B. L. D. E. ASSOCIATION'S
S. B. ARTS AND K. C. P. SCIENCE COLLEGE
Smt. Bangaramma Sajjan Campus, Shri B. M. Patil Road (Solapur Road), Vijayapur-586 103
Accredited with CGPA of 2.99 at 'B++' Grade in 4th Cycle by NAAC
(Affiliated to Rani Channamma University, Belagavi)

DEPARTMENT OF CHEMISTRY

BSC I SEMESTER

CHEMISTRY LAB MANUAL

Name of the Student :_____

Reg. No. :_____

DEPARTMENT OF CHEMISTRY

LABORATORY INSTRUCTIONS

1. **Wear apron & proper footwear**
2. **Keep the working table clean**
3. **Use the chemicals economically**
4. **Don't smell the chemicals closely**
5. **Place the reagent bottles to shelf after use**
6. **Never attempt to taste the chemicals**
7. **Avoid hurried movement in the laboratory**
8. **Avoid eating, & drinking in the laboratory**
9. **Make sure to close gas & water taps before leaving the laboratory**
10. **Handle the reagent bottles and instruments carefully**
11. **Clean the glass wares after use**

EXPERIMENT NO-1

CALIBRATION OF GLASSWARES, BURETTES, PIPPETTES AND VOLUMETRIC FLASK

All volumetric glassware are calibrated in mL at room temperature (25 ºC). For ordinary purpose the volume marked on an apparatus by the manufacturer may be considered reliable. In relative measurements like double titration, any errors in volume if present get cancelled. For an accurate work any such small error must be determined i.e. apparatus must be calibrated.

CALIBRATION OF BURETTES

Burettes are most simply calibrated by Ostawald's method with the help of small pipette (2mL), the volume of which has been accurately determined. The calibration procedure is as discussed below:

Fill the well cleaned burette with air filled distilled water, taking care that no air bubble remains in the jet of the burette. Clamp it in vertical position and deliver 2 mL of water from zero mark in a previously weighed small flask. Determine the weight of water delivered by weighing it again. Withdraw successfully 2 mL of water and weigh after each delivery. From the weights of 2, 4, 6...mL... etc. on the burette, calculate the correct volumes. Tabulate the differences (corrections) corresponding to 2, 4, 6....50mL. Also plot a graph between the burette reading as abscissa and corrections as ordinates.

CALIBRATION OF PIPETTE'S

It is carried out by weighing the water they deliver from the fixed mark. Thoroughly clean the pipette to be calibrated by cleaning mixture and then wash with tap water and distilled water. Stuck the air free distilled water into the pipette up to the mark and deliver it, keeping the pipette almost upright, into a weighed small flask. When the liquid stops running, allow the pipette to drain for about 15 seconds, touch the tip of pipette against the side of the vessel so as to remove the last drop of water which collects at the tip. Determine the weight of the water delivered by weighing the flask again. From the weight of the water calculate the true volume of the pipette.

CALIBRATION OF VOLUMETRIC FLASK

Weigh accurately a thoroughly cleaned and dried flask on a robust balance. Fill the flask with air-free distilled water so that the lower edge of the meniscus stands at the fixed mark on the neck. Remove any drop of water above the mark by a piece of filter paper. Dry the outer surface and weigh the flask again. After having determined the weight of water contained in the flask up to the mark, obtain the true volume of the vessel from the table

given below. In case the error is considerable, etch a new ring on the neck.

Apparent specific weight and apparent specific volume of water weighed in air

Temp (ºC)	Apparent weight of 1 mL of water(g)	Volume corresponding to an apparent weight of 1g water(mL)	Temp (ºC)	Apparent weight of 1 mL of water(g)	Volume corresponding to an apparent weight of 1 g water(mL)
10	0.9986	1.0013	18	0.9976	1.0024
11	0.9985	1.0014	19	0.9974	1.0026
12	0.9984	1.0015	20	0.9972	1.0028
13	0.9983	1.0017	21	0.9970	1.0030
14	0.9982	1.0018	22	0.9967	1.0033
15	0.9981	1.0019	23	0.9965	1.0035
16	0.9979	1.0021	24	0.9963	1.0037
17	0.9977	1.0023	25	0.9960	1.0040

EXPERIMENT NO-2

ESTIMATION OF SODIUM CARBONATE AND SODIUM HYDROGEN CARBONATE PRESENT IN A MIXTURE

AIM: To estimate the amount of sodium carbonate and sodium hydrogen carbonate present in a mixture

CHEMICALS REQUIRED: Na_2CO_3, $NaHCO_3$, HCl, Phenolphthalein, Methyl orange etc.

