

# 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.

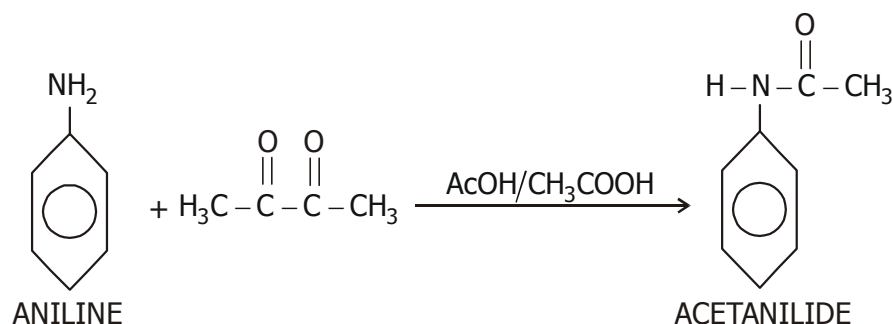
Transfer the contents of the flask into 250 ml ice-cold water. Filter the crude at the Pump. Yellow colored precipitate is formed on the filter paper.

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 ( $\text{Na}_2\text{CO}_3$ ) - 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  $\text{KMnO}_4$ .

Heat under reflux until the purple color of  $\text{KMnO}_4$  disappears (1 to 4 hours).

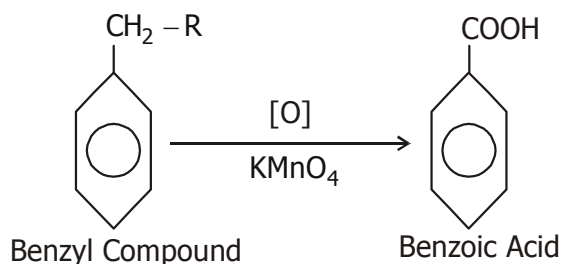
Allow the mixture to cool and filter. Carefully acidify the filtrate with Conc. HCl.

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.HNO <sub>3</sub>                | - 3.5 ml |
| 3. Conc. H <sub>2</sub> SO <sub>4</sub> | - 5 ml   |

**PROCEDURE :**

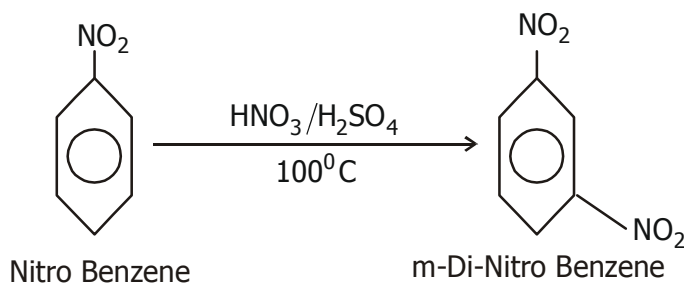
In 100 ml of round-bottomed flask, 3.5 ml of Conc.HNO<sub>3</sub> & 5 ml of Conc. H<sub>2</sub>SO<sub>4</sub> are taken. 3ml of Nitro Benzene is added in small portions and shaken well. For each addition, reflux the addition on a water bath for about 30 minutes with a continuous shaking.

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

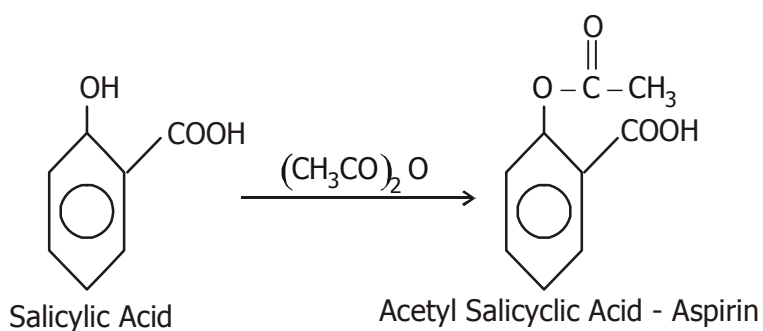
**PROCEDURE :**

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.

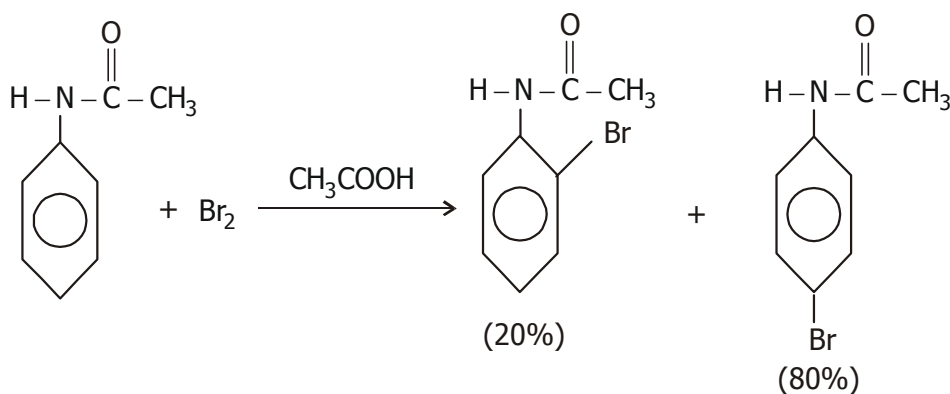
Filter the precipitate and see that no moisture is present and collect the entire mixture and stored it.

