

1) **Acetyl derivative** : Dissolve 0.5 gms of amine in 2ml of HCl and add a little crushed ice-introduce a solution of 5 grams of hydrated sodium acetate in 25 ml of water followed by 5 ml of acetic anhydride, shake the mixture in cold until the smell of $(\text{CH}_3\text{CO})_2$ disappear, collect the solid derivative and recrystallise from ethanol.



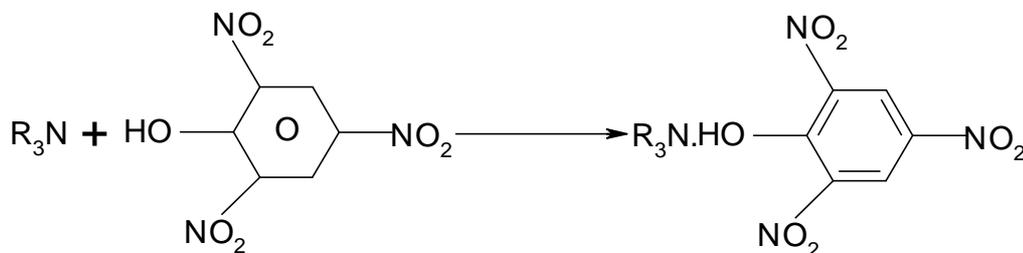
Acetyl derivative

2) **Benzoyl derivative** : Suspend 1 gm of the substance in 5ml of 10% NaOH solution in a boiling tube and add 2ml of benzoylchloride with const shaking and cool in water. Shake vigorously for 5-10 minutes until the odour of Benzoylchloride has disappeared. Filter off the solid derivative and recrystallise it from ethanol.



Derivatives of 3° Amines :

Picrate derivative : Dissolve the given amine (0.5 g) in a minimum quantity of ethyl alcohol (or) benzene. Add a saturated solution (2-3ml) of picric acid in the same solvent. Picrate separates out on mixing. In case no solid forms on mixing, heat the mixture on water bath and allow it to cool slowly. Filter the product, and recrystallise from dilute alcohol.



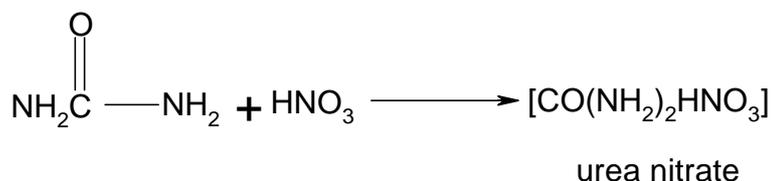
Derivatives of Amides :

Hydrolysis of Amides : Place 1 gm of amide and sodium hydroxide (20 ml, 10%) in a round bottomed flask. Reflux the mixture gently for half an hour until the hydrolysis is complete. Cool, and acidify the solution with dil H_2SO_4 or dil HCl. The acid separates out. Allow the mixture to stand in the ice water for five minutes then filter the solid recrystallise from hot water.



Derivatives of urea :

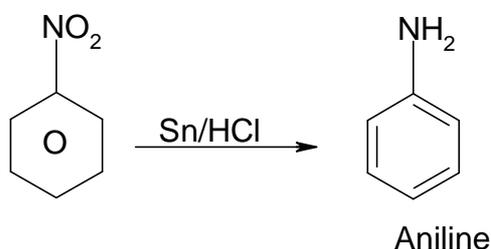
1) Urea nitrate derivatives : Dissolve 1 gm of urea in about 5 ml of water and add 2 ml of conc HNO_3 with stirring. White crystals of the urea nitrate separated. Filter and dry it. Recrystallise from ethanol.



Urea oxalate : Dissolve 1 gm of urea in water (4 ml) and add a solution of oxalic acid (1.2 gms in 15 ml water) on stirring with a glass rod. Filter the crystalline urea oxalate. Recrystallize from ethanol.

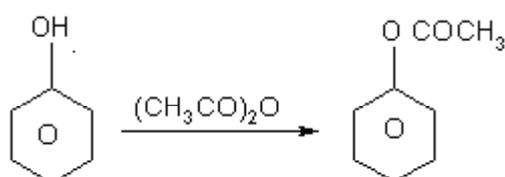
Derivatives of Nitro compounds:

1) Reduction test: Place 1 ml of compound in R.B. flask, add granulated Sn-metal, 3 grams to it, add 2ml of ethanol. Fit reflux condenser and add conc HCl 10 ml in small portions with vigorous shaking, reflux the mixture gently on water bath for 30 minutes. Cool it add 40% NaOH solution, until the solution alkaline. Extract the sol, several times with ether. Distill of the ether and recrystallise the derivative.



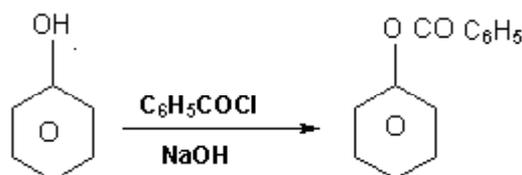
DRIVATIVES OF PHENOLS

Acetyl derivative : Dissolve 1 gm of phenols in 2ml of HCl and add a little crushed ice. Introduce a sol of 5 gms of sodium acetate in 250 ml of water followed by 5ml of acetic anhydride. Shake the mixture in cold until the smell of acetic anhydride disappearsw. Collect the solid derivative and recrystallize it from ethanol.



Benzoyl derivative :

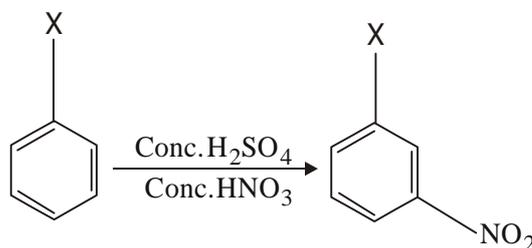
1ml of compound is taken in a R.B. flask. To this add 5 ml of 10% NaOH and 2ml of Benzoyl chloride. Shake the flask vigorously for about 30 minutes. The completion of reaction is indicated by the disappearance of smell of benzoyl chloride add about 30ml of cold water to the flask, filter it and recrystallize from ethanol.

**Picrate**

0.2 grams of the substance is dissolving 2 c.c of Benzene, to this add 2 c.c of picric acid the solution is shaken well and then filtered. The solid is washed with benzene and it is dried. Its melting point is determined.

Derivatives of Hydro carbons : /extraelement compound**Nitro derivative :**

Prepare a mixture of conc H_2SO_4 (4ml) and conc HNO_3 (4ml) and add to this slowly with shaking the organic compound (1ml). Heat in a hot water bath for 15-20 minutes. Pour the reaction mixture into ice cold water. Filter and recrystallise from dil alcohol.



X = H, Cl, Br, SO_3H

Final Report:**The given compound contains :**

Layer	Aromatic/Aliphatic And its its Melting	Functional Group	Derivatives and its Melting Point
Organic layer			
Aqueous layer			

MELTING POINTS & BOILING POINTS OF DERIVATIVES**M.P./B.P.**

56 ⁰	Acetone, derivative, idoform, m.p. 119 2, 4 - dinitroph enythrazone 128 ⁰ , Semicarbazone m.p. 187 ⁰
132 ⁰	Chlorobenzene, derivative, 2, 4 - dinitrochlorobenzene m.p. 52 ⁰
179 ⁰	Benzaldehyde, derivative, benzoic acid, m.p. 121 ⁰ , Phenylhydrazone, m.p. 157 ⁰ , 2, 4 - dinitrophenylhydrazone m.p. 235 ⁰ Semicarbaone, m.p. 214 ⁰ .
181 ⁰	Phenol, derivative benzoate m.p.69 ⁰ , tribromophenol - m.p. 93 ⁰ aryloxyacetic acid, 99 ⁰ , Picric acid, m.p. 122 ⁰
183 ⁰	Aniline, derivative, acetyl m.p. 114 ⁰ , benzoyl, m.p. 162 ⁰ , tribromo, m.p. 118 ⁰
196 ⁰	Salicylaldehyde, derivative phenylhydrazone, m.p. 143 ⁰ , Semicarbazone, m.p. 230 ⁰ , 2, 4 - dinitrophenyl hydrazone, m.p. 250 ⁰ .
193 ⁰	Dimethylaniline, derivative, picrate, m.p. 163 ⁰
198 ⁰	Methyl benzoate, derivative, benzoic acid, m.p. 121 ⁰
201	P. Cresol, derivative, benzoate, m.p. 71 ⁰ , aryloxyacetic acid, m.p. 136 ⁰
202	Acetophenone, derivative, Semicarbozonone, 202 ⁰ , 2, 4 dinitro phenylhydrazone m.p. 249 ⁰ , Oxime m.p. 59 ⁰ , Phenylhydrazone m.p. 105 ⁰ .
210	O-Chloroaniline, derivative, acetyl m.p. 87 ⁰ , benzoyl m.p. 99 ⁰
213	Ethyl benzoate, derivative benzoic acid m.p. 121 ⁰
175	O-Chlorophenol, derivative, aryloxyacetic acid, m.p. 145 ⁰
44 ⁰	O-Nitrophenol, derivative, benzoate m.p. 59 ⁰ , aryloxyacetic acid, m.p. 158 ⁰
48 ⁰	Benzophenone, derivative, semicarbazone, m.p. 164 ⁰ , oxime m.p. 141 ⁰ Phenylhydrazone m.p. 137 ⁰ , 2, 4 - dinitrophenylhydrazone, m.p. 238 ⁰
94 ⁰	α - Naphthol, derivative, picrate, m.p. 149 ⁰ , benzoate, m.p. 56 ⁰
102 ⁰	Fructose, derivative, Osazone, m.p. 205 ⁰
110 ⁰	Resorcinol, derivate, benzoate, m.p. 117 ⁰

