NETAJI SUBHAS OPEN UNIVERSITY

Choice Based Credit System
(CBCS)

SELF LEARNING MATERIAL

HCH
CHEMISTRY

CC-CH-01

Under Graduate Degree Programme

PREFACE

In a bid to standardize higher education in the country, the University Grants Commission (UGC) has introduced Choice Based Credit System (CBCS) based on five types of courses *viz. core, discipline specefic generic elective, ability and skill enhancement* for graduate students of all programmes at Honours level. This brings in the semester pattern, which finds efficacy in sync with credit system, credit transfer, comprehensive continuous assessments and a graded pattern of evaluation. The objective is to offer learners ample flexibility to choose from a wide gamut of courses, as also to provide them lateral mobility between various educational institutions in the country where they can carry their acquired credits. I am happy to note that the university has been recently accredited by National Assessment and Accreditation Council of India (NAAC) with grade ''A''.

UGC (Open and Distance Learning Programmes and Online Programmes) Regulations, 2020 have mandated compliance with CBCS for UGC 2020 programmes for all the HEIs in this mode. Welcoming this paradigm shift in higher education, Netaji Subhas Open University (NSOU) has resolved to adopt CBCS from the academic session 2021-22 at the Under Graduate Degree Programme (BDP) level. The present syllabus, framed in the spirit of syllabi recommended by UGC, lays due stress on all aspects envisaged in the curricular framework of the apex body on higher education. It will be imparted to learners over the six semesters of the Programme.

Self Learning Materials (SLMs) are the mainstay of Student Support Services (SSS) of an Open University. From a logistic point of view, NSOU has embarked upon CBCS presently with SLMs in English / Bengali. Eventually, the English version SLMs will be translated into Bengali too, for the benefit of learners. As always, all of our teaching faculties contributed in this process. In addition to this we have also requisitioned the services of best academics in each domain in preparation of the new SLMs. I am sure they will be of commendable academic support. We look forward to proactive feedback from all stakeholders who will participate in the teaching-learning based on these study materials. It has been a very challenging task well executed, and I congratulate all concerned in the preparation of these SLMs.

I wish the venture a grand success.

Professor (Dr.) Subha Sankar Sarkar
Vice-Chancellor

Netaji Subhas Open University
Under Graduate Degree Programme
Choice Based Credit System (CBCS)
Subject : Honours in Chemistry (HCH)
Course : Practical Paper - I
Course Code : CC - CH- 01

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Netaji Subhas Open University

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UG Chemistry
(HCH)

Course Name : Practical Paper - I
Course Code : CC - CH - 01

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Basic Laboratory Knowledge

Basic Laboratory Knowledge

It is most important way to gather scientific knowledge is to perform laboratory work, without which perfection can never be attained. Performance of Laboratory work requires a sound knowledge of theoretical background, acquaintance of laboratory work requires a sound knowledge of theoretical background, acquaintance with apparatus, appliances and of course an analytical mind. Keeping in mind this has been written as a suitable guide-book on Practical Physical Chemistry for the B.Sc. (Hons.) Course. This covers all practical experiments of CC-CH-01 under UGC guideline for CBCS system and also contain relevant questions and answers. Laboratory is a place for learning the experimental skills. You are strongly advised to be careful at all times. Without any apron and glasses students must not enter into the laboratory. It is recommended not to perform unauthorized experiments. This will ensure your safety as well as the safety of your fellow-students. Even a small accident involving minor injury must be reported to the counsellor. The following instructions should be observed during the laboratory work.

You must wear a laboratory coat or apron over your clothes while working in the chemistry laboratory. This will save you from injury and protect your clothes from damage.

ii) Handle the hot glass carefully; it cools very slowly and may be very hot without appearing so.

iii) Protect your eyes from any spurting of acid or a corrosive chemical. In case of such spurting into the eyes, immediately wash with lot of water and go to a doctor.

iv) You must not reach across lighted burners as it may result in an accident.

v) Wash your apparatus thoroughly with a washing powder.

vi) While heating substances, do not point the tube towards your neighbor or to yourself. A suddenly formed bubble may eject the contents violently and dangerously.

vii) When diluting sulphuric acid, pour the acid slowly and carefully into the water with constant stirring. Never add water to the acid as it may result in the liberation of a lot of heat.

viii) Read the label on the bottle carefully before using the required chemical. Never pour back the unused reagent into the bottle.

ix) Never touch or taste a chemical or solution as most of chemicals are either corrosive or poisonous.

x) Always bring your container to the reagent shelf and do not take the bottles to your desk.

xi) Do not insert the pipette or dropper into the reagent bottles; this helps in avoiding any possible contamination.

xii) Graduated cylinders and bottles are not to be heated because these break very easily and their volume also changes.

xiii) At the end of the experiment, clean and dry the glass apparatus and wipe off the top of the working table. Ensure that the gas and water taps are closed before you leave the laboratory.

Laboratory First-Aid:

If a corrosive substance falls on your skin, immediately wash the spot with large quantities of water, followed by remedial action indicated below:

Acid spill : Treat with sodium bicarbonate or ammonium carbonate (2M) solution; then apply vaseline or a soothing cream.

Base spill : Treat with acetic acid (1 M) followed by vaseline or a soothing cream

Bromine :Treat with 2 M ammonia; keep the affected part dipped in dilute sodium bisulphite solution till bromine is washed off. Finally apply vaseline.

Phenol :Wash with ethanol and then take hospital treatment.

The most common accidents in the chemistry laboratory involve cuts, burns or fire. The first-aid to be given in each case is below:

Cuts : If you have a cut, wash the wound well with cold water immediately. If bleeding is severe, apply pressure directly on to the wound to stop the bleeding. Then an antiseptic cream can be applied to the wound; it should be followed by proper dressing of the wound.

Burns : Wash the burnt part with cold water for some time and then apply Burnol to it.

Fire : A small fire in a beaker, caused by the vapours of an inflammable liquid can be extinguished by covering it with a watch glass. If the clothes catch fire, one should lie on the flow and, fire can be put off by wrapping a thick blanket around the body

Reagents Required for Qualitative Analysis

1. Strength of Concentrated Acids and Bases:

Name	Specific Gravity	Normality (Approximate)
Hydrochloric Acid	1.19	12 N
Sulphuric Acid	1.84	36 N
Nitric Acid	1.42	16 N
Glacial Acetic Acid	1.05	17 N
Syrupy Phosphoric Acid	1.71	15 N
Liquor Ammonia	0.83	18 N

2. Preparation of Dilute Acids and Bases Solutions:

Name	Preparation of Solution	Strength
Hydrochloric Acid	Dissolve 83.3 ml of conc. HCl in 416.7 ml of distilled water to prepare 500 ml solution	2N
Hydrochloric Acid	Dissolve 166.6 ml of conc. HCl in 333.4 ml of distilled water to prepare 500 ml solution	4N
Sulphuric Acid	Dissolve 83.3 ml of conc. H_2SO_4 in 416.7 ml of distilled water to prepare 500 ml solution	6N
Sulphuric Acid	Dissolve 55.5 ml of conc. H_2SO_4 in 444.5 ml of distilled water to prepare 500 ml solution	4N
Acetic Acid	Dissolve 117.6 ml of glacial acetic acid in 382.4 ml of distilled water to prepare 500 ml solution	4N
Acetic Acid	Dissolve 58.2 ml of glacial acetic acid in 441.8 ml of distilled water to prepare 500 ml solution	2N
Ammonium Hydroxide Solutin	Dissolve 111 ml of liquorl NH_3 in 389 ml of distilled water to prepare 500 ml solution	4N
Sodium Hydroxide Solution	Dissolve 50 g of NaOH in 500 ml of distilled water to prepare 500 ml solution	10%;0.6N

3. Preparation of Aqua Regia:

Prepared by mixing 1 volume of conc. HNO_3 and with 3 volume of conc. HCl.

4. Preparation of Some Common Indicators:

Name	Preparation of Solution	Strength
Ba – diphenylamine Sulphonate	Dissolve 0.2 g of the dye staff in 100 ml of distilled water	0.2%
Methyl orange (pH range 3.1 – 4.4)	Dissolve 0.05 g of the dye staff in 100 ml of distilled water	0.05%
Phenolphthalein (pH range 8.3 – 10)	Dissolve 0.5 g of the dye staff in 100 ml of 50% of ethanol	0.5%
Calcon	Dissolve 0.4 g of the dye staff in 100 ml of methanol	0.4%
Starch Solution	Prepare a paste of 1 g of soluble starch with a little water and pour it into 100 ml of boiling water with constant stirring. Boil the mixture 2-3 minutes more.	1%

5. Equivalent Weight of Some Common Reagents:

Name	Molecular Weight	Equivalent Weight
Potassium permanganate $KMnO_4$	158	158/5 = 31.6
Potassium dichromate $K_2Cr_2O_7$	294.18	294.18/6 = 49.03
Oxalic Acid $H_2C_2O_4.2H_2O$	126	126/2 = 63
Mohr's Salt $(NH_4)SO_4.FeSO_4.\ 6H_2O$	392.13	392.13/1 = 392.13
Sodium Carbonate Na_2CO_3	106	106/2 = 53
Hydrochloric Acid HCl	36.5	36.5/1 = 36.5
Sulphuric Acid H_2SO_4	98	98/2 = 49
Sodium Hydroxide NaOH	40	40/1 = 40

6. Some Common Rack Reagents:

Sl. No.	Name	Preparation of Solution	Strength
1	Ammonium carbonate	Dissolve 80 g of $(NH_4)_2CO_3$ in 430 ml of distilled water and add 70 ml of liquor NH_3.	4 N
2	Barfoed's Reagent	Dissolve 5 g of cupric acetate in 100 ml of distilled water and add 1 ml of acetic acid.	
3	Benedict's solution	Dissolve 17.3 g of $CuSO_4.5H_2O$ in 100 ml of distilled water. Dissolve 173 g of sodium acetate and 100 g of anhydrous Na_2CO_3 in 800 ml of distilled water. Mix this two solution, a bluish green solution is obtained.	
4	Br_2 – water	Dissolve 11 ml of Br_2 in 1000 ml of distilled water.	
5	Calcium chloride	Dissolve 13.25 g of $CaCl_2$ in distilled water and then diluted to 250 ml with distilled water.	0.5 N
6	Denige's Reagent	Dissolve 5 g of yellow HgO in 20 ml of conc. H_2SO_4. Add 80 ml of distilled water carefully. Cool and filter.	
7	2,4 Dinitrophenyl hydrazine sulphate	Dissolve 2 g of 2,4-DNP in 100 ml of methanol, add 4 ml of conc. H_2SO_4	
8	Fehling's solution-A	Dissolve 34.5 g of $CuSO_4.5H_2O$ in 500 ml of distilled water and add few drops of conc. H_2SO_4.	
9	Fehling's solution-B	Dissolve 175 g of Rochelle salt (Potassium-Sodium tartaret) with 70 g of NaOH in 500 ml of distilled water.	
10	Ferric chloride solution	Dissolve 1 g of $FeCl_3$ in 100 ml of distilled water.	1%

11	Iodine solution	Dissolve 20 g of KI in 50 ml of distilled water and add 8 g of I_2. Dilute the to 1000 ml.	0.1 N
12	Lime water	Shake 0.6 g of lime with 250 ml of distilled water and filter the mixture. Keep the filtrate in well-stoppered bottle.	0.4 N
13	Molisch's Reagent	Dissolve 10 g of α- Naphthol in 100 ml of alcohol	10%
14	Reinhardt solution	Dissolve 67 g of $MnSO_4.4H_2O$ in 250 ml of distilled water, add this solution to the mixture of 133 ml conc. H_2SO_4 and 250 ml of distilled water then add 133 ml of H_3PO_4.	
15	Schieff's Reagent	Dissolve 0.5 g of Rosaniline hydrochloride in 250 ml of distilled water. Cool and saturated the solution with SO_2 gas till the solution becomes colourless.	
16	Silver nitrate	Dissolve 1.7 g of $AgNo_3$ in 100 ml of distilled water and add 1-2 drops of liquor NH_3.	0.1 N
17	Starch- KI solution	Dissolve a paste of 1 g of starch in 100 ml of boiling distilled water. Add 1 g of KI and few drops of $CHCl_3$.	1%
18	Tollen's Reagent	Add 5-6 drops of 10% NaOH solution to 25 ml of 0.1 N $AgNO_3$ solution. Mixed thoroughly and allow to stand. Decant of the supernatant liquid and just dissolve the precipitate with strong NH_3 solution by adding dropwise.	

Module – I (Inorganic Chemistry)

Unit : 1 ❐ Estimation of ions

Structure

1.0 Objectives

1.1 Introduction

1.2 Preparation of Standard Solution

  1.2.1 Primary standard substances

  1.2.2 Secondary standard substances

  1.2.3 Strength of a solution

1.3 Estimation of Na_2CO_3 and NaOH present in a mixture by using standard HCl (N/20) solution

1.4 Estimation of Na_2CO_3 and $NaHCO_3$ present in a mixture by using standard HCl (N/20) solution

1.5 Oxidation-Reduction Titrations or Redox titrations

1.6 Standardisation of given $KMnO_4$ solution with standard Oxalic acid solution

1.7 Estimation of Fe(II) using standard $K_2Cr_2O_7$ solution

1.8 Estimation of Fe(III) using standard ~ (N/20) $K_2Cr_2O_7$ / $KMnO_4$ Solution

  1.8.1 Procedure-I ($KMnO_4$ method)

  1.8.2 Procedure-II ($K_2Cr_2O_7$ method)

1.9 Estimation of Ca^{+2} using standard $KMnO_4$ solution

1.10 Estimation of Cu^{+2} iodometrically

1.11 Estimation of Cr^{+3} using $K_2Cr_2O_7$ solution

1.12 Summary

1.13 Questions

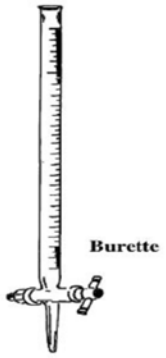
1.0 Objectives

In this Unit a learner will acquire the laboratory based knowledge on:

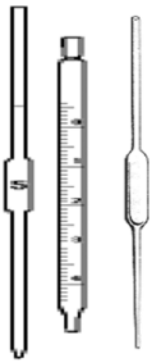
- Preparation of standard substances.
- Equivalent weights of oxidants and reductants.
- Different types of strength of a solution.
- Theory, principle and procedure for the estimation of various ions in the mixtures using alkalimetry and acidimetry titration.
- Oxidation-Reduction Titrations or Redox titration.
  Estimation of ions in the mixtures using iodometric titration.

1.1 Introduction

A chemistry laboratory is one of the best places in the world where one can see miracles happening. It is a workshop for the chemists and the place where the students learn the basics of applications of chemistry. Here, the students learn the techniques of identification, estimation and preparation of chemical substances. But the chemistry laboratory is such a place where people should be very careful. Different type of chemicals present in the lab may cause hard on exposure, contact or mishandling. It is very important for a student to know how to work with equipment and what precautions should be taken. Generally a chemistry laboratory contains multiple glasswares some of which are shown below.



Burette

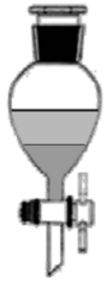


Pipette

Test-tube

Measuring cylinder

Conical flask



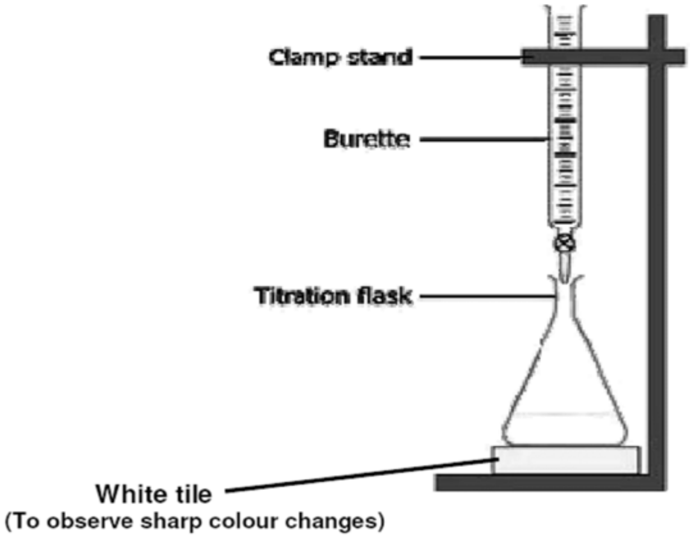
Separating funnel

Volumetric flask

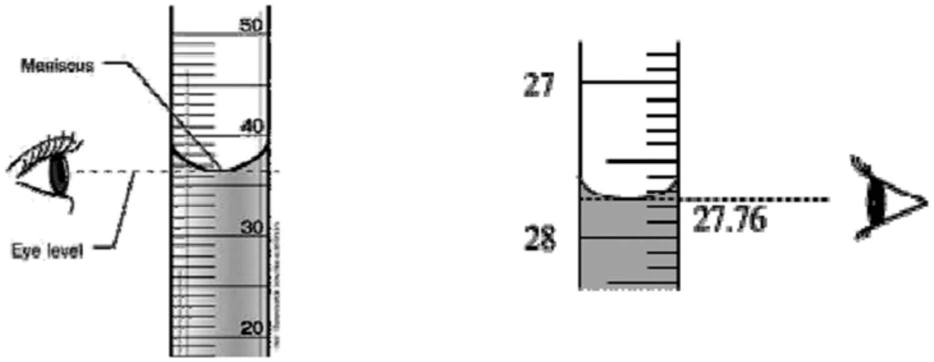
Beaker

Filter funnel

TITRATION ASSEMBLY



Correct method to note down the readings



Graduated Cylinder
The reading is 36.5 ml.

Burette
The reading is 27.8 ml

1.2 Preparation of Standard Solution

Solution whose strength is known is termed as standard solution. The substances are present in these solutions are classified into two classes i) Primary standard substances and ii) Secondary standard substances.

1.2.1 Primary standard substances

The substances are considered Primary standard should satisfy the following requirements –

a) The substance must be easily obtained in the highly pure state.
b) It is highly soluble in solvent (water).
c) It should neither hydroscopic nor be oxidised by air.
d) Its equivalent weight should be high so that weighing error is negligible.
e) It should not involve any chemical reaction with components (e.g. CO_2, H_2O, H_2S etc.) present in air during weighing.

Example: Oxalic acid ($H_2C_2O_4.2H_2O$); Anhydrous Na_2CO_3 ; Potassium bromate ($KBrO_3$) ; Zinc acetate [$Zn(CH_3COO)_2.2H_2O$] ; Potassium dichromate ($K_2Cr_2O_7$) ; Potassium iodate (KIO_3); etc.

1.2.2 Secondary standard substances:

The strength of the solution can not be known by dissolving a definite weight of substance in a known volume of solution. Its strength can be determined by titrating against a primary standard solution. The strength of the solution is not constant it changes on day long standing.

Example: H_2SO_4; HCl; HNO_3; NaOH; KOH; $KMnO_4$; Sodium thiosulphate ($Na_2S_2O_3.5H_2O$); EDTA ; etc.

1.2.3 Strength of a solution:

Normality (N): It is defined as the number of gram-equivalent weight of the solute dissolved in one litre of the solution.

Equivalent weight of acid = Molecular weight / basicity

Equivalent weight of base = Molecular weight / acidity

Equivalent weight of salt = Molecular weight / No. of +charge(s)
Equivalent weight of oxidant/reductant = Molecular weight / No. of electron transferred

Molarity (M): It is defined as the number of gram moles of the solute dissolved in one litre of the solution. [gram mole = molecular weight when expressed in terms of gram]

1.3 Estimation of Na_2CO_3 and NaOH present in a mixture by using standard HCl (N/20) solution

Principle:

During the neutralisation of Na_2CO_3 solution by strong acid like HCl occurs in two steps as a result two equivalence points are observed on the titration curve.

$$Na_2CO_3 + HCl = NaHCO_3 + NaCl \text{ [pH = 8.3 at this equivalence point]}$$

$$NaHCO_3 + HCl = NaCl + H_2O + CO_2 \text{ [pH = 3 to 4 at this equivalence point]}$$

So at the half neutralisation point phenolphthalein (pH range = 8.3 – 10) will show its colour change from pink to colourless.

If the mixture is titrated using methyl orange as indicator (pH range = 3.1 - 4.4) complete neutralisation will occur that means titre value corresponds to total amount of Na_2CO_3 and NaOH by changing the colour yellow to pink (or red).

$$\tfrac{1}{2} \text{ mole } Na_2CO_3 = 1 \text{ mole NaOH} = 1 \text{ equivalent}$$

$$\therefore 1000 \text{ ml (N) HCl solution} \equiv 53 \text{ g of } Na_2CO_3 \equiv 40 \text{ g of NaOH}$$

Chemicals required:

i) Standard ~ (N/20) Na_2CO_3 solution [0.6625 g in 250 ml of water]

ii) ~(N/20) HCl solution

iii) Phenolphthalein indicator [0.5% in alcohol]

iv) Methyl orange [0.05% in water]

v) Unknown Na_2CO_3 + NaOH mixture

[Mix 15 ml (N) NaOH solution and 30 ml (N) Na_2CO_3 solution and dilute to 1 litre.

Procedure:

A. Preparation of standard 250 ml (N/20) Na_2CO_3 solution

B. Dissolve near about 0.6625g Na_2CO_3 (note accurate weight of taken amount) in 250mL volumetric flask, dilute up to the mark with distilled water and then shake to form a uniform solution.

Table – 1:

Initial weight (g)	Final weight (g)	Amount of Na_2CO_3 taken (g)	Strength of the solution (N/20)
W_1	W_2	$W_1 - W_2 = W$	$S_1 = W/0.6625$ $= f$

C. Standardisation HCl solution against standard Na_2CO_3 solution using methyl orange as indicator.

Pipette out of 25 ml of standard Na_2CO_3 solution in a 250 ml conical flask and add 1-2 drops of methyl orange indicator. Solution turns to yellow colour. Titrate with the same HCl solution with constant shaking until the pink (or red) colour just appeared. Record the burette reading (V). Repeat process three times.

Table -2:

No. of obs.	Volm. of Na_2CO_3 (ml)	Burette reading		Volm. of HCl (ml)	Mean volm. of HCl (ml)	Strength of HCl soln. (N/20)
		Initial	Final			
1.	25	0	...	...	V	S= (25 x W/0.6625)/V = (25 x f)/V
2.	25	...	...	...		
3.	25	...	...	...		

Calculation:

$$V \times S = V_1 \times S_1 \;;\; V \times S = 25 \times f(N/20) \;;\; \therefore S = 25 \times f/V \; (N/20)$$

D. Titration of the supplied solution:

Pipette out of 25 ml of the supplied solution in a 250 ml conical flask and add 1-2 drops of phenolphthalein indicator. The solution turns to pink. Titrate the solution with the standard HCl solution with constant shaking until the pink colour just discharged. Burette reading (V_1) correspond to the half amount of Na_2CO_3 and full amount of NaOH.

To the above titrated solution add 2-3 drops of methyl orange indicator. Solution turns to yellow colour. Titrate with the same standard HCl solution with constant shaking until the pink (or red) colour just appeared. Burette reading (V_2) correspond to the half amount of Na_2CO_3. Repeat process three times.

Table -3:

No. of obs.	Volm. of solution (Na_2CO_3 + NaOH) (ml.)	Phenolphthalein				Methyl orange	
		Burette reading		Volm. of HCl (ml)	Mean volm. of HCl (ml)	Volm. of HCl (ml)	Mean volm. of HCl (ml)
		Initial	Final				
1.	25	0	...	...		...	
2.	25	...	...	...	V_1	...	V_2
3.	25	...	...	...		...	

(E) Calculation:

a) Strength of HCl solution = S (N/20)

b) Using Phenolphthalein as indicator:

Half amount of Na_2CO_3 + full amount of NaOH in 25 ml of the supplied solution $\equiv V_1$ ml S (N/20) HCl solution

$\equiv V_1 \times S/20$ ml (N) HCl solution

c) Using methyl orange as indicator:

Half amount of $Na_2CO_3 \equiv V_2$ ml S (N/20) HCl solution

$\equiv V_2 \times S/20$ ml (N) HCl solution

Full amount of Na_2CO_3 in 25 ml mixture $\equiv 2\ V_2 \times S/20$ ml (N) HCl solution

We know that, 1000 ml (N) HCl solution $\equiv$ 53 g of Na_2CO_3

$\therefore 2\ V_2 \times S/20$ ml (N) HCl solution $\equiv 0.053 \times 2\ V_2 \times S/20$ g of Na_2CO_3 in 25 ml

$\equiv 0.0053 \times V_2 \times S \times 40$ g of Na_2CO_3 in 1 lit.

Again full amount of NaOH in 25 ml mixture $\equiv (V_1 - V_2)$ ml S(N/20) HCl solution

$\equiv (V_1 - V_2) \times S/20$ ml (N) HCl solution

We know that, 1000 ml (N) HCl solution ≡ 40 g of NaOH

∴ $(V_1 - V_2)$ x S/20 ml (N) HCl solution ≡ 0.04 x $(V_1 - V_2)$ x S/20 g of NaOH in 25 ml

≡ 0.002 x $(V_1 - V_2)$ x S g of NaOH in 25 ml

≡ 0.002 x $(V_1 - V_2)$ x S x 40 g of NaOH in 1 lit.

∴ The amount of Na_2CO_3 in the supplied mixture = 0.0053 x V_2 x S x 40 g of Na_2CO_3 / lit.

The amount of NaOH in the supplied mixture = 0.002 x $(V_1 - V_2)$ x S x 40 g of NaOH/ lit.

1.4 Estimation of Na_2CO_3 and $NaHCO_3$ present in a mixture by using standard HCl (N/20) solution

Principle:

During the neutralisation of Na_2CO_3 solution by strong acid like HCl occurs in two steps as a result two equivalence points are obsedved on the titration curve.

Na_2CO_3 + HCl = $NaHCO_3$ + NaCl [pH = 8.3 at this equivalence point]

$NaHCO_3$ + HCl = NaCl + H_2O + CO_2 [pH = 3 to 4 at this equivalence point]

So at the half neutralisation point phenolphthalein (pH range = 8.3 – 10) will show its colour change from pink to colourless.

If the mixture is titrated using methyl orange as indicator (pH range = 3.1 – 4.4) complete neutralisation will occur that means titre value corresponds to total amount of Na_2CO_3 and $NaHCO_3$ by changing the colour yellow to pink (or red).

½ mole Na_2CO_3 = 1 mole HCl = 1 equivalent

∴ 1000 ml (N) HCl solution ≡ 53 g of Na_2CO_3 ≡ 84 g of $NaHCO_3$

Chemicals required:

i) Standard ~ (N/20) Na_2CO_3 solution [0.6625 g in 250 ml of water]

ii) ~ (N/20) HCl solution

iii) Phenolphthalein indicator [0.5% in alcohol]

iv) Methyl orange [0.05% in water]

v) Unknown Na_2CO_3 + NaOH mixture

[Mix 15 ml (N) $NaHCO_3$ solution and 35 ml (N) Na_2CO_3 solution and dilute to 1 litre.]

Procedure:

A. Preparation of standard 250 ml (N/20) Na_2CO_3 solution

Dissolve near about 0.6625g Na_2CO_3 (note accurate weight of taken amount) in 250mL volumetric flask, dilute up to the mark with distilled water and then shake to form a uniform solution.

Table – 1:

Initial weight (g)	Final weight (g)	Amount of Na_2CO_3 taken (g)	Strength of the solution (N/20)
W_1	W_2	$W_1 - W_2 = W$	$S_1 = W/0.6625$ $= f$

B. Standardisation HCl solution against standard Na_2CO_3 solution using methyl orange as indicator.

Pipette out of 25 ml of standard Na_2CO_3 solution in a 250 ml conical flask and add 1-2 drops of methyl orange indicator. Solution turns to yellow colour. Titrate with the same HCl solution with constant shaking until the pink (or red) colour just appeared. Record the burette reading (V). Repeat process three times.

Table -2:

No. of obs.	Volm. of Na_2CO_3 (ml)	Burette reading		Volm. of HCl (ml)	Mean volm. of HCl (ml)	Strength of HCl soln. (N/20)
		Initial	Final			
1.	25	0	...	...	V	$S = 25 \times \frac{w}{0.6625}$ $= \frac{25 \times f}{v}$
2.	25	...	...	...		
3.	25	...	...	...		

C. Titration of the supplied solution:

Pipette out of 25 ml of the supplied solution in a 250 ml conical flask and add 1-2 drops of phenolphthalein indicator. The solution turns to pink. Titrate the solution with the standard HCl solution with constant shaking until the pink colour just discharged. Burette reading (V_1) correspond to the half amount of Na_2CO_3 and full amount of $NaHCO_3$.

To the above titrated solution add 2-3 drops of methyl orange indicator. Solution turns to yellow colour. Titrate with the same standard HCl solution with constant shaking until the pink (or red) colour just appeared. Burette reading (V_2) correspond to the half amount of Na_2CO_3. Repeat process three times.

Table -3:

No. of obs.	Volm. of solution (Na_2CO_3 + $NaHCO_3$) (ml.)	Phenolphthalein				Methyl orange	
		Burette reading		Volm. of HCl (ml)	Mean volm. of HCl (ml)	Volm. of HCl (ml)	Mean volm. of HCl (ml)
		Initial	Final				
1.	25	0	...	...	V_1	...	V_2
2.	25	...	...	...		...	
3.	25	...	...	...		...	

E. Calculation:

d) Stre
ngth of HCl solution = S (N/20)

e) Using Phenolphthalein as indicator:
Half amount of Na_2CO_3 + full amount of $NaHCO_3$ in 25 ml of the supplied solution

$\equiv V_1$ ml S (N/20) HCl solution

$\equiv V_1 \times S/20$ ml (N) HCl solution

f) Using methyl orange as indicator:

Half amount of Na_2CO_3 $\equiv V_2$ ml S (N/20) HCl solution

$\equiv V_2 \times S/20$ ml (N) HCl solution

Full amount of Na_2CO_3 in 25 ml mixture ≡ 2 V_2 x S/20 ml (N) HCl solution
We know that, 1000 ml (N) HCl solution ≡ 53 g of Na_2CO_3

∴ 2 V_2 x S/20 ml (N) HCl solution ≡ 0.053 x 2 V_2 x S/20 g of Na_2CO_3 in 25 ml
≡ 0.0053 x V_2 x S x 40 g of Na_2CO_3 in 1 lit.
Again full amount of $NaHCO_3$ in 25 ml mixture ≡ (V_1 – V_2) ml S(N/20) HCl solution
≡ (V_1 – V_2) x S/20 ml (N) HCl solution

We know that, 1000 ml (N) HCl solution ≡ 84 g of $NaHCO_3$

∴ (V_1 – V_2) x S/20 ml (N) HCl solution ≡ 0.084 x (V_1 – V_2) x S/20 g of $NaHCO_3$ in 25 ml
≡ 0.0042 x (V_1 – V_2) x S g of $NaHCO_3$ in 25 ml

≡ 0.0042 x (V_1 – V_2) x S x 40 g of $NaHCO_3$ in 1 lit.