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 $\text{NaHCO}_3$ : Take a little amount of mixture in a test tube, to this a saturated solution of $\text{NaHCO}_3$ 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  $\text{NaHCO}_3$  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  $\text{CO}_2$  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  $\text{MgSO}_4$  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  $\text{MgSO}_4$ , 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  $\text{CO}_2$  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  $\text{MgSO}_4$  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
<b>PHYSICAL CHARACTERISTICS:</b>		
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		
<b>II. Solubility: Take a small amount of compound in a test tube and add 3-ml of solvent</b>		
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 <sub>3</sub>	Soluble in 5% NaHCO <sub>3</sub> 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 :

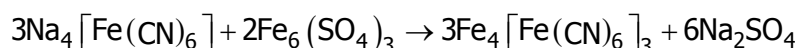
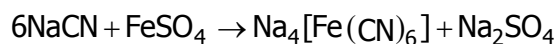
Heat a small amount of given compound on spatula	1) Burns with non-luminous and non-smoky flame.	Aliphatic compound
	2) Burns with Luminous and smokes flame	Aromatic compound
	3) Burns with sugar smell	Carbohydrates

### 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 hot 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.

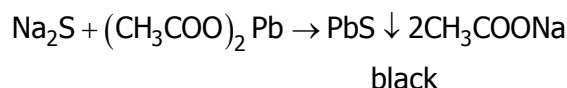
#### i) Test for Nitrogen :

Take 2ml of sodium Nitrogen is fusion extract add freshly prepared $\text{FeSO}_4$ and heated. Add conc $\text{H}_2\text{SO}_4$ slowly .	Prussian blue colour is observed	Nitrogen present observed
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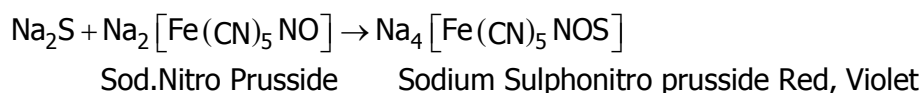


**ii) Test for Sulphur :**

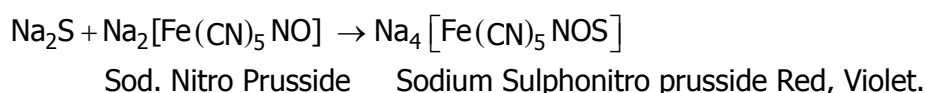
- |  |  |                    |
|--|--|--------------------|
| a) Acidify the sodium extract (2ml) with dil. acetic acid (2ml) and add a few drops (4-5) of lead acetate solution | A black precipitate of Lead sulphide is formed | Sulphur is present |
|--|--|--------------------|

**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:**

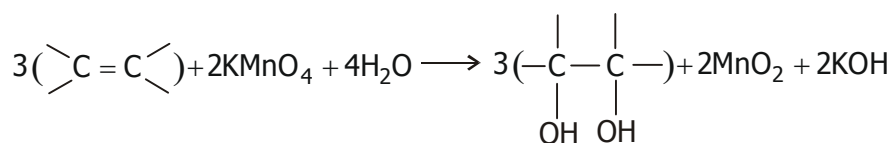
- |   |  |                      |
|---|--|----------------------|
| Acidify the sodium-fusion extract (2 ml) with dilute nitric acid (2-3 ml). Boil the solution gently for 1-2 minutes. Add silver nitrate solution (0.5 ml) to the above solution | i) A white ppt is formed which is soluble in $\text{NH}_4\text{OH}$        | Presence of Chlorine |
|   | ii) A pale yellow ppt is formed which is soluble in $\text{NH}_4\text{OH}$ | Presence of bromide. |
|   | iii) Yellow ppt is formed which is insoluble in $\text{NH}_4\text{OH}$     | 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 |

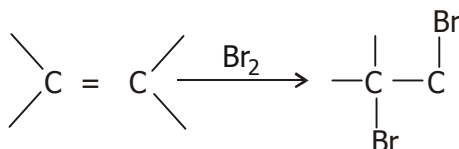


### ii) Br<sub>2</sub> in CCl<sub>4</sub> :

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%) Br<sub>2</sub> in CCl<sub>4</sub>.

Decolourisation takes place  
Decolourisation doesn't take place

Unsaturated compound  
Saturated compound



## DETECTION OF FUNCTIONAL GROUPS

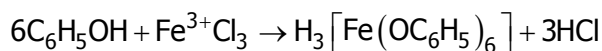
### TEST FOR PHENOLS

#### i) With neutral FeCl<sub>3</sub> test :

The compound to be dissolved in alcohol and add 1 (or) 2 drops of 5% FeCl<sub>3</sub> Solution.