- 114⁰ Acetanilide, derivative, P - bromoacetanilide, m.p. 167⁰, P - nitroacetanilide, m.p. 214⁰
- 121 Benzoic acid, derivative, anilide, m.p. 162⁰, S. Benzyl isothiouranium, m.p. 167⁰
- 128 Benzamide, derivative, benzoic acid, m.p. 121⁰
- 132 Urea, derivative, nitro, m.p. 163⁰, oxalate m.p. 170⁰
- 133 Cinnamic acid, derivative, anilide, m.p. 153⁰, S. Benzyl ISO thiouranium m.p. 152⁰
- 141⁰ m - Nitro benzoic acid, derivative, anilide, m.p. 153⁰, amide, m.p. 142⁰, S.benzyl iso thiouranium, m.p. 159⁰
- 146⁰ Glucose, derivative, Osazone, m.p. 205⁰
- 156 Salicylic acid, derivative, anilide, m.p. 135⁰ acetyl, m.p. 136, Nitro m.p. 226⁰
- 280 Sulphanilic acid, derivative, amide m.p. 164⁰

SPECIAL REAGENTS USED IN THE ORGANIC LABORATORY

Alcoholic potash : 1) 10g of pure caustic potash in the form of pellets are dissolved in 10ml . The solution is agitated with 10% of anhydrous sodium sulphate till it becomes clear and then decanted.
Or

2) 15g of caustic potash are agitated with 500 ml of 95% alcohol at the ordinary temperature until solution is complete. After settling, the clear solution is decanted.

Bromine in carbon tetrachloride : 2ml of liquid bromine are dissolved in 50ml of dry carbon tetrachloride.

Benedict's solution : (reagent for aliphatic aldehydes and reducing sugars.) this solution is prepared by dissolving 17.3gms of sodium citrate and 100 gms of anhydrous sodium carbonate in about 800ml of water and then mixing the two solutions and making up to litre.

Barfoed's reagent : 6.6gms of cupric acetate and 1ml of glacial acetic acid are dissolved in water and made up to 100ml

Borsche's reagent : 1% methyl alcoholic solution of 2;4 dinitrophenyl hydrazine. Very valuable for detecting carbonyl groups.

1gm of solid is refluxed with 100ml of methyl alcohol till dissolved.

Chromic acid mixture : 10g of commercial chromic anhydride are dissolved in a mixture of 60 ml of water and 8ml of conc. sulphuric acid. 1ml of the solution contains 0.5g. of available oxygen. (A rough calculation of the reagent necessary for oxidizing 1g. of the substance should always be made before hand.)

Denige's reagent (Acid mercuric sulphate). 5g. of mercuric oxide are dissolved in a solution of 20 ml of concentrated sulphuric acid and 100 ml of water while the mixture is still hot.

Fehling's solution . (1) 6.9g. of copper sulphate crystals are dissolved in 40ml of water and diluted to 100ml.

(2) 15 g. of sodium hydroxide and 36g. of Rochelle salt are dissolved separately in 30ml of water each, mixed and diluted to 100 ml after cooling.

Equal volumes of (1) and (2) are mixed before use.

Hydroxylamine reagent for ketones. (1) 7.25 g. of hydroxylamine hydrochloric are dissolved in 9 ml of water and diluted to 35 ml by adding absolute alcohol.

(2) 10 gms of pure sodium hydroxide are dissolved in 20 ml of water and diluted to 140ml by adding absolute alcohol. One part of (1) and four parts of (2) are mixed before use.

Iodine solution : 2g. iodine, 10g of potassium iodide and 30ml of water are ground together in a mortar till the solids have dissolved.

Luca's reagent for alcohols : 13.6 g of anhydrous zinc chloride are dissolved in 10.5g. of concentrated hydrochloric acid.

Mayer's reagent (potassium mercuri-iodide). 10g. of potassium iodide and 2.8g. mercuric chloride are dissolved in 200 ml of water.

Nylaners'solution. 4g. of Rochelle salt and 2g. of bismuth subnitrate are dissolved in 100ml of 8% caustic soda.

Potassium permanganate for oxidation. 61.1g. of permanganate are dissolved in a litre of distilled water 1ml of the solutions contains 0.01g. of available oxygen.

Phenylhydrazine reagent. (1) 4 ml of the pure light coloured base and 4c.c of glacial acetic acid are dissolved in 10 ml of water. Alternatively, 4g. of phenyl hydrazine hydrochloride are dissolved in 16 ml of water, 6g. of sodium acetate crystals are added and one drop of glacial acetic acid. This composition is very useful for preparing the osazones of sugars. (2) To test for ketones, 0.3ml of glacial acetic acid, 7 ml of water, 2 ml of light coloured phenylhydrazine are mixed together. (This lasts for a few days only and should be made afresh.) 4 drops of the reagent are added to one drop of ketone in 2 ml of water or alcohol and the mixture heated by immersing in a boiling water -bath for 5 minutes.

Sodium hypochlorite : 100 g, of freshly made bleaching powder are ground into a thick cream with 450 ml of water and 84 g. of anhydrous sodium carbonate are added with stirring. The mixture is shaken well, and after keeping for some time the precipitated calcium carbonate is filtered and the clear solution used.

Saturated sodium bisulphite solution. Sodium carbonate crystals (200g) are added with water insufficient to dissolve them and sulphur dioxide is passed till the solid disappears and a pale green solution is obtained. On standing, this solution deposits crystals. The solutions prepared as described above is more effective than the commercial bisulphate and is recommended for use even in preparative work.

Schiff's reagent : 0.2g. of pure fuchsine (p-rosaniline) as hydrochloride) or acetate is dissolved in 20 ml of water and saturated with sulphur dioxide. After the solution has become colourless, it is filtered., diluted to 200 ml with water and preserved in dark bottles.

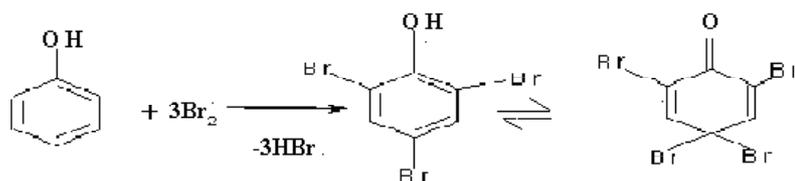
Seliwanoff's reagent : 0.05g. of resorcinol is dissolved in 100 c.c of concentrated hydrochloric acid and diluted with an equal volume of water.

Tollen's reagent : Commercial ammonia (sp.gr. 0.90) is diluted with an equal volume of water and 10g. of silver nitrate are dissolved in 100 c.c of this diluted ammonia. A 10 percent aqueous solution of caustic soda is also prepared and kept separate. The two are mixed in equal volumes just before use.

VIVA QUESTIONS

- 1) Why is the sodium fusion extract acidified better testing for Halogens?
 - A) The acidification of sodium fusion extract is necessary before adding silver nitrate solution to prevent the precipitation of silver hydroxide (or) oxide.
- 2) Why use add H_2SO_4 rather than HCl in test for nitrogen?
 - A) On boiling the alkaline solution some ferric ions are produced by the oxidation of ferrous ions by air both ferrous and ferric hydroxides dissolve on adding dil H_2SO_4 . The ferrocyanide reacts with ferric ions to produce the prussian blue colour of ferric ferrocyanide.

The alkaline solution should not be acidified by HCl/because the yellow colour due to the ferric chloride formed causes prussian blue to appear greenish.
- 3) Why would we only use sodium fusion extract for the detection of Nitrogen, sulfur, halogens?
 - A) In Lassaigne's test, the organic compound is fused with a piece of sodium metal to convert covalent compounds into ionic compounds (NaCN , Na_2S , NaX). Lithium is not used in Lassaigne's test since it reacts slowly and its compounds are generally covalent. Potassium can also not be used since it reacts evidently and cannot be handled.
- 4) Why should ferrous sulfate solution be fresh and saturated in the test for the detection of nitrogen?
 - A) A freshly prepared FeSO_4 solution is used in Lassaigne's test for nitrogen as on keeping FeSO_4 solution oxidizes to basic ferric sulphate and cannot be used for detection.
- 5) Why does o-nitro phenol give no colour with FeCl_3 solution?
 - A) Nitro phenols can be expressed as meromeric structures with a +ve charge on the nitrogen atom and competing with ferric ions in their influence or electron pair thus weakening the iron-oxygen bond.
- 6) Which type of phenols give Libermann reaction?
 - A) Only those phenols possessing a free para position respond to this test.
- 7) Bromination of phenol faster in water (or) CCl_4 ?
 - A) The advantage of bromine in water over bromine in CCl_4 is that the more polar solvent greatly increases the rate of bromination by the ionic mechanism. Of course it is impossible with this solvent to observe the evolution of hydrogen bromide. An excess of bromine water reacts with phenol to a yellow tetrabromoderivative, 2, tetrabromo cyclohexadienone.

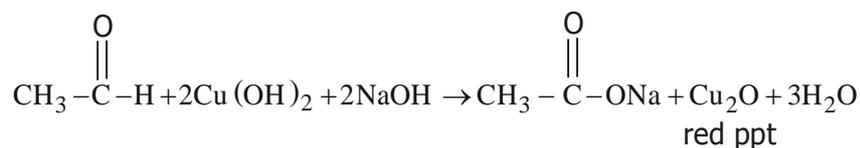


2,4,4,6 - tetra bromo cyclo hexadieneone

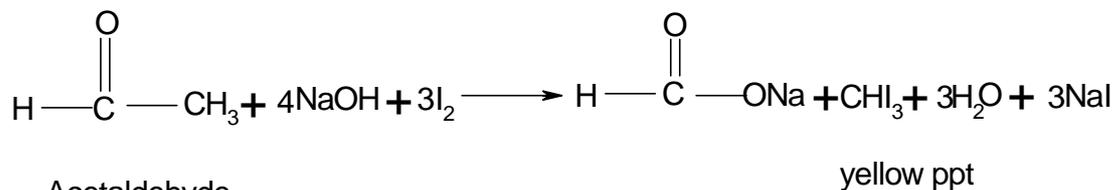
8) How will you distinguish between benzaldehyde and acetaldehyde?

A) Acetaldehyde gives Fehling's test and Iodo form test. Benzaldehyde does not.

Fehling test :



Iodo form test :



Acetaldehyde

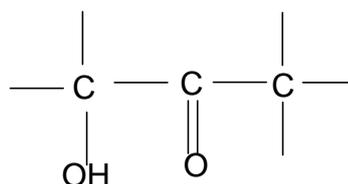
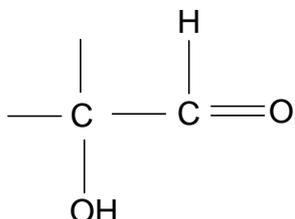
9) How will you distinguish between reducing and non reducing sugars?

A) Those Saccharides which reduce Fehling's reagent and Tollen's reagent are called reducing sugars, and those which do not, non-reducing sugars. The ability to reduce (or) not to reduce Fehling's and Tollen's reagents depends on certain characteristic structural features.

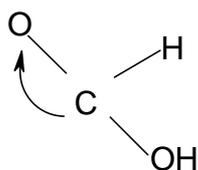
Structural features of reducing sugars:

1) They contain α - hydroxyaldehyde (or) α -hydroxy ketone functions

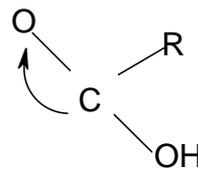
2)

 α - hydroxy aldehyde α - hydroxy ketone

- 3) They contain cyclic hemiacetal (or) hemiketal structures in equilibrium with the open chain form having a free CHO (or) C=O group as the case may be. Such sugars, there bore, reduce Fehling's and Tollen's reagents.



Hemi acetal



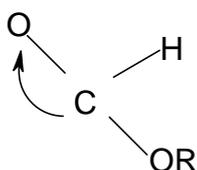
Hemi ketal

Structural features a-non-reducing sugars :

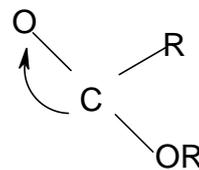
- 1) They do not contain free aldehyde (or) ketone groups with OH on the carbon adjacent to carbonyl group.

They contain acetal (or) ketal structure that is stable. Their cyclic structures cannot be opened into an open chain form having a free carbonyl group. Thus they are unable to reduce Fehling's (a) Tollen's

- 1) reagent: For the same reason, non reducing sugars do not exhibit mutarotation.



Acetal

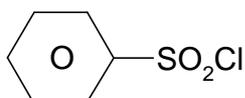


Ketal

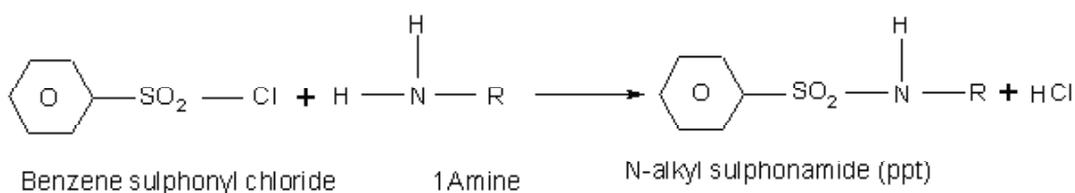
Reducing sugars : glucose, fructose (mono sacharides) maltose, lactose (di)

Nonreducing sugars: Sucrose

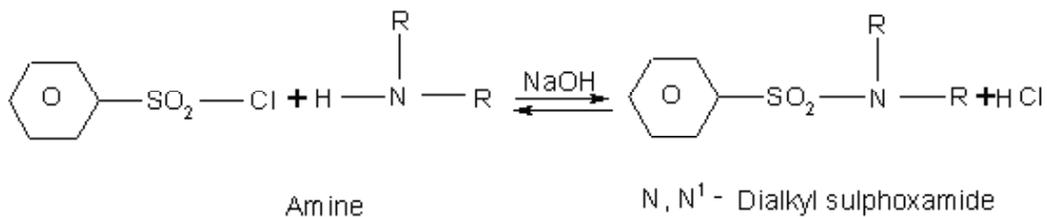
- 10) How will you distinguish between glucose and starch?
- A) Starch does not reduce Tollen's reagent and Fehling solution. It does not form an osazone with phenyl hydrazine. While glucose can give Tollen's test and Fehling test. It also form osazone.
- 11) What is Hinsberg reagent? By using it how will you distinguish between 1°, 2° and 3° Amines?
- A) Benzene sulphonyl chloride is called. Hinsberg reagent.



- a) Primary amines react with benzene sulphonyl chloride to form N-alkyl benzene sulphonamide.



- a) Secondary amines react with benzene sulphonyl chloride to form N, N¹-diakyl benzene sulphonamide.



- b) 3^o amines do not react since they do not possess a replaceable hydrogen.
- 12) What is the function of adding boiling chips to the liquid during distillation?
- A) Bumping is minimized by adding one (or) two boiling chips, which are small pieces of porous tile, to the flask, the escaping gas bubbles from the boiling chips will break the surface of the liquid and thus promote smooth boiling and prevent bumping. It must be noticed that whenever.

PRACTICAL - III :: PHYSICAL CHEMISTRY

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EXPERIMENT- 1**DETERMINATION OF PARTITION
CO-EFFICIENT OF I_2 IN CCl_4 & WATER**

Aim : To determine the value of partition co-efficient of Iodine between Carbon Tetrachloride and water.

CHEMICALS REQUIRED:

1. 1% Iodine in CCl_4
2. Carbon Tetra Chloride
3. 0.1N Hypo Solution
4. 0.01 N Hypo Solution
5. Starch Indicator
6. 10% Potassium Iodide Solution

PREPERATION OF SOLUTIONS :

1% Iodine in CCl_4 : One gm Iodine is weighed accurately and dissolved in 100 ml CCl_4 .

0.1N Hypo :- About 24.819 gm of sodium thiosulphate pentahydrate is weighed accurately. And then transferred into a 500 ml standard flask through funnel. The substance is dissolved in minimum quantity of water and then made up to the mark by adding distilled water

0.01N Hypo : Transfer the above prepared solution 50ml i.e 0.1N hypo from burette into a 500ml standard flask and then it made up to the mark with distilled water.

Starch Indicator : About one gm of starch powder is weighed and pastent with few ml of cold water and pour this solution drop by drop into 100ml of boiling water and boil for few minutes.

10%Potassium, Iodide : 10gms of potassium Iodide is weighed and dissolved into 100ml distilled water.

Procedure :

Take three 250 ml wel stopper conical flasks or iodine flaks or ambered coloured reagent bottles, Pipette out 20ml , 30ml and 40 ml of iodine in CCl_4 into the above iodine flasks respectively which are marked as A,BC . Now make up the total volume of the iodine solution to 50 ml by addintg CCl_4 solution in 30 ml,20ml and 10ml of CCl_4 respectiv ely. Add 50ml of distilled water to each flask, there by total volume is 100ml.Now shake the contents of the flask very thoroughly for about 90 minutes. Now separate aqueous and organic phases by means of separating funnel. The concentration of Iodine is calculated by titration each phase with Hypo solution using starch indicator.

TITRATION OF ORGANIC LAYER :

Pipette out 5ml of Organic Layer into a 250ml conical flask. To this add 10ml of 10% Potassium Iodide Solution. Shake thoroughly, add 10ml distilled water and titration is done to the solution with 0.1N Hypo Solution. Few drops of starch Indicator is added when the solution is in Pale yellow and continues the titration until the colorless solution is obtained.

Note : The burette readings and repeat the titration until two concurrent readings are obtained.

TITRATION OF AQUEOUS LAYER :

Pipette out 10ml of aqueous layer into a 250ml conical flask and add 10ml-distilled water and titrated the solution with 0.01N hypo solution. Starch is used as indicator and the end point is colorless.

REPORT :

The Partition Co-efficient Of Iodine between CCl_4 and water is _____.

CALCULATIONS :**ORGANIC LAYER**

S.No	Volume of Organic layer (ml)	Burette Reading Initial (ml)	Burette Reading final (ml)	Volume of hypo consumed (V1) ml (0.1) N
1	5ml	0		
2	5ml	0		
3	5ml	0		

Volume of Hypo $V_1 =$

Concentration of Hypo $N_1 = 0.1\text{N}$

Volume of Organic layer $V_2 = 5\text{ml}$

Concentration of Organic layer $N_2 =$

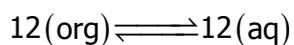
$$V_1 N_1 = V_2 N_2$$

$$N_2 = \frac{V_1 N_1}{V_2}$$

Concentration of $[I_2]_{org} =$

AQUEOUS LAYER

S.No	Volume of Aqueous layer (ml)	Burette Reading Initial (ml)	Burette Reading final (ml)	Volume of hypo consumed (V1) ml (0.1) N
1	10ml	0		
2	10ml	0		
3	10ml	0		



Volume of Hypo $V_1 =$

Concentration of Hypo $N_1 =$

Volume of I in Aqueous layer $V_2 =$

Concentration of I in Aqueous layer $N_2 =$

$$\begin{aligned} V_1 N_1 &= V_2 N_2 \\ N_2 &= \frac{V_1 N_1}{V_2} \end{aligned}$$

Concentration of $[I_2]_{Aq} =$

$$\text{Partition coefficient} = \frac{[I_2]_{org}}{[I_2]_{Aq}}$$

NOTE: Partition coefficient can also be calculated as follows.

$$\text{Partition Co-efficient} = \frac{(\text{Vol. of hypo consumed by org. layer})}{(\text{Vol. of hypo consumed by aqueous layer})} \times 100$$

The Partition Co-efficient Of Iodine between CCl_4 and water is _____

EXPERIMENT- 2**DETERMINATION OF
EQUILIBRIUM CONSTANT**

AIM : To determine the equilibrium constant for the equilibrium. $KI_3 \rightleftharpoons KI + I_2$

CHEMICALS REQUIRED :

- 1) 0.05 N of KI solution in 250ml
- 2) 10% of KI in 100ml
- 3) 0.01N Hypo in 250ml
- 4) 1% of I_2 in CCl_4
- 5) Starch indicator in 100ml
- 6) CCl_4
- 7) 0.01N Potassium dichromate solution in 250ml

PREPARATION OF REAGENTS:

0.05N KI solution in 250 ml : About 2.125gms of Potassium Iodide is weighed accurately and then transferred in to 250ml standard flask through funnel . The substance is dissolved in minimum quantity of water and then made up ;to the mark by adding distilled water.

1% I_2 in CCl_4 : One gram of iodine is weighed accurately and dissolved in 100ml ccl_4 .

0.01N Hypo : About 2.5gms of sodium thiosulphate pentahydrate is weighed accurately and then transferred in to a 500ml standard flask through funnel; The substance is dissolved in minimum quantity of wager and then made up ;to the mark by adding distilled water.

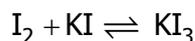
Starch indicator : About one gram of starch is weighed and pasted with few ml of cold water and pour this solution drop wise into 100ml of boiling water. Boil the solution cool it and used as starch indictor

10% POTASSIUM IODIDE : About 10gms of potassium Iodide is wieghed and dissolved in 100ml of distilled water.

0.1N Potassium dichromate :

About 1.114gms of pure potassium dichromate is weighed accurately and then transfered into a 250ml conical flask through funnel wash the funnel with water dissolve the substance and made up to the mark.

PRINCIPLE : When KI solution is added to the solution of I_2 , they reacts to form KI_3 .The Equilibrium state exists between I_2 and KI to form KI_3 .



Equilibrium constant

$$K = \frac{[KI_3]_{(Eq)}}{[KI]_{(Eq)} \cdot [I_2]_{(Eq)}}$$

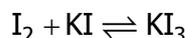
On determining $[KI_3]_{(Eq)}$, $[KI]_{(Eq)}$, $[I_2]_{(Eq)}$ we can calculate Equilibrium constant.

The concentration of iodine $[I_2]_{(Eq)}$ can be determined by the partition co-efficient method.

PROCEDURE:

STANDARDISATION OF SODIUM THIOSULPHATE : 20 ml of potassium dichromate solution is pipetted out into a conical flask and add 5 ml of 4N HCl and 10ml of 10% KI are added, now the conical flask is covered with watch glass and kept in dark room for few minutes the liberated iodine dissolves in the excess of potassium iodide present in it. Then the sol is diluted to about 100 ml of distilled water. Now titrate the solution with Hypo till the brown colour of the solution changes to straw yellow colour. Then one or two ml of starch solution is added then the solution is turns to blue coloured again titrate this solution against sodium thiosulphate solution until the blue colour changes to green colour. This is the end point. Repeat the titration until the concurrent values are obtained.

Determination of Equilibrium constant for



Take two 250ml Iodine flasks marked as A and B. Take 30ml, 40ml of Iodine (I_2) in CCl_4 in flasks A and B respectively. Make the volumes of the flasks up to 50ml with CCl_4 . Add 50ml of 0.05N KI solution to each flask. Fix stopper to the flask and shake about 90 to 120 minutes. A separating funnel separates Organic layer aqueous layers. The concentration of I_2 in each phase is calculated by titrating with 0.01N hypo solution.

DETERMINATION OF CONCENTRATION OF I_2 IN ORGANIC LAYER : Pipette out 5ml of Organic layer. Add 5ml of 10% KI solution. Shaken for few minutes and add 10ml of water. Titrating with 0.01N hypo solution till the solution turns to straw yellow in colour then add one to two ml of starch indicator and continue the titration until the deep blue coloured solution changes to colourless solution.

DETERMINATION OF CONCENTRATION OF I_2 IN AQUEOUS LAYER : Pipette out 10ml of aqueous layer and add 10ml of water and titrating with 0.01N hypo solution till the solution turns to straw yellow in colour then add one to two ml of starch indicator and continue the titration until the deep blue coloured solution changes to colourless solution.

Then the rate of Equilibrium or Equilibrium constant

$$K = \frac{[KI_3]_{(Eq)}}{[KI]_{(Eq)} \cdot [I_2]_{(Eq)}}$$

REPORT :

The Equilibrium constant of the reaction is _____

CALCULATIONS:

Weight of weighing bottle substance $W_2 =$ _____gms

Weight of bottle after transferring the substance $W_1 =$ _____gms

Weight of the substance transferred $W = W_2 - W_1$

Te concentration of potassium dichromate $= \frac{(W_2 - W_1) \times 0.1}{1.225}$

STANDARDISATION OF SODIUM THIOSULPHATE

S.No	Volume of potassium dichromate	Burette Reading of Initial (ml)	Burette Reading final (ml)	Volume hypo consumed (V_1) ml
1	20	0		
2	20	0		
3	20	0		

Volume of potassium dichromate $V_1 = 20$ ml

Concentration of potassium dichromate $N_1 =$

Volume of Hypo $V_2 =$

Concentration of Hypo $N_2 = V_1 N_1 = V_2 N_2$

$$N_2 = \frac{V_1 N_1}{V_2}$$

Concentration of Hypo = _____N

TITRATION OF ORGANIC LAYER:

S.No	Volume of Organic layer (ml)	Burette Reading Initial (ml)	Burette Reading final (ml)	Volume of hypo consumed (V_1) ml
1	5	0		
2	5	0		
3	5	0		

CALCULATIONS & OBSERVATIONS

Volume of Hypo $V_1 =$

Concentration of Hypo $N_1 = 0.1N$

Volume of Organic layer $V_2 = 5ml$

Concentration of Organic layer $N_2 = V_1 N_1 = V_2 N_2$

$$N_2 = \frac{V_1 N_1}{V_2}$$

Concentration of $[I_2]_{org} =$

$$\text{Partition co-efficient} = \frac{[I_2]_{org}}{[I_2]_{Eq}}$$

$$[I_2]_{Eq, Free} = \frac{[I_2]_{org}}{\text{Partition Coefficient}}$$

TITRATION OF AQUEOUS LAYER:

S.No	Volume of Organic layer (ml)	Burette Reading Initial (ml)	Burette Reading final (ml)	Volume of hypo consumed (V_1) ml
1	10	0		
2	10	0		
3	10	0		

CALCULATIONS :

Volume of Hypo $V_1 =$

Concentration of Hypo $N_1 =$

Volume of I in Aqueous layer $V_2 =$

Concentration of I in Aqueous layer $N_2 =$

$$V_1 N_1 = V_2 N_2$$

$$N_2 = \frac{V_1 N_1}{V_2}$$

$$\text{Concentration of } [I_2]_{\text{Aq total}} = \frac{(\text{Conc. of hypo}) \times (\text{Volume of hypo})}{(\text{Volume of Organic layer}) \times (2)}$$

$$\text{Concentration of KI, } [KI] = \text{_____ N}$$

$$\text{Concentration of Hypo sol} = \text{_____ N}$$

$$\text{Partition Co-efficient} = 85.5$$

$$[I_2]_{\text{Eq Free}} = \text{_____ N};$$

$$[I_2]_{\text{Aq total}} = [I_2]_{\text{Eq total}} = \text{_____ N}$$

$$[KI_3]_{\text{Eq}} = [I_2]_{\text{Eq total}} - [I_2]_{\text{Eq Free}}$$

$$[KI]_{\text{Eq}} = [KI] - [KI_3]_{\text{Eq}}$$

$$\text{Equilibrium Constant, } K = \frac{[KI_3]_{\text{Eq}}}{([KI]_{\text{Eq}} \times [I_2]_{\text{Eq}})}$$

EXPERIMENT- 3**DETERMINATION OF CRITICAL SOLUTION TEMPERATURE**

AIM : To determine the Critical Solution Temperature (C.S.T) of Phenol–Water System.

CHEMICALS REQUIRED :

80 % Phenol - 100 ml.

PROCEDURE :

In a boiling tube, take 10 ml of Phenol. To this add 2 ml of Water. The boiling tube is placed in 250ml beaker containing water. Thermometer is also placed in a boiling tube. On stirring the solution, white turbidity is obtained. On continuous heating of the solution, the clear solution appears.

The temperature is noted (clearing temperature). Then on continuous cooling by vigorous stirring, again the clouding will appear. The temperature is noted (Clouding Temperature-). Similarly the procedure will follow for the addition of 4ml, 6ml, 8ml, 10ml of water.

Similarly in another test tube take 10ml of water. To this add 2ml of Phenol. Clearing and Clouding Temperatures are noted and also for the addition of 4ml, 6ml, 8ml, 10ml of Phenol.

The average of Clearing and Clouding Temperature is called Miscibility Temperature. The maximum Miscibility Temperature is called Critical Solution Temperature.

REPORT :

The Critical Solution Temperature of Phenol – Water System is _____°C.

CALCULATIONS:**WATER IN PHENOL SYSTEM :**

S.No	Volume of 80% Phenol (ml)	Volume of Water (ml)	Clearing Temperature (T_1)	Clouding Temperature (T_2)	Miscibility Temperature $T=(T_1+T_2)/2$
1	10	02			
2	10	04			
3	10	06			
4	10	08			
5	10	10			

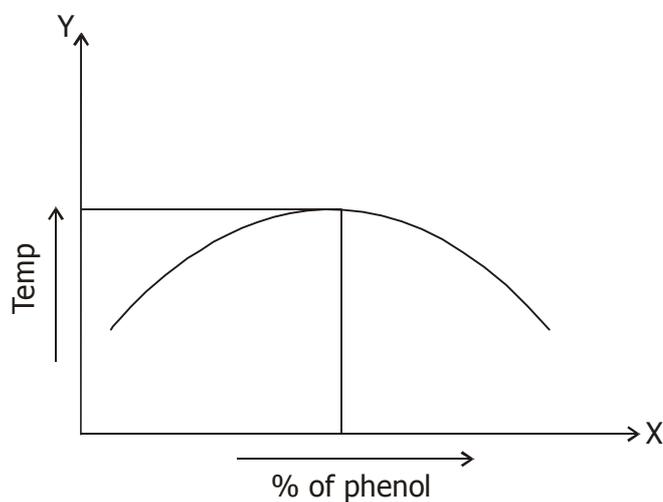
PHENOL IN WATER SYSTEM :

S.No	Volume of 80% Phenol (ml)	Volume of Water (ml)	Clearing Temperature (T_1)	Clouding Temperature (T_2)	Miscibility Temperature $T=(T_1+T_2)/2$
1	02	10			
2	04	10			
3	06	10			
4	08	10			
5	10	10			

The Percentage of Phenol can be calculated using the formulae=

$$\frac{(\text{Vol. of Phenol} \times \text{Density of water}) \times 100}{\{(\text{Vol. of Phenol} \times \text{Density of Phenol}) + (\text{Vol. of water} \times \text{Density of Water})\}}$$

The CST of Phenol – Water System from graph is _____°C.



EXPERIMENT- 4**DETERMINATION OF EFFECT OF ELECTROLYTE ON CST**

AIM : To determine the effect of electrolyte on Critical Solution Temperature of Phenol–Water System.

CHEMICALS REQUIRED :

- 1) 80% Phenol = 80ml Phenol + 20ml water.
- 2) 0.1 N NaCl

PROCEDURE :

From 0.1N NaCl solution 0.02N, 0.04N, 0.06N, 0.08N NaCl solutions are prepared. In a boiling tube 5ml of Phenol solution and 5ml of 0.02 N NaCl are taken. The boiling tube with stirrer and thermometer is placed in a beaker in which water will be taken and the boiling tube is clamped to retort stand. On stirring the solution, white cloudiness is appeared. On heating the solution gradually at certain temperature, the cloudiness disappears. The temperature is noted. Again on continues cooling, at certain temperatures a clear solution becomes cloudy. The temperature is noted. The average of these two temperatures will gives the Critical Solution Temperature. Similarly, the procedure will follows for 0.04 N, 0.06 N, and also for given unknown solution.

Draw a graph between Critical Solution Temperature and concentration of Electrolyte. A straight line will be formed with a positive slope.

REPORT :

The Concentration of unknown NaCl solution is 0.02 N. On addition of NaCl, the Critical Solution Temperature of Phenol – Water System increases.

CALCULATIONS:

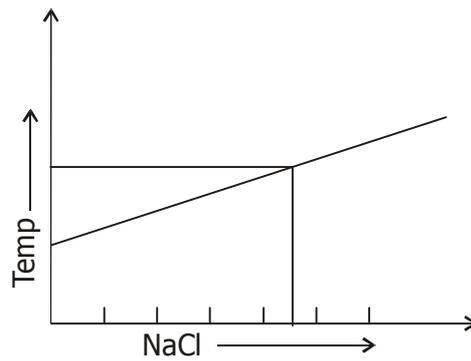
S.No	NaCl Solution		Volume of Water (T_1)	Clearing Temperature (T_2)	Clouding Temperature $T=(T_1+T_2)/2$	Miscibility Temperature
	Conc.	Volume				
1	0.02 N	5 ml	5 ml			
2	0.04 N	5 ml	5 ml			
3	0.06 N	5 ml	5 ml			
4	0.08 N	5 ml	5 ml			
5	0.1 N	5 ml	5 ml			
6	X N	5 ml	5 ml			
7	Y N	5 ml	5 ml			

From graph:

The concentration of unknown NaCl Solution (X)= _____ N.

The concentration of unknown NaCl Solution (Y)= _____ N.

GRAPH FOR DETERMINING THE EFFECT OF ELECTROLYTE ON CST :



EXPERIMENT- 5

DETERMINATION OF CO-EFFICIENT
OF VISCOSITY

AIM : Determination of co-efficient of viscosity of a liquid by Oswald's method.

APPARATUS REQUIRED :

Viscometer, beaker, pipette, rubber tube, pinch cocks, retort stand.

CHEMICALS REQUIRED :

- 1) Chromic Acid
- 2) Water
- 3) Acetone and
- 4) Given liquid.

PRINCIPLE :

The fractional force acting between two layers at a distance of 1 cm with a velocity difference of 1 cm/sec is called Co-efficient Of Viscosity. It is denoted by the symbol " η ", units are c-poise.

PROCEDURE :

Clean the Viscometer using Chromic Acid. Again Viscometer is rinsed with Water for two to three times.

The Pinch cock is adjusted so that the time of flow of Water is determined for two to three times and notes the average value (t_w). The Viscometer is cleaned with acetone and dries.

The time of flow of the liquid is determined for 2 or 3 times and note the average value (t_l).

Calculate the Co-efficient of viscosity of the given liquid by using the given formula,

$$\eta_l = \frac{t_l \times d_l}{t_w \times d_w} \times \eta_w$$

PRECAUTIONS :

1. The Viscometer should be cleaned with Chronic Acid.
2. The Viscometer should be clamped vertically using retort stand.

REPORT :

The co-efficient of Viscosity of a given liquid is _____ c-poise.

CALCULATIONS :

S.NO.	Time of flow of water (t_w sec)	Average (t_w sec)	Time of flow of given liquid (t_{l1})	Average (t_{l1} sec)
1				
2				
3				

Viscosity of Water, $\eta_w = \text{_____ c-poise}$

Density of water, $d_w = \text{_____ gm/cc}$

Density of liquid, $d_{l1} = \text{_____ gm/cc}$

Time flow of given liquid, $d_{l1} = \text{_____ sec}$

Time flow of water, $t_w = \text{_____ sec}$

Density of second liquid (d_{l2}) = _____ gm/cc

$$\eta_{l1} = \frac{t_{l1} \times d_{l1}}{t_w \times d_w} \times \eta_w$$

= _____ c-poise

S.NO.	Time of flow of water (t_w sec)	Average (t_w sec)	Time of flow of given liquid (t_{l_2})	Average (t_{l_2} sec)
1				
2				
3				

Viscosity of Water, $\eta_w = \text{_____}$ c-poise

Density of water, $d_w = \text{_____}$ gm/cc

Density of liquid, $d_{l_2} = \text{_____}$ gm/cc

Time flow of given liquid, $t_{l_2} = \text{_____}$ sec

Time flow of water, $t_w = \text{_____}$ sec

Density of second liquid (d_{l_2}) = _____ gm/cc

$$\eta_{l_2} = \frac{t_{l_2} \times d_{l_2}}{t_w \times d_w} \times \eta_w$$

= _____ c-poise

EXPERIMENT- 6**DETERMINATION OF FIRST ORDER RATE CONSTANT [ESTER HYDROLYSIS]**

AIM : To determine the relative strength of two acids by ester hydrolysis

APPARATUS :

1. Conical flask.
2. Burette.
3. Pipette.

CHEMICALS REQUIRED :

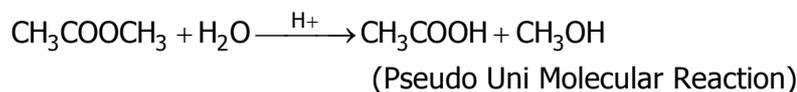
1. Methyl Acetate
2. Hydrochloric Acid
3. Sodium Hydroxide (NaOH)
4. Oxalic Acid.
5. Phenolphthalein.

PREPARATION OF SOLUTIONS :

- a) 1N and 2N HCl: 22.5 ml and 45 ml of Conc. HCl is taken in a 250 ml volumetric flask and make up them up to the mark with distilled water.
- b) 0.5N NaOH solution: 10 gms of NaOH is taken in the 500 ml volumetric flask. Dissolve it in distilled water and make up to the mark with distilled water.
- c) 0.5N Oxalic Acid: Accurately 6.3 gms of oxalic acid is weighed and transferred into 100ml volumetric flask. The substance is dissolved in distilled water and make up to the mark with distilled water.

PRINCIPLE:

The hydrolysis of methyl acetate in presence of an acid may be represented as



The Rate of reaction is given by

$$\left(\frac{Dx}{Dt}\right) = \left(\frac{2.303}{t}\right) \times \log\left(\frac{a}{(a-x)}\right) \rightarrow (1 \text{ order})$$

As Acetic acid is produced during the reaction, the reaction may be studied by the titration of unknown concentration of reaction mixture with a standard Alkali at suitable intervals of time.

The increasing in the acidity of the solution will have increase of amount of alcohol produced and hence the amount of methyl acetate is hydrolyzed.

$V_{\infty} = V_0$ is directly proportional to "a"

$(V_{\infty} = V_t)$ is directly proportional to (a-x)

$$x = \left(\frac{2.303}{t} \right) \times \log \left(\frac{V_{\infty} - V_0}{V_{\infty} - V_t} \right)$$

PROCEDURE :

Standardize 1N and 2N HCl by Known Concentration of NaOH solution, 100 ml of 1N HCl is taken in a conical flask and 10ml of pure methyl acetate is taken in a test tube. Both the Conical flask and the test tubes are placed in water bath to bring them into room temperature. Measure exactly 5ml of Methyl Acetate and add to 100 ml of 1N HCl in a Conical flask with Stopper.

When exactly half of the amount in the pipette is been discharged, the stopwatch is started. Mixture is shaken well and maintain at a constant Temperature. Now titrated with NaOH solution using phenolphthalein as indicator. The volume of Alkali required for titration is noted and is taken as " V_0 ". Similarly, 5ml of reaction mixture is taken out in successive intervals of time 10, 20, 30, 40 and 50 minutes. 5ml of reaction mixture is taken in a conical flask and 20ml of ice – cold water and titrated with NaOH using Phenolphthalein as indicator.

To obtain complete hydrolysis, the reaction mixture is kept in a water bath maintained at 50°C for about half an hour.

After the hydrolysis is completed, it is cooled at room temperature and titrated the 5ml of the reaction mixture with NaOH

Solution and is taken as, V_{∞} .

METHOD OF CALCULATION :

The initial volume of titrant, NaOH is V_0 at T_0 °C is proportional to the amount of HCl present I the reaction mixture at zero time.

When there is an Acetic Acid present as the hydrolysis, proceeds $V_{\infty} - V_0$, directly proportional to initial concentration of ester. At successive intervals of time $V_{\infty} - V_t$ is proportional to the concentration of esters at time "t".

$$K = \left(\frac{2.303}{t} \right) \times \log \frac{(V - V_0)}{(V_{\infty} - V_t)} \text{ sec}^{-1}$$

Same procedure and calculation is repeated for 2N HCl solution

Relative Strength of two acids is given by $\frac{K_2}{K_1}$

REPORT :

The Rate Constant for Hydrolysis of Methyl Acetate by 1N HCl and 2N HCl are

$$K_1 = \dots\dots\dots$$

$$K_2 = \dots\dots\dots$$

Relative Strength of Acids, $\frac{K_2}{K_1} = \dots\dots\dots$

CALCULATIONS :

Normally of Oxalic acid :

$$N_1 = \frac{\text{Amount of Oxalic acid}}{63.035} \times \frac{1000}{250}$$

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

STANDARDIZATION OF SODIUM HYDROXIDE SOLUTION :

S.No.	Volume of Oxalic acid (V_1 ml)	Burette Readings		Volume of NaOH solution (V_2 ml)
		Initial	Final	
1	20			
2	20			
3	20			

Where Volume of Oxalic acid Solution

$$V_1 = 20.0 \text{ ml}$$

Normality of Oxalic acid Solution $N_1 = \text{---} \text{ N}$

1

Volume of Sodium Hydroxide solution $V_2 =$

Normality of Sodium Hydroxide solution $N_2 = \text{---} \text{ N}$

We know that $V_1 N_1 = V_2 N_2$

Therefore, $N_2 = \frac{V_1 N_1}{V_2}$

Calculations for determining Rate constants:

For 1 N HCl :

S.No.	Time(t) Minutes	Burette initial reading (ml)	Burette final reading (ml)	Volume of NaOH Consume (V_t ml)	$(V_\infty - V_t)$ ml	$\text{Log}(V_\infty - V_t)$	$K_1 = (2.303/t) \times$ $\text{Log}(V_\infty - V_0) /$ $(V_\infty - V_t)$
1	0						
2	10						
3	20						
4	30						
5	40						
6	50						
7	60						
8	V_∞						

Average $K_1 =$

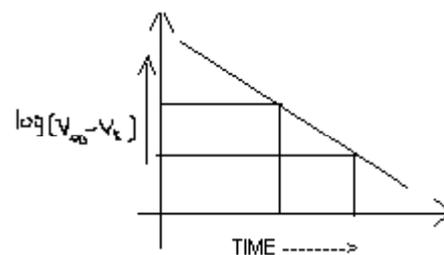
$$V_0 = \text{_____ ml}, \quad V_\infty = \text{_____}$$

$$V_\infty - V_0 = \text{_____ ml}$$

From Graph

$$\text{Slope} = \text{_____}$$

$$\text{Slope} = \frac{K_1}{2.303} \Rightarrow K_1 = \text{Slope} \times 2.303$$



S.No.	Time(t) Minutes	Burette initial reading (ml)	Burette final reading (ml)	Volume of NaOH Consume (V_t ml)	$(V_\infty - V_t)$ ml	$\text{Log}(V_\infty - V_t)$	$K_2 = (2.303/t) \times$ $\text{Log}(V_\infty - V_0) /$ $(V_\infty - V_t)$
1	0						
2	10						
3	20						
4	30						
5	40						
6	50						
7	60						
8	V_∞						

Average $K_2 =$

$$V_0 = \dots\dots\dots \text{ml}, V_\infty = \dots\dots\dots$$

$$V_\infty - V_0 = (\dots\dots\dots) - (\dots\dots\dots)$$

$$= \text{___ ml}$$

From Graph: Slope = $K / 2.303$,

$$K = 2.303 * \text{slope}$$

CALCULATIONS :

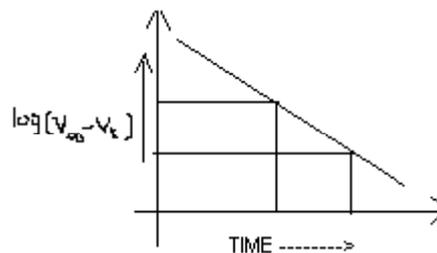
Rate Constant of 1N HCl, $K_1 = \text{___ sec}^{-1}$,

Rate Constant of 2N HCl, $K_2 = \text{___ sec}^{-1}$

Relative Strength of acids = K_2 / K_1 ,

=

=



EXPERIMENT- 7**CONDUCTOMETRIC TITRATION OF STRONG ACID Vs STRONG BASE**

AIM : To determine the strength of the given HCl Solution conductometrically .

CHEMICALS REQUIRED :

1. NaOH Solution
2. HCl
3. Oxalic acid.
4. Phenolphthalein.

PREPARATION OF STANDARD OXALIC ACID SOLUTION (0.1N) :

About 3.15 Gms of Oxalic acid di hydrate is weighed accurately and dissolved in small amount of distilled water and made up to the mark in a 250 ml Volumetric flask.

PREPARATION OF 0.1N SODIUM HYDROXIDE :

About 1 Gm of Sodium Hydroxide is dissolved in small amount of water and diluted to 250 ml and Standardized against standard Oxalic acid Solution.

THEORY : The conductivity of HCl solution is very high due to mobility of H^+ ions in it. When a solution of strong alkali is added to the solution of Strong acid, the highly conducting H_3O^+ ions are replaced by Na^+ ions is considerably Smaller than H_3O^+ and hence addition of alkali to the acid is always accompanied by a decrease in conductivity. When all the H_3O^+ ions are replaced, i.e.; after the endpoint, further addition of NaOH results in increase in conductivity.

From the plot of the Conductance Vs Volume of NaOH added, the end point can be calculated.

PROCEDURE :**STANDARDIZATION OF SODIUM HYDROXIDE SOLUTION :**

20 ml of Oxalic acid is pipetted out in to a Conical flask and is diluted to 30 ml with distilled water. To the solution, two drops of Phenolphthalein indicator is added and then titrated against Sodium Hydroxide taken in a burette. The end point is colorless to pale pink. The experiment is repeated till concurrent readings are obta

DETERMINATION OF STRENGTH OF GIVEN HCL SOLUTION : The given unknown HCl solutin in 100ml V.f. is made upto the mark and then 10ml of the given Unknown HCl Solution is taken in a 100 ml beaker. To this 40 ml of distilled water is added. The electrode of the cell is dipped in the solution. The conductivity of the solution is noted before adding the alkali. The standardized Sodium Hydroxide is added from a Burette with 1 ml of increment and by shaking thoroughly, the Contents of the beaker the conductivity values are noted. The values of ob-

served conductivities are plotted ordinate against volume of Sodium Hydroxide added as abscissa.

The concentration of Hydrochloric acid is determined using the end point from the graph.

PRECAUTIONS :

After each addition of the titrant from the burette, the solution should be thoroughly stirred and then the reading should be taken.

REPORT :

The strength of the Hydro Chloric acid is _____ Gms / Litre

CALCULATIONS :

$$N = \frac{\text{Amount of Oxalic acid}}{63.035} \times \frac{1000}{250}$$

$$= \text{_____} N$$

STANDARDIZATION OF SODIUM HYDROXIDE SOLUTION :

S.No.	Volume of Oxalic acid (V_1 ml)	Burette Readings		Volume of NaOH solution (V_2 ml)
		Initial	Final	
1	20			
2	20			
3	20			

We know that $V_1 N_1 = V_2 N_2$

Where Volume of Oxalic acid Solution $V_1 = 20.0$ ml

Normality of Oxalic acid Solution $N_1 = \text{_____} N$

Volume of Sodium Hydroxide solution $V_2 = \text{_____} ml$

Normality of Sodium Hydroxide solution $N_2 = \text{_____} N$

$$\text{Therefore, } N_2 = \frac{V_1 N_1}{V_2}$$

\therefore Normality of Sodium Hydroxide $N_2 = \text{.....} N$

DETERMINATION OF AMOUNT OF HYDRO CHLORIC ACID :

Where Volume of Sodium Hydroxide solution from graph $V_2 = \text{--- ml}$

Normality of Sodium Hydroxide solution $N_2 = \text{--- N}$

Volume of Hydrochloric acid solution $V_3 = 10.0 \text{ ml}$

Normality of Hydrochloric acid in the mixture $N_3 = \text{--- N}$

$$V_2 N_2 = V_3 N_3$$

Therefore,

$$N_3 = \frac{V_2 N_2}{V_3}$$

Strength of HCl acid = Normality of HCl acid in solution * Eq.Wt. of HCl

$$= N_3 * 36.5 = \text{--- Gms / liter.}$$

REPORT:

Amount of HCl present in the given solution = gms/liter

EXPERIMENT- 8**TITRATION OF POTASSIUM DI CHROMATE
VERSUS FERROUS AMMONIUM SULPHATE
(MOHR'S SALT)**

AIM : To determine the strength and amount of the ferrous salt present in the given solution potentiometrically.

APPARATUS AND CHEMICALS REQUIRED :

Potentiometer, calomel electrode, platinum electrode, potassium dichromate (N/10) and solution of ferrous salt (~N/10). 2N sulphuric acid etc.

