B.Sc. CHEMISTRY LAB MANUAL

1st Semester

Prepared By
Pure & Applied Science Dept.
Chemistry

MIDNAPORE CITY COLLEGE

CHEMISTRY HONOURS

[Choice Based Credit System]

(Semester Programme)

SEMESTER-I

C1P1: Organic Chemistry Lab

1. Separation of components of a binary solid mixture

Basic Concept: Synthesis of organic compounds often involves reactions that result in the formation of a mixture of products. Again, when some parts of a tree are extracted in an attempt to isolate a targeted compound, invariably a mixture of compounds appears. Isolation of the desired compound, therefore, needs exclusion of the unwanted companions. This constitutes the principle of separation of a mixture of compounds into its components. Wide variety of techniques including solvent extraction, fractional crystallisation and steam distillation, chromatography etc. is employed for this purpose. Increase in the number of components in the mixture requires technique with enhanced sophistication and clinical accuracy for separation. In the following section separation of a mixture of only two components utilising the difference in solubility of components in a suitable solvent is discussed.

If one component dissolves in a particular solvent and the other does not, the mixture may be shaken with appropriate solvent to dissolve the soluble component. Filtration separates the insoluble component from the soluble one. Then the soluble component has to be regenerated from its solution. Acidification, basification, evaporation etc. may be needed for this regeneration purpose.

General Procedure of Separation:

1. Test the solubility of the supplied Binary Mixture by adding a pinch of the sample in (~ 2 mL) each of the following two solvents and shake well to find the solvent in which a part of the mixture is soluble.

Solvents: (i) 10% NaOH solution, (ii) 6 (N) HCI.

2. Add (~ 25 mL) of the appropriate solvent (identified in step 1) to the rest of the mixture taken in a 100 mL beaker and stir well with a glass rod for 15 - 20 minutes.
3. Filter under suction and collect the filtrate in a 250 mL beaker.

4. Wash the residue obtained in step 3 with the same solvent used in step 2. Then wash the residue with water, dry and collect as the ‘Insoluble Part’
5. Precipitate the soluble component from the filtrate obtained in step 3 either by acidifying with conc. HCl (if 10% NaOH solution is used for dissolution) or basifying with 20% NaOH solution (if 6(N) HCl solution is used for dissolution) as the case may be. Filter off the precipitate, wash with water, dry and collect the solid as the soluble parts.

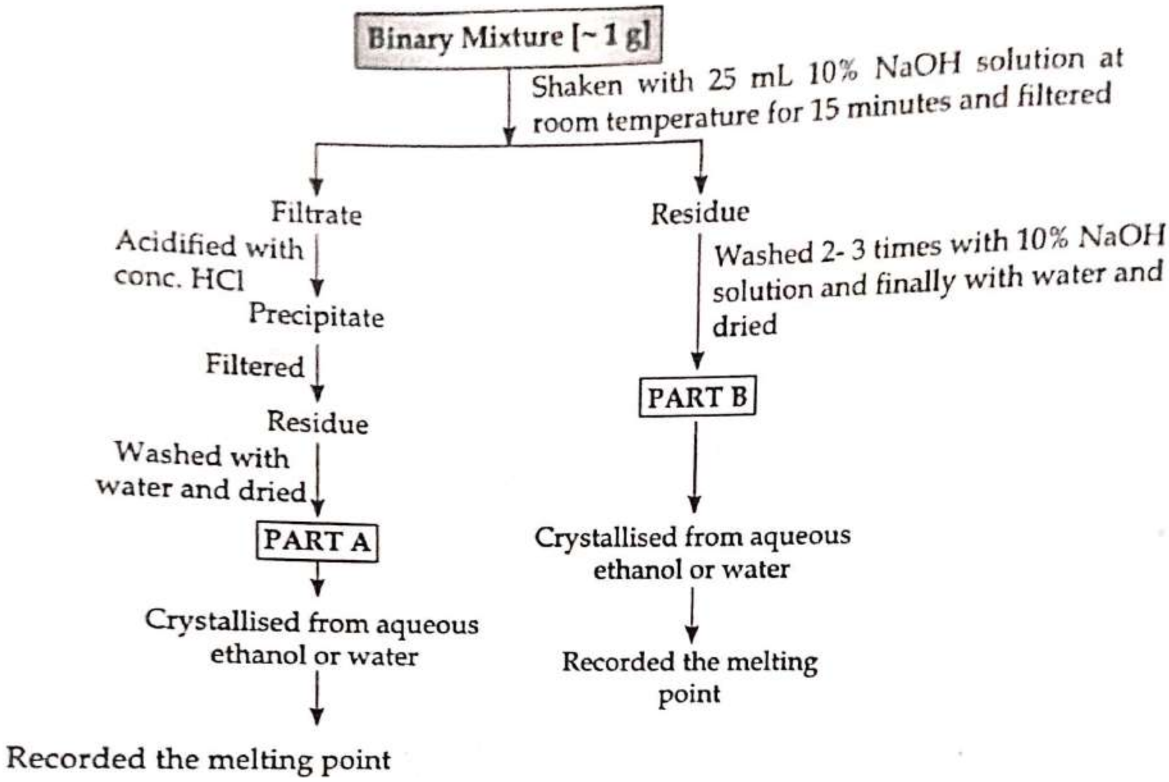
Reporting of Separation of Components of Unknown Binary Solid Mixture:

Chemical required	Apparatus required
6(N) HCl	Test tube
Conc. HCl	100 ml beaker
10% NaOH	Measuring cylinder

Chemical required	Apparatus required
20% NaOH	Glass rod
Distilled water	Suction filtering apparatus with small Buchner funnel

TYPE I [Mixture of Acidic (PART A) and Neutral (PART B) Components]: 0.2 g of the given binary mixture (preferably in powdered form, if crystalline sample is given, it should be ground thoroughly with the pestle to make it powder) is vigorously shaken separately with 2-3 mL of each of 6(N) HCl and 10% NaOH solution at room temperature for 5 minutes.

6(N) HCl	10% NaOH
Insoluble	Partly Soluble

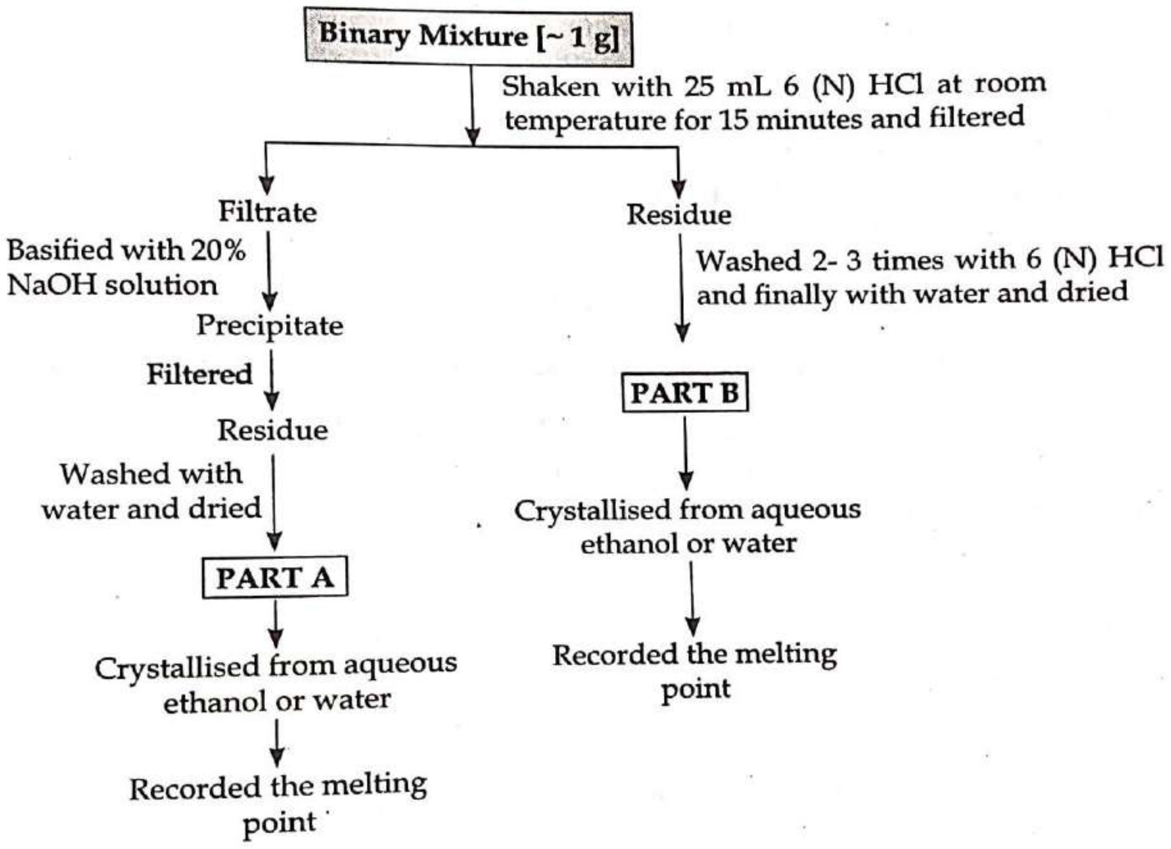


Melting point of part A=

Melting point of part B=

TYPE II [Mixture of Basic (PART A) and Neutral (PART B) Components] : 0.2 g of the given binary mixture (preferably in powdered form, if crystalline sample is given, it should be ground thoroughly with the pestle to make it powder) is vigorously shaken separately with 2-3 mL of each of 6(N) HCl and 10% NaOH solution at room temperature for 5 minutes.

10% NaOH	**6(N) HCl**
Insoluble	Partly Soluble



Melting point of part A=

Melting point of part B=

2. Boiling point determination: Here are varieties of methods by which a sample's boiling point can be determined, including distillation, reflux, and by using a Thiele tube. The most straightforward method uses a Thiele tube.

Distillation Method

There are simpler methods than a distillation to measure a compound's boiling point, and it is recommended to explore other options (e.g. Thiele tube) if this is the only goal. However, if materials are limited, or if purification is planned anyhow, a distillation can be used to determine a compound's boiling point (Figure 1).

A simple distillation should suffice for most situations, and at least 5 mL of sample should be used in the distilling flask along with a few boiling stones or stir bar. As the bulk of the material distills, the highest temperature is noted on the thermometer corresponds to the boiling point. A major source of error with this method is recording too low a temperature, before hot vapors fully immerse the thermometer bulb. Be sure to monitor the thermometer periodically, especially when the distillation is active. Record the barometric pressure along with the boiling point.

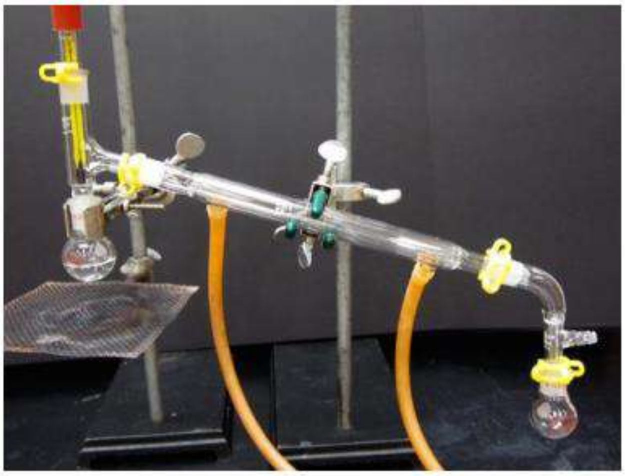


Figure 1

Reflux Method

A reflux setup can also be used to determine a compound's boiling point. Reflux is when a liquid is actively boiling and condensing, with the condensed liquid returning to the original flask. It is analogous to a distillation setup, with the main difference being the vertical placement of the condenser.

If materials are available, the best reflux setup for this application is shown in Figure 2 and uses a microscale condenser and digital thermometer. The setup uses ~5 mL of liquid, and a few boiling stones or stir bar. The condenser is attached to the round bottomed flask, with the lower water hose connected to the water spigot and the upper water hose draining to the sink. It is important to check that the joint connecting the flask and condenser is securely fastened. The liquid is brought to a boil on a sand bath, and the thermometer is placed low into the apparatus such that an inch separation exists between the boiling liquid surface and the bottom of the thermometer. In this position, the thermometer can accurately measure the hot vapors and the temperature will stabilize at the compound's boiling point. Record the barometric pressure along with the boiling point.

Although it might seem prudent to plunge the thermometer directly into the boiling liquid, it is possible the liquid may be superheated, or hotter than its boiling point. After determining the boiling point, the flask should be raised from the sand bath to cool, and condenser kept running until the flask is only warm to the touch. At this point the setup can be dismantled.

If a microscale condenser is not available, an alternative reflux method can also be used as shown in Figure 2. Roughly 5mL of sample is placed in a medium test tube (18 x 150 mm) with thermometer clamped inside so it does not touch the sides of the glass. The apparatus is carefully heated on a sand bath such that reflux happens controllably and vapors do not escape from the tube. The temperature during reflux will eventually stabilize (this takes some time), and the highest temperature noted corresponds to the compound's boiling point. The boiling points measured with this method may have significant error if the boiling point is very low or high (<70°C or >150°C) as low boiling compounds boil away too easily and high boiling compounds tend to cool too easily.

Figure 2

Thiele Tube Method

Thiele Tube Theory

The Thiele tube method is one of the simplest methods to determine a compound's boiling point, and has the advantage of using small amounts of material (less than 0.5 mL of sample). The sample is placed in a small tube along with an inverted capillary tube. The setup is attached to a thermometer and heated inside a Thiele tube to slightly higher than the compound's boiling point (which is evidenced by a continuous stream of bubbles emerging from the capillary tube). The tube is then allowed to cool, and the moment liquid is drawn into the capillary tube, the temperature is the compound's boiling point.

This method utilizes the definition of boiling point: the temperature where the compound's vapor pressure equals the applied (atmospheric) pressure. The inverted capillary tube acts as a reservoir to trap the compound's vapors. As the apparatus is heated, the air initially trapped in the capillary tube expands and causes bubbles to emerge from the tube (Figure 3). With further heating, the compound's vapors eventually displace all of the trapped air, which is why heat is applied until there is a continuous stream of bubbles.

When the apparatus is cooled, eventually the pressure inside the capillary tube (due solely to the compound's vapors) will match the atmospheric pressure, at which point the bubbles will slow and liquid will be drawn into the tube. The temperature where this begins is the compound's boiling point.

Thiele Tube Procedure

1. Obtain a Thiele tube and clamp it to a ring stand in the fume hood. The tube is normally filled with clear mineral oil, but it may have darkened from oxidation or spilled compounds. If the oil is quite dark, it should be replaced. The oil should be filled to at least 1cm higher than the top triangular arm and if too low the oil will not circulate as needed (Figure 3a).

2. Insert a thermometer into a one-holed rubber stopper with a slit down one side. Attach a small glass vial ("Durham tube", or 66 x 50 mm culture tube) to the thermometer with a small rubber band. The bottom of the vial should be flush with the bottom of the thermometer.

3. Fill the vial about half-full with sample.

4. Insert a capillary tube into the sample (the same type that is used for melting points), open end down and sealed end up.

5. Place the rubber stopper and thermometer assembly into the Thiele tube, adjusting the height so that the sample is midway (if possible) inside the tube. The rubber band should be higher than the top of the mineral oil, keeping in mind that the oil may expand somewhat during heating. The thermometer should not touch the sides of the glass, and if it does it should be clamped in such a way that it no longer touches.
6. Heat the oil gently on the side arm of the Thiele tube with a micro-burner if available, or Bunsen burner using a back and forth motion. As the oil warms and becomes less dense, it will rise and travel up the triangular portion of the tube. The cooler, denser oil will sink, thereby creating a current. This method is an excellent way to indirectly and slowly heat the sample.
7. Although bubbles should not be seen in the Thiele tube as it warms, they commonly are seen if the tube had been used previously for boiling point determinations. In this method, the rubber band occasionally breaks causing the sample to fall into the oil and contaminate it. If the oil is not subsequently changed, the sample may boil when heated in the tube. It is okay to continue heating a Thiele tube if bubbles are seen.
8. Studies of this method have determined that it is best to heat the oil gently and in a continual manner, as stopping and starting have caused the results to suffer.
9. Continue heating until a vigorous stream of bubbles emerges from the tip of the capillary tube (Figure 3d), such that individual bubbles can barely be distinguished. The purpose of this step is to expunge the air originally present in the capillary tube and replace it with the sample's vapor. Do not heat so vigorously that the entire sample boils away. When bubbles are vigorously emerging from the capillary tube, the vapor

pressure inside the tube is greater than the atmospheric pressure (the oil is at a higher temperature than the boiling point).

10. Turn off the burner and allow the apparatus to cool. The bubbles will slow and eventually stop. At some point the vapor pressure inside the capillary tube will equal the atmospheric pressure and liquid will be drawn into the tube (Figure 3e). The boiling point should be recorded as the temperature when liquid *just* begins to enter the capillary tube.

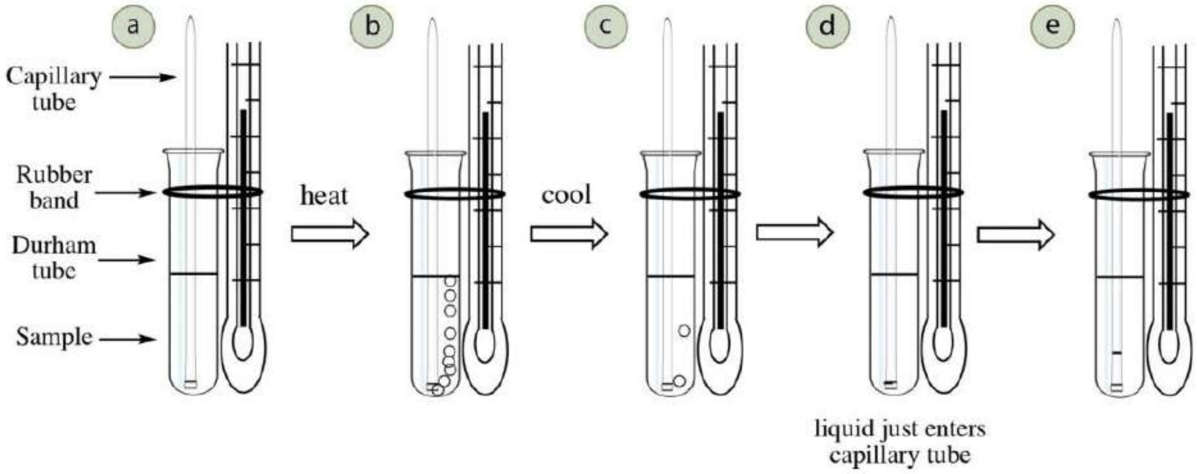


Figure 3

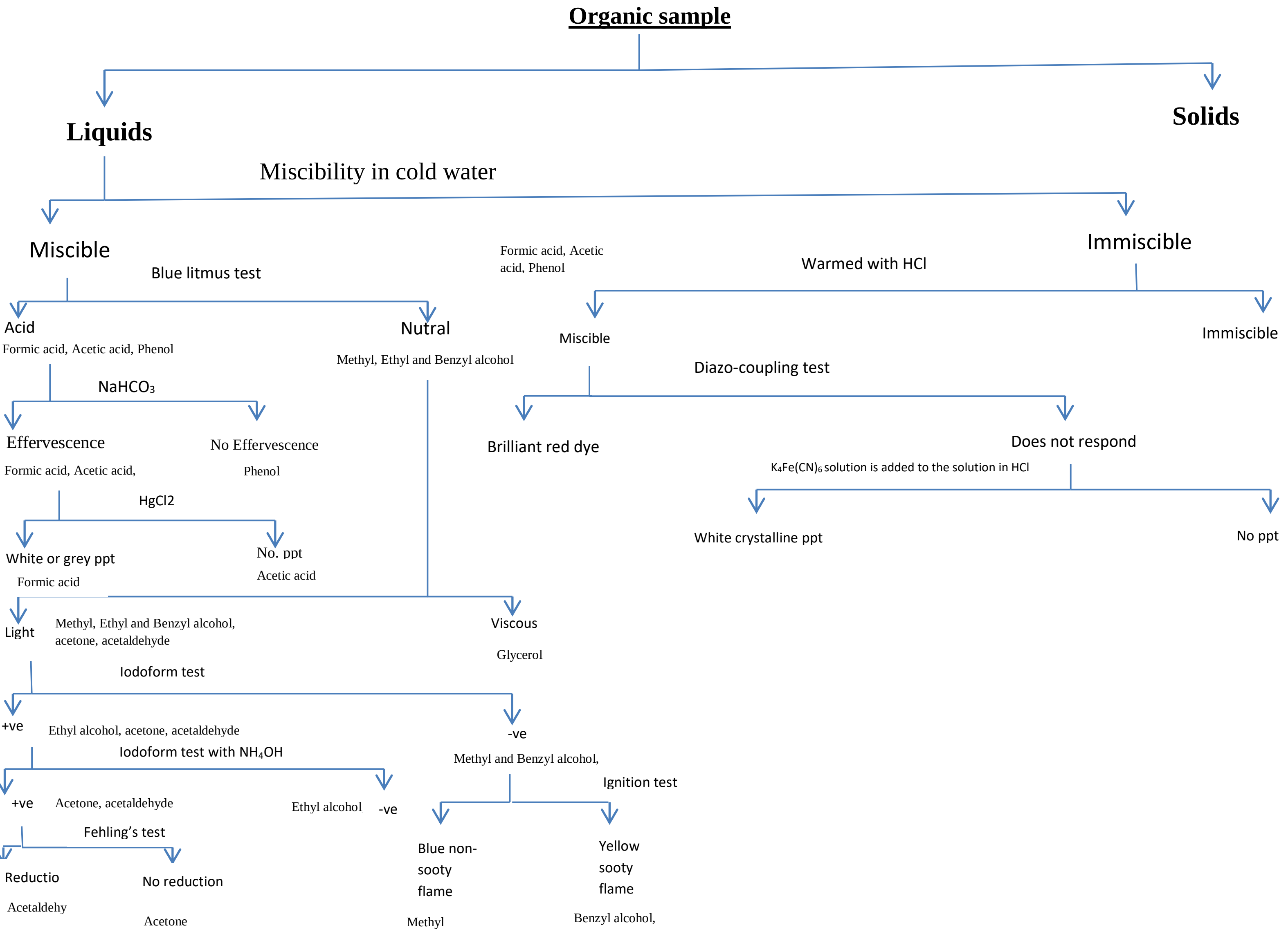
3.Identification of a Pure Organic Compound

The sample supplied may be any one of the following types:

1. Pure solid

2. Pure liquid

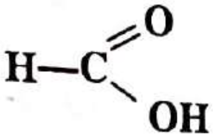
The following preliminary tests will be performed with the given sample;


Organic sample
Liquids
Solids
Miscibility in cold water
Miscible
Immiscible
Blue litmus test
Formic acid, Acetic acid, Phenol
Warmed with HCl
Acid
Formic acid, Acetic acid, Phenol
Nutral
Methyl, Ethyl and Benzyl alcohol
Miscible
Immiscible
Diazo-coupling test
NaHCO₃
Effervescence
Formic acid, Acetic acid,
No Effervescence
Phenol
Brilliant red dye
Does not respond
K₄Fe(CN)₆ solution is added to the solution in HCl
HgCl2
White or grey ppt
Formic acid
No. ppt
Acetic acid
White crystalline ppt
No ppt
Light
Methyl, Ethyl and Benzyl alcohol, acetone, acetaldehyde
Viscous
Glycerol
Iodoform test
+ve
Ethyl alcohol, acetone, acetaldehyde
-ve
Methyl and Benzyl alcohol,
Iodoform test with NH₄OH
Ignition test
+ve
Acetone, acetaldehyde
Ethyl alcohol
-ve
Fehling's test
Reductio
Acetaldehy
No reduction
Acetone
Blue non-sooty flame
Methyl
Yellow sooty flame
Benzyl alcohol,

Preparation of neutral solution: Solid sodium carbonate is added pinch by pinch to aqueous solution of suspension of organic sample taken in a beaker with continuous stirring with a glass rod till the effervescence ceases and a little sodium carbonate remains in excess. Then dilute nitric acid is added to it till the solution becomes distinctly acidic and finally ammonium hydroxide solution is added till the smell of ammonia persists after thorough mixing. Excess of ammonia is then boiled off completely and the solution is concentrated if necessary. The one-third portion of O.S is then used for special and confirmatory tests to identify a particular compound.

Liquid Compounds

1. Formic acid



Physical characteristics and preliminary test :

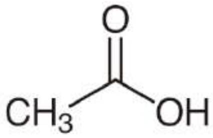
1. State : Liquid
2. Colour : Colorless
3. Odour : Strong pungent odour
4. Miscibility : Miscible with water in all proportions
5. Litmus : Blue litmus paper turns red
6. Action of heat : Completely volatilises without leaving any residue
7. Action of H_2SO_4 : Evolution of carbon monoxide in the cold and there is brisk evolution of carbon monoxide on warming which burns with a blue flame
8. Ignition test : Blue non-sooty flame

Special Tests

Experiment	Observation

1. Silver mirror test: Silver mirror test is performed with silver nitrate. This is added to O.S or neutral solution of O.S.	1. White ppt. of silver formate - blackens on warming due to reduction to metallic silver. N.B: The reduction is prevented in presence or ammonia. **(***difference from acetic acid***)**
2. $FeCl_3$ test: A few drops of freshly prepared feric chloride solution is added to neutral solution of O.S. The resulting solution is divided into two parts.	2. A red colour develops.
(a) Dilute HCI is added to another part.	(a) The red colour is discharged and yellow colour of $FeCl_3$ appears.
(b) One part is boiled.	(b) A brown ppt. of basic ferric formate.
3. Denige's reagent: Denige's reagent is added to a neutral solution or O.S. and boiled.	3. A white sand-like ppt.
4. Mercuric chloride test: A few drops of neutral solution of O.S. is added to a little $HgCl_2$ solution and warmed.	4. White ppt. of mercurous formate.
Then excess of neutral solution is added and warmed.	Grey ppt. of metalic mercury. **(***difference from acetic acid***)**

2. Acetic acid



Physical characteristics and preliminary test :

1. State : Liquid
2. Colour : Colorless
3. Odour : Characteristics smell of vineger
4. Miscibility : Miscible With water
5. Litmus : Blue litmus paper turns red
6. Action of heat : Completely volatilises without

	leaving any residue
7. Ignition test	**: Blue non-sooty flame**

Special Tests

Experiment	Observation
1. Denige's reagent: Denige's reagent is added to cool neutral solution of O.S. and then boiled. Very dilute solution of KMnO4 is added to the resulting solution.	1. No ppt. from cold or hot solution. No change of permanganate color.
2. $FeCl_3$ test: A few drops of freshly prepared feric chloride solution is added to neutral solution of O.S. The resulting solution is divided into two parts.	2. A red colour develops.
(a) Dilute HCI is added to another part.	(a) The red colour is discharged and yellow colour of $FeCl_3$ appears.
(b) One part is boiled.	(b) A brown ppt. of basic ferric formate.
3. $AgNO_3$ test: $AgNO_3$ solution is added to concentrated neutral solution of O.S. and boiled.	3. A white ppt. which does not turn black on boiling. **(***difference from acetic acid***)**
4. Mercuric chloride test: $HgCl_2$ solution is added to solution of O.S.	4. No ppt. (*Distinction from formic acid*) [N.B. : A white ppt. is obtained with ammonium acetate but no grey or black ppt. comes down.]
5. Cacodyl oxide test (C.T): The neutral solution of O.S. is heated to dryness and than thc residue is mixed with equal parts of arsenious oxide in a test tube and then heated. Thumb is held at the mouth of the test tube and the thumb is inhaled.	5. A characteristic obnoxious smell of cacodyl oxide. [N.B: The vapour should not be inhaled directly as it is highly poisonous. The test tube must be discards as the test is over.] (Adv.: *Better do not perform this test)*

3. Methyl Alcohol

CH_3-OH

Physical characteristics and preliminary test :

1. State	**: Liquid**
2. Colour	**: Colorless**
3. Odour	**: Pungent but faint alcoholic**
4. Miscibility	**: Miscible With water**
5. Litmus	**: Neutral**
6. Action of heat	**: Volatilises**
7. Ignition test	**: Blue non-sooty flame**

Special Tests

Experiment	Observation
1. Oxidation test : A Cu-spiral is made repeatedly red hot and introduced into 2 ml of O.S. kept in a test tube dipped in a beaker containing cold Water. The solution is then divided into four pan ts.	1.
(a) Schiffis test : One part is added to Schiff s.	(a) Pink color which deepens slowly.
(b) Tollen's test: Another part is added to Tollen's reagent and heated in a water-bath.	(b) Bright mirror of silver on the side of the test tube.
(c) Resorcinol test: A mixture of 0.5 ml of oxidised liquid and a drop of 0.5% aq. Solution of resorcinol is added carefully down the side of the test tube held in an inclined position containing 2ml of conc. H_2SO_4.	(c) A reddish -violet ring appears at the junction of two liquid layers. A white ppt. changing to reddish-violet appear in the aq. Layer above the ring after a little while.
2. Denige's reagent: To about 5ml of aq. Solution of o.s. in a porcelain basin placed on ice-water, 2-3 ml of 2.5% soln. of $KMnO_4$ soln. is added followed by few drops of conc. H_2SO_4 when a brown color developes. The brown color is destroyed by addition of saturated soln. of oxalic acid. A freshly prepared soln.of schiffs reagent is added dropwise to it with stirring.	2. A violet color develops deepening on standing.
3. Oil of wintergreen test: 0.5 ml of o.s. and 3 drops of conc. H2SO4 are added to 0.5 g of salicylic acid and heated for one minute and finally the reaction mixture is	3. Characteristics smell of methyl salicylate.

poured into 50 ml of water taken in a beaker. 4. **Iodoform test** in NaOH is performed (vide test 3a for ethanol)	4. The test is negative i.e., no yellowish ppt. of iodoform (*distinction from ethyl alcohol and acetone*)

4. Ethanol

CH_3CH_2OH

Physical characteristics and preliminary test :

1. State	**: Liquid**
2. Colour	**: Colorless**
3. Odour	**: Pungent but faint alcoholic**
4. Miscibility	**: Miscible with water**
5. Litmus	**: Neutral**
6. Action of heat	**: Volatilises**
7. Ignition test	**: Blue non-sooty flame**

Special Tests

Experiment	Observation
1. Oxidation test : A Cu-spiral is made repeatedly red hot and introduced into 2 ml of O.S. kept in a test tube dipped in a beaker containing cold Water. The solution is then divided into four parts.	1.
(a) Schiff's test : One part is added to Schiff s.	(a) Pink color which deepens slowly.
(b) Tollen's test: Another part is added to Tollen's reagent and heated in a water-bath.	(b) A silver mirror is disposited on the walls of the test tube.
(c) To another part equal volume of very dilute solution of sodium nitroprusside solution is added followed by a few drops of NaOH solution.	(c) Wine-red color develops.
(d) To another part a very dilute solution of sodium nitroprusside solution is added followed by a few drops of piperidine.	(d) A deep red color develops.
2. Ethyl acetate formation: About 0.2 ml of O.S. and an equal volume of glacial acetic acid and a little conc. H_2SO_4 (or 0.2 g of fused sodium acetate) are taken in a test tube and warmed in a water-bath for about 5 min. the mixture is then	2. Pleasant fruity smell.

poured into water taken in a beaker to which a little Na_2CO_3 has been added. **3. Iodoform test:** (a) To 2 ml of aq. soln. of o.s. an equal volume of a conc. solution of iodine in potassium iodide is added and then dil. NaOH solution is added dropwise with stirring until violet color of iodine disappears. Then the mixture is warmed and cooled under tap with shaking. (b) The iodoform test is repeated by adding NH_4OH instead of NaOH.	3. (a) Yellow ppt. of iodoform and its characteristic smell. (*distinction from methanol*) (b) No ppt. of iodoform. (*distinction from acetone*)

5. Chloroform

$CHCl_3$

Physical characteristics and preliminary test :

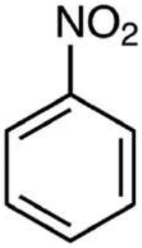
1. State : Liquid
2. Colour : Colorless
3. Odour : Sweet
4. Miscibility : Immiscible with water and much heavier than water
5. Litmus : Neutral
6. Action of heat : Volatilises
7. Ignition test : Yellow sooty flame

Special Tests

Experiment	Observation
1. Hydrolysis test: O.S. is treated with aq. KOH or NaOH solution and boiled. The mixture is acidified with conc. HNO_3 and then $AgNO_3$ is added. **2. Fehlings test:** O.S and Fehlings solution (I + II equal vol.) is warmed with constant shaking. **3. Resorcinol test:** A little powdered resorcinol and few drops of O.S. is taken in a basin, about 1 ml of conc. solution of NaOH is added to it, then the mixture is warmed gently.	1. Curdy white ppt. soluble in NH_4OH but reappears on addition of conc. HNO_3. 2. A yellowish red ppt. 3. A brilliant reddish colouration is developed in aq. layer. 4. Intolerable obnoxious smell of carbylamine. (*Not recommended to perform)*

4. Carbylamine test: Few drops of O.S. aniline and alc. KOH are warmed in a diy test tube and the ensuing gas is smelt by placing the thumb at the mouth of the test tube and then holding tfie thumb near the nostrils.	

6. Nitrobenzene



Physical characteristics and preliminary test :

1. State	**: Liquid**
2. Colour	**: Pale yellow**
3. Odour	**: Characteristic smell of bitter almonds**
4. Miscibility	**: Immiscible with water**
5. Litmus	**: Neutral**
6. Action of heat	**: Volatilises without leaving any residue**
7. Ignition test	**: Yellow sooty flame**

Special Tests

Experiment	Observation
1. Caustic soda test : About 0.2 ml of O.S. is heated with conc. solution of caustic soda.	1. The color darkens.
2. Reduction and diazocoupling test: 0.5 ml is reduced by tin or zinc and dil. HCl for 5 minutes. The decanted solution is cooled and very dilute cold solution of $NaNO_2$ is added to it. The diazotised soln. is added to cold alkaline soln. of. β-naphthol.	2. Brilliant scarlet-red dye.
3. Muliken-Barker test: An aq. ethanolic solution of few drops of given sample is boiled with a pinch of zinc dust	3. Grey or black ppt..

and little solid NH_4Cl. The mixture is cooled and filtered into Tollen's reagent.	

7. Acetone

CH_3COCH_3

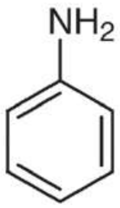
Physical characteristics and preliminary test :

1. State	**: Liquid**
2. Colour	**: Colorless**
3. Odour	**: Pleasant ethereal odour**
4. Miscibility	**: Miscible with water**
5. Litmus	**: Neutral**
6. Action of heat	**: Completely Volatilises without leaving any residue**
7. Ignition test	**: Blue non-sooty flame**

Special Tests

Experiment	Observation
1. Brady's test : A small amount of O.S. is added to 2-4-dinitrophenylhydrazine solution	1. Yellow ppt. on mixing.
2. Denige's test: An equal volume of Denige's reagent is added to an aqueous solution of O.S and the test tube is then kept in a boiling water bath for few minutes.	2. Heavy white ppt. of double compound of acetone and basic mercuric sulphate.
3. Legal's test: A few drops of a very dil. solution of sodium nitroprusside is added to 2-3 ml of aqueous solution of O.S. followed by a few drops of dil. NaOH solution.	3. A ruby red (reddish-purple) color develops which disappears on warming but reappears on cooling.
4. Iodoform test: (a) iodoform test is performed with I2 in KI solution and NaOH solution. (b) the iodoform test is repeated by adding NH_4OH solution instead of NaOH solution.	4. (a) Yellow ppt. of CHI_3 having characteristics sweeet smell. (b) Yellow ppt. of CHI_3 having characteristics sweet smell. (*Distinction from ethanol*)

8. Aniline



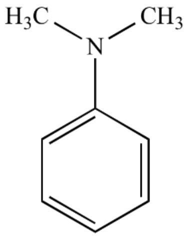
Physical characteristics and preliminary test :

1. State : Liquid
2. Colour : Colorless when freshly distilled but turns brown on exposure to light and air
3. Odour : Characteristic aromatic smell
4. Miscibility : Immiscible with water but soluble in dil. HCI
5. Litmus : Neutral
6. Action of heat : Completely volatilises without leaving any residue
7. Ignition test : Yellow sooty flame

Special Tests

Experiment	Observation
1. Bleaching powder test: A few drops of bleaching powder solution is added to a dilute solution of O S. in HCl.	1. Purple-violet colouration.
2. Potassium dichromate test: A drop of O.S. is added to 5 to 6 drops of conc. H_2SO_4 taken in a spot plate and the mixture is stirred well with glass rod. Then a drop of $K_2Cr_2O_7$ solution is added to it.	2. Intense blue colour develops.
3. Diazocoupling test: 5-6 drops of O.S are dissolved in dil. HCl in a test tube and cooled in ice-water. Then 3-4 drops of very dilute ice cold solution of sodium nitrite are added to it. Then the solution is added dropwise to 2 mL of ice-cold alkaline solution of β-naphthol; finally solution should remain mild alkaline	3. Brilliant scarlet-red dye.

9. *N,N*-Dimethylaniline



Physical characteristics and preliminary test :

1. State : Liquid
2. Colour : Colorless when freshly distilled

but turns brown on exposure to light and air

3. Odour : Characteristic bad smell
4. Miscibility : Immiscible with water but soluble in dil.HCI

5. Litmus : Neutral
6. Action of heat : Completely volatilises without leaving any residue
7. Ignition test : Yellow sooty flame

Special Tests

Experiment	Observation
1. Bleaching powder test: A few drops of bleaching powder solution is added to a dilute solution of O S. in HCl.	1. Purple-violet colouration.
2. Potassium dichromate test: A drop of O.S. is added to 5 to 6 drops of conc. H_2SO_4 taken in a spot plate and the mixture is stirred well with glass rod. Then a drop of $K_2Cr_2O_7$ solution is added to it.	2. Intense blue colour develops.
3. Nitrous acid test: 5-6 drops of O.S are dissolved in dil. HCl in a test tube and cooled in ice-water. Then 3-4 drops of very dilute ice cold solution of sodium nitrite are added to it.	3. A colour appears at this stage. (No red dye after addition to alkaline 2-naphthol solution) (*distinction from aniline*)
4. **Malachite green test**: See test of benzaldehyde below. Use benzaldehyde and this sample.	4. An intense green colouration

10. Benzaldehyde

C_6H_5CHO

Physical characteristics and preliminary test :

1. State : Liquid
2. Colour : Colorless
3. Odour : Characteristic smell of bitter almonds

4. Miscibility : Immiscible with water
5. Litmus : Neutral
6. Action of heat : Volatilises
7. Ignition test : Yellow sooty flame

Special Tests

Experiment	Observation
1. 2,4-D.N.P test: A few drops of 2,4-D.N.P solution is added to 1 mL alcoholic solution given sample.	1. Reddish yellow ppt. forms immediately simply on mixing.
2. Tollen's test: An alcoholic solution of the given sample is added to 2 mL of Tollen's reagent, warmed gently.	2. Black ppt.
3. Malachite green test: 0.5 ml of O.S is heated with 1 ml of dimethyl aniline and a small bit of anhydrous $ZnCl_2$ in a dry test tube for one minute. The leucobase produced is oxidised with lead dioxide in a solution of acetic acid and excess conc. HCl is added.	3. A intense green coloration.

Solid compounds

1. Oxalic acid [$(COOH)_2$]

Physical characteristics and preliminary test :

1. State : Solid
2. Colour : Colorless
3. Texture : Crystaline
3. Odour : Odourless
4. Solubility : Soluble in cold water
5. Litmus : Blue litmus turns red
6. Action of heat : Volatilises completely without charring when heated slowly and a sublimation is formed but decomposed with evolution of gases when heated strongly
7. Ignition test : Blue non-sooty flame

Experiment	Observation
1. H_2SO_4 test: A small amount of O.S. is heated with conc. H_2SO_4 and the evolved gas is passed into lime water.	1. Lime water turns milky.
2. Soda-lime test: A small amount of O.S. is heated in a hard glass test tube with sodalime.	2. The gas burns at the mouth of the test tube.
3. Calcium chloride test: Calcium chloride solution is added to neutral solution of O.S. The ppt is divided into two parts	3. A white ppt. forms immediately.

(i) Dil. acetic acid is added to one portion.	(i) The ppt does not dissolve. (*Distinction from tartaric and succinic acids*)
(ii) Dil. HCl or dil. HNO_3 is added to another portion.	(ii) The ppt. dissolves
4. Silver nitrate test : $AgNO_3$ solution is added to neutral solution of O.S. The ppt. is divided into three parts : (il Dil. NaOH is added to one portion. (ii) Dil. HNO_3 is added to another portion. (iii) The third portion is warmed, dried and heated strongly in a dry test tube	4. A white crystalline ppt. (i) The ppt. dissolves (ii) The ppt. dissolves (iii) Metallic silver is formed
5. Denige's test (C.T.): Denige's reagent is added to neutral solution or aqueous solution of O.S.	5. White ppt. in the cold which does not dissolve
6. Potassium permanganate test: A little of dil. H_2SO_4 is added to a solution of O.S or neutral soln. of O.S. The solution is warmed and dil. $KMnO_4$ solution is added drop by drop with shaking.	6. The pink colour of permanganate disappears.

2. Citric acid

Physical characteristics and preliminary test :

1. State : Solid
2. Colour : Colorless
3. Texture : Crystaline
3. Odour : Odourless
4. Solubility : Soluble in cold water
5. Litmus : Blue litmus turns red
6. Action of heat : Charring with evolution of acid-smelling vapour
7. Ignition test : Blue non-sooty flame

Experiment	Observation
1. H_2SO_4 test: A small amount of O.S. is heated with conc. H_2SO_4 .	1. Slow charring.
2. Calcium chloride test: An equal volume of calcium chloride solution is added to neutral solution of O.S. The mixture is shaken vigorously inner side of the test tube is scratched with glass rod and finally boiled.	2. No ppt. appears even on shaking and scratching but white crystalline ppt. appears after boiling for several minutes.
	3. A curdy white ppt (i) The ppt. dissolves

3. Silver nitrate test : $AgNO_3$ solution is added to neutral solution of O.S. The ppt. is divided into three parts : (i) Dil. NH_4OH is added to one portion. (ii) Dil. HNO_3 is added to another portion. (iii) The third portion is warmed, dried and heated strongly in a dry test tube	(ii) The ppt. dissolves (iii) No metallic silver is formed
4. Denige's test (C.T.): Denige's reagent is added to neutral solution or aqueous solution of O.S. and then a drop of 2% $KMnO_4$ solution is added.	4. No ppt. in the cold but the color of permanganate discharges with appearance of heavy white turbidity on boiling.

3. Succinic acid

Physical characteristics and preliminary test :

1. State : Solid
2. Colour : Colorless
3. Texture : Crystaline
3. Odour : Odourless
4. Solubility : Soluble in cold water
5. Litmus : Blue litmus turns red
6. Action of heat : Melts and then boils giving off extremely irritating vapours. A sublimate is forme d at the cooler part of the test tube
7. Ignition test : Blue non-sooty flame

Experiment	Observation
1. H_2SO_4 test: Few crystals of O.S. is warmed conc. H_2SO_4 and then heated strongly.	1. O.S dissolves without charring. Slight chairring occurs on strong heating and the solution turn brown with evolution of SO_2.
2. Calcium chloride test: An equal volume of Calcium chloride solution is added to neutral solution of O.S. The mixture is shaken vigorously inner side of the test tube is scratched with glass rod and finally boiled.	2. A white ppt. soluble in acetic acld. (*Distiction from oxalic macid*)
3. Silver nitrate test : $AgNO_3$ solution is added to neutral solution of O.S.	3. Buff-colored ppt. soluble in dil. HCl.
4. Denige's test (C.T.): Denige's reagent is added to neutral solution or aqueous solution of O.S. and then a drop of 2% $KMnO_4$ solution is added.	4. No ppt. in the cold but the color of permanganate presists.
5. Fluorescein test: A small quantity of the sample ix mixed with resorcinol and	5. A beautiful reddish green fluorescence, intesifies to a beautiful green fluorescence on addition of alkali..

2 / 3 drops of c. sulfuric acid and heated. Then poured into large volume of water.	

4. Resorcinol

Physical characteristics and preliminary test :

1. State : Solid
2. Colour : Colorless
3. Texture : Crystaline
3. Odour : Odourless
4. Solubility : Soluble in cold water
5. Litmus : feebly acidic
6. Action of heat : Melts and volatiles
7. Ignition test : Yellow sooty flame

Experiment	Observation
1. H_2SO_4 test: Few crystals of O.S. is warmed with conc. H_2SO_4.	1. O.S dissolve without charring.
2. Ferric chloride test: A few drops of $FeCl_3$ solution is added to aqueous solution of O.S.	2. Bluish-violet color.
3. Bromine writer test: Bromine writer is added to aq. solution of O.S. and shaken.	3. White ppt.
4. Tollen's test: Aqueous solution of O.S is added to Tollen’s reagent and warmed.	4. Black ppt of silver mirror.
5. Fluorescein test: A small quantity of O.S. is mixed with succinic acid / phathalic acid and 2 drops conc. Sulfuric acid and heated. Then poured into a large volume of water.	5. An intense reddish-green fluorescein, intesifies to a beautiful green fluorescence on addition of alkali.
6. O.S. is mixed with 3 - 4 drops $CHCl_3$ and gently heated on a basin with NaOH solution.	6. A brilliant reddish colouration is developed in aq. layer.

5. Urea

Physical characteristics and preliminary test :

1. State : Solid
2. Colour : Colorless
3. Texture : Crystaline
3. Odour : Odourless
4. Solubility : Soluble in cold water
5. Litmus : Neutral
6. Action of heat : Melts and gives off characteristic smell of NH_3
7. Ignition test : Blue non-sooty flame

Experiment	Observation
1. Nitrous acid test: Dil. HCl and dil. $NaNO_2$ solution is added to aq. Solution of O.s in a test tube and shaken.	1. Effervescence with evolution of gas.

2. Nitric acid test: 2 mL of conc. HNO_3 is added to aqueous concentrated solution of O.S.	2. A white crystalline ppt.
3. Oxalic acid test: A concentrated solution of oxalic acid is added to conc. solution of O.S.	3. A white crystalline ppt.
4. Biuret test: About 0 5 g of O.S. is heated gently# to melt. The heating is continued till the molten mass solidifies at once when test tube is taken out of flame. If there is no solidification the process is repeated. The residue is cooled and dissolved in I ml of NaOH solution by warming and shaking. The solution is cooled again and a drop or two of a very dilute copper sulphate solution is added to it.	4. A pink or violet colour develops. [#strong and rapid heaing leads to formation of cyanuric acid and then the test will fail]

6. Benzoic acid

Physical characteristics and preliminary test :

1. State : Solid
2. Colour : White
3. Texture : Plate-shaped or needle shaped Crystal
3. Odour : Odourless
4. Solubility : Insoluble in cold water but Soluble in hot water
5. Litmus : Blue litmus turns red
6. Action of heat : Melts and sublimates
7. Ignition test : Yellow sooty flame

Experiment	Observation
1. H_2SO_4 test: A small amount of O.S. is warmed with conc. H_2SO_4.	1. Dissolves without charring.
2. Soda-lime test: A small amount of O.S. is heated in a hard glass test tube with sodalime.	2. Characteristics smell of benzene.
3. Denige's test: Denige's reagent is added to neutral solution of O.S.	3. White ppt. dissolves on boiling but appears on cooling.
4. Ferric chloride test: (a) A drop or two of freshly prepared solution of $Fecl_3$ is added to neutral solution of O.S. (b) Dilute HCl is added to it.	4. (a) a buff-colored ppt. (Distinction from salicylic acid) (b) buff-colored ppt dissolves with appearance of white ppt.
5. Esterification test: About 0.1 g of O.S and 2 mL of dehydrated alcohol are taken in a clean test tube and shaken well. Then a few drops of conc. H_2SO_4 is added and the test tube is waremd in a hot water bath. The test tube is cooled and content	5. Characteristics fruity smell of ester.

of the test tube is poured into 50 mL of dilute sodium cxarbonate solution taken in a beaker.	

7. Salicylic acid

Physical characteristics and preliminary tests:

1. State : Solid
2. Colour : White
3. Texture : needle shaped Crystal
3. Odour : Odourless
4. Solubility : Sparingly soluble in cold water but readily Soluble in hot water
5. Litmus : Blue litmus turns red
6. Action of heat : Melts and sublimes
7. Ignition test : Yellow sooty flame

Experiment	Observation
1. H_2SO_4 test: A small amount of O.S. is warmed with conc. H_2SO_4.	1. The solid dissolved, charring occurs after some time, solution darkens and gas evolve.
2. Soda-lime test: A small amount of O.S. is heated in a hard glass test tube with sodalime.	2. Characteristics smell of phenol.
3. Denige's test: Denige's reagent is added to neutral solution of O.S.	3. White ppt. dissolves on boiling but appears on cooling.
4. Ferric chloride test: A drop or two of freshly prepared solution of $Fecl_3$ is added to neutral solution of O.S. (a) Dilute HCl is added to it. (b) acetic acid is added to another part.	4. An intense violet color (*Distinction from benzoic acid*) (a) The color discharges (b) The color persists
5. Oil of wintergreen test: About 0.1 g of O.S and 1 mL of methanol and few drops of conc. H_2SO_4 are warmed in aclean dry test tube.	5. A characteristics pungent fragnant odor which intensifies on pouring the mixture to dil. Sodium carbonate solution.

8. Tartaric acid

Physical characteristics and preliminary test :

1. State : Solid
2. Colour : Colorless
3. Texture : Crystalline
3. Odour : Odourless
4. Solubility : Soluble in cold water
5. Litmus : Blue litmus turns red
6. Action of heat : Chars and gives off smell of burnt sugar
7. Ignition test : Blue non-sooty flame

Experiment	Observation
1. H_2SO_4 test: A small amount of O.S. is warmed with conc. H_2SO_4.	1. charrs immediately.
2. Calcium chloride test: Excess of calcium chloride solution is added to neutral solution of O.S. shaken and inside of the test tube is scratched with a glass rod.	2. A white crystalline ppt. soluble in hot dilute acetic acid.
4. Silver nitrate test : (a) $AgNO_3$ solution is added to neutral solution of O.S. (b) Addition of AgNO3 solution is continued till the precipitation is complete. Then dil. NH4OH is added dropwise with constant shaking till the ppt. almost and not completely dissolved as revealed by slight turbidity.	4. (a) A white crystalline ppt. (b) shining silver mirror forms at the inner of the test tube. (*Distinction from oxalic, citric, succinic acids)*
5. Denige's test (C.T.): Denige's reagent is added to neutral solution or aqueous solution of O.S.	5. Permanganate color discharges immediately without turbidity.

9. Glucose

Physical characteristics and preliminary test :

1. State : Solid
2. Colour : Colorless
3. Texture : Crystalline
3. Odour : Odourless
4. Solubility : Soluble in cold water
5. Litmus : Neutral
6. Action of heat : Charrs and gives off smell of burnt sugar
7. Ignition test : Blue non-sooty flame

Experiment	Observation
1. H_2SO_4 test: A small amount of O.S. is warmed with conc. H_2SO_4.	1. No charring in cold but darkens on heating immediately.
2. Sodium hydroxide test: 2 ml of 3% solution of NaOH is added to conc. solution of O.S. and the mixture is heated. The mixture is then acidified with dil. HNO_3.	2. The solution turns first yellow and then raddish brown.
3. Tollen's test: 5 ml of aqueous solution of O.S. is added to equal volume of Tollen's reagent taken in a clean test tube and then the test tube is placed in a beaker of boiling water bath for a few minutes.	3. Black or grey precipitate or shining silver mirror.
4. Fehling's test: The sample is added to a mixture of Fehling A and Felling B and heated for 1 minute.	4. Brick red precipitate.
5. Lead acetate test: Lead acetate solution is added to solution of o.s and the mixture is boiled for few seconds. Then dil. NH_4OH solution is added dropwise till just sufficient to produce a permanat white ppt. then the mixture is boiled again.	5. The white ppt. turns salmon-pink in color.

10. Cane sugar

Physical characteristics and preliminary test :

1. State : Solid
2. Colour : Colorless
3. Texture : Crystalline
3. Odour : Odourless
4. Solubility : Soluble in cold water
5. Litmus : Neutral
6. Action of heat : Charrs and gives off smell of burnt sugar
7. Ignition test : Blue non-sooty flame

Experiment	Observation
1. H_2SO_4 test: A small amount of O.S. is warmed with conc. H_2SO_4.	1. Immediate charring even in cold.
2. Sodium hydroxide test: 2 ml of 3% solution of NaOH is added to conc. Solution of O.S. and the mixture is heated. The mixture is then acidified with dil. HNO_3.	2. No chharing but sometimes a light yellow color develops.

3. Fehling's test: (a) The sample is added to a mixture of Fehling A and Felling B and heated for 1 minute. (b) A little of aq. Solution of o.s is boiled with dil. HCl or dil. $H2SO_4$ for few minutes. The solution is then made alkaline with NaOH solution. The solution is added to 2 ml of Fehling solution and warmed. **4. Lead acetate test:** Lead acetate solution is added to solution of o.s and the mixture is boiled for few seconds. Then dil. NH_4OH solution is added dropwise till just sufficient to produce a permanat white ppt. then the mixture is boiled again.	3. (a)No ppt. (b) Red ppt of Cu_2O. 4. The white ppt. does not change color.

C2P2: Physical Chemistry Lab

Experiment 1: Determination of pH of unknown solution (buffer), by color matching method:

Theory:

P^H of a solution is defined as the negative logarithm of its H^+ ion activity i.e,

$$P^H = -\log a_{H^+}$$

In case of solution of low ionic strength

$$P^H = -\log c_{H^+}$$

The solution having applicable capacity to resist the change in its P^H due to addition of acid or base are called buffer solutions. Usually they consist of a mixture of a weak acid or base and its salt.

In case of a mixture of a weak acid and its salt [provided the solution is not very acidic (P^H>4)]. P^H of the solution can be expressed as

$$P^H = pK_a + \log \frac{[\mathrm{Salt}]}{[\mathrm{acid}]}$$

And I case of a mixture of weak base and its salt [provided the solution is not very basic (P^H<10)].

$$P^H = pK_b + \log\frac{[\text{salt}]}{[\text{base}]}$$

Both the equations are known as Henderson equation for weak acid and weak base respectively and will be valid only within the P^H range 4 to10.

As indicator is a substance which can indicate, generally by colour change, the specific physic-chemical condition of a chemical system.

The acid-base indicator or neutralization indicators are substance which exhibit different colours according to the hydrogen ion concentration of their environment. It is therefore possible to obtain a idea of the P^H of a given solution by adding a little of a suitable indicator to the same. Colour changes are believed to be due to some structural changes. In solution the acidic form (In_A) and the basic (In_B) of an indicator will be in equilibrium.

$$In_A \rightleftharpoons H^+ + In_B$$

The equilibrium constant called indicator constant (K_{In}) corresponding to this equilibrium is

$K_{In} = a_{In}a_{H^+}/a_{InA} = [H^+][In_B]/[In_A]$, in solution of low ionic strength

Or, $P^H = pK_{In} + \log\frac{[InB]}{[InA]}$

The colour of the indicator as perceived by the eye is determined by the ratio of the concentrations of the acid and alkaline forms i.e, by $[In_B]/[In_A]$

The value of $[In_B]/[In_A]$ determines the actual shade of colour as a mixture of two colours (predominant colours in acidic and basic medium). Thus by changing the P^H of the solution one can developed by an indicator. If a solution of known P^H exhibits a particular shade of colour, with a definite amount of indicator, then another solution (of unknown P^H) which exhibits the same shade of colour, with the same amount of indicator, must also posses the same P^H.

Apparatus required:

1. 100 mL volumetric flask-3
2. 500 mL bottle-2
3. Burette-1
4. 10 mL pipette-1
5. 250 mL conical flask-1
6. Hard glass test tubes of equal diameter-10

Procedure:

1) Prepare 100 mL standard 0.5(N) oxalic acid solution in a volumetric flask by accurate weighing.
2) Prepare 250 mL~0.5(N) NaOH solution.
3) Standardize the prepare NaOH solution against the 0.5(N) oxalic acid solution, taking 10 mL of the acid as aliquot and using phenolphthalein as indicator.
4) Determine the strength of the alkali: Prepare 100 mL of exact 0.4(N) NaOH solution by proper dilution.
5) Prepare 250 mL~0.5(N) CH_3COOH solution and Standardize it against prepared ~ 0.5(N) NaOH solution.
6) Determine the strength of CH_3COOH solution. Prepare 100 mL of exact 0.4(N) CH_3COOH solution by proper dilution.
7) Take 10 hard glass test tubes by approximately equal diameter, lebel them from 1 to 9 and prepare the following buffer solutions by proper mixing of exact 0.4(N) NaOH and 0.4(N) CH_3COOH.

Test tube No.	**Volume of CH_3COOH(mL)**	**Volume of NaOH(mL)**	**Volume of H_2O(mL)**	**Total volume(mL)**	**P^H**

8) In the remaining test tube pipette out exactly 10 mL of the unknown buffer. To each of these test tubes add 5 drops of the indicator. Mix thoroughly to develop uniform colour in each test tube. Identify the p^H of the buffer solution by colour matching.

Experimental Result:

1) Room temperature
2) **Preparation of 100 mL 0.5(N) oxalic acid:**
   Required weight (3.15 gm) of oxalic acid was taken in a 100 mL volumetric flask and volume was made up to the mark by deionized water.
3) **Preparation of 250 mL approximately 0.5(N) NaOH solution:**
   5 gm NaOH solid was taken in a glass bottle and~250 mL deionized water was added (using measuring cylinder) to make 250 mL~0.5(N) NaOH solution.
4) **Standardization of the prepared NaOH solution:**

Volume of 0.5(N) Oxalic acid (mL)	Burette reading		Volume of NaOH(mL)	Average volume of NaOH(mL)
	Initial(mL)	Final(mL)		

5) **Preparation of 100 mL exact 0.4(N) NaOH solution:**

Required volume of prepared NaOH solution = $\frac{100\times0.4}{\text{strength of NaOH solution}}$ mL

…… mL prepared NaOH solution was taken (using burette) in a 100 mL volumetric flask and rest of the volume was made by adding deionized water up to the mark.

6) **Preparation of 250 mL~0.5(N) acetic acid:**

7.4 mL of the acetic acid was taken in a glass bottle and~250 mL deionized water was added (using measuring cylinder) to make 250 mL~0.5(N) CH_3COOH solution.

7) **Standardization of the prepared CH_3COOH solution:**

Vol. of~0.5(N) acetic acid (mL)	Burette reading		Vol. of standardization NaOH solution used (mL)	Average vol. of NaOH (mL)
	Initial(mL)	Final(mL)		

Strength of CH_3COOH solution:

8) **Preparation of 100 mL exact 0.4(N) CH_3COOH solution:**

Required volume of prepared CH_3COOH solution= $\frac{\mathbf{100\times0.4}}{\boldsymbol{Strength\ of}\ \textbf{CH3COOH solution}}$ **mL.**

…..mL prepared CH_3COOH solution was taken (using burette) in a 100 mL volumetric flask and rest of the volume was made by adding deionized water up to the mark.

9) **Preparation of buffer solution:**

Test Tube No.	Volume of CH_3COOH(mL)	Volume of NaOH(mL)	Volume of H_2O (mL)	Total volume (mL)	P^H
1	0.5	0.5	4.5	10.0	3.72
2	0.5	1.0	4.0	10.0	4.05
3	0.5	1.5	3.5	10.0	4.27
4	0.5	2.0	3.0	10.0	4.45
5	0.5	2.5	2.5	10.0	4.63
6	0.5	3.0	2.0	10.0	4.80
7	0.5	3.5	1.5	10.0	4.99
8	0.5	4.0	1.0	10.0	5.23
9	0.5	4.5	0.5	10.0	5.57

Conclusion:

The colour of the test tube containing unknown buffer matched with the colour of the test tube no …… having p^H …… Therefore p^H of the unknown buffer solution is…..

Experiment 2: Determination of heat of neutralization of a strong acid by a strong base:

Theory:

The molar heat of neutralization $(-\Delta H_{neut})$ of an acid can be defined as the heat change associated with the complete neutralization of its dilute aqueous solution containing one mole of H^+ ions by a dilute aqueous solution of a base containing one mole OH^- ions.

Let us consider a neutralization reaction of strong acid (HA) by a strong base (BOH) in aqueous solution. Since both are completely dissociated in aqueous solution we can represent the neutralization reaction as

$$H^+ (aq) + A^- (aq) + B^+ (aq) \rightarrow A^- (aq) + B^+ (aq) + H_2O$$

$$\text{Or, } H^+ (aq) + OH^- (aq) \rightarrow H_2O$$

Thus the neutralization of strong acid with strong base can be considered as the combination or reaction of H^+ ions with OH^- ions. In other words molar heat of neutralization is the formation of 1 mole of water from one mole each H^+ and OH^- ions. Therefore molar heat of neutralization is constant irrespective of the strong acid or the strong base used.

Heat measurements are performed by carrying out the reaction in a special container called a calorimeter. The heat given off by the neutralization reaction is absorbed by the reaction solution and the calorimeter. Both the solution and calorimeter increases in temperature due to the absorbed heat and this increase can be measured with a thermometer.

Total Heat of neutralization ($-\Delta H_{neu}$)

= Heat gained by salt solution + heat gained calorimeter

= [Mass of salt solution × Sp. Heat capacity of salt solution× Δt of salt solution]+[Calorimeter constant × Δt of calorimeter]

Molar heat of neutralization $(-\Delta H_{neut})$

$$= \frac{Total\ heat\ of\ neutralization(-\mathbf{\Delta Hneu})}{No.of\ moles\ of\ acids\ neutralized}$$

To evalute the calorimeter constant (also known as its heat capacity) in J/ºC, adds a known mass of hot water to a known mass of cold water which is in the calorimeter. Heat is lost by the hot water and is absorbed by the cold water and the calorimeter.

Heat lost by Hot water = Heat gained by cold water + Heat gained by calorimeter

Or, Mass of hot water × Sp. Heat capacity of water × Δt of Hot water = [Mass of cold water × Sp. Heat capacity of water × Δt of cold water]+[Mass of calorimeter × Sp. Heat capacity of calorimeter × Δt of calorimeter].

where, [Mass of calorimeter × Sp. Heat capacity of calorimeter]=Calorimeter constant

Δt is found by plotting temperature versus time for the system in the calorimeter and extrapolating the results to find Δt the instant of mixing.

Apparatus required:

1) Glass calorimeter,
2) 100 mL conical
3) 100 mL beaker,
4) 25 mL pipette
5) Stop watch
6) 500 mL glass bottle.

Chemicals required: Oxalic acid , HCl, NaOH and Phenolphthalein

Procedure:

a) Determination of calorimetric constant:

1) Pipette out 25/50 mL of distilled water into a clean and dry calorimeter with stirrer. This is the cold water. Suspend a digital thermometer into water.

2) Pipette out 25/50 mL of distilled water into a 100 mL conical flask. Heat this water to 20-30ºC above the temperature of the cold water. Remove the heat source and place a digital thermometer within the flask.

3) Be sure to note the starting time when measuring temperatures. Starting with the hot water, simultaneously measure the hot and cold water (in the calorimeter) and record the temperature of the mixture at 1 minutes intervals for 8-10 minutes.

4) Clean and dry the beaker and calorimeter for the neutralization reaction.

5) Plot graphs of temperature vs time (in minutes as abscissa) for hot water, cold water and mixture. Extrapolate the three straight lines beyond the data points. Indicate the temperature of hot water and cold water and that of the mixture at the time of mixing in the graph as shown in Figure 3.1.Evalute the calorimeter constant.

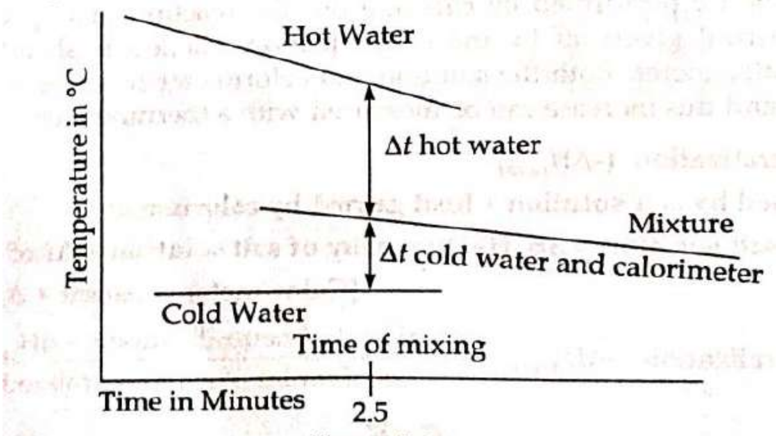


Figure-3.1

b) Acid-Base neutralization:

1) Prepare~2(N) HCl and~2(N) NaOH solutions. Standardize the prepared NaOH solution by taking 25 mL supplied oxalic acid solution [strength 1(N)] using phenolphthalein indicator. Determine the strength of NaOH is molarity.

2) Standardize the prepared acid solution against standard NaOH solution, taking 25 mL of the acid as aliquot and using phenolphthalein as indicator. Calculate the strength of acid in molarity.

3) Pipette out 25/50 mL of NaOH solution into a 100 mL beaker.

4) Pipette out 25/50 mL of assigned acid solution into the clean dry calorimeter. Suspend digital thermometers in both the acid and the base solution. Start the timer.

5) Note the temperature of both acid and base at 1 minute interval (total 5 readings for each acid and base). [Since both the acid and base have been at room temperature for several hours, we can safely assume that both are at he same temperature.(Check the thermometer)].

6) Quickly add the base to the acid in the calorimeter, stir gently and note the time. Record the solution temperature every minute for 8-10 minutes.

7) Plot the graphs of temperature vs.time (in minutes as abscissa) for acid, base and the mixture. Extrapolate the straight lines beyond the data points. Indicate the temperature of the acid, base and the mixture in the graph as shown in Figure 3.2. Evalute the heat of neutralization.

8) Be sure to neutralization all of the acidic hydrogens of the acid (strength of base should be slightly higher than that of acid as same volume of acid and base are mixed to react). Detremine the moles of water formed in the system from the molarity and volumes of acid and base used and calculate molar heat of neutralization.

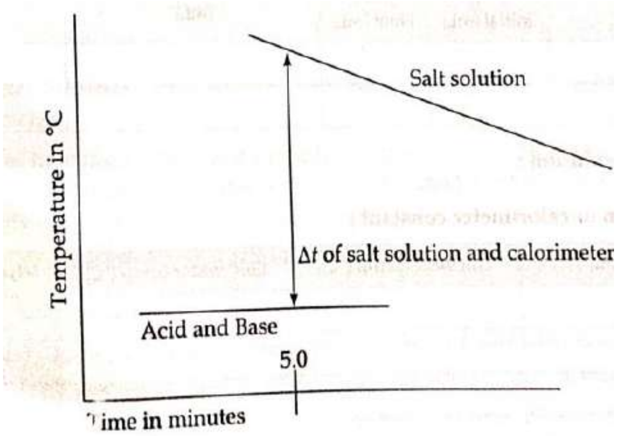


Figure-3.2

Experimental result:

1) Determination of strength of NaOH using 1N oxalic acid:

Vol. of 1(N) oxalic acid (mL)	**Burette reading**		**Vol. of NaOH used (mL)**	**Average vol. of NaOH(mL)**
	Initial(mL)	**Final(mL)**		
25				
25				

Strength of NaOH solution:

2) Determination of strength of HCl:

Vol. of HCl (mL)	**Burette reading**		**Vol. of NaOH used (mL)**	**Average vol. of NaOH(mL)**

	Initial (mL)	**Final (mL)**		
25				
25				

Strength of HCl solution:

3) Determination of calorimeter constant:

Time (min)	**Hot water temp(^{0}C)**	**Cold water(^{0}C)**	**Mixed water temp(^{0}C)**
0			
0.5			
1.0			
1.5			
2.0			
2.5	**Mixing of Hot and Cold water**		

Time(min)	**Hot water temp (^{0}C)**	**Cold water temp temp (^{0}C)**	**Mixed water temp (^{0}C)**
3.0			
4.0			
5.0			
6.0			
7.0			
8.0			

4) **Determination of Heat of neutralization:**

Time (min)	**Acid solution temperature (^{0}C)**	**Base solution temperature (^{0}C)**	**Salt solution temperature (^{0}C)**
0			
1.0			
2.0			
3.0			
4.0			
5.0	Mixing of Acid and Base		
6.0			
7.0			
8.0			
9.0			
10.0			

Calculation:

1) **Calorimeter constant:** Heat lost by Hot water = Heat gained by cold water + Heat gained by calorimeter
    - Mass of hot water × Sp. Heat capacity of water × Δt of Hot water = [Mass of cold water × Sp. Heat capacity of water × Δt of cold water]+[Mass of calorimeter ×Sp. Heat capacity of calorimeter × Δt of calorimeter]
    - [Mass of calorimeter × Sp. Heat capacity of calorimeter]= Calorimeter constant = … J/^{o}C.
2) **Heat of neutralization:**
    a) **If acid and base have different temperature:** Heat gained by acid solution + Heat gained by base solution + Heat gained by Calorimeter.
        - Total Heat of neutralization ($-\Delta H_{neut}$) = [Mass of acid solution × Sp. Heat capacity of acid solution × Sp. Heat capacity of calorimeter]
    b) **If acid and base have same temperature:** Heat of neutralization = Heat gained by salt solution + heat gained by calorimeter.
        -
        - Total Heat of neutralization ($-\Delta H_{neut}$) = [Mass of salt solution × Sp. Heat capacity of salt solution × Δt of salt solution]+[Calorimeter constant × Δt of Calorimeter]

Calculation of moles of acid used in neutralization reaction :

Strength of HCl (say) = M

So, 1000 mL HCl solution contains M mole HCl

25/50 mL HCl solution contains $\frac{\mathrm{M}\times(25 \text{ or } 50)}{1000}$ mole HCl.

Heat of neutralization for $\frac{\mathrm{M}\times(25 \text{ or } 50)}{1000}$ mole HCl= X joule (say)

Therefore, Heat of neutralization for 1 mole HCl, $(-\Delta H_{neut})$

= X/ M × (25 or 50) KJ mol^{-1}

Experiment 3: Study of kinetics of acid-catalyzed hydrolysis of methyl acetate:

Theory:

The acid catalysed hydrolysis reaction of ester can be represented as

$$R_1COOR_2 + H_2O + H^+ \rightleftarrows R_1COOH + R_2OH$$

The rate equation is represented as

$$-\frac{d[R_1COOR_2]}{dt} = k[R_1COOR_2][H^+][H_2O]$$

$= k_1[R_1COOR_2]$, where $k_1 = k[H^+][H_2O]$ = constant, (in large excess of water,$[H_2O]$ remains constant and H^+ being the catalyst $[H^+]$ is constant)

Therefore the reaction becomes first order w.r.t ester. Integration of this equation with the boundary conditions, when t= 0, $[R_1COOR_2] = C_0$ and at time t, $[R_1COOR_2] = C$, gives

$$K_1 = (2.303/t)\log (C_0/C)$$

The progress of the catalysed reaction may be studied by withdrawing measured volume of aliquot from the reaction mixture at different intervals of time and titrating with standard alkali solution using phenolphthalein indicator. The volume of alkali required at any instant is equivalent to be the sum of weak acid (produced as a result of hydrolysis) and the acid used as catalyst (a constant quantity).

If V_0, V_n and V_∞ be the volumes of alkali required for the same volume of aliquot at the beginning, at time $t = t_n$ and at the end of the reaction (at infinite time) respectively then,

$$C_0 \propto (V_\infty - V_0) \text{ and } C \propto (V_\infty - V_n)$$

Then, $k_1 = \frac{2.303}{t_n} log \frac{(V\infty - V0)}{(V\infty - Vn)}$

To avoid the measurement of V_0 the equation may be represented in the form

$$\Delta t_n = t_n - t_1 = \frac{2.303}{k_1} log \frac{(V\infty - V1)}{(V\infty - Vn)}$$

Where V_n and V_1 are the volumes of alkali required at times t_n and t_1 respectively.

Plot of $log \frac{(V\infty - V1)}{(V\infty - Vn)}$ vs Δt_n will give a straight line passing through the origin and the slope k_1 may be determined by

$$K_1 = \text{slope} \times 2.303$$

Apparatus required:

1) 100 mL dry conical flask-1
2) 500 mL bottle for NaOH.
3) 2 mL pipette; 5 mL pipette-1 each
4) 250 mL conical flask-5
5) Sufficient ice cold water; water bath
6) **Stop watch**

Chemicals required: Methyl acetate, NaOH, and Phenolphthalein

Procedure:

1) Prepare 250 mL of approximately 0.1(N) NaOH solution.
2) Prepare 100 mL 1(N) HCl solution
3) Pipette out 50 mL of prepared HCl solution (catalyst solution) in a 100 mL dry conical flask, add 5 mL of ester using a pipette. Start the stop watch at the time of half discharge. Mix the solution thoroughly by swirling motion.
4) At 5-7 minutes intervals take 2 mL aliquot and add to 50 mL ice cold water taken in a 250 mL conical flask. Note the time of half discharge. Titrate rapidly against the prepared~0.1(N) NaOH solution taken in a burette, using phenolphthalein as indicator. Take at least 6 readings.
5) The remaining solution is heated at about 60ºC in a water bath~for 40 minutes with an air condenser fitted in the mouth of conical flask. The solution is allowed to cool to room temperature. Pipette out 2mL of it in 50 mL water taken in a 250 mL conical flask and titrate with~0.1(N) NaOH solution; using phenolphthalein as indicator. The titre value correspond to V∞.

6) Plot a graph of $log\frac{(V\infty - V1)}{(V\infty - Vn)}$ vs Δt_n and draw the best fit straight line passing through the origin.
7) Calculate the value of 'k_1' from the slop of the graph.

Experimental result:

1) Room temperature

2) Preparation of 250 mL~0.1(N) NaOH solution: Dissolve 1 g NaOH in 250 mL deionized water.

3) Preparation of 100 mL 1(N) HCl solution: Dissolve~9mL conc. HCl in 91 mL deionized water

4) Recording of data for ester hydrolysis:

Time(t)	Time(t_n)in sec	$\Delta t_n = t_n - t_1$	Volume of NaOH(V_n mL)	(V_∞-V_1) mL	(V_∞-V_n)mL	$log\frac{(V\infty - V1)}{(V\infty - Vn)}$

5) Determination of V_∞:
V_∞ = Volume of NaOH required to standardize 2 mL reaction mixture after heating at about 60ºC in a water bath.

6) Plotting of graph:

$log\frac{(V\infty - V1)}{(V\infty - Vn)}$						
Δt_n(Sec)						

Calculation: Observed rate constant, k_1=slope×2.303

Conclusion: Threfore observed rate constant for the acid catalyzed hydrolysis of methyl acetate at …..ºC is…..sec^{-1}.

Experiment 4: Study of kinetics of decomposition of H_2O_2

Theory:

The reaction between H_2O_2 and KI in dilute H_2SO_4 medium is represented as

$$H_2O_2+2KI+H_2SO_4=I_2+2H_2O+K_2SO_4$$

Suggested reaction mechanism is

$$H_2O_2+I^-=H_2O+OI^- \quad \text{….(slow)}$$

$$OI^-+2H^++I^-=H_2O+I_2 \quad \text{…….(fast)}$$

The first step being the slowest step is the rate determining step. The differential rate becomes

$-\frac{d[H_2O_2]}{dt}=k[H_2O_2][I^-]$, where k is the rate constant and other terms have their usual significance.

Therefore kinetically the reaction is of second order (overall). But if the concentration of iodide ion is kept constant [by adding $Na_2S_2O_3$ continuously whereby the $S_2O_3^-$ ions react with the liberated iodine (I_2) and regenerate I^- according to the equation, $I_2+2S_2O_3^{2-}=S_4O_6^{2-}+2I^-$] the reaction becomes kinetically first order w.r.t.[H_2O_2] only. Under this condition the rate equation may be expressed as

$$-\frac{d[H_2O_2]}{dt}=k_1[H_2O_2], \text{ where } k_1=k[I^-]$$

If the initial (at time t=0) concentration of H_2O_2 is a and at time t, $[H_2O_2]$ = (a-x), (where, x= amount of H_2O_2 reacted), integration of the above equation gives

$$K_1=\frac{2.303}{t}\log\frac{a}{a-x}$$

If both ‘a’ and (a-x) are represented in terms of their $Na_2S_2O_3$ equivalent , we have

$V_0 \propto a$ (where V_0 is the titre value of thiosulphate for the total iodine liberated by a fixed volume of H_2O_2 solution of concentration ‘a’ after complete decomposition).

And $V_t \propto x$ (where V_t is the titre value of the same thiosulphate solution for the iodine liberated by the same H_2O_2 solution undergoing reaction at time t)

The rate equation may then be express as

$$K_1 = \frac{2.303}{t} \log V_0/V_0\text{-}V_t$$

$$\text{Or, } \log V_0/V_0\text{-}V_t = k_1 t/2.303$$

A plot of V_0/V_0-V_t vs. t will give a straight line passing through the origin and from the slope k_1 may be determined, k_1= slope× 2.303.

Apparatus required:

1) 500 mL conical flask-2
2) 500 mL glass bottle for thiosulphate-1
3) Burette-1
4) 250 mL volumetric flask for KI-1
5) 10 mL pipette
6) Watch glass
7) Stop watch

Chemicals required: H_2O_2 , Sodium thiosulphate,KI,12N H_2SO_4,1% Ammonium molybdate solution, Starch

Procedure:

1) Prepare 100 mL ‘2 volume’ H_2O_2 solution. in a glass bottle.
2) Prepare 250 mL of 0.1(N) sodium thiosulphate solution in glass bottle. Fill the burette with sodium thiosulphate solution.
3) Take 10 mL 12 (N) H_2SO_4 in a 500 mL conical flask. Add 10 mL of prepared H_2O_2 solution followed by addition of 50 mL of water. Then add approximately 2 gm soli KI. Add 2 mL 1% ammonium molybdate solution. Cover the conical flask with a watch glass and keep it in dark for 1 minute. Add about 50 mL of water and titrate the liberated iodine with sodium thiosulphate solution using starch as indicator. Record the volume of thiosulphate (V_0).
4) Take 250 mL of 0.4% KI solution (dissolve 1 gm KI in 250 mL deionized water) in a 500 mL conical flask. Add 15 mL 12(N) sulphuric acid and 5 L of freshly prepared starch solution. Add 10 mL of prepared H_2O_2 solutions and at the time of half discharge start stop watch.
   Run immediately sodium thiosulphate solution from the burette from the burette into the mixture in excess to discharge the blue colour. Wait for appearance of blue colour and record the time (t) of reappearance of colour, volume of thiosulphate used (V_t). Again run thiosulphate into the mixture in excess to discharge the blue colour, record time (t) of reappearance of colour, and total volume of thiosulphate used (V_t).Take at least 6 readings.

5) Plot log [V_0/(V_0-V_t)] vs. t in millimeter graph paper and draw the best fit straight line passing through the origin. Calculate ‘k_1’ value from the slope of the graph.

Experimental result:

1) Room temperature
2) Preparation of 250 mL~0.1(N) sodium thiosulphate solution: Dissolve~6.2 gm $Na_2S_2O_3$ in 50 mL deionized water.
3) Determination of V_0 :
   V_0 = titre value of thiosulphate for the total iodine liberated by 10 mL of’’2 volume’ H_2O_2 solution after complete decomposition.

4) **Titre value of thiosulphate at different times:**

Time(t)	Time (t) in sec	Volume of $S_2O_3^{2-}$ used (V_t mL)	(V_0-V_t) mL	log V_0/V_0-V_t

5) **Plotting of graph:**

log V_0/V_0-V_t						
t(sec)						

Calculation: Observed rate constant, k_1=slope× 2.303

Conclusion: Therefore observed rate constant for the decomposition of H_2O_2 at ….. ^{0}C is …….Sec^{-1}.

Experiment 5: Determination of heat of solution of oxalic acid from solubility measurement

Theory:

The dissociation of a solid into a liquid is usually accompanied by heat change (heat is either evolved or absorbed). For equilibrium between a solid non-electrolyte and its saturated solution (pure solvent+ pure solute ⇌ Saturated solution) the thermodynamics equilibrium constant (k) is given by

$K=a_2=S$, solubility of the non electrolyte (assuming the saturated solution to be ideal).

Since the solubility of a solid non electrolyte in its saturated solution at a particular temperature, is a special case of the equilibrium constant we can determine the heat of solution using the van't Hoff equation, i.e,

$$\frac{d\ln S}{dT} = \frac{\Delta \overline{H}}{RT^2} \quad \text{……..(1)}$$

Integrating equation (1) we get,

$$\log S = -\frac{\Delta \overline{H}}{2.303RT} + \text{constant}$$

where R is gas constant, S is the solubility in moles per 1000g of solvent at temperature T, and $\Delta \overline{H}$ is the average heat of solution per mole over the temperature range used at the saturation concentration.

Thus, by obtaining the solubility at different temperatures ,and by applying the van't Hoff equation,it is possible to determine the heat of solution ($\Delta \overline{H}$) from the slope of logS vs 1/T plot.In this experiment oxalic acid dihydrate is assumed to be non-electrolyte (being weak acid) and its dissotiation is considered to be ideal.

Here, $\Delta \overline{H}$ obtained differs from the heat of solution at infinite dilution,which is the heat of solution usually given in literature,by an amunt equivalent to the heat of dilution from saturation to infinite dilution.

Apparatus required:

1) 500 mL glass bottle and 100 mL volumetric flask
2) 10 mL pipette-1
3) 2 mL pipette-1
4) Burette-1
5) 250 mL stoppered bottle-1
6) 100 mL conical flask-1
7) Temperature controlled water bath

Chemicals required: NaOH, Oxalic acid, Phenolphthalein

Procedure:

1) Prepare 100 mL 0.1(N) oxalic acid and 500 mL~0.2(N) NaOH solution. Determine the strength of NaOH solution using standard Oxalic acid solution 0.1(N) and phenolphthalein indicator.[Pipette out 10 mL 0.1(N) oxalic acid in a 100 mL conical flask. Titrate the solution with prepared NaOH solution using 2 drops of phenolphthalein until the solution becomes pink].
2) Prepare 50 mL saturated solution of oxalic acid in a 100 mL conical flask (or in a 250 mL stopper bottle) at room temperature. Pipette out 2 mL of the solution into 100 mL conical flask using a tip (stuffed with cotton) attached to the pipette end(so as to prevent any solid particle from entering into the pipette).Add 2 drops of phenolphthalein and titrate using standard NaOH solution.
3) The saturated solution is brought to equilibrium at 3-4 different (higher) temperatures (at a gap of 3^{o}C) using temperature controlled hot water bath and at a lower temperature using ice cooled bath.
4) At each temperature pipette out 2 mL of the solution into 100 mL conical flask using a tip (stuffed with cotton) attached to the pipette end (so as to prevent any solid particle from entering into the pipette). Add 2 drops of phenolphthalein and titrate using standard NaOH solution.
5) From the titre value calculate solubility of oxalic acid in normality at different temperatures. Transform the solubility into moles of oxalic acid /1000 gm of water for each temperatures using the following equation:

   Solubility (S)= $\frac{S_T \times M}{20}$ moles/100 gm of water at temperature T
6) Plot log(S) vs 1/T and obtain ΔH (J/mol) from the slope.

Experimental data:

Determination of strength of NaOH using 0.1(N) oxalic acid:

Volume of 0.1(N) oxalic acid (mL)	Burette reading		Volume of NaOH used(mL)	Average volume of NaOH(mL)
	Initial(mL)	Final(mL)		

Strength of NaOH solution:

Determination of heat of solution of oxalic acid:

Sl.No.	Temperature(^{o}C)		Burette reading		log(S)		

		Volume of NaOH consumed	Initial(mL)	Final(mL)	Solubility (S) moles/1000gm		1/T(K^{-1})	

Calculation:

A straight line is obtained on plotting log(S) vs 1/T. From the slope = $\Delta\overline{H}$ /2.303R, we can calculate the average heat of solution per mole ($\Delta\overline{H}$) over the temperature range used.

GE1: Lab

1. Estimation of Fe(II) Ions by Titrating it with $K_2Cr_2O_7$ Solution using Internal Indicator

Principle:

In acid medium Fe(II) in a solution may be estimated by direct titration with a standard solution of $K_2Cr_2O_7$ in presence of either H3PO4 or ammonium bifluoride (NH_4HF_2) using barium diphenylaminesulphonate (BDS) as indicator. Under this condition $K_2Cr_2O_7$ quantitatively oxidizes Fe^{2+} to Fe^{3+}:

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

$$\therefore\ 1/6 \text{ mol } Cr_2O_7^{2-} \equiv 1 \text{ mol } Fe^{2+} = 1 \text{ equivalent}$$

$$\therefore\ 1000 \text{ ml } 1 \text{ N } K_2Cr_2O_7 \text{ solution} \equiv 55.85 \text{ gm } Fe^{2+}$$

H_3PO_4 (or NH_4HF_2) stabilizes Fe3+ by complex formation which is essential for indicator action of BDS.

Chemicals required:

a) standard N/20 $K_2Cr_2O_7$ solution (to be prepared by accurate weighing)
b) N/20 Mohr's salt solution
c) 4 N H_2SO_4
d) Syrupy H_3PO_4 or NH_4HF_2
e) saturated aqueous solution of BDS indicator

Procedure:

Pipette out an aliquot of 25 ml from the supplied Mohr's salt solution in a 250 ml conical flask. Add 25 ml of 4 N H_2SO_4, 3 ml syrupy H_3PO_4 (or 1-2 gm of NH_4HF_2) and 3-4 drops of BDS indicator. Titrate with standard N/20 $K_2Cr_2O_7$ solution until the colour of the solution just changes from green to violet. Calculate the amount of iron in gm per litre present in the supplied solution.

Results:

Table: Estimation of Fe^{2+} ion solution

Serial No.	Volume of Mohr's salt solution (ml)	Volume of $K_2Cr_2O_7$ (ml)	Mean volume of $K_2Cr_2O_7$ (ml)	Strength of $K_2Cr_2O_7$
1	25		x (say)	y N (say)
2	25			

Calculations:

$$1000 \text{ ml } 1 \text{ N } K_2Cr_2O_7 \equiv 55.85 \text{ gm } Fe^{2+}$$

$$\therefore \text{ x ml y N } K_2Cr_2O_7 \equiv 55.85 \times x \times y/1000 \text{ gm } Fe^{2+}$$

$$\text{Now 25 ml solution contains } Fe^{2+} = 55.85 \times x \times y/1000 \text{ gm}$$

$$\therefore \text{ 1000 ml solution contains } Fe^{2+} = (55.85 \times x \times y/1000) \times 1000/25 \text{ gm}$$

So, the amount of Fe(II) ions present in the supplied solution = _______ gm per litre.

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2. Estimation of Cu (II) ions iodometrically using $Na_2S_2O_3$.

Principle:

Cu(II) is Iodometrically estimated by treating with an excess of KI solution and titrating the liberated iodine with a sodium thiosulphate ($Na_2S_2O_3.5H_2O$) solution which is standardized against a standard $K_2Cr_2O_7$ solution.

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

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

$$\therefore \text{ 2 moles of } Cu^{2+} \equiv 1 \text{ mol } I_2 \equiv 2 \text{ moles of } S_2O_3^{2-}$$

$$\therefore \text{ 1 mol } S_2O_3^{2-} \equiv 1 \text{ mol } Cu^{2+} \equiv 1 \text{ equivalent}$$

$$\therefore \text{ 1000 ml 1 N } Na_2S_2O_3 \text{ solution} \equiv 63.55 \text{ gm } Cu^{2+}$$

Sodium thiosulphate solution is standardized against a standard $K_2Cr_2O_7$ solution:

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

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

Chemicals required:

a) Standard N/20 $K_2Cr_2O_7$ solution (to be prepared by accurate weighing)
b) N/20 $Na_2S_2O_3.5H_2O$ solution
c) 15% KI solution
d) 4 N H_2SO_4
e) Freshly prepared 1% starch solution

Procedure:

1. Standardization of the supplied $Na_2S_2O_3$ solution:

Pipette out an aliquot of 25 ml from the supplied N/20 $K_2Cr_2O_7$ solution in a 500 ml conical flask. Add 25 ml of 4 N H_2SO_4 and 10 ml 15% KI solution. Cover the flask with a watch glass and keep it in the dark for 5 minutes. Take it out and dilute the mixture with 150 ml distilled water by properly rinsing the watch glass and the inner side of the conical flask. Titrate rapidly the liberated iodine by the supplied thiosulphate solution until the color of the solution turns straw-yellow. Add 2 ml of freshly prepared 1% starch solution and shake to obtain a bluecoloured solution. Continue the titration until the blue colour is just discharged and a clear light-green solution appears. Repeat the titration twice.

2. Estimation of Cu(II):

Pipette out 25 ml of the supplied solution in a 500 ml conical flask, dilute to 100 ml with distilled water. Add 10 ml 15% KI solution and titrate the liberated iodine with standard thiosulphate solution till the solution assumes a straw-yellow colour. Add 2 ml of starch indicator. The solution turns intense blue. Continue the titration till the milky-white precipitate of CuI appears. Record the titre value and calculate the amount of Cu(II) in the supplied solution.

Results:

Table 1: Standardization of thiosulphate solution

Serial No.	Volume of $K_2Cr_2O_7$ solution (ml)	Volume of thiosulphate solution (ml)	Mean volume of thiosulphate solution (ml)	Strength of thiosulphate solution
1	25			y N (say)
2	25			

Table 2: Estimation of Cu^{2+} ion solution

Serial No.	Volume of supplied copper solution (ml)	Volume of thiosulphate solution (ml)	Mean Volume of thiosulphate solution (ml)
1	25		x (say)
2	25		

Calculations:

$$V_{Cr_2O_7^{2-}} \times S_{Cr_2O_7^{2-}} = V_{S_2O_3^{2-}} \times S_{S_2O_3^{2-}}$$

$$\therefore\ S_{S_2O_3^{2-}} = V_{Cr_2O_7^{2-}} \times S_{Cr_2O_7^{2-}} / V_{S_2O_3^{2-}} = y\ N$$

$$1000\ \text{ml}\ 1\ N\ Na_2S_2O_3\ \text{solution} \equiv 63.55\ \text{gm}\ Cu^{2+}$$

$$\therefore\ x\ \text{ml}\ y\ N\ Na_2S_2O_3\ \text{solution} \equiv 63.55 \times x \times y/1000\ \text{gm}\ Cu^{2+}$$

$$\text{Now 25 ml solution contains } Cu^{2+} = 63.55 \times x \times y/1000\ \text{gm}$$

$$\therefore\ 1000\ \text{ml solution contains } Cu^{2+} = (63.55 \times x \times y/1000) \times 1000/25\ \text{gm}$$

So, the amount of Cu(II) ions present in the supplied solution = ________ gm per litre.

3. Estimation of oxalic acid by titrating it with $KMnO_4$.

Principle:
In dilute H_2SO_4 medium MnO_4^- quantitatively oxidizes $C_2O_4^{2-}$ to CO2 and it is reduced to Mn^{2+}:

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

$$\therefore\ MnO_4^-/5 \equiv C_2O_4^{2-}/2 = 1 \text{ equivalent}$$

$$\therefore\ 1000 \text{ ml } 1 \text{ N } C_2O_4^{2-} \equiv 1000 \text{ ml } 1 \text{ N } MnO_4^-$$

It is an example of autocatalytic reaction in which Mn2+, a product of the reaction, acts as the catalyst.
KMnO4 solution must be standardized against standard oxalic acid solution in 4 N H2SO4 medium at 70-80 ^{0}C. Purple coloured KMnO4 acts as a self-indicator. Its strength may be calculated using the relation:

$$V_{MnO_4^-} \times S_{MnO_4^-} = V_{C_2O_4^{2-}} \times S_{C_2O_4^{2-}}$$

Chemicals required:

a) Standard N/20 oxalic acid, H2C2O4.2H2O [F.W. = 126.05 gm]; strength = (W/0.7879) N/20 where W is the weight of H2C2O4.2H2O per 250 ml of the solution

b) N/20 KMnO4 solution

c) 4 N H2SO4

d) N/20 oxalic acid solution

Procedure:

1. Standardization of KMnO4 solution:

Pipette out an aliquot of 25 ml of N/20 standard oxalic acid in a 250 ml conical flask. Add 25 ml of 4 N H2SO4 and heat to about 70-80 ^{0}C. Titrate the hot solution with supplied KMnO4 solution until the solution turns light pink colour that is stable for □30 seconds. Repeat the titration to have a concordant reading. Calculate the strength of KMnO4 solution.

2. Estimation of oxalic acid solution:

Pipette out an aliquot of 25 ml of N/20 oxalic acid in a 250 ml conical flask. Add 25 ml of 4 N H2SO4 and heat to about 70-80 ^{0}C. Titrate the hot solution with standard KMnO4 solution until the solution turns light pink colour that is stable for 30 seconds. Repeat the titration to have a concordant reading. Calculate the amount of the supplied oxalic acid in gram per litre.

Results:

Table 1: Standardization of $KMnO_4$ solution

Serial No.	Volume of oxalic acid (ml)	Strength of oxalic acid	Volume of $KMnO_4$ (ml)	Mean volume of $KMnO_4$ (ml)	Strength of $KMnO_4$
1	25				y N (say)
2	25				

Table 2: Estimation of oxalic acid solution

Serial No.	Volume of oxalic acid (ml)	Volume of $KMnO_4$ (ml)	Mean volume of $KMnO_4$ (ml)
1	25		x (say)
2	25		

Calculations:

$$V_{MnO_4^-} \times S_{MnO_4^-} = V_{C_2O_4^{2-}} \times S_{C_2O_4^{2-}}$$
$$\therefore\ S_{MnO_4^-} = V_{C_2O_4^{2-}} \times S_{C_2O_4^{2-}}/V_{MnO_4^-} = y\ N \text{ (say)}$$

$$1000 \text{ ml } 1 \text{ N } KMnO_4 \equiv 63 \text{ gm oxalic acid}$$
$$\therefore\ x \text{ ml } y \text{ N } KMnO_4 \equiv 63 \times x \times y/1000 \text{ gm oxalic acid}$$

$$\text{Now 25 ml solution contains oxalic acid} = 63 \times x \times y/1000 \text{ gm}$$
$$\therefore\ 1000 \text{ ml solution contains oxalic acid} = (63 \times x \times y/1000) \times 1000/25 \text{ gm}$$

So, the amount of oxalic acid present in the supplied solution = _______ gm per litre.

4. Estimation of water of crystallization in Mohr's salt by titrating with $KMnO_4$.

Principle:
In dilute H2SO4 medium MnO4- quantitatively oxidizes Fe2+ to Fe3+ and itself is reduced to Mn2+:

$$MnO_4^- + 5Fe^{2+} + 8H^+ \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$
$$\therefore\ MnO_4^- \equiv 5Fe^{2+}$$
$$\text{or }\ MnO_4^-/5 \equiv Fe^{2+} = 1 \text{ equivalent}$$

Mohr's salt (Fe2+) solution may be estimated by titrating it in 4 N H2SO4 medium with a standard solution of KMnO4 at room temperature in presence of H3PO4. Theoretical molecular weight of Mohr's salt [FeSO4.(NH4)2SO4.nH2O] = (284 + 18n); where n = number of molecules of water of crystallization in Mohr's salt. Since equivalent weight of Mohr's salt is equal to its molecular weight, so (284 + 18n) = E; where E = equivalent weight of Mohr's salt. By accurate weighing of Mohr's salt and expressing the strength of its aqueous solution in gm per litre, the number of water molecules present as solvent of crystallization can easily be calculated.

Chemicals required:
a) standard N/20 oxalic acid solution
b) N/20 KMnO4 solution
c) 4 N H2SO4

d) syrupy phosphoric acid
e) 19.6 gm per litre Mohr’s salt solution

Procedure:

1. Standardization of N/20 KMnO4 solution:

Pipette out an aliquot of 25 ml of N/20 standard oxalic acid in a 250 ml conical flask. Add 25 ml of 4 N H2SO4 and heat to about 70-80 ^{0}C. Titrate the hot solution with supplied KMnO4 solution until the solution turns light pink colour that is stable for 30 seconds. Repeat the titration to have a concordant reading. Calculate the strength of KMnO4 solution.

2. Standardization of Mohr’s salt solution:

Pipette out an aliquot of 25 ml of Mohr’s salt solution in a 250 ml conical flask. Add 25 ml of 4 N H2SO4 and 3 ml of syrupy H3PO4. Titrate the solution with standard KMnO4 solution until the solution turns light pink colour that is stable for 30 seconds. Repeat the titration to have a concordant reading. Calculate the number of water molecules present as solvent of crystallization in Mohr’s salt.

Results:

Table 1: Standardization of $KMnO_4$ solution

Serial No.	Volume of oxalic acid (ml)	Strength of oxalic acid	Volume of $KMnO_4$ (ml)	Mean volume of $KMnO_4$ (ml)	Strength of $KMnO_4$
1	25				y N (say)
2	25				

Table 2: Standardization of Mohr’s salt solution

Serial No.	Volume of Mohr’s salt solution (ml)	Volume of $KMnO_4$ (ml)	Mean volume of $KMnO_4$ (ml)
1	25		x (say)
2	25		

Calculations:

$$V_{MnO_4^-} \times S_{MnO_4^-} = V_{C_2O_4^{2-}} \times S_{C_2O_4^{2-}}$$

$$\therefore\ S_{MnO_4^-} = V_{C_2O_4^{2-}} \times S_{C_2O_4^{2-}}/V_{MnO_4^-} = y\ N\ (\text{say})$$

$$1000\ \text{ml}\ 1\ N\ KMnO_4 \equiv 31.6\ \text{gm}\ KMnO_4 \equiv (284 + 18n)\ \text{gm Mohr's salt}$$

$$\therefore\ x\ \text{ml}\ y\ N\ KMnO_4 \equiv (284 + 18n) \times x \times y/1000\ \text{gm Mohr's salt}$$

$$\text{Now 25 ml solution contains Mohr's salt} = (284 + 18n) \times x \times y/1000\ \text{gm}$$

$$\therefore\ \text{1000 ml solution contains Mohr's salt} = (284 + 18n) \times x \times y/1000 \times 1000/25\ \text{gm}$$

$$\text{Now } (284 + 18n) \times x \times y \times /25 = 19.6\ \text{gm/litre}$$

So, the number of water molecules (n) present as solvent of crystallization in Mohr's salt is _.

5. Estimation of sodium carbonate and sodium hydrogen carbonate present in a mixture.

Method: Indicators change colour within well defined pH ranges: phenolphthalein changes from colourless to red in the range 8.0 - 9.6; methyl orange changes from red to yellow in the range 3.1 - 4.4. The pH just after the neutralization point depends upon the strength of the acid / base, ie., their p*Ka* / p*Kb*.

Hydrochloric acid is standardized against previously standardized sodium hydroxide using phenolphthalein as indicator: HCl + NaOH = NaCl + H2O.

The decomposition of carbonate by acid takes place in two steps: (i) CO32– + H+ = HCO3–. (ii) HCO3– +H+ = H2O + CO2. At the end of step (i), the pH will be near about 8 or 9. After the complete neutralization, the next drop of HCl will bring down the pH to near about 3 or 4. The Na2CO3 content of the given sample is determined by titration against standard hydrochloric acid using methyl orange as indicator: Na2CO3 + 2HCl = 2NaCl + H2O + CO2. The equivalent weight of Na2CO3 is half its molecular weight (*M*). This means *M*/2 g of Na2CO3 is equivalent to 1000 ml of 1 N HCl. It also means that the molarity of a solution of Na2CO3 is half its normality.

The total amount of carbonate and bicarbonate in the mixture is determined by titration against standard hydrochloric acid using methyl orange as indicator: CO32– + HCO3 – + 3H+ = 2H2O + 2CO2. Another titration using phenolphthalein as indicator will give the concentration of carbonate. CO3 2– + H+ = HCO3 –. If the above titre values are *Vm* and *Vp* respectively, then carbonate is equivalent to 2*Vp* and bicarbonate is equivalent to *Vm* – 2*Vp*.

Note that in the second titration the pH change is relatively slow near the neutralization point, therefore the colour change is not sharp and the titration has to be done slowly.

Procedure:

(i) Standardization of hydrochloric acid: Transfer 25 ml of sodium hydroxide solution to a 250 ml conical flask using a pipette. Dilute with a little water (about 10 ml) and add 1-2 drops of phenolphthalein. Titrate against hydrochloric acid taken in a burette. Repeat till concordant titre values are obtained. Calculate the normality of the acid using the given normality of sodium hydroxide.

(ii) *Estimation of Na2CO3 content of the given sample*: *A* : Weigh accurately about 0.6 g of the sample (*w* g) into a 100ml standard flask. Dissolve in distilled water and make upto the mark with distilled water. Titrate 25 ml of this solution against standard hydrochloric acid (normality, *Na*) using 1-2 drops of methyl orange as indicator. When the colour becomes very faint yellow, continue the titration dropwise until the colour becomes orange or a faint pink. Repeat the titrations till concordant values (*Va*) are obtained. Calculate the normality ($Nb = VaNa/25$) of the

sodium carbonate solution and the percentage purity of the sample. [Amount of Na2CO3 in the weighed sample, $m = (100/1000) \times (Nb/2) \times M$; percentage purity = $100m/w$]. *B* : Repeat the above experiment by accurately weighing about 0.15 g of the solid sample to a 250 ml titration flask (ie., conical flask), dissolving it in water and diluting to about 40 ml and titrating as before. Calculate the percentage purity. The amount of Na2CO3 in the weighed sample is, $m = (Na \times Va / 1000) \times (M / 2)$.

Estimation of Na2CO3 and NaHCO3 in a mixture: Accurately weigh about 2.0 g of the mixture and prepare a solution in distilled water in a 250 ml standard flask. Slowly titrate 25 ml of this solution against standard hydrochloric acid using phenolphthalein as indicator. Repeat to concordance (*Vp* ml). Now titrate the same volume using methyl orange as indicator. Repeat to concordance (*V*m ml). Calculate the number of equivalents, in the titrated volume(ie., 25.0 ml), of Na2CO3 ($Ecarb = Na \times 2 \times Vp/1000$) and NaHCO3 [$Ebicarb = Na \times (Vm - 2Vp)/1000$]. Hence calculate the respective amounts and percentages in the given sample.

Qualitative Analysis of Single Solid Organic Compound

Background

Organic chemists often must identify unknown compounds. In some cases, such as a reaction, you may have a good idea of what the compound in question is. However in other cases, such as when you isolate a compound from a natural source, you may have no idea what the compound might be. In this experiment you will determine the identity of an unknown compound. First,you will need to purify your compound, then you will need to identify its functional group (it will contain only one), and finally you will need to make a derivative of the compound. You will confirm your results with boiling or melting point, IR, and NMR.

Impurities in your compound will make it extremely difficult to identify. Thus, before you do anything else, you will need to make sure your unknown compound is pure. Consider each of the following purification techniques you have learned over the courseof the year.

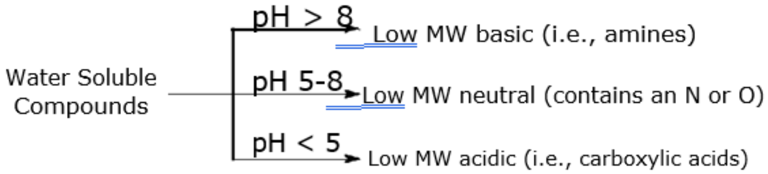
1. *Recrystallization:* Works well for solid compounds. You will need to find an appropriate recrystallization solvent. Consider a variety of solvents and mixed solvent systems.

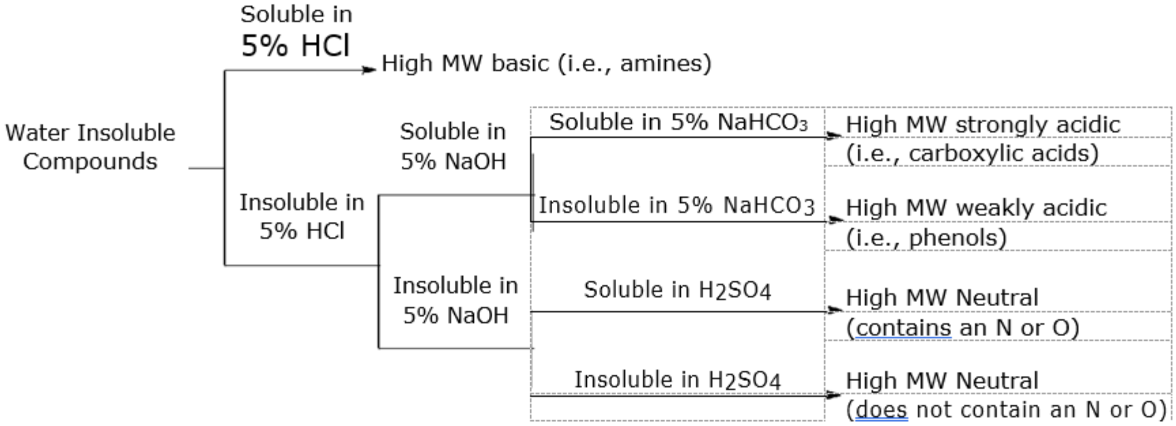
2. *Distillation:* Works well for liquids that have a boiling point of <250 ◦C. (Note: Fractional distillation may be required if you suspect impurities close to the boiling point of your unknown.)
3. *Column Chromatography:* Works well for UV active compounds. You will need to use TLC to identify a solvent system that will separate your unknown from any impurities.

After you have purified your unknown, verify that it is pure enough to proceed by measuring the boiling or melting point. Note that while you will not know what the melting point or boiling point of your unknown should be, the narrowness is an excellent indicator of whether or not your product is pure. Also pay attention to the appearance of your unknown and see if it has changed (hopefully for the better) during the course of the purification process.

Once your unknown is pure, you will need to identify its functional group. Your unknown will have one major functional group (alcohol, ketone, aldehyde, amide, amine, carboxylic acid, or ester). Additionally, your unknown compound may or may not contain an aromatic ring. To determine the functional group, it is recommended that you start with solubility tests, and then conduct functional group classification tests. IR spectroscopy may also be useful at this point.

Solubility can sometimes provide a surprisingly useful amount of information. First, you will test your unknown's solubility in water. Compounds with 4 carbons or less will easily dissolve in water, whereas compounds with 8 carbons or more will be insoluble. Compounds containing 5----7 carbons may or may not dissolve (often they will display "partial" solubility). If your compound dissolves in water, you will also want to check the pH of the solution. Amines will typically be basic, and carboxylic acids will typically be acidic. Most other compounds will be neutral. Compounds that are insoluble in water should then be subjected to a solubility test in 5% HCl. Typically, only amines will be soluble in HCl because they form water-soluble hydrochloride salts when they react with HCl. Compounds that are not soluble in HCl, should be subjected to testing in basic solutions (5% NaOH and 5% $NaHCO_3$). Both strong and weak acids (Carboxylic acids and phenols) will be deprotonated by NaOH to form water-soluble alkoxides. Only strong acids like carboxylic acids will react with $NaHCO_3$. Compounds that are not soluble in base should then be reacted with a very strong acid, sulfuric acid (note that in the case of sulfuric acid, "solubility" is also indicated by any type of reaction such as heat, gas generation, or a color change). Compounds that cannot become protonated by sulfuric acid at all (i.e., alkanes, alkyl halides, and aromatic carbons) will still remain insoluble. These solubility tests are summarized in the flow charts below.





The results from the solubility tests can significantly help in determining which classification tests should then be performed, or at least narrow down the list. By no means do you need to conduct all classification tests. In fact, you should do your best to select only tests that will provide you with additional information about your unknown and/or confirm results. Also, make sure that your glassware is clean and dry so you do not get any false positive or false negative results. Keep in mind that a negative result for a classification test provides useful information, so be sure to keep track of negative results as well as positive results. Also, for each classification test that you perform, be sure to run a blank, and one or more controls. These will help you to determine if a reaction actually occurred. A blank includes everything but the unknown, and a control includes a compound for which the outcome is known in place of the unknown. Controls can be positive (a compound you know will react) or negative (a compound that you know will not react). The classification tests are summarized in the table below.

Functional group	Test	Test no	Notes
Elemental analysis	Lassaigne test	C-1	Test for nitrogen, sulphur, halogens
Amine	Basicity test Bleaching powder test Dye test	C-2 C-3 C-4	Test for aromatic amine
Nitro	Reduction test Muliken and barker test	C-5 C-6	Test for aromatic nitro group
Amido	Nitrous acid test Hydrolysis test	C-7 C-8	Test for amido group
Phenolic –OH	Ferric chloride test Back dye test	C-9 C-10	Test for phenolic-OH
Carboxylic acid	Bicarbonate test Esterification test	C-11 C-12	Test for carboxylic acid
Aldehyde	Benedict test Tollens test	C-13 C-14	Test for aldehyde
Ketone	2,4-Dinitrophenyl hydrazine test	C -15	Test for ketone

At this point, you should be able to use your boiling or melting point data combined with the results of your functional group data to develop a hypothesis as to what your unknown might be or at least narrow down the list to only a few candidates. Note that due to the accuracy (or lack thereof) of our thermometers, your boiling or melting points may be up to 15 °C lower than the literature values.

Once your functional group has been determined, you will prepare a derivative of your unknown. To prepare a derivative, you will select a suitable reaction that converts your unknown into a different functional group for which the boiling or melting point is known. This is particularly useful because compounds that have similar boiling or melting points will often have derivatives that differ significantly in terms of boiling or melting point. You should then be able to identify your unknown using this information.

Finally, you can confirm the identity of your product using IR and NMR. Note that these measurements can be taken at any time during the course of the lab after you purified your product. In fact, it is recommended that you conduct them sooner rather than later as they may provide valuable information as to the identity of your unknown (e.g., IR may reveal your functional group).

Lab Notebook Preparation A

Before coming to lab on the first day of this experiment, the following items must be in your lab notebook:

1. Title of experiment
2. Date the experiment is to be performed
3. Outline of your plan for determining the identity of your unknown
4. Hazards of and appropriate precautions for the safe handling of unknown organic compounds
5. References

Lab Notebook Preparation B

Before coming to lab on the day you plan to prepare a derivative, the following items must be in your lab notebook:

1. Title of experiment
2. Date the experiment is to be performed
3. List of possible unknowns

4. The chemical reaction(s) you are attempting (with skeletal structures…R groups are okay if you do not know the identity of your unknown yet)
5. For each reaction you are attempting, include a table with information about your starting materials. Include molecular weight, molar equivalents, and mmoles to be used. For solids include grams. For liquids, include grams, density, and volume. For solutions, include the concentration and volume. (Note: You will not be able to completely fill in the table if you do not know the identity of your unknown yet. If that is the case, list whatever data you can.)
6. Any relevant physical properties (i.e., melting points or boilingpoints of possible unknowns and their derivatives)
7. Hazards of and appropriate precautions for the specific reaction(s) you are conducting
8. References

Safety Notes

- Assume that all unknowns are flammable and harmful by inhalation, ingestion, and skin absorption. Do not inhale their vapors and avoid contact with eyes, skin and clothing.

Directions

1. Purify your unknown using distillation, recrystallization, or column chromatography. It is recommended that purify the entire unknown provided so that you have enough pure material for all of the tests.
2. Measure the boiling or melting point of your unknown to confirm its purity.
3. Confirm with your instructor that the boiling or melting point you obtained for your unknown is within 15 ◦C of the reported literature value before proceeding.
4. Test the solubility of your unknown in water. (If your unknown is a solid, crush it into a fine powder.)
    a. Add approximately 30 mg of your unknown to a test tube or smallvial.
    b. Add 1 mL of water and shake vigorously for approximately 30 seconds. If the unknown appears to be soluble, test the pH of the solution and then skip to step 9.
5. Test the solubility of your unknown in 5% HCl. (If your unknown is a solid, crush it intoa fine powder.)
    a. Add approximately 30 mg of your unknown to a test tube or small vial.

   b. Add 1 mL of 5% HCl and shake vigorously for approximately 30 seconds. If the unknown appears to be soluble, skip to step 9.

6. Test the solubility of your unknown in 5% NaOH. (If your unknown is a solid, crush it into a fine powder.)
   a. Add approximately 30 mg of your unknown to a test tube or small vial.
   b. Add 1 mL of 5% NaOH and shake vigorously for approximately 30 seconds. If the unknown appears to be insoluble, skip to step8.
7. Test the solubility of your unknown in 5% $NaHCO_3$. (If your unknown is a solid, crush it into a fine powder.)
   a. Add approximately 30 mg of your unknown to a test tube or small vial.
   b. Add 1 mL of 5% $NaHCO_3$ and shake vigorously for approximately 30 seconds.
8. Note whether your unknown is soluble or insoluble and then skip to step 9.
9. Test the solubility of your unknown in concentrated H_2SO_4. (If your unknown is a solid, crush it into a fine powder.)
   a. Add approximately 30 mg of your unknown to a test tube or small vial.
   b. Add 1 mL of concentrated H_2SO_4 and shake vigorously for approximately 30 seconds.
   c. Note whether your unknown is soluble or insoluble. (Any indication of a reaction such as heat, gas generation, or a color change also indicates solubility.)
10. Conduct classification tests as needed. See directions for specific tests below.
11. Confirm the identity of your functional group with your instructor before proceeding.
12. Prepare one or more derivatives of your unknown. See directions for specific derivatives below.
13. Measure the melting point of any derivatives.
14. Confirm with your instructor that the melting point you obtained for your derivative is within 15 ◦C of the reported literature value.

Classification Tests

C-1 Elemental Analysis

This reaction tests for the presence of nitrogen, sulfur and halogens (Cl / Br / I).

Safety Notes: Sodium can cause serious burns and the sodium-lead alloy may react violently with some substances. Wear gloves, avoid contact, and keep the sodium-lead alloy away from other chemicals.

Recommended Controls: butylamine, acetamide, bromobenzene

Procedure:

1. In the fume hood or under a snorkel, place 0.25 g of 10% sodium-lead alloy in a small, dry test tube held vertically by a clamp.
2. Melt the alloy with a Bunsen burner flame and continue heating until the sodium vapor rises about 1 cm up the tube.
3. Using a Pasteur pipet, add 2 drops of the unknown (or 10 mg of a solid) directly onto the molten alloy so that it does not touch the sides of the tube.
4. Heat gently to start the reaction, remove the flame until the reaction subsides, then heat the tube strongly for a minute or two, keeping the bottom a dull red color.
5. Let the tube cool to room temperature.
6. Dropwise add 1.5 mL of water and heat gently for a minute or so until the excess sodium has decomposed and gas evolution ceases.
7. Filter the solution through a Pasteur pipet with a small plug of cotton, wash the cotton with 1 mL of water, and combine the wash water with the filtrate. (Use a rubber bulb to expel any liquid that adheres to the cotton.) The filtrate should be colorless or just slightly yellow. If it is darker, repeat the fusion with stronger heating or more of the alloy.

To test for nitrogen:

1. Put 5 drops of the sodium fusion solution into a small test tube.
2. While stirring, add enough solid sodium bicarbonate, to saturate it (a little excess solid should be present).

3. Add 1 drop of this solution to a test tube containing 10 drops of PNB reagent (*p*-nitrobenzaldehyde in dimethyl sulfoxide) and note any color change.

To test for halogens:

1. Acidify 10 drops of the sodium fusion solution with dilute nitric acid.
2. Boil it gently under the hood for a few minutes.
3. Add a drop or two of 0.3 M aqueous silver nitrate, and note the color and volume of any precipitate that forms. (If a voluminous precipitate forms, let the precipitate settle and then remove the solvent using a pipet.)
4. Add 2 mL of 3 M aqueous ammonia to the solid, shake vigorously, and note your observations.
5. To test further for bromine and iodine, acidify 1 mL of the original sodium fusion solution with 1 M sulfuric acid, boil for a few minutes, and add 0.5 mL of dichloromethane and a then a drop of freshly prepared chlorine water. Shake and look for a color in the dichloromethane layer.

To test for sulfur:

1. Put 1ml of sodium-extract into a test tube.
2. Add 1 ml dil. NaOH solution followed by 2-3 drops of sodium nitroprusside (freshly prepared).

Interpretation*:* In the PNB test, a purple color indicates the presence of nitrogen (green indicates sulfur). In the halogen tests, formation of a voluminous precipitate on addition of silver nitrate indicates that a halogen is present, and the color of the precipitate (a silver halide) may suggest which halogen: white for chlorine, pale yellow for bromine, and yellow for iodine. If only a faint turbidity is produced, it may be caused by traces of impurities or by incomplete sodium fusion. If the precipitate is silver chloride, it will dissolve in aqueous ammonia; silver bromide is only slightly soluble and silver iodide is insoluble. In the chlorine water test, a red-brown color is produced by elemental bromine and a violet color by elemental iodine. In the sulfur test, a violet or purple color indicates the presence of sulfur.

C-2 Basicity Test

This test is useful if you have already determined that you have an amine. It is used to distinguish alkyl amines from aromatic amines.

Recommended Controls: p-toluidine, dibutylamine

Procedure for water-soluble compounds:

1. Dissolve 4 drops of your unknown (0.10 g of a solid) in 3 mL of water.

2. Measure the pH of the solution using pH paper.

Procedure for water-insoluble compounds:

1. Dissolve 4 drops of your unknown (0.10 g of a solid) in 3 mL of a pH 5.5 acetate-acetic acid buffer.

2. Mix thoroughly.

Interpretation: Water-soluble alkyl amines give pH values above 11, whereas water-soluble aromatic amines have pH values below 10. Water-insoluble alkyl amines should dissolve in the buffer, but water-insoluble aromatic amines will not dissolve.

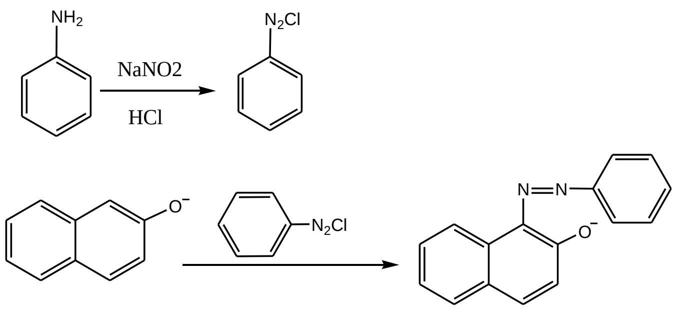
C-3 Bleaching powder test

Procedure:

1. Dissolve 0.05 g of your unknown in 5 mL of water.
2. Add 3-4 drops of bleaching powder solution.
3. Shake vigorously.

Observation: Transient purple color which soon turns brown or light purple color.

C-4 Dye test:

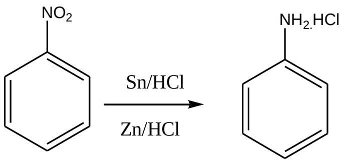


Procedure:

1. 0.1 g of organic sample is dissolved in 5ml of dil. HCl.
2. The mixture is cooled at 0-5 °C in an ice-bath.
3. Then add 1ml of ice cold solution of dil. $NaNO_2$.
4. The mixture is added to ice-cold alkaline solution of β-naphthol (excess).

Interpretation: Red or orange red dye (brown or reddish purple or violet dye indicates the presence of two amino groups; soluble dye indicates the presence of SO_3H or Ar-OH along with Ar-NH_2 group).

C-5 Reduction followed by Dye test



1. A mixture of 0.1 g of organic sample, few pieces of granulated tin or zinc and 3ml of Conc. HCl is warmed gently with occasional shaking till the reaction is complete.
2. The mixture is cooled.
3. Filtered, if required, diluted and diazo-coupling reaction is performed.

Observation: Brilliant red or scarlet dye obtained.

Interpretation: A group reducible to –NH_2 group. Normally an aromatic nitro compound is indicated.

C-6 Mulliken and Barker Test

Procedure:

1. 0.1 g of organic sample is dissolved in 5 ml of 50% alcohol.
2. A little solid NH_4Cl or 10% $CaCl_2$ solution and a pinch of Zn-dust is added to it.
3. The mixture is boiled for a few minutes.
4. Then the mixture is cooled and allowed to stand for 5 minutes and then filtered.
5. With the filtrate following three tests are performed:

a) A portion of the solution is added to Tollen's reagent and then warmed in a water bath.

b) Two drops of benzoyl chloride and 2 drops of conc. HCl are added to another portion of the filtrate followed by 12 drops of $FeCl_3$ solution.

c) The last portion of the filtrate is warmed with a little Fehling's solution.

Observation: From the part (a), a silver mirror or black or grey precipitation is obtained. From part (b), a wine-red color of ferric hydroxamate is present, from last part (c), a red precipitation is obtained.

Interpretation: A nitro group is reduced to –NHOH that oxidises Ag^+ to Ag, and Cu^{++} to Cu^+ (Cu_2O)

C-7 Nitrous Acid Test

Procedure:

1. A little of the aqueous solution of organic sample is treated with a few drops of HNO_2 ($NaNO_2$ and HCl).

Interpretation: Effervescence due to evolution of N_2 gas. Indicates presence of $–NH_2$ (aliphatic) / -$CONH_2$

C-8 Hydrolysis Test

Procedure:

0.2 g of organic sample is heated with 2 ml of 50% NaOH solution.

Observation: Characteristics smell of NH_3 which turns mercurous nitrate paper black or copper sulphate paper deep blue.

Interpretation: Primary amide ($-CONH_2$) is hydrolysed to organic acid and ammonia. The latter gives the above observations.

C-9 Ferric Chloride [Must be freshly prepared]

This reaction tests for the presence of phenols.

Recommended Control: Phenol / resorcinol

Procedure:

1. Dissolve 1 drop of the unknown (40 mg of a solid) in 1 mL of water. If (you know based on the results of your solubility tests that the unknown is insoluble in water, use 0.5 mL of water and 0.5 mL of methanol instead of 1 mL of water.)
2. Add two drops of 2.5% ferric chloride solution.

Interpretation: Formation of an intense red, green, blue, or purple color suggests a phenol or an easily enolizable compound (such as an β-diketone or β-ketoester). Yhe colour specis is $(ArO)_6Fe^{3-}$

Some phenols do not react under these conditions.

C-10 Back Dye Test

This reaction tests for the presence of phenols.

Procedure:

1. A few drops of aniline dissolved in dil. HCl.
2. Few drops of cold dil. $NaNO_2$ solution is added.
3. Then the clear solution is added to the cold solution of organic sample in NaOH.

Observation: A brilliant red dye is obtained.

Interpretation - Phenolic OH group present and confirmed; test is very good for resorcinol, naphthols etc.

C-11 Bicarbonate Test

This reaction tests for the presence of carboxylic acid (or any good acidic compounds e.g., picric acid, 2,4-dinitrophenol)

Procedure:

1. A small amount of organic sample is sprinkled over aqueous solution of sodium bicarbonate.

Interpretation: Effervescence due to the evolution of CO_2.

C-12 Esterification Test

This reaction tests for the presence of carboxylic acid.

1. 0.5 g of organic sample is taken in a dry test tube.
2. To this, add 1 ml of dehydrated ethanol.
3. Then 2-3 drops of conc. H_2SO_4 is added and heated for 5 minutes in a water bath.
4. The mixture is then poured into a beaker containing large volume of Na_2CO_3 solution.

Interpretation: Characteristics sweet smell (fruity) of ester.

C-13 Benedict's Test

This reaction tests for the presence of aldehydes. Note that most ketones and aromatic aldehydes will not react.

Recommended Controls: butanal

Procedure:

1. Add 2 drops of the unknown (80 mg if it is a solid) to 2 mL of water.
2. Add 2 mL of Benedict's reagent.
3. Heat the mixture to a boil.
4. Observe if a precipitate forms, and note its color.

Interpretation: Benedict's reagent contains copper(II) sulfate, sodium citrate, and sodium carbonate. Aldehydes will react with the Cu^{2+} from the copper(II) sulfate to form copper(I) oxide which appears as a yellow or orange precipitate (it may look a little green in the blue reaction solution). Note that most ketones and aromatic aldehydes will not react.

C-14 Tollen's Test

This reaction tests for the presence of aldehydes. [#a-Hydroxyketones e.g., benzoin responds to this test]

Recommended Controls: benzaldehyde

Procedure:

1. Measure 2 mL of 0.3 M aqueous silver nitrate into a test tube and add 1 drop of 3 M sodium hydroxide.
2. Add 2 M aqueous ammonia drop by drop, with shaking, until the precipitate of silver oxide just dissolves (avoid an excess of ammonia).
3. Add 1 drop of the unknown (40 mg of a solid) to this solution, shake the mixture, and let it stand for 10 minutes. (If a silver mirror is observed at this point, this is considered a positive result.)
4. Heat the mixture in a 35 °C water bath for 5 minutes.
5. Immediately after the test has been completed, dissolve any solid residue in 1M nitric acid and then dispose of the solution in the designated waste container.

Interpretation: Formation of a silver mirror on the inside of the test tube is a positive test for an aldehyde. (Note that if the tube is not sufficiently clean, a black precipitate or a suspension of metallic silver may form instead.)

C-15 2,4-Dinitrophenylhydrazine

This reaction tests for the presence of aldehydes and ketones.

Safety Notes: 2,4-Dinitrophenylhydrazine (DNPH) is harmful if absorbed through the skin. Wear gloves and avoid contact.

Recommended Controls: cyclohexanone, benzaldehyde

Procedure:

1. Dissolve 1 drop of the unknown (40 mg of a solid) in 1 mL of 95% ethanol (use more ethanol if necessary to completely dissolve the unknown).
2. Add this solution to 2 mL of the DNPH reagent.
3. Shake and let the mixture stand for 15 minutes or until a precipitate forms. (If a precipitate is observed at this point, this is considered a positive result.)
4. Scratch the inside of the test tube and observe if a precipitate forms, and note its color.

Interpretation: Formation of a crystalline yellow or orange-red precipitate indicates an aldehyde or ketone. The color of the precipitate may give a clue to the structure of the carbonyl compound (unconjugated aliphatic aldehydes and ketones usually yield a yellow precipitate, while aromatic and α,β-unsaturated aldehydes and ketones yield a orange-red precipitate).