PERIYAR INSTITUTE OF DISTANCE EDUCATION (PRIDE)

PERIYAR UNIVERSITY

SALEM - 636 011.

B.Sc. CHEMISTRY

THIRD YEAR

PRACTICAL – III : (ORGANIC ANALYSIS AND GRAVIMETRIC CHEMISTRY)

PRACTICAL – IV : (ORGANIC PREPARATION AND PHYSICAL CHEMISTRY EXPERIMENT)

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PRACTICAL – III : (ORGANIC ANALYSIS AND GRAVIMETRIC CHEMISTRY)

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UNIT – I

ORGANIC PREPARATIONS

1.0 INTRODUCTION:

In the laboratory organic compounds are prepared by involving different types of reactions. Some of the important types of reaction which are included in our syllabus are

1. Oxidation
2. Hydrolysis
3. Nitration
4. Bromination
5. Benzoylation
6. Diazotization

In order to obtain maximum yield of the product, conditions like temperature, relative proportion of chemicals, concentration of the reagents, duration of heating etc., have to be carefully maintained.

In the following pages the preparation of some simple organic compounds (involving single stage) are described.

The students will be expected to submit for evaluation the crude product in a dry condition as well as a small portion of the product in a pure, recrystallized state.

1.2 OXIDATION

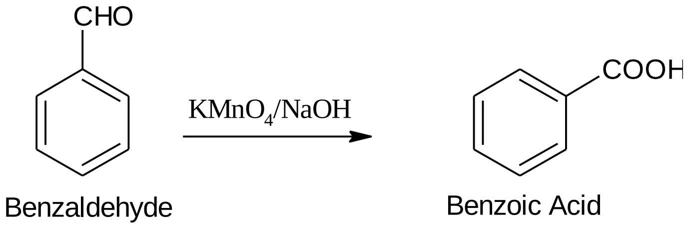
1.2 a) PREPARATION OF BENZOIC ACID FROM BENZALDEHYDE

Aim:

To prepare a maximum quantity of benzoic acid from benzaldehyde.

Principle:

Benzaldehyde is readily oxidized to benzoic acid by treating with alkaline potassium permanganate.



Chemical Required:

1. Benzaldehyde = 5ml
2. Anhydrous sodium carbonate = 5g
3. Potassium permanganate = 6g
4. Sodium bisulphite = 8g

Procedure:

About 5g of anhydrous sodium carbonate are dissolved in about 25ml of water in a 500ml R.B. flask. 5ml of benzaldehyde and a few porcelain chips are added. The flask is then fitted with a reflux water condenser and kept in position. The flask is gently heated on a wire gauze.

When the mixture begins to boil, a saturated solution of about 6g of potassium permanganate is added to the flask from the top of the condenser in small quantities at a time, until the solution in the flask remains slightly pink. The contents of the flask are boiled for about 30 minutes. Sodium benzoate is formed in solution and hydrated manganese dioxide is precipitated.

The heating is then stopped and the flask is cooled. The contents are transferred into a beaker. A saturated solution of sodium bisulphite is added to the beaker followed by 1:1 dilute sulphuric acid, added in small quantities at a time. The contents are stirred well until the precipitated manganese dioxide is dissolved and the solution remains distinctly acidic. Colourless crystals of benzoic acid are precipitated. The contents of the beaker are cooled very well. The precipitated crystals are filtered off at the pump. The crystals are washed with a little cold water, dried and weighed.

Recrystallisation:

About one gram of the sample is recrystallised from boiling water and dried.

Report:

The yield of benzoic acid =

1.3 HYDROLYSIS

Aromatic esters and amides can be easily hydrolysed by boiling with aq NaOH solution. On acidification the aromatic acid is precipitated.

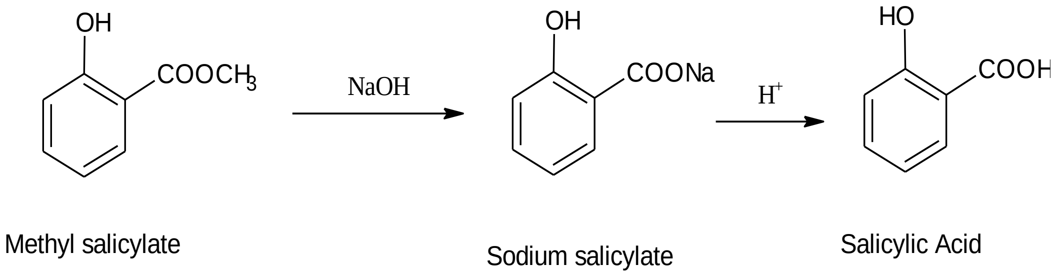
1.3a) PREPARATION OF SALICYLIC ACID FROM METHYL SALICYLATE

Aim:

To prepare a maximum quantity of salicylic acid from methyl salicylate.

Principle:

Methyl salicylate is easily hydrolysed by sodium hydroxide solution and the acid is precipitated by adding hydrochloric acid.



Chemicals Required:

1. Methyl salicylate = 5ml
2. 10% sodium hydroxide solution = 30ml

Procedure:

About 5 ml of methyl salicylate and 30 ml of 10% NaOH solution are placed in R.B. flask. A few porcelain chips are introduced into it. The flask is fitted with a reflex condenser and held in position. It is heated on a wire gauze until no oily drops of methyl salicylate are seen in the R.B. flask. The heating is then discontinued and the flask is cooled.

The contents are poured into a beaker containing 200 ml water and stirred well. About 10 ml of 1:1 HCl solution is added in small quantities at a time till the solution is slightly acidic. It is tested by placing a drop of the solution on a blue litmus paper which turns red.

A white precipitate of salicylic acid is readily formed in the beaker on cooling. It is filtered off using buchner funnel, washed well with water and dried.

Recrystallisation:

About 1g of the salicylic acid is dissolved in boiling water and recrystallised .White crystals of salicylic acid are separated and dried.

Report:

The yield of salicylic acid =

1.3b) BENZOIC ACID FROM ETHYL BENZOATE

Aim:

To prepare a Maximum quantity of Benzoic acid from ethyl benzoate

Principle:

Ethyl benzoate is hydrolysed to sodium benzoate and ethanol when heated with aqueous NaOH solution. From sodium benzoate, benzoic acid is liberated by the addition of a mineral acid like HCl.

$$C_6H_5COOC_2H_5 + NaOH \longrightarrow C_6H_5COO^-Na^+ + C_2H_5OH$$

$$C_6H_5COO^-Na^+ + HCl \longrightarrow C_6H_5COOH\downarrow + NaCl$$

Procedure:

Ethyl benzoate (4ml) and 10% aq. NaOH (25ml) are mixed in a round bottom flask. A bit of broken porcelain is added to prevent bumping. The round bottom flask is fitted with a reflux condenser and heated over a wire-gauze steadily till the oily layer of ester disappears (about 30-45minutes). Then, the contents of the flask are cooled and transferred into a 250ml beaker. The flask is rinsed with about 5ml water and the rinsings are also added to the beaker. To free the benzoic acid from the salt solution, con HCl is added, drop by drop, with constant stirring, till the solution is distinctly acidic (test with litmus paper). Benzoic acid is liberated in the solid form. The contents of the beaker are cooled, and the precipitated benzoic acid is filtered off at the pump. Washed with cold water, dried using filter paper.

Recyrstallisation

About 0.5g of the crude benzoic acid is dissolved in 5ml of boiling water, filtered, poured into a watch glass and allowed to cool slowly. After the crystals are formed the liquid is poured off and the crystals are dried with bits of filter paper.

Report:

The yield of benzoic acid =

1.4 NITRATION

Nitration of an aromatic compound is an example of aromatic electrophilic substitution.

$$HNO_3 + 2H_2SO_4 \rightleftharpoons NO_3^+ + H_3O^+ + 2HSO_4^-$$

Nitronium ion

Nitronium ion acts as electrophile which is obtained from nitric acid. For aromatic compounds containing deactivating groups like – NO_2 and

– SO_3H fuming sulphuric acid or fuming nitric acid is used.

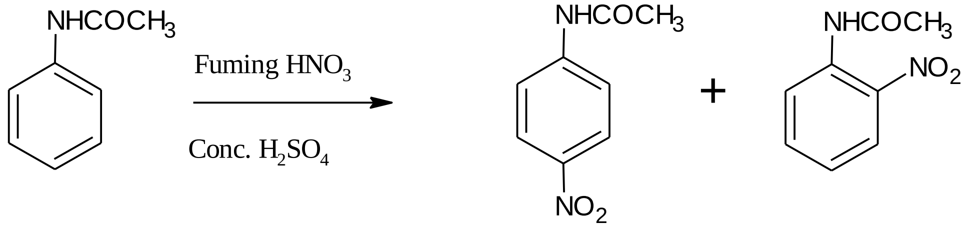
1.4a) p-NITROACETANILIDE FROM ACETANILIDE:

Aim:

To prepare a maximum quantity of p-Nitroacetanilide from Acetanilide.

Principle:

Acetanilide on nitration with con HNO_3 and H_2SO_4 gives para nitro acetanilide as major product.



acetanilide

p-nitroacetanilide (major product)

o-nitroacetanilide (minor product)

Procedure:

Acetanilide (7g) is dissolved in 7ml glacial acetic acid in a conical flask. Con sulphuric acid (15ml) is added very slowly, with constant shaking. The flask is cooled in a freezing mixture of crushed ice and crude common salt. Then, fuming nitric acid (3ml) is added, very slowly with gentle shaking to the flask so that the temperature does not rise above 20^0C. The contents of the flask are shaken vigorously for about an hour. Then, it is poured into cold water in a thin stream, slowly with shaking. The product is allowed to stand for an hour, filtered off at the pump, and then washed with water.

The ortho-isomer obtained as the minor product is removed by stirring the above product with water and adding sufficient amount of sodium carbonate till the liquid portion becomes alkaline to litmus. The mixture is then boiled for a few minutes. The ortho-product undergoes hydrolysis and goes in to solution, but the para-product is not affected and remains in the solid state. This solid is filtered off. Washed with water, dried and the yield is noted.

Recrystallisation:

About 1g of the crude sample is recrystallised from hot rectified spirit.

Report:

The yield of para nitro acetanilide =

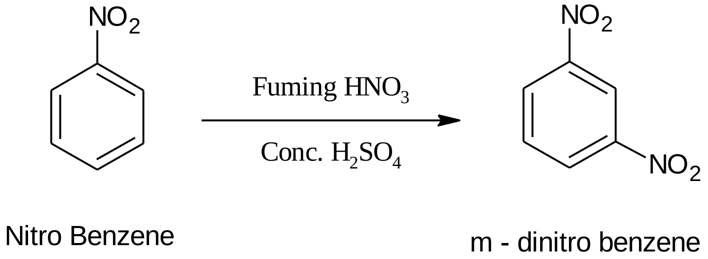
1.4b) PREPARATION OF M-DINITROBENZENE FROM NITROBENZENE

Aim:

To prepare a maximum quantity of meta dinitrobenzene from nitrobenzene.

Principle:

By employing a mixture of fuming nitric acid and concentrated sulphuric acid, the nitrobenzene is converted into meta-dinitrobenzene.



Chemicals Required:

1. Nitrobenzene = 6 ml
2. Fuming nitric acid = 8 ml
3. Conc. H_2SO_4 = 10 ml

Procedure:

In a 250ml RB flask, 8ml of fuming nitric acid is placed. 10ml of conc.H_2SO_4 is slowly added to the flask with constant shaking. After each addition the flask is shaken well and cooled in ice water. A few pieces of porcelain bits are introduced into the RB flask. It is fitted with reflux condenser. The nitrobenzene (6ml) is added in small portions to the mixture in the RB flask with constant shaking. The flask is heated on a water bath for about 30 minutes. To test the completion of the reaction, a drop of the reaction mixture is shaken with cold water taken in a test tube. The formation of a yellow solid shows the reaction is complete. If it is not so, the heating may be continued for some more time. The flask is allowed to cool in air and the contents are poured into 200ml water in a beaker with vigorous stirring. A yellow precipitate of m-dinitrobenzene is obtained. It is filtered at the pump, washed with cold water and dried.

Recrystallisation:

A small portion of the sample is recrystallised from rectified spirit heated on a water bath. The colourless crystals of m-dinitrobenzene are filtered and dried.

Report:

The yield of m-dinitrobenzene =

1.5 BROMINATION

Bromination is an example of electrophilic aromatic substitution. Aromatic compounds containing activating groups like -OH, $-NH_2$ and $-NHCOCH_3$ can easily be brominated when treated with a solution of Br_2 in CH_3COOH.

Liquid Br_2 is highly corrosive. Therefore solution of Br_2 in CH_3COOH can be prepared in bulk and the required amount can be added from a burette.

1.5a) PREPARATION OF P-BROMOACETANILIDE FROM ACETANILIDE

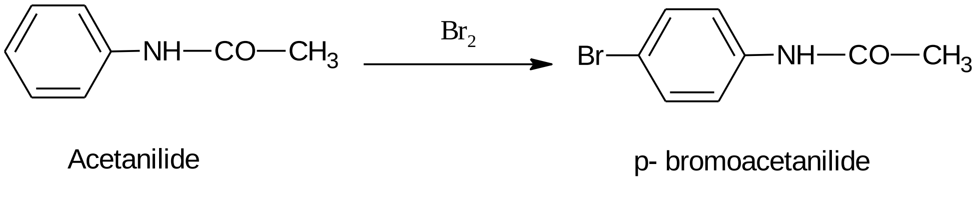
Aim:

To prepare a maximum quantity of P-bromoacetanilide from acetanilide.

Principle:

Primary amines do not yield monosubstituted products by direct reaction with reagents such as bromine (or) nitrating mixture.

When the amino group is protected as in the case of acetanilide, the substitution reaction readily occurs with bromine. Acetanilide produces p-bromoacetanilide as the main product. Though a little amount of ortho-isomer is formed, it is easily converted into the para isomer on recrystallisation.



Chemicals Required:

1. Acetanilide = 7g
2. Acetic acid (Glacial) = 25ml
3. Bromine in glacial acetic acid = 3ml of Br_2 in 13ml of acetic acid

Procedure:

About 7g of finely powdered acetanilide is dissolved in 25ml of glacial acetic acid in a R.B. flask. In another conical flask, 3ml of bromine liquid is dissolved in 13ml of acetic acid and transferred into a burette or a separating funnel. The bromine solution is added slowly into the R.B. flask containing acetanilide and shaken well to make thorough mixing. The flask may be cooled in ice cold water. When all the bromine has been added, the solution will have an orange colour due to excess of bromine. The R.B. flask is well shaken and the contents are poured into a beaker containing 200ml water. A little amount of sodium bisulphite is added to remove the orange colour. The precipitated p-bromoacetanilide is filtered at the pump using Buchner funnel and dried.

Recrystallisation:

A small amount of the crude acetanilide is dissolved in a dilute solution of alcohol and recrystallised. Colourless crystals of

p-bromoacetanilide are separated and dried.

Report:

The yield of p-bromoacetanilide =

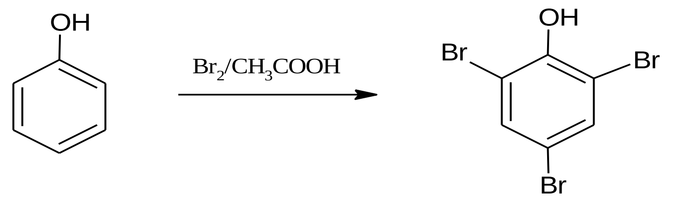
1.5b) 2,4,6 – TRIBROMO PHENOL FROM PHENOL:

Aim:

To prepare a maximum amount of 2,4,6 – tribromo phenol from phenol.

Principle:

Phenol when treated with an excess of bromine in glacial acetic acid, gives symmetrical tribromo phenol .



phenol 2,4,6 - tribromophenol

Chemicals required:

1. Phenol - 2ml
2. Glacial acetic acid - 5ml
3. Bromine in glacial acetic acid - 13ml

Procedure:

Phenol is dissolved in about 5ml of glacial acetic acid in a conical flask fitted with a cork. A solution of bromine in glacial acetic acid (3ml bromine in 10ml glacial HOAc) is taken in a boiling test tube. Using a dropper, about 1ml of bromine in acetic acid is added at a time to the contents of the flask and shaken well. The addition of bromine is continued till the colour of the solution in the flask becomes yellow. The flask is corked well and shaken vigorously for about 10-15 minutes. About 100ml of cold water is then added to the conical flask, and the mixture is shaken vigorously for two minutes. Colourless crystals of tribromo phenol that separateout are filtered off at the pump, washed with water, dried and weighed.

Recrystllisation:

About 1g of crude sample is recrystallized from hot 1:1 aqueous alcohol.

Report:

The yield of tribromo phenol =

1.6 BENZOYLATION (SCHOTTEN-BAUMANN REACTION)

Aromatic amines and phenols undergo Benzoylation. Benzoyl chloride is the reagent used. Benzoylation proceeds smoothly and the benzoyl derivative separates as a solid. NaOH is used to remove HCl formed in the reaction and also it hydrolyses excess of benzoyl chloride.

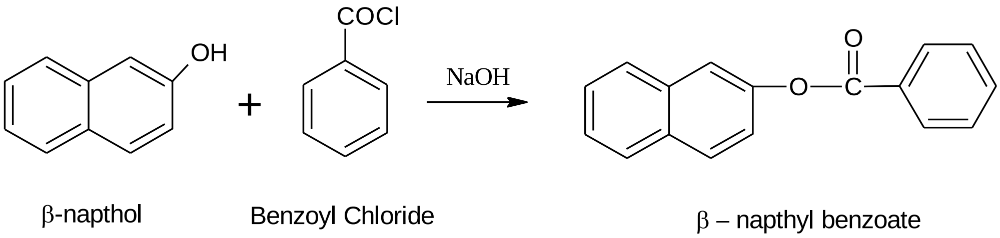
1.6a) PREPARATION OF β -NAPHTHYL BENZOATE FROM β -NAPHTHOL

Aim:

To prepare a maximum quantity of β-naphthyl benzoate from β-naphthol.

Principle:

In basic solution, β-naphthol is benzoylated using benzoyl chloride. This reaction is called Schotten Baumann reaction.



Chemicals Required:

1. β -Naphthol = 2g
2. 10% sodium hydroxide = 50ml
3. Benzoyl Chloride = 3ml

Procedure:

In a RB flask 50ml of 10% NaOH is taken. To this 2g of β-naphthol is added and dissolved in it. Then 3ml of benzoyl chloride is added to the flask and mouth is closed by a cork. The flask is shaken well for about 30 minutes. If there is smell of benzoyl chloride, some more NaOH is added and shaken well. Then the reaction mixture is transferred to a beaker containing about 200ml of water. Light brown β-naphthyl benzoate separates out. It is filtered and washed with NaOH solution first and then with water and dried.

Recrystallisation:

A portion of it is recrystallised from alcohol and dried.

Report:

The yield of β-naphthyl benzoate =

1.7 DIAZOTIZATION

It is a process of converting aromatic primary amines to diazonium salts using aq solution of $NaNO_2$ and HCl at 0 - 5 °C. The diazonium salt formed couples with aromatic amines to give azo dyes.

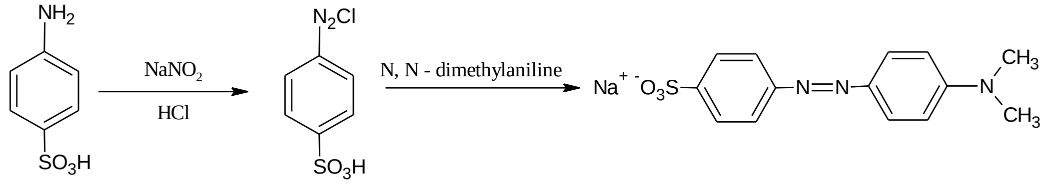
1.7a) METHYL ORANGE FROM SULPHANILIC ACID

aim:

To prepare a maximum quantity of methyl orange from sulphanilic acid.

Principle:

Methyl orange is prepared by coupling diazotised sulphanilic acid with N, N dimethyl aniline in the presence of excess hydrochloric acid.



Chemicals required:

1	Sulphanilic acid	3g
2	Anhydrous sodium carbonate	1g
3	Sodium nitrite	1g
4	Dimethyl aniline	2ml
5	Sodium chloride	8g
6	Con.HCl	3ml
7	NaOH (20% solution)	15ml
8	NaCl	8g
9	Rectified spirit	20ml

Procedure:

The sodium carbonate is dissolved in 50ml of water and sulphanilic acid is added and dissolved by boiling the solution. The mixture is cooled in ice and sodium nitrite in water is added to the content. To the ice cold solution, conc hydrochloric acid is added drop by drop with constant stirring and the temperature being maintained between 0 to 5 °C. To the diazotised solution, an ice cold solution of dimethyl aniline in 10ml dilute hydrochloric acid is added with continuous stirring. The solution is made alkaline by adding 15ml of 20% sodium hydroxide solution and the dye is salted out by adding sodium chloride. The mixture is heated to boiling, cooled in an ice bath. The orange coloured dye is filtered, washed with little ethanol and dried.

Report:

The yield of methyl orange dye =

UNIT – II

GRAVIMETRIC ANALYSIS

2.0 Introduction:

Gravimetric analysis is a type of quantitative analysis based on the process of weighing. This involves converting the element or radical to be determined into a pure stable compound of known composition, which can be readily converted into a form suitable for weighing. From its weight, the weight of the element or radical is calculated. Normally the constituent being determined is precipitated from a solution in a form which is slightly soluble so that no appreciable loss occurs when the precipitate is separated by filtration and weighed.

Apparatus used in Gravimetric Analysis:

The following types of apparatus are commonly used in gravimetric analysis.

Crucibles:

The crucibles used for collecting and weighing the precipitate are of two types (i) Crucibles made of silica which are used when the precipitates are ignited to constant weight. (ii) Sintered crucibles are used for the precipitates which are weighed after drying in air oven.

Silica crucibles:

These crucibles are made up of fused silica. Even though these are explosive, they are preferred over porcelain crucible because (i) they can be safely exposed to sudden change in temperature without any risk of fracture; (ii) they are not attacked by acids even at high temperatures. (Exception HF and H_3PO_4)

Precaution in using Crucibles:

1. The crucible should be thoroughly washed, cleaned, dried and ignited before use.
2. Any stain on the surface of the crucible or lid is removed by immersing the crucible in an acidified concentrated solution of $K_2Cr_2O_7$ and then washed. A little dil.HNO_3 added to the crucible before washing. If the stain still persists, the crucible surface is rubbed with moist sand, washed, dried wiping with filter paper and then heated on a low non-luminous flame at first. The flame is then gradually raised into its full length. Heating is continued for further 5 to 10 minutes. If the stain still persists then it has become a part of the crucible and it is now harmless. All these operations are known as Tarring of Crucibles.

3. A tarred crucible is always handled by a pair of tongs. The crucible should not be touched with fingers as moisture and dust from the fingers will stick to it and make heavier.
4. A non-luminous flame must be used to heat the crucible.
5. Wet crucible should not be placed on flame as it will crack.

Clay-pipe Triangle:

It is used for supporting crucibles during the process of heating on a burner. It is formed by passing three pieces of iron wires through small lengths of heat resisting clay tubes and then twisting the ends to form a triangle. It can be attached to the stand by bending the wire ends round.

Desiccator:

It is a covered glass container designed for cooling crucibles in a dry atmosphere. In the lower part it carries a drying agent like anhydrous $CaCl_2$ or dry lime or Conc.H_2SO_4. The crucible to be kept in desiccators is placed on a porcelain disc having holes of suitable size. The ground glass rims of the desiccators and that of its cover are lightly coated with Vaseline to make it air tight.

Care and use of the Desiccator:

1. The desiccators must be kept covered except when actually placing or removing the crucible.
2. Before placing a hot crucible in the desiccator, the former should be cooled for a while and then transferred into the latter.
3. To open a desicctor, it is held firmly on the table with left hand, the knob of the cover is held by right hand and pulled aside by sliding it in sideways.
4. If necessary, the cover should be placed on the table with its greased surface pointing upwards.
5. For replacing the cover, its rim is allowed to slide over the rim of the jar gently.
6. The desiccators must be held firmly with both hands while carrying it to the balance room and returning it to the table.

Filter paper (Whatmann):

When there is a necessity for high temperature ignition and the precipitate not reduced by carbon, the use of filter papers is most sought after. The quantitative filter papers employed must be practically ash free. Whatmann filter papers are widely used in most of the laboratories. Whatmann No. 41 with very loose texture gives very fast filtration and is best suited for coarse and gelatinous precipitates like $Al(OH)_3$ and $Fe(OH)_3$. Whatman No. 40 with moderately open texture, gives fairly rapid filtration and is suited for majority of precipitates like calcium oxalate, AgCl, etc., Whatmann No.42 with very close texture is used for filtering very fine precipitates like $BaSO_4$.

Filter Crucibles – Sintered Glass Crucible:

Sintered glass crucible is made of a resistance glass like pyrex or borosil glass and has a porous disc of sintered, ground glass fused in the body of the crucible, few millimeter above the lower end. The filter disc is available in different degrees of porosity. No.4 porosity is suitable for very fine precipitates, while No. 3 precipitates of medium particle size. A crucible with 30ml capacity is most widely used.

Sintered crucibles have many advantages. (i) Since they are made of glass, are resistant to most of the reagents except HF and hot alkalis (ii) They can be conveniently handled and are readily cleaned. (iii) They can be dried to a constant weight at 100-150^{0}C.

Experimental techniques in gravimetric analysis:

The various operations involved in the gravimetric estimation of an element or radical are (i) Precipitation, (ii) Digestion, (iii) Filtration and washing and (iv) Drying and ignition.

Precipitation:

It is the process of converting a soluble substance into an insoluble precipitate. It is usually carried out in a 400 ml beaker of high resistance glass (pyrex or borosil) provided with a glass cover and a glass rod for stirring. The conditions of precipitation differ from case to case. In general, the following points must be remembered during a precipitation process.

1. Precipitation should be carried out in solutions with supersaturation as low as possible, since particle size is related to supersaturation.
2. Care should be taken to avoid co-precipitation and post-precipitation. Co-precipitation is the phenomenon by which normally soluble substances are taken up by the precipitate and post-precipitation is the phenomenon in which the impurity in the form of sparingly soluble compound is precipitated on the surface of the precipitate after its formation.

   To reduce the effects of supersaturation, co-precipitation and post-precipitation and to obtain better results, the following conditions must be effected or followed:

1. The solution from which the radical is to be precipitated and that of the precipitant (i.e., the reagent added for precipitation) should be in a moderately dilute form.
2. Both or at least one of the two solutions should be heated to almost boiling before precipitation, i.e., the precipitation should be effected in hot solution only.
3. The precipitant should be added slowly in a thin stream with stirring and without splashing. This is achieved by allowing the reagent to flow down the sides of the beaker or along the glass rod used for stirring.
4. Only a moderate excess of the reagent is to be added, as excess reagent may redissolve the precipitate formed and also make the washings during filtration a tedious process.
5. Solutions should never be boiled during precipitation.
6. Precipitations should be done is scratch free beakers, as precipitate that gets lodged in scratches may be lost introducing serous error.
7. After adding the required amount of the precipitating reagent, the precipitate must be allowed to settle. To check whether the precipitation is complete, few drops of the precipitant are added to the supernatant liquid, if there is no turbidity, then the precipitation is complete.

Digestion:

Most precipitates require digestion before filtration. Digestion is usually carried out on a water bath or on a hot plate or even using low flame if there is no bumping. During digestion process, the precipitate is kept in contact with the liquid from which it was formed. Digestion reduces the amount of absorbed impurities and makes the precipitate more granular, a form which can be easily filtered.

Filtration and Washing:

During the process of filtration the precipitate is separated from the mother liquor. Washing is done to remove the last traces of mother liquor from the precipitate.

A precipitate should not be allowed to remain in unwashed condition for a long time, as the mass will crack and cake together. Then it will be virtually impossible to wash it free of soluble impurities.

Drying and Ignition of the Precipitate:

The precipitate after washing must be obtained in a dry state suitable for weighing. In some cases the precipitate obtained need to be ignited to produce another compound, which is suitable for weighing. To dry the precipitate obtained on the filter paper, the funnel along with the filter paper and its contents is placed in a hot air oven maintained at a temperature between 100^0 and 105^0C. To avoid any contamination the funnel may be covered using a cover glass. The funnel should be kept in the air oven till the precipitate and the paper are completely dried.

For drying the precipitate in a sintered crucible, the crucible is removed from the adapter, covered with cover glass, placed in a 100 ml beaker and then kept in a hot air oven maintained at the required temperature, till the precipitate dries completely.

Common Errors:

The following is a list of errors common to all gravimetric estimations.

1. Incomplete and improper precipitation, i.e., adding too little or too large volume of the precipitant rapidly to the solution of the radical to be determined.
2. Incomplete washing and using unnecessarily large amount of wash liquid.
3. Careless handling leading to the loss of some of the precipitate during filtration and washing.
4. Defective ignition of the precipitate leading to its reduction or change in the composition.
5. Errors in weighing the crucible with or without the precipitate.

The condition of the experiment should be suitably designed so as to reduce these errors to the minimum.

Calculation:

Weight of empty crucible (W_1) =

Weight of crucible + $BaCl_2.2H_2O$ (W_2) =

Weight of $BaCl_2.2H_2O$ (W_2 - W_1) (A) =

Weight of silica crucible + anhydrous $BaCl_2$ (W_3) =

Weight of anhydrous $BaCl_2$ (W_3 - W_1) (B) =

weight of water (A–B) =

Percentage of water $\frac{A-B}{A}\times 100$ =

2.1 ESTIMATION OF WATER OF HYDRATION IN CRYSTALLINE BARIUM CHLORIDE

Aim:

To estimate the percentage of water of hydration in crystalline barium chloride.

Principle:

When hydrated barium chloride is heated, it loses its water of crystallization and a residue of anhydrous barium chloride is left behind.

$$BaCl_2.2H_2O \xrightarrow{\Delta} BaCl_2 + 2\,H_2O$$

A known weight of Barium chloride crystals are heated and the weight of anhydrous salt determined. From the results the percentage of water is calculated.

Procedure:

A porcelain or silica crucible is heated to dull redness over a clay pipe triangle for about 15 minutes. While heating the crucible, a non-luminous flame is to be used. At first, the crucible is heated by waving the flame under it and later it is strongly heated. After heating, the crucible is removed to a desiccator, allowed to cool for about half an hour and weighed.

About one gram of hydrated barium chloride is introduced in it and the crucible is again weighed. It is then heated strongly, keeping the lid slightly titled to one side for the water vapour to escape. Heating is continued for half an hour. The crucible and anhydrous $BaCl_2$ are then cooled in a desiccator and weighed. Heating, cooling and weighing are repeated till the weight becomes constant. A duplicate is conducted.

Result:

The percentage of water of hydration in crystalline Barium chloride

CRUCIBLE: I

Calculation:

Weight of crucible + lid (W_1) =

Weight of crucible + lid + $BaSO_4$ (W_2) =

Weight of $BaSO_4$ (W_2 - W_1) =

233.24g of $BaSO_4$ contains 137.34g of barium

Weight of barium in (W_2 - W_1)g of $BaSO_4$ = 0.5886 x (W_2 - W_1)

=

Weight of barium present in the whole of the given solution (100ml) $\Big\}$ = 0.5886 x $(W_2 - W_1)$ x 5

=

2.2 ESTIMATION OF BARIUM AS BARIUM SULPHATE

Aim:

To estimate the amount of barium present in the whole of the given barium chloride solution.

Principle:

The solution is made up to a definite volume. A measured volume of it is then treated with dilute K_2SO_4 and the barium is precipitated as $BaSO_4$.The precipitated $BaSO_4$ is filtered and weighed. From the weight of $BaSO_4$, the weight of barium present in the whole of the given solution is calculated.

$$BaCl_2 + K_2SO_4 \rightarrow BaSO_4 \downarrow + 2KCl$$

Procedure:

The given $BaCl_2$ solution is made up to 100ml in a standard flask.20ml of the solution is pipetted out into a 250ml beaker, diluted to about 150ml, 5ml of pure dilute HCl is added. The solution is heated to boiling. To the boiling solution about 15ml of 5% K_2SO_4 is added drop by drop stirring the solution continuously, till the precipitation is complete. The mixture is boiled for few more minutes to make the precipitate granular.

The liquid is then allowed to cool and settle. The clear supernatant liquid is tested for complete precipitation by adding a few drops of K_2SO_4 along the side of the beaker. Formation of turbidity at the point where the K_2SO_4 meets the clear liquid indicates incomplete precipitation. Then more K_2SO_4 is to be added till the precipitation is complete.

The solution is filtered by decantation through filter paper (whatman no.40). The precipitate is thoroughly washed with small quantities of hot distilled water till the washings does not give a precipitate with $BaCl_2$ (free

CRUCIBLE: II

Calculation:

Weight of crucible + lid (W_1) =

Weight of crucible + lid + $BaSO_4$ (W_2) =

Weight of $BaSO_4$ ($W_2 - W_1$) =

233.24g of $BaSO_4$ contains 137.34g of barium

Weight of barium in ($W_2 - W_1$)g of $BaSO_4$ = 0.5886 x ($W_2 - W_1$)

=

Weight of barium present in the whole
of the given solution (100ml) } = 0.5886 x ($W_2 - W_1$) x 5

=

from sulphate). The precipitate is then transferred completely into the filter paper.

Any particles sticking to the sides of the beaker are removed by a policeman rod. Finally the precipitate in the filter is washed once again. After the water has completely drained off, the funnel is kept in the air oven for drying.

When dry, the paper is removed from the funnel and folded in the form of a packet so as to enclose the precipitate taking special care not to previously heated to constant weight. tear the paper. The packet is placed point down in a crucible which is The crucible is then mounted on a clay pipe triangle loosely covered by the lid and heated by a low flame. When all the moisture has been expelled, the flame is increased slightly so as to slowly carbonise the paper. The paper should not be allowed to inflame as it may cause the expulsion of fine particles of the precipitate owing to the rapid escape of the products of combustion. If by chance, the paper inflames, the flame is extinguished by momentarily closing the crucible with lid.

When the charring of the paper is complete the temperature is raised to dull redness and all the carbon burnt off with free access of air. The crucible is then cooled and the residue moistened with a drop of dil.H_2SO_4 to convert any sulphide formed to sulphate. The crucible is then heated till no more fumes are evolved. It is then maintained at red hot for 15 minutes.

If there is any deposit of carbon on the lid, it should be heated separately by holding it in the flame with a pair of tongs. The crucible and lid are then allowed to cool in a desiccator till the weight becomes constant.

From the weight of $BaSO_4$, the weight of barium in the whole of the given solution can be calculated. A duplicate is also conducted.

Result:

The weight of barium present in the
whole of the given solution =

CRUCIBLE: I

Weight of empty sintered crucible (W_1) =

Weight of sintered crucible with Barium chromate precipitate } W_2 =

Weight of Barium chromate $W_2 - W_1$ =

253.34g of $BaCrO_4$ contains 137.34g of barium

Weight of barium present in ($W_2 - W_1$) g of $BaCrO_4$ = 0.5421x ($W_2 - W_1$)

=

Weight of barium present in the whole of the given solution (100ml) } = 0.5421x ($W_2 - W_1$) x 5

=

2.3 ESTIMATION OF BARIUM AS BARIUM CHROMATE

Aim:

To estimate the amount of barium present in the whole of the given $BaCl_2$ solution by precipitating it as barium chromate.

Principle:

Barium is precipitated as barium chromate in acetic acid medium by the addition of potassium chromate. The precipitated barium chromate is filtered in a sintered glass crucible, washed, dried at 120°C and weighed as barium chromate.

$$BaCl_2 + K_2CrO_4 \rightarrow BaCrO_4 + 2KCl$$

Procedure:

The given barium chloride solution is made upto 100ml in a standard flask. Exactly 20ml of this made up solution is pipetted out into a clean 250ml beaker. Exactly 1ml of 6M acetic acid and 10ml of 3M ammonium acetate are then added and the solution is diluted to 100ml with distilled water. The solution is heated to boiling in a water bath and to the hot solution 15-20ml of 5% potassium chromate solution is added slowly with constant stirring. The heating is continued for further 15minutes and the precipitate is allowed to settle. The clear supernatant liquid must be yellow in colour. A little more 5% K_2CrO_4 solution is added down the sides of the beaker into the supernatant liquid to test the completion of precipitation. When there is no turbidity, the precipitation is complete.

The clear solution is filtered in a previously weighed crucible. The precipitate is washed with hot water and the washings are also filtered and filtration is continued till the filtrate is free from chloride and chromate ions (tested with $AgNO_3$ and $BaCl_2$ solution). The precipitate is then completely transferred into the sintered crucible. Any precipitate adhering to the sides of

CRUCIBLE: II

Weight of empty sintered crucible (W_1) =

Weight of sintered crucible with Barium chromate precipitate } W_2 =

Weight of Barium chromate $W_2 - W_1$ =

253.34g of $BaCrO_4$ contains 137.34g of barium

Weight of barium present in ($W_2 - W_1$) g of $BaCrO_4$ = 0.5421x ($W_2 - W_1$)

=

Weight of barium present in the whole } =

of the given solution (100ml) 0.5421x $(W_2 – W_1)$ x 5

=

the beaker is removed using policeman rod. When filtration is complete, 4 drops of ethanol are added to the precipitate and allowed to drain off.

The crucible is then dried at 120 °C for an hour in an air oven. It is then cooled in a desiccator and when quite cold it is weighed. The heating, cooling and weighings are repeated to constant weight. A duplicate experiment is conducted simultaneously.

From the weight of barium chromate precipitate, the amount of barium present in the whole of the given solution can be calculated.