- 1) 0.1N Ferrous Ammonium sulphate solution; About 9.8035gms of Ferrous Ammonium Sulphate is weighed accurately transfer the substance through funnel dissolve in small amount of 2N H_2SO_4 and made up to the mark with 2N Sulphuric acid.
- 2) 0.1N Potassium dichromate solution: About 1.225 gms of potassium dichromate is weighed accurately, transfer the substance through the funnel and made up to the mark with distilled water.

PRINCIPLE :

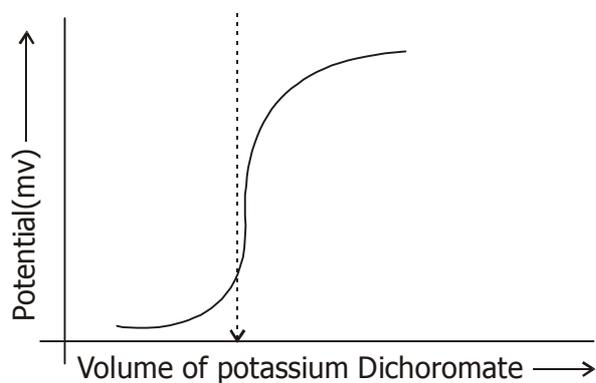
When dichromate solution is added to a solution containing ferrous ions, the ferrous ions get oxidized to ferric ions and a platinum electrode is dipped in the solution to pick up redox potential developed. The potential arising in a system containing species of oxidized and reduced state is given by.

$$E_{red} = E_{red}^0 - \frac{RT}{nF} * \ln \frac{a_{red}}{a_{ox}}$$

The Potential developed depends on the activities of the species (or concentrations of the species taking the activity coefficient as unity in dilute solutions) and it may be combined with another half cell (calomel electrode) to determine the change of activities on adding the oxidizing agent. After the oxidation of all ferrous ions into ferric ions, the redox system will be $Cr_2O_7^{2-}/Cr^{3+}$ which has a different redox potential. This forms the basis of potentiometric titrations redox systems.

PROCEDURE;

The given Ferrous salt solution in 100ml volumetric flask is made up to the mark with 2N sulphuric acid. Pipette out 20ml of the ferrous salt solution into a 100ml beaker. Add equal quantity of dilute sulphuric acid and dip a bright platinum electrode and calomel electrode into the solution. Titrate the solution in the beaker against potassium dichromate taken in the burette



from graph volume of potassium dichromate $V_1 = \text{_____ml}$

Normality of potassium dichromate $N_1 = 0.1 \text{ N}$

Volume of ferrous Ammonium sulphate $V_2 = 10\text{ml}$

Normality of ferrous Ammonium sulphate $N_2 = \text{_____ml}$

We know that

$$V_1 N_1 = V_2 N_2$$

Therefore, $N_2 = \frac{V_1 N_1}{V_2}$

Amount of ferrous Ammonium sulphate present in the given 100ml of solution

$$= N_2 * 392.14 * 100 / 1000$$

$$= \text{_____gms/liter.}$$

REPORT:

Amount of ferrous Ammonium sulphate present in the given 100ml of solution = _____

MOLECULAR WEIGHTS AND EQUIVALENT WEIGHTS OF SOME SUBSTANCES

	Mol.wt	Eq .wt
1. Hydrochloric acid (HCl)	36.5	36.5
2. Sulphuric acid (H_2SO_4)	98	49
3. Sodium Carbonate (Na_2CO_3)	106	53
4. Sodium hydroxide (NaOH)	40	40
5. Oxalic acid ($\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$)	126	63
6. Hypo ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$)	248.19	248.19
7. Potassium permanganate (KMnO_4)	158	31.6
8. Potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$)	249.18	49.03
9. Copper sulphate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$)	249.6	249.6
10. Ferrous Ammonium Sulphate ($(\text{NH}_4)_2 \text{FeSO}_4 \cdot 5\text{H}_2\text{O}$)	392.14	392.14
11. Potassium Iodide (KI)	166	166
12. Sodium chloride (NaCl)	58.44	58.44

Table - 1
CONCENTRATED ACIDS

Acids	Specific gravity	% By-Weight	Approximate Normally
Hydrochloric acid	1.19	37.9	12 N
Nitric Acid	1.42	69.8	16 N
Sulphuric acid	1.84	96.0	36 N
Acetic acid (glacial)	1.05	99.5	17 N
Phosphoric acid	1.71	86.0	15 N

TABLE - 2
INDICATORS

Phenolphthalein	1%	Dissolve one gram of phenolphthalein in 100 ml of alcohol.
Methyl orange	0.1%	Dissolve one gram of methyl orange in one litre water
Starch	1%	Make a paste of 1 gm starch and add it to 100 ml of boiling water. Cool it and use.
D.P.A.	1%	Dissolve one gram Diphenyl amine indicator in 100 ml of conc. H_2SO_4

TABLE - 3
DENSITIES AND VISCOSITY OF LIQUIDS AT 27°C

LIQUID	DENSITY dl	VISCOSITY
Water	0.9965	0.894
Benzene	0.8737	0.596
Toluene	0.8625	0.526
Carbon Tetra Chloride	1.584	0.843
Chloroform	1.480	0.542
Acetone	0.792	0.361

TABLE - 4
SPECIFIC CONDUCTANCE OF POTASSIUM CHLORIDE (MHO CM - 1)

Temp °C	1N KCl	0.1 N KCl	0.01 KCl
25	0.11180	0.01288	0.001413
27	0.11574	0.01377	0.001418
30	0.12160	0.01412	0.001552
32	0.1288	0.01462	0.001610
35	0.1310	0.01539	0.001693
40	0.1400	0.01661	0.008360

STOCK SOLUTIONS

PHYSICAL CHEMISTRY

For 25 students

1) Determination of partition Co-efficient of Iodine in CCl_4 and water

- a) CCl_4 = 5 liters
- b) 1% Iodine in CCl_4 = 1.5 liters (15 Gms I_2 in 1.5 liters of CCl_4)
- c) 0.5N Hypo = 2 liters (250 Gms in 2 liters)
- d) 0.05N Hypo = 2 liters (25 Gms in 2 liters)
- e) Starch = (1 Gm in 100 ml)
- f) 10 % KI = 1 liter (100 Gms in 1 liter)

2) Determination of rate of equilibrium Constant:

- a) 0.05 N of KI = 2 liters (17 Gms in 2 liters)
- b) 10 % of KI = 1 liter (100 Gms in 1 liter of water)
- c) 0.01 Hypo = 2 liters (5 Gms of Hypo in 2 liters)
- d) 0.1 $\text{NK}_2\text{Cr}_2\text{O}_7$ = 1 liter (4.9 gms of $\text{k}_2\text{Cr}_2\text{O}_7$ in one liter)
- e) 1 % of I_2 in CCl_4 = 1.5 liters (15 Gms of I_2 in 1.5 liter CCl_4)
- f) CCl_4 = 2.5 liters
- g) Starch Indicator = 1 Gm Starch dissolved in 100 ml of hot water

3) Determination of rate of C.S.T of Phenol – Water System:

80% of Phenol = 2.5 liters (2 liters of Phenol + 500 ml of water)

[To the 2 liters of phenol add 500 ml of water drop by drop slowly while stirring with glass rod.]

4) Determination of effect of electrolyte on C.S.T:

- 1. 80 % Phenol = 1.2 liters (960 ml of Phenol + 240 ml of water)
- 2. 0.1 N NaCl = 6 liters (6 Gms NaCl / liter)

5) Determination of First Order rate Constant:

1. Methyl Acetate = 250 ml
2. 1 N HCl = 2.5 Liters (225 ml Conc. HCl + 2275 ml Water)
3. 2 N HCl = 2.5 Liters (450 ml Conc. HCl + 2050 ml Water)
4. 0.5 N NaOH = 5 Liters (20 Gms of NaOH / Liters) i.e. 100 Gms in 5 liters.

1) Conductometric titration:

1. 0.1 N HCl = 1 liter (9 ml HCl in 1 liter)
2. 0.1 N NaOH = 1 liter (4 Gms NaOH per Liter)
(Distribute 10 to 15ml of 1N Unknown solution in 100ml volumetric flask
And make up by distilled water)

2) Potentiometric titration:

- 1) 0.1N $K_2Cr_2O_7$ = 2 liters (9.8 gms in 5liters)
- 2) 2N H_2SO_4 = 5liters (275ml conc. H_2SO_4 in 5 liters)
- 3) 1N Ferrous ammonium sulphate = 500ml (unknown)
(Distribute 10 to 13ml of 1N Unknown solution in 100ml volumetric flask
And make up by 2N sulphuric acid)