Violet (or) Blue colour is observed

Phenol is present



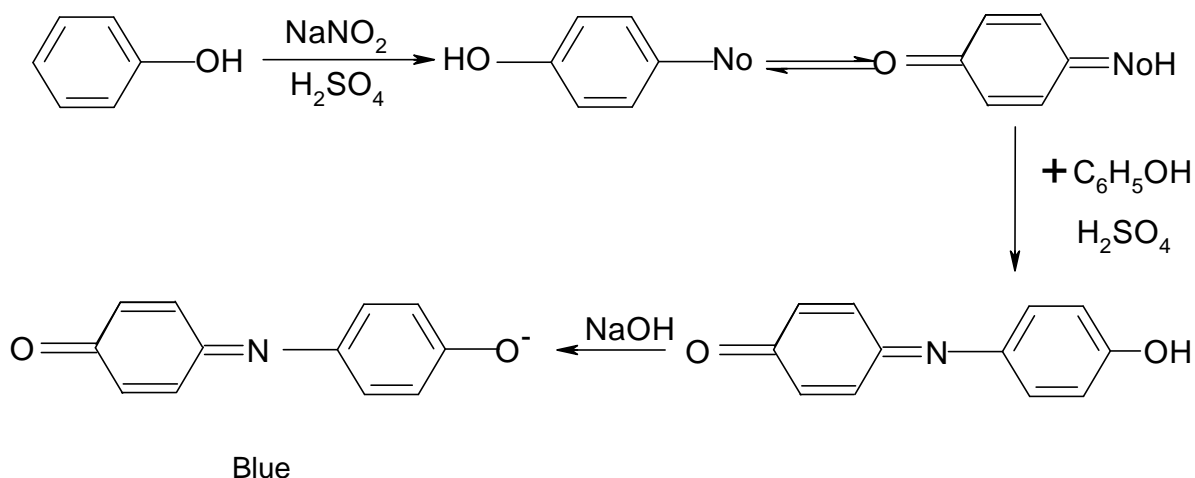
#### ii) Liebermann's nitroso

##### 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

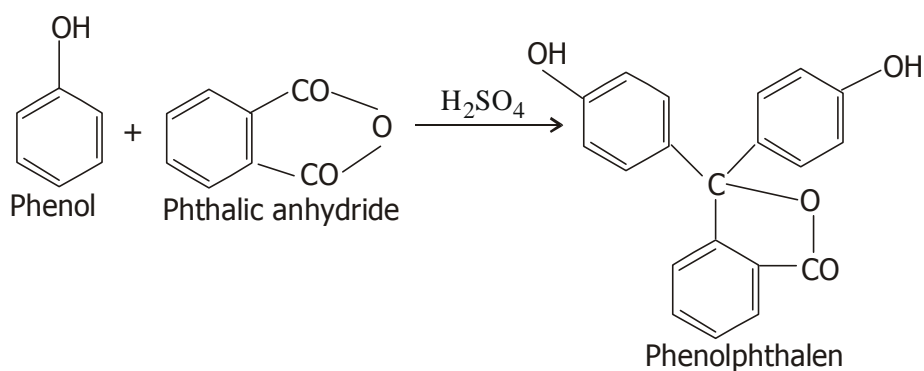


### iii) Phthalein Test :

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  
 $\alpha$  - Naphthol  
 $\beta$  - Naphthol



## II. TEST FOR CARBOXYLIC ACIDS

### i) $\text{NaHCO}_3$ Test :

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

Brisk effervescence is observed

Carboxylic acid is present

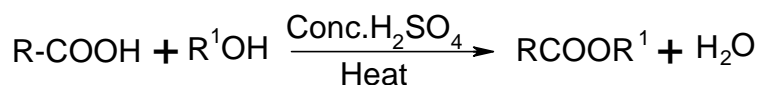


### ii) Ester Test :

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  $\text{Na}_2\text{CO}_3$  solution

Fruity smell is observed

Carboxylic acid is present



### iii) $\text{FeCl}_3$ 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

$\alpha$  - Hydroxy acids

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

$\beta$  - substituted aromatic hydroxy acids

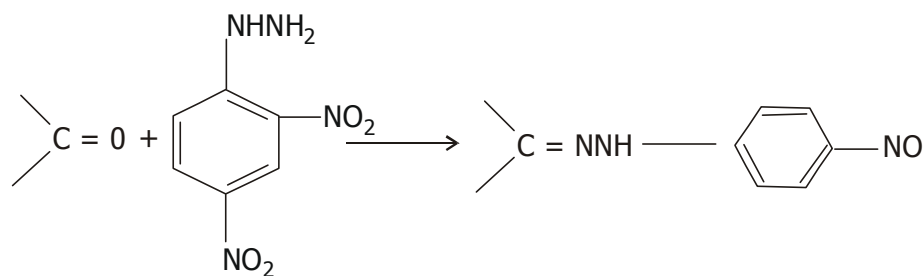
## III. TEST FOR CARBONYL COMPOUNDS

### i) Reaction with 2,4 DNP<sup>1</sup>

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

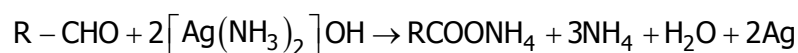
May be a carbonyl compound

**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

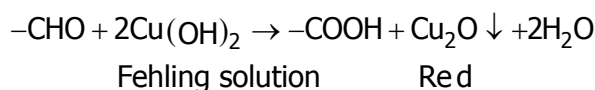
May be aldehyde is present

**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

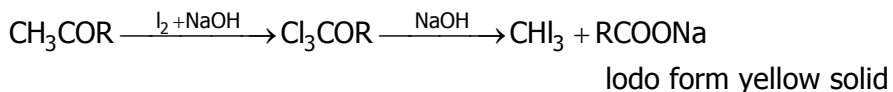
**v) Iodo form test :**

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

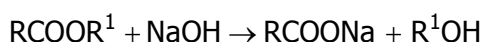
May be ketone



**vi) Test for esters :****i) Phenol phthalin test (Hydrolysis) :**

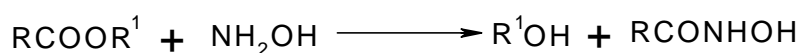
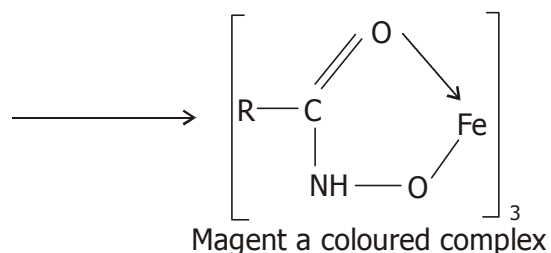
Add the given compound (0.1) to a dilute solution of NaOH (1% 12 ml). Add a drop of phenolphthalein. Add more NaOH to obtain pink colour. Now boil the solution for 5 minutes

Pink colour disappears      May be ester

**ii) Hydroxylamine test :**

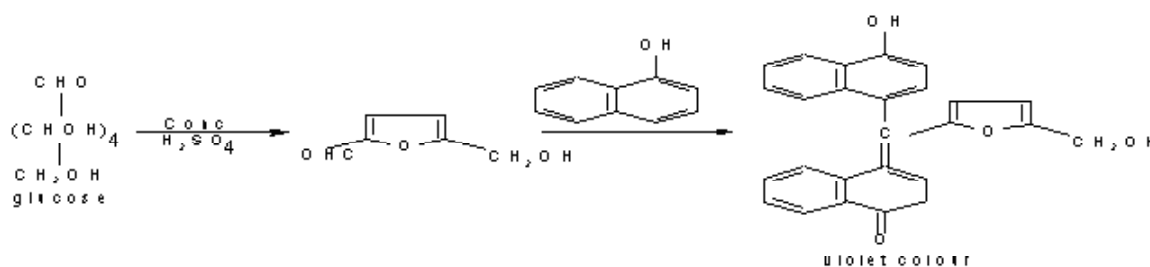
Mix the compound with hydroxylamine hydro chloride (1 ml) and sodium hydroxide (0.2 ml) and heat the mixture to boiling. Cool and add HCl (2 ml) and then add ferric chloride solution (1-2 drops)

Magenta colour is formed      Ester is present

**v) Test for carbohydrates :****i) Molisch's test :**

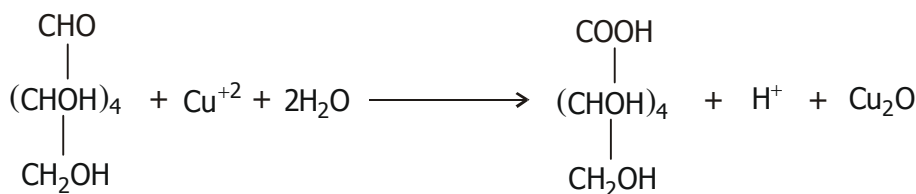
Add an alcoholic solution of  $\alpha$ -NaPhthol (10%) to an aqueous solution of substance. Then add conc H<sub>2</sub>SO<sub>4</sub> (1 ml) carefully along the sides of the test tube. Allow to stand for 2 minutes.