Result:

The weight of barium present in the

whole of the given solution =

CRUCIBLE: I

Calculation:

Weight of sintered glass crucible (W_1) =

$$\left.\begin{matrix}\text{weight of sintered glass crucible} + \\ \text{Lead chromate preciptate}\end{matrix}\right\} \square\ \square W_2) =$$

Weight of Lead Chromate = $(W_2\text{-}W_1)$ =

323.21g of lead chromate contains 207.21 g of lead.

$$\left.\begin{matrix}\text{Weight of Lead present in} \\ (W_2 - W_1)\text{g of lead Chromate}\end{matrix}\right\} = 0.6411 \text{ x } (W_2\text{-}W_1)$$

=

$$\left.\begin{matrix}\text{weight of lead present in the} \\ \text{whole of the given solution (100ml)}\end{matrix}\right\} = 0.6411 \text{ x } (W_2\text{-}W_1) \text{ x } 5$$

=

CRUCIBLE: II

Calculation:

Weight of sintered glass crucible (W_1) =

$$\left.\begin{matrix}\text{weight of sintered glass crucible} + \\ \text{Lead chromate preciptate}\end{matrix}\right\} \square\ \square W_2) =$$

Weight of Lead Chromate = $(W_2\text{-}W_1)$ =

323.21g of lead chromate contains 207.21 g of lead.

$$\left.\begin{array}{l}\text{Weight of Lead present in}\\ (W_2 - W_1)\text{g of lead Chromate}\end{array}\right\} = 0.6411 \text{ x } (W_2 - W_1)$$

=

$$\left.\begin{array}{l}\text{weight of lead present in the}\\ \text{whole of the given solution (100ml)}\end{array}\right\} = 0.6411 \text{ x } (W_2 - W_1) \text{ x } 5$$

=

2.4 ESTIMATION OF LEAD AS LEAD CHROMATE

Aim:

To estimate the amount of lead present in the whole of the given lead acetate solution by precipitating it as lead chromate.

Principle:

Lead is precipitated as $PbCrO_4$ by adding potassium chromate solution.

$$Pb(CH_3COO)_2 + K_2CrO_4 \rightarrow PbCrO_4 + 2CH_3COOK$$

The lead chromate is separated and weighed as such. From the weight of $PbCrO_4$, the weight of lead is calculated.

Procedure:

The given solution is diluted to 100ml in a standard flask. 20ml of the solution is pipetted out into a beaker and NH_4OH is added drop by drop till a permanent pink colour is formed. Dilute CH_3COOH is then added to make the solution slightly acidic. It is then diluted to 125 ml and heated to boiling. To the hot solution a 4% solution (about 10 ml) of Potassium chromate is added slight excess with constant stirring. The mixture is then boiled for 5 to 10- minutes to make the precipitate granular. The precipitate is then allowed to settle. The supernatant liquid must be coloured slightly yellow. This indicates that the K_2CrO_4 solution is sufficient. The precipitate is then filtered using a previously dried and weighed sintered glass crucible. It is washed with hot water dried at 120^0C, cooled and weighed. Heating cooling and weighings are repeated to get constant weight.

A duplicate is conducted. From the weight of $PbCrO_4$, the weight of lead in the whole of the given solution can be calculated.

Result:

The amount of lead present in the whole of the given solution =

CRUCIBLE: I

Calculation:

Weight of Empty sintered crucible (W_1) =

$$\left.\begin{array}{l}\text{weight of sintered crucible} + \\ \text{Calcium Oxalate monohydrate}\end{array}\right\} \square W_2) =$$

Weight of Calcium Oxalate monohydrate (W_2-W_1) =

146.1g of l Calcium Oxalate monohydrate contains 40.08g of Calcium.

$$\left.\begin{array}{l}\text{Weight of Calcium present in} \\ (W_2 - W_1)\ \text{g of } CaC_2O_4.H_2O\end{array}\right\} = 0.2744 \text{ x } (W_2\text{-}W_1)$$

=

$$\left.\begin{array}{l}\text{weight of Calcium present in the} \\ \text{whole of the given solution (100ml)}\end{array}\right\} = 0.2744 \text{ x } (W_2\text{-}W_1) \text{ x } 5$$

=

2.5 ESTIMATION OF CALCIUM AS CALCIUM OXALATE MONOHYDRATE

Aim:

To estimate the amount of calcium present in the whole of the given calcium chloride solution by precipitating it as calciumoxalate monohydrate.

Principle:

Calcium is precipitated as calcium oxalate by treating the hot calcium chloride solution with ammonium oxalate solution and slowly neutralized with ammonia. Calcium oxalate is filtered, washed and dried at 105^0C to constant weight and weighed as calcium oxalate monohydrate.

$$CaCl_2 + (NH_4)_2(C_2O_4) \rightarrow CaC_2O_4 \downarrow + 2NH_4Cl$$

Procedure:

The given calcium salt solution is made upto 100ml in a standard flask. Exactly 20ml of this solution is pipetted out into a clean 400ml beaker. A drop of methyl orange indicator is added. Then NH_4OH is added in drops till the pink colour just turns yellow. About 5ml of dil HCl is added. The solution is diluted to 100ml with distilled water and then heated to boiling.

To the hot solution about 20ml of saturated ammonium oxalate is added slowly in drops with stirring. Then ammonium hydroxide solution is added until the solution is distinctly alkaline (Shown by distinct ammonia smell).

The heating is then continued for another half an hour over a flame for the digestion of the precipitate. The precipitate is allowed to settle and the supernatant liquid is tested for completeness of precipitation by adding a little ammonium oxalate along the sides of the beaker.

CRUCIBLE: II

Calculation:

Weight of Empty sintered crucible (W_1) =

$$\left.\begin{array}{l}\text{weight of sintered crucible} + \\ \text{Calcium Oxalate monohydrate}\end{array}\right\} \quad \square W_2) =$$

Weight of Calcium Oxalate monohydrate (W_2-W_1) =

146.1g of l Calcium Oxalate monohydrate contains 40.08g of Calcium.

$$\left.\begin{array}{l}\text{Weight of Calcium present in} \\ (W_2 - W_1)\ \text{g of } CaC_2O_4.H_2O\end{array}\right\} = 0.2744 \text{ x } (W_2\text{-}W_1)$$

=

$$\left.\begin{array}{l}\text{weight of Calcium present in the} \\ \text{whole of the given solution (100ml)}\end{array}\right\} = 0.2744 \text{ x } (W_2\text{-}W_1) \text{ x } 5$$

=

A sintered crucible is washed, dried at 105^0C and weighed. The clear supernatant liquid is first transferred and precipitate is washed thoroughly (5 to 6 times) with dil.ammonium oxalate (1%) solution and the washings are filtered by decantation.

Washing is continued till the filtrate does not show the presence of chloride when tested with $AgNO_3$ containing a little HNO_3. The whole of the precipitate is transferred to the crucible and allowed to drain. The precipitate is then dried in an air oven at 105^0-110^0C. It is then cooled in a desiccator and weighed. Heating, cooling and weighings are continued till constant weight is obtained. From the weight of calcium oxalate monohydrate precipitate, the weight of calcium can be calculated. A duplicate experiment is conducted simultaneously.

Result:

The amount of calcium present in the

whole of the given solution =

CRUCIBLE: I

Calculation:

Weight of Empty sintered crucible (W_1) =

$\left.\begin{array}{l}\text{weight of sintered crucible} + \\ \text{Silver Chloride precipitate}\end{array}\right\}$ □ □W_2) =

Weight of Silver chloride precipitate (W_2-W_1) =

143.32g of Silver Chloride contains 35.45g of Chloride.

$\left.\begin{array}{l}\text{Weight of Chloride present in} \\ \quad (W_2 - W_1)\text{ g of AgCl precipitate}\end{array}\right\}$ = 0.2473 x (W_2-W_1)

=

$\left.\begin{array}{l}\text{weight of Chloride present in the} \\ \text{whole of the given solution (100ml)}\end{array}\right\}$ = 0.2473 x (W_2-W_1) x 5

=

2.6 ESTIMATION OF CHLORIDE AS SILVER CHLORIDE

Aim:

To estimate the amount of chloride present in the whole of the given solution as silver chloride.

Principle:

Chloride ion is precipitated as silver chloride with excess of $AgNO_3$ in the presence of dilute nitric acid. The precipitated silver chloride is filtered, washed in diminished light conditions.

$$KCl + AgNO_3 \rightarrow AgCl\downarrow + KNO_3$$

Procedure:

The given chloride solution is made upto 100 ml in a standard flask. Exactly 20ml of this solution is pipetted out into a clean beaker provided with a cover glass and a glass rod. The beaker and cover glass should be covered with thin brown or black paper. About 5 ml of dil.HNO_3 is added and the solution is diluted to 100ml with distilled water. To the cold solution about 20 ml of 0.1N $AgNO_3$ is added drop by drop with constant stirring. The addition is to be continued till the precipitate coagulates and settles down. The beaker is placed over a water bath and heated gently for half an hour. The supernatant liquid is tested for completion of precipitation by adding little silver nitrate solution along the sides of the beaker.

The solution is filtered by decantation through a previously weighed sintered glass crucible, covered with brown or black paper. The precipitate is washed with water containing little dilute nitric acid. Washing is continued till the filtrate gives no precipitate when tested with dilute hydrochloric acid.

CRUCIBLE: II

Calculation:

Weight of Empty sintered crucible (W₁) =

$$\left.\begin{array}{l}\text{weight of sintered crucible} + \\ \text{Silver Chloride precipitate}\end{array}\right\} \square \qquad \square W_2) =$$

Weight of Silver chloride precipitate $(W_2\text{-}W_1)$ =

143.32g of Silver Chloride contains 35.45g of Chloride.

$$\left.\begin{array}{l}\text{Weight of Chloride present in} \\ \quad (W_2 - W_1)\text{ g of AgCl precipitate}\end{array}\right\} = 0.2473 \text{ x } (W_2\text{-}W_1)$$

=

$$\left.\begin{array}{l}\text{weight of Chloride present in the} \\ \text{whole of the given solution (100ml)}\end{array}\right\} = 0.2473 \text{ x } (W_2\text{-}W_1) \text{ x } 5$$

=

The precipitate is then transferred into the sintered crucible and any particles adhering to the sides of the beaker and glass rod are removed using a policeman. The crucible is then dried in an air oven at 130^0C for one hour. It is then cooled in a desiccator and weighed.

Heating, cooling and weighings are repeated till constant weight is obtained. A duplicate experiment is conducted simultaneously.

Result:

The amount of chloride present in
the whole of the given solution =

CRUCIBLE: I

Calculation:

Weight of crucible + lid (W_1) =

Weight of crucible + lid + $BaSO_4$ (W_2) =

Weight of $BaSO_4$ (W_2-W_1) =

233.34g of barium sulphate contains 96g of sulphate

$$\left.\begin{array}{c}\text{Weight of Sulphate present in}\\ (W_2 - W_1)\text{ g of }BaSO_4\end{array}\right\} = 0.4114 \times (W_2-W_1)$$

=

$$\left.\begin{array}{l}\text{Weight of sulphate present in the}\\ \text{whole of the given solution (100ml)}\end{array}\right\} = 0.4114 \times (W_2-W_1) \times 5$$

=

CRUCIBLE: II

Calculation:

Weight of crucible + lid (W_1) =

Weight of crucible + lid + $BaSO_4$ (W_2) =

Weight of $BaSO_4$ (W_2-W_1) =

233.34g of barium sulphate contains 96g of sulphate

$$\left.\begin{array}{c}\text{Weight of Sulphate present in}\\ (W_2 - W_1)\text{ g of }BaSO_4\end{array}\right\} = 0.4114 \times (W_2-W_1)$$

=

$$\left.\begin{array}{l}\text{Weight of sulphate present in the}\\ \text{whole of the given solution (100ml)}\end{array}\right\} = 0.4114 \times (W_2-W_1) \times 5$$

=

2.7 ESTIMATION OF SULPHATE AS BARIUM SULPHATE

Aim:

To estimate the amount of Sulphate present in the whole of the given solution as Barium Sulphate.

Principle:

Sulphate is estimated by precipitating it as barium sulphate by adding barium chloride solution in presence of dilute hydrochloric acid. The precipitate is filtered, washed, dried and weighed. From the weight of barium sulphate, the weight of sulphate in the whole of the given solution is calculated.

$$CuSO_4 + BaCl_2 \rightarrow BaSO_4 \downarrow + CuCl_2$$

Procedure:

The given sulphate solution is made upto 100ml. 20ml of this solution is pipetted out into a clean beaker. It is diluted to 100ml. About 5ml of dilute hydrochloric acid is added. The resulting solution is heated to boiling. To the boiling solution, a hot solution of $BaCl_2$ is added drop by drop and it is further boiled for about 5 minutes. The mixture is then cooled and tested for complete precipitation. It is filtered through quantitative filter paper and washed (free of chloride) with hot water (Tested with $AgNO_3$).

The precipitate is dried in an air oven and ignited along with the filter paper. It is cooled, one drop of dilute H_2SO_4 is added and is carefully heated, it is cooled in a desiccator and the weight of the crucible is found.

Heating, cooling and weighings are repeated till concordant values are obtained. A duplicate is conducted. From the weight of barium sulphate, weight of sulphate is calculated.

Result:

$$\left.\begin{array}{r}\text{The amount of sulphate present in the}\\ \text{whole of the given solution}\end{array}\right\} =$$

CRUCIBLE: I

Calculation:

Weight of empty sintered crucible (W_1 g) =

$$\left.\begin{array}{l}\text{weight of sintered crucible} + \\ \text{Nickel complex}\end{array}\right\}$$ □W_2 g) □□

Weight of nickel dimethyl glyoxime complex (W_2-W_1) g =

288 g of nickel dimethyl glyoxime complex contains 58g of Nickel.

$$\left.\begin{array}{l}\text{Weight of Nickel present in} \\ \quad (W_2 - W_1)\text{ g of nickel dimethyl glyoxime complex}\end{array}\right\} = 0.2034 \times (W_2 - W_1)\text{ g}$$

=

$$\left.\begin{array}{l}\text{weight of Nickel present in the} \\ \text{whole of the given solution(100ml)}\end{array}\right\} = 0.2034 \times (W_2 - W_1) \times 5$$

=

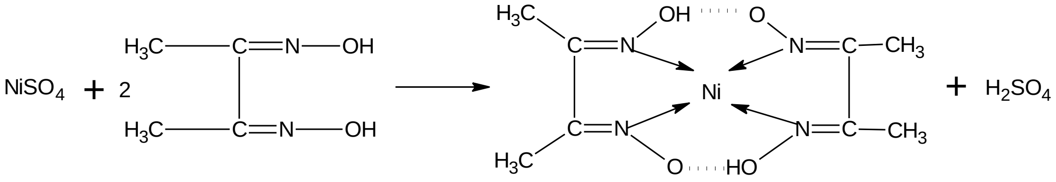
2.8 ESTIMATION OF NICKEL AS NICKEL DIMETHYL GLYOXIME

Aim:

To estimate gravimetrically the amount of nickel present in the whole of the given solution of Nickel salt.

Principle:

Nickel in a solution is precipitated as dimethyl glyoxime complex by the addition of alcoholic solution of dimethyl glyoxime to a hot, strong acid solution of the nickel compound and then adding slight exccess of ammonium hydroxide. The precipitated nickel complex is filtered, washed and dried at 110^0C.



Procedure:

The given nickel salt solution is made upto 100ml in a standard flask. Exactly 20ml of this solution is pipetted out into a clean 400ml beaker. About 5ml of 1:1 HCl is added and the solution is diluted to 100ml with distilled water. The solution is then heated to about 80^0C. To the hot solution about 20ml of 1% alcoholic solution of dimethyl glyoxime reagent is added in drops with stirring. Immediately dilute ammonium hydroxide solution is added dropwise, directly to the solution and not along the sides of the beaker till the solution is slightly alkaline (indicated by the smell of NH_3 coming out). A rosy red precipitate of nickel dimethyl glyoxime complex will be obtained. The solution is heated on a water bath for about an hour and the precipitate is allowed to settle. The supernatant liquid is then tested for

CRUCIBLE: II

Calculation:

Weight of empty sintered crucible (W_1 g) =

$$\left.\begin{array}{l}\text{weight of sintered crucible} +\\ \text{Nickel complex}\end{array}\right\}$$ □W_2 g) □□

Weight of nickel dimethyl glyoxime complex (W_2-W_1) g =

288 g of nickel dimethyl glyoxime complex contains 58g of Nickel.

$$\left.\begin{array}{l}\text{Weight of Nickel present in}\\ \quad (W_2 - W_1)\text{ g of nickel dimethyl glyoxime complex}\end{array}\right\} = 0.2034 \times (W_2 - W_1)\text{ g}$$

=

$$\left.\begin{array}{l}\text{weight of Nickel present in the}\\ \text{whole of the given solution(100ml)}\end{array}\right\} = 0.2034 \times (W_2 - W_1) \times 5$$

=

completion of precipitation by adding a little more of the dimethyl glyoxime reagent into it.

When the precipitation is complete, it is filtered through a previously cleaned, dried and weighed crucible by decantation. The precipitate is washed with hot water until the washings gives no reaction for chloride when tested with silver nitrate solution containing little HNO_3. The entire precipitate is washed, transferred to the crucible, and the particles sticking to the sides of the beaker and glass rod are removed using the policemen. When filtration is complete, the precipitate is dried in an air oven at 110^0C for an hour. It is allowed to cool in a desiccator and weighed. Heating, cooling and weighings are repeated till the weight becomes constant. A duplicate experiment is conducted simultaneously. From the weight of the dimethyl glyoxime complex, the weight of nickel present in the whole of the given solution is calculated.

Result:

Amount of nickel present in the
whole of the given solution =

Notes:

1. Addition of excess of the precipitant (DMG) should be avoided since the reagent itself is capable of dissolving the complex formed.
2. The Ni-DMG Complex is creeping over the glass surface. Therefore, while filtering, never pour the solution beyond half the volume of the sintered crucible.

CRUCIBLE: I

Calculation:

Weight of empty sintered crucible (W_1) =

$$\left.\begin{array}{c}\text{weight of sintered crucible} +\\ \text{magnesium oxinate}\end{array}\right\} (W_2) =$$

Weight of magnesium oxinate (W_2-W_1) =

348.312 g of hydrated magnesium oxinate contains 24.312 of Mg.

$$\therefore \left.\begin{array}{r}\text{Weight of magnesium in } (W_2 - W_1)\text{g}\\ \text{of magnesium oxinate}\end{array}\right\} =$$

$$0.06896 \times (W_2 - W_1)\ \text{g}$$

=

$$\therefore \left.\begin{array}{r}\text{Weight of Magnesium in the}\\ \text{whole of the given solution}\end{array}\right\} =$$

$$0.06896 \times (W_2 - W_1)\ \text{g} \times 5$$

=

2.9 ESTIMATION OF MAGNESIUM AS OXINATE

Aim:

To estimate gravimetrically, the amount of magnesium present in the whole of the given solution by precipitating it as magnesium oxinate.