∴ The amount of Na_2CO_3 in the supplied mixture = 0.0053 x V_2 x S x 40 g of Na_2CO_3 / lit.

The amount of $NaHCO_3$ in the supplied mixture = 0.0042 x (V_1 – V_2) x S x 40 g of $NaHCO_3$/ lit.

1.5 Oxidation-Reduction Titrations or Redox titrations

a) **Oxidation-reduction** : The terms oxidation and Reduction are defined as :-

Oxidation is the process in which an atom or ion loses electron(s). For example ferrous ion (Fe^{+2}) is converted to ferric ion by loss of an electron as $Fe^{+2} - e^- \longrightarrow Fe^{+3}$. Here Fe^{+2} loses electron, is the reducing agent and is oxidised to Fe^{+3} by losing an electron.

Reduction is the process in which there is a gain of electron(s). Chlorine atom is converted to chloride ion by gain of electron. i.e. $Cl + e^- \longrightarrow Cl^-$. Here Cl atom is oxidising agent and is reduced to Cl^- by gaining an electron.

Oxidation and reduction simultaneously take place in any chemical reaction.

b) Equivalent weight of some oxidising and reducing agents:

Oxidising agents	**Ion-Electron equation**	**Equivalent weight**
1. Potassium permanganate (Acidic solution)	$MnO_4^- + 8H^+ + 5e^- = Mn^{+2} + 4H_2O$	Mol. Wt./5
2. Potassium permanganate (Neutral solution)	$MnO_4^-\ 2H_2O + 3e^- = MnO_2 + 4OH^-$	Mol. Wt./3
3. Potassium permanganate (Alkaline solution)	$MnO_4^- + e^- = MnO_4^{-2}$	Mol. Wt./1
4. Potassium dichromate	$Cr_2O_7^{-2} + 14H^+ + 6e^- = 2Cr^{+3} + 7H_2O$	Mol. Wt./6
Reducing agent	**Ion-Electron equation**	**Equivalent weight**
• Oxalic acid	$C_2O_4^{-2} = 2CO_2 + 2e^-$	Mol. Wt./2
• Ferrous sulphate	$Fe^{+2} = Fe^{+3} + e^-$	Mol.Wt./1
• Sodium thiosulphate	$2S_2O_3^{-2} = S_4O_6^{-2} + 2e^-$	Mol. Wt./2

(C) Comparison of the oxidising and reducing property of a system:

The oxidising and reducing property of a system is measured by its reducing potential. Hence the standard reduction potentials of the various systems indicating their oxidising or reducing power. For example, standard reduction potential of acidified $KMnO_4$ is +1.52V and that of acidified $K_2Cr_2O_7$ is +1.30V in the redox reactions. Hence acidified $KMnO_4$ is stronger oxidising agent than acidified $K_2Cr_2O_7$ in redox reactions.

1.6 Standardisation of given $KMnO_4$ solution with standard Oxalic acid solution

Principle : As a reductant oxalic acid acts as follows:

$$C_2O_4^{-2} - 2e^- = 2CO_2$$

Equivalent weight of oxalic acid = Mol. Wt./2 = 126.066/2 = 63.033

∴ 250 ml. (N/20) oxalic acid solution ≡ 63.033/80 = 0.7879 g of oxalic acid.

Reaction:

$$2MnO_4^- + 5\,C_2O_4^{-2} + 16H^+ = 2Mn^{+2} + 10CO_2 + 8H_2O$$

Chemicals required:

a) Oxalic acid

b) ~ ~ (N/20) $KMnO_4$ solution

[Dissolve ˜1.6 g of $KmnO_4$ in 500 ml distilled water, boil the mixture for about 20-30 mins., cool, diluted to 1lit., then filter off through glass wool and store in an amber coloured bottle.]

c) 4(N) H_2SO_4

d) Indicator : $KMnO_4$ solution act as a self-indicator

Procedure:

A. Preparation of standard 250 ml. (N/20) oxalic acid solution

Dissolve near about 0.7879g oxalic acid (note accurate weight of taken amount) in 250mL volumetric flask, dilute up to the mark with distilled water and then shake to form a uniform solution.

$$\therefore \text{Strength of prepared oxalic acid solution} = \frac{\text{Actual weight of oxatic acid taken}}{0.78.79}\left(\frac{N}{20}\right)$$

$$= S_1\ (N)$$

Table-1:

Initial weight (g)	Final weight (g)	Amount of oxalic acid taken (g)	Strength of the solution (N/20)
W_1	W_2	$W_1 - W_2 = W$	= W/0.7879

B. Standardisation of given $KMnO_4$ solution with standard Oxalic acid solution

Take $KMnO_4$ solution in a burette. Pipette out 25 ml of the standard oxalic acid solution in a 250 ml conical flask. Add 25 ml of 4(N) H_2SO_4 in it and warm the mixture up to 60-70^{0}C. Titrate the solution by ~ (N/20) $KMnO_4$ solution in hot condition until a faint pink colour stable for 30 sec. Note the volume (V_1).

Table-2:

No. of obs.	Volm. of Oxalic acid (ml)	Burette reading		Volm. of $KMnO_4$ (ml)	Mean volm. of $KMnO_4$ (ml)	Strength of $KMnO_4$ soln. (N/20)
		Initial	Final			
1.	25	0	...	...	V_2	S_2= (25 xW/0.7879) /V_2
2.	25	...	...	...		
3.	25	...	...	...		

C. Calculation:

$V_1 \times S_1 = V_2 \times S_2$

i.e., $25 \times W/0.7879(N/20) = V_2 \times S_2$

$\therefore$ Strength of $KMnO_4$ solution $(S_2)=(25\times W/0.7879)/V_2$ (N/20)

1.7 Estimation of Fe(II) using standard $K_2Cr_2O_7$ solution

Principle: Because of the higher standard reduction potential than that of Fe^{+3} Potassium dichromate quantitatively oxidised Fe^{+2} to Fe^{+3} in acid medium.

Reaction:

$$K_2Cr_2O_7 + 7H_2SO_4 + 6FeSO_4 = K_2SO_4 + Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 7H_2O$$

Ionically:

$$Cr_2O_7^{-2} + 6Fe^{+2} + 14H^+ = 2Cr^{+3} + 6Fe^{+3} + 7H_2O$$

Indicator : Sodium or Barium diphenylamine sulphonate (BaDS) is usually used as indicator. Freshly prepared Diphenylamine may also be used as indicator. But BaDS works better as its solution can resist aerial oxidation and can be stored for a long time. BaDS gives a very sharp colour change from colourless through green to red-violet. To use BaDS or diphenylamine as indicator H_3PO_4 or F^- (NH_4HF_2) should be added prior to the start of the titration to lower the reduction potential of Fe^{+2}/Fe^{+3} system. N-phenyl anthranilic acid ($E^0 = +1.08V$) or 5,6 dimethyl ferroin ($E^0 = +1.06V$) may also be used as indicator and in these case addition of H_3PO_4 or F^- is not necessary.

End point: Bluish-violet or purple colour.

Procedure:

A. Preparation of standard 250 ml ˜(N/20) $K_2Cr_2O_7$ solution.

Dissolve near about 0.6129 g $K_2Cr_2O_7$ (note accurate weight of taken amount) in 250mL volumetric flask, dilute up to the mark with distilled water and then shake to form a uniform solution.

Equivalent weight of $K_2Cr_2O_7$ = Mol. Wt./6 = 294.18/6 = 49.03

$$\therefore 250 \text{ ml (N/20) } K_2Cr_2O_7 \text{ solution} \equiv \frac{49.03 \, x \, 250}{20 \, x \, 1000} \equiv 0.6129 \text{ g of } K_2Cr_2O_7$$

Table- 1:

Initial weight (g)	Final weight (g)	Amount of $K_2Cr_2O_7$ taken (g)	Strength of the solution (N/20)
W_1	W_2	$W_1 - W_2 = W$	S = W/0.6129

B. Titration with standard $K_2Cr_2O_7$ solution

Take standard $K_2Cr_2O_7$ solution in burette. Pipette out 25 ml of Mohr's salt (ferrous salt) solution in a 250 ml conical flask. Add 150 ml of distilled water. Now pour 5 ml conc. H_2SO_4 and 5 ml of syrupy H_3PO_4. Add 2-3 drops of BaDS indicator. Titrate with $K_2Cr_2O_7$ solution with constant shaking till red-violet or purple colour appeared. Note the burette reading. Repeat the experiment three times.

Table-2:

No. of obs.	Volm. of Fe^{+2} salt soln. (ml)	Burette reading		Volm. of $K_2Cr_2O_7$ (ml)	Mean volm. of $K_2Cr_2O_7$ (ml)
		Initial	Final		
1.	25	0	...	...	V
2.	25	...	...	...	
3.	25	...	...	...	

C. Calculation:

25 ml of Morh's salt or (Fe^{+2})solution ≡ V ml W/0.6129 (N/20) $K_2Cr_2O_7$ solution

≡ V x W/0.6129 ml (N/20) $K_2Cr_2O_7$ solution

We know, 1000 ml (N/20) $K_2Cr_2O_7$ solution ≡ 1000 ml (N/20) mohr's solution

≡ 1000 ml (N/20) Fe^{+2}

≡ 55.85/20 g of Fe

≡ 2.779 g of Fe

∴ 1 ml (N/20) $K_2Cr_2O_7$ solution ≡ 0.002779 g of Fe

∴ V x W/0.6129 ml (N/20) $K_2Cr_2O_7$ solution ≡ 0.002779 x V x W/0.6129 g of Fe

25 ml Mohr's salt solution contain 0.002779 x V x W/0.6129 g of Fe

250 ml ... ... 0.002779 x V x W/0.6129 x 10 g of Fe

Or 1 lit or 1000 ml ... ... 0.002779 x V x W/0.6129 x 10 x 4 g of Fe

1.8 Estimation of Fe (III) using standard ˜ (N/20) $K_2Cr_2O_7$ / $KMnO_4$ Solution

Principle :

Fe^{+3} in the given solution first reduced to Fe^{+2} with $SnCl_2$ in hot 6(N) HCl medium. After cooling the solution to the room temperature excess $SnCl_2$ is removed by adding $HgCl_2$ solution, a silky white precipitate appears. This ensure the complete removable of excess $SnCl_2$.

$$2Fe^{+3} + Sn^{+2} = 2Fe^{+2} + Sn^{+4}$$

$$Sn^{+2} + HgCl_2 = Hg_2Cl_2\downarrow + Sn^{+4} + 2Cl^-$$

The reduction may be carried out by using A.R. Al – foil in 5-6(N) HCl acid medium.

$$3Fe^{+3} + Al = 3Fe^{+2} + Al^{+3}$$

Titration of the solution with a standard ˜(N/20) $KMnO_4$ in 2(N) H_2SO_4 medium in presence of Zimmermann-Reinhardt reagent will correspond to the amount of Fe. Here $KMnO_4$ oxidised Fe^{+2} to Fe^{+3} and itself gets reduced to Mn^{+2}.

$$MnO_4^- + 8\,H^+ + 5\,Fe^{+2} = Mn^{+2} + 4\,H_2O + 5\,Fe^{+3}$$

$$\therefore\ MnO_4^- \equiv 5\ Fe^{+2}$$

$$\text{Or, } 1/5\ MnO_4^- \equiv Fe^{+2} \equiv 1 \text{ equivalent}$$

$$\therefore\ 1000 \text{ ml (N) } KMnO_4 \text{ solution} \equiv 55.847 \text{ g of Fe.}$$

Or;

Titration of the solution with a standard ˜(N/20) $K_2Cr_2O_7$ in 2(N) H_2SO_4 medium in presence of syrupy ortho phosphoric acid and BaDS as indicator will correspond to the amount of Fe. Here $K_2Cr_2O_7$ oxidised Fe^{+2} to Fe^{+3} and itself gets reduced to Cr^{+3}.

$$Cr_2O_7^{-2} + 14\,H^+ + 6\,Fe^{+2} = 2Cr^{+3} + 6\,Fe^{+3} + 7\,H_2O$$

$$\therefore\ Cr_2O_7^{-2} \equiv 6\ Fe^{+2}$$

$$\text{Or, } 1/6\ Cr_2O_7^{-2} \equiv Fe^{+2} \equiv 1 \text{ equivalent}$$

$$\therefore\ 1000 \text{ ml (N) } K_2Cr_2O_7 \text{ solution} \equiv 55.847 \text{ g of Fe.}$$

Chemicals Required :

A. For $KMnO_4$ method
  - i) 5% $HgCl_2$ solution
  - ii) 15% $SnCl_2$ solution
  - iii) Zimmermann-Reinhardt reagent
  - iv) Fe^{+3} solution
  - v) Standard ˜(N/20) oxalic acid solution
  - vi) ˜(N/20) $KMnO_4$

B. For $K_2Cr_2O_7$ method
  - i) Standard ˜(N/20) $K_2Cr_2O_7$ solution
  - ii) Fe^{+3} solution
  - iii) Al foil
  - iv) Syrupy ortho phosphoric acid
  - v) BaDS indicator

1.8.1 Procedure-I ($KMnO_4$ method)

A. Preparation of 250ml (N/20) oxalic acid solution:

Dissolve near about 0.7879g oxalic acid (note accurate weight of taken amount) in 250mL volumetric flask, dilute up to the mark with distilled water and then shake to form a uniform solution.

∴ Strength of prepared oxalic acid solution $= \dfrac{\text{Actual weight of oxatic acid taken}}{0.78.79}\left(\dfrac{N}{20}\right)$

$= S_1$ (N)

Table -1

Initial weight (g)	Final weight (g)	Amount of oxalic acid taken (g)	Strength of the solution (N/20)
W_1	W_2	$W_1 - W_2 = W$	$S_1 = W/0.7879$

B. Standardisation of $KMnO_4$ solution against standard oxalic acid solution

Take $KMnO_4$ solution in a burette. Pipette out 25 ml of the standard oxalic acid solution in a 250 ml conical flask. Add 25 ml of 4(N) H_2SO_4 in it and warm the mixture up to 60-70^{0}C. Titrate the solution by ˜ (N/20) $KMnO_4$ solution in hot condition until a faint pink colour stable for 30 sec. Note the volume (V_2).

Table – 2

No. of obs.	Volm. of Oxalic acid (ml)	Burette reading		Volm. of $KMnO_4$ (ml)	Mean volm. of $KMnO_4$ (ml)	Strength of $KMnO_4$ soln. (N/20)
		Initial	Final			
1.	25	0	...	...	V_2	S_2= (25 xW/0.7879)/V_2
2.	25	...	...	...		
3.	25	...	...	...		

C. Reduction with $SnCl_2$ and Estimation of Fe(III):

Pipette out 25 ml of the supplied Fe (III) solution in a 500 ml conical flask.Add 20 ml conc. HCl and heat nearly to boiling (approx. 90^{0}C) then reduce with 15% $SnCl_2$ solution adding drop wise with constant shaking until the yellow colour of the mother solution is just disappeared. Add 1-2 drops of excess $SnCl_2$ solution. Add 10 ml of 5% $HgCl_2$ solution at a time and shake the mixture gently. Allow to stand for 5 minutes a silky white precipitate of Hg_2Cl_2 appears.

Dilute the above reduced solution with 250 ml distilled water to maintain the acidity of the solution below the 0.8(N), add 25 ml of Zimmermann-Reinhardt reagent and titrate with standard ˜(N/20) $KMnO_4$ solution till pink colour stands for 15 sec. Note the consumed volume (V_3 ml).

Table – 3 Estimation of Fe(III)

No. of obs.	Volm. of Fe(III) soln. (ml)	Burette reading		Volm. of $KMnO_4$ (ml)	Mean volm. of $KMnO_4$ (ml)
		Initial	Final		
1.	25	0	...	...	V_3
2.	25	...	...	...	
3.	25	...	...	...	

D. Calculation:

Strength of KM_nO_4 solution:

$V_1 \times S_1 = V_2 \times S_2$

i.e., $25 \times W/0.7879(N/20) = V_2 \times S_2$

$\therefore S_2 = (25 \times W/0.7879)/V_2\ (N/20)$

Estimation of Fe (III):

25 ml given Fe (III) solution $\equiv V_3$ ml S_2 (N/20) KM_nO_4 solution

$\equiv V_3 \times S_2/20$ ml (N) KM_nO_4 solution

We have, 1000 ml (N) KM_nO_4 solution $\equiv$ 55.847 g of Fe

$\therefore V_3 \times S_2/20$ ml (N) KM_nO_4 solution $\equiv 0.055847 \times V_3 \times S_2/20$ g of Fe in 25 ml.

$\therefore 0.002792 \times V_3 \times S_2$ g of Fe in 25 ml.

25 ml of the supplied solution contain $0.002792 \times V_3 \times S_2$ g of Fe

$\therefore$ 1000 ml ... ... $0.002792 \times V_3 \times S_2 \times 40$ g of Fe

$\therefore$ The amount of iron in the supplied solution $= 0.002792 \times V_3 \times S_2 \times 40$ g / lit.

1.8.2 Procedure-II ($K_2Cr_2O_7$ method)

A. Preparation of standard ˜(N/20) $K_2Cr_2O_7$ solution.

Dissolve near about 0.6129 g $K_2Cr_2O_7$ (note accurate weight of taken amount) in 250mL volumetric flask, dilute up to the mark with distilled water and then shake to form a uniform solution.

Table – 1:

Initial weight (g)	Final weight (g)	Amount of $K_2Cr_2O_7$ taken (g)	Strength of the solution (N/20)
W_1	W_2	$W_1 - W_2 = W$	S = W/0.6129

B. Reduction with Aluminium foil and Estimation of Fe(III)::

Pipette out 25 ml of the supplied Fe (III) solution in a 500 ml conical flask. Add 20 ml conc. HCl and heat nearly to boiling (approx. 90^0C) with few pieces of Al foil. Add more pieces of Al foil, if required, until the yellow colour of the mother solution is just disappeared.

Dilute the above reduced solution with 200 ml distilled water then add 5 ml of conc. H_2SO_4 and 5 ml of syrupy H_3PO_4 followed by 3-5 drops of Barium diphenylamine sulphonate indicator. Titrate with standard ˜(N/20) $K_2Cr_2O_7$ solution till the solution gets red-violet colouration. Note the consumed volume (V ml).

Table – 2:

No. of obs.	Volm. of Fe(III) salt soln. (ml)	Burette reading		Volm. of $K_2Cr_2O_7$ (ml)	Mean volm. of $K_2Cr_2O_7$ (ml)
		Initial	Final		
1.	25	0	...	...	V
2.	25	...	...	...	
3.	25	...	...	...	

Calculation:

25 ml given Fe(III) solution ≡ V ml S (N/20) $K_2Cr_2O_7$ solution
≡ V x S /20 ml (N) $K_2Cr_2O_7$ solution
We have, 1000 ml (N) $K_2Cr_2O_7$ solution ≡ 55.847 g of Fe
∴ V x S /20 ml (N) $K_2Cr_2O_7$ solution≡ 0.055847 x V x S /20 g of Fe in 25 ml.
≡ 0.002792 x V x S g of Fe in 25 ml.

25 ml of the supplied solution contain 0.002792 x V x S g of Fe
∴ 1000 ml ... ... 0.002792 x V x S x 40 g of Fe

∴ The amount of iron in the supplied solution = 0.002792 x V x S x 40 g / lit.

1.9 Estimation of Ca^{+2} using standard $KMNO_4$ solution

Principle:
Calcium is precipitated as calcium oxalate by treating a hot hydrochloric acid solution with ammonium oxalate or oxalic acid neutralizing with NH_4OH solution (1:1).

$$Ca^{++} + C_2O_4^{=} + H_2O = CaC_2O_4.H_2O.$$

This precipitation of Ca^{+2} as oxalate is quantitative at a pH of 4.The precipitate is then dissolved in hot dil. H_2SO_4 to liberate equivalent amount of oxalic acid. Since $KMnO_4$ is powerful oxidising agent, oxidises quantitatively oxalic acid to CO_2.

$$CaC_2O_4 + H_2SO_4 = CaSO_4 + H_2C_2O_4$$

$$2\ KMnO_4 + 3\ H_2SO_4 + 5\ H_2C_2O_4 = K_2SO_4 + 2\ MnSO_4 + 10\ CO_2 + 8\ H_2O$$

Chemicals required:

a) Standard (N/10) oxalic acid solution
b) Standard ~(N/10) $KMnO_4$ solution
c) 6% ammmonium oxalate solution
d) 4(N) H_2SO_4 solution
e) 2(N) HCl solution
f) NH_4OH (1:1) solution
g) Methyl orange indicator

h) Supplied solution

[Dissolve 13.875 g of anhydrous $CaCl_2$ in 250 ml of distilled water and supply 7-8 ml as stock solution.]

i) Conc. HCl

Procedure:

A. Preparation of 250 ml N/10 oxalic acid solution

Dissolve near about 1.575g oxalic acid (note accurate weight of taken amount) in 250mL volumetric flask, dilute up to the mark with distilled water and then shake to form a uniform solution.

Table -1:

Initial weight (g)	Final weight (g)	Amount of oxalic acid taken (g)	Strength of the solution
W_1	W_2	W_1 - W_2 = W	S = W/1.575(N/10) = f (N/10)

B. Standardisation of $KMnO_4$ solution against standard oxalic acid solution

Take $KMnO_4$ solution in a burette. Pipette out 25 ml of the standard oxalic acid solution in a 250 ml conical flask. Add 25 ml of 4(N) H_2SO_4 in it and warm the mixture up to 60-70^{0}C. Titrate the solution by $^{\sim}$(N/10) $KMnO_4$ solution in hot condition until a faint pink colour stable for 30 sec. Note the volume (V).

Table -2

No. of obs.	Volm. of Oxalic acid (ml)	Burette reading		Volm. of $KMnO_4$ (ml)	Mean volm. of $KMnO_4$ (ml)	Strength of $KMnO_4$ soln.
		Initial	Final			
1.	25	0	...	...	V	S_1= (25 x f/V) (N/10) = f_1 (N/10)
2.	25	...	...	...		
3.	25	...	...	...		

C. Estimation of Ca^{+2}

i) Transfer the supplied solution in a 100 ml volumetric flask. Wash the container 4-5 times with distilled water and transfer to the volumetric flask carefully. Make up the volume with distilled water.

ii) Pipette out 25 ml of the Ca-salt solution in a 250 ml beaker. Diluted to 100 ml with distilled water (i.e., by adding 75 ml of distilled water). Add 1 drop of methyl orange indicator. Add small quantities of NH_4OH solution until the solution smells faintly of NH_3. Then add 2(N) HCl solution dropwise with stirring until a faint pink colour appears, then add 5 ml of conc. HCl. Heat the solution to boiling. To this hot solution add slowly 15-20 ml of 6% ammonium oxalate solution with constant stirring with a glass- rod. Now add NH_4OH (1:1) drop wise until the smell of NH_3 persists. A white precipitation of Ca-oxalate comes down. The beaker is than allowed to stand on low flame on an asbestos board (or on water bath) for 20-30 minutes. The precipitate will settle down leaving a clear solution at the top. Complete precipitation is tested by a few more drops of the ammonium oxalate solution down the inclined side of the beaker.

The precipitate is carefully filtered off by Whatman 42. Rinse the beaker 4-5 times with hot water. Now wash the filter paper and precipitate by hot water until it is free from oxalate & Cl^-.

[To test for oxalate ion : Take about 1 ml of the filtrate in a clean test tube and add few drops of CH_3COOH and few drops of clear $CaCl_2$ solution. Formation of white ppt. indicate the presence of $C_2O_4^=$ in filtrate.

To test for Cl^- ion: Take about 1 ml of the filtrate in a clean test tube, acidify with HNO_3 then add 1-2 drops of $AgNO_3$ solution. Curdy white ppt. indicates the presence of Cl^- in the filtrate.]

Place the funnel containing precipitate on a 250 ml conical flask. Pierce the filter paper with a glass rod and wash down the precipitate with a jet of hot water completely in to the conical flask. Boil the mixture. Now add 4(N) H_2SO_4 (i.e., 1:8) into the filter paper to dissolve any adhering oxalate precipitate and wash it down again with hot water. Add excess amount of 4(N) H_2SO_4 to dissolve the precipitate of oxalate if require.

iii) The solution is diluted to 150 ml with distilled water, head on a asbestos board to about 60-70^{0}C and then titrate with standard $KMnO_4$ solution, until pink colour appears.

Table-3

No. of obs.	Volm. of Ca^{+2} soln. (ml)	Burette reading		Volm. of $KMnO_4$ (ml)	Mean volm. of $KMnO_4$ (ml)
		Initial	Final		
1.	25	0	...	...	
2.	25	...	...	...	V_1
3.	25	...	...	...	

C. Calculation

25 ml of Ca^{+2} solution $\equiv V_1$ ml of f_1 (N/10) $KMnO_4$ solution

$\equiv V_1 \times f_1$ ml of (N/10) $KMnO_4$ solution

1000 ml of (N) $KMnO_4$ $\equiv$ 20 g of Ca^{+2}

$\therefore$ 1 ml of N/10 $KMnO_4$ $\equiv$ 0.002 g of Ca^{+2}

$\therefore$ $V_1 \times f_1$ ml of (N/10) $KMnO_4$ solution $\equiv 0.002 \times V_1 \times f_1$ g of Ca^{+2}

$\therefore$ 25 ml solution contain $0.002 \times V_1 \times f_1$ g of Ca^{+2}

$\therefore$ 1000 ml ... . $0.002 \times V_1 \times f_1 \times 40$ g of Ca^{+2}

$\therefore$ Ca^{+2} present in the solution $= 0.002 \times V_1 \times f_1 \times 40$ g of Ca^{+2} / lit.

1.10 Estimation of Cu^{+2} iodometrically

Iodometry refers to the titration of iodine liberated in a quantitative redox reaction by a standard solution of a reducing agent like sodium thiosulphate. ***Iodimetry,*** is the titration of a reducing agent with standard solution of iodine.

$$I_2 + 2e^- = 2I^- \qquad E^0 = +0.54\ V$$

$$2S_2O_3^{=} = S_4O_6^{=} + 2e^- \qquad E^0 = -0.08\ V$$

$$I_2 + 2S_2O_3^{=} = 2I^- + S_4O_6^{=} \qquad E^0 = +0.46\ V$$

Standarisation of ˜(N/20) $Na_2S_2O_3$ solution

Principle:

Thiosulphate solution is standardised against a primary standard substance like $K_2Cr_2O_7$. In acid medium $Cr_2O_7^{=}$ quantitatively oxidises KI to I_2 and the liberated I_2 is titrated with the thiosulphate solution using starch as indicator.

$$Cr_2O_7^{-2} + 14\,H^+ + 6\,I^- = 2\,Cr^{+3} + 7\,H_2O + 3\,I_2$$

$$I_2 + 2\,S_2O_3^{-2} = 2\,I^- + S_4O_6^{-2}$$

Chemicals Required:

a) Standard (N/20) $K_2Cr_2O_7$ solution
b) ˜ (N/20) $Na_2S_2O_3$ solution
   [Dissolve 12.5 – 13 g of $Na_2S_2O_3 .5H_2O$ in 500 ml of boiled distilled water and diluted to 1 litre. Add 3-4 drops of $CHCl_3$ to improve the stability of the solution and store in a amber colour bottle].
c) 4(N) H_2SO_4
d) 10% KI solution
e) 1% starch solution

Procedure:

Step - 1: Preparation of standard 250 mL ˜ (N/20) $K_2Cr_2O_7$ solution

Dissolve near about 0.6129 g $K_2Cr_2O_7$ (note accurate weight of taken amount) in 250mL volumetric flask, dilute up to the mark with distilled water and then shake to form a uniform solution.

Equivalent weight of $K_2Cr_2O_7$ = 294.18/6 = 49.03

Table – 1:

Initial weight (g)	Final weight (g)	Amount of $K_2Cr_2O_7$ taken (g)	Strength of the solution (N/20)
W_1	W_2	$W_1 - W_2 = W$	S = W/0.6129

Step-2 : Standardisation of ˜ (N/20) Sodium thiosulphate solution:

Pipette out 25 ml of standard $K_2Cr_2O_7$ solution in a 500 ml conical flask, add 25 ml of 4(N) H_2SO_4 and 10 ml 10% KI solution. Cover the flask with a watch glass and keep in a dark place for 3 minutes. Add 150 ml of distilled water, titrate the liberated I_2 with ˜ (N/20) $Na_2S_2O_3$ solution till straw yellow colour appears. Add 2 ml of 1% starch solution then solution turns to blue and continue the titration until blue colour just changes to light green. Repeat the experiment thrice.

Table -2:

No. of obs.	Volm. of $K_2Cr_2O_7$ (ml)	Burette reading		Volm. of $Na_2S_2O_3$ soln. (ml)	Mean volm. of $Na_2S_2O_3$ soln. (ml)
		Initial	Final		
1.	25	0	...	...	V_1
2.	25	...	...	...	
3.	25	...	...	...	

A. Calculation:

Standardisation of $Na_2S_2O_3$ solution;

Strength of $K_2Cr_2O_7$ solution = S = (W/0.6129) N/20 = f (N/20)

Volume of $K_2Cr_2O_7$ solution taken = V ml = 25 ml

Strength of $Na_2S_2O_3$ solution = S_1 = ?

Volume of $Na_2S_2O_3$ solution = V_1 ml

$\therefore$ $V \times S = V_1 \times S_1$

$\therefore$ Strength of $Na_2S_2O_3$ solution = $S_1 = 25 \times f/V_1$ (N/20) = f_1 (N/20)

Step-3 : Estimation of Cu^{+2} iodometrically

Principle:

Copper is estimated iodometrically based upon the reaction

$$Cu^{+2} + 4\,I^- = 2CuI \downarrow + I_2$$

The precipitation of CuI causes the rise of formal potential of the Cu^{+2}/Cu^{+} to about 0.858 Volt

(from $E^{0}_{Cu^{+2}/Cu^{+}}$ = 0.15 volt). As a result Cu^{+2} oxidises I^{-} to I_2 ($E^{0}_{I_2/2IH^{-}}$ = 0.54 volt) quantitavely and the liberated iodine is then titrated with standard $Na_2S_2O_3$ solution using starch as indicator. The precipitate of CuI adsorbs some iodine. Ammonium thiocyanate is thus added. The SCN^{-} ions liberates the adsorbed iodine due to the preferential adsorption over CuI.