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<sub>2</sub>O 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

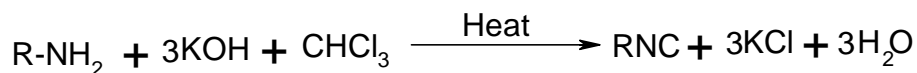
Carbohydrate is present

**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

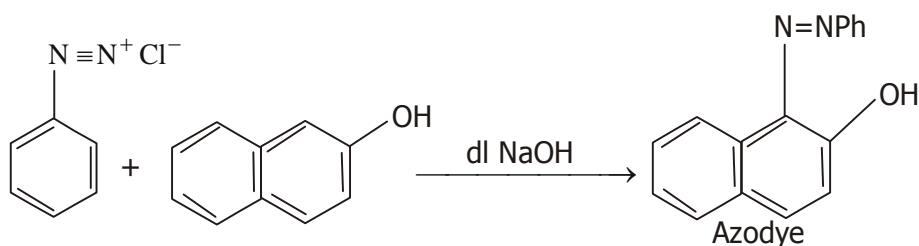
May be 1° amine.

**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<sub>2</sub> 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.

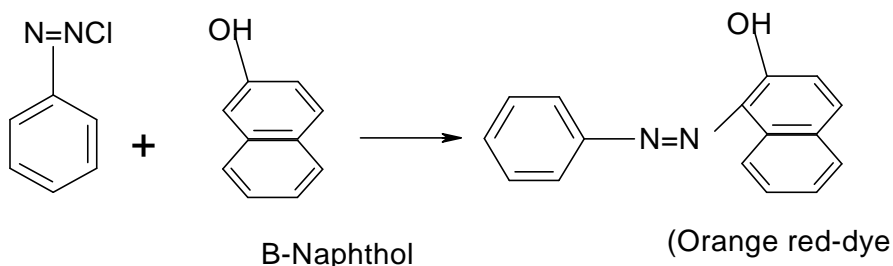
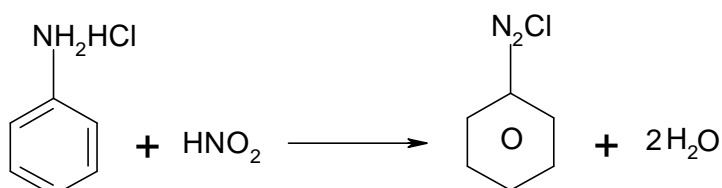
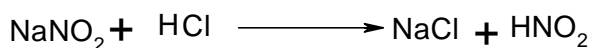


### iii) Nitrous acid test :

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  $\text{NaNO}_2$  slowly by means of dropper. After completion of reaction add a sol of  $\beta$ -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

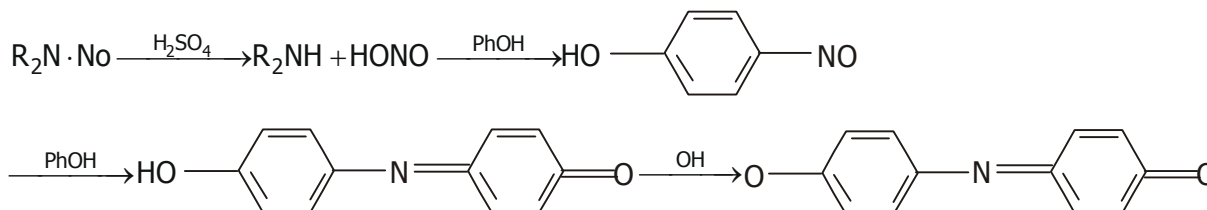


### TEST FOR 2° AMINEi) Liber mannitroso test :

Dissolve the compound in dil HCl and cool in ice. Add few ml or 10%  $\text{NaNO}_2$  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  $\text{H}_2\text{SO}_4$  by the sides of test tube

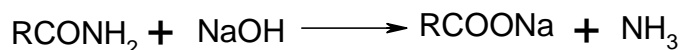


### 3) TEST FOR 3<sup>o</sup> AMINES:

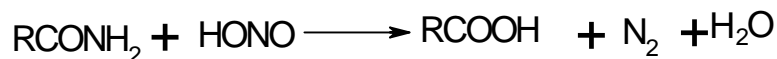
- |   |                            |                                 |
|---|----------------------------|---------------------------------|
| i) Dissolve the compound in few ml of dil HCl and add 2 ml of 10% $\text{K}_4[\text{Fe}(\text{CN})_6]$ solution | White ppt is observed      | 3 <sup>o</sup> Amine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

### VII. Test for Amides

- |   |                           |              |
|---|---------------------------|--------------|
| i) To the compound add few ml of 10% NaOH reflux (or) boil until $\text{NH}_3$ 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% $\text{NaNO}_2$ solution | Brisk effervescence are obtained due to the evolution of $\text{N}_2$ | May be Amide |
|---|---|--------------|

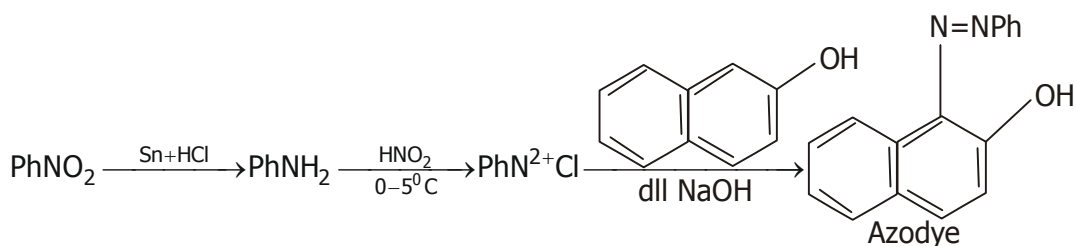


### Test for aromatic amides :

- |  |                               |                |
|--|-------------------------------|----------------|
| 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 $\text{H}_2\text{SO}_4$ to the organic compound	Soluble insoluble (two layers air for med)	Aromatic hydrocarbons Aliphatic
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**Test with chloroform :**

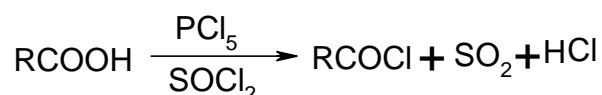
i) Heat anhydrous aluminium hydrochloride gently in a test tube and add organic compound and chloroform (2-3 drops)	Orange (or) red Blue Biphenyl (purple) Orange to red	Benzene Naphthalene Ar x
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**PREPARATION OF DERIVATIVES FOR VARIOUS FUNCTIONAL GROUPS****Derivatives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

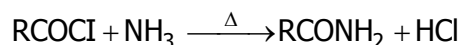
The acid is first converted to acid chloride and the acid chloride is then converted to the amide, anilide derivatives.

**Preparation of acid chloride by using thionyl chloride:**

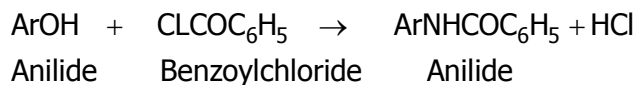
Place 1 gram of the acid into the round bottomed flask and add 5 ml of  $\text{SOCl}_2$  and reflux the contents in a water bath for 30 minutes. Distill off excess of thionyl chloride and cool the residue. It is used for the preparation of acid derivatives.

**Amide derivative :**

Treat the acid chloride with 10ml of conc  $\text{NH}_3$  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  $\text{C}_6\text{H}_6$ , warm on water bath, cool and filter if a solid separates out. If the solid aniline does not separate, wash the  $\text{C}_6\text{H}_6$  layer with water, dil HCl, dil NaOH finally with water. Dry remaining  $\text{C}_6\text{H}_6$  solution over anhydrous sodium sulphate (or) anhydrous  $\text{CaCl}_2$ . Remove the solvent by distillation and recrystallise the residue from  $\text{C}_6\text{H}_6$  (or) alcohol.



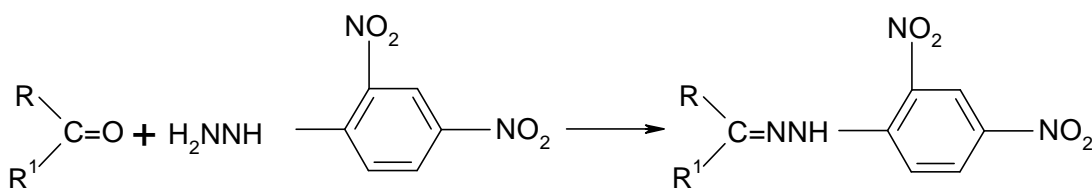
### S-BENZYL THIO URANYL CHLORIDE

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

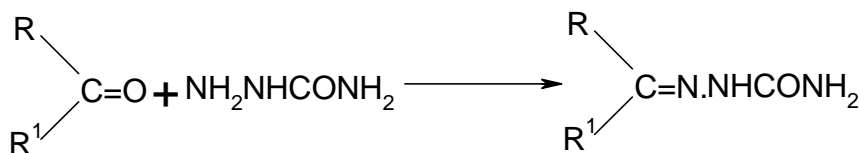
0.5 grams of substance or 2 ml of the given substance dissolved in 1 .c.c of methanol, to this 2 c.c of 2,4 –DNP solution is added and shake well. Then yellow precipitate is formed, it is recrystallised from alcohol.



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 :

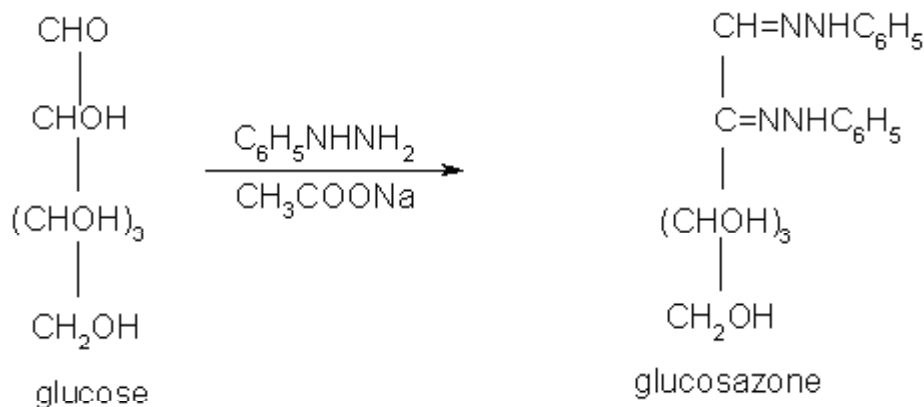
**Hydrolysis of Ester:** Place 1 gm of ester and sodium hydroxide (20 ml, 10%) in a round bottomed flask. Reflux the mixture gently for half an hour until the hydrolysis is complete. Cool, and acidify the solution with dil  $\text{H}_2\text{SO}_4$  dil HCl. The acid separates out. Allow the mixture to 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.



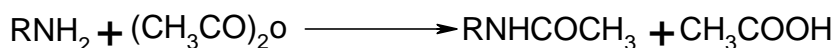
### ii) Acetate derivative :

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.



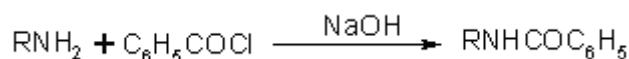
## Derivatives of Amines :

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.



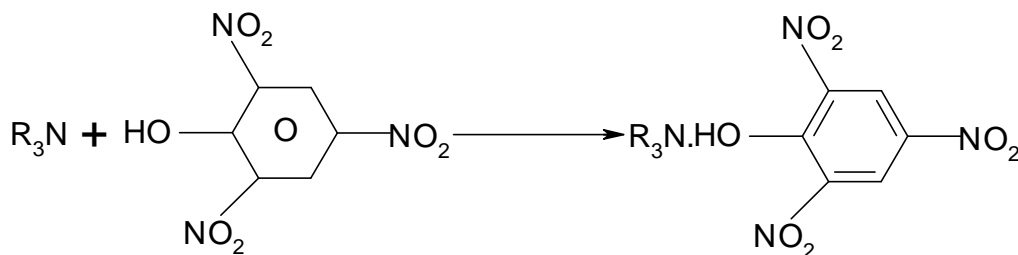
Acetyl derivative

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.



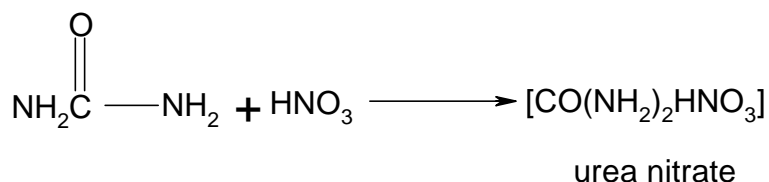
## Derivatives of Amides :

**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  $\text{H}_2\text{SO}_4$  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 :

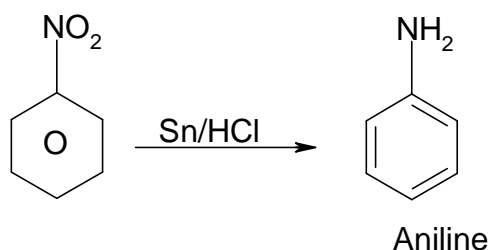
**1) Urea nitrate derivatives :** Dissolve 1 gm of urea in about 5 ml of water and add 2 ml of conc  $\text{HNO}_3$  with stirring. White crystals of the urea nitrate separated. Filter and dry it. Recrystallise from ethanol.



**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.

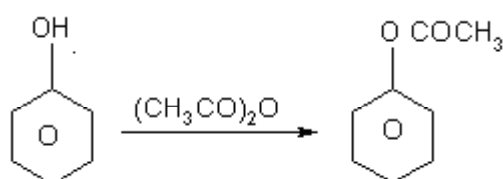
## Derivatives of Nitro compounds:

**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.



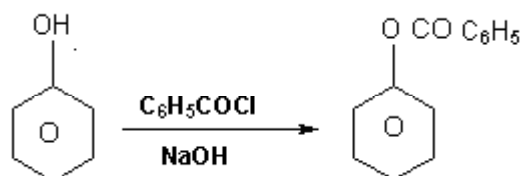
## DRIVATIVES OF PHENOLS

**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 :**

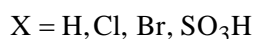
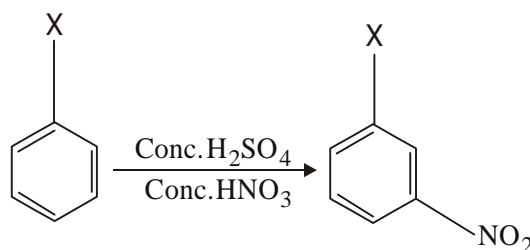
1ml of compound is taken in a R.B. flask. To this add 5 ml of 10% NaOH and 2ml of Benzoyl chloride. Shake the flask vigorously for about 30 minutes. The completion of reaction is indicated by the disappearance of smell of benzoyl chloride add about 30ml of cold water to the flask, filter it and recrystallize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

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

- 114<sup>0</sup> Acetanilide, derivative, P - bromoacetanilide, m.p. 167<sup>0</sup>, P - nitroacetanilide, m.p. 214<sup>0</sup>
- 121 Benzoic acid, derivative, anilide, m.p. 162<sup>0</sup>, S. Benzyl isothiouranium, m.p. 167<sup>0</sup>
- 128 Benzamide, derivative, benzoic acid, m.p. 121<sup>0</sup>
- 132 Urea, derivative, nitro, m.p. 163<sup>0</sup>, oxalate m.p. 170<sup>0</sup>
- 133 Cinnamic acid, derivative, anilide, m.p. 153<sup>0</sup>, S. Benzyl ISO thiouranium m.p. 152<sup>0</sup>
- 141<sup>0</sup> m - Nitro benzoic acid, derivative, anilide, m.p. 153<sup>0</sup>, amide, m.p. 142<sup>0</sup>, S.benzyl iso thiouranium, m.p. 159<sup>0</sup>
- 146<sup>0</sup> Glucose, derivative, Osazone, m.p. 205<sup>0</sup>
- 156 Salicylic acid, derivative, anilide, m.p. 135<sup>0</sup> acetyl, m.p. 136, Nitro m.p. 226<sup>0</sup>
- 280 Sulphanilic acid, derivative, amide m.p. 164<sup>0</sup>

## 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.

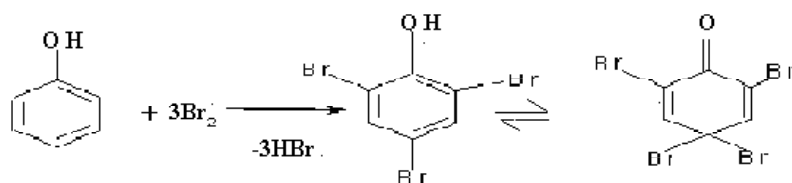
**Tollen's reagent** : Commercial ammonia (sp.gr. 0.90) is diluted with an equal volume of water and 10g. of silver nitrate are dissolved in 100 c.c of this diluted ammonia. A 10 percent aqueous solution of caustic soda is also prepared and kept separate. The two are mixed in equal volumes just before 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  $\text{H}_2\text{SO}_4$  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  $\text{H}_2\text{SO}_4$ . 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 ( $\text{NaCN}$ ,  $\text{Na}_2\text{S}$ ,  $\text{NaX}$ ). 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  $\text{FeSO}_4$  solution is used in Lassaigne's test for nitrogen as on keeping  $\text{FeSO}_4$  solution oxidizes to basic ferric sulphate and cannot be used for detection.
- 5) Why does o-nitro phenol give no colour with  $\text{FeCl}_3$  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)  $\text{CCl}_4$ ?
  - A) The advantage of bromine in water over bromine in  $\text{CCl}_4$  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.



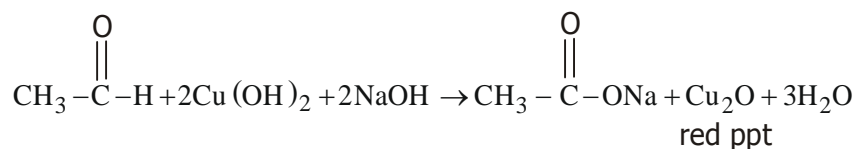


2,4,4,6 - tetra bromo cyclo hexadieneone

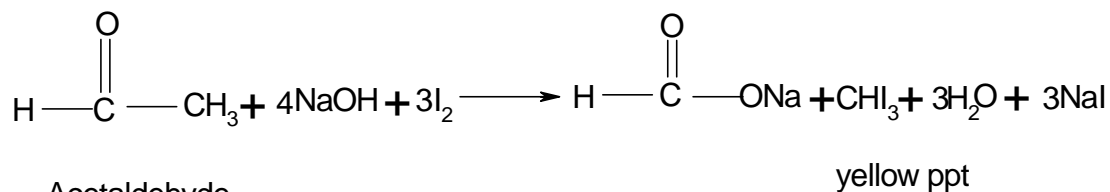
8) How will you distinguish between benzaldehyde and acetaldehyde?

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

Fehling test :



Iodo form test :



Acetaldehyde

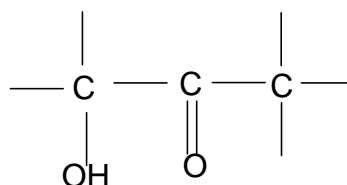
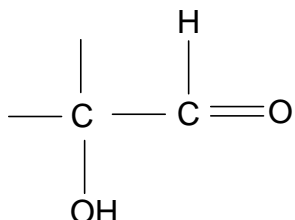
9) How will you distinguish between reducing and non reducing sugars?

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.

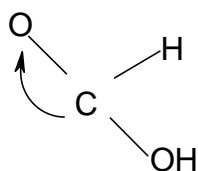
**Structural features of reducing sugars:**

1) They contain  $\alpha$  - hydroxyaldehyde (or)  $\alpha$ -hydroxy ketone functions

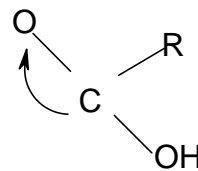
2)

 $\alpha$  - hydroxy aldehyde $\alpha$  - 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



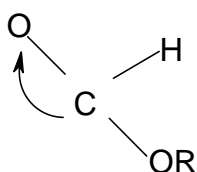
Hemi ketal

Structural features a-non-reducing sugars :

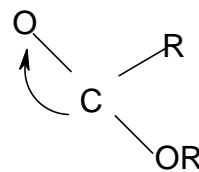
- 1) They do not contain free aldehyde (or) ketone groups with OH on the carbon adjacent to carbonyl group.

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

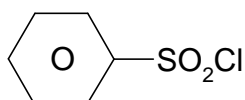


Ketal

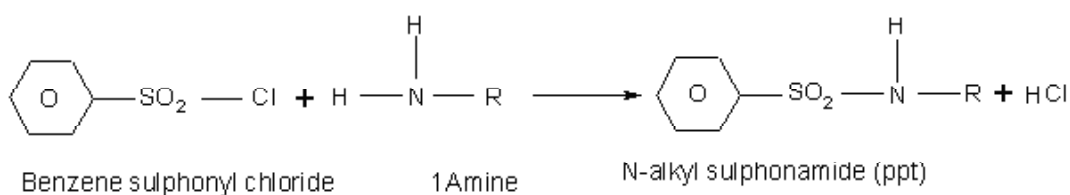
Reducing sugars : glucose, fructose (mono sacharides) maltose, lactose (di)

Nonreducing sugars: Sucrose

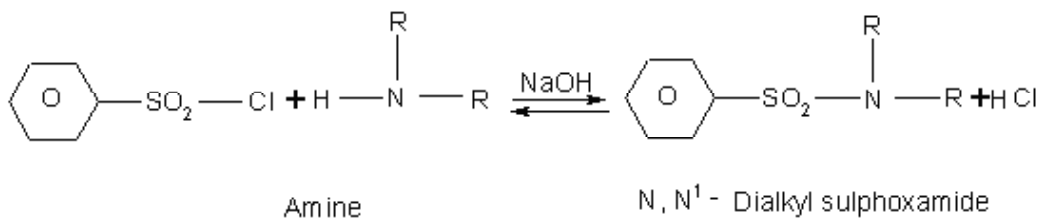
- 10) How will you distinguish between glucose and starch?
- A) Starch does not reduce Tollen's reagent and Fehling solution. It does not form an osazone with phenyl hydrazine. While glucose can give Tollen's test and Fehling test. It also form osazone.
- 11) What is Hinsberg reagent? By using it how 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, N<sup>1</sup>-diakyl benzene sulphonamide.



- b) 3<sup>o</sup> 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  $\text{CCl}_4$  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  $N_2 =$

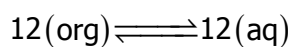
$$V_1 N_1 = V_2 N_2$$

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

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.

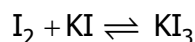
**Starch indicator :** About one gram of starch is weighed and pasted with few ml of cold water and pour this solution drop wise into 100ml of boiling water. Boil the solution cool it and used as starch indictor

**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

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

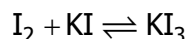
On determining  $[KI_3]_{(Eq)}$ ,  $[KI]_{(Eq)}$ ,  $[I_2]_{(Eq)}$  we can calculate Equilibrium constant.

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  $N_2 =$

$$V_1 N_1 = V_2 N_2$$

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

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

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

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

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

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

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

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

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

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

**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			

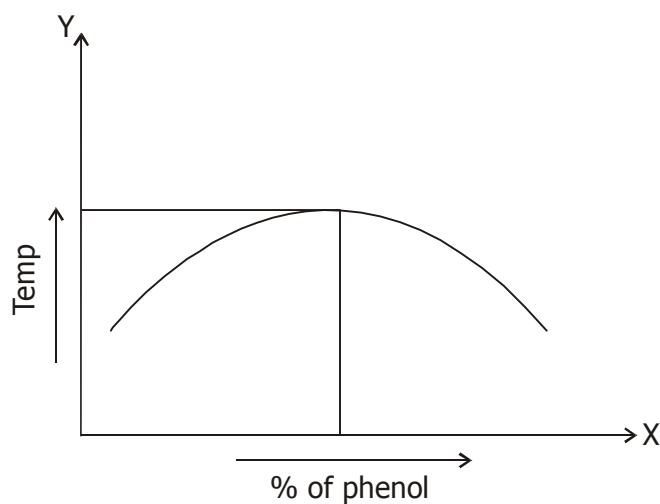
**PHENOL IN WATER SYSTEM :**

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			

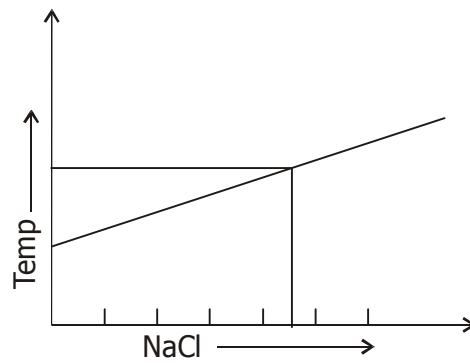


From graph:

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 " $\eta$ ", 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,  $\eta_w =$  \_\_\_\_\_ c-poise

Density of water,  $d_w =$  \_\_\_\_\_ gm/cc

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

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

Time flow of water,  $t_w =$  \_\_\_\_\_ 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 :**

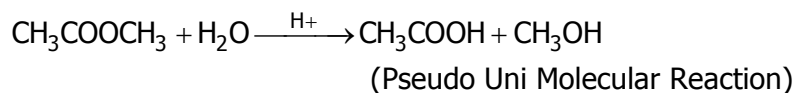
1. Methyl Acetate
2. Hydrochloric Acid
3. Sodium Hydroxide (NaOH)
4. Oxalic Acid.
5. Phenolphthalein.

**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,  $V_{\infty}$ .

### 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 :

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

$$= \dots\dots\dots N$$

**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  $N_1 = \text{---} N$

↓

Volume of Sodium Hydroxide solution  $V_2 =$

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

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 <sub>t</sub> ml)	(V <sub>∞</sub> - V <sub>t</sub> ) ml	Log(V <sub>∞</sub> - V <sub>t</sub> )	K <sub>1</sub> = (2.303 / t) × Log(V <sub>∞</sub> - V <sub>0</sub> ) / (V <sub>∞</sub> - V <sub>t</sub> )
1	0						
2	10						
3	20						
4	30						
5	40						
6	50						
7	60						
8	V <sub>∞</sub>						

Average K<sub>1</sub> =

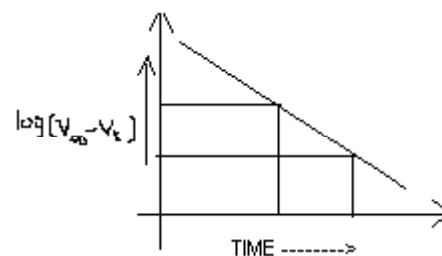
$$V_0 = \text{_____ ml}, \quad V_\infty = \text{_____}$$

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

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	$V_\infty$						

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 :**

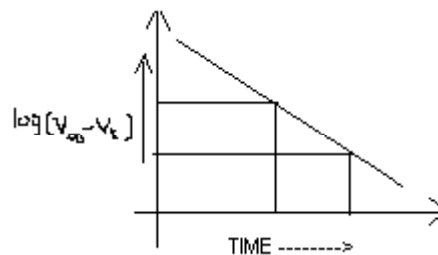
Rate Constant of 1N HCl,  $K_1 = \text{___ sec}^{-1}$ ,

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.

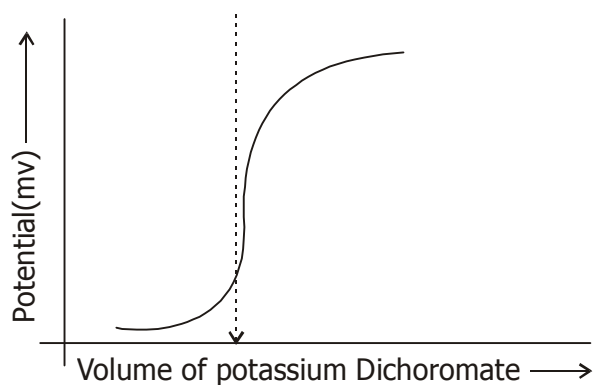
$$E_{red} = E_{red}^0 - \frac{RT}{nF} * \ln \frac{a_{red}}{a_{ox}}$$

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 ( $H_2C_2O_4 \cdot 2H_2O$ )	126	63
6. Hypo ( $Na_2S_2O_3 \cdot 5H_2O$ )	248.19	248.19
7. Potassium permanganate ( $KMnO_4$ )	158	31.6
8. Potassium dichromate ( $K_2Cr_2O_7$ )	249.18	49.03
9. Copper sulphate ( $CuSO_4 \cdot 5H_2O$ )	249.6	249.6
10. Ferrous Ammonium Sulphate ( $(NH_4)_2 FeSO_4 \cdot 5H_2O$ )	392.14	392.14
11. Potassium Iodide (KI)	166	166
12. Sodium chloride (NaCl)	58.44	58.44

**Table - 1**  
**CONCENTRATED ACIDS**

<b>Acids</b>	<b>Specific gravity</b>	<b>% By-Weight</b>	<b>Approximate Normally</b>
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**

<b>LIQUID</b>	<b>DENSITY dl</b>	<b>VISCOSITY</b>
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  $\text{CCl}_4$  and water

- a)  $\text{CCl}_4$  = 5 liters
- b) 1% Iodine in  $\text{CCl}_4$  = 1.5 liters (15 Gms  $\text{I}_2$  in 1.5 liters of  $\text{CCl}_4$ )
- 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  $\text{I}_2$  in  $\text{CCl}_4$  = 1.5 liters (15 Gms of  $\text{I}_2$  in 1.5 liter  $\text{CCl}_4$ )
- f)  $\text{CCl}_4$  = 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)