Principle:

Magnesium in a given volume of the solution is precipitated as oxine complex by the addition of dilute solution of oxine to the ammoniacal solution of the magnesium salt containing ammonium chloride. The precipitate is filtered, washed and dried at 105^0C and weighed as magnesium oxinate $Mg(OC_9H_6N)_2.2H_2O$.

$$\mathrm{MgSO_4 + 2C_9H_7ON + 2H_2O \rightarrow Mg(OC_9H_6N)_2.2H_2O} \downarrow + H_2SO_4$$

Procedure:

The whole of the given magnesium solution is made up to 100ml in a standard flask. Exactly 20ml of this solution is pipetted out into a clean beaker provided with a cover glass and a glass rod. The solution is diluted to 100ml into which 2g of ammonium chloride is added followed by ammonium hydroxide solution till it is just alkaline. The solution is heated to about 80^0C. To the hot solution about 20ml of 2% solution of oxine in 2N acetic acid is added very slowly with stirring until small excess is present. The supernatant liquid must be yellow in colour. A large excess of the reagent is to be avoided. The mixture is boiled until the yellow precipitate becomes crystalline. The precipitate is then digested over a hot water bath for half an hour. The supernatant liquid is then tested for completion of precipitation. The precipitate is then filtered by decantation through a clean, dried and weighed sintered crucible. The precipitate is washed with hot

CRUCIBLE: II

Calculation:

Weight of empty sintered crucible (W$_1$) =

$$\left.\begin{array}{c}\text{weight of sintered crucible} +\\ \text{magnesium oxinate}\end{array}\right\}$$ □W$_2$) □□

Weight of magnesium oxinate (W$_2$-W$_1$) =

348.312 g of hydrated magnesium oxinate contains 24.312 of Mg.

$$\left.\begin{array}{r}\therefore \text{Weight of magnesium in } (W_2 - W_1)\text{g}\\ \text{of magnesium oxinate}\end{array}\right\} =$$

$$0.06896 \times (W_2 - W_1)\text{ g}$$

=

$$\left.\begin{array}{c}\therefore \text{Weight of Magnesium in the}\\ \text{whole of the given solution}\end{array}\right\} =$$

$$0.06896 \times (W_2 - W_1)\text{ g} \times 5$$

=

water containing little ammonium hydroxide several times. The precipitate is then transferred to the crucible and the particles sticking to the sides of the beaker and glass rod are removed by policeman. After the filtration is over, the precipitate is dried in an oven at 100-105^{0}C, cooled in a desiccator and finally weighed. The process of heating, cooling and weighing is repeated to constant weight. A duplicate experiment is conducted simultaneously. From the weight of the magnesium oxinate, the weight of the magnesium in the whole of the given solution is calculated.

Result:

$$\left.\begin{array}{c}\text{Amount of magnesium present}\\ \text{in the whole of the given solution}\end{array}\right\} =$$

CRUCIBLE: I

Calculation:

Weight of empty sintered crucible (W_1) g =

$$\left.\begin{array}{c}\text{weight of sintered crucible}+\\ \text{cuprous thiocyanate}\end{array}\right\}\ \square W_2)\text{ g}\qquad \square\square$$

$$\left.\begin{array}{l}\text{Weight of cuprous thiocyanate}\\ \qquad\text{precipitate }(W_2\text{-}W_1)\text{ g}\end{array}\right\} =$$

243.92 g of cuprous thiocyanate contains 126.08 of copper.

$\therefore$ (W_2-W_1) g cuprous thiocyanate

contains =

$$0.5228\times(W_2-W_1)\text{ g of Cu}$$

=

$$\therefore\left.\begin{array}{r}\text{Amount of copper present in the}\\ \text{whole of the given solution}\end{array}\right\} =$$

$$0.5228\times(W_2-W_1)\text{ g}\times 5$$

=

2.10 ESTIMATION OF COPPER AS CUPROUS THIOCYANATE

Aim:

To estimate the amount of copper present in the whole of the given solution by precipitating it as cuprous thiocyanate.

Principle:

The copper present in a definite volume of the made up solution is precipitated as cuprous thiocyanate in acid solution by the addition of ammonium thiocyanate in the presence of sulphurous acid.

$$2CuSO_4 + SO_2 + 2NH_4CNS + 2H_2O \rightarrow Cu_2(CNS)_2 + (NH_4)_2SO_4 + 2H_2SO_4$$

The cuprous thiocyanate is filtered, washed and dried at 110^0C and weighed.

Procedure:

The given copper salt solution is made upto 100ml in a standard flask. Exactly 20ml of this solution is pipetted out into clean 400ml beaker. About 5ml of dilute H_2SO_4 is added followed by 20ml of saturated solution of sulphurous acid. The solution is diluted to 100ml and heated to boiling. 20 ml of 10% freshly prepared ammonium thiocyanate is added in drops with constant stirring till the reagent is in slight excess. The supernatant liquid must be colourless. The precipitate is allowed to stand overnight, and tested for completion of precipitation by adding the ammonium thiocyanate reagent along the sides of the beaker.

The supernatant liquid is filtered through a previously cleaned, dried and weighed sintered crucible. The precipitate is washed with cold water containing 1ml of 10% ammonium thiocyanate solution and 5 drops of saturated sulphurous acid solution per 100ml of water. The precipitate is finally washed with 20% alcohol several times to remove excess of ammonium thiocyanate.

CRUCIBLE: II

Calculation:

Weight of empty sintered crucible (W_1) g =

$$\left.\begin{array}{c}\text{weight of sintered crucible} + \\ \text{cuprous thiocyanate}\end{array}\right\}$$ □W_2) g □□

$$\left.\begin{array}{l}\text{Weight of cuprous thiocyanate} \\ \qquad\text{precipitate } (W_2\text{-}W_1) \text{ g}\end{array}\right\} =$$

243.92 g of cuprous thiocyanate contains 126.08 of copper.

$\therefore$ (W_2-W_1) g cuprous thiocyanate

contains =

$$0.5228 \times (W_2 - W_1)\ \text{g of Cu}$$

=

$$\therefore \left.\begin{array}{c}\text{Amount of copper present in the} \\ \text{whole of the given solution}\end{array}\right\} =$$

$$0.5228 \times (W_2 - W_1)\ \text{g} \times 5$$

=

The precipitate is dried to constant weight at 110^0-120^0C and weighed as cuprous thiocyanate. A duplicate experiment is conducted simultaneously. From the weight of cuprous thiocyanate precipitate obtained, the amount of copper present in the whole of the given solution is calculated.

Result:

$$\left.\begin{array}{c}\text{Amount of copper present in the whole} \\ \text{of the given solution}\end{array}\right\} =$$

2.11SOLUTIONS AND REAGENTS FOR GRAVIMETRIC ESTIMATIONS

The following is the list of solutions and reagents commonly required for gravimetric estimations. Each student may be given the solution in the order of 20ml which would contains about 0.2g to 0.3g of the respective metal ion to be precipitated. Probable errors that may be introduced in the process of estimations will be eliminated by preparing the solutions and reagents in distilled water.

1. **Estimation of Barium as Barium sulphate**

Barium Chloride solution : 30.00 g of AR barium Chloride dissolved in water and made up to 500ml in a standard flask.

Precipitating agent : 2N sulphuric acid (56ml of con H_2SO_4 diluted to 1 litre)

Potassium sulphate : 20gms of K_2SO_4 in 1 litre.

Whatmann No. 40 filter Paper circles.

2. **Estimation of Sulphate as barium Sulphate**

Potassium sulphate : 25.0g of AR K_2SO_4 is accurately weighted and made to 500 ml in a standard flask. 20-24 ml of the solution may be given to each student.

Copper sulphate : 40.00gs in 500ml

Barium chloride Solution : 25.0 or 30.0g of barium chloride in 500ml whatmann No.40 filter paper circles.

3. **Estimation of chloride in a soluble chloride**

Sodium chloride : 15.0g in 500ml of distilled water.

Potassium chloride : 20g in 500ml

$AgNO_3$ solution : 20gm in 1 litre

4. **Estimation of calcium as calcium oxalate mono hydrate**

Given solution : Calcium chloride About 20g of anhydrous calcium carbonate is accurately weighed and dissolved in hydrochloric acid and made upto 500ml in standard flask.

Ammonium oxalate : Saturated solution

5. Estimation of barium as barium chromate:

Given solution : $BaCl_2$ solution. 30g of barium chloride in 500ml

Potassium chromate 4% solution (40gms in one litre)

6. Estimation of lead as lead chromate:

Lead acetate : About 40.0g of lead acetate is Accurately weighted and made upto 500ml.

Potassiumchromate : 5% solution in 750ml

7. Estimation of nickel as nickel dimethyl glyoxime;

Nickel sulphate ($NiSO_4.6H_2O$) - 30gm in 500ml

Nickel sulphate ($NiSO_4.7H_2O$) - 36g in 500ml

Dimethyl glyoxime - 10gm of dimethyl Glyoxime dissolved in 1litre of alcohol.

8. Estimation of magnesium as magnesium oxinate:

Magnesium solution - 20.0g of magnesium sulphate in 500ml

Oxine solution - About 20.0g of oxine and 100ml of glacial acetic acid are warmed for few minutes and diluted to 1litre.

9. Estimation of copper cuprous thiocyanate:

Given solution : $CuSO_4$ solution. About 35.0g of copper sulphate is accurately weighed and made up to 500ml.

10% ammonium thiocyanate : 100gms of ammonium thiocyanate in 1 litre.

UNIT - III

ORGANIC QUALITATIVE ANALYSIS

3. 0 Introduction:

The aim of organic qualitative analysis is to identify a given organic substance and to confirm its nature by performing a set of known standard reactions with it.

Millions of known organic compounds are easily and effectively classed into a limited number of (25 or 30) groups depending on their nature of functional group present. A compound belonging to a particular class will exhibit characteristic reactions of the atoms or group of atoms present in it.

In general, organic compounds are considered to be derivatives of hydrocarbons (aliphatic or aromatic). The substituents or linking atoms or groups in an organic molecule are invariably inorganic atoms or groups such as halogens, oxygen and hydrogen, nitrogen and hydrogen, sulphur, etc., which lead to the formation of halogen compounds, alcohols, aldehydes, ketones, esters, amines, amides, thiols, etc., A good understanding of the reactions of these simple class of organic compounds is an essential requirement before attempting to take up qualitative analysis of substance.

Unlike inorganic analysis, in which the ionic reactions are instantaneous and well-defined, organic reactions involve simultaneous occurrence of a wide possible reactions and hence the analysis includes a number of stages. For accurate analysis of a substance, one must follow a systematic procedure. Besides this, an over-all knowledge of reactions and careful observations are also a must for an analyst.

In any qualitative organic analysis, the systematic procedure includes the following steps:

Purity of Organic Compound:

Generally, a sharp melting point indicates that the substance is pure. In case of a liquid, its boiling points is determined.

Qualitative elements test or Lassaigne’s test:

The presence or absence of elements, such as nitrogen, halogens and sulphur as confirmed by Lassigne’s test, will shed more light on the nature of the class of compounds to which it belongs. For instance, if nitrogen is present, one may test for amines, amides, nitro compounds etc. in case of absence of nitrogen, one need not attempt, to perform the experiments belonging to these classes; one can readily test the compound for acids, phenols, esters, etc.

Solubility test:

Solubility of an organic substance illustrates the exact nature of the substance more easily. For this purpose, the given organic substance is dissolved in simple solutions and solvents – H_2O, NaOH, dil.HCl, $NaHCO_3$, etc. The presence or absence of certain class of compounds can be ascertained by means of this test.

Nature of functional group test:

The class to which an organic compound belongs is determined by this method.

Preparation of Derivatives:

Confirmation of the presence of a functional group in an organic compound is conclusively established only after preparing solid derivatives for the compound. In organic qualitative analysis, the preparation of a suitable solid derivative is required as a last proof of the functional group.

In the following pages, a systematic procedure for organic qualitative analysis is described. It comprises three sections of reactions discussed earlier.

When an unknown organic compound is subjected to the following tests in the order, its identification will be much easier.

3.1 Determination of boiling point of liquids:

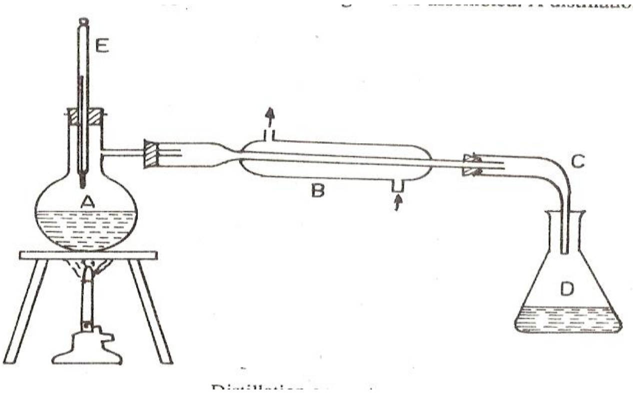
A sharp boiling point confirms that,

i. The liquid is pure.

ii. A definite boiling is also observed in the case of constant boiling mixtures.

The two liquids of the above type may easily be differentiated by carrying out distillation at varied external pressures. A pure liquid, always boils at definite temperature without a change in its composition; whereas the constant boiling mixture changes its boiling point and its composition.

Experimental determination of boiling point:



In general, the boiling point of a liquid is determined by simple distillation. For this purpose, the apparatus shown in figure is assembled. A distillation flask A of 100 ml capacity is fitted to a water condenser B. Water is regulated through the condenser as shown in figure. An adapter C is attached to the condenser and the distillate is collected in a conical flask or boiling test tube. The liquid is then placed in the flask A, a few porcelain bits are added and the thermometer E is fixed in position. The flask is now heated directly on a wire gauze (for high boiling liquids) or on a water bath (for low boiling liquids below 80 ° C b.p.). A pure liquid will boil at a constant temperature until all liquid boiled off. This temperature recorded is the boiling point of the given liquid.

Precautions to be observed in the experiment:

i. Always place a few bits of unglazed porcelain into the R.B. flask containing the liquid. This will ensure steady, gentle boiling.

ii. The thermometer should be so arranged that the top of the bulb is just level with the centre of the side-aim of the distilling flask.

iii. Water condenser can safety be used when boiling point of a liquid does not exceed 140 ° .

iv. Low boiling (below 80 ° C) liquids should be heated on a water bath for safety reasons.

3.2 ANALYSIS OF ORGANIC COMPOUNDS

3.2.1 A SYSTEMATIC PROCEDURE OF ORGANIC QUALITATIVE ANALYSIS

EXPERIMENT	OBSERVATION	INFERENCE
I. Preliminary Tests		
1. Colour and appearance	a) Yellow colour liquid	May be aromatic nitro compounds
	b) Brown or dark coloured solid or liquid	May be aromatic amines or phenols.
	c) Colourless solid	Absence of amines, phenols and nitro compounds
2. Odour of the substance	a) Phenolic odour	May be phenols.
	b) Aniline like smell	May be aromatic amines
	c) Pleasant odour	May be aromatic ketones or aldehydes or aromatic esters.
	d) Nocharactenistic odour	Absence of esters amines, aldehydes, ketones and phenols.
3. Solubility Test Solubility of the substance is tested in the following solvents		
a) In water	i) Soluble in cold condition	May be carbohydrates or aliphatic diamide.
	ii) Soluble in hot condition	May be aromatic acids.
	iii) Insoluble	Absence of acids, sugars and diamides.
In dil HCl	a) Soluble and reappeared on adding NaOH solution	Presence of aromatic Amines.
	b) Insoluble	Absence of amines.

4. Litmus Test Aqueous solution of the substance is tested with litmus paper.	a) Blue litmus turns red. b) Red litmus turns blue. c) Neutral to litmus.	May be acids or phenols. May be aromatic amines. Absence of phenols and amines.
5. Test for elements **Preparation of sodium fusion extract (Lassaigne's Test)** A small piece of dry sodium metal is fused in a fusion tube. To this a little of the substance is added and the tube is heated gently until the reaction subsides and then heated to redness. The red hot end of the tube is plunged into 5 ml of distilled water in a mortar. The contents are ground well, boiled in a china dish and filtered. The filtrate is used for the following tests.		
a) Test for nitrogen To about 2ml of the extract, a strong solution of freshly prepared ferrous sulphate is added. The solution is boiled, cooled and then dil. HCl is added.	(i) A blue or green precipitate or solution is obtained. (ii) No blue or green precipitate or solution is obtained.	Presence of nitrogen. Absence of nitrogen.
(b) Test for sulphur To about 2ml of the extract, a freshly prepared solution of sodium nitroprusside is added.	(i) A purple colour is obtained. (ii) No purple colour is obtained	Presence of sulphur. Absence of sulphur.
c) Test for Halogens To about 2ml of the extract dil.HNO_3 is added. The solution is boiled, cooled and then silver nitrate ($AgNO_3$) solution is added.	(i) A curdy white precipitate, completely soluble in NH_4OH is obtained. (ii) A pale yellow precipitate, sparingly soluble in NH_4OH is	Presence of chlorine Presence of bromine.

	obtained.	
	(iii) A pale yellow precipitate, insoluble in NH_4OH is obtained.	Presence of Iodine.
	(iv) No characteristic precipitate is obtained.	Absence of halogens (chlorine, bromine and iodine).
6. Test for aliphatic or aromatic character		
(a) A little of the substance is burnt in a nickel spatula.	(i) Burns with a luminous, smoky flame.	The substance is aromatic.
	(ii) Burns with non-luminous flame.	The substance is aliphatic.
(b) A little of the substance is heated with a mixture of 1 ml of conc. HNO_3 and 1 ml of conc. H_2SO_4 in a test tube and then poured into beaker, containing water.	(i) A yellow precipitate or solution.	The substance is aromatic.
	(ii) No yellow precipitate or solution.	The substance is aliphatic
7. Test For saturation Or unsaturation		
(a) A little of substance is shaken with 1 ml of water or alcohol and then bromine water is added drop by drop.	(i) Decolorisation takes place readily.	Presence of unsaturated compound.
	(ii) Decolorisation takes place with the formation of white or yellow precipitate.	Presence of saturated compounds like amines and phenols.
	(iii) No Decolourisation.	Presence of saturated compound.
(b) A little of the substance is treated with a dilute solution of potassium permanganate ($KMnO_4$) and a little sodium carbonate.	(i) Decolorisation takes place.	May be unsaturated compound.
	(ii) $KMnO_4$ colour changes to brown or black	Presence of saturated compound (easily oxidisable compounds)

8. A little of the substance is added to 1ml of a strong solution of sodium bicarbonate.	Vigorous effervescence takes place. No specific reaction	Presence of carboxylic acids. Absence of acids.
9. A little of the substance is warmed with 2ml of 10% NaOH solution	a) Dissolves readily in the cold condition and the substance is regenerated on adding dil. HCl. b) Solution turns yellow or brown. c) Ammonia gas is evolved and it gives dense white fumes with a glass rod dipped in conc. HCl. d) Oily layer disappears on boiling and on acidification with con HCl white precipitate is formed. e) Oily drops are seen on the sides of the test tubes. f) No characteristic change in cold and in hot condition.	Presence of acids or phenols. May be carbohydrates or aldehydes. May be amides. Presence of esters. Presence of anilides. Absence of amides, phenols, acids, carbohydrates, esters and anilide.
10. A little of the substance is heated with sodalime strongly.	Ammonia gas is evolved and it gives dense white fumes with a glass rod dipped in conc. HCl	May be amides
11. A little of the substance is warmed with 2ml of conc H_2SO_4.	a) The substance chars with the smell of burnt sugar.	May be carbohydrates.

	b) Charring takes place with effervescence. c) A white precipitate is formed which is soluble in H_2O. d)No specific reaction	May be polyhydricphenol. Presence of amines. Absence of amines, polyhydricphenols and carbohydrates.
12.A little of the subs- substance is dissolved in water or alcohol and neutral $FeCl_3$ solution is added.	a) A violet or blue or green colour is obtained. b) Buff coloured precipitate. c) No specific reaction.	Presence of phenolic group. Presence of acids. Absence of phenols and acids.
13. A little of the substance is shaken with Borsche’s reagent.Few drops of con HCl added and boiled in a water bath.	A yellow precipitate is obtained. No yellow precipitate is obtained.	May be aldehydes or ketones. Absence of aldehydes or ketones.
14. A little of the substance is treated with Tollens reagent and heated on a water bath.	A black precipitate or silver mirror is formed.	Presence of aldehydes or reducing sugars or polyhydric phenols.
II. TEST FOR FUNCTIONAL GROUPS (CONFIRMATIVE TESTS) (Note: It is necessary to do all the preliminary test from (1 – 14)] to fix the functional group. After identifying the functional group the test for the particular group alone is performed.)		
1. Test for Acids (a) To about 2 ml of sodium hydroxide solution one drop of phenolphthalein indicator is added (Pink colour appears). To this the substance dissolved in water or alcohol is added drop by drop in excess. (b) A little of the subs-	Pink colour disappears. A pleasant fruity odour	Presence of carboxylic acid. Presence of carboxylic

substance is mixed with a few drops of alcohol and two drops of conc. H_2SO_4, The mixture is gently warmed and poured into a dilute solution of sodium carbonate.	is noted.	acid.
(c) Fluorescein test: A little of the substance is mixed with a pinch of resorcinol and 1ml of conc. H_2SO_4. The mixture is gently warmed and poured into a beaker containing 100ml water. To this NaOH solution is added and stirred well.	An intense greenish yellow fluorescence is produced. No intense greenish yellow fluorescence is produced.	Presence of dicarboxylic acid. Presence of monocarboxylic acid.

2. Test for phenols (Liebermann’s test)		
a) A little of the substance is mixed with a few crystals of sodium nitrite and 3 or 4 drops of conc. H_2SO_4. This is gently warmed and poured into a beaker containing water. To this NaOH is added and stirred well.	A red solution is obtained. This turns blue or green on adding NaOH solution.	Presence of phenolic group.
(b) Phthalein fusion test A little of the substance is mixed with a pinch of phthalic anhydride and 1ml of conc. H_2SO_4 , the mixture is gently warmed and poured into a beaker containing water. To this NaOH is added with stirring.	(i) A pink or red colour is obtained.	Presence of phenolic group.
	(ii) An intense greenish yellow fluorescence is obtained.	Presence of dihydric phenols like resorcinol.
(c) Azo-dye test A few drops of aniline are dissolved in about 5 ml of dil HCl. To this 5ml of a strong solution of sodium nitrite is added in drops with constant shaking and cooling in ice cold water. To the above diazotised solution, 1g of substance dissolved in NaOH is added.	a) A scarlet red dye is obtained.	Presence of phenols such as resorcinol or naphthol.
(d) About one ml of Fehling solution (A) is mixed with one ml of Fehling solution (B). The mixture is added to a little of the substance dissolved	A red brown precipitate is obtained.	Presence of dihydric phenols.
	No red brown	Presence of monohydric

in water or alcohol shaken well and heated in a water bath.	precipitate	phenols.
3. Test for carbohydrates		
Molish's test (a) To a little of the substance in water few drops of an alcoholic solution of α -naphthol are added. To this mixture concH_2S0_4 is added along the sides of the test tube without shaking,	A violet or purple ring is obtained at the junction of the two layers and the colour spreads slowly throughout the solution.	Presence of carbohydrates.
(b) A little of the substance is mixed with 2ml of Tollen's reagent. This is shaken well and heated in a boiling water bath.	A black precipitate or a bright silver mirror is formed.	Presence of carbohydrates. (reducing sugars).
(Preparation of tollen's reagent To about 1ml of $AgNO_3$ solution, 10% NaOH solution is added drop wise till a black precipitate is obtained. To this, NH_4OH solution is added just to dissolve the precipitate and then shaken well.)		
(c) About one ml of Fehling's solution A is mixed with one ml of Fehling's solution B. 'This mixture is added to a little of the substance dissolved in water, shaken well and heated in a boiling water bath.	A red brown precipitate is obtained.	Presence of carbohydrates (reducing sugars)
(d) To about 2ml of H_2O a pinch of phenyl hydrazinehydrochloride is	A bright yellow	Presence of

added, To this sodium acetate is added and shaken well until the solution becomes clear. A little of the substance is added and heated in a boiling water bath.	precipitate is obtained.	carbohydrates.
4. Test for amides		
(a) A little of the substance is heated with a 5ml of 10% NaOH solution till no more ammonia is evolved. It is then cooled and acidified with conc HCl	A white precipitate is obtained	Presence of an aromatic amide.
(b) Biuret test A little of the substance is heated in a dry test-tube for a few minutes. It is cooled and the residue is dissolved in 2ml of dil $CuSO_4$ solution and then 10% NaOH solution is added dropwise.	A violet colour is obtained.	Presence of diamides (urea).
Test for amines **(a) Action on nitrous acid** A little of the substance is dissolved in about 3ml of dil HCI. To this a strong solution of sodium nitrite is added drop-wise cooling the mixture in ice cold water.	(i) A clear solution is obtained (ii) A yellow oily liquid Separates,	Presence of aromatic primary amine. Presence of secdndary amine.

(i) To the above clear solution β-naphthol in NaOH is added.	A scarlet red dye is obtained.	Presence of aromatic primary amine.
(ii) The above yellow oily liquid is mixed with 2 drops of phenol, a few drops of conc H_2SO_4 gently warmed and poured into a beaker containing water. To this NaOH solution is added and stirred well.	A red solution is obtained which turns blue or green on adding NaOH.	Presence of aromatic secondary amine.
(iv) Carbylamine test A little of the substance is treated with 2 drops of chloroform and 2ml of alcoholic KOH and warmed.	A characteristic foul smell of isocyanide is noted.	Presence of aromatic primary amine.
6. Test for aldehydes and ketones		
(i) Schiff's reagent test A little of the substance is shaken with Schiff's reagent	A pink colour is formed slowly.	Presence of aldehydes and ketones.
(ii) Tollen's reagent test A little of the substance is warmed with 2ml of Tollens reagent on a water bath.	A black precipitate is obtained. No black precipitate.	Presence of aldehydes. Presence of ketones.
(iii) Sodium bisulphite test A little of the substance is shaken with 1ml of saturated sodium	White crystalline precipitate is obtained.	Presence of aldehydes and ketones.

bisulphite solution.		
(iv) Borsche's reagent test A little of the substance is shaken with 1ml. of Borsch's reagent and 2 drops of conc. HCl. Gently heated and then cooled well.	A yellow precipitate is obtained.	Presence of aldehydes and ketones.
(v) Semicarbazide test A small amount of semicarbazide hydrochloride is dissolved in 2ml of water. To this a little amount of sodium acetate is added and then warmed to get a clear solution A little of the substance is mixed with this clear solution and warmed on a water bath.	White crystalline precipitate is obtained.	Presence of aldehydes and ketones.
(vi) Nitroprusside test A little of the substance is mixed with freshly prepared sodium nitroprusside solution and sodium hydroxide is added drop by drop in excess.	Wine red colour is obtained.	Presence of ketones.
(iii) Iodoform test A little of the substance is mixed with 1ml of sodium hydroxide and 1ml of iodine solution and warmed on a water bath.	A pale yellow precipitate is obtained.	Presence of ketones. (Methyl ketones)

Test for anilides 1)Substance is heated with NaOH solution	Oily drops on the sides of the test tube appeared.	Presence of anilide.
2) Dye test Small amount of the substance is boiled with con HCl. The soln is cooled diazotised with $NaNO_2$ solution and coupled with β-naphthol in NaOH soln at low temperature.	A scarlet red dye is formed.	Presence of anilide is confirmed.
3) Small amount of the substance is dissolved in glacial CH_3COOH Br_2 in CH_3COOH solution is added in drops with shaking and poured into water.	Pale yellow precipitate is formed.	Presence of anilide.
Confirmatory tests for Nitro compounds		
Mulliken and Barker's test 1) Substance is dissolved in ethanol.NH_4Cl and Zn dust are added. It is heated for 3minutes and filtered. The filtrate is treated with Tollen's reagent and heated gently on a water bath.	Black precipitate or silver mirror is formed.	Presence of nitro group is confirmed.
Dye test: Substance is mixed with con HCl and a piece of tin. It is heated well and filtered. The filtrate is diazotised and coupled with β-naphthal in NaOH.	Scarlet red dye is formed.	Presence of nitro group confirmed.

Test for Esters		
1) Hydrolysis Small amount of the substance is boiled with 5ml of 20% NaOH . Then the solution is cooled and acidified with con HCl.	White precipitate is formed.	Presence of esters confirmed.
2)Hydroxamic acid test To 3 drops of substance added a pinch of hydroxylamine hydrochloride. 5ml of 10% NaOH is added. The contents is gently boiled cooled and acidified with con HCl. To the mixture added few drops of $FeCl_3$ solution.	A violet or deep red or brown colour appeared.	Esters confirmed.

3.2.2 Preparation of derivatives:

1) Carboxyl acids:

a) S-Benzyl thiuronium salt:

About 0.5gm of the substance is dissolved in hot water and a drop of phenolphthalein is added. The acid is neutralized with NaOH solution. Two drops of NH_4Cl and a solution of 1gm of S- benzyl thiuronium chloride in 5ml of H_2O are added. The solution is cooled. White derivative is obtained. It is filtered and dried.

b) Amide dvt:

About 0.5gm of the substance is mixed with equal quantity of $SOCl_2$ in a mortar. The mixture is ground well till the evolution of fumes stops. To this added few ml of concentrated NH_3 stirred well and small amount of water added. The amide obtained is filtered and dried.

2) Derivatives for Phenols:

a) Benzoyl dvt: To 1gm of given phenol added 5ml of benzoyl chloride and 20ml of 10% NaOH. It is shaken well for 10 minutes after closing the test tube with cork. Then the contents are poured into water. White solid is obtained. It is filtered and dried.

b) Bromination: (Bromo dvt)

About 0.5gm of the substance is treated with saturated Br_2/H_2O till the yellow colour due to excess of Br_2 persists. This solution when diluted with H_2O bromo derivative crystallises out.

3) Carbohydrates:

a) Osazone dvt: 0.5gm of phenyl hydrazine hydrochloride is dissolved in 2ml of H_2O. About 0.5gm sodium acetate crystals are added followed by drop of strong acetic acid. This reagent is added to a saturated solution of sugar solution. The mixture is heated on a water bath for 10 minutes. When it is cooled yellow crystals of osazone obtained. It is filtered and dried.

4) Derivative of Esters:

Acid derivative (Hydrolysis)

About 1ml of the substance is mixed with 10ml of 20% solution of NaOH and boiled the solution till the oily layer disappears. It is cooled and acidified with con HCl. White precipitate of aromatic acid is formed. It is filtered and dried.

5) Derivatives for amines:

Dye derivative for primary amine:

In a test tube small amount of the substance is dissolved in con HCl and cooled in ice water. In another test tube 1gm of sodium nitrite is dissolved in H_2O and ice cooled. Both the above solutions are mixed together at ice cold temp. To this solution β-naphthol dissolved in NaOH is added. Scarlet red dye is obtained.

Benzoyl dvt: 0.5gm substance in alcohol is mixed with benzoyl chloride and 10ml of 10% NaOH. Shaken well for 10 minutes and poured into water. While precipitate formed is filtered and dried.

6) Derivatives for Nitro compounds:

Azo-dye derivative

About 0.5gm of the substance is dissolved in alcohol. To this added one gm of Zn dust and dil HCl and boiled. After reduction the solution is diazotised with $NaNO_2$ soln at $0^\circ C$. then coupled with β-naphthol in NaOH Scarlet red dye is obtained.

7) Derivatives for anilides:

Bromo derivative: 1gm of given anilide is dissolved in acetic acid. To this added Br_2 in CH_3COOH solution drop wise with shaking. When the reation micture is yellow in colour it is poured into water. The precipitate formed is filtered and dried.

8) Diamide derivatives:

a) Urea oxalate: A saturated solution of diamide is mixed with a saturated solution of oxalic acid and shalken well. Urea oxalate is precipitated as white solid. It is filtered and dried.

b) Urea nitrate: To a saturated solution of urea added con HNO_3 in drops and shaken well. White precipitate is formed. It is filtered and dried.

9) Derivatives for aldehydes and ketones

a) 2,4-dinitro phenyl hydrazone dvt:

To a small amount of the substances added 1ml of Borche's reagent and con HCl. It is heated for 10 minutes on a boiling water bath. Then poured into water. Yellow crystals are formed. It is filtered and dried.

b) Semi carbazone derivative:

A small amount of the substance in alcohol is mixed with semi carbazide hydrochloride and sodium acetate solution. It is boiled in water bath for about 15 minutes and poured into ice water. White precipitate formed is filtered and dried.

3.2.3 PREPARATION OF SPECIAL REAGENTS:

1. Alcoholic potash: 30% KOH in rectified spirit. Allow soln. to settle (for 24 hours). Decant clear soln.
2. Alcoholic silver nitrate solution: 2% soln. of $AgNO_3$ in rectified spirit. Decant clear soln.
3. Borsche's reagent: 1% soln. of 2, 4 – dinitrophenyl – hydrazine in rectified spirit (or methyl alcohol). Heat till clear soln. appears. Cool, filter.
4. Bromine in CCl_4 : 4ml liq. Bromine in 100ml CCl_4.
5. Bromine water : Saturated soln. of Br_2 in water.
6. Bromine in HOAc: 4% soln. (1ml Br_2 in 75ml HOAc).
7. Fehling's solution-A: 7% $CuSO_4$ in water.
8. Fehling's solution-B: 35g Rochelle salt and 15g NaOH dissolved separately in 40ml of water. The solns are mixed. The volume made upto 100ml (1ml of soln. A and 1ml of soln. B mixed for test).
9. Neutral $FeCl_3$ solution: To 1ml of ferric chloride soln. add aq. Ammonia till permanent brown ppt. appears. Add dil. HOAc, drop by drop, till ppt just dissolves.
10. Phenylhydrazine reagent: 10ml phenylhydrazine + 10ml glacial HOAc + 30ml water.
11. Potassium permanganate solution: 2% $KMnO_4$ in water.
12. Schiff's reagent: 1g p-rosaniline hydrochloride dissolved in 100ml water, decolourised by passing sulphur dioxide. Soln. is filtered, diluted to 500ml with distilled water, kept in brown bottle.
13. Sodium. bisulfite soln. : Satd. Soln. of $NaHSO_3$ in water.
14. Sodium. nitroprusside soln: 1% soln. in water.
15. Tollen's reagent – A: 10g silver nitrate dissolved in 100ml of dilute aq. Ammonia.
16. Tollen's reagent – B: 10g of NaOH dissolved in 100ml water. (When required, 1ml of A mixed with 1ml of B and used for test).

3.2.4 MODEL PROCEDURE FOR THE ANALYSIS OF A GIVEN ORGANIC SUBSTANCE

<table>
<tr><th>EXPERIMENT</th><th>OBSERVATION</th><th>INFERENCE</th></tr>
<tr><td>1. Colour and Appearance</td><td>Coloured solid</td><td>May be acids or amides or carbohydrates</td></tr>
<tr><td>2. Odour of the substance</td><td>No phenolic or aniline like odour or pleasant odour.</td><td>Absence of phenols, amines and ketones.</td></tr>
<tr><td>3. Solubility test
Solubility of the substance is tested in the following solvents
a) In water</td><td>Soluble in the cold conditions</td><td>May be the presence of carbohydrates or diamides.</td></tr>
<tr><td>4. Litmus test
Aqueous solution of the substance is tested with litmus paper.</td><td>Neutral to litmus.</td><td>May be presence of amides or carbohydrates or aldehydes or ketones.</td></tr>
<tr><td colspan="3">5. Test for elements
Preparation of solution fusion extract (Lassaigne’s test)
A small piece of dry sodium metal is fused in a fusion tube. To this a little of the substance is added and the tube is heated gently until the reaction subsides and then heated to redness. The red hot end of the tube is plunged into 5ml of distilled water in a mortar. The contents are ground well, boiled in a china dish and filtered. The filtrate is used for the following tests.</td></tr>
<tr><td>a) Test for nitrogen
To about 2ml of the extract, a strong solution of freshly prepared ferrous sulphate is added. The solution is boiled, cooled and then dil. HCl acid is added.</td><td>A blue solution is obtained.</td><td>Presence of nitrogen.</td></tr>
</table>

(b) Test for sulphur To about 2ml of the extract, a freshly prepared solution of sodium nitroprusside is added.	No violet colour solution.	Absence of sulphur.
c) Test for halogens To about 2ml of the extract dil. HNO_3 is added. The solution is boiled, cooled and then silver nitrate solution is added.	No characteristic precipitate is obtained.	Absence of halogens.
6. Test for aliphatic or aromatic character		
(a) A little of the substance is burnt in a nickel spatula.	Burns with a non-luminous flame.	The substance is aliphatic
(b) A little of the substance is heated with a mixture of 1ml of conc. HNO_3 and 1ml of conc. H_2SO_4 in a test tube and then poured into beaker. Containing water.	No yellow precipitate or solution is obtained.	The substance is aliphatic.
7. Test for saturation or unsaturation		
(a) A little of substance is shaken with 1ml of water or alcohol and then bromine water is added drop by drop.	No decolorisation takes place.	Presence of saturated compound.
(b) A little of the substance is treated with a 2% solution of potassium permanganate ($KMnO_4$)	No decolorisation takes place.	Presence of saturated compound.

8. A little of the substance is added to 1ml of a strong sodium bicarbonate.	No virgorous effervescence takes place.	Absence of acids.
9. A little of the substance is warmed with 2ml of 10% NaOH solution	NH_3 gas is evolved and it gives dense white fumes with a glass rod dipped in.HCl.	May be presence of amides.
10. A little of the substance is heated with sodalime strongly.	Ammonia gas is evolved.	May be presence of amides.
11. A little of the substance is warmed with 2ml of conc. H_2SO_4.	No charring takes place.	Absence of carbohydrates.
12. A little of the substance is dissolved in water or alcohol and neutral $FeCl_3$ solution is added.	No violet or blue or green colour is obtained.	Absence of phenolic group.
II. Test for nitrogen compounds		
1. Test for amides		
(a) A little of the substance is heated with 5ml of 10% NaOH solution till no more ammonia is evolved. It is then cooled and acidified with conc. HCl.	No characteristic white precipitate is obtained.	Presence of an aliphatic amide.
(b) Bluret test		
A little of the substance is heated in a dry test-tube for a few minutes. It is cooled and the residue is dissolved in	A violet colour is obtained.	Presence of diamide.

2 ml of dil. $CuSO_4$ solution and then 10% NaOH solution is added dropwise. **2. Test for amines** A little of the substance is dissolved in 3ml of dilute HCl to which added a strong solution of $NaNO_2$ in drop wise cooling the mixture in ice cold water.	No scarlet red dye is formed.	Absence of primary amine.
3.Test for nitro compounds:		
Mulliken and Barker's test A little of the substance is dissolved in a few ml of alcohol to which 1ml of strong solution of $CaCl_2$ is added followed by a pinch of zinc dust. The contents are boiled and filtered. To the filtrate tollens reagent is added and warmed. **4.Test for anilides:** To a little of the substance added about 5ml of 10% NaOH and gently warmed.	No black precipitate or silver mirror. No oily drops are seen on the sides of the test tube.	Absence of nitro compounds. Absence of anilides.
Derivative for diamide: A little of the substance in water is shaken with a saturated solution of oxalic acid. Urea oxalate is precipitated. It is filtered and dried.		

Report:

The given organic substance is

- (i) aliphatic
- (ii) presence of nitrogen and absence of sulphur and halogens
- (iii) Saturated
- (iv) Contains the functional group – diamide.

Aqueous Layer:

Bottle No:	Volume taken (ml)	Burette reading (ml)		Volume of N/100 thiosulphate (ml)
		Initial	Final	
I	20			
	20			
II	20			
	20			

Calculations:

Aqueous Layer

Volume of Sodium thiosulphate V_1 =

Strength of sodium thiosulphate N_1 =

Volume of aqueous layer V_2 =

Strength of I_2 in aqueous layer $N_2 = \frac{V_1 N_1}{V_2}$

UNIT - IV

4.1 DISTRIBUTION LAW

4.1a) DISTRIBUTION COEFFICIENT OF IODINE BETWEEN CARBON TETRACHLORIDE AND WATER

Aim:

To determine the partition coefficient of iodine between water and carbon tetrachloride.

Principle:

When a solute is added to a system of two immiscible solvents, it distributes itself in a constant ratio between the two solvents. The ratio of the concentration of solute in the two layers is known as partition coefficient. Deviations from this occur when the solute undergoes chemical changes in one of the phases. In this case the molecular condition of the solute (Iodine) is the same in both the solvents and so

$$K = \frac{Cccl_4}{Caq}$$

Where, K = partition coefficient.

Caq = Concentration of Iodine in water layer.

$Cccl_4$ = concentration of Iodine in carbon tetrachloride.

Material Required:

1. N/10 Sodium thiosulphate solution
2. N/100 sodium thiosulphate solution
3. Saturated solution of Iodine in carbontetrachloride
4. Indicator – starch solution
5. Approximately 10% Potassium Iodide Solution
6. Carbon tetrachloride
7. Burette, pipette, conical flasks, etc.,

Carbon Tetrachloride layer:

Bottle No:	Volume taken (ml)	Burette reading (ml)		Volume of N/10 thiosulphate (ml)
		Initial	Final	
I	5			
	5			
II	5			
	5			

Organic Layer

Volume of Sodium thiosulphate V_1 =

Strength of sodium thiosulphate N_1 =

Volume of organic layer V_2 =

Strength of I_2 in organic layer $N_2 = \frac{V_1 N_1}{V_2}$

Partition Coefficient $K_D = \frac{\text{Concentration of } I_2 \text{ in organic layer}}{\text{Concentration of } I_2 \text{ in aqueous layer}}$

=

Procedure:

In two dry stoppered bottles, solutions are taken as given in the table1.

Table 1:

Bottle No:	Volume of saturated Iodine Solution (ml)	Volume of carbon tetrachloride (ml)	Volume of water (ml)
1	30	0	100
2	25	5	100

The bottles are stoppered and shaken well in a mechanical shaker for about 60 minutes. After equilibrium has been attained, the bottles are placed in a thermostat (For our convenience in a trough of Water) for 20 to 30 minutes till the two clear layers separate.

Now, from bottle I, 20ml of the aqueous layer (upper layer) is pipetted out into a well cleaned conical flask. 1ml of starch indicator added.It is titrated against N/100 thiosulphate solution taken in the burette till the end point is reached. The end point is the just disappearance of blue colour. The titration is repeated for concordant values.

5ml of the carbontetrachloride (lower) layer from the same bottle is pipetted out into a well cleaned conical flask containing 10ml of 10% Potassium iodide solution. Then 1 ml of starch indicator is added and the solution is titrated against N/10 thiosulphate taken in the burette. The end point is the just disappearance of blue colour. The titration is repeated for concordant values.

The partition coefficient of Iodine between carbontetrachloride and water for the second bottle is calculated as before.

Result:

$$\left.\begin{array}{l}\text{The partition coefficient of Iodine}\\ \text{between carbontetrachloride and water}\end{array}\right\} =$$

OBSERVATIONS AND CALCULATIONS

Bottle No:	Volume taken (ml)	Burette reading (ml)		Volume of N/10 thiosulphate (ml)
		Initial	Final	
I	20			
	20			
II	20			
	20			

Bottle No:	Volume taken (ml)	Burette reading (ml)		Volume of N/10 thiosulphate (ml)
		Initial	Final	
I	5			
	5			
II	5			
	5			

Model calculation

The equilibrium constant of the reaction, (K)

$$KI + I_2 \rightleftharpoons KI_3$$

$$K = \frac{[KI_3]}{[KI][I_2]}$$

Where,

$[KI_3]$ = Concentration of I_3^- *at equilibrium*

$[KI]$ = Concentration of KI *at equilibrium or unreacted*

$[I_2]$ = Concentration of free I_2 *in aqueous layer*

Concentration of I_2 in organic layer $c_1 = \frac{5 \text{ x conc of thio}}{\text{volume of thio}}$

Concentration of I_2 in aqueous layer$c_2 = \frac{10 \text{ x conc of thio}}{\text{volume of thio}}$

4.1b) DETERMINATION OF THE EQUILIBRIUM CONSTANT FOR THE REACTION $KI + I_2 \rightleftharpoons KI_3$

Aim

To determine the equilibrium constant of the reaction between Potassium iodide and iodine.

Principle

When iodine is distributed between Potassium iodide and carbon tetrachloride, a part of the Iodine is complexed with Potassium iodide to form KI_3. The reaction may be written as

$$KI + I_2 \rightleftharpoons KI_3$$

The equilibrium constant, $K = \dfrac{[KI_3]}{[KI][I_2]}$

The equilibrium constant can be calculated by knowing the concentration of free iodine and Potassium Iodide. If the equilibrium constant is known, the concentration of the unknown solution of KI can be calculated.

Materials Required

i. I_2/CCl_4 solution

ii. M/10 KI solution

iii. N/10 Thio solution

iv. Starch indicator solution

v. Reaction bottles [250ml]

vi. Burette, Pipette, Conical flasks, etc.

Procedure

Exactly 50ml of M/10 KI solution taken in a clean stoppered reaction bottle is mixed with exactly 50ml of a saturated solution of iodine in carbon-tetrachloride. The bottle is shaken well nearly for an hour. It is then set aside for about 20 minutes in a water trough so that equilibrium is attained. Exactly 10 ml of the aqueous layer is pipetted out into a clean conical flask.

The partition coefficient of iodine betweenCCl$_4$ and water = 80 (K_D)

Concentration of free iodine C_3 $= \dfrac{C_1}{K_D}$ moles/lit.

Concentration of I_2 in

aqueous layer, $[I_2]$ C_2 = combined iodine +conc of free iodine

$C_2 = [KI_3] + [I_2]_{\text{free}}$

concentration of $[KI_3]$

at equilibrium C_4 = $C_2 - \frac{C_1}{K_D}$

= $C_2 - C_3$

concentration of

unreacted KI C_5 = initial concentration of KI – $(C_2 – C_3)$

= $0.1 – (C_2 – C_3)$

Equilibrium constant = $\frac{[KI_3]}{[KI][I_2]}$

= $\frac{C_4}{C_5 \times C_3}$

=

A little of potassium iodide salt is added to it. The liberated iodine is titrated against standard sodium thiosulphate solution taken in a clean burette, using starch as indicator. The end point is the disappearance of blue colour. Another titration is performed to determine the concordant values. From the titre value the concentration of iodine in aqueous layer is found out (c_2).Similarly by titrating 5ml of organic layer with N/10 thio soln the concentration of I_2 in organic layer is calculated. (c_1)

From the values of c_1, c_2, K_D and strength of KI solution equilibrium constant is calculated.

Report

i. The equilibrium constant for the

reaction $KI + I_2 \rightleftarrows KI_3$ =

Tabulation:

V_0 = $V_\infty =$

S. No	Time in minutes	Volume of Sodium hydroxide (ml)	$(V_\infty - V_t)$ (ml)	Log $(V_\infty - V_t)$	$K = \frac{2.303}{t} \log \frac{V_\infty - V_0}{V_\infty - V_t}$ Min^{-1}
				Average	=

V_0 = volume of NaOH at zero time.

V_∞ = volume of NaOH at infinite time.

V_t = volume of NaOH at ‘t’ time.

Calculation:

1. $K = \frac{2.303}{t} \log \frac{V_\infty - V_0}{V_\infty - V_t} \text{ min}^{-1}$

4.2 KINETICS

4.2a) RATE CONSTANT FOR ACID CATALYSED HYDROLYSIS OF AN ESTER

Aim:

To determine the rate constant of the hydrolysis of methyl acetate at room temperature by an acid (Hydrochloric Acid)

Principle:

When methyl acetate is hydrolysed in the presence of an acid as catalyst, the following reaction takes place,

$$CH_3COOCH_3 + H_2O \xleftrightarrow{H^+} CH_3COOH + CH_3OH$$

The rate of the reaction is proportional to the concentration of methyl acetate only. The large amount of water does not affect the rate constant. So, it is an example for pseudo-unimolecular reaction and the rate equation will be $\frac{dx}{dt} = k[\text{methylacetate}]$

And thus kinetics is first-order with respect to methyl acetate.

Acetic acid is produced during the hydrolysis and it can be titrated with standard alkali solution. From the titre values the rate constant can be calculated by using the equation.

$$K = \frac{2.303}{t} \log \frac{V_\infty - V_0}{V_\infty - V_t} \text{ min}^{-1}$$

Where, K = rate constant

t = time in minutes

$V\infty$ = final volume of alkali solution (The reaction completed)

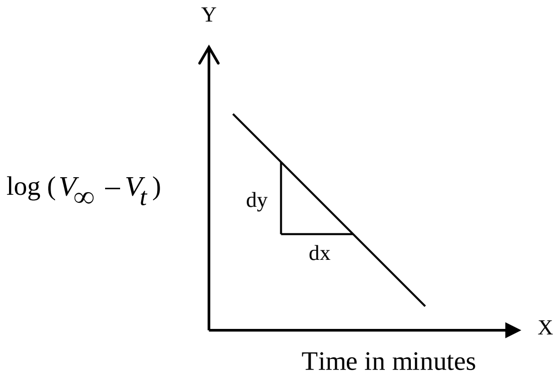
V_0 = the volume of alkali at time ‘0’

V_t = the volume of alkali at time‘t’

Materials Required:

1. Methyl acetate
2. 0.5 N Hydrochloric acid
3. 0.2 N Sodium hydroxide
4. Phenolphthalein indicator
5. Burette, Pipette, Conical flask, Stop Watch

Graph: log $(V_\infty - V_t)$ Vs Time in minutes



From the graph, $\text{Slope} = \frac{\text{-K}}{2.303}$

$$K = -2.303 \times \text{Slope}$$

$$\text{Slope} = \frac{-\,dy}{dx}$$

$$K = -2.303 \times \frac{-\,dy}{dx} \text{ minute}^{-1}$$

Procedure:

About 100 ml of 0.5 N HCl is taken in a clean dry narrow mouth bottle. About 200 ml of the methyl acetate is taken in another bottle. Both are kept in a water bath for about half an hour to attain room temperature.

10 ml of methyl acetate ester is pipetted out into the bottle containing hydrochloric acid. A stopwatch is started when half of the quantity of the ester has been added to the acid. When all the ester has been added the mixture is shaken well. Immediately 5ml of reaction mixture is pipetted out into a conical flask containing 25ml of ice water (To arrest the reaction) and titrated with NaOH taken in the Burette. The titre value gives $V_\circ$.

At 5th minute, 5ml of the reaction mixture is pipetted out into the conical flask containing some pieces of ice to freeze the equilibrium. One drop of phenolphthalein indicator is added and it is titrated against sodium hydroxide (0.2N) taken in the burette (V_5). Similarly the experiment is repeated at regular intervals (V_t). In the meantime 25ml of the reaction mixture is separately pipetted out in a flask and heated on a water bath (with care) for an hour.Then the flask is kept in the thermostat to attain room temperature. From this 5 ml of the mixture is pipetted and titrated as usual against the sodium hydroxide. This titre value gives the V_∞. Using $V_\circ$, V_t and V_∞ values the rate constant is calculated.

The rate constant can also be graphically determined as follows. The value of log (V_∞ - V_t) is taken in Y-axis and time is taken in the X-axis. A linear graph is obtained, which proves the reaction to be I order. From the slope the rate constant can be determined.

Result:

The rate constant for the hydrolysis of methyl acetate

I. Calculated Value =

II. Graphical value =

Observation:

S.No	Time in minutes	Volume of thio (ml) V_t	$V_\infty - V_t$	$\frac{1}{V_\infty - V_t}$	$k = \frac{1}{t} \times \frac{V_t}{V_\infty(V_\infty - V_t)}$ lit/mol/min

V_t= volume of thio at time ‘t’.

V_∞= volume of thio at infinite time.

Calculation:

$$k = \frac{1}{t} \times \frac{V_t}{V_\infty(V_\infty - V_t)}$$

4.2b) RATE CONSTANT FOR THE REACTION BETWEEN PERSULPHATE AND IODIDE

Aim:

To determine the rate constant of the reaction between potassium persulphate and potassium Iodide.

Principle:

Iodide is liberated when potassium persulphate and potassium iodide are allowed to react.

$$K_2S_2O_8 + 2KI \leftrightarrow 2K_2SO_4 + I_2$$

The actual mechanism may be shown as

$$[S_2O_8]^{2-} + I^- \rightarrow [S_2O_8I]^{3-} \qquad 1)\,\text{slow process}$$

$$[S_2O_8I]^{3-} + I^- \rightarrow 2SO_4{}^{2-} + I_2 \qquad 2)\,\text{fast process}$$

As the slowest step determine the rate of reaction, the process (1) gives the rate expression as

$$\frac{dx}{dt} = K[I^-][S_2O_8]^{2-}$$

Hence the reaction is of the second order. The rate of the reaction can be determined by measuring the rate of liberation of iodine. The liberated iodine is titrated against standard thiosulphate solution at various time intervals using starch as indicator. The titre values are directly proportional to the concentration of iodine liberated. Hence these titre values are equal to the values of x. Using the titre values the rate constant can be determined as follows.

$$K = \frac{1}{t}\left[\frac{x}{a(a-x)}\right] \text{ lit/mol/min}$$

Materials Required:

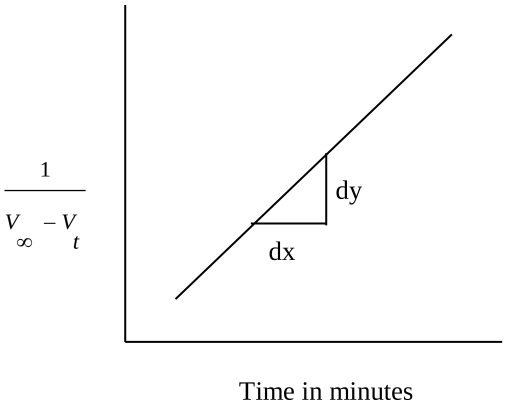
1. 100 ml of N/10 KI solution
2. 500 ml of N/100 thiosulphate solution
3. 200 ml of N/10 $K_2S_2O_8$ solution
4. Starch indicator solution
5. Burette, pipette, Conical flask, Stop watch, etc.,

Procedure:

100 ml of N/10 Potassium persulphate and 100ml of N/10 potassium iodide are taken in separate reagent bottles and kept in a trough of water

Graph:

$\frac{1}{V_\infty - V_t}$ Vs Time



K= Slope

$$= \frac{dy}{dx}$$

(thermostat to attain room temperature). Then the KI solution is added to the persulphate solution. When half of iodide solution is added a stop watch is started. The whole of KI is added, the bottle is shaken and kept in a thermostat.

Now, at the 5th minute 10ml of the reaction mixture is pipetted into a conical flask containing ice water. The solution is titrated against N/100 thiosulphate solution taken in the burette using starch as indicator. The end point is the disappearance of blue colour.

Similarly 10ml of the reaction mixture is withdrawn at 10, 15, 20, 25, 30, 35, etc., minutes and the titrations done with each solution as above(V_t). V_t values are proportional to x values. 50ml of the reaction mixture is pipetted out into a well clean conical flask. 2 g of potassium iodide is added and the contents are heated in a waterbath at 50^0-60^0c for about 30 minutes. It is then cooled to room temperature and 10ml of this solution is titrated against N/100 thiosulphate solution (using starch indicator) to get the titre value at infinite time ($V\infty$).It is proportional to the initial concentration ‘a’ of the potassium persulphate and potassium iodide.

The rate constant is calculated using the formula

$$K = \frac{1}{t}\left[\frac{x}{a(a-x)}\right]$$

$$= \frac{1}{t}\left[\frac{V_t}{V_\infty(V_\infty - V_t)}\right]$$

The value of K is also verified from the graph. A graph is drawn by taking the concentration term 1/ $(V_\infty - V_t)$ on the Y- axis and time‘t’ on the X- axis. A linear graph is obtained. A slope is taken.

Result:

The rate constant of the reaction between $K_2S_2O_8$ and KI

i) Calculated value =

ii) Graphical Value =

Observations:

S. NO	Time (sec)	Volume of Thio (cc)	$x = (V_0 - V_t)$ mole/lit.	$K_o = (V_0 - V_t)/t$ mole/lit/sec.

V_0 = Volume of thio at zero time

V_t = Volume of thio at‘t’ time

$x = (V_0 - V_t)$

$K_o = (V_0 - V_t)/t$ mole/lit/sec.

4.2c) KINETICS OF IODINATION OF ACETONE

Aim:

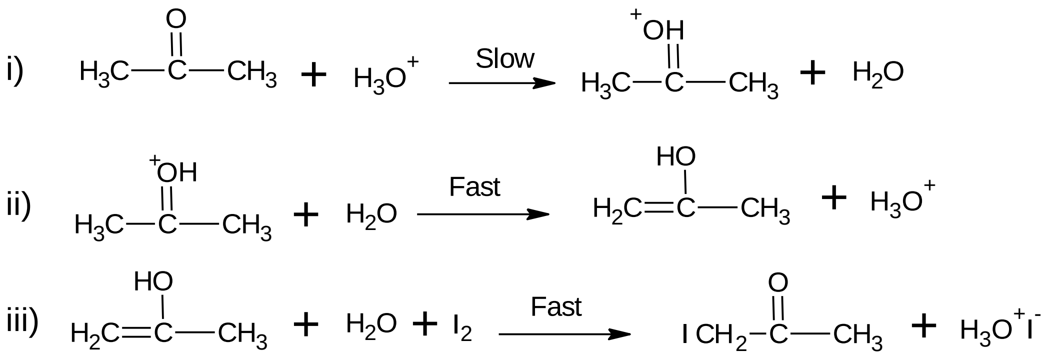
To determine the rate constant of the acid-catalysed iodination of acetone.

Principle:

Iodination of acetone in presence of acid is represented by the equation.

$$CH_3COOCH_3+I_2 \rightarrow I\text{-}CH_2\text{-}CH_3+HI$$

It is found to be zero order with H_3O^+ respect to iodine. The reaction is supposed to take place in the following three steps:



The rate of the overall reaction is governed by the slow step. This step does not involve the concentration of Iodine. Therefore, the rate law for this reaction is

$$-(dc/dt)=k_0[CH_3COCH_3][H_3O^+]$$

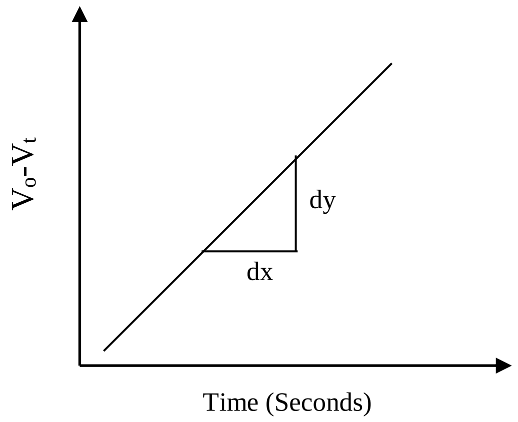
This rate equation does not include $[I_2]$ factor, hence it will be zero order with respect to iodine.

Materials Required:

1. Acetone
2. Iodine solution (N/10)
3. 1 M sulphuric acid
4. 0.2 M sodium acetate (quencher)
5. N/200 sodium thiosulphate solution

Graph:

(V_o-V_t) Vs Time in seconds



$$K_o = \text{slope} = \frac{dy}{dx}$$

Procedure:

Exactly 10ml of acetone is pipetted out into a clean reaction bottle. Exactly 10ml of 1M sulphuric acid solution is added and kept in a thermostat. To this added 10ml of 0.1N iodine solutions. When half of the solution is added, a stop watch is started. Immediately 5ml of reaction mixture is pipetted out and added to sodium acetate solution (to stop the reaction).It is titrated with N/200 thio solution using starch as indicator (V_0) at regular time intervals 5 ml of reaction mixture is pipetted out into a clean conical flask containing sodium acetate (10 ml) with ice-cold water.This solution is titrated against standard sodium thiosulphate solution using starch as indicator (V_t). From the titre values the rate constant (k_0) of the reaction is determined. A graph is drawn between (V_o-V_t) and time‘t’. The slope of which gives the rate constant k_0.

Result:

The rate constant for the iodination of acetone = moles $lit^{-1}sec^{-1}$

Calculation :

Weight of the solvent (A) W_1 =

Freezing point of the pure solvent (A) T_1 =

Weight of the solute (B) W_2 =

$$\left.\begin{array}{l}\text{Freezing point of pure solvent (A)} + \text{substance(B)} \\ \text{of the known molecular weight } (T_2{}^0C)\end{array}\right\} =$$

Molecular weight of the solute M_2 =

Depression in freezing point $\Delta T_f = T_1{}^0 - T_2{}^0$

Molal depression constant $K_f = \frac{\Delta T_f W_1 M_2}{1000 W_2}$

4.3 RAST METHOD

4.3a) DETERMINATION OF MOLECULAR WEIGHT

Aim:

To determine i) The molal depression constant of the given solvent and ii) the molecular weight of the given solute.

Principle:

The melting point of a pure substance (A) is a characteristic constant. If another solid (B) is added to (A), the melting point of (A) is lowered if there is no chemical reaction between them. This is known as the depression (or) lowering of the freezing point. This is expressed by the following expression.

$$\Delta T_f = K_f \times \frac{1000\ W_2}{W_1 \times M_2}$$

Where, T_f = Depression of freezing point

K_f = Molar depression constant of (A)

W_1 = Weight of substance (A) - solvent

W_2 = Weight of substance (B) – solute

M_2 = Molecular weight of (B) – solute

K_f can be calculated, provided the remaining quantities are known. Similarly M_2 can be found out.

Material Required:

1. Solvent (A) - Naphthalene
2. Diphenyl (B) - Known molecular weight
3. Unknown substance (C)
4. Thermometer 1/10th degree accuracy
5. Water bath
6. Freezing point apparatus

Calculation of Molecular Weight:

Weight of the solvent (A) W_1 =

Melting point of the pure solvent (A) $T_1{}^0C$ =

Weight of the unknown substance (C) W_2 =

$\left.\begin{array}{l}\text{Freezing point of pure solvent (A)} + \text{substance} \\ \text{(C) of the unknown molecular weight}\end{array}\right\}$ $T_2{}^0C$ =

Depression in freezing point $\Delta T_f = T_1^0 - T_2^0$

Molecular weight of the solute M_2 =

$$\frac{K_f \times 1000 \times W_2}{W_1 \times \Delta T_f}$$

Procedure:

Determination of molal depression constant, K_f of the solvent:

About 5gm of the solvent is taken in inner tube of the freezing point apparatus. A thermometer and a stirrer are introduced through the holes in the cork. It is then immersed along with the outer jacket in the waterbath and heated. The temperature at which the substance begins to melt is noted. This gives the melting point of the substance. The content is heated to about 5^0C above the melting point so that it becomes a clear solution. The apparatus is removed from the bath and cooled in air with stirring. The temperature at which the first crystal appears is noted. This is the freezing point. In practice these two temperatures will be slightly different. Hence, the mean of the two temperatures gives the melting point of the solvent taken (T_1^o). 0.5g of the solute (B) is weighed accurately and added to the solvent taken. The mixture is heated to get a homogeneous solution and cooled well to get the solid mixture. Now the melting point of the solid mixture (T_2^o) is taken as before. The difference in melting points gives T_f of solvent (A). K_f can be calculated from

$$K_f = \frac{\Delta T_f W_1 M_2}{1000 W_2}$$

Determination of molecular weight of unknown substance:

The whole procedure is now repeated using the substance (C) solute, for which molecular weight is to be calculated.

Result:

1) The molal depression canstant of given solvent =

2) Molecular weight of the given solute =

Tabulation:

S.No	Volume of Phenol (ml)	Weight of Phenol (Volume x density) (g)	Weight of water (same as volume) (g)	% of Phenol	Miscibility temperature (heating) ^0C	Turbidity Temperature (Cooling) ^0C	Average Temperature ^0C

Calculation:

Density of phenol = 1.071gm/cc

1. Percentage of Phenol =

$$\frac{\text{weight of Phenol}}{\text{Weight of water} + \text{Weight of Phenol}} \times 100$$

4.4 HETEROGENEOUS EQUILIBRIUM

4.4a) CRITICAL SOLUTION TEMPERATURE (PHENOL – WATER SYSTEM)

Aim:

To determine the critical solution temperature of phenol water system.

Principle:

When two partially miscible liquids (Phenol and water) are mixed together we get two layers, one containing the other dissolved in it. Here in the phenol water system, the lower layer is the solution of water in phenol and upper layer is the solution of phenol in water. When the temperature of the mixture of liquids increased the solubility of one in the other increases and becomes equal the solution becomes homogeneous. The temperature at which this happens is called upper critical solution temperature.

Material required:

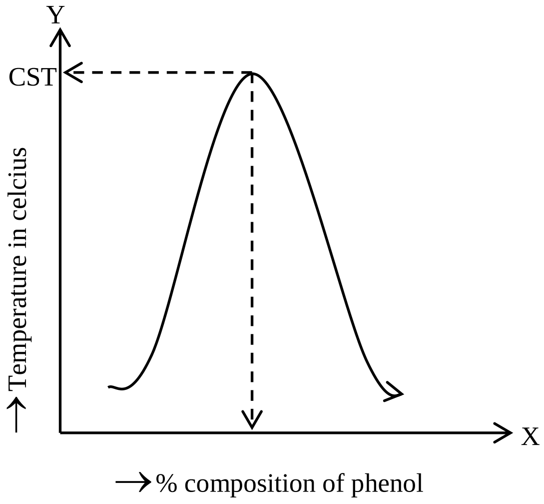
1. Phenol (distilled)
2. Distilled water
3. Freezing point apparatus
4. Pipette – graduated
5. Thermometer to read with 1/10 accuracy
6. Beaker (400ml) – water bath.

Procedure:

5ml of pure phenol is taken in the inner tube of the freezing point apparatus. 2ml of water is added. Thermometer and stirrer are inserted through the holes provided for them in the cork. The bulb of the thermometer must be well immersed in the solution. The solution is stirred well. The apparatus is placed in the beaker containing water. The portion containing the solution must be well immersed in water. Water in the beaker

Graph:

% of phenol Vs Miscibility temperature ^{0}c



is heated gradually to raise the temperature. The temperature at which the solution becomes homogeneous is noted. The apparatus is removed from the bath and allowed to cool in air. The temperature at which the turbidity appears is noted. The mean of these two temperatures is the miscibility temperature.The above experiment is repeated by adding 4,6,8,10,12,14ml of distilled water and their corresponding miscibility temperatures are noted.

Similarly, 5ml of distilled water is taken and 2ml of phenol is added and the experiment is done as above successively for by adding 4, 6, 8, 10,12ml of phenol.

A graph is drawn with % composition of phenol on the X-axis and miscibility temperature on the Y-axis. The temperature corresponding to the maximum of the curve is the critical solution temperature. (CST)

Result:

$$\left.\begin{array}{r}\text{i) The critical solution temperature of}\\ \text{phenol - water system}\end{array}\right\} =$$

$$\left.\begin{array}{r}\text{i) The percentage composition of}\\ \text{Phenol at CST}\end{array}\right\} =$$

Tabulation:

S. No	Percentage of NaCl Solution	Miscibility Temperature (Heating) ^0C	Turbidity Temperature (Cooling) ^0C	Average Temperature ^0C

4.4b) EFFECT OF IMPURITY ON CST -
DETERMINATION OF STRENGTH OF GIVEN NaCl SOLUTION

Aim:

To study the effect of impurity such as sodium chloride on phenol – water system and to determine the concentration of the given Sodium Chloride solution.

Principle:

The addition of impurities will affect the critical solution temperature. This is due to the solubility of the impurities in one (or) both components. The change in the critical solution temperature is directly proportional to the concentration of the impurity added.

Material Required:

1. Phenol (distilled)
2. Distilled water
3. 1% Sodium Chloride (2.5 g in 250 ml of water) – 250 ml
4. Freezing point apparatus
5. Thermometer, Water bath, Standard flask 100 ml

Procedure:

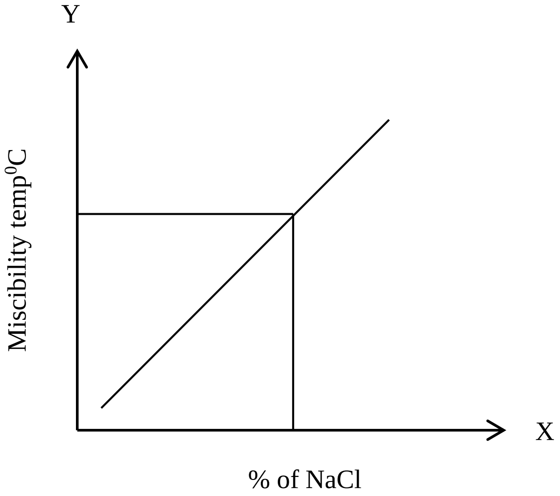
From 1% Sodium Chloride solution 0.8%, 0.6%, 0.4%, 0.2% Solution of Sodium Chloride are prepared as follows

0.8% Sodium Chloride = 80 ml of 1% NaCl + 20 ml of water in a 100 ml standard flask.

0.6% Sodium Chloride = 60 ml of 1% NaCl + 40 ml of water in a 100 ml standard flask.

Graph:

Miscibility temp Vs % of NaCl



0.4% Sodium Chloride = 40 ml of 1% NaCl + 60 ml of water in a 100 ml standard flask

0.2% Sodium Chloride = 20 ml of 1% NaCl + 80 ml of water in a 100 ml standard flask

5 ml of Phenol and 5 ml of 0.2% sodium chloride are taken in the inner tube of the freezing point apparatus. The solution is stirred well and the CST for this mixture is found out. The experiment is repeated for 0.4%, 0.6%, 0.8%, 1% and unknown solution of sodium chloride.

The concentration of the given sodium chloride could be found from graph. The strength of sodium chloride is taken on the X-axis and CST taken on the Y-axis. A vertical to the X-axis is drawn from the CST of the given sodium chloride and the percentage of given NaCl is noted.

Result:

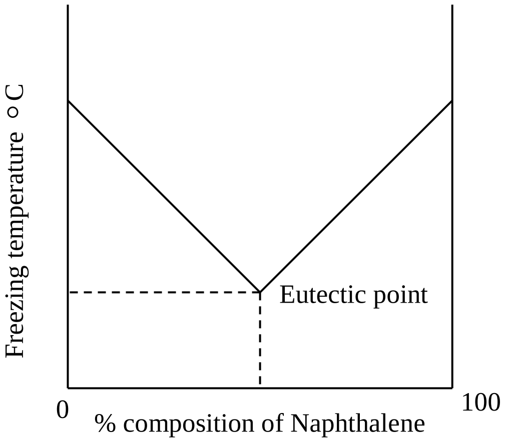
The strength of the given sodium chloride solution =

Observations and Calculation:

S.No	Weight of Naphthalene (g)	Weight of Diphenyl	% Naphthalene	% Diphenyl	Freezing point (Temperature) (^{0}C)
1	3	0	100	0	
2	3	0.5	85.7	14.3	
3	3	1.0	75	25	
4	3	1.5	66.6	33.3	
5	3	2	60	40	
6	0	3	0	100	
7	0.5	3	14.3	85.7	
8	1	3	25	75	
9	1.5	3	33.3	66.6	
10	2	3	40	60	

Model graph:

Percentage of naphthalene Vs freezing temperature



4.4c) SIMPLE EUTECTIC SYSTEM (NAPHTHALENE -BIPHENYL SYSTEM)

Aim:

To construct a phase diagram for a binary mixture and to determine the eutectic temperature and the corresponding composition.

Principle:

When a binary mixture is cooled, a solid separates out and the composition of the solid depends upon the nature of the substance. If the components are chemically dissimilar each lowers the freezing point of the other. The solids crystallize out separately and, a eutectic system is obtained. The temperature at which the separation results is known as eutectic temperature.

Materials Required:

Diphenyl and Naphthalene

Procedure:

Using the inner and outer tubes, the freezing points of pure naphthalene and that of pure Diphenyl are separately found out. The mixture of these two substances in various proportions varying from 10% to 90% of each of the components are so taken that the total weight of the mixture remains constant. The freezing point of each mixture is separately found out. The freezing points are plotted against their corresponding composition. From the curve the eutectic temperature and eutectic composition is recorded.

Result:

The eutectic temperature and eutectic composition of Naphthalene-Diphenyl was found to be

1. Eutectic temperature:
2. Eutectic composition:

S. No	Heating		Cooling	
	Time in minutes	Temperature ^{0}C	Time in minutes	Temperature ^{0}C

4.4 d) TRANSITION TEMPERATURE OF THE GIVEN SALT HYDRATE

Aim:

To determine the transition temperature of the given salt hydrate.

Procedure:

When a salt hydrate is heated the temperature is regularly increases and attains a steady constant temperature during which the transition takes place. This temperature is called transition temperature. After the complete change, the temperature again rises regularly on the other hand, if the substance has been heated above its transition point and if cooled slowly in air, its temperature will fall at a definite rate till the transition point is reached. After the change is complete the temperature falls regularly.

Materials Required:

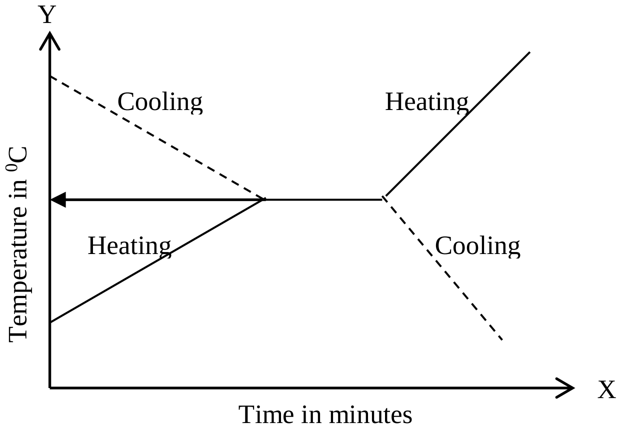
1. Salt – hydrate
2. Stop watch
3. Freezing point apparatus
4. Thermometer to read 1/10 degree accuracy.
5. Water bath (beaker containing Water)

Procedure:

The salt hydrate is taken in the inner tube of the freezing point apparatus to half its capacity. The bulb of the thermometer must be well immersed in the salt hydrate. The whole apparatus is placed in the bath and gradually heated.

When the temperature reaches the low value of range of temperature, then for every half a minute the temperature is noted. The substance must be stirred well during heating. Heating is continued till the temperature rises

Graph: Temperature Vs Time



by 5^0C above its transition temperature. The whole apparatus is removed from the water bath and cooled in air.

Now the stopwatch is again started from zero noting down the thermometer reading simultaneously. The temperature is noted for every half a minute during cooling. The cooling is continued till the contents are cooled 5^0C below the transition temperature.

A graph is drawn by taking temperature on Y-axis and time on X-axis. The temperature corresponding to the point of intersection of the two curves is the transition temperature.

Result:

$$\left.\begin{array}{l}\text{The transition temperature of the} \\ \text{given salt hydrate}\end{array}\right\} =$$

Tabulation:

S. No	Strength of KCl solution	Specific conductance k (mho cm^{-1})	Conductance (mho)	Cell constant $= \frac{\text{Specific conductance}}{\text{Conductance}}$ (cm^{-1})

Calculation:

Strength of KCl solution =

Specific conductance of KCl solution=

Conductance of KCl solution =

$$\text{Cell constant of the given cell} = \frac{\text{Specific conductance}}{\text{Conductance}}$$

$= \quad cm^{-1}$

UNIT - V

ELECTRO CHEMISTRY EXPERIMENTS

5.1 CONDUCTOMETRIC EXPERIMENTS

5.1a) DETERMINATION OF CELL CONSTANT

Aim:

To determine the cell constant of a given conductivity cell.

Principle:

In a conductivity cell electricity is conducted by an electrolytic solution in between the two platinum electrodes.

$$k = \frac{l}{a} \times \text{conductance}$$

$$k = x \times \text{conductance}$$

Where,
x = cell constant
k = specific conductance
l = distance between 2 electrodes
a = area of the electrodes

The cell constant is obtained by using KCl solution of known strength. The cell with known cell constant (x) can be used to determine specific conductance (k) of any solution.

Materials Required:

1. Exactly 0.1 and 0.01 N solutions of KCl
2. Conductivity Bridge
3. Conductivity cell
4. Beaker

Procedure:

The conductivity cell is washed well and rinsed with 0.1 N (or) 0.01 N KCl solution. Sufficient volume of 0.1 N (or) 0.01 N KCl solution is taken in a beaker and the cell is immersed in the same and its conductance is measured using the conductivity bridge. Form the specific conductivity and measured conductance values, the cell constant is calculated.

i.e., cell constant = $\frac{\text{Specific conductance (k)}}{\text{measured conductance}}$

Result:

The cell constant of the given conductivity cell =

Cell constant=

S. No	Strength of KCl (C)	Conductance (mho)	Specific conductance k = cell constant × conductance (mho cm^{-1})	Equivalent conductance $\lambda = \frac{1000}{C} \times k$ mho cm^{2} equ^{-1}

Calculation:

Specific conductance (k) = cell constant × Conductance (mho cm^{-1})

Equivalent conductance (λ) = $\frac{1000}{C} \times k$ (mho cm^{2} equ^{-1})

5.1b) EQUIVALENT CONDUCTANCE OF STRONG ELECTROLYTE

Aim:

To determine the equivalent conductance of given strong electrolyte using conductivity cell of known cell constant.

Principle:

In a conductivity cell electricity is conducted by an electrolytic solution in between the two platinum electrodes.

The cell constant is known from the following equation,

$$k = \frac{l}{a} \times \text{conductance}$$

$$k = \text{cell constant} \times \text{conductance}$$

Where, k = specific conductance

l = distance between 2 electrodes

a = area of the electrodes

The cell constant is obtained by using KCl solution of known strength.

The cell of known cell constant can be used to determine K, specific conductance of any solution.

The equivalent conductance (λ) of the given electrolyte is calculated by using the formula,

$$\lambda = \frac{1000}{C} \times k \text{ mho cm}^2 \text{ equ}^{-1}$$

Where, λ = equivalent conductance

k = Specific conductance

C = Strength of KCl Solution.

Procedure:

The cell constant is determined using 0.1N KCl and 0.01N KCl solution using conductivity cell. The conductance of the given solutions at various concentrations are measured using the conductivity bridge. From the cell constant and the conductance values, the specific conductivity and equivalent conductivity values are computed.

Result:

Equivalent conductance of the given KCl solutions =

Tabulation:

S.No	Volume of NaOH (ml)	Conductance (mho)

Calculation:

Volume of Sodium hydroxide V_1 =

Strength of sodium hydroxide N_1 =

Volume of HCl V_2 =

Strength of given HCl N_2 =

5.1c) CONDUCTOMETRIC TITRATINS (HCL VS NaOH)

Aim:

To determine the strength of hydrochloric acid solution by conductometric titration using standard sodium hydroxide.

Principle:

The conductance of HCl is due to the greatest mobility of H^+ ions. H^+ ions are substituted by less mobile Na^+ ions during the addition of NaOH. So, the conductivity of HCl solution decreases gradually till the end point, during the titration. After the neutralisation point, conductivity increases due to increase in the concentration of OH^- ions.

$$H^{+} + Cl^{-} + Na^{+} + OH^{-} \rightarrow Na^{+}Cl^{-} + H_{2}O$$

A graph is plotted between the conductivity values and the volume of sodium hydroxide solution added. Two straight lines are obtained. The point of intersection of two straight lines gives the equivalence point.

Materials Required:

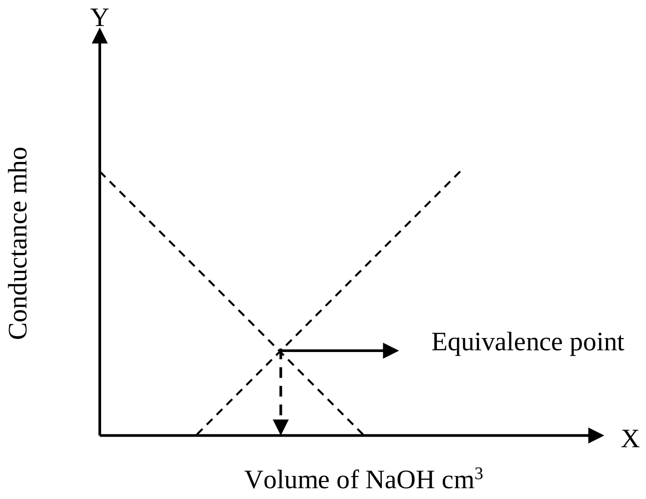
1. Sodium hydroxide - Known strength
2. Hydrochloric acid ~ 0.1N
3. Conductivity bridge
4. Conductivity cell
5. Burette, pipette
6. Beaker

Procedure:

10 ml of given acid (HCl) solution is pipetted out into a clean beaker. It is diluted initially by adding about 40 ml of distilled water. The conductivity cell is dipped in it. It is stirred well. The standard sodium hydroxide solution is added from the burette in small portions (about

Graph:

Conductance Vs volume of alkali



0.2 ml) and the conductivity is measured for each addition. The conductance of solutions decreases till equivalence point and then increases due to the formation of free hydroxide ions.

Atleast five readings should be taken beyond the end point. A graph is plotted between the conductance value and the volume of sodium hydroxide added. The end point is represented by the point of intersection of two straight lines.

Result:

The strength of the given HCl solution =

Tabulation:

S. No	Concentration (c)	Conductance (mhos) (C)	$k = (C) \times$ cell constant	$\lambda c = \frac{1000 \times k}{c}$	$\alpha = \frac{\lambda_c}{\lambda_0}$	$k_a = \frac{c\alpha^2}{1-\alpha}$
1.	0.1N					
2.	0.05N					
3.	0.02N					
4.	0.01					
5.	0.005N					
6.	0.002N					
7.	0.001N					

5.1d) DISSOCIATION CONSTANT OF A WEAK ACID

Aim:

To determine the equivalent conductance of a weak electrolyte at various concentrations and its dissociation constant.

Principle:

The equivalent conductance is the product of observed specific conductance and volume in ml containing one gram equivalent of the electrolyte. The equivalent conductance of strong electrolytes do not very much with concentration. In the case of weak electrolytes, equivalent conductance increases and specific conductance decreases with dilution. The equivalent conductance of the weak electrolyte (λ_c) at different concentrations are determined by measuring the conductance of these solutions. A plot of λ_c vs $\sqrt{C}$ will result in a parabola.

The degree of dissociation (α) of the electrolyte at different concentrations can be obtained from the equation.

$\alpha = \frac{\lambda_c}{\lambda_o}$ Where λ_0 is the equivalent conductance of the weak electrolyte at infinite dilution.

The dissociation constant of a weak electrolyte is given by Ostwald's dilution law, viz., $k_a = \frac{C\alpha^2}{1-\alpha}$

By knowing the values of C, and α, k_a is determined.

Materials Required:

1. Analar KCl
2. N/10 Acetic acid
3. Conductivity Cell
4. Conductivity water
5. Burette, pipette, Standard flasks

Calculation:

Cell constant of the conductivity cell = cm^{-1}

Equivalent conductance of $CH_3COOH(\lambda_0)$

at Infinite dilution = 390 mho cm^2

The conductance of CH_3COOH(c) = mhos

The equivalent conductance (λ_c) of

CH_3COOH (c) = conductance × cell constant

=

Degree of dissociation α = $\frac{\lambda_c}{\lambda_0}$

=

Dissociation constant of CH_3COOH K_a = $\frac{\alpha^2 C}{1-\alpha}$

= moles/lit.

Procedure:

Exactly $\frac{N}{10}$ KCl solution is prepared and its resistance is measured. From this value, the cell constant of the given conductivity cell calculated.

A 0.1N solution of a weak electrolyte, (acetic acid) is prepared using conductivity water and its exact strength is determined by titrating it against standard sodium hydroxide solution using phenolphalein indicator. From this stock solution, exactly 0.0025N, 0.005N, 0.01N, 0.02N, 0.05N, etc. solutions are prepared using conductivity water. Each solution is then taken in a beaker, the conductivity cell whose cell constant is determined previously is dipped into it. The conductance of the solution is measured by conductivity bridge.

From the measured conductance and cell constant, the specific conductance and hence equivalent conductance of each solution is calculated. Using the equivalent conductance at infinite dilution (λ_0) of acetic acid, the degree of dissociation (α) is calculated at different concentrations. The dissociation constant of the acid is calculated using Ostwald’s dilution law.

Result:

The dissociation constant of the

weak electrolyte (CH_3COOH), k_a =

Observations and calculations:

Volume of the acid solution = 20 ml.

S. No	Volume of NaOH (ml)	EMF (Volt)	ΔE (Volt)	ΔV (ml)	$\Delta E/\Delta V$

Strength of HCl acid soloution $= \dfrac{V_{NaOH} \times N_{NaOH}}{V_{HCl}} =$ N

5.2 POTENTIOMETRY

5.2a) POTENTIOMETRIC TITRATION

(Acid-base titration)

Strong acid Vs strong Base

Aim:

To titrate HCl against NaOH by Potentiometric method using Quinhydrone electrode.

Principle:

The potential of an electrode dipping in the solution of an electrolyte depends on the concentration of the ion with which it is in equilibrium. The change in potential with concentration during a titration provides an accurate indication of the equivalence point. For example the cell given below,

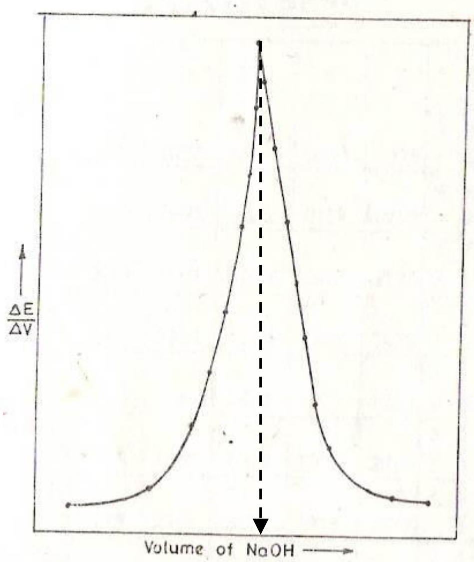
$$\mathrm{Hg, Hg_2Cl_2} \mid \mathrm{KCl}_{\text{(Saturated)}} \;\Big\Vert\; \begin{array}{c}\text{Acid solution}\\ \text{containing}\\ \text{Quinhydrone}\end{array} \;\Big|\; \mathrm{Pt}$$

will have a certain emf depending on the [H^+] of the solution. If an acid solution is added with an alkali in a cell having Quinhydrone electrode as cathode and standard Calomel electrode as anode, as the concentration of H^+ decreases the emf of the cell goes on decreasing. On adding small portions of a standard solution of alkali to the acid, the emf of the cell will change slowly at first, because the change in the electrode potential depends on the fraction of the hydrogen ions removed.

When the amount of alkali added approaches equivalence point, the fraction of the H^+ ion removed by each drop of alkali solution rapidly increases and there is a corresponding rapid change in emf. After the equivalence point, an excess of alkali is added, the emf again shows a slow change. Consequently when the emf of the cell (E) is plotted vs the

Graph:

Volume of NaOH Vs $\frac{\Delta E}{\Delta V}$



Potentiometric Titration
HCl vs. NaOH solution

volume of alkali (V) added, we get a curve. The point of inflexion is the end point. It can also be found by plotting $\Delta E/\Delta V$ against V where $\Delta E/\Delta V$ is maximum at the end point. These potentiometric titrations are used when colour indicators are not available. We get accurate end point. These can be carried out on a micro scale.

Procedure:

Exactly 20 ml of the acid solution is pipetted out in to a clean 250 ml beaker and diluted considerably so that the electrode dips well. A pinch of Quinhydrone is added and saturated. A platinum electrode is dipped in it. It is then connected to calomel by a salt bridge and included in the potentiometer circuit. The emf is determined. About 1ml portion of the alkali is added and at each addition, emf is determined. Near the end-point 0.1 ml portion may be added. Both graphs E vs V and $\Delta E/\Delta V$ vs V are plotted and the end-point is found. From the end point strength of HCl is calculated.

Result:

$$\text{Strength of given HCl solution}\} \qquad =$$

APPENDIX-I: Strength of common acids and bases

Reagent	Specific gravity	Normality(N)	Volume*(ml)
Hydrochloric acid	1.18	11.3	89
Nitric acid	1.42	16.0	63
Sulphuric acid	1.84	36.0	28
Acetic acid	1.05	17.4	58

* Volume required to make 1 litre of approximately 1N solution.

APPENDIX-II: Gravimetric factors

Element	Atomic Mass	Predicated Composition	Molecular Mass	Calculation factor
Pb	207.19	$PbCrO_4$	323.19	$\frac{Pb}{PbCrO_4}$ = 0.6411
Ba	137.34	$BaSO_4$ $BaCrO_4$	233.34 253.34	$\frac{Ba}{BaSO_4}$ = 0.5886 $\frac{Ba}{BaSO_4}$ = 0.5421
Ca	40.08	$CaC_2O_4.H_2O$	146.08	$\frac{Ca}{CaC_2O_4.H_2O}$ = 0.2744
Mg	24.312	Mg-Oxinate (Mg-$C_9H_6ON)_2.2H_2O$	348.312	$\frac{Mg}{Mg-Oxinate}$ = 0.06896
Ni	58.71	Ni $(DMG)_2$ Ni $(C_4H_7O_2N_2)_2$	288.71	$\frac{Ni}{Ni\,(DMG)2}$ = 0.2034

Cu	63.54	$Cu_2(CNS)_2$	243.92	$\frac{2Cu}{Cu2(CNS)2}$ = 0.5228
Chloride	35.45	AgCl	143.32	$\frac{Cl}{AgCl}$ = 0.2473

APPENDIX-III: Transition temperature of commonly used hydrated salts

Hydrated salt	Transition temperature
Sodium thiosulphate – $Na_2S_2O_3.5H_2O$	49.5
Strontium chloride – $SrCl_2.6H_2O$	60.5
Sodium acetate – $CH_3COONa.3H_2O$	58.3
Manganous chloride – $MnCl_2.4H_2O$	58.5
Sodium bromide – $NaBr.2H_2O$	50.8

APPENDIX-IV: Melting point of solvents and solutes used in molecular weight determination by Rast method

Substance	Molecular weight	Melting point
Naphthalene	128	80 – 82
Biphenyl	154	69 – 72
p-dichlorobenzene	147	54 – 56
p-nitro toluene	137	50 – 54
Benzophenone	182	49 – 51

Diphenylamine	169	52 – 54
Acetanilide	135	113 – 115
Benzamide	121	128 –129

APPENDIX-V: Molal depression constant of solvents

Solvent	Freezing point [^{0} C]	K_f [deg/mol]
Camphor	258.6	40.0
m-dinitrobenzene	90.0	10.6
Diphenyl	69.0	8.0
Diphenylamine	53.0	8.6
Napthalene	80.0	6.9

APPENDIX-VI: Boiling points of some common organic compounds

Substance	Boiling point [$^\circ$ C]
Benzene	80
Toluene	110
p-xylene	138
m-xylene	139
Ethyl alcohol	78
Methyl ethyl ketone	80
Ethyl acetate	77
Dimethyl ketone	102
Acetic acid	118

APPENDIX-VII specific conductance of KCl

(ohm^{-1} cm^{-1} or siemen cm^{-1}

Temp ^{0}c	0.1N KCl	0.02N KCl	0.01N KCl
10	0.00933		0.001020
20	0.01167	0.002501	0.001278
21	0.01191	0.002553	
22	0.01215	0.002606	
23	0.01239	0.002659	
24	0.01264	0.002712	
25	0.01288	0.002765	
26	0.01313	0.002819	
27	0.01337	0.002873	
28	0.01362	0.002927	
29	0.01387	0.002981	
30	0.01412	0.003036	0.001552
31	0.01437	0.003091	
32	0.01462	0.003146	
33	0.01488	0.003201	
34	0.01513	0.003256	
35	0.01559	0.003312	

B.Sc. CHEMISTRY
THIRD YEAR
PRACTICAL – III : ORGANIC PREPAERATIONS AND GERAVIMETRIC ANALYSIS
Model question paper

Time: 6 hours **Maximum Marks: 100**

ORGANIC PREPARATION
(or)
B.P.DETERMINATION: 30 Marks
GERAVIMETRIC ANALYSIS: 70 marks

1. a) Determine the Boiling Point of the given liquid

   (or)

   b) Prepare maximum quantity of benzoic acid from ethyl benzoate Recrystallise a portion of it and submit the crude and recrystallised sample for evaluation.
2. Estimate gravimetrically the amount of Barium present in the whole of the given Barium chloride solution, by converting it into Barium sulphate. Get the weighings attested by the Examiners.

B.Sc. CHEMISTRY
THIRD YEAR
PRACTICAL – IV : ORGANIC QUALITATIVE ANALYSIS AND PHYSICAL CHEMISTRY EXPERIMENTS

Model question paper

Time: 6 hours **Maximum Marks: 100**

ORGANIC ANALYSIS: 50 Marks
PHYSICAL EXPERIMENT: 50 Marks

I. Analyse the given organic compound and report on the following.

a) Whether aliphatic or aromatic.
b) Saturated or unsaturated
c) Special elements present.
d) Functional group present

Submit a colour reaction or derivative in support of functional group present.

II. students may be given a question (by a lot system) from the following physical chemistry experiments.

1. Determine the rate constant of the acid catalyzed hydrolysis of the given ester at room temperature
2. Determine the molecular weight of the given solute. You are provided with a suitable solvent, whose K_f value is _______________
3. Determine the transition temperature of the hydrated salt by thermometric method.
4. Determine the distribution coefficient of Iodine between Carbon tetrachloride and water at room temperature

5. Find out the concentration of the given sodium chloride solution. You are provided with pure phenol and 1% solution of Sodium Chloride.
6. Determine the rate constant of the reaction between Potassium Iodide and Potassium persulphate at room temperature.
7. Determine the molar depression constant K_f of the given solvent. You are provided with a solute of known molecular weight.
8. Determine the strength of the given Hydrochloric acid solution conductometrically using a standard Sodium Hydroxide solution.
9. Find out the cell constant of the given conductivity cell, using 0.1M and 0.01M potassium chloride solutions, whose specific conductivities are given. Determine the equivalent conductance of the two solutions of known concentration.