Chemicals Required:

a) Standard (N/20) $K_2Cr_2O_7$ solution
b) Standard (N/20) $Na_2S_2O_3$ solution
c) 4(N) H_2SO_4
d) KI solution
e) 1% starch solution
f) NH_4SCN
g) $CuSO_4$ solution
[Dissolve 12.434 g $CuSO_4.5H_2O$ in 100 ml of distilled water and add 1-2 drops of conc. H_2SO_4 to prepare (N) solution. 4-6 ml may be supplied for determination of Cu^{+2}].

Procedure for the estimation of Cu^{+2} using standard thiosulphate solution:

i) Transfer the supplied solution in a 100 ml volumetric flask. Wash the container 4-5 times with distilled water and transfer to the volumetric flask carefully. Make up the volume with distilled water.

ii) Pipette out 25 ml of the copper sulphate solution into 250 ml conical flask. Add dilute solution of NH_4OH (1:1) until a slight permanent precipitate of cupric hydroxide is just formed (with excess of NH_4OH the precipitate dissolves forming a blue colouration). Add 2 ml of glacial acetic acid; the solution will be slightly acidic and will dissolve any precipitate formed. Cool the solution (pH – 3). Add about 1 g of KI, mix it well and cover the flask with a watch glass and allow to stand for 1 minute in dark place. A precipitate appears and the solution becomes brown. Rinse down the sides of the wall of the flask and dilute to about 100 ml. Titrate with standard thiosulphate solution from the burette until the brown colour due to iodine changes to very light yellow. Add 2 ml of starch solution; colour of the solution becomes blue. Continue adding thiosulphate solution from burette slowly with stirring until blue colour begins to fade. Now add about 1-2 g of ammonium thiocyanate. Continue the titration with thiosulphate adding it dropwise with stirring until with one drop, the blue colour is discharged and the colour changes to white. Note the volume of thiosulphate consumed. Repeat the experiment three times.

No. of obs.	Volm. of Cu-salt solution (ml)	Burette reading		Volm. of $Na_2S_2O_3$ soln. (ml)	Mean volm. of $Na_2S_2O_3$ soln. (ml)
		Initial	Final		
1.	25	0	...	...	V_2
2.	25	...	...	...	
3.	25	...	...	...	

Table – 3:

Calculation:

25 ml Cu^{+2} salt solution ≡ V_2 ml of f_1 (N/20) $Na_2S_2O_3$ solution

≡ V_2 x f_1/20 ml of (N) $Na_2S_2O_3$ solution

We know that, 1000 ml of (N) $Na_2S_2O_3$ ≡ 63.357 g of copper

[since g. Eq. Wt of Cu = g. Atomic wt./1]

∴ 1 ml ... ... ≡ 0. 063357 g of copper

∴ V_2 x f_1/20 ml of (N) $Na_2S_2O_3$ solution ≡ 0. 063357 x V_2 x f_1/20 g of copper

∴ 25 ml of the cupric salt solution contain 0. 063357 x V_2 x f_1/20 g of copper

∴ 1000 ml ... ... 0. 063357 x V_2 x f_1/20 x 40 g of copper

∴ Amount of Cu = 0. 063357 x V_2 x f_1/20 x 40 g/lit.

1.11 Estimation of Cr^{+3} using $K_2Cr_2O_7$ solution

Principle:

Ammonium persulphate quantitatively oxidised Cr^{+3} to $Cr_2O_7^{=}$ in sulphuric acid medium in presence of $AgNO_3$ as catalyst. $Cr_2O_7^{=}$ so formed is then estimated by adding measured excess of standard Mohr's salt solution. the excess Mohr's salt being back titrated with the standard $K_2Cr_2O_7$ solution using Barium diphenylsulphonate (BaDS) as indicator.

$$2Cr^{+3} + 3S_2O_8^{-3} + 7H_2O = Cr_2O_7^{=} + 6SO_4^{-2} + 14H^{+}$$

$$Cr_2O_7^{=} + 6Fe^{+2} + 14H^{+} = 2Cr^{+3} + 6Fe^{+3} + 7H_2O$$

$$\therefore 2 \text{ moles } Cr^{+3} \equiv 1 \text{ mole of } Cr_2O_7^{-2} \equiv 6 \text{ moles of } Fe^{+2}$$

Or, 1 mole $Fe^{+2} \equiv$ 1/6 mole of $K_2Cr_2O_7 \equiv$ 1/3 mole mole of Cr $\equiv$ 1 equivalent

$\therefore$ 1000 ml (N) Mohr's salt solution $\equiv$ 49.03 g of $K_2Cr_2O_7$ $\equiv$ 51.996/3 or 17.332 g of Cr

Chemicals Required:

a) Standard 250 ml ˜ (N/20) $K_2Cr_2O_7$ solution
b) Standard 250 ml ˜ (N/20) Mohr's salt solution
c) Conc. H_2SO_4
d) 10% ammonium persuphate solution
e) 1.5% $AgNO_3$ solution
f) Syrupy H_3PO_4
g) Barium diphenylsulphonate indicator (BaDS)

Procedure:

A. Prepare standard 250 ml ˜ (N/20) $K_2Cr_2O_7$ solution [0.6129 g $K_2Cr_2O_7$ in 250 ml water]

B. Prepare ˜ (N/20) $Na_2S_2O_3$ solution [Dissolve 12.5 – 13 g of $Na_2S_2O_3 .5H_2O$ in 500 ml of boiled distilled water and diluted to 1 litre. Add 3-4 drops of $CHCl_3$ to improve the stability of the solution and store in a amber colour bottle].

C. Transfer the supplied solution in 100 ml of volumetric flask. Wash the container carefully. Dilute the solution with distilled water up to the mark.

D. Standardize the Mohr's salt solution by standard $K_2Cr_2O_7$ solution using usual procedure

Take standard $K_2Cr_2O_7$ solution in burette. Pipette out 25 ml of Mohr's salt (ferrous salt) solution in a 250 ml conical flask. Add 150 ml of distilled water. Now pour 5 ml conc. H_2SO_4 and 5 ml of syrupy H_3PO_4. Add 2-3 drops of BaDS indicator. Titrate with $K_2Cr_2O_7$ solution with constant shaking till red-violet or purple colour appeared. Note the burette reading. Repeat the experiment three times. Repeat the experiment thrice.

E. Estimation of Cr^{+3}

i) Oxidation: Pipette out 25 ml of prepared stock solution in 500 ml conical flask. Add 10 ml 1.5% $AgNO_3$ solution and 30 ml of 10% ammonium persuphate solution. Now carefully pour 8 ml of conc. H_2SO_4. Stir the mixture gently. Cover the mouth of the conical flask with watch glass. Heat the mixture slowly and then boil it for about 20 minutes.

ii) Back titration of the excess Mohr's salt solution: Cool the solution. Add 100 ml of distilled water. Add 50 ml of the standard Mohr's salt solution with a pipette. Add 3 ml of syrupy H_3PO_4 and 3-4 drops of Barium diphenylsulphonate indicator (BaDS). Titrate the excess Mohr's salt with standard ˜ (N/20) $K_2Cr_2O_7$ solution. [mentioned above].

F. Experimental Results:

Table-1: Preparation of standard 250 ml ˜ (N/20) $K_2Cr_2O_7$ solution

Initial weight (g)	Final weight (g)	Amount of $K_2Cr_2O_7$ taken (g)	Strength of the solution (N/20)
W_1	W_2	$W_1 - W_2 = W$	W/0.6129

∴ Strength of the $K_2Cr_2O_7$ solution = W/0.6129 x N/20 = $\frac{W}{0.6129 \times 20}$ (N)

= S(N)

Table -2: Standardization of ˜ (N/20) Mohr's salt solution:

No. of obs.	Volm. of Mohr's salt soln. (ml)	Burette reading		Volm. of $K_2Cr_2O_7$ (ml)	Mean volm. of $K_2Cr_2O_7$ (ml)
		Initial	Final		
1.	25	0	...	...	V
2.	25	...	...	...	
3.	25	...	...	...	

∴ Strength of Mohr's salt solution = V x S / 25 (N) = S_1 (N)

Table-3: Estimation of Cr^{+3} :

No. of obs.	Volm. of $K_2Cr_2O_7$ + Mohr's salt (ml)	Burette reading		Volm. of $K_2Cr_2O_7$ (ml)	Mean volm. of $K_2Cr_2O_7$ (ml)
		Initial	Final		
1.	25 + 50	0	...	...	V_1
2.	25 + 50	...	...	...	
3.	25 + 50	...	...	...	

G. Calculation:

i) Strength of $K_2Cr_2O_7$ solution = S (N)

ii) Strength of Mohr's salt solution = S_1 (N)

iii) Estimation of Cr:

25 ml Mohr's salt solution ≡ V ml S (N) $K_2Cr_2O_7$ solution

25 ml K_2 Cr_2 O_7 solution + 50 ml Mohr's salt solution ≡ V_1 ml S (N) $K_2Cr_2O_7$ solution

Mohr's salt consumed by $K_2Cr_2O_7$ in 25 ml diluted stock solution ≡ $(2V - V_1)$ ml S(N) $K_2Cr_2O_7$ solution

≡ $(2V - V_1)$ x S ml (N) $K_2Cr_2O_7$ solution

≡ $(2V - V_1)$ x S ml (N) Mohr's salt solution

We have, 1000 ml (N) Mohr's salt solution ≡ 17.332 g of Cr

∴ $(2V - V_1) \times S$ ml (N) Mohr's salt solution ≡ $0.017332 \times (2V - V_1) \times S$ g of Cr

25 ml of the stock solution contain $0.017332 \times (2V - V_1) \times S$ g of Cr

∴ 1000 ml ... ... $0.017332 \times (2V - V_1) \times S \times 40$ g of Cr

∴ Amount of Cr present = $0.017332 \times (2V - V_1) \times S \times 40$ g/ lit.

1.12 Summary

- Primary standard substances are the substances from which a standard solution can be prepared by direct weighing a define amount of it followed by dissolution and dilution to a definite volume.
- A secondary standard substance is one, the strength of the solution of which can't be known by dissolving a definite weight of the substance in a known volume of the solution.
- For the calculation of a titration generally the strength of a solution is expressed in normality (N).
- We have to maintain the conditions such as pH, temperature time of addition of indicator etc. for each titration as the procedure discussed for individual experiments to obtain accurate result.
- Acidified $KMnO_4$ is stronger oxidising agent than acidified $K_2Cr_2O_7$ in redox reactions.
- Iodometry refers to the titration of iodine liberated in a quantitative redox reaction by a standard solution of a reducing agent like sodium thiosulphate. Iodimetry, is the titration of a reducing agent with standard solution of iodine.

1.13 Questions

Q-1: In permanganometry no external indicator is used- why?

Ans: $KMnO_4$ act as self indicator for its pink colour.

Q-2: What is the formula of Mohr's salt?

Ans: $(NH_4)_2SO_4.FeSO_4.6H_2O$

Q-3: What type of salt it is?

Ans: It is a double salt.

Q-4: Why $KMnO_4$ is not use as Primary standard?

Ans: a) It is not available in pure sate.

b) Trace of organic matters present in distilled water helps to decomposition of $KMnO_4$ in solution.

$$4MnO_4^- + 2H_2O = 4MnO_2 + 4OH^- + 3O_2$$

c) $KMnO_4$ solution decomposes in bright sun light.

d) Solid MnO_2 obtained in reaction also catalyse the decomposition of $KMnO_4$.

Q-5: Why $KMnO_4$ is behaves more powerful oxidising agent in acid medium compare to other medium?

Ans: $KMnO_4$ act as a powerful oxidant in acid medium due to its higher standard reduction potential value. But the potential value falls and thus oxidising power decreases with decrease of concentration of H^+ ie., increase of pH value of the medium.

In acid medium : $MnO_4^- + 8H^+ + 5e \longrightarrow Mn^{+2} + 4H_2O$ $E^0 = 1.51V$

In neutral medium: $MnO_4^- + 2H_2O + 3e \longrightarrow MnO_2 + 4OH^-$ $E^0 = 0.59V$

In alkaline medium: $MnO_4^- + e \longrightarrow MnO_4^{-2}$ $E^0 = 0.56V$

Q-6: What is the basic criteria of choosing indicator in redox titration?

Ans: The standard reduction potential of the indicator should be higher than reductant and lower that of the oxidant.

Q-7: Why removal of mineral acid is essential for precipitation of Ca- oxalate?

Ans: Because Ca-oxalate is soluble in mineral acid.

Q-8: Why in the titration of oxalic acid with $KMnO_4$ pink colour disappears slowly at the beginning but rapidly afterwards?

Ans: The reaction between oxalic acid and $KMnO_4$ is slow; so the pink colour disappears slowly at the beginning, but once the reaction starts, Mn^{+2} formed and accelerate the rate of reaction.

Q-9: Why this reaction is carried out at hot condition?

Ans: To make the reaction rate fast.

Q-10: What is Zimmernmann – Reinhardt (Z.R) solution?

Ans: The solution consists of $MnSO_4$, H_3PO_4 and H_2SO

Module - II (Organic Chemistry)

Unit 2 ❐ Separation of Organic Compounds

Structure

2.0 Objectives

2.1 Introduction

2.2 Crystallization Techniques

2.3 Separation of p-Toluidine /Benzoic acid

2.4 Separation of p-Nitrotolune / p- Anisidine

2.5 Separation of Benzoic acid / Phloroglucinol (3,5- dihydroxy phenol)

2.6 Summary

2.7 Questions

2.0 Objectives

At the end of this unit the learner is expected to be able to:

- Train basic organic laboratory techniques.
- Learn basic procedures for isolation and purification of organic compounds.
- Use acid-base chemistry for separation of organic compounds.
- Separate a mixture of a neutral and a basic organic compound by solvent extraction technique.
- Describe the theory behind the above.

2.1 Introduction

The separation of mixtures of compounds to give the single pure components is of great practical importance in chemistry. A mixture of organic compounds may be in the solid or liquid form or may consist of a solid dissolved or suspended in a liquid. If a solid and a liquid are present it is usually unwise to expect separation to be accomplished by filtration because the liquid phase almost certainly contains some dissolved solid and traces of the liquid component may be difficult to remove from the solid compound. The methods of isolating pure samples of the components from a mixture may be either physical or chemical. Separations can be achieved by differences in physical properties, such as differences in boiling point, or by chemical means, wherein differences in physical properties are enhanced by chemical reactions. The chemical method of separating two compounds depends on their differing solubility in water, ether, dilute acid or alkali. In this chapter we will consider some separations of compounds based on differences in Chemical procedures.

2.2 Crystallization Techniques

Solid organic compounds when obtained from any chemical reaction or mixture, are usually contaminated with small amount of other compounds, known as impurities, which are produced or mixed along with the desired product. The purification of impure crystalline compounds is usually effected by crystallization from a suitable solvent or mixture of solvents.

The purification of solids by crystallization is based upon differences in their solubility in a given solvent or mixture of solvents. The crystallization process consists of the following sequential process:

i) Dissolve the impure substance in some suitable solvent at or near the boiling point.
ii) Filter the hot solution to remove insoluble materials or dust if any present.
iii) Evaporate the solution to concentrate the mixture and then cool thus causing the dissolved substance to crystallize out.
iv) Separate the crystals from the supernatant solution (i.e, mother-liquor).
v) The resulting solid, after drying, is tested purity by determining m.p.

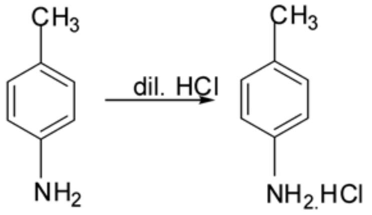
List of common solvents for crystallization:

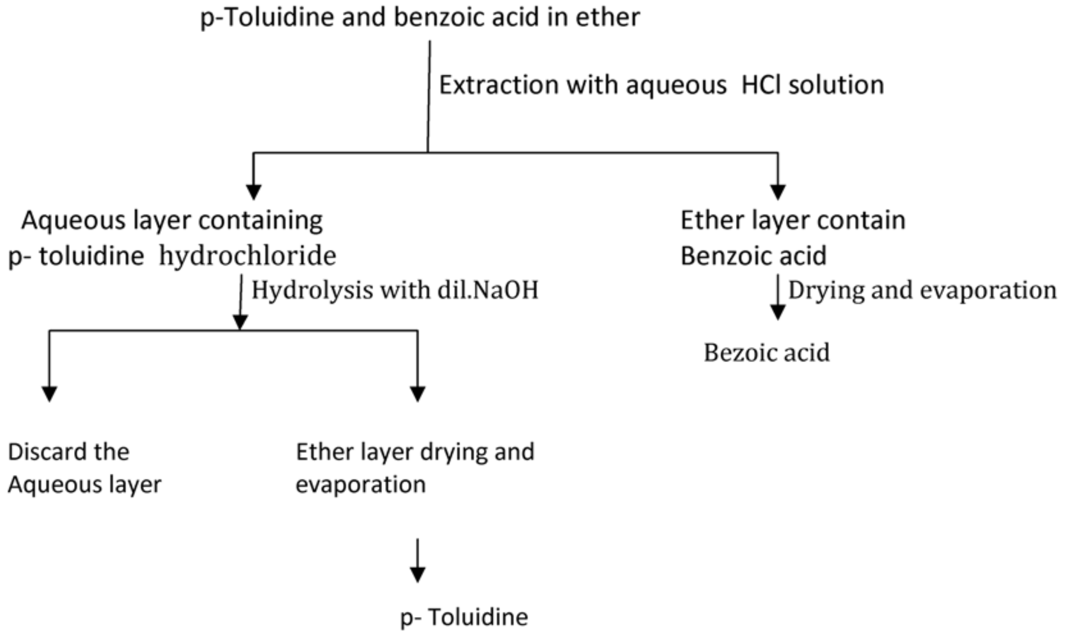
Solvent	b.p (^0C)
Water	100
Methanol	64.5
Ethanol	78
Acetone	56
Chloroform	61
Benzene	80

2.3 SEPERATION OF p-TOLUIDINE/Benzoic Acid

Principle:

It is a mixture of two compounds of different nature. One is acidic and other basic in nature. p - Toludine is basic in nature so it is soluble in dil. HCl solution on other hand benzoic acid is acidic and thus soluble in alkaline solution.





Procedure:

The procedural instructions are given below in sequential order. You are expected to go through the complete procedure and prepare a broad mental outline of the same.

1. Clean the separating funnel first with soap water and then with plenty of distilled water. Grease the stopcock to ensure its smooth movement.

2 Close the stopcock and mount the separatory funnel in the ring support, on an iron stand. If the ring support is not available, you may use a tripod stand for the purpose.

3. Weigh 2 g of the mixture on a rough weighing balance and dissolve it in about 30 ml of solvent ether in a conical flask.

4. Transfer the solution to the separatory funnel after ensuring that the stopcock is closed. Wash the conical flask with a little (5 mL) of ether and pour this also into the separatory funnel. This ensures complete transfer of the mixture.

5 Add about 20 ml of 2 (N) hydrochloric acid solution to the solution.

6. Gently swirl the contents of the funnel to mix them. Release the pressure build up inside the flask. This pressure is due to the evaporation of highly volatile ether. To release the pressure, carefully turn the funnel upside down then the stopper may be cautiously open and then closed. You will hear the sound of escaping vapours.

7. Allow the mixture to stand in the funnel (on the ring support) until the two immiscible layers are separated. .

8. Remove the stopper and draw off the lower layer into a 100 ml conical flask labelled 'A'

9. Put additional 5 ml of H_20 in the funnel, shake the contents, allow the layers to separate and draw off the lower layer (water layer) again in flask 'A'.

10. Pour about 15 ml of saturated aqueous solution of sodium chloride in the separatory funnel shake vigorously for about a minute and allow the layers to separate. Draw out the lower layer and discard it.

11. Place little amount of anhydrous Na_2SO_4 to dehydrate the ether layer.

12. Pour the ether layer into a conical flask labeled 'B'.

RECOVERY OF SEPARATED COMPOUNDS :

By following the above procedure you will obtain two flasks containing the separated compounds.

Flask 'A' :p-toluidine as p-toluidine hydrochloride in water.

Flask 'B' : Benzoic acid in ether.

The desired compounds can be obtained as follow:

Recovery of p-toluidine from Part A (water layer): As said above p-toluidine can be recovered by hydrolysing the solution with aqueous alkali. Take flask 'A' containing the solution of p-toluidine hydrochloride and add dilute NaOH solution dropwise into it with constant shaking. Continue addition till the solution becomes alkaline. This can be checked with the help of a pH paper. When pH of the solution approaches $\approx$ 10, you may see the separation of p-toluidine as a solid. It may so happen that you may get the solid even after adding little more of NaOH solution. This can be because of a low melting point of toluidine (43°C).

If you get the solid, filter it and dry the crystals in the folds of filter paper. Report the amount of p-toluidine obtained and determine the m.p.

If you get oily mass or emulsion instead of solid then proceed with the process given below.

Transfer the above solution from flask 'A' to a separatory funnel mounted on a ring stand. Put about 20 ml of ether into it and gently swirl it so as to dissolve any p-toluidine droplets sticking on the walls. Transfer this ether also to the separatory funnel. Gently swirl the separatory funnel to extract p-toluidine into ether. Keep the funnel for some time so as to allow the layers to separate. Collect the aqueous layer again in the flask 'A' and pour the ethereal layer to flask labelled 'C'. Repeat the process with another 20 ml of solvent ether.

Dry the ethereal fraction in flask 'C' by putting in some anhydrous sodium sulphate crystals. Decant the ether solution from flask 'C' into another flask. Put about 5 ml of ether into flask 'C' and thoroughly rinse the flask along with drying agent. Wait for a minute or two and mix this ether with the previous lot by completely decanting it. Take care not to transfer the drying agent. Evaporate the ether on a steam bath, or preferably distil it.

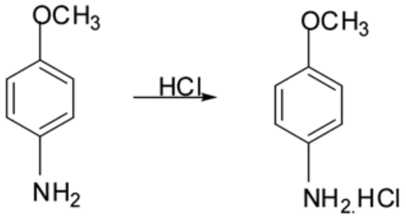
Recovery of Benzoic acid from Part B (ether layer): Evaporate the ether solution from flask 'B' by placing it over a steam bath. Scratch the solid with a neat spatula and weigh it. Report the amount of Benzoic aci obtained and save the sample and determine m.p.

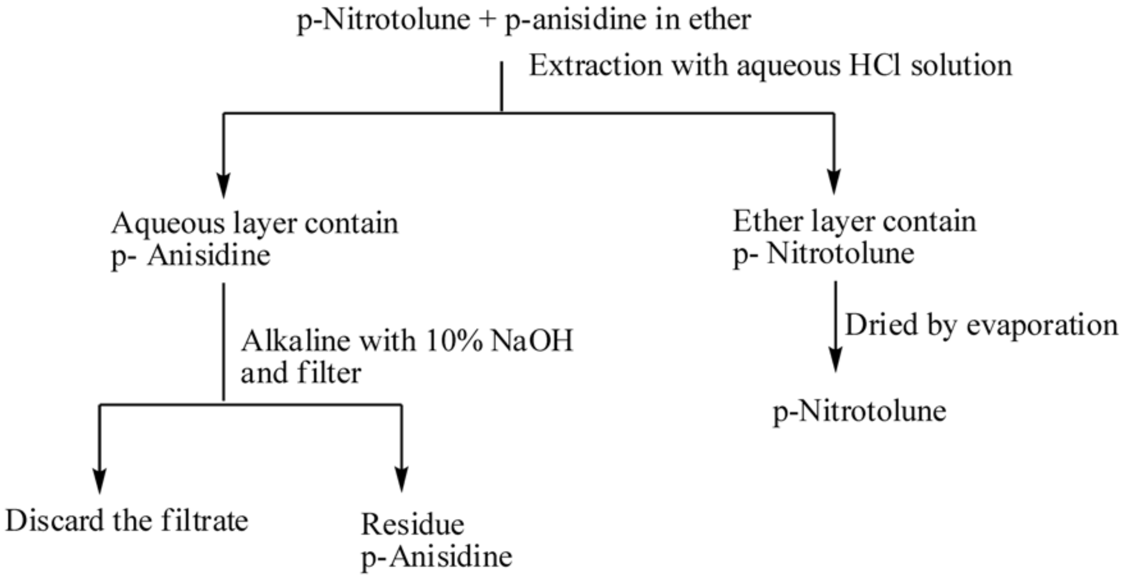
Crystallisation: Take the benzoic acid in a beaker. Dissolve it in minimum volume of distilled water by heating. Now add drop by drop distilled water to make the solution turbid. Boil the mixture till it becomes transparent. Filter the solution in hot condition. Cool the filtrate.

Needle shape crystals of benzoic acid are separated out. Filter, dry and collect the product and note the m.p. (121.5^{0}C)

2.5 Separation of p-Nitrotolune / p- Anisidine

It is a mixture of two compounds of different nature. One is neutral and other basic in nature. P- Anisidine is basic in nature so it is soluble in dil. HCl solution on other hand p- Nitrotolune is neutral and thus insoluble in acid.





Procedure:

The procedural instructions are given below in sequential order. You are expected to go through the complete procedure and prepare a broad mental outline of the same.

1. Clean the separating funnel first with soap water and then with plenty of distilled water. Grease the stopcock to ensure its smooth movement.

2 Close the stopcock and mount the separatory funnel in the ring support, on an iron stand. If the ring support is not available, you may use a tripod stand for the purpose.

3. Weigh 2 g of the mixture on a rough weighing balance and dissolve it in about 30 ml of solvent ether in a conical flask.

4. Transfer the solution to the separatory funnel after ensuring that the stopcock is closed. Wash the conical flask with a little (5 ml) of ether and pour this also into the separatory funnel. This ensures complete transfer of the mixture.

5 Add about 20 ml of 2 (N) hydrochloric acid solution to the solution.

6. Gently swirl the contents of the funnel to mix them. Release the pressure build up inside the flask. This pressure is due to the evaporation of highly volatile ether. To release the pressure, carefully turn the funnel upside down then the stopper may be cautiously open and then closed. You will hear the sound of escaping vapours.

7. Allow the mixture to stand in the funnel (on the ring support) until1 the two immiscible layers are separated. .

8. Remove the stopper and draw off the lower layer (water layer) into a 100 ml conical flask labelled 'A'

9. Put additional 5 ml of H_20 in the funnel, shake the contents, allow the layers to separate and draw off the lower layer again in flask 'A'.

10. Pour about 15 ml of saturated aqueous solution of sodium chloride in the separatory funnel shake vigorously for about a minute and allow the layers to separate. Draw out the lower layer and discard it.

11. Place little amount of anhydrous Na_2SO_4 to dehydrate the ether layer.

12. Pour the ether layer into a conical flask labelled 'B'.

RECOVERY OF SEPARATED COMPOUNDS :

By following the above procedure you will obtain two flasks containing the separated compounds.

Flask 'A' :p-Anisidine as p-Anisidine hydrochloride in water.

Flask 'B' : p-Nitrotolune in ether.

The desired compounds can be obtained as follow:

Recovery of p-Anisidine from part A: As said above p-Anisidine can be recovered by hydrolysing the solution with aqueous alkali. Take flask 'A' containing the solution of p-Anisidine hydrochloride and add dilute NaOH solution dropwise into it with constant shaking. Continue addition till the solution becomes alkaline.

This can be checked with the help of a pH paper. When pH of the solution approaches ≈ 10, you may see the separation of p-Anisidine as a solid. It may so happen that you may get the solid even after adding little more of NaOH solution. This can be because of a low melting point of p-Anisidine.

If you get the solid, filter it and dry the crystals in the folds of filter paper. Report the amount of p-Anisidine obtained and determine the m.p.

If you get oily mass or emulsion instead of solid then proceed with the process given below.

Transfer the above solution from flask 'A' to a separatory funnel mounted on a ring stand. Put about 20 ml of ether into it and gently swirl it so as to dissolve any p-Anisidine droplets sticking on the walls. Transfer this ether also to the separatory funnel. Gently swirl the separatory funnel to extract p-Anisidine into ether. Keep the funnel for some time so as to allow the layers to separate. Collect the aqueous layer again in the flask 'A' and pour the ethereal layer to flask labeled 'C'. Repeat the process with another 20 ml of solvent ether.

Dry the ethereal fraction in flask 'C' by putting in some anhydrous sodium sulphate crystals. Decant the ether solution from flask 'C' into another flask. Put about 5 ml of ether into flask 'C' and thoroughly rinse the flask along with drying agent. Wait for a minute or two and mix this ether with the previous lot by completely decanting it. Take care not to transfer the drying agent. Evaporate the ether on a steam bath, or preferably distil it.

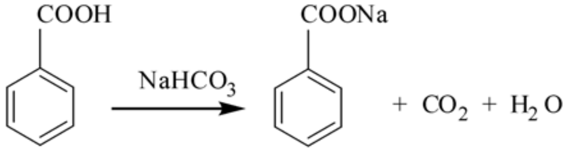
Recovery of p- Nitrotolune from part B: Evaporate the ether solution from flask 'B' by placing it over a steam bath. Scratch the solid with a neat spatula and weigh it. Report the amount of p- Nitrotolune obtained and save the sample and determine m.p.

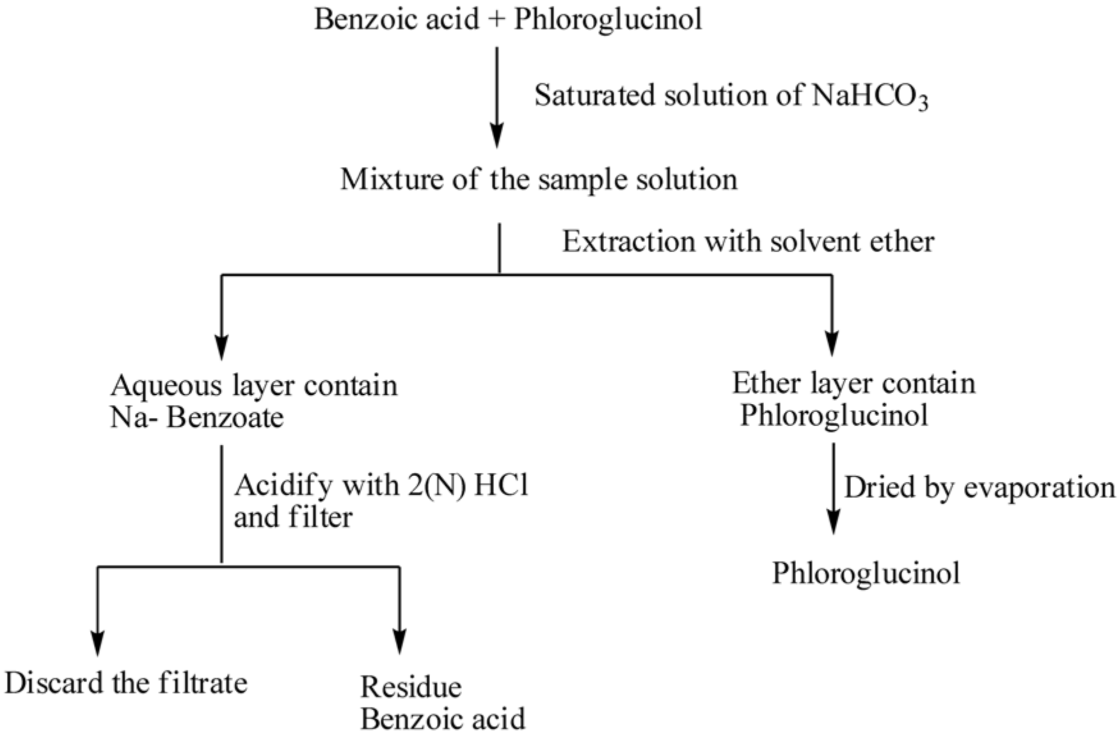
Crystallization: Take the p- Nitrotolune and p- Anisidine in two separate beaker. Dissolve it in minimum volume of alcohol by heating. Now add drop by drop distilled water to make the solution turbid. Cool, filter, dry and collect the product and note the m.p.

[Melting Point of p- Anisidine is 57^0C and p- Nitrotolune is 52^0C]

2.5 Separation of Benzoic acid / Phloroglucinol (3,5- dihydroxy phenol)

It is a mixture of two compounds of different nature. One is strong acid compare to other. Benzoic acid is stronger than phloroglucinol for this reason benzoic acid reacts with $NaHCO_3$ to produce sodium benzoate but phloroglucinol remain unreacted.





Procedure:

The procedural instructions are given below in sequential order. You are expected to go through the complete procedure and prepare a broad mental outline of the same.

1. Clean the separating funnel first with soap water and then with plenty of distilled water. Grease the stopcock to ensure its smooth movement.

2 Close the stopcock and mount the separatory funnel in the ring support, on an iron stand. If the ring support is not available, you may use a tripod stand for the purpose.

3. Weigh 2 g of the mixture on a rough weighing balance and take the whole mixture in a 250 ml beaker.

4. Now add saturated solution of sodium bicarbonate slowly by stirring till all the CO_2 is liberated.

4. Transfer the solution to the separatory funnel after ensuring that the stopcock is closed. Wash the conical flask with a little (5 ml) of ether and pour this also into the separatory funnel. This ensures complete transfer of the mixture.

5 Add about 30 – 40 ml ether to the solution.

6. Gently swirl the contents of the funnel to mix them. Release the pressure build up inside the flask. This pressure is due to the evaporation of highly volatile ether. To release the pressure, carefully turn the funnel upside down then the stopper may be cautiously open and then closed. You will hear the sound of escaping vapours.

7. Allow the mixture to stand in the funnel (on the ring support) until the two immiscible layers are separated. .

8. Remove the stopper and draw off the lower layer (water layer) into a 100 ml conical flask labelled 'A'

9. Put additional 5 ml of H_20 in the funnel, shake the contents, allow the layers to separate and draw off the lower layer again in flask 'A'.

10. Pour about 15 ml of saturated aqueous solution of sodium chloride in the separatory funnel shake vigorously for about a minute and allow the layers to separate. Draw out the lower layer and discard it.

11. Place little amount of anhydrous Na_2SO_4 to dehydrate the ether layer.

12. Pour the ether layer into a conical flask labelled 'B'.

RECOVERY OF SEPARATED COMPOUNDS :

By following the above procedure you will obtain two flasks containing the separated compounds.

Flask 'A' : Benzoic acid as sodium benzoate in water.

Flask 'B' : Phloroglucinol in ether.

The desired compounds can be obtained as follow:

Recovery of Benzoic acid from part A: The aqueous layer in flask 'A', which contains the sodium salt of benzoic acid, is now worked up on by adding dil. HCl to neutralize sodium salt. When neutralization is complete filtered and dried.

Crystallisation: Take the benzoic acid in a beaker. Dissolve it in minimum volume of distilled water by heating. Now add drop by drop distilled water to make the solution turbid. Boil the mixture till it becomes transparent. Filter the solution in hot condition. Cool the filtrate.

Needle shape crystals of benzoic acid are separated out. Filter, dry and collect the product and note the m.p.

Recovery of Phloroglucinol from part B: Evaporate the ether solution from flask 'B' by placing it over a steam bath. 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 determine m.p.

[Melting point of benzoic acid = 121.5^0C and Phloroglucinol = 218^0C]

2.6 Summary

- The purification of solids by crystallization is based upon differences in their solubility in a given solvent or mixture of solvents.
- p-Toludine is basic in nature so it is soluble in dil. HCl solution on other hand benzoic acid is acidic and thus soluble in alkaline solution.
- p-Anisidine is basic in nature so it is soluble in dil. HCl solution on other hand p-Nitrotolune is neutral and thus insoluble in acid.
- Benzoic acid is stronger than phloroglucinol for this reason benzoic acid reacts with NaHCO3 to produce sodium benzoate but phloroglucinol remain unreacted.

2.7 Questions

Q1. Which is known as mother liquor?

Ans: Mother liquor is the part of a solution that is left over after crystallization. It is encountered in chemical processes including sugar refining.

Q2. How insoluble impurities from solution are removed during crystallization?

Ans: Insoluble impurities from solution during crystallization are removed by filtration. The solution is filtered to remove insoluble impurities.

Q3. Which factors govern the nature of the crystallization process?

Ans: The nature of the crystallization process is governed by both thermodynamic and kinetic factors

Q4. What is the basic principle for the separation of p-Toluidine and Benzoic acid from mixtures?

Ans: See text 2.4

Q5. What is the basic principle for the separation of p-Nitrotolune and p- Anisidine from mixtures?

Ans: See text 2.5

Q6. What is the basic principle for the separation of Benzoic acid and Phloroglucinol from mixtures?

Ans: See text 2.6

Q7. Which is stronger acid between Benzoic acid and phloroglucinol?

Ans: Benzoic acid

Q8. What is the nature of p-Anisidine?

Ans: P-Anisidine is basic in nature

Unit 3 ❐ Determination of Boiling Point of Organic Compounds

Structure

3.0 Objectives
3.1 Introduction
3.2 Procedure
3.3 Summary
3.4 Questions

3.0 Objectives

In this Unit a learner will acquire the laboratory based knowledge on:

- The determination of the boiling points of various organic compounds and to use these to identify unknowns.
- The instruments used for the above experiment.

3.1 Introduction

Organic chemistry is a branch of chemistry that deals with learning of composition and synthesis of organic chemical compounds. Organic compounds refer to the compounds which contain carbon in its composition. The boiling point of a liquid may be defined as the temperature at which the vapour pressure of the liquid is equal to the atmospheric pressure exerted upon the liquid surface. The boiling point of a liquid increases if non-volatile impurities are present in it. It is important to check the boiling points for a liquid organic compound to find its purity, elucidation of structures etc. Here we will learn to determine the boiling point of liquid organic compounds like benzene and benzaldehyde using laboratory apparatus.

3.2 Procedure

Boiling point can be taken as a test for the purity of a liquid. A pure liquid will have a certain definite boiling point only at a particular pressure, as the boiling point is affected both by impurities and by the ambient or external pressure. Impurities generally raise the boiling point. Since boiling point is the temperature at which the vapour pressure of a Liquid becomes equal to the ambient pressure, the boiling point of a liquid will be higher at higher pressures, and the liquid will boil at a lower temperature if the pressure is reduced.

Unless only minute quantities of the liquid are available the boiling-point is usually determined by simple distillation. For this purpose, the apparatus shown in Fig. 2 is assembled. A pear-shaped flask, A (between 10 – 25 ml) is chosen for determination of boiling point of liquid. The flask when charged with liquid should be one-half to two-third full. Now place few pieces of porous bead into the liquid. The flask is then fitted with a thermometer E (range 200^{0}C or 360^{0}C) attached cork so that the bulb of the thermometer is just at the centre of the neck and placed just below the vapour exit tube of the distilling flask. The flask is carefully connected with a water condenser B and then heat with a semi-luminous Bunsen flame with care.

Initially the temperature will rise rapidly until it near the boiling point of the liquid, then slowly, and finally will remain practically constant. Note the temperature. This is the boiling point of the liquid.

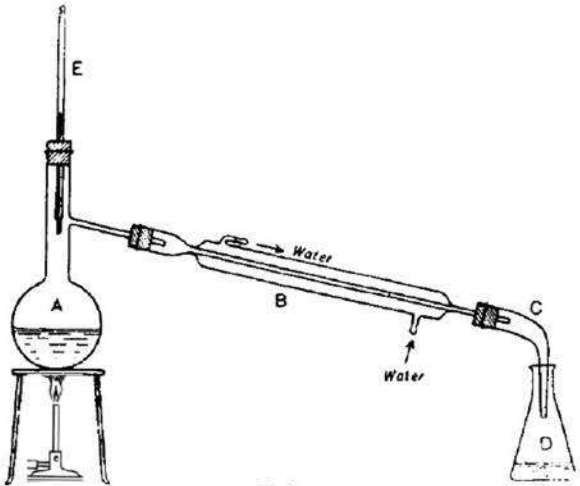


Fig. 1

Boiling point of the organic compounds which will be given to the students for practice, should preferably be less than 160 ^{o}C. Boiling Point of some organic compound are given below.

Name of the compound	**Boiling Point (^{0}C)**
Ethanol	78.37
Cyclohexane	81
Chloroform	61.2
Ethyl methyl ketone	79.64
Cyclohexanone	155.6
Acetylacetone	140
Anisole	153.8
Crotonaldehyde	104
Mesityl oxide	130

3.3 Summary

- The boiling point of a liquid is the temperature at which the vapour pressure of the liquid is equal to the atmospheric pressure exerted upon the liquid surface.
- Boiling point is affected both by impurities and by the ambient or external pressure and thus it can be taken as a test for the purity of a liquid compound.
- The boiling point of a liquid will be higher at higher pressures and vice versa.
- The boiling point of a liquid increases if non-volatile impurities are present in it.

3.5 Questions

Q1. What is the boiling point of Ethanol?

Ans: 78.37°C

Q2. What is the boiling point of benzaldehyde?

Ans: 178°C

Q3. Explain why carboxylic acids have a higher boiling point than hydrocarbons?

Ans: Carboxylic acids have a higher boiling point as they have the capacity to form hydrogen bonds. These bonds provide these molecules with extra stability that further allows these molecules to form additional bonds by employing dispersion forces.

Q4. What is the boiling point of water in hilly regions?

Ans: It is less than 100 °C.

Q5. What is the definition of boiling point?

Ans: see text

Unit 4 ❐ Identification of pure Organic Compounds by chemical test(s)

Structure

4.0 Objectives
4.1 Introduction
4.2 Identification of Organic Compounds
4.2.1 Preliminary studies of Pure Sample
4.2.2 Preparation of neutral solution of acid
4.3 Identification of a Oxalic acid by Chemical Tests
4.4 Identification of a Tartaric acid by Chemical Tests
4.5 Identification of a Citric acid by Chemical Tests
4.6 Identification of a Succinic acid by Chemical Tests
4.7 Identification of a Resorcinol by Chemical Tests
4.8 Identification of a Urea by Chemical Tests
4.9 Identification of a Glucose by Chemical Tests
4.10 Identification of a Sucrose by Chemical Tests
4.11 Identification of a Benzoic acid by Chemical Tests
4.12 Identification of a Salicylic acid by Chemical Tests
4.13 Identification of a Formic acid by Chemical Tests
4.14 Identification of a Acetic acid by Chemical Tests
4.15 Identification of a Methyl alcohol by Chemical Tests
4.16 Identification of a Ethyl alcohol by Chemical Tests
4.17 Identification of a Acetone by Chemical Tests
4.18 Identification of a Aniline by Chemical Tests
4.19 Identification of a N,N-dimethye aniline by Chemical Tests
4.20 Identification of a Benzaldehyde by Chemical Tests
4.21 Identification of a Chloroform by Chemical Tests
4.22 Identification of a Nitrobenzene by Chemical Tests
4.23 Summary
4.24 Questions

4.0 Objectives

At the end of this unit the learner is expected to be able to:

- Preliminary studies of pure sample
- Preparation of neutral solution of acid
- Identification of a few organic compounds by chemical tests

4.1 Introduction

The organic compound supplied as sample, solid or liquid, is to be detected as a whole by systemetic quantative analytical methods.

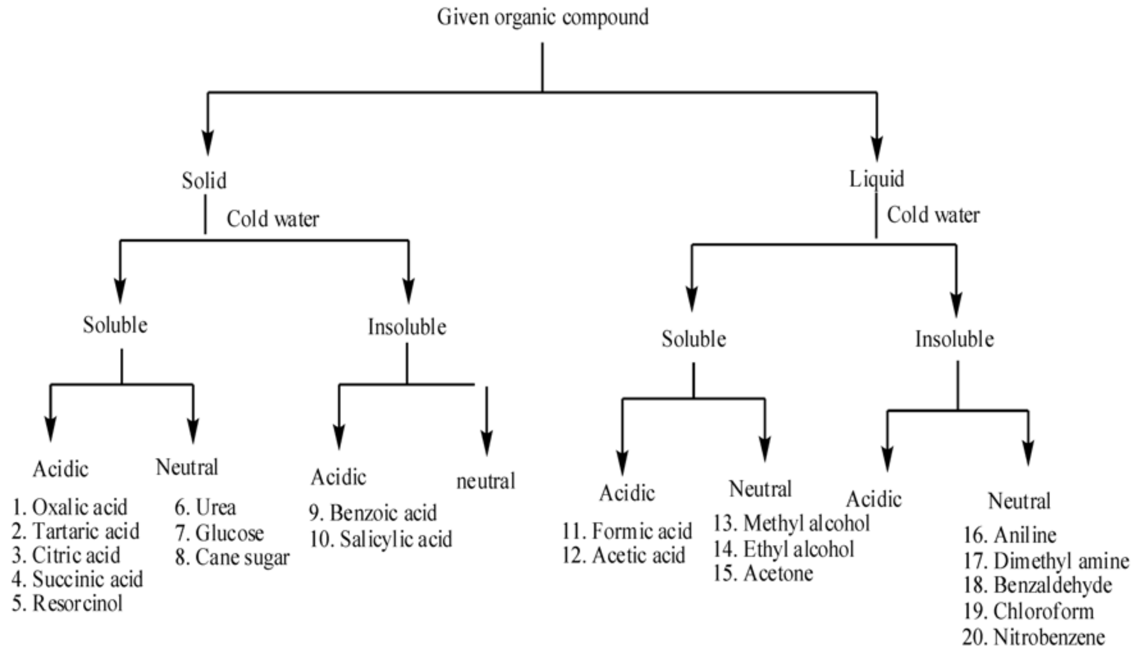
The following samples will be provided for analysis in the pure form.

Solid	**Liquid**
S-1. Oxalic acid	L-11. Formic acid
S-2. Tartaric acid	L-12. Acetic acid
S-3. Citric acid	L-13. Methyl alcohol
S-4. Succinic acid	L-14. Ethyl alcohol
S-5. Resorcinol	L-15. Acetone
S-6. Urea	L-16. Aniline
S-7. Glucose	L-17. Dimethyl aniline
S-8. Cane sugar (Sucrose)	L-18. Benzaldehyde
S-9. Benzoic acid	L-19. Chloroform
S-10. Salicylic acid	L-20. Nitrobenzene

4.2 Identification of Organic Compounds

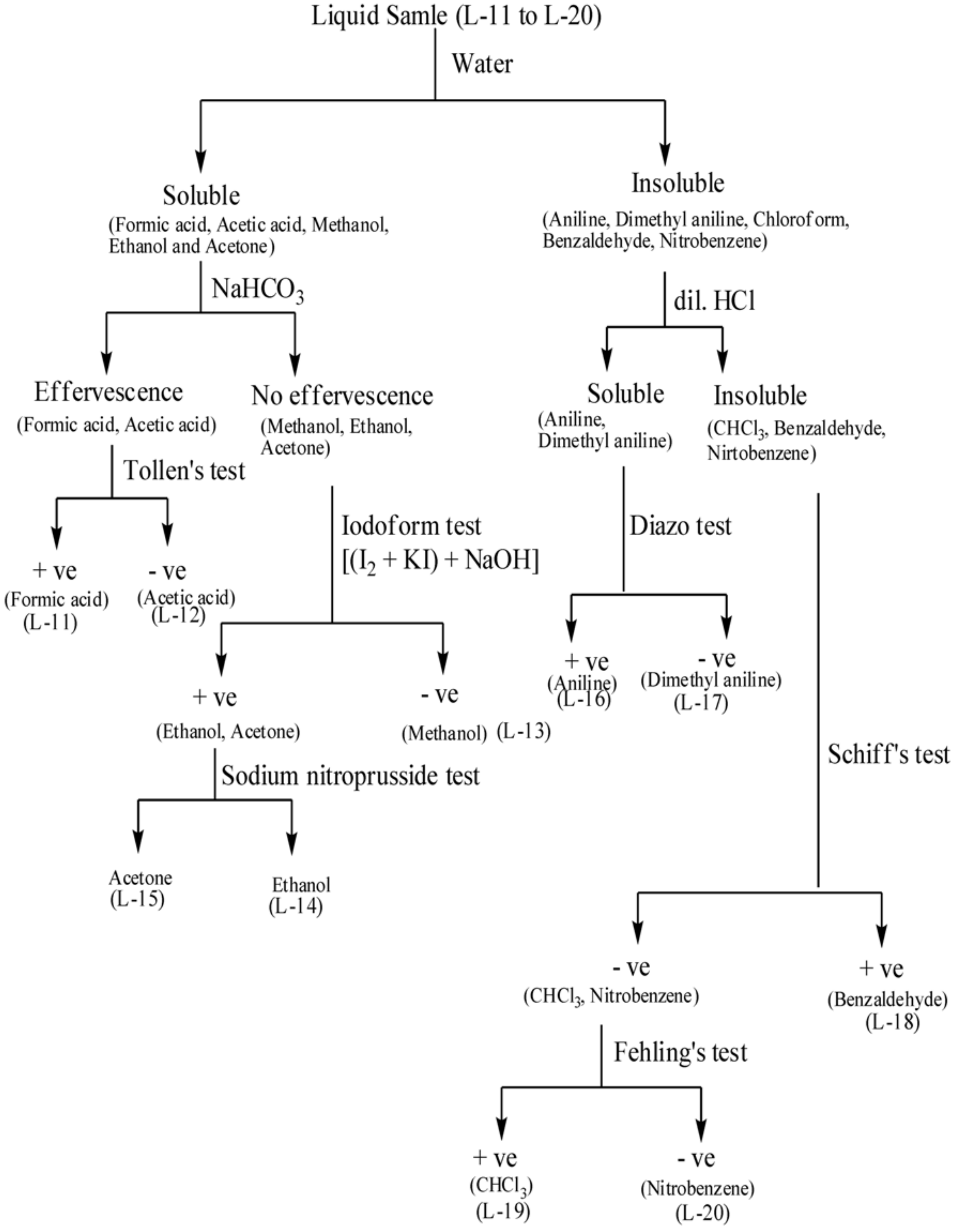
An organic compound supplied to the student may be solid or liquid, soluble or insoluble in cold water, acidic or neutral. So it is great important to the student for preliminary identification of the supplied sample belongs to the listed above. In each case small amount of sample (0.1 – 0.2 g) and reagent (2 ml) are to be taken for testing.

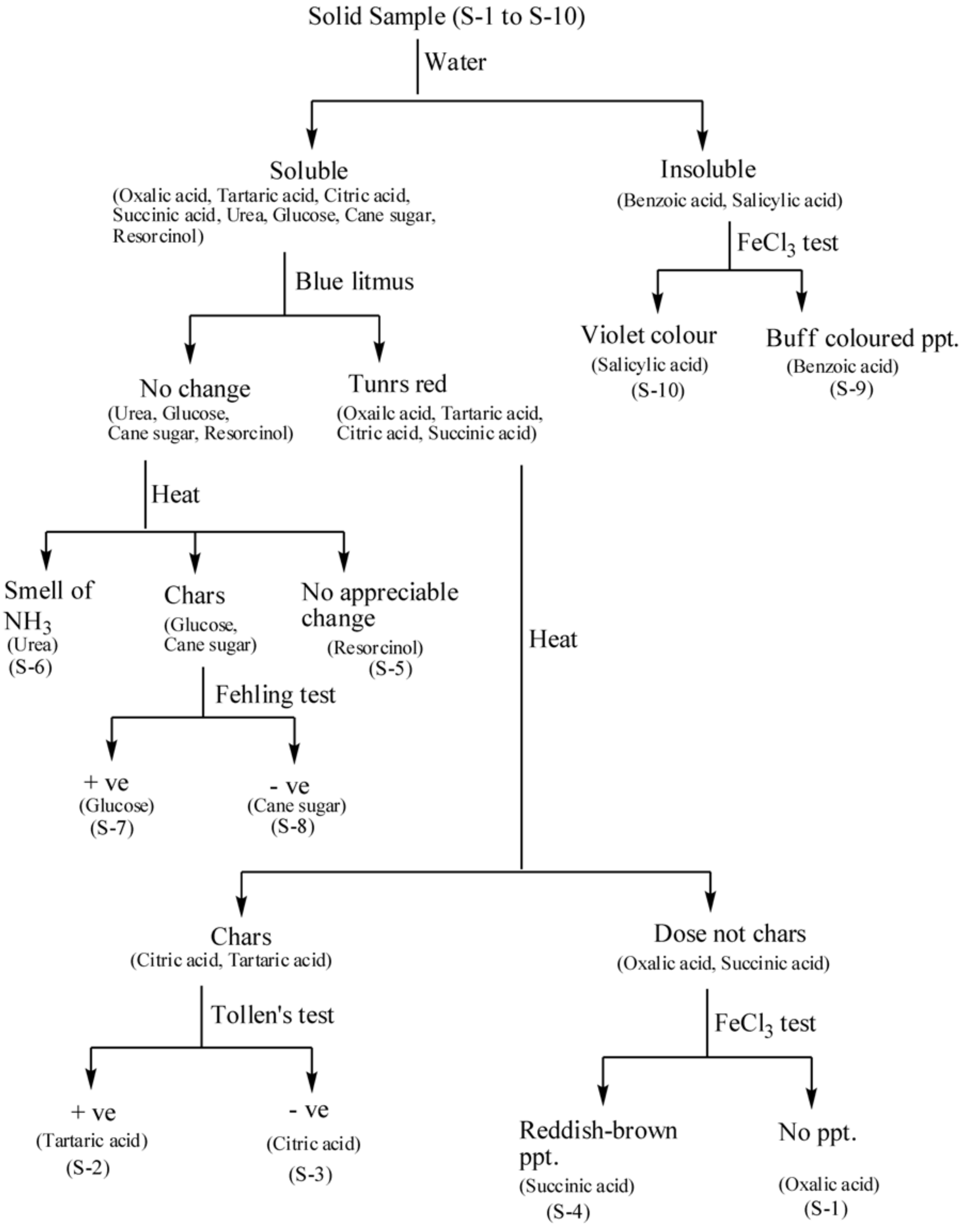
For liquid sample particularly, specific gravity and odour are the vital characteristic to identify them. As for example, among water soluble liquids specific gravity is less, should belong to CH_3OH, C_2H_5OH and $CH_3.CO.CH_3$. Liquids with pungent smell are HCOOH and CH_3COOH. $CHCl_3$ is sweet smelling water insoluble with specific gravity greater than water. Aniline and dimethyl anilne is insoluble in water but soluble in dil. HCl. Benzaldehyde and Nitrobenzene both are insoluble in acid and alkali. Based on above, the given compound under investigation can be classified as follows:



4.2.1 Preliminary studies of Pure Sample:

The given sample should be treated with some solvents, acidic/basic, reaction condition as follows and classified depending upon their nature and reactivity.


Liquid Samle (L-11 to L-20)
Water
Soluble
(Formic acid, Acetic acid, Methanol, Ethanol and Acetone)
Insoluble
(Aniline, Dimethyl aniline, Chloroform, Benzaldehyde, Nitrobenzene)
$NaHCO_3$
Effervescence
(Formic acid, Acetic acid)
No effervescence
(Methanol, Ethanol, Acetone)
Tollen's test
+ ve
(Formic acid)
(L-11)
- ve
(Acetic acid)
(L-12)
Iodoform test
[(I_2 + KI) + NaOH]
+ ve
(Ethanol, Acetone)
- ve
(Methanol) (L-13)
Sodium nitroprusside test
Acetone
(L-15)
Ethanol
(L-14)
dil. HCl
Soluble
(Aniline, Dimethyl aniline)
Insoluble
($CHCl_3$, Benzaldehyde, Nirtobenzene)
Diazo test
+ ve
(Aniline)
(L-16)
- ve
(Dimethyl aniline)
(L-17)
Schiff's test
- ve
($CHCl_3$, Nitrobenzene)
+ ve
(Benzaldehyde)
(L-18)
Fehling's test
+ ve
($CHCl_3$)
(L-19)
- ve
(Nitrobenzene)
(L-20)

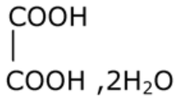

Solid Sample (S-1 to S-10)
Water
Soluble
(Oxalic acid, Tartaric acid, Citric acid, Succinic acid, Urea, Glucose, Cane sugar, Resorcinol)
Insoluble
(Benzoic acid, Salicylic acid)
$FeCl_3$ test
Violet colour
(Salicylic acid)
(S-10)
Buff coloured ppt.
(Benzoic acid)
(S-9)
Blue litmus
No change
(Urea, Glucose, Cane sugar, Resorcinol)
Tunrs red
(Oxailc acid, Tartaric acid, Citric acid, Succinic acid)
Heat
Smell of NH_3
(Urea)
(S-6)
Chars
(Glucose, Cane sugar)
No appreciable change
(Resorcinol)
(S-5)
Fehling test
+ ve
(Glucose)
(S-7)
- ve
(Cane sugar)
(S-8)
Heat
Chars
(Citric acid, Tartaric acid)
Dose not chars
(Oxalic acid, Succinic acid)
Tollen's test
+ ve
(Tartaric acid)
(S-2)
- ve
(Citric acid)
(S-3)
$FeCl_3$ test
Reddish-brown ppt.
(Succinic acid)
(S-4)
No ppt.
(Oxalic acid)
(S-1)

4.2.2 Preparation of neutral solution of acid

It is necessary to prepare neutral solution if the sample is acidic in nature. Dissolve half of the original sample (supplied) in water in a beaker. Add solid Na_2CO_3 pinch by pinch to the solution with continuous stirring with the help of a glass rod till the effervescence ceases. Dissolve little excess Na_2CO_3 to make the solution alkaline (test with red litmus paper). Now add drop wise dil. HNO_3 till the solution becomes distinctly acidic (test with blue litmus paper). Now add dil. NH_4OH solution till the smell of ammonia persists after through mixing. Boil the solution to remove excess ammonia and concentrate if require.

4.3 Identification of Oxalic Acid by Chemical Tests

S-1. OXALIC ACID



$$\begin{array}{l} COOH \\ | \\ COOH\ ,2H_2O \end{array}$$

Physical characteristics:

1. State : Solid
2. Colour : White/ Colourless
3. Odour : Odourless
4. Texture : Crystalline
5. Solubility : Soluble in cold water
6. Litmus : Blue litmus turns to red

Preliminary Test:

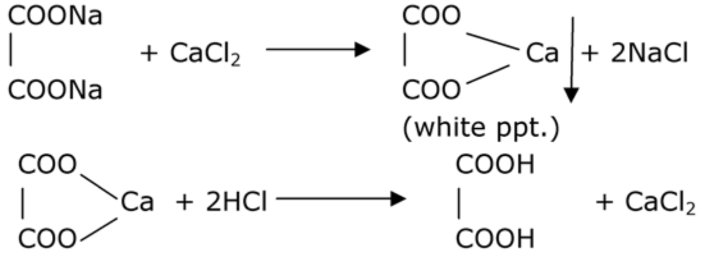
1. Ignition Test : Burns with non-sooty blue flame

Special Tests:

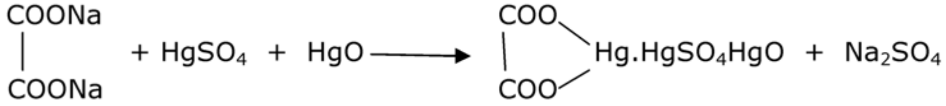
Experiment	Observation
1. **Calcium Chloride Test**: Few drops of $CaCl_2$ solution is added to the neutral solution of the sample. The precipitate is devided into two parts. i) In first part dilute acetic acid is added ii) In second part dil. HCl is added	1. A white precipitate is formed i) The ppt. does not dissolve ii) The ppt. dissolve and clear solution obtained
2. Denige's Test: Denige's reagent is added to the neutral solution of the sample	2. White precipitate is obtained which is insoluble on heating
3. Silver Nitrate Test: Add few drops of $AgNO_3$ to the neutral or slightly alkaline sample solution. The white precipitate is divided into three parts i) Add NH_4OH solution in one part of the ppt. ii) Add dil. HNO_3 in second part of the ppt. iii) Heat the third part gently to dryness and then heat strongly	3. White ppt. is formed i) The ppt. dissolves ii) The ppt. dissolves iii) Black metallic silver is formed
4. Potassium permanganate Test: The sample solution is warmed after adding few drops of dil. H_2SO_4 . Now add few drops of dil. $KMnO_4$ solution.	4. The pink colour of $KMnO_4$ solution disappears.
5. Manganous sulphate Test: Take 1 ml of $MnSO_4$ solution in a test tube and alkaline with dil. NaOH solution. A white ppt. of $Mn(OH)_2$ is formed. Heat the mixture gently till the white ppt. turns to brown due to formation of MnO(OH). Then add sample solution drop wise to the mixture.	5. The brown ppt. dissolves and red/ pinkish red colour appears.
6. Conc. H_2SO_4 Test: Heat little amount of the sample with conc. H_2SO_4.	6. A colourless gas evolves which clear lime solution to milky.

Explanations and Reactions:

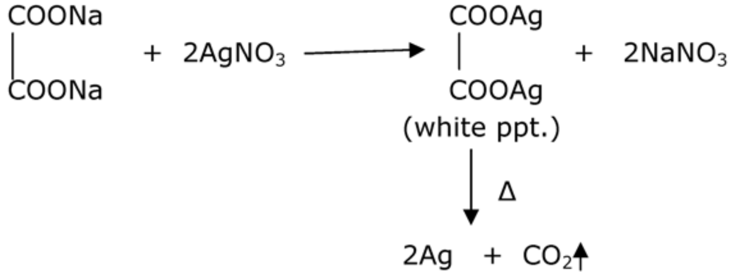
1.



2.



3.



4. $H_2C_2O_4$ + $2KMnO_4$ + $3H_2SO_4$ $\longrightarrow$ K_2SO_4 + $MnSO_4$ + $2H_2O$ + $10CO_2$

5. $MnSO_4 + 2NaOH \longrightarrow Mn(OH)_2 + Na_2SO_4$
(white)
$\downarrow$ [O] Aerial oxidation
MnO(OH) (brown)

$Na_2C_2O_4 + MnO(OH) \longrightarrow Na_3[Mn(C_2O_4)_3] + H_2O$

6. $H_2C_2O_4.\ 2H_2O + H_2SO_4 \longrightarrow CO_2\uparrow + CO\uparrow + [H_2SO_4 + 3H_2O]$

$CO_2 + Ca(OH)_2 \longrightarrow CaCO_3\downarrow$

4.4 Identification of TARTARIC ACID by Chemical Tests

S-2. TARTARIC ACID

$HO_2C.CH(OH) - CH(OH)CO_2H$

Physical characteristics:

1. State : Solid
2. Colour : White/ Colourless
3. Odour : Odourless
4. Texture : Crystalline
5. Solubility : Soluble in cold water
6. Litmus : Blue litmus turns to red

Preliminary Test:

1. Ignition Test : Burns with non-sooty blue flame

Special Tests:

Experiment	**Observation**
1. Calcium Chloride Test: Few drops of $CaCl_2$ solution is added to the neutral solution of the sample. The precipitate is divided into two parts.	1. A white precipitate is formed
iii) In first part dilute acetic acid is added and warmed	iii) The ppt. dissolve
iv) In second part dil. HCl is added and warmed	iv) The ppt. dissolve and clear solution obtained

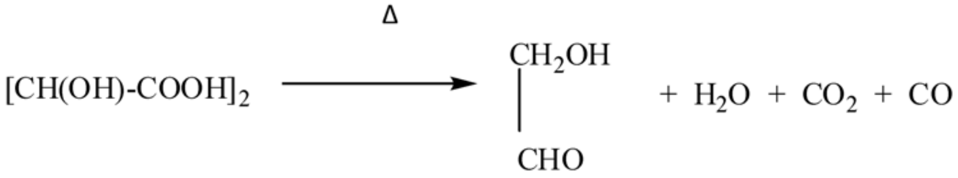
2. **Mohler's Test:** Take about 1 ml of neutral sample solution in a test tube and evaporate to dryness (no charring). Add a particle of resorcinol and 2-3 drops of conc. H_2SO_4 and warm (this test can be done by taking original sample).	2. A violate colouration
3. **Denige's Test:** Same volume of Denige's reagent and the sample solutions are mixed in a test tube. Boil the mixture then add 1-2 drops of 1% $KMnO_4$ solution.	3. Pink colour of permanganate discharges immediately without turbidity.
4. **Silver Mirror Test:** Take little amount of neutral sample solution in a clean test tube. Now add $AgNO_3$ solution drop wise till the precipitation is completed. Then add dil. NH_4OH solution drop wise so that ppt. almost dissolves but not completely. Place the mixture in a water-bath.	4. A white ppt. and a shining mirror of silver forms at the inner side of the test tube.
5. **Conc. H_2SO_4 Test:** Place little amount of the sample in a test tube and warm with few drops of conc. H_2SO_4	5. Chars immediately.
6. **Fenton's Test:** Take about 4-5 ml of the neutral sample solution in a test tube and then add 1-2 drops of freshly prepared $FeSO_4$ solution and 1 drop of dil. H_2O_2 solution. Now add excess NaOH solution.	6. A violet colouration.

Explanations and Reactions:

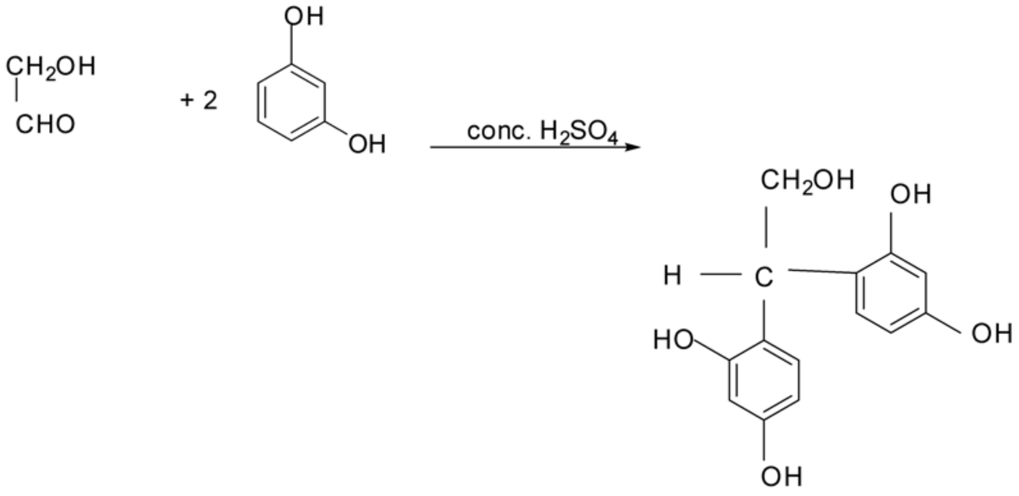
1. $CaCl_2$ test:

$$[CH(OH)COONa]_2 + CaCl_2 \xrightarrow{\Delta} [CH(OH)COO]_2\ Ca + 2NaCl$$

2. Mohler's test:

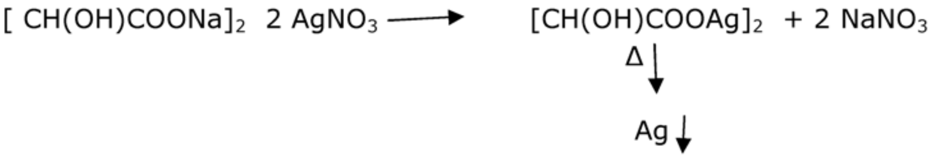


$$[CH(OH)\text{-}COOH]_2 \xrightarrow{\Delta} \begin{array}{l} CH_2OH \\ | \\ CHO \end{array} + H_2O + CO_2 + CO$$



(Violet colour)

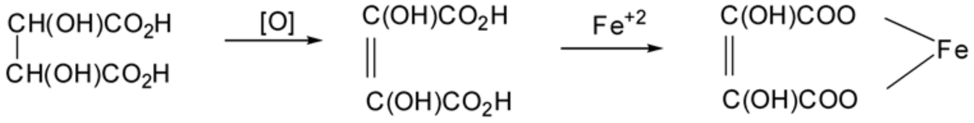
3. Mirror Test:



$$[\ CH(OH)COONa]_2\ \ 2\ AgNO_3 \longrightarrow [CH(OH)COOAg]_2 + 2\ NaNO_3$$

$$[CH(OH)COOAg]_2 \xrightarrow{\Delta} Ag\downarrow$$

4. Fenton's Test:

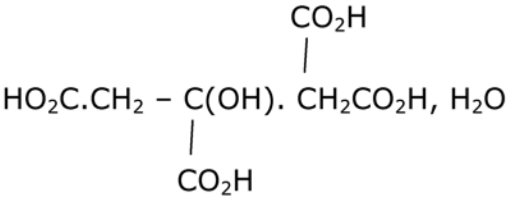


Dihydroxy maleic acid

Deep violet colour

4.5 Identification of CITRIC ACID by Chemical Tests

S-3. CITRIC ACID



$$HO_2C.CH_2 - \underset{\substack{|\\CO_2H}}{C}(OH).\ \overset{\substack{CO_2H\\|}}{C}H_2CO_2H,\ H_2O$$

Physical characteristics:

1. State : Solid
2. Colour : White/ Colourless
3. Odour : Odourless
4. Texture : Crystalline
5. Solubility : Soluble in cold water
6. Litmus : Blue litmus turns to red

Preliminary Test:

1. Ignition Test : Burns with non-sooty blue flame

Special Tests:

Experiment	**Observation**
1. Calcium Chloride Test: Take about 2 ml of the neutral sample solution in a test tube. Then add about equal volume of $CaCl_2$ solution. Shake the mixture and scratch the inner side of the wall of the test tube with a glass rod. Boil the mixture gently.	1. No precipitate appears on shaking or scratching, but white crystalline ppt. appears on boiling.
2. Siver Nitrate Test: Take little amount of the neutral sample solution in a clean test tube. Now add $AgNO_3$ solution drop wise till the precipitation is completed. Then add dil. NH_4OH solution drop wise so that ppt. almost dissolves but not completely. Place the mixture in a water-bath.	2. Curdy white ppt. is formed , which is soluble in NH_4OH solution but no silver mirror is obtained.
3. Denige's Test: Same volume of Denige's reagent and the neutral sample solutions are mixed in a test tube. Boil the mixture then add 1-2 drops of 1% $KMnO_4$ solution.	3. The pink colour of the permanganate solution will discharge with appearance of white ppt.
4. Cadmium Chloride Test: Take about 2 ml of the neutral sample solution in a test tube and add about 2 ml of aqueous solution of $CdCl_2$.	4. A gelatinous white ppt. appears. This is insoluble in hot water but soluble in hot acetic acid.

Explanations and Reactions:

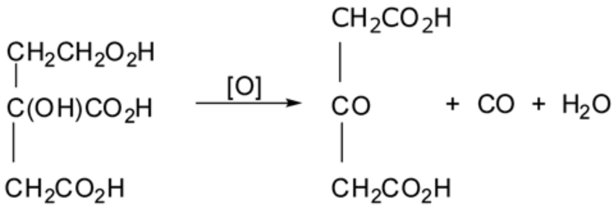
1. $CaCl_2$ test:

   $2C_6H_5O_7Na_3 + 3CaCl_2 \longrightarrow Ca_3(C_6H_5O_7)_2 + 6NaCl$

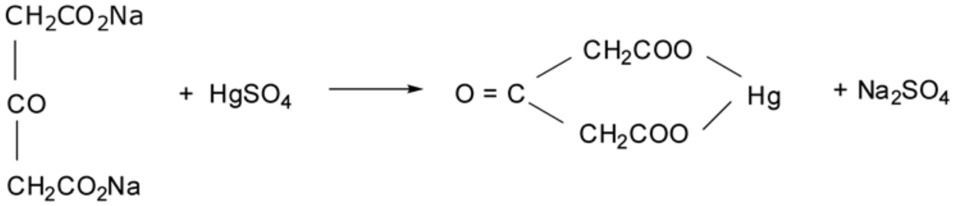
2. $AgNO_3$ test:

   $C_3H_4(OH).(COONa)_3 + 3AgNO_3 \longrightarrow C_3H_4(OH).(COOAg)_3 + 3NaNO_3$

3. Denige's test:



Acetone dicarboxylic acid



Acetone dicarboxylic acid

4.6 Identification of Succinic Acid by Chemical Tests

S-4. SUCCINIC ACID

$HOOC.CH_2.CH_2.COOH$

Physical characteristics:

1. State : Solid
2. Colour : White/ Colourless
3. Odour : Odourless
4. Texture : Crystalline
5. Solubility : Soluble in cold water
6. Litmus : Blue litmus turns to red

Preliminary Test:

1. Ignition Test : Burns with non-sooty blue flame

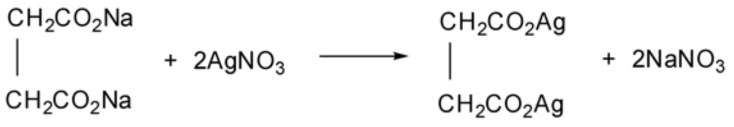
Special Tests:

Experiment	Observation
1. **Calcium Chloride Test**: Take about 2 ml neutral sample solution in a test tube and then add about equal volume of $CaCl_2$ solution. Shake the mixture, boil and scratch the inner side of the wall of the test tube with a glass rod.	1. White precipitate appears which is soluble in acetic acid.
2. **Silver Nitrate Test:** Take about 2 ml neutral sample solution in a test tube and add few drops of $AgNO_3$ solution.	2. White precipitate is obtained which is soluble in dil. NH_4OH solution.
3. **Ferric Chloride Test:** Take about 2 ml neutral sample solution in a test tube and add 1-2 drops of freshly prepared 1% $FeCl_3$ solution.	3. Buff-colour precipitate is obtained which is soluble in dil. HCl.
4. **Denige's Test:** Same volume of Denige's reagent and the neutral sample solutions are mixed in a test tube. Boil the mixture then add 1-2 drops of 1% $KMnO_4$ solution.	4. No precipitate is obtained and the colour of the permanganate persists.

5. Fluorescein Test: Place little amount of the mixture of the sample and resolcinol with 1:2 weight ration in a dry test tube. Add few drops of conc. H_2SO_4. Now, i) Heat the mixture gently ii) Pour the deep red solution in about 200 ml of water in a beaker. iii) The solution of the beaker is then alkaline with dil. NaOH solution.	5. i) Form a deep red solution ii) Deep red solution changes to orange yellow, which emits an intense green fluorescence. iii) The solution changes to bright red and fluorescence intensified.
6. Conc. H_2SO_4 Test: Place little amount of the sample in a test tube and heat with few drops of conc. H_2SO_4	6. The sample dissolves without charring but slightly charring occurs on strong heating.

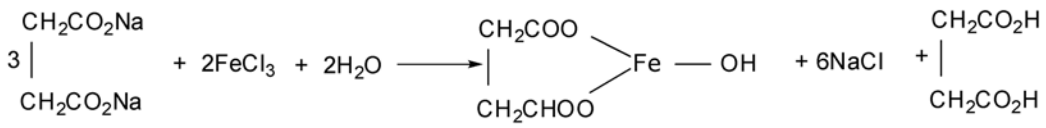
Explanations and Reactions:

1. Silver nitrate test:



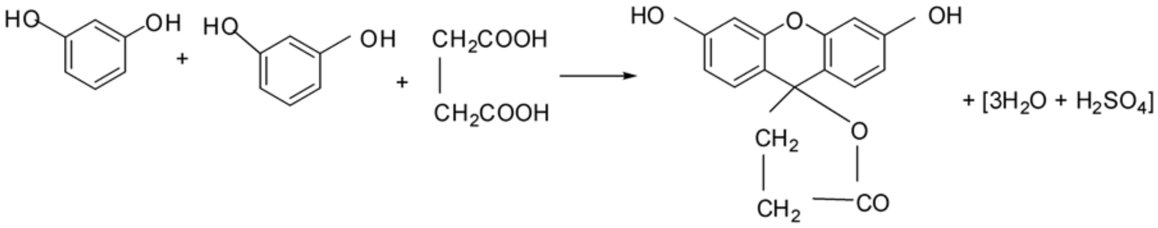
$$\begin{array}{l}CH_2CO_2Na\\ |\\ CH_2CO_2Na\end{array} + 2AgNO_3 \longrightarrow \begin{array}{l}CH_2CO_2Ag\\ |\\ CH_2CO_2Ag\end{array} + 2NaNO_3$$

2. Ferric chloride test:



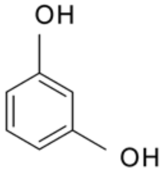
$$3\begin{array}{l}CH_2CO_2Na\\ |\\ CH_2CO_2Na\end{array} + 2FeCl_3 + 2H_2O \longrightarrow \begin{array}{l}CH_2COO\\ |\\ CH_2CHOO\end{array}\!\!>Fe-OH + 6NaCl + \begin{array}{l}CH_2CO_2H\\ |\\ CH_2CO_2H\end{array}$$

3. Fluorescein test:



4.7 Identification of RESORCINOL by Chemical Tests

S-5. RESORCINOL



Physical characteristics:

1. State : Solid
2. Colour : White/ Pink (Actual colour is white but becomes pink on exposure to light)
3. Odour : Odourless
4. Texture : Crystalline
5. Solubility : Soluble in cold water
6. Ph paper : Slightly acidic

Preliminary Test:

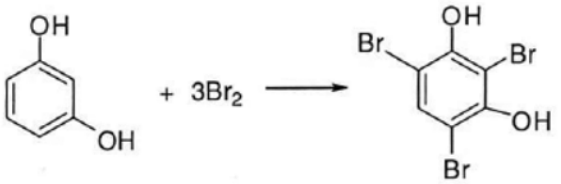
1. Ignition Test : Burns with yellow-sooty flame

Special Tests:

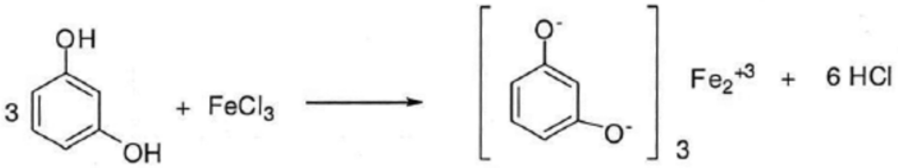
Experiment	Observation
1. **Bromine Water Test:** Take about 2 ml of the sample solution in a test tube and add few drops of Br_2-water. Shake the mixture.	1. White precipitate is obtained.
2. **Fehling's Solution Test:** Take about 2 ml of the sample solution in a test tube and then add Fehling's solution (I + II). Boil the mixture.	2. Red precipitate of Cu_2O is obtained.
3. **Tollen's Test:** Take about 2-3 ml of the sample solution in a test tube and add little amount of Tollen's reagent. Warm the mixture in a water bath.	3. Black ppt. or silver mirror will form.
4. **Ferric Chloride Test:** Add 1-2 drops of freshly prepared 1% $FeCl_3$ to about 2 ml of the sample solution.	4. Bluish-violet colouration.
5. **Fluoroscein Test:** Place little amount of the mixture of the sample and succinic anhydride/ succinic acid with 1:2 weight ration in a dry test tube. Add few drops of conc. H_2SO_4. Now, heat the mixture gently. Pour a drop of the solution in about 200 ml of water in a beaker. The solution of the beaker is then alkaline with dil. NaOH solution.	**5.** An intense green fluorescence.

Explanations and Reactions:

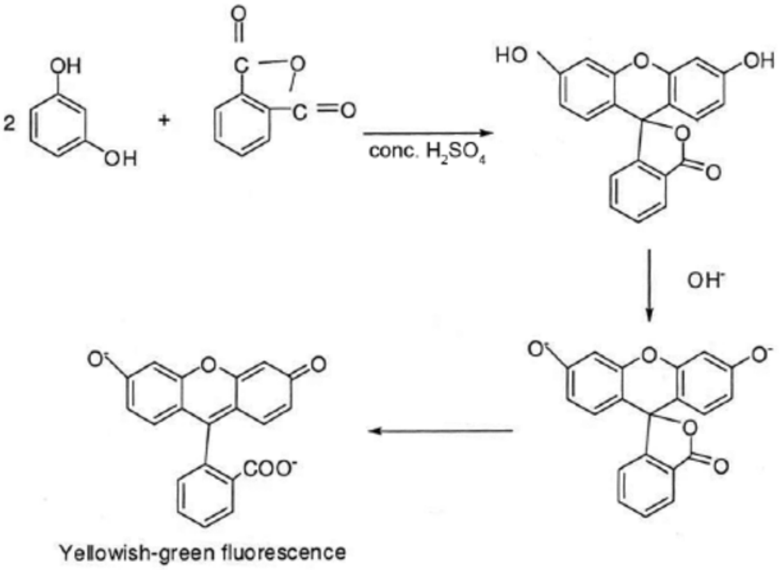
1. Bromine water test:



2. FeCl$_3$ test:

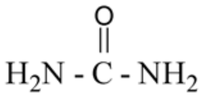


3. Fluorescein test:



4.8 Identification of UREA by Chemical Tests

S-6. UREA



$$H_2N-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2$$

Physical characteristics:

1. State : Solid
2. Colour : Colourless
3. Odour : Odourless
4. Texture : Crystalline
5. Solubility : Soluble in cold water
6. Litmus : Neutral

Preliminary Test:

1. Ignition Test : Burns with non-sooty blue flame

Special Tests:

Experiment	Observation
1. Nitrous Acid Test: Take 2 ml of the sample solution in a test tube and then add little amount of $NaNO_2$. Now add 1 ml of dil. HCl and shake the mixture. Hold a baryta moist glass rod over the mouth of the test tube.	1. Effervescence with evolution of gas. Baryta water turns milky.
2. Nitric Acid Test: Take about 2 ml of the sample solution in a test tube and then add about 1 ml of conc. HNO_3 (if require add little excess).	2. A white precipitate of urea nitrate is obtained.
3. Biuret Test: Take about 0.5 g of the sample in a dry test tube and heat gently till melts. Remove the test tube out of flame. The molten mass will solidify. If it is not, repeat the process, till it solidify on cooling. Dissolve the residue in about 1 ml of NaOH solution by shaking or warm if require. Cool the solution. Now add 1-2 drops of dil. $CuSO_4$ solution.	3. Colouless gas comes out with smell of NH_3 A pink or violet colour develops.

Explanations and Reactions:

1. Nitrous acid test:

$$H_2N\text{ - }CO\text{ - }OH_2 + 2\,HNO_2 \longrightarrow CO_2 + N_2 + 3H_2O$$

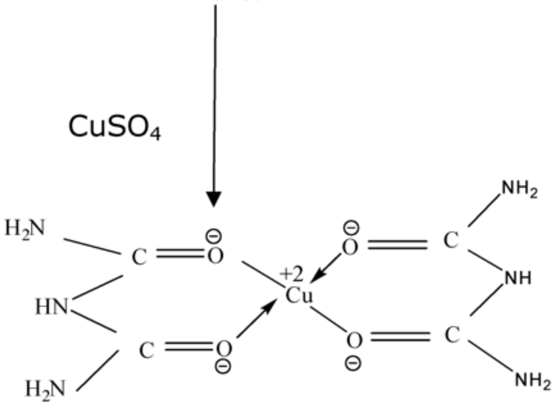
2. Nitric acid test:

$$CO(NH_2)_2 + HNO_3 \longrightarrow \underset{\text{Urea nitrate}}{CO(NH_2)_2.HNO_3}$$

3. Biuret test:

$$H_2N\text{ - }CO\text{ - }NH\text{ -}\boxed{H\ +\ H_2N}\text{- }CO\text{ - }NH_2 \xrightarrow[\Delta]{}$$

$$\underset{\text{Biuret}}{H_2N\text{ - }CO\text{ - }NH\text{ - }CO\text{ - }NH_2} + NH_3$$



Copper biurate sulphate

(Violet colour)

4.9 Identification of Glucose by Chemical Tests

S-7. GLUCOSE

$$C_6H_{12}O_6 \quad \text{or} \quad HOCH_2(CHOH)_4CHO$$

Physical characteristics:

1. State : Solid
2. Colour : Colourless
3. Odour : Odourless
4. Texture : Crystalline
5. Solubility : Soluble in cold water
6. Litmus : Neutral

Preliminary Test:

1. Ignition Test : Burns with non-sooty blue flame
2. Action of heat : Melts, turns to black on futher heating due to charring.

Special Tests:

Experiment	Observation
1. Conc. H_2SO_4 Test: Place little amount of the sample in a dry test tube and add about 0.5 ml of conc. H_2SO_4. Warm the mixture carefully.	**1.** Intially no change in colour but darkens on heating.
2. Molisch's Test: Take about 2-3 ml of the sample solution in a test tube. Add 2-3 drops of 15% ethanolic solution of α- naphthol. Then add 1-2 ml of conc. H_2SO_4 carefully down the side of the inclined tst tube so that a seperate layer of conc. H_2SO_4 can be formed at the bottom of the test tube.	**2.** A red coloured ring gradually changes to blue or violet colour at the junction of the two liquids.
3. Sodium hydroxide Test: Dissolve little amount of the sample in about 2 ml of dil. NaOH solution in a test tube. Heat the mixtre and then acidify with dil. HNO_3	**3.** First the solution turns to yellow and then to reddish brown.

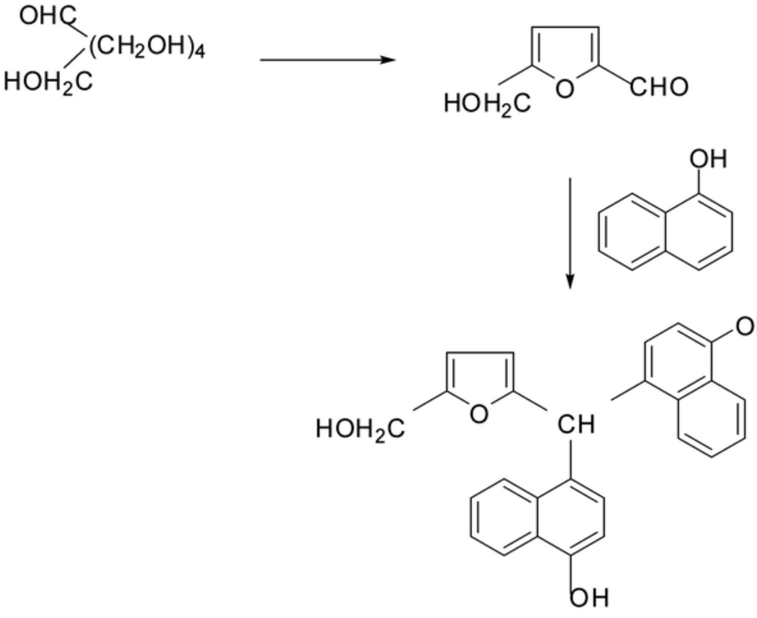
4. Fehling's Test: Place little amount of the sample in a test tube and disolve in about 1 ml of distilled water. Now add 2 ml of Fehling's solution (I + II). Boil the mixture gently.	**4.** Red precipitate of Cu_2O is obtained.
5. Tollen's Test: Dissolve about 0.5 g of the sample in about 1 ml of distilled water in a test tube. Add about 1 ml of Tillen's reagent and shake the mixture and then place in a water bath.	**5.** Black ppt. or shining mirror of silver will deposite on the inner wall of the test tube.
6. Lead acetate Test: Dissolve about 0.5 g of the sample in 2 ml of distilled water in a test tube. Add few drops of Lead acetate solution. Heatl the mixture just to boil. Add dil. NH_4OH solution dropwise till just sufficient to produce a parmanent white precipitate. The mixture is then biled agin.	**6.** The white precipitate turns salmon-pink.
7. Barfoed's Test: Dissolve little amount of the sample in 1 ml of distilled water in a test tube. Now add about 1-2 ml of Barfoed's reagent and place the mixture in a water bath.	**7.** Red precipitate of Cu_2O is appeared.

Explanations and Reactions:

1. Conc. H_2SO_4 test:

$$C_6H_{12}O_6 + H_2SO_4 \longrightarrow 6\,C + [\,6H_2O + H_2SO_4]$$

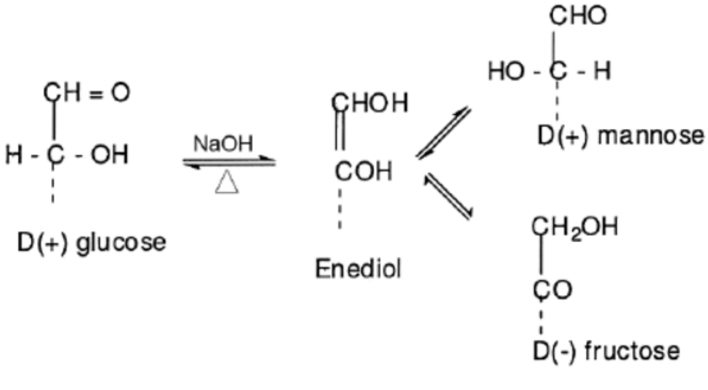
2. Molisch's test:



Red - violet colour

3. Sodium hydroxide test:

Lobry-de-Van Ekenstein rearrangement occurs when D(+)- glucose is warmed with NaOH to give a mixture of D(+)- glucose, D(+)- mannose and D(-)-fructose.



4.10 Identification of Sucrose by Chemical Tests

S-8. CANE SUGAR or SUCROSE

$C_{12}H_{22}O_{11}$

Physical characteristics:

1. State	: Solid
2. Colour	: Colourless
3. Odour	: Odourless
4. Texture	: Crystalline
5. Solubility	: Soluble in cold water
6. Litmus	: Neutral

Preliminary Test:

1. Ignition Test : Burns with non-sooty blue flame
2. Action of heat : Melts, turns to black on futher heating due to charring.

Special Tests:

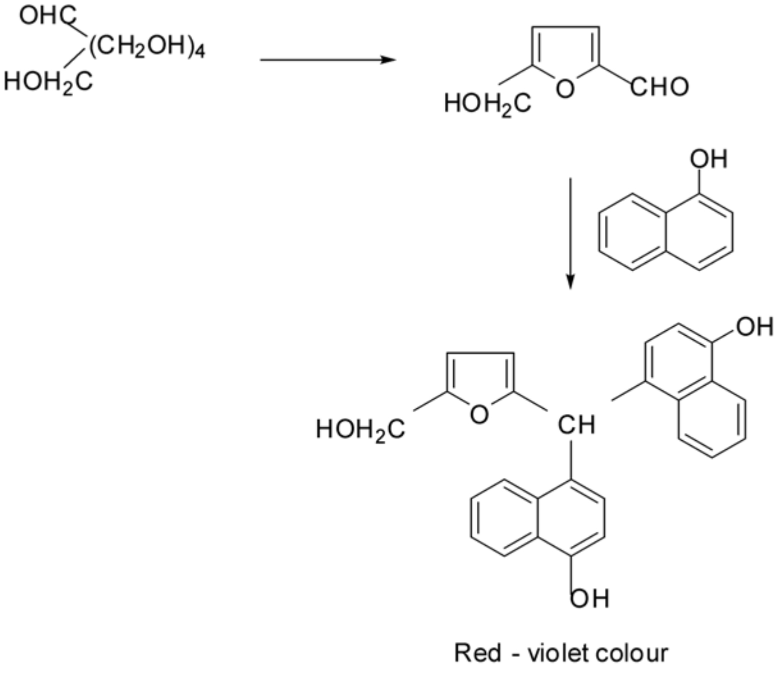
Experiment	Observation
1. **Conc. H_2SO_4 Test:** Place little amount of the sample in a dry test tube and add about 0.5 ml of conc. H_2SO_4.	1. Immediate charring even cold condition (Distinction from glucose).
2. **Molisch's Test:** Take about 2-3 ml of the sample solution in a test tube. Add 2-3 drops of 15% ethanolic solution of ∝- naphthol. Then add 1-2 ml of conc. H_2SO_4 carefully down the side of the inclined tst tube so that a seperate layer of conc. H_2SO_4 can be formed at the bottom of the test tube.	2. A red coloured ring gradually changes to blue or violet colour at the junction of the two liquids.
3. **Sodium hydroxide Test:** Dissolve little amount of the sample in about 2 ml of dil. NaOH solution in a test tube. Heat the mixtre and then acidify with dil. HNO_3	3. Light yellow colour develops

4. Lead acetate Test: Dissolve about 0.5 g of the sample in 2 ml of distilled water in a test tube. Add few drops of Lead acetate solution. Heatl the mixture just to boil. Add dil. NH_4OH solution dropwise till just sufficient to produce a parmanent white precipitate. The mixture is then biled agin.	4. The colour of the white precipitate dose not change (Distinction from glucose).
5. Seliwanoff's Test: Dissolve little amount of the sample in a test tube in about 1 ml of distilled water. Add 1 ml of conc. HCl and heat on a water bath until it turns to red. Now add few crystals of resolcinol and warm.	5. A wine-red colour followed by formation of brown precipitate. Dark red colouration is obtained when the precipitate dissolves in ethanol.
6. Fehling's Test: Place little amount of the sample in a test tube and disolve in about 1 ml of distilled water. Now add 2 ml of Fehling's solution (I + II). Boil the mixture gently.	6. No red precipitate of red Cu_2O.

Explanations and Reactions:

1. Molisch's test:

Cane sugar first breacks into gluose and fructose.

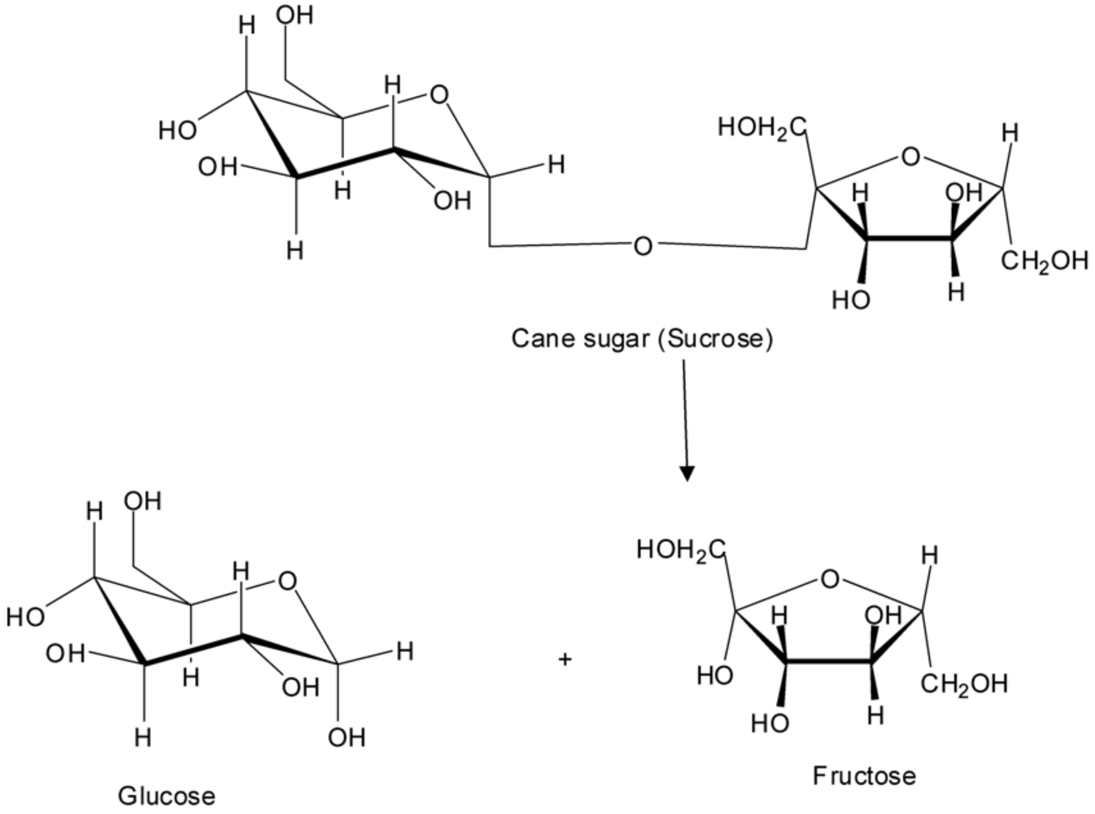


Red - violet colour

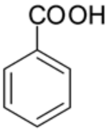
2. Fehling’s test:

Sucrose dose not respond in fehling’s test, as it is non-reducing sugar. This is due to the fact that one glucose and one fructose molecules are joint togather through –CHO and C=O group respectively in sucrose.

Hydrolysis of cane sugar (sucrose):



4.11 Identification of Benzoic Acid by Chemical Tests



S-9. BENZOIC ACID

Physical characteristics:

1. State : Solid
2. Colour : Colourless
3. Odour : Odourless
4. Texture : Crystalline
5. Solubility : Soluble in hot water
6. Litmus : Blue litmus turns red

Preliminary Test:

1. Ignition Test : Burns with yellow sooty flame
2. Action of heat : Melts and sublimes with copious white fume.

Special Tests:

Experiment	**Observation**
1. Conc. H_2SO_4 Test: Take little amount of the sample in a test tube and warm with little amount of conc. H_2SO_4.	1. Sample dissolves without charring.
2. Ferric chloride Test: Take little amount of the neutral sample solution in a test tube and add 1-2 drops of freshly prepared 1% $FeCl_3$ solution. Now add dil. HCl to the precipitate.	2. A buff-colour precipitate is obtained which dissolves in acid and white precipitate appears.
3. Sodalime Test: Place little amount of the sample in a test tube and mixed with sodalime. Heat the mixture.	3. Characteristic smell of benzene comes out.

4. **Esterification Test:** Dissolve about 0.2 g of the sample in about 1 ml of dehydrated alcohol in a dry and clean test tube. Add 2-3 drops of conc. H_2SO_4 and warm the mixture in a water bath. Cool the mixture. Pour this mixture in a beaker contain about 50 ml of dil. $NaHCO_3$ solution.	4. Characteristic fruity smell of ester.

Explanations and Reactions:

1. Ferric chloride test:

$$3C_6H_5COONa + 2FeCl_3 + 3H_2O \longrightarrow (C_6H_5COO)_3\,Fe.Fe(OH)_3 + 3HCl + 3NaCl$$

$$(C_6H_5COO)_3\,Fe.Fe(OH)_3 + 6HCl \longrightarrow 3\,C_6H_5COOH + 2FeCl_3 + 3H_2O$$

2. Sodalime test:

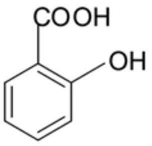
$$C_6H_5COOH + 2NaOH \xrightarrow{\Delta} C_6H_6 + Na_2CO_3 + H_2O$$

3. Estarification test:

$$C_6H_5COOH + C_2H_5OH \longrightarrow \underset{\text{(ester)}}{\underset{\text{Ethyl benzoate}}{C_6H_5COOC_2H_5}} + H_2O$$

4.12 Identification of Salicylic Acid by Chemical Tests

S-10. SALICYLIC ACID



Physical characteristics:

1. State	: Solid
2. Colour	: White
3. Odour	: Odourless
4. Texture	: Needle shaped crystals
5. Solubility	: Soluble in hot water
6. Litmus	: Blue litmus turns red

Preliminary Test:

1. Ignition Test : Burns with yellow sooty flame
2. Action of heat : Melts and sublimes on gentle heating.

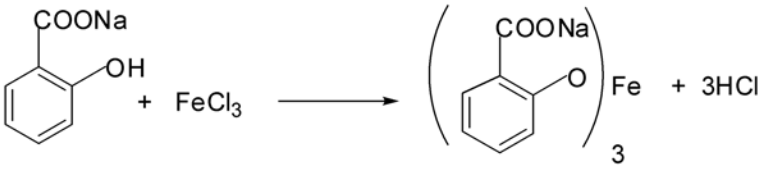
Special Tests:

Experiment	Observation
1. Conc. H_2SO_4 Test: Take little amount of the sample in a test tube and warm with little amount of conc. H_2SO_4.	1. The sample dissolves and charring occurs after some time and solution darkens.
2. Ferric chloride Test: Take little amount of the neutral sample solution in a test tube and then add 1-2 drops of freshly prepared 1% $FeCl_3$ solution. The solution is then devided into two parts in two different test tubes. i) Add dil. HCl in one part ii) Add dil. acetic acid in another part	2. An intense violet colouration (Distinction from benzoic acid) i) Colour discharged ii) Colour persists
3. Bromine water Test: Take little amount of the sample in a test tube and dissolve it in about 1 ml of alcohol. Neutralise the mixture with $NaHCO_3$ solution and then add excess of Br_2- water.	3. Pale yellow crystalline precipitation.

4. **Phthalein Test (Fluoroscein Test):** Place little amount of the mixture of the sample and succinic anhydride/ succinic acid with 1:2 weight ration in a dry test tube. Add few drops of conc. H_2SO_4. Now, heat the mixture gently. Pour a drop of the solution in about 200 ml of water in a beaker. The solution of the beaker is then alkaline with dil. NaOH solution.	4. Red or greenish yellow fluorescence.
5. **Oil of wintergreen Test:** Take little amount of the sample in a dry test tube and dissolve it into about 1 ml of methanol then add few drops of conc. H_2SO_4 and warm the mixture. Cool the mixture. Pour into about 20 ml aqueous solution of Na_2CO_3.	5. A characteristic smell of oil of wintergreen and the smell intensifies in Na_2CO_3 solution.

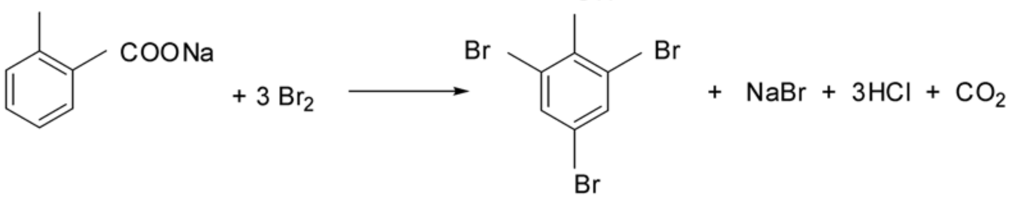
Explanations and Reactions:

1. Ferric chloride test:



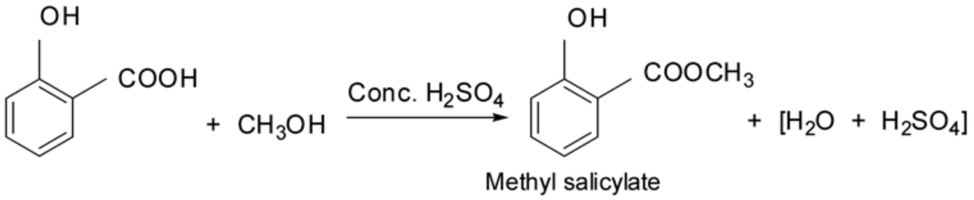
(Violet colour)

2. Bromine water test:



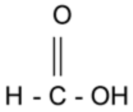
2,4,6-tribromo phenol

3. Oil of wintergreen test:



4.13 Identification of FORMIC ACID by Chemical Tests

L-11. FORMIC ACID



$$H-\overset{\overset{\displaystyle O}{\|}}{C}-OH$$

Physical characteristics:

1. State : Liquid
2. Colour : Colourless
3. Odour : Pungent odour
4. Miscibility : Miscible in water
5. Litmus : Blue litmus turns red

Preliminary Test:

1. Ignition Test : Burns with non- sooty blue flame

Chemical Tests:

Experiment	Observation
1. **Ferric chloride Test:** Take little amount of the neutral sample solution in a test tube. Now add freshly prepared 1% $FeCl_3$ solution. Devide the resulting solution in two parts in two different test tube. i) Boil one part ii) Add dil. HCl in the other part	1. A red colour develops. i) A brown ppt. will form ii) The red colour discharged and yellow colour develops of $FeCl_3$.

2. **Tollen's Test:** Take about 1 ml netral solution of the sample in a test tube. Add few drops of Tollen's reagent and place the mixture in a water bath.	2. First white precipitate forms due to the formation of silver formate but blackens on warming (or shining silver mirror is formed in side of the wall of the test tube).
3. **Denige's Test:** Take about 0.5 ml netral sample solution in a test tube and mixed with Denige's reagent and boil.	3. Sand like white precipitate appears.

Explanations and Reactions:

1. Ferric chloride test:

$$3HCOONa + FeCl_3 = \underset{\text{(Red colour)}}{(HCOO)_3Fe} + 3NaCl$$

$$(HCOO)_3Fe + 2H_2O = (HCOO)Fe(OH)_2 + 2HCOOH$$

(Basic ferric formate)

Brown ppt.

2. Silver nitrate test:

$$HCOOH + 2[Ag(NH_3)_2]^+ + 2OH^- = 2Ag + CO_2 + 2H_2O + 4NH_3$$

4.14 Identification of Acetic Acid by Chemical Tests

L-12. ACETIC ACID

$CH_3 - COOH$

Physical characteristics:

1. State : Liquid
2. Colour : Colourless
3. Odour : Characteristic smell of vinegar
4. Miscibility : Miscible in water
5. Litmus : Blue litmus turns red

Preliminary Test:

1. Ignition Test : Burns with non- sooty blue flame

Chemical Tests:

Experiment	Observation
1. Ferric chloride Test: Take little amount of the neutral sample solution in a test tube. Now add freshly prepared 1% $FeCl_3$ solution. Devide the resulting solution in two parts in two different test tube. i) Boil one part ii) Add dil. HCl in the other part	1. A red colour develops. i) A brown ppt. will form ii) The red colour discharged and yellow colour develops of $FeCl_3$.
2. Tollen's Test: Take about 1 ml netral solution of the sample in a test tube. Add few drops of Tollen's reagent and place the mixture in a water bath.	2. A white precipitate appears, does not turns black on heating (*Distinction from formic acid*).
3. Denige's Test: Take about 0.5 ml netral sample solution in a test tube and mixed with Denige's reagent and boil.	3. No precipitate appears at hot and cold conditions. (*distinction from formic acid*).
4. Cacodyl oxide Test: Take about 1 ml netral solution of the sample in a test tube. Heat gently to dryness. The resultant residue is then mixed with equal amount of As_2O_3 in the test tube and heat. Place the thumb at the mouth of the test tube and then inhale the thumb.	4. A characteristic unpleasant (disagreeable) smell of cacodil oxide. [N.B. : The vapour is highly poisonous so it should not be inhaled directly. Discard the test tube after performing the test do not use it further.]

Explanations and Reactions:

1. Ferric chloride test:

$$3CH_3COONa + FeCl_3 = \underset{\text{(Red colour)}}{(CH_3COO)_3Fe} + 3NaCl$$

$$(CH_3COO)_3Fe + 2H_2O = (CH_3COO)Fe(OH)_2 + 2CH_3COOH$$

(Basic ferric acetate)
Brown ppt.

2. Tollen's test:

$$CH_3COONa + AgNO_3 = CH_3COOAg + NaNO_3$$

3. Cacodyl oxide test:

$$4CH_3COONa + As_2O_3 \longrightarrow \underset{\text{(Cacodyl oxide)}}{(CH_3)_2As-O-As(CH_3)_2} + CO_2 + 2Na_2CO_3$$

4.15 Identification of Methyl Alcohol by Chemical Tests

L-13. METHYL ALCOHOL

$$CH_3 - OH$$

Physical characteristics:

1. State : Liquid
2. Colour : Colourless
3. Odour : Characteristic smell of alcohol
4. Miscibility : Miscible in water
5. Litmus : Neutral

Preliminary Test:

1. Ignition Test : Burns with non- sooty blue flame

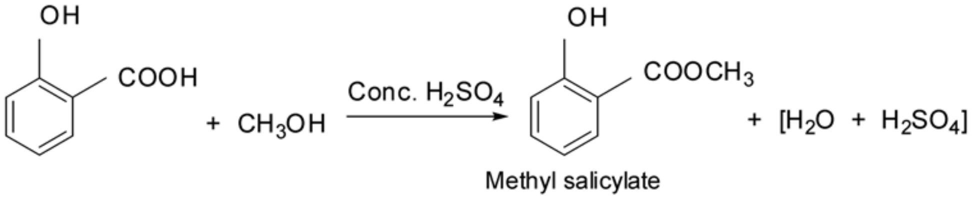
Chemical Tests:

Experiment	Observation
1. Oil of Wintergreen Test: Take about 0.5 ml of the sample in a dry test tube and add about 0.5 g of salicylic acid and then pour few drops of conc. H_2SO_4. Heat the mixture. Cool, then transfer to 50 ml of water in a clean beaker.	1. Characteristic smell of oil of wintergreen (due to formation of methyl salicylate).
2. Denige's Test: Take about 1 ml of the sample and diluted it to about 5 ml by distilled water and pour in a porcelain basin and place it on an ice bath. Add 2-3 ml of 3% $KMnO_4$ solution followed by 2-3 drops of conc. H_2SO_4. A brown colour develops. Now add saturated solution of oxalic acid slowly till the brown colour is discharged. Now add dropwise freshly prepared Schiff's base with stirring.	2. A violet colour develops deepening on standing.
3. Oxidation Test: Take about 2 ml of the sample in a dry test tube and place the tube in a beaker containing cold water. Now introduce red hot Cu-spiral wire repeatedly in the sample. Divide the solution into four parts. **i) Schiff's Test:** Schiff's reagent is added to one part. **ii) Resorcinol Test:** Add a drop of 0.5% aqueous solution of resorcinol to the another part. Now transfer this mixture carefully along to the side of the test tube, held inclined position, containing about 2 ml conc. H_2SO_4.	3. i) Pink colouration which deepens gradually. ii) A reddish-violet ring appears at the junction of the two liquids layer. White precipitate in the aqueous layer slowly changes to reddish-violet.

iii) **Rimini's Test:** Mix about 0.5 ml of of 1% freshly prepared aqueous solution of phenyl hydrazine hydrochloride and 0.5 ml of 1% aqueous solution of sodium nitroprusside to the third part . Now add excess 10% NaOH solution.	iii) Intense indigo colour.
iv) **Tollen's Test:** Add about 0.5 ml of the Tollen's reagent to the rest part and hold the mixture in a water bath.	iv) Black ppt. or shiny silver mirror inside the wall of the test tube.

Explanations and Reactions:

1. Oil of Wintergreen test:



4.16 Identification of Ethyl Alcohol by Chemical Tests

L-14. ETHYL ALCOHOL

$CH_3.CH_2 - OH$

Physical characteristics:

1. State : Liquid
2. Colour : Colourless
3. Odour : Characteristic smell of alcohol
4. Miscibility : Miscible in water
5. Litmus : Neutral

Preliminary Test:

1. Ignition Test : Burns with non- sooty blue flame

Chemical Tests:

Experiment	Observation
1. Ester Formation: Add about 0.5 ml of glacial acetic acid in about 0.5 ml of the sample and few drops of conc. H_2SO_4. Place the mixture in a water bath for about 5 mins. Pour the reactents into water with little amount of Na_2CO_3 in a beaker. (Instead of glacial acetic acid fused sodium acetate 0.5 g can be used)	1. Pleasant fruity smell.
2. Iodoform Test: Take 1 ml of the sample in a test tube and dilute with 1 ml of water. Add about 2 ml of conc. Solution of iodine in KI. Now add dropwise 10% NaOH solution till the colour of iodine disappears [avoid excess NaOH) and warm the mixture and cool under tap water with shaking.	2. Yellow crystals with sweet smell of iodofom appear.
3. Oxidation Test: Take about 2 ml of the sample in a dry test tube and place the tube in a beaker containing cold water. Now introduce red hot Cu-spiral wire repeatedly in the sample. Divide the solution into three parts. **i) Schiff's Test:** Schiff's reagent is added to one part.	3. i) Pink colouration which deepens gradually.

ii) Sodium nitroprusside Test: To the another part of of the oxidised sample equal volume of 1% sodium nitroprusside is added and then add few drops of 10% NaOH solution.	ii) A deep blue colouration.
iii) Tollen's Test: Add about equal volume of the Tollen's reagent to the rest part of the oxidised sample and placed in a water bath for 3-4 minutes.	iii) Black ppt. or shiny silver mirror inside the wall of the test tube.

Explanations and Reactions:

1. Ester Formation:

$$CH_3CH_2 - OH + CH_3COOH \;=\; CH_3COOC_2H_5 \;+\; H_2O$$

2. Iodoform test:

$$CH_3CH_2 - OH + 4I_2 + 6NaOH = CHI_3 + HCOONa + 5NaI + 5H_2O$$

3. Sodium nitroprusside test:

$$CH_3CH_2 - OH + CuO \;= CH_3CHO + H_2O + Cu$$

$CH_3CHO + Na_2[Fe(CN)_5NO] + OH^- \longrightarrow Na_2[Fe(CN)_5NO - CH_2CHO]$ (Blue colour)

4.17 Identification of Acetone by Chemical Tests:

L-15. ACETONE

$$CH_3 - CO - CH_3$$

Physical characteristics:

1.	State	: Liquid
2.	Colour	: Colourless
3.	Odour	: Characteristic pleasant smell
4.	Miscibility	: Miscible in water
5.	Litmus	: Neutral

Preliminary Test:

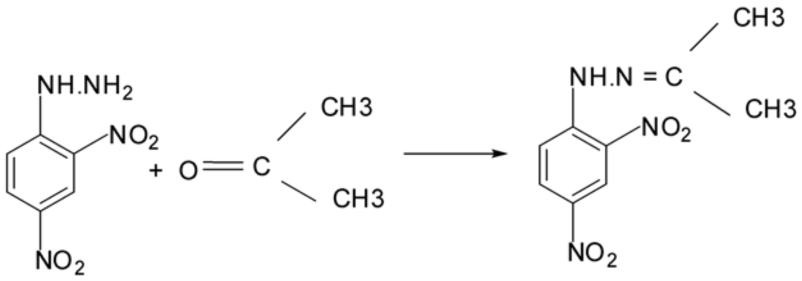
1. Ignition Test : Burns with non- sooty blue flame

Chemical Tests:

Experiment	Observation
1. **DNP Test:** Take 0.5 ml of the sample in a dry test tube and add few drops of 2,4- dinitrophenyl hydrazine sulphate reagent.	1. Yellow precipitate will form.
2. **Sodium nitroprusside Test:** Take 0.5 ml of the sample solution and diluted with 1-2 ml of water then add few drops of 1% sodium nitroprusside solution followed by few drops of 10% NaOH solution.	2. A reddish purple (Ruby red) colour develops. The colour disappears on warming and reappears on cooling.
3. **Iodoform Test:** Take 0.5 ml of the sample in a test tube and diluted to 1 ml with water. Add about 1 ml of conc. Solution of iodine in KI. Now add dropwise 10% NaOH solution till the colour of iodine disappears [avoid excess NaOH) and warm the mixture and cool under tap water with shaking.	3. Yellow crystalline precipitate with sweet smell of iodofom appears.

Explanations and Reactions:

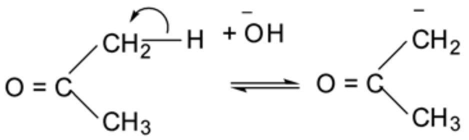
1. DNP Test:



2. Sodium nitroprusside test:

$CH_3COCH_3 + Na_2[Fe(CN)_5NO] + OH^- \longrightarrow Na_2[Fe(CN)_5 NO– CH_2COCH_3]$
(Ruby red colour)

In presence of alkali acetone converted to first $CH_3COCH_2^-$, which reacts with $[Fe(CN)_5NO]^{-2}$ to give highly coloured $[Fe(CN)_5 NO– CH_2COCH_3]^{-2}$

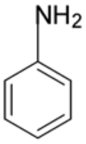


3. Iodoform test:

$$CH_3COCH_3 + 3I_2 + 4NaOH = CHI_3 + CH_3COONa + 3NaI + 3H_2O$$

4.18 Identification of Aniline by Chemical Tests

L-16. ANILINE



Physical characteristics:

1. State : Liquid
2. Colour : Reddish brown *
3. Odour : Characteristic smell
4. Miscibility : Immiscible in water but soluble in dil. HCl
5. Litmus : Neutral

Preliminary Test:

1. Ignition Test : Burns with yellow sooty flame

* [Colour of the freshly distilled liquid is colourless but turns brown on exposure in air and light.]

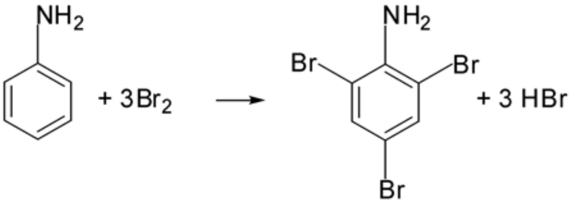
Chemical Tests:

Experiment	**Observation**
1. Bromine water Test: Take about 0.5 ml of the sample and dissolve in 1 ml of dil. HCl and then add about 0.5 ml of bromine water.	**1.** White precipitate.
2. Diazo-coupling Test: Take three test tubes. a) In first tube take 0.5 ml of the sample and dissolve it into 1 ml of dil. HCl. b) In second test tube prepare 1ml 10% $NaNO_2$ solution. c) In third test tube dissolve about 10 mg β – naphthol in 5 ml 10% NaOH. Place the three mixtures in an ice bath. When the solutions are throughly chilled, tranfer $NaNO_2$ solution (b) into acidified sample solution (a). Now pour a drop of this diazotised mixture to alkaline sodium β - naphthoxide solution.	2. Brilliant red dye will form.

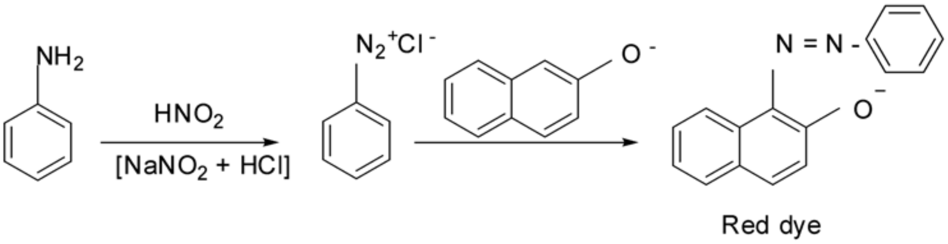
3. Bleaching Powder Test: Take 1-2 drops of the sample in a test tube and dissolve it into about 1 ml of dil. HCl. Now add few drops of bleaching powder solution.	3**.** Purple or violet colouration.
4. Carbylamine Test: Take 2-3 drops of the sample in a test tube and add 2-3 drops of chloroform and 1-2 ml of alcohol and a bead of KOH or NaOH. Warm the mixture.	4. A colourless gas comes out with a irritating smell of iso-cyanide.
5. Potassium dichromate Test: Place a drop of the sample in spot plate and add 3-4 drops of conc. H_2SO_4. Stir the mixture well with a glass rod. Now pour a drop of $K_2Cr_2O_7$ solution.	5. Intense blue colouration.

Explanations and Reactions:

1. Bromine water test:

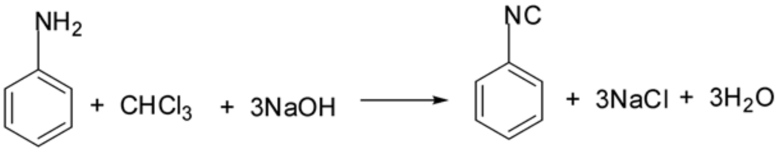


2. Diazo- coupling reaction:



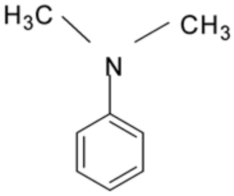
Red dye

3. Carbylamine test:



4.19 Identification of N,N-dimethyl aniline by Chemical Tests

L-17. N,N- dimethyl aniline



Physical characteristics:

1. State : Liquid
2. Colour : Brown *
3. Odour : Characteristic bad smell
4. Miscibility : Immiscible in water but soluble in dil. HCl
5. Litmus : Neutral

* [Colour of the freshly distilled liquid is colourless but turns brown on exposure in air and light.]

Preliminary Test:

1. Ignition Test : Burns with yellow sooty flame

Chemical Tests:

Experiment	**Observation**
1. **Potassium ferrocyanide Test:** take 0.5 ml of the sample in a test tube and dissolve it in 1 ml of dil. HCl then add few drops of $K_4Fe(CN)_6$ solution. boil the mixture.	1. A white precipitate will form which dissolves on boiling.
2. **Nitrous acid Test:** Take three test tubes. a) In first tube take 0.5 ml of the sample and dissolve it into 0.5 ml of dil. HCl. b) In second test tube prepare 1ml $NaNO_2$ solution. c) In third test tube take 10% NaOH. Place the three solutions in an ice bath. When the solutions are throughly chilled, tranfer $NaNO_2$ solution (b) into acidified sample solution (a). Now pour dil. NaOH solution in the mixture.	2. Either red colour develops or a white precipitate of p- nitoso dimethylaniline hydrochloride appears. Solution or precipitate turns green.
3. **Diazo – coupling Test:** Take three test tubes. a) In first tube take 2-3 drops of aniline and add few drops of conc. HCl. b) In second test tube prepare 1ml 10% $NaNO_2$ solution. c) In third test tube dissolve about 0.5 ml of the sample in about 1 ml of dil. HCl. Place the three mixtures in an ice bath. When the solutions are throughly chilled, tranfer $NaNO_2$ solution (b) into acidified sample solution (a). Now pour a drop of this diazotised mixture to the acidify sample solution.	3. Rose-red colour develops.

4. Malachite green Test: Take about 1 ml of the sample in a dry test tube and mixed with about 0.5 ml benzaldehyde and a small bit of anhydrous $ZnCl_2$. Boil the mixture for about 1 minute. Cool. Now add about 2 ml of glacial acetic acid and 0.5 g lead dioxide. Boil the mixture gently for oxidation of the resultant mixture. Cool the mixture and add excess conc. HCl.	4. Intense green colouration.

Explanations and Reactions:

1. Potassium ferrocyanide test:

$$C_6H_5N(CH_3)_2 + HCl \longrightarrow C_6H_5N(CH_3)_2.HCl$$

$$2C_6H_5N(CH_3)_2.HCl + 2HCl + K_4[Fe(CN)_6] \longrightarrow \underset{\text{(White ppt.)}}{[C_6H_5N(CH_3)_2]_2 . H_4Fe(CN)_6} + 4KCl$$

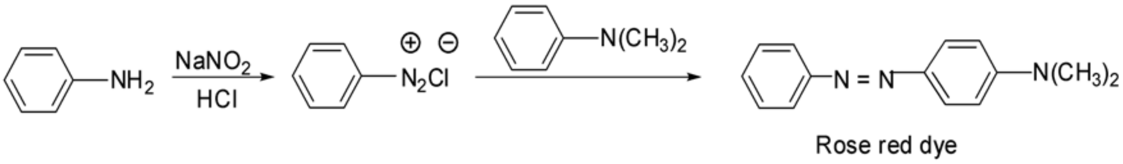
Nitrous acid test:

$$C_6H_5N(CH_3)_2.HCl + NaNO_2 \longrightarrow \underset{\text{(Red colour or white ppt).}}{ON - C_6H_5 - N(CH_3)_2.HCl} + NaCl + H_2O$$

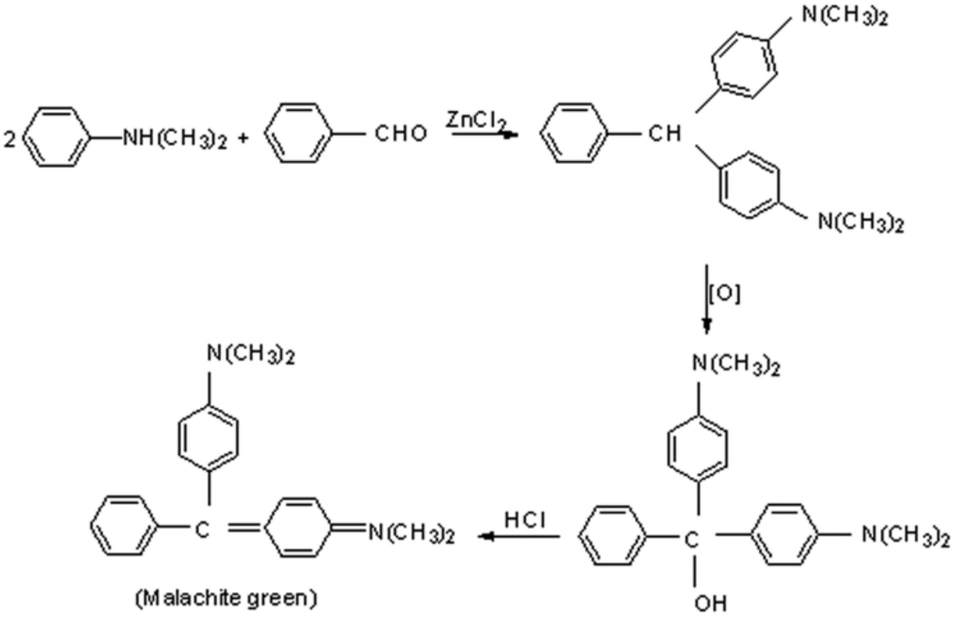
$$\downarrow$$

$$\underset{\text{(Green)}}{ON - C_6H_5 - N(CH_3)_2} + NaCl + H_2O$$

2. Diazo-coupling test:

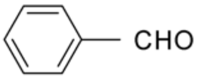


2. Malachite green test:



4.20 Identification of Benzaldehyde by Chemical Tests:

L-18. BENZALDEHYDE



Physical characteristics:

1. State : Liquid
2. Colour : Colourless
3. Odour : Characteristic odour of bitter almonds

4. Miscibility : Immiscible with water
5. Litmus : Neutral (for freshly distilled)

* [Colour of the freshly distilled liquid is colourless but turns brown on exposure in air and light.]

Preliminary Test:

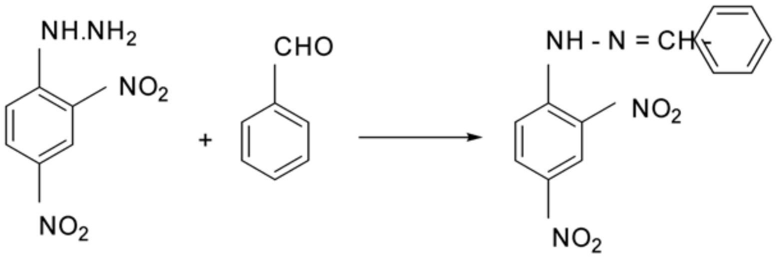
1. Ignition Test : Burns with yellow sooty flame

Chemical Tests:

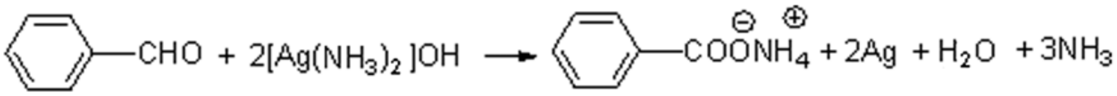
Experiment	**Observation**
1. *Schiff's Test:* *Take about 2 ml of* Schiff's reagent in a test tube and add a drop of the sample and the mixture is then shaken.	1. Pink or purple colour develops immediately.
2. Fehling's Test: Take about 2 ml of Fehling's solution (I & II) in a test tube and add 2-3 drops of the sample and warm.	2. No red precipitate of Cu_2O.
3. Tollen's Test: Take about 1 ml of Tollen's reagent in a test tube and pour few drops of the sample. Shake the mixture and place in a water bath.	3. Black ppt. or silver mirror form on the sides of the test tube.
4. 2,4- DNP Test: Add 2,4- Dinitro phenyl hydrazine sulphate reagent to 0.5 ml of the sample in a dry test tube.	4. Red or reddish yellow ppt. forms immediately.
5. Malachite green Test: Take about 0.5 ml of the sample in a dry test tube and mixed with about 1 ml of benzaldehyde and a small bit of anhydrous $ZnCl_2$. Boil the mixture for about 1 minute. Cool. Now add about 2 ml of glacial acetic acid and 0.5 g lead dioxide. Boil the mixture gently for oxidation of the resultant mixture. Cool the mixture and add excess conc. HCl.	5. Intense green colouration.

Explanations and Reactions:

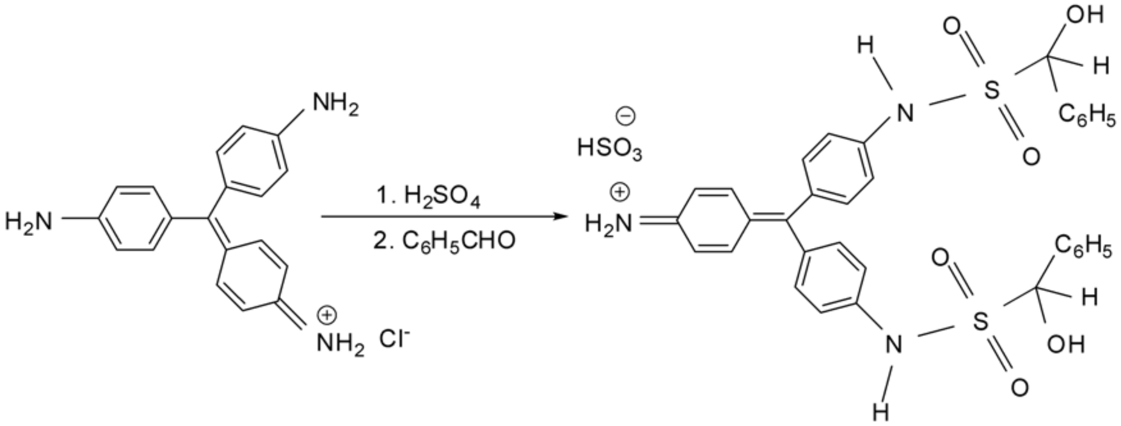
1. 2,4- DNP test:



2. Tollen's test:



3. Schiff's test:



4. Malachite green test: See N,N-dimethyl aniline

4.21 Identification of Chloroform by Chemical Tests

L-19. CHLOROFORM

$CHCl_3$

Physical characteristics:

1. State : Liquid
2. Colour : Colourless
3. Odour : Sweet smell
4. Miscibility : Immiscible with water
5. Litmus : Neutral (for freshly distilled)

Preliminary Test:

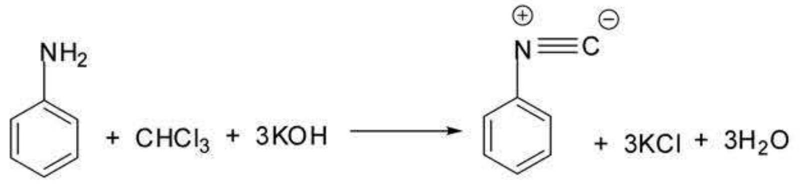
1. Ignition Test : Burns with yellow sooty flame (Because $CHCl_3$ has aromatic like C/H ratio i.e. C : H = 1 : 1)

Chemical Tests:

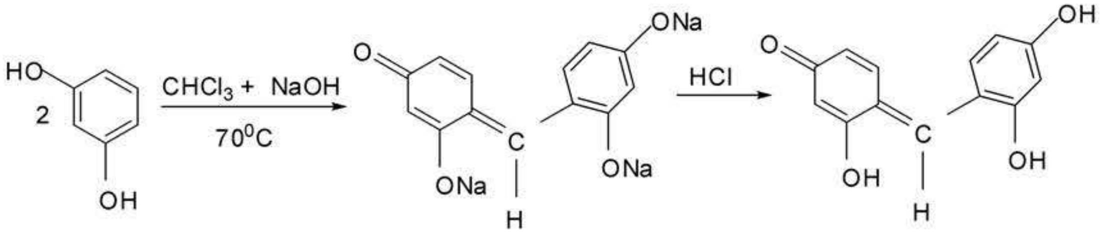
Experiment	Observation
1. Carbylamine Test: Take 2-3 drops of aniline and few drops of the sample and 1 ml of methanol in a dry test tube. Add a bead of KOH and warm the mixture.	1. A penetrating disgusting smell of iso-cyanide.
2. Resorcinol Test: Take little powdered resorcinol and few drops of the sample. Add about 1 ml conc. NaOH and warm the mixture. Add slightly excess HCl.	2. A brilliant red colour forms in the aqueous layer. Brilliant red colour changes to pale yellow.
3. β- Naphthol Test: Take little amount of β - Naphthol and 0.5 ml of the sample in a test tube. Add about 1 ml of 10% NaOH solution and heat.	3. A blue colour, fades to greenish brown.
4. Fehling's Test: Take 0.5 ml of the sample in a test tube and add about 1 ml of Fehling's solution (I & II). Heat the mixture with constant shaking.	5. A yellowish- red precipitate.
6. Silver nitrate Test: Take about 0.5 ml of the sample solution in a test tube and add about 1 ml of dil. NaOH or KOH solution and boil. Acidfy the mixture with conc. HNO_3 then add 1-2 drops of $AgNO_3$ solution.	6. Curdy white precipitate, soluble in NH_4OH solution.

Explanations and Reactions:

1. Carbylamine test:



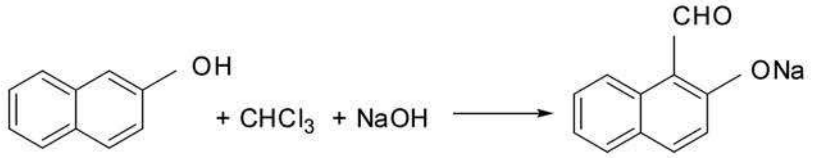
2. Resorcinol test:



Brilliant red colour

Pale yellow colour

3. β- Naphthol Test:



4. Fehling's test:

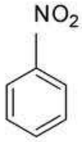
$$CHCl_3 + 2Cu(OH)_2 + 3KOH = Cu_2O\downarrow + K_2CO_3 + 3KCl$$
$$5H_2O$$

5. Silver nitrate test:

$$CHCl_3 + 4NaOH = HCOONa + 3NaCl + 2H_2O$$
$$\Big\downarrow AgNO_3$$
$$3AgCl\downarrow + 3NaNO_3$$

4.22 Identification of Nitrobenzene by Chemical Tests

L-20. NITRO BENZENE



Physical characteristics:

1. State : Liquid
2. Colour : pale yellow
3. Odour : Characteristic odour of bitter almonds
4. Miscibility : Immiscible with water
5. Litmus : Neutral

Preliminary Test:

1. Ignition Test : Burns with yellow sooty flame

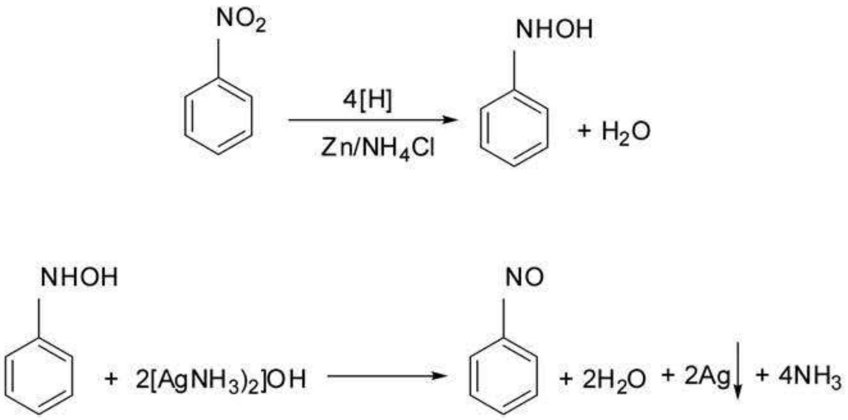
Chemical Tests:

Experiment	Observation
1. **Mulliken-Barker Test:** Take 0.2 ml of the sample in a test tube and boil in a water bath after adding about 0.1 g of Zn-dust and 0.2 g NH_4Cl and 5 ml of alcohol for 5 minutes. Filter the solution. Add 2-3 drops of Tollen's reagent to the filtrate and wormed.	**1.** Greyish black precipitate.
2. Diazo-coupling Test: Take about 0.5 ml of the sample in a test tuibe and boil with 3 ml of c. HCl and a piece of metallic Sn for 5 minutes. In second test tube prepare 1 ml 10% $NaNO_2$ solution. In third test tube dissolve about 10 mg. of β –	2. Red or orange dye appears.

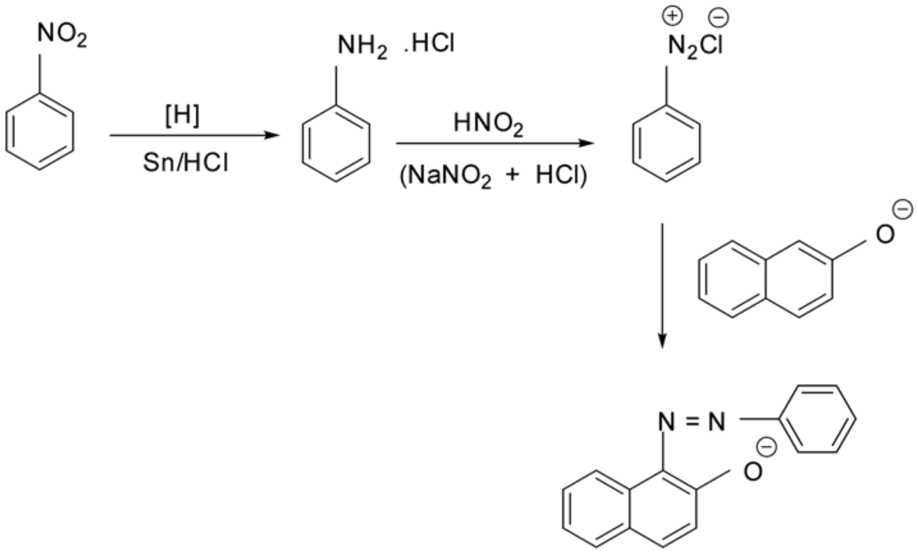
naphthol in 5 ml 10% NaOH. Place the three mixtures in an ice bath. When the solutions are throughly chilled, tranfer $NaNO_2$ solution into reduced sample solution. Now pour a drop of this diazotised mixture to alkaline sodium β - naphthoxide solution.	
3. **Caustic soda Test:** Take about 0.2 ml of the sample in a test tube and add about 1 ml of NaOH solution and then boil the mixture gently.	3. The colour darkens.

Explanations and Reactions:

1. Mulliken-Barker test:



2. Diazo-coupling test:



4.23 Summary

- For identification of organic compounds, state, specific gravity, solubility, acidic/basic nature, and odour are the vital characteristic.
- Oxalic acid and Tartaric acid both gives white precipitate on calcium chloride test.
- Tartaric acid gives a violate colouration on Mohler's Test.
- Citric acid does not give white precipitate on calcium chloride test.
- Resorcinol gives an intense green fluorescence in fluorescence test.
- Urea is identified by Biurate test to form pink or violet colouration.
- Glucose gives positive result in Fehling's and Tollen's test.
- Sucrose does not give red precipitate in Fehling's test.
- Benzoic acid produces fruity smell on Esterification Test.
- Formic acid develop red colour in Ferric chloride Test
- Methanol gives positive result on Oil of Wintergreen Test.
- Pleasant fruity smell
- develops on esterification of ethanol.

- Yellow crystalline precipitate with sweet smell of iodofom appears on iodoform reaction of acetone.
- Aniline produce Brilliant red dye in Diazo-coupling Test.

4.24 Question

Q-1: Why chloroform burns with sooty flame?

Ans: Its aromatic behaviour due to C:H=1:1.

Q-2: Will back-dye test be responded by all phenolic compounds?

Ans: Ortho and para substituted phenols do not response to this test.

Q-3: Glucose is a reducing sugar but sucrose is not – explain with a test.

Ans: Glucose responses on Fehling's or Tollen's test but sucrose is not.

Q-4: Name a test which is given by both glucose and sucrose.

Ans: Molisch's test.

Q-5: Name at least two compounds responding to fluorescence test.

Ans: Resorcinol and succinc acid

Q-6: What type of compounds responding haloform test?

Ans: Compounds containing $CH_3 - CO -$ group or a group can be converted to keto-methyl, eg., $CH_3 - CHOH -$, during chemical reaction will response to haloform test.

Q-7: Both the ethyl alcohol and acetone response on Iodoform test. How can you distinguish between them?

Ans: Acetone gives iodoform in presence of both NaOH and NH_4OH but ethyl alcohol gives in presence of NaOH only.

Q-8: How can you distinguish between aliphatic and aromatic aldehyde?
Ans: By Fehling's test.

Q-9: What is the characteristic property by which aldehyde and ketone can be distinguished?
Ans: Reducing property of aldehyde.

Unit 5 ❐ Preparations of Organic Compounds

Structure :

5.0 Objectives

5.1 Introduction

5.2 Purification methods of Crystallisation

5.3 Solvents for crystallization

5.4 Calculation of percentage yield

5.5 General discussion for the preparation, purification, Melting point check and percentage yield calculation of organic compounds

5.6 Experiment-1: Application of Nitration of aromatic compounds in Organic synthesis; Preparation of m-Dinitrobenzene

5.7 Experiment-2: Application of Condensation reactions in Organic synthesis; Preparation of Chalcone and Phthalimide

5.7.1 Preparation of Benzalacetophenone (Chalcone)

5.7.2 Preparation of Phthalimide

5.8 Experiment-3: Application of Hydrolysis reaction in Organic synthesis; Preparation of Phthalic acid

5.9 Experiment-4: Application of Acetylation reaction in Organic synthesis; Preparation of acetanilide

5.10 Experiment-5: Application of Benzoylation reaction in Organic synthesis; Preparation of Benzanilide

5.11 Experiment-6: Application of Side chain oxidation of aromatic compounds in Organic synthesis; Preparation of paranitrobenzoic acid

5.12 Experiment-7: Application of Diazo coupling reactions of aromatic amines in Organic synthesis; Preparation of phenylazo-β-naphthol (para red)

5.13 Experiment-8: Application of Bromination of acetanilide using green approach (Bromate-Bromide method) in Organic synthesis; Preparation of p-bromoacetanilide

5.14 Experiment-9: Selective reduction of m-dinitrobenzene to m-nitroaniline in Organic synthesis; Preparation of m-Nitroaniline

5.15 Experiment-10: Green 'multi-component-coupling' reaction in Organic synthesis; Preparation of β-Dimethylaminopropiophenone hydrochloride by Mannich Reaction

5.16 Summary

5.17 Questions

5.18 Further Readings

5.0 Objectives

The topic in this course will provide hands-on opportunities to develop and apply the knowledge of an experiment in organic synthesis. The student will be able to:

- learn and apply basic techniques used in the organic laboratory for preparation, purification and identification of organic compounds.
- employ the major techniques used in organic chemistry laboratory for analyses such as crystallization, melting point determination.
- will correctly calculate reaction yield for relevant lab experiments.
- analyse the given procedure of an experiment and suggest or recommend improvements.

5.1 Introduction

In the previous units of Block-2 you have learned about the experimental techniques used in the organic laboratory. In this unit we will discuss about the Preparation, purification, Melting point check and percentage yield calculation of organic compounds. After practicing the following organic synthesis, you will acquire expertise in this field and will be able to perform new reaction if procedure is supplied.

5.2 Purification methods of Crystallisation

The compounds directly obtained by means of chemical reactions are, only in rare cases, pure; they must therefore be subjected to a process of purification before they can be further utilized. For this purpose, the operations most frequently employed is crystallisation.

The crude solid product obtained directly as the result of a reaction is generally amorphous or not well crystallised. In order to obtain the compound in uniform, well-defined crystals, as well as to separate it from impurities like filter-fibres, inorganic substances, by-products, etc., it is dissolved, usually with the aid of heat, in a proper solvent, filtered from the impurities remaining undissolved, and allowed to cool gradually. For the crystallization process the quantity of solvent taken at first should be insufficient to dissolve the substance completely even on heating; then; more of the solvent is gradually added, until all of the substance is just dissolved. The dissolved compound then separates out in a crystallised form, while the dissolved impurities are retained by the mother-liquor (Crystallisation by Cooling). Many compounds are so easily soluble in all solvents, even at the ordinary temperature, that they do not separate from their solutions on mere cooling. In this case, in order to obtain crystals, a portion of the solvent must be allowed to evaporate (Crystallisation by Evaporation).

5.3 Solvents for crystallization

As solvents fororganic compounds, the following substances are principally used:

CLASS I. Water,
Alcohol,
Ether,
Petroleum Ether
Glacial Acetic Acid,
Benzene.

Also mixtures of these:

CLASS II. Water + Alcohol,
Water + Glacial Acetic Acid,
Ether + Petroleum Ether,
Benzene + Petroleum Ether

Less frequently used than these are: carbon disulphide, acetone, chloroform, ethyl acetate, methyl alcohol, amyl alcohol, toluene, xylene etc. But rarely used solvents are: pyridine, phenol, nitrobenzene, aniline, and others. If a compound is very difficultly soluble, solvents with high boiling points are used, as toluene, xylene, nitrobenzene, aniline, phenol, and others.

5.4 Calculation of percentage yield

Let us consider that, Molecular weight of starting material taken = M_1
Molecular weight of final product obtained = M_2
Weight of starting material taken = X
Weight of the final product obtained (Practical yield) = Y

Then, theoretically M_1 g starting material will give M_2 g of final product.

Therefore, Theoretical Yield of product = $\frac{M_2 \times X}{M_1}$ g

Percentage yield of the product $= \frac{\text{Practical yield}}{\text{Theoretical yield}} \times 100 \quad = \frac{Y \times M_1 \times 100}{M_2 \times X}$

5.5 General discussion for the preparation, purification, Melting point check and percentage yield calculation of organic compounds

There is a need to proper plan for the preparation of organic compounds in the laboratory. For this following points to be keep in minds-

- Read the procedure in details before preforming the reaction
- Check the availability of the reagents and instruments required for the reaction in your laboratory
- Check if there is any possibility of accident, poisonous gas evolution during the reaction or during the handling of chemicals.
- After completing the reaction, crude product should be collected after workup process as described the procedure. Note the amount of the crude product.
- Crude product should be purified and dried before recording the melting point.

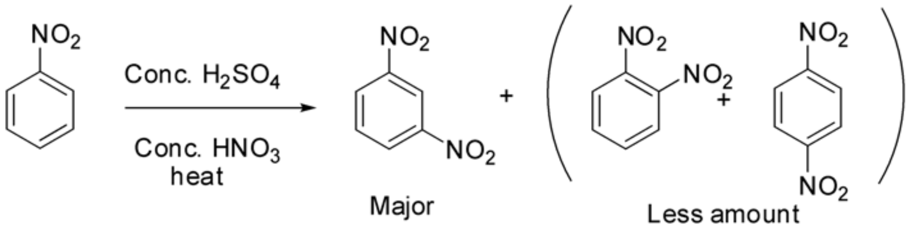
5.6 Experiment-1: Application of Nitration of aromatic compounds in Organic synthesis; Preparation of m-Dinitrobenzene

Introduction: Benzene rings are components of many important natural products and other useful organic compounds. Therefore, the ability to put substituents on a benzene ring, at specific positions relative to each other, is a very important factor in synthesizing many organic compounds. The two main reaction types used for this are both substitutions: Electrophilic Aromatic Substitution and Nucleophilic Aromatic Substitution. The benzene ring itself is electron-rich, which makes Nucleophilic Aromatic Substitution difficult, unless there are a number of strongly electron withdrawing substituents on the ring. Electrophilic Aromatic Substitution, on the other hand, is a very useful method for putting many different substituents on a benzene ring, even if there are other substituents already present. Electrophilic Aromatic Substitution chapter describes the factors involved in the regioselectivity for Electrophilic Aromatic Substitution reactions using benzene rings, which already have substituents on them. In this experiment you will put a nitro (-NO_2) group on a benzene ring. The actual electrophile in the reaction is the nitronium ion (NO_2^+), which is generated in situ.

Reaction: Aromatic compounds may be nitrated, i.e., the hydrogen atoms replaced by nitro (-NO_2) groups, with concentrated nitric acid in the presence of concentrated sulphuric acid. The function of the sulphuric acid is to furnish a strongly acid medium and to convert the nitric acid into the highly reactive nitronium ion NO_2^+ which is the real nitrating agent:

$$HNO_3 + 2H_2SO_4 \rightleftharpoons NO_2^+ + H_3O^+ + 2HSO_4^-$$

For an example nitration of nitrobenzene on treatment with mixed acid (conc. H_2SO_4 and fuming HNO_3) produces m-Dinitrobenzene.



Instruments required:

- Round-bottomed flask (100ml)
- Reflux condenser
- Steam bath
- Glass beads
- Stand and clamp
- Filter with suction pump

Chemicals required:

- Concentrated sulphuric acid (10 ml)

- Fuming nitric acid (8 ml)
- Nitrobenzene (6 ml)
- Rectified spirit

Experimental Procedure: Place 10 ml. of concentrated sulphuric acid and 8 ml of fuming nitric acid, in a 100 ml. round-bottomed flask; add a few fragments of porcelain or of glass beads. Attach a reflux condenser and place the apparatus in a fume chamber. Add slowly dropwise 6 ml. of nitrobenzene with shaking the flask to ensure thorough mixing. After complete addition, heat the mixture on water bath for 30 min with occasional shaking. Then allow the mixture to cool and pour it cautiously with vigorous stirring into about 200 ml. of ice cold water; the dinitrobenzene soon solidifies. Filter with suction, wash thoroughly with cold water to make it acid free, and allow to drain water as completely as possible. Place the crude m-dinitrobenzene on a blotting paper, dry on air and note the weight of crude m-dinitrobenzene.

Purification by recrystallization: Transfer the crude dinitrobenzene to a conical flask fitted, add minimum amount of methanol or rectified spirit and heat on a water bath until all the crystalline solid dissolves. If the resulting solution is not quite clear, filter it through a filter paper on a funnel in hot condition. Colourless crystals of m-dinitrobenzene are deposited on cooling. Note the weight of recrystallized product, calculate its percentage yield and check its melting point.

Calculation of percentage yield:

Molecular weight of starting material i.e. nitrobenzene ($C_6H_5NO_2$) = 123

Molecular weight of product i.e. m-dinitrobenzene ($C_6H_4N_2O_4$) = 168

Theoretical Yield: 123g nitrobenzene gives 168g of m-dinitrobenzene

Therefore, Xg of nitrobenzene should give $\frac{168\times X}{123}$g of m-dinitrobenzene

If practical yield of product is Y g, then the percentage yield of the product

$$= \frac{\text{Practical yield}}{\text{Theoretical yield}} \times 100$$

$$= \frac{Y \times 123 \times 100}{168 \times X}$$

Where, X = Weight of nitrobenzene taken
Y = Weight of the m-dinitrobenzene obtained

Submit the product to your instructor in a paper wrapped and labelled including your name(s). Note down the experimental results following the chart given below.

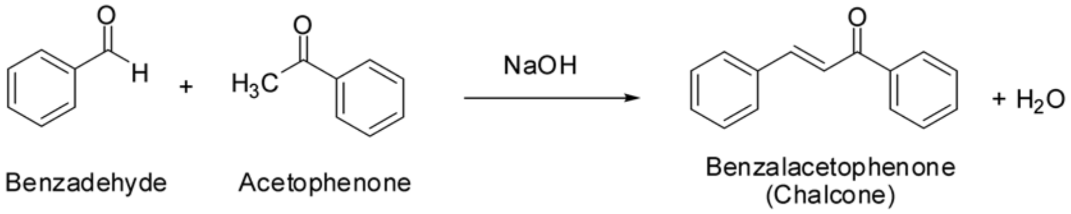
Weight of nitrobenzene taken	Theoretical Yield of m-dinitrobenzene	Weight of crude m-dinitrobenzene obtained	Weight of recrystallized m-dinitrobenzene obtained	percentage yield of product	Melting Point of recrystallized m-dinitrobenzene

5.7 Experiment - 2: Application of Condensation reactions Organic synthesis; Preparation of Chalcone and Phthalimide

Introduction: In a condensation reaction, two molecules or parts thereof combine, releasing a small molecule. When this small molecule is water, it is known as a dehydration reaction. Other possible lost molecules include hydrogen chloride, methanol, and acetic acid. It is a versatile class of reactions that can occur in acidic or basic conditions or in the presence of a catalyst. In this experiment you will prepare i) Benzalacetophenone or Chalcone and ii) Pthalimide by the use of condensation reaction.

5.7.1 Preparation of Benzalacetophenone (Chalcone)

Reaction: Chalcones can be prepared by the aldol condensation reaction between benzaldehyde and acetophenone in the presence of sodium hydroxide as a catalyst.



Instruments required:

- Round-bottomed flask (100ml)
- mechanical stirrer
- Ice chest
- Stand and clamp
- Buchner funnel with suction pump

Chemicals required:

- Sodium hydroxide (2.2 g)
- Acetophenone (5.2 g)
- Benzaldehyde (4.6 g)
- Rectified spirit

Experimental Procedure: Place a solution of 2.2 g. of sodium hydroxide in 20 ml. of water and 13 ml. of rectified spirit in a 100 ml. r.b. flask provided with a mechanical stirrer. Immerse the flask in a bath of crushed ice, pour in 5.2 g. of freshly-distilled acetophenone, start the stirrer, and then slowly add 4.6 g. of pure benzaldehyde. Keep the temperature of the mixture at about 25° (the limits are 15-30°) and stir vigorously for 2-3 hours. Remove the stirrer and cool the reaction mixture in an ice chest. Filter the solid product with suction on a Buchner funnel, wash with cold water until the washings are neutral to litmus. Place the crude chalcone on a blotting paper, dry on air and note the weight of crude chalcone. This substance should be handled with great care since it acts as a skin irritant.

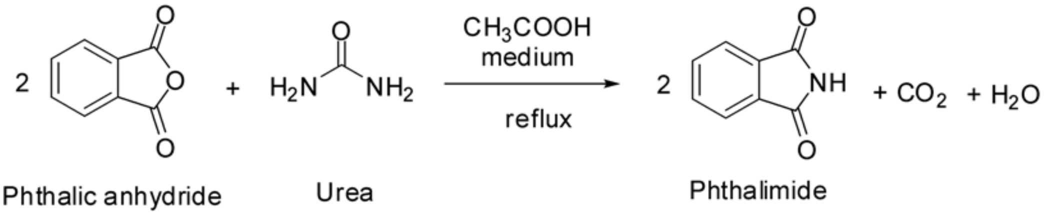
Purification by recrystallization: Transfer your weighed crude chalcone into a conical flask. Then add the minimum amount of hot 95% ethanol required to just dissolve your crude product. After dissolving your product, cork the flask and allow the mixture to cool slowly. When it appears that crystallization is complete, place the mixture in an ice water bath for 5 minutes. Filter it through a filter paper crystal of chalcone and dry on air. Note the weight of recrystallized product, calculate its percentage yield and check its melting point.

Submit the product to your instructor in a paper wrapped and labelled including your name(s). Note down the experimental results following the chart given below.

Weight of acetophenone taken	**Theoretical Yield of chalcone**	**Weight of crude Chalcone obtained**	**Weight of recrystallized Chalcone obtained**	**percentage yield of product**	**Melting Point of recrystallized chalcone**

5.7.2 Preparation of Phthalimide

Reaction: Phthalimide can be prepared by refluxing Phthalic anhydride and Urea in acetic acid medium using the Condensation reaction.



Instruments required:

- Round-bottomed flask (100ml)
- Condenser
- Stand and clamp
- Bunsen burner
- Buchner funnel with suction pump

Chemicals required:

Phthalic anhydride (5 g)

Urea (2.5 g)

Glacial acetic acid (10 ml)

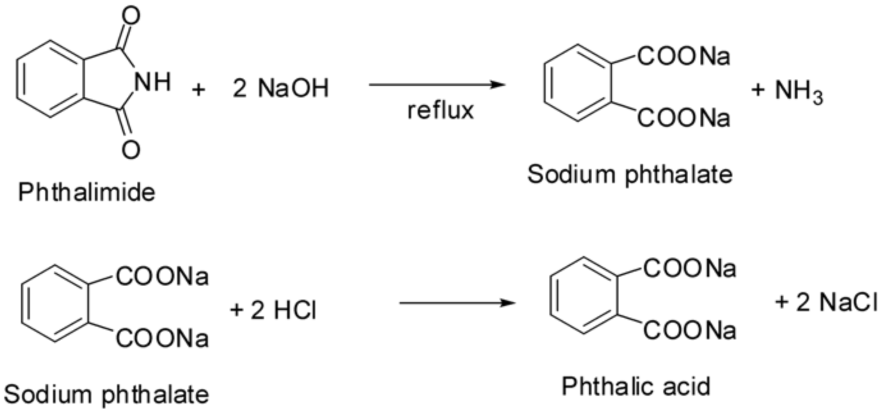
Experimental Procedure: Take 5 g. of Phthalic anhydride, 2.5 g urea and 10 ml glacial acetic acid in a 100 ml r.b. flask fitted with a condenser. Heat the mixture to reflux on a Bunsen burner for 1 hour. Then cool the reaction mixture at room temperature and the mixture get solidifies on cooling. Pour 20-30 ml water in the mixture with shaking. Filter the solid phthalimide on a Buchner funnel and wash it with cold water to make it acid free. Recrystallize the crude phthalimide from hot water and note the weight of obtained product, calculate its percentage yield and check its melting point.

Submit the product to your instructor in a paper wrapped and labelled including your name(s). Note down the experimental results following the chart given below.

Weight of Phthalic anhydride taken	**Theoretical Yield of phthalimide**	**Weight of crude phthalimide obtained**	**Weight of recrystallized phthalimide obtained**	**percent age yield of product**	**Melting Point of recrystallized phthalimide**

5.8 Experiment-3: Application of Hydrolysis reaction in Organic synthesis; Preparation of Phthalic acid

Reaction: Phthalimide on hydrolysis with 10% aqueous NaOH solution produces Sodium phthalate. Aqueous solution of sodium phthalate on treatment with conc. HCl produces Phthalic acid.



Instruments required:

- Round-bottomed flask (100ml)
- Beaker
- Condenser
- Stand and clamp
- Bunsen burner
- Buchner funnel with suction pump

Chemicals required:

- Phthalimide (5 g)
- NaOH (5 g)
- conc. HCl

Experimental Procedure: Take 5 g. of Phthalimide in a 100 ml r.b. flask fitted with a condenser. Pour 50 ml 10% NaOH (5 gm NaOH in 50 ml water) in it and put some glass beads into the solution. Heat the mixture to reflux on a Bunsen burner for 30 minutes. Then cool the reaction mixture at room temperature and transfer the mixture in a 250 ml beaker. Cool the beaker in ice. After cooling acidify the mixture strongly by adding conc HCL with stirring. Filter the white solid Phthalic acid on a Buchner funnel and wash it with water to make it acid free. Recrystallize the crude phthalimide from hot water and note the weight of obtained product, calculate its percentage yield and check its melting point.

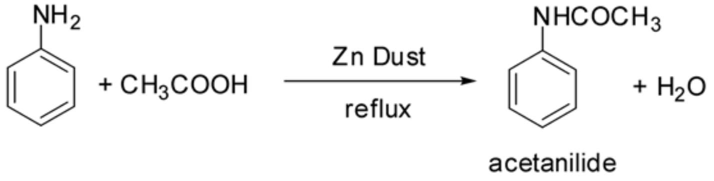
Submit the product to your instructor in a paper wrapped and labelled including your name(s). Note down the experimental results following the chart given below.

Weight of phthalimide taken	Theoretical Yield of Phthalic acid	Weight of crude Phthalic acid obtained	Weight of recrystallized Phthalic acid obtained	percentage yield of product	Melting Point of recrystallized Phthalic acid

5.9 Experiment - 4 : Application of Acetylation reaction in Organic synthesis; Preparation of acetanilide

Acetyl derivatives of aromatic amines may be prepared either with acetic anhydride or acetic acid or with a mixture of both reagents. Acetylation reaction using acetic anhydride is simple and provides good yield of product. But acetic anhydride is a banned item and hence we will perform acetylation using acetic acid.

Reaction: Acetanilide is produced when aniline is refluxed with excess glacial acetic acid in presence of catalytic amount of Zn dust. The zinc reduces the coloured impurities in the aniline and also helps to prevent oxidation of the amine during the reaction.



Instruments required:

- Round-bottomed flask (100ml)
- Beaker
- Refluxing condenser
- Stand and clamp
- Bunsen burner
- Buchner funnel with suction pump

Chemicals required:

- Aniline (10 ml)
- Glacial acetic acid (20 ml)
- Zinc dust
- Charcoal

Experimental Procedure: Take 10 ml aniline and 20 ml glacial acetic acid in a dry 100 ml r.b. flask fitted with a condenser. Put pinch of zinc dust and some glass beads into the solution. Reflux the mixture on a Bunsen burner for 2-3 hour. Pour the hot liquid cautiously in a thin stream into a 500 ml beaker containing 200 ml of ice-water with continuous stirring. Solid acetinalide will precipitate. Filter the solid acetinalide on a Buchner funnel and wash it with water to make it acid free. Dry the solid over air and note the weight of obtained crude product, calculate its percentage yield and check its melting point.

Purification of acetinalide (if gummy texture appears)

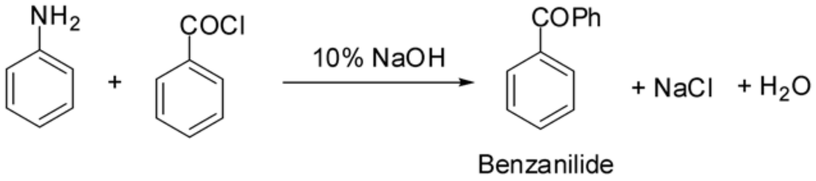
Place the moist acetanilide in a beaker and add gradually about 300 ml. of boiling water. It must be remembered that the crude acetanilide melts slightly below 114°; the substance may therefore melt when heated with water. All the material, liquid or solid, must be dissolved: the addition of a little alcohol will assist the process of solution. Filter, if necessary, through a Buchner funnel. If the solution is coloured, add 1 g. of decolourising charcoal before filtration. Solid acetinalide precipitates on cooling. Filter and dry upon filter paper in the air. The acetanilide may also be recrystallized using toluene as solvent.

Submit the product to your instructor in a paper wrapped and labelled including your name(s). Note down the experimental results following the chart given below.

Weight of Phthalic anhydride taken	Theoretical Yield of acetinalide	Weight of crude acetinalide obtained	Weight of pure acetinalide obtained	percentage yield of product	Melting Point of pure acetinalide

5.10 Experiment - 5 : Application of Benzoylation reaction in Organic synthesis ; Preparation of Benzanilide

Reaction: Aniline on treatment with benzoyl chloride in presence of NaOH produces Benzanilide in good yield. This reaction is also called *Schotten-Baumann* reaction.



Instruments required:

- Stoppered conical flask
- Buchner funnel with suction pump

Chemicals required:

- Aniline (5 ml)
- 10 % aqueous NaOH solution
- benzoyl chloride (7 ml)

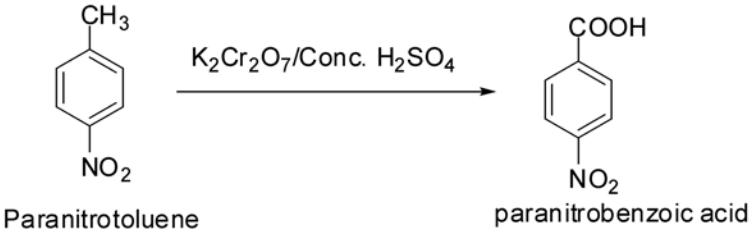
Experimental Procedure: Place 5 ml of aniline and 45 ml. of 10 % aqueous NaOH solution in a stoppered conical flask, and then add 7 ml of benzoyl chloride, stopper, and shake vigorously for 10-15 minutes. Heat is evolved in the reaction. The crude benzoyl derivative separates as white solid mass. Complete the reaction. If the odour of benzoyl chloride is detected (smell cautiously) add few ml of NaOH and make sure that the reaction mixture is alkaline. Dilute with water. Filter off the product with suction on a Buchner funnel, break up the mass on the filter (if necessary), wash well with water, and drain. Collect the Benzanilide and dry in the air and note the weight of obtained crude product, calculate its percentage yield and check its melting point. Recrystallize from hot alcohol (or methylated spirit); filter the hot solution through a Buchner funnel.

Submit the product to your instructor in a paper wrapped and labelled including your name(s). Note down the experimental results following the chart given below.

Weight of aniline taken	Theoretical Yield of Benzanilide	Weight of crude Benzanilide obtained	Weight of pure Benzanilide obtained	percentage yield of product	Melting Point of Benzanilide

5.11 Experiment - 6 : Application of Side chain oxidation of aromatic compounds in Organic synthesis; Preparation of paranitrobenzoic acid

Reaction: Paranitrotoluene on oxidation with potassium dichromate/conc H_2SO_4 produces paranitrobenzoic acid.



Instruments required:

- 100 ml r.b. flask
- refluxing condenser
- Bunsen burner
- 250 ml beaker
- Buchner funnel with suction pump

Chemicals required:

- para-nitrolotulene (5 gm)

- Conc H_2SO_4 (20 ml)
- saturated $NaHCO_3$ solution
- charcoal
- potassium dichromate (15 gm)

Experimental Procedure: Add slowly 20 ml of conc H_2SO_4 into a 100 ml r.b. flask containing 30 ml water and then add 15 gm potassium dichromate into the solution. It will form a warm solution mixture. Heat is evolved during mixing. 5 gm para-nitrolotulene is then added to the warm solution for 5-10 minutes with shaking the flask. Fit a refluxing condenser and put some glass beads into the solution. Reflux the mixture on a Bunsen burner for 30 minutes. Bring the reaction mixture at room temperature and pour the mixture slowly into a 250 ml beaker containing 100 ml ice water. Stir the mixture during this addition. The crude para-nitrobenzoic acid separates as solid mass. Filter off the product with suction on a Buchner funnel, wash with 5 % H_2SO_4, and drain. Collect the para-nitrobenzoic acid and dry in the air and note the weight of obtained crude product, calculate its percentage yield.

Purification of para-nitrobenzoic acid

Dissolve the crude para nitrobenzoic acid in minimum amount of saturated $NaHCO_3$ solution. Add little amount of decolourising charcoal and heat the mixture (don't boil). Filter through a Buchner funnel after cooling. Acidify the filtrate by 15% H_2So_4. Solid para-nitrobenzoic acid will be precipitated. Filter the solid through a Buchner funnel and wash with little amount of cold water and dry. Check the melting point of pure para-nitrobenzoic acid.

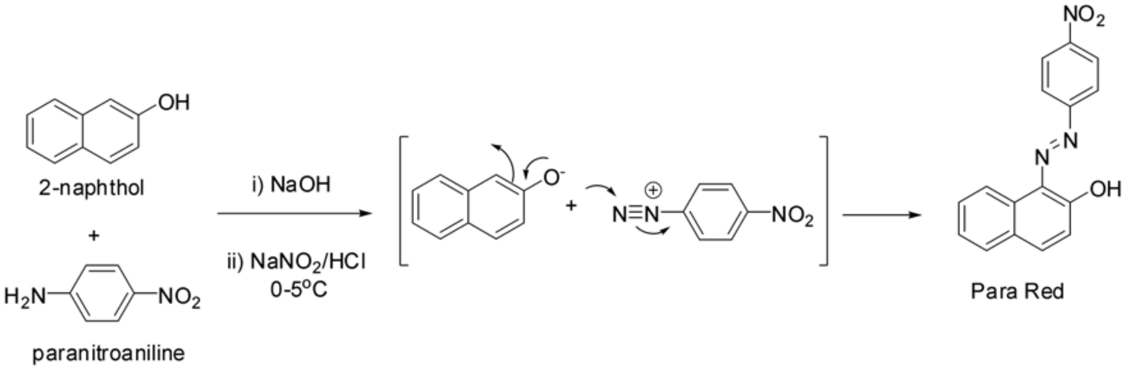
Submit the product to your instructor in a paper wrapped and labelled including your name(s). Note down the experimental results following the chart given below.

Weight of para-nitrolotulene taken	Theoretical Yield of para nitrobenzoic	Weight of crude para nitrobenzoic obtained	Weight of pure para nitrobenzoic obtained	percentage yield of product	Melting Point of para nitrobenzoic

5.12 Experiment - 7 : Application of Diazo coupling reactions aromatic amines in Organicsynthesis; Preparation of phenylazo-*β*-naphthol (para red)

Diazonium ions are weak electrophiles, however, they undergo coupling with activated aromatic nuclei such as aryl amines, phenols and aromatic heterocyclic compounds. However, the careful control of the pH of the reaction medium is necessary for the success of the process. Aromatic azo-compounds are coloured. Several of those compounds synthesized by the diazo-coupling are employed as dye-stuffs. In this experiment you will prepare phenylazo-β-naphthol (i.e. called para red, a dye-stuff) by the use of diazo coupling reactions of aromatic amines

Reaction: Para red is prepared by diazo coupling reactions of 2-napthol with p-nitrobenzenediazonium salt.



Instruments required:

- 250 ml. conical flask
- 250 ml beaker
- Thermometer
- Glass rod
- Ice bath
- Buchner funnel with suction pump

Chemicals required:

- paranitroaniline (5 gm)
- Conc HCl (16 ml)

- $NaNO_2$ (4 gm)
- β-naphthol
- glacial acetic acid (30-35 ml.)
- 10% sodium hydroxide solution

Experimental Procedure:

Dissolve 5 g. of paranitroaniline in a mixture of 16 ml. of concentrated hydrochloric acid and 16 ml. of water contained in a 250 ml. conical flask. Place a thermometer in the solution and immerse the flask in a bath of crushed ice; cool until the temperature of the stirred solution falls below 5°C. Dissolve 4 g. of sodium nitrite in 20 ml. of water and chill the solution by immersion in the ice bath; add the sodium nitrite solution in small volumes (1-2 ml. at a time) to the cold paranitroaniline hydrochloride solution, and keep the latter well stirred. Heat is evolved by the reaction. The temperature should not be allowed to rise above 10°C (add a few grams of ice to the reaction mixture if necessary) otherwise appreciable decomposition of the diazonium compound and of nitrous acid will occur. Prepare a solution of 7.8 g. of β-naphthol in 45 ml. of 10 % sodium hydroxide solution in a 250 ml. beaker; cool the solution to 5° C by immersion in an ice bath, assisted by the direct addition of about 25 g. of crushed ice. Stir the naphthol solution vigorously and add the cold diazonium salt solution very slowly: a red colour develops and red crystals of phenylazo-β-naphthol (para red) soon separate. When all the diazonium salt solution has been added, allow the mixture to stand in an ice bath for 30 minutes with occasional stirring. Filter the crystals through a Buchner funnel with gentle suction, wash well with water, and drain thoroughly. Recrystallize the product from glacial acetic acid (30-35 ml.). Filter the recrystallized product with suction, wash with a little alcohol (or methylated spirit) to eliminate acetic acid, and dry upon filter paper. The yield of deep red crystals is about 3 g. Pure phenylazo-β-naphthol has m.p. 131°C ; if the m.p. is low, recrystallize the dry product from alcohol.

Submit the product to your instructor in a paper wrapped and labelled including your name(s). Note down the experimental results following the chart given below.

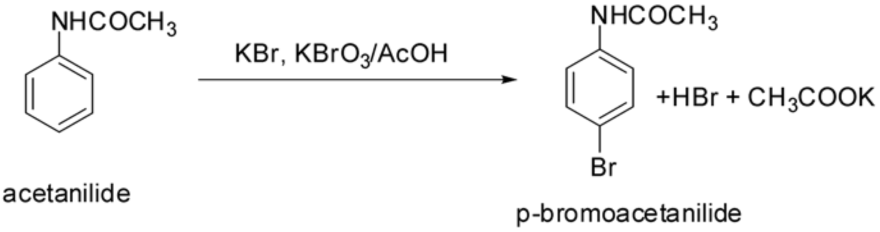
Weight of paranitroaniline taken	**Theoretical Yield of para red**	**Weight of crude para red obtained**	**Weight of pure para red obtained**	**percentage yield of product**	**Melting Point of para red**

5.13 Experiment - 8 : Application of Bromination of acetanilide using green approach (Bromate-Bromide method) in Organic synthesis ; Preparation of p-bromoacetanilide

The traditional experiment involves the use of Br_2-AcOH and is described in several laboratory textbooks. However, liquid bromine is extremely corrosive and is hazardous to handle. To avoid risks in using liquid bromine, methods to generate bromine in situ have been developed now a day. In acidic medium, $KBrO_3$-KBr is known to release bromine according to equation.

$5\ KBr + KBrO_3 + 6\ CH_3COOH = 3\ Br_2 + 3\ H_2O + 6\ CH_3\ COOK$

Reaction: p-bromoacetanilide is prepared by Bromination of acetanilide on treatment with KBr and $KBrO_3$ in acetic acid medium using green approach.



Instruments required:

- 100 ml. conical flask fitted with a cork
- 250 ml beaker
- Glass rod
- Buchner funnel with suction pump

Chemicals required:

- acetanilide - 5 g
- Glacial Acetic acid - 20 ml
- Potassium bromide – 7.5 g
- Potassium bromate – 2.5 g

Experimental Procedure:

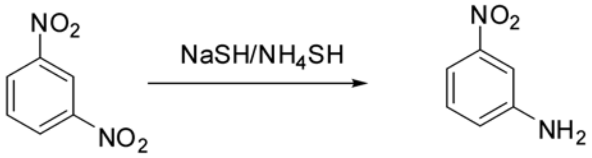
5 gm acetanilide is dissolved in glacial acetic acid (20 ml) in a 100 ml conical flask fitted with a cork (warming if necessary). The flask is cooled under water to room temperature. In another conical flask dissolve 7.5 gm potassium bromide and 2.5 gm potassium bromate in 20 ml water. Add the bromate-bromide mixture to the acetinalide solution slowly at room temperature keeping the cork closed and with shaking. The reaction mixture was then stirred occasionally with for additional 1 hour. Then add the reaction mixture to a beaker containing 100 ml of ice-cold water stirring all the while with a glass rod. The developed light brown colour disappeared. The precipitate of p-bromoacetanilide separated out (If no precipitate is formed then neutralize the acid by sodium hydroxide solution). The white crystals were filtered through Buchner funnel and the solid was dried. Recrystallize the crude product from ethanol. M.P. of p-bromoacetanilide = 165 ^{o}C

Submit the product to your instructor in a paper wrapped and labelled including your name(s). Note down the experimental results following the chart given below.

Weight of p-nitro aniline taken	**Theoretical Yield of p-bromo acetanilide**	**Weight of crude p-bromo acetanilide obtained**	**Weight of pure p-bromo acetanilide obtained**	**percent age yield of product**	**Melting Point of p-bromo acetanilide**

5.14 Experiment - 9 : Selective reduction of m - dinitrobenzene to m-nitroaniline in Organic synthesis; Preparation of m-Nitroaniline

Reaction: m-Nitroaniline is prepared by partial reduction of m-dinitrobenzene on treatment with NaSH or NH_4SH.



Instruments required:

- 250 ml beaker
- Refluxing condenser
- Glass rod
- Buchner funnel with suction pump

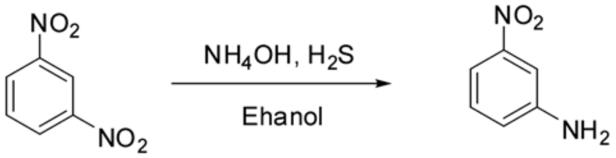
Chemicals required:

- m-dinitrobenzene
- sodium sulfide
- hydrogen sulfide
- ammonium chloride
- ammonium hydroxide
- ethanol

Experimental Procedure:

A solution of 11 grams of crystalline sodium sulfide ($Na_2S.9H_2O$) in 20 cc. water is treated with hydrogen sulfide until the solution is completely saturated. In this way a clear solution of sodium hydrosulfide (NaSH) is obtained. In a beaker, another solution is prepared containing 1 grams of ammonium chloride in 40 cc. hot water, and to this solution is added, at 90°C, 8 grams of pure m-dinitrobenzene, stirring the mixture vigorously enough to produce a fine emulsion. The temperature is allowed to fall to 85°C and then, with continued vigorous stirring, the previously prepared hydrosulfide solution is added slowly from a dropping funnel during the course of 15 minutes, maintaining the temperature between 80 and 85°. When the addition has been completed, stirring is continued for 5 minutes without further heating and then the mixture is cooled to 20° by the addition of 50 gm ice. The end-point of the reaction may be recognized by the fact that a drop of the reaction solution on a filter paper gives a black streak of metallic sulfide with an iron or copper sulfate solution. Stirring is continued for about 1 hour more at room temperature, and then the m-nitroaniline, which has separated in yellow crystals, is filtered with suction and washed with cold water. The crude product can be recrystallized from boiling water. The mp of pure recrystallized m-nitraniline is 114° C.

Alternative Experimental Procedure:



10 g of m-dinitrobenzene is dissolved in 40 g of ethanol and the solution is cooled down, upon which a portion of the m-dinitrobenzene separates out. This solution is further treated with 8 g of concentrated ammonium hydroxide solution (each 1 g of m-dinitrobenzene requires 0.8 g of concentrated ammonium hydroxide solution). The reaction flask with its content is tared, the mixture is saturated with hydrogen sulfide at room temperature and after saturation is complete the flask is heated under reflux for 30 minutes. Then the reaction flask content is cooled to room temperature and hydrogen sulfide again passed into it to solution until there is an increase of 6 g in weight (or 0.6 g for every gram of m-dinitrobenzene used). If correct weight is not reached hydrogen sulfide is again passed into the mixture. The solution is diluted with water, the precipitated crude 3-nitroaniline is filtered, washed with water, and extracted by warming with dilute hydrochloric acid. 3-Nitroaniline hydrochloride is converted to 3-nitroaniline base by neutralizing with ammonium hydroxide. Finally, 3-nitroaniline is recrystallized from water yielding 70-80% of product which melts at 114° C.

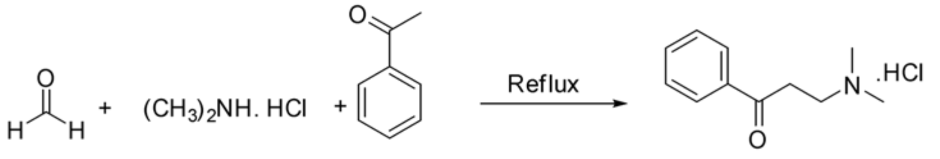
Submit the product to your instructor in a paper wrapped and labelled including your name(s). Note down the experimental results following the chart given below.

Weight of m-dinitro benzene taken	Theoretical Yield of m-Nitroaniline	Weight of crude m-Nitroaniline obtained	Weight of pure m-Nitroaniline obtained	percent age yield of product	Melting Point of m-Nitroaniline

5.15 Experiment-10 : Green 'multi-component-coupling' reaction in Organic synthesis ; Preparation of β - Dimethy laminopropiophenone hydrochloride by Mannich Reaction

This multi-component condensation of a non-enolizable aldehyde, a primary or secondary amine and an enolizable carbonyl compound affords aminomethylated products. The iminium derivative of the aldehyde is the acceptor in the reaction. The involvement of the Mannich Reaction has been proposed in many biosynthetic pathways, especially for alkaloids.

Reaction: The Mannich reaction consists in the condensation of formaldehyde with ammonia or a primary or a secondary amine and a compound containing at least one hydrogen atom of pronounced reactivity; the active hydrogen atom may be derived from a methylene group activated by a neighbouring keto group, or from a nitroparaffin, or it may be the o- or p-hydrogen atoms in phenols. Thus when acetophenone is boiled in alcoholic solution with formaldehyde and dimethylamine hydrochloride, the Mannich base β-dimethylaminopropiophenone hydrochloride is readily formed.



β-dimethylaminopropiophenone hydrochloride

Instruments required:

- 100 ml. conical flask fitted with a cork
- 250 ml beaker
- Glass rod
- Buchner funnel with suction pump

Chemicals required:

- dimethylamine hydrochloride – 5.3 g
- paraformaldehyde – 2 g
- acetophenone – 6 g
- ethanol – 10 ml
- concentrated hydrochloric acid
- acetone

***β*-Dimethylaminopropiophenone hydrochloride**. Place 5.3 g of dry dimethylamine hydrochloride, 2.0 g. of powdered paraformaldehyde and 6.0g. (6 ml.) of acetophenone in a 50 ml. round bottomed flask attached to a reflux condenser. Introduce 10 ml. of 95 percent, ethanol to which 0.1 ml. of concentrated hydrochloric acid has been added, and reflux the mixture on a water bath for 2 hours; the reaction mixture should ultimately be almost clear and homogeneous. Filter the yellowish solution (if necessary) through a hot water funnel transfer the filtrate to a 100 ml. wide-mouthed conical flask and, while still warm, add 40 ml. of acetone. Allow to cool to room temperature and leave in a refrigerator overnight. Filter the crystals at the pump, wash with 15 ml. of acetone, and dry for 6 hours at 40-50°C: Recrystallize the crude product by dissolving in 8 ml. of hot rectified spirit and slowly adding 40 ml. of acetone to the solution; collect the solid which separates by suction filtration and dry at 70°C. The m.p. of purified material is 155-156°C.

Submit the product to your instructor in a paper wrapped and labelled including your name(s). Note down the experimental results following the chart given below.

Weight of acetophenone taken	Theoretical Yield of product	Weight of crude product obtained	Weight of pure product obtained	percent age yield of product	Melting Point of β-Dimethyl aminopropio-phenone hydrochloride

5.16 Summary

- If a compound is very difficultly soluble, solvents with high boiling points are used for crystallization, as toluene, xylene, nitrobenzene, aniline, phenol, and others.
- The function of the sulphuric acid in nitration of aromatic compounds is to furnish a strongly acid medium and to convert the nitric acid into the highly reactive nitronium ion NO^{2+} which is the real nitrating agent.
- Chalcones can be prepared by the aldol condensation reaction between benzaldehyde and acetophenone in the presence of sodium hydroxide as a catalyst.
- Phthalimide can be prepared by refluxing Phthalic anhydride and Urea in acetic acid medium using the Condensation reaction.
- Acetyl derivatives of aromatic amines may be prepared either with acetic anhydride or acetic acid or with a mixture of both reagents.
- Schotten-Baumann reaction is the reaction between aniline and benzoyl chloride in presence of NaOH to produce Benzanilide in good yield.
- Diazonium ions are weak electrophiles, however, they undergo coupling with activated aromatic nuclei such as aryl amines, phenols to produce azo-dye compounds.
- Liquid bromine is extremely corrosive and is hazardous to handle.

- This multi-component condensation reaction of a non-enolizable aldehyde, a primary or secondary amine and an enolizable carbonyl compound affords aminomethylated products.

5.17 Questions

Q1. What is the function of zinc dust in the preparation of acetanilide?

Ans: i) It reduces the coloured impurities present in aniline. ii) It prevents oxidation of aniline during the reaction.

Q2. What is the colour of para-red dye?

Ans: deep red

Q3. What is diazotisation reaction?

Ans: It is the reaction of primary aromatic amines with nitrous acid to form diazonium salt. The reaction is carried out at low temperature (below 5°C)

Q4. What is coupling reaction?

Ans: It is the reaction of diazonium salts with highly activated benzene rings such as phenolic ring. The reaction involves electrophilic substitution and the product obtained is generally a dye.

Q5. What is Mannich Reaction reaction?

Ans: The Mannich reaction is an organic reaction which consists of an amino alkylation of an acidic proton placed next to a carbonyl functional group by formaldehyde and a primary or secondary amine or ammonia. The final product is a β-amino-carbonyl compound also known as a Mannich base.

Q6. Why is crystallisation done?

Ans. Crystallisation enables to prepare a substance in state of highest purity.

Q7. What is meant by 'saturated solution'?

Ans. A solution in which no more of solute can be dissolved at a particular temperature is known as saturated solution.

Q8. What is the formula to evaluate percentage yield?

Ans: see text 5.4

Q9. What is nitrating mixture?

Ans: Mixture of Conc.HNO_3 & Conc.H_2SO_4

Q10. What is the formula of Phthalimide?

Ans: See text 5.7.1

5.18 Further Readings

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