APPARATUS: Burette, Pipette, volumetric Flask, Conical Flask, Beaker, Funnel, Watch Glass, Glass rod

PRINCIPLE:

Neutralisation of Na_2CO_3 solution by using HCl occurs in two steps.

$$Na_2CO_3 + HCl \longrightarrow NaHCO_3 + NaCl \text{ (pH- 8.3 at Eq. Pt.)}$$

$$NaHCO_3 + HCl \longrightarrow NaCl + H_2O + CO_2$$

So for first neutralisation phenolphthalein (pH-3.1- 10.0) should be used as indicator where the colour change in pink to colourless. At this stage Na_2CO_3 consumes only half amount of HCl required for complete neutralisation. Then methyl orange (pH – 3.1 – 4.4) is added to this titrated solution and titration is continued with HCl solution till colour changes from yellow to red, this titre value corresponds to complete neutralisation of $NaHCO_3$ (i.e. $NaHCO_3$ derived from Na_2CO_3 plus the amount of $NaHCO_3$ present in original mixture).

PROCEDURE:

Rinse the burette with 0.05N HCl and fill with same. Pipette out 25CC of the mixture Na_2CO_3 and $NaHCO_3$ solution. Add 2-3 drops of phenolphthalein indicator and titrate with 0.05N HCl from burette till colour changes from pink to colourless. Note the B.R. reading in the first table. Then to this titrated solution add 2-3 drops of methyl orange indicator and continue the titration with 0.05N HCl till colour changes from yellow to red. Note this B.R in second table. First take pilot readings and repeat the titration of three concurrent readings.

OBSERVATIONS:

1. Solution taken in burette – 0.05N HCl solution.
2. Solution taken in conical flask – mixture of Na_2CO_3 and $NaHCO_3$.
3. Indicator – Phenolphthalein
4. End point – pink to colourless and yellow to red.

TABLE – 1: Titration using phenolphthalein indicator

Burette level	Pilot Reading	Accurate Burette readings in CC			Mean Burette reading(MBR)X
		1	2	3	
Final level					
Initial level					
Difference					

TABLE– 2: **Titration using methyl orange indicator**

Burette levels	**Pilot Reading**	**Accurate readings in CC**			**Mean Burette reading(MBR) Y**
		1	**2**	**3**	
Final level					
Initial level					
Difference					

CALCULATION:

Estimation of Na_2CO_3:

1. Volume of HCl required for half mole of Na_2CO_3 = X CC = ___CC.
2. Volume of HCl required for 1 mole of Na_2CO_3 = 2X CC = ___CC.
3. Since 1000CC of 1N HCl solution = 53gm of Na_2CO_3.

Therefore 25CC of supplied mixture contains = $\frac{53\times2X\times0.05}{1000}$ = N = ___g of Na_2CO_3(W).

Hence the amount of Na_2CO_3 present in the sample supplied – W x 40 g/litre = ___g/litre.

Estimation of $NaHCO_3$:

Volume of HCl required for $NaHCO_3$ in mixture = Y – 2X = ___CC.

Since 1000ml of 1N HCl = 84gm of $NaHCO_3$.

Therefore 25ml of supplied mixture contains = $\frac{84 \text{ x } (Y-2X)}{1000}$ = W =___g of $NaHCO_3$.

Hence amount of $NaHCO_3$ present in the sample supplied = W x 40 gm/litre = ___ g/litre

EXPERIMENT NO-3

DETERMINATION OF ALKALI CONTENT IN CLEANSING AGENTS

CHEMICAL REQUIRED: 0.5N NaOH and 0.5N HNO_3. NaOH was standardized using standard oxalic acid and standardized NaOH was used to prepare standard HNO_3, Soap samples, Chloroform ($CHCl_3$), Sodium Hydroxide (NaOH), Methyl Orange, Nitric acid (HNO_3) and Sodium Carbonate (Na_2CO_3).

APPARATUS: Burette, Pipette, volumetric Flask, Conical Flask, Beaker, Funnel, Watch Glass, Glass rod

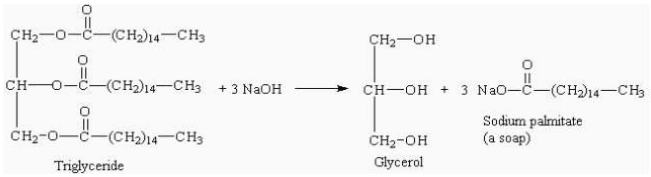
THEORY:

Soap is a sodium or potassium salts of various naturally occurring fatty acids. It is produced by saponification or basic hydrolysis reaction of a fat or oil. Sodium carbonate or sodium hydroxide is used to neutralize the fatty acid and convert it to the salt. The fatty acids, stearic, palmitic, myristic, lauric and oleic acids, contribute to lathering and washing properties of the soaps. The chemical characteristics of soap depend on several factors: the strength and purity of alkali, the kind of oil used, completeness of saponification and age of the soap. Such chemical characteristics include moisture content, total fatty acids (TFM), pH, free alkali, and percent chloride.

General Overall Hydrolysis Reaction

Fat + NaOH → glycerol + sodium salt of fatty acid

Soap is an anionic surfactant used in conjunction with water for washing and cleaning. Although the reaction is shown as one step reaction, it is in fact two steps. The net effect as that the ester bonds are broken. The glycerol turns back into an alcohol. The fatty acid portion is turned in to a salt because of the presence of a basic solution of the NaOH. In the carbonyl group, one oxygen now has a negative charge that attracts the positive sodium ion. The fats and oils used in soap making come from animals or plant sources. Each fat or oil is made up of a distinctive mixture of several different triglycerides. In a triglyceride molecule, three fatty acid molecules are attached to one molecule of glycerin. There are many types of triglycerides; each type consists of its own particular combination of fatty acid. Fatty acids are the components of fats and oils that are used in soap making.



Hydrolysis of a Triglyceride (fat)

The alkali used in soap making was obtained from ashes of plants, but they are now made commercially. The alkali mainly used is a soluble salt of an alkali metal like sodium or potassium. The alkalis used in soap making are NaOH (sodium hydroxide) and KOH (potassium hydroxide). Sodium carboxylates are the common toilet soaps. Potassium carboxylates or potassium soaps are obtained when saponification of a fat or oil is carried with potassium hydroxide. Potassium soaps are softer than sodium soaps and they are used for special purposes when rapid solution is desired eg: in making shaving creams or liquid soaps. The composition of sodium or potassium carboxylates constituting soap depends on the percentage of fatty acidsbonded to glycerol in the original triglycerides. Solid fats give mixture with higher proportion of sodium or potassium salts of higher fatty acids (palmitic acid, stearic acid) and give hard soaps. The vegetable oils give mixtures with a greater proportion of unsaturated fatty acids (oleic acid and linoleic acid) and give soft soaps.

PROCEDURE:

Determination of Total Alkali Content in the Soap Samples

1. Exactly weigh 5gm of soap sample and dissolve in 100 mL hot water.
2. Add about 40 mL of 0.5 N HNO_3 to make it acidic.
3. Heat the mixture until fatty acids are floating as a layer above the solution.
4. Cool the solution in ice water to solidify the fatty acids.
5. Separate the fatty acids through filtration and treat the aqueous solution with 50 mL chloroform to remove the remaining fatty acids.
6. Measure the total volume of aqueous solution and 10 mL of aqueous solution is titrate against 0.5N NaOH using methyl orange as indicator.

OBSERVATION AND CALCULATION:

1. Total volume of the aqueous solution =V=_____ml
2. 10 ml of aqueous solution required = t = _____mL of NaOH
3. V ml of aqueous solution requires = V x t /10 = A ml.
4. Amount of NaOH required by acid in aqueous solution = A ml
5. Volume of HNO_3 required,

$$B\ ml = \frac{A \times \text{Normality of NaOH}}{\text{Normality of } HNO_3}$$

6. Volume of HNO_3 required for neutralizing NaOH = C=40 – B
7. Amount of NaOH in 1000 cc of soap solution (E) = $\frac{C \times 40 \times \text{Normality of } HN_3 g)}{1000}$

8. 250 cc of soap solution contains (F) $=\frac{E \times 250)}{1000\ g}$

$$2NaOH \rightarrow Na_2O + H_2O$$

9. 80 gram of NaOH 62 g of Na_2O

10. F g of NaOH requires (Y) $=\frac{(62 \times F)}{(80\ g)}$ Na_2O

11. Weight of soap taken = 5 g

12. % of alkalinity = (Y x 100) / w = _____.

Result: Percentage of alkalinity = ____%

EXPERIMENT NO-4

ESTIMATION OF Fe^{+2} PRESENT IN A GIVEN SOLUTION

AIM: To estimate the amount of iron (II) present in a given solution

PREPARATION OF 0.05 N POTASSIUM DICHROMATE SOLUTION:

Weigh exactly 0.6125grams of potassium dichromate in a clean dry watch glass and dissolve it in minimum volume of distilled water in a beaker. Then transfer the solution to 250ml measuring flask and collect the washings in the same volumetric flask. Wash the beaker 3 to 4 times with the distilled water and transfer quantitatively to the same volumetric flask. Dilute the solution up to mark and shake well before use.

PROCEDURE:

Dilute the given ferrous sulphate solution exactly up to 250 ml with distilled water. Shake the solution before use. Pipette out exactly 25 ml of this solution into a clean conical flask. To this add two test tube full of dilute H_2SO_4 and one test tube full of Na_2HPO_4 (disodium hydrogen phosphate) and three drops of diphenylamine indicator. Titrate this solution against standard potassium dichromate taken in the burette. At the end point the colour changes from green to violet. Take one pilot and three accurate readings.

OBSERVATIONS:

1. Weight of the empty watch glass (W_1) = ---- g
2. Weight of the watch glass + substance (W_2) = ---- g
3. Weight of the substance taken (W_3) = ($W_2 - W_1$) = ---- g

I. Solution in burette = standard potassium dichromate.

II. Solution in conical flask = 25ml of ferrous sulphate solution + 2 test tube dilute H_2SO_4 + 1 test tube Na_2HPO_4 + 3 drops of diphenylamine as indicator.

III. Color change = Green to violet

REACTION:

$$K_2Cr_2O_7 + 4H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3[O]$$
$$[2\ FeSO_4 + H_2SO_4 + [O] \rightarrow Fe_2(SO_4)_3 + H_2O] \times 3$$

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

From the above reaction it is clear that
$K_2Cr_2O_7 \equiv 6FeSO_4.7H_2O \equiv 3[O]$

$\therefore$ Equivalent weight of $K_2Cr_2O_7$ =

$$\frac{Molecular\ weight}{2\times\ Number\ of\ available\ oxygen}=\frac{294}{2\times 3}=49$$

$$\therefore\ \text{The substance to be weighed} = \frac{NEV}{1000}=\frac{0.05\times 49\times 250}{1000}=0.6125\ grams$$

Burette Reading	Pilot Reading	Correct Reading			Mean Burette Reading
		I	II	III	
Final					
Initial					
Difference					

CALCULATION:

$N_1V_1 = N_2V_2$
N_1 = Normality of $FeSO_4.7H_2O$
V_1 = Volume of $FeSO_4.7H_2O$
N_2 = Normality of $K_2Cr_2O_7$.
V_2 = Volume of $K_2Cr_2O_7$.

$$\therefore\ V_1=\frac{N_2V_2}{V_1}=\frac{0.05\times M.B.R.}{25.}$$

1. Grams/Liter of $FeSO_4.7H_2O$ = $Normality\times Equivalent\ weight$

2. Amount of $FeSO_4.7H_2O$ in 250ml = $\frac{Normality\times Equivalent\ weight}{4}$

Second Method of Calculation:

Chemical Factor from the Reaction:

$K_2Cr_2O_7 \equiv 3[O] \equiv 6FeSO_4.7H_2O \equiv 6Fe^{+2}$

$$\frac{K_2Cr_2O_7}{6}=\frac{3[O]}{6}=FeSO_4.7H_2O=Fe^{+2}$$ i.e. $\frac{249}{6}=\frac{16}{2}=278=55.82$

49 parts of $K_2Cr_2O_7$ = 8 parts of oxygen = 278 parts of $FeSO_4.7H_2O$ = 55.82 parts of Fe^{+2}.
Equivalent weight of $FeSO_4.7H_2O$ = 278.
1000ml of 1N $K_2Cr_2O_7$ = 278grams of $FeSO_4.7H_2O$ = 55.82grams of Fe^{+2}.
1ml of 1N $K_2Cr_2O_7$ = 0.0278grams of $FeSO_4.7H_2O$ = 0.05582grams of Fe^{+2}.
1ml of 0.1N $K_2Cr_2O_7$ = 0.0278grams of $FeSO_4.7H_2O$ = 0.005582grams of Fe^{+2}.
1ml of 0.05N $K_2Cr_2O_7$ = 0.0139grams of $FeSO_4.7H_2O$ = 0.002791grams of Fe^{+2}.

1) Amount of $FeSO_4.7H_2O$ present in 250ml of dilute solution = 0.0139 × M. B. R. × 10
2) Amount of Fe^{+2} present in 250ml of dilute solution = 0.00279 × M. B. R. × 10

EXPERIMENT NO-5

ESTIMATION OF $KMnO_4$ BY TITRATING WITH OXALIC ACID

AIM: To prepare the standard solution of oxalic acid and to estimate the amount of $KMnO_4$ present in the given solution

APPARATUS: Burette, Pipette, Conical flask, Measuring flask, Beaker, Funnel etc.

CHEMICALS: Oxalic acid, $KMnO_4$, H_2SO_4 (2N) etc.

THEORY: This is an example of Redox titration in which oxalic acid gets oxidized to CO_2 and potassium permanganate gets reduced to manganese sulphate. This reaction is carried out in acid medium by adding two test tubes of 2N sulphuric acid and then heated to 60-80 ^{0}c to evolve CO_2 formed during the reaction readily. In this titration $KMnO_4$ solution (titrant) acts as a self-indicator.

PROCEDURE:

A) Preparation of standard Oxalic acid (0.05N) solution

In a clean & dry watch glass weigh accurately 0.7875g of oxalic acid transferred to beaker carefully and dissolves by adding distilled water. It is then transferred to 250 ml volumetric flask using funnel. Volume is made up to zero mark and shaken well to get homogenous solution.

B) Estimation of $KMnO_4$ using standard Oxalic acid (0.05N) solution

The burette is washed with water and rinsed with $KMnO_4$ solution and filled with the same solution up to the zero mark. The pipette is washed with water, rinsed with oxalic acid solution and 25cc of oxalic acid solution pipette in to clean conical flask. To this two test tube full of dil. H_2SO_4 is added and heated to 60-80 ^{O}c. It is then titrated against the $KMnO_4$ solution till the colour changes from colourless to light pink. The burette reading is recorded. Above procedure is repeated to get 3 accurate reading.

OBSERVATIONS

1) Mass of empty watch glass =W_1=_____g

2) Mass of watch glass + substance =W_2= _____g

3) Mass of substance = W_3= _____g

4) Solution taken in burette = $KMnO_4$ solution

5) Solution taken in conical flask = standard oxalic acid + 2 test tube of dil. H_2SO_4

6) Indicator used = $KMnO_4$ itself

7) Colour change = colourless to light pink

REACTION:

$2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_20 + 5(0)$

$(H_2C_2O_4 + (O) \longrightarrow H_20 + 2CO_2) \times 5$

$2KMnO_4 + 3H_2SO_4 + 5H_2C_2O_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 8H_20 + 10CO_2$

BURETTE READINGS

Burette levels	**Pilot Reading**	**Accurate Burette Readings in ml**			**Mean Burette reading(MBR)**
		1	**2**	3	
Final level					
Initial level					
Difference					

CALCULATION:

1. $N_1V_1 = N_2V_2$

   $N_1 = N_2V_2 / V_1$ (Where N_2 = Normality of Oxalic acid = 0.05N; V_2 = Volume of Oxalic acid = 25ml)

2. $N_1 =$ 0.05 x 25/ MBR = ------ N N_1 = Normality of $KMnO_4$
   V_1 = Volume of $KMnO_4$

3. Grams / dm^3 of KMnO4 = Normality of $KMnO_4$ X Equivalent weight of $KMnO_4$

   = N_1 x 31.6

   = ---------- g / dm^3

4. Grams / 250cc of $KMnO_4$ = N_1 x 31.6 / 4 = -------- g / 250 cc

RESULTS:

1. MBR = ---------- ml
2. Normality of $KMnO_4$ = -------- N
3. Grams / dm^3 of $KMnO_4$ = ---------- g / dm3
4. Grams / 250 cc of $KMnO_4$ = ---------- g / 250 cc

EXPERIMENT NO-6

DATERMINATION OF TOTAL HARDNESS OF WATER

AIM: To determine the total hardness of the water

PRINCIPLE:

Hardness of water is due to the presence of calcium and magnesium salts in water. Ethylenediaminetetracetic acid [EDTA] forms complexes with a large number of cations including Ca^{+2} *and* Mg^{+2} ions. Accordingly, it is possible to determine the total hardness of water using EDTA reagent.

The EDTA molecule (H_4Y) has two easily replaceable hydrogen atoms and the resulting ion after ionisaion may be represented as H_2Y^{2-}. The latter forms complexes with metal ion as follows ;

$$M^{+2} + H_2Y^{2-} \rightarrow MY^{2-} + 2H^+$$

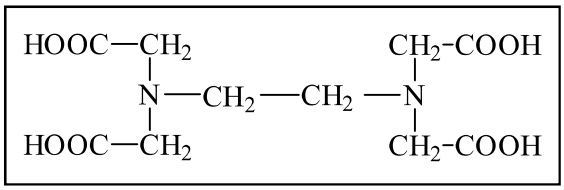
Where M^{2+} is Ca^{2+} *and* Mg^{2+} in water. Reaction (1) can be carried out quantitatively at a pH of 10 using eriochrome black – T indicator. Since the reaction involves the liberation of H^+ ions, a buffer mixture has to be added to maintain a pH of 10. The buffer mixture used in the titration is $NH_3 - NH_4Cl$. The hardness of water is usually expressed in terms of ppm (parts per million) of $CaCO_3$. Since EDTA (free acid) is sparingly soluble, its disodium salt, Na_2H_2Y, is used for preparing the reagent.

PREPARATION OF 0.05N DISODIUM SALT OF EDTA SOLUTION:

Weigh exactly 4.653grams disodium salt of EDTA in a clean dry watch glass and dissolve in minimum volume of distilled water in a beaker. Then transfer the solution to 250ml measuring flask and collect the washings in the same volumetric flask. Wash the beaker 3 to 4 times with the distilled water and transfer quantitatively to the same volumetric flask. Dilute the solution up to mark and shake well before use.

PROCEDURE:

Pipette out exactly 25ml of the given water sample into a clean conical flask. Add 1 test tube full of $NH_3 - NH_4Cl$ buffer and a pinch of eriochrome blak – T indicator. Titrate this solution against EDTA till the colour changes from wine red to clear blue. Let the volume of EDTA consumed be ‘x’ml.



OBSERVATIONS:

1. Weight of the empty watch glass (W_1) =

2. Weight of the watch glass + substance (W_2) =

3. Weight of the substance (W_3) = ($W_2 - W_1$) =

Molarity of EDTA = $\frac{Weight\ of\ EDTA\ taken \times 4}{Molecular\ mass\ of\ disodium\ salt\ of\ EDTA} = z\ (say)$

I. Solution in burette = standard disodium salt of EDTA.

II. Solution in pipette = Hard water sample.

III. Solution in conical flask = 25ml of hard water sample + 1 test tube full of NH_3–NH_4Cl buffer + a pinch of Eriochrome black – T indicator

IV. Colour change = wine red to clear blue.

Burette Reading	**Pilot Reading**	**Correct Reading**			**Mean Burette Reading**
		I	II	III	
Final					
Initial					
Difference					

CALCULATION:

1000ml of 1M EDTA = 100gram of $CaCO_3$ (molecular mass $CaCO_3$ =100)

$$\text{x ml of z M of EDTA} = \frac{\text{x} \times \text{z} \times 100}{1000 \times 1} = a\ gram\ \ CaCO_3.$$

25ml of hard water contains 'a' grams of $CaCO_3$. Therefore, $10^6\ ml$ of hard water = $\frac{a \times 10^6}{25}\ gram\ of\ CaCO_3.$

EXPERIMENT NO-7

ESTIMATION OF PHENOL VOLUMETRICALLY

AIM: To estimate the amount of phenol in a given solution by bromination method

APPARATUS: Stoppard conical flask, Burette, Pipette, Measuring flask Etc

CHEMICALS:

1. 0.1N Brominating mixture
2. 0.1N Sodium thiosulphate
3. Given phenol solution
4. 10% potassium iodide solution
5. Conc. Hydrochloric acid and starch solution

PRINCIPLE:

Quantity of phenol presents in the given solution is determined by bromination method using known and excess volume of brominating mixture .The excess of brominating mixture present(un used) is liberated quantitatively in the form of iodine with the addition of 10% KI solution which is determined by titrating against 0.1N sodium thiosulphate solution using starch as an indicator .The volume of brominating mixture added in terms of 0.1N sodium thiosulphate is determined by performing blank titration. Here by knowing the volume of 0.1N brominating mixture consumed by phenol solution their quantity can be calculated.

PROCEDURE:

1. MAIN TITRATION: The given phenol solution in 250ml measuring flask in diluted up to the mark and is shaken well. Pipette out 25ml of this diluted solution in each of the three stopper bottles. Add about 50ml of water and 5ml of conc. Hydrochloric acid to these bottles separately .Then add 25ml of 0.1N brominating mixture to each bottle from the burette gives pale yellow colour ppt. Keep the bottle aside for 10 minutes. For the completion of bromination.

Then added the same quantity of brominating mixture to the remaining stopper bottles and keep them aside with occasional shaking. Takeout first bottle, add 2 test tubes full of 10% KI solution. Then titrate the liberated iodine immediately against 0.1 N sodium thiosulphate solution till it becomes pale yellow. Then add starch solution, continue the addition of drop wise till colourless. Perform similar titrations with two more remaining solutions to get concurrent readings. Note down the burette readings.

2. BLANK TITRATION: Pipette out 25ml of 0.1N brominating mixture in stopper bottle. To this add about 50ml of water and 5ml conc. Hydrochloric acid followed by 1 test tubes full of 10% KI solution. Titrate the liberated iodine immediately against 0.1N sodium thiosulphate solution taken in burette as in main titration. Perform two more similar titrations to get concurrent readings.

REACTIONS:

$KBrO_3 + 5KBr + 6HCl \longrightarrow 6KCl + 3Br_2 + 3H_2O$

$C_6H_5OH + 3Br_2 \longrightarrow C_6H_2Br_3OH + 3HBr$

$2KI + Br_2$ (excess) $\longrightarrow 2KBr + I_2$

$I_2 + 2Na_2S_2O_3 \longrightarrow 2NaI + Na_2S_4O$

CONVERSION FACTOR:

For Phenol

From the above equations

1 mole of phenol = 3 mole of Br_2 = 3 mole of I_2 = 6 atoms of iodine.

1 mole of phenol = 60,000 ml of 0.1N $Na_2S_2O_3.5H_2O$

1 ml of 0.1N $Na_2S_2O_3.5H_2O$ = 1 mole of phenol / 60,000

= 94/60000

= 0.001567 g.

Quantity of phenol present in given solution = Brominating mixture consumed in terms of 0.1N $Na_2S_2O_3.5H_2O$ X 0.001567 X 10 g

1. MAIN TITRATION

Burette Levels	I	II	III	Mean `a` ml
Final level				
Initial level				
Difference				

Mean=(I+II+III)/3

2. BLANK TITRATIONS:

Burette Levels	I	II	III	Mean `y` ml
Final level				
Initial level				
Difference				

OBSERVATIONS AND CALCULATIONS:

1. Quantity of 0.1N Brominating mixture added to 25ml of dilute phenol solution ..... 25 ml

2. 0.1N sodium thiosulphate solution required to react with 25ml of Brominating mixture (blank titration reading) ..... x ml

3. 0.1N sodium thiosulphate solution required to react excess of Brominating mixture present (main titration) ..... y ml

4. Quantity of Brominating mixture consumed in terms of 0.1 N sodium thiosulphate solution = x - y = z ml

5. Quantity of phenol present in given solution = z x 0.001567 x 10 g

EXPERIMENT NO-8

ESTIMATION OF ANILINE VOLUMETRICALLY

AIM: To estimate the amount of aniline in a given solution by bromination method

APPARATUS: Stoppard conical flask, Burette, Pipette, Measuring flask Etc

CHEMICALS:

1. 0.1N Brominating mixture
2. 0.1N Sodium thiosulphate
3. Given aniline solution
4. 10% potassium iodide solution
5. Conc. Hydrochloric acid and starch solution

PRINCIPLE:

Quantity of aniline presents in the given solution is determined by bromination method using known and excess volume of brominating mixture .The excess of brominating mixture present(un used) is liberated quantitatively in the form of iodine with the addition of 10% KI solution which is determined by titrating against 0.1N sodium thiosulphate solution using starch as an indicator .The volume of brominating mixture added in terms of 0.1N sodium thiosulphate is determined by performing blank titration.

Here by knowing the volume of 0.1N brominating mixture consumed by phenol solution their quantity can be calculated.

PROCEDURE:

1. MAIN TITRATION

The given aniline solution in 250ml measuring flask in diluted up to the mark and is shaken well. Pipette out 25ml of this diluted solution in each of the three stopper bottles. Add about 50ml of water and 5ml of conc. Hydrochloric acid to these bottles separately .Then add 0.1N brominating mixture to each bottle from the burette till pale yellow colour persists. Add further 5ml more of brominating mixture .Note down the exact quantity added KI the bottle aside for about 10min.For the completion of bromination.

Then added the same quantity of brominating mixture to the remaining stopper bottles and keep them aside with occasional shaking. Take out first bottle; add 2 test tubes full of 10% KI solution. Then titrate the liberated iodine immediately against 0.1N sodium thiosulphate solution till it becomes pale yellow. Then add starch indicator, continue the addition of drop wise till colourless. Perform similar titrations with two more remaining solutions to get concurrent readings .Note down the burette readings.

2. **BLANK TITRATION:**

Pipette out 10ml of brominating mixture in stopper bottle .To this add about 50ml of water and 5ml conc. Hydrochloric acid followed by 2 test tubes full of 10% KI solution. Titrate the

liberated iodine immediately against 0.1N sodium thiosulphate solution taken in burette as in main titration. Perform two more similar titrations to get concurrent readings.

REACTIONS:

$KBrO_3 + 5KBr + 6HCl \longrightarrow 6KCl + 3Br_2 + 3H_2O$

$C_6H_5NH_2 + 3Br_2 \longrightarrow C_6H_2Br_3NH_2 + 3HBr$

$2KI + Br_2 \text{ (excess)} \longrightarrow 2KBr + I_2$

$I_2 + 2Na_2S_2O_3 \longrightarrow 2NaI + Na_2S_4O_6$

CONVERSION FACTOR:

For aniline
From the above equations
1 mole of 0.1N $Na_2S_2O_3.5H_2O$ = 1 mole of aniline / 60,000
= 93/60,000 = 0.00155 grams.
Quantity of aniline present in given solution = Brominating mixture consumed in terms of 0.1N $Na_2S_2O_3.5H_2O$ X 0.00155 X 10 grams

1. MAIN TITRATION

Burette Levels	I	II	III	Mean `a` ml
Final level				
Initial level				
Difference				

2. **BLANK TITRATIONS**

Burette Levels	I	II	III	Mean `y` ml
Final level				
Initial level				
Difference				

OBSERVATIONS AND CALCULATIONS:

1. Quantity of 0.1N Brominating mixture added to 25ml of dilute aniline solution.....x ml
2. 0.1N sodium thiosulphate solution required to react with 10ml of Brominating mixture (blank titration reading) ..... y ml
3. 0.1N sodium thiosulphate solution required to entire quantity of Brominating mixture added = xy / 10 = z ml
4. 0.1N sodium thiosulphate solution required to react excess of Brominating mixture present (main titration reading) ..... = a ml
5. Quantity of Brominating mixture consumed in terms of 0.1 N sodium thiosulphate solution z-a=b ml
6. Quantity of aniline present in given solution = bx0.00155x10 gms.

PART-B: ORGANIC CHEMISTRY

EXPERIMENT NO-1

Selection of suitable solvents for the purification/crystallization of organic compound

The choice of a solvent is of course determined primarily by its suitability for the actual recrystallization of the given crude product. If two or more solvents appear to be almost equally suitable for the recrystallization, the final choice should depend on the inflammability (and therefore risk in use) of the solvent, and also on its cost. It is assumed that a solvent which might have any chemical action on the compound has already been debarred. The chief solvents normally available are:

Solvent	B.P.	Inflammability	Remarks
Distilled water	100 ^{o}C	Non-inflammable	To be used whenever suitable
Ether	35 ^{o}C	Inflammable	Avoid when possible
Acetone	56 ^{o}C	Inflammable	Should preferably be dried before use
Methanol	65 ^{o}C	Inflammable	Toxic
Benzene	81 ^{o}C	Inflammable	Toxic
Acetic acid(glacial)	118 ^{o}C	Not readily Inflammable	Hygroscopic. Hot liquid gives pungent fumes. Frequently used to dissolve strong oxidizing agent
Chloroform	61 ^{o}C	Non-inflammable	May contain traces of HCl, due to oxidation or hydrolysis
Carbon tetrachloride	77 ^{o}C	Non-inflammable	May contain traces of HCl, due to oxidation or hydrolysis

Experimental Directions for Recrystallisation

The complete process of recrystalization consists of the following stages,

(1) Choice of a Solvent:

(2) Repetition of recrystallization on Larger Scale

(3) Drying of recrystallized Material.

(4) Checking the Purification.

(1) Choice of a Solvent

Generalised consideration for selection of solvent is based on the dissolving power of the compound. Alcohol will usually dissolve other hydroxy compounds, benzene will dissolve hydrocarbons.

- Place about 0.1 g of the crude powdered compound in a clean dry test-tube, and add sufficient of the possible solvent just to cover the compound. If the compound

dissolves readily in the cold, the solvent is obviously unsuitable. If it does not dissolve, warm the mixture gently over a very small Bunsen flame until the liquid boils: it is advantageous at this stage to hold the forefinger loosely over the mouth of the tube to prevent undue loss of vapour. Continue adding the liquid if necessary until almost all the substance has dissolved.

- If a large amount of the solvent is required (e.g., one-half to two-thirds of the tube) then the low solubility renders the solvent unsuitable. If an almost clear solution is obtained, cool by immersing the tube preferably in a mixture of ice and water, or alternatively in cold water. (If benzene is the solvent, cold water alone must be used, as benzene will itself crystallise in ice-water.) Shake the mixture gently in the tube. If crystallisation does not rapidly start, the failure may be due to lack of suitable nuclei for crystal-growth. Therefore scratch the tube below the surface of the solution with a glass rod: the fine scratches on the walls form excellent sites for crystal-growth, and crystals often form rapidly after scratching.
- Repeat this process with various other possible solvents (using a fresh clean tube for each test) until the best solvent has been selected, and then note carefully the approximate proportions of the solute and the solvent for efficient recrystallization.
- Sometimes the crude substance may contain an insoluble impurity, and on cooling the solution it may be difficult to judge how much of the solid matter is merely undissolved impurity and how much is solute which has subsequently crystallised from solution. To avoid this difficulty, the hot solution should be filtered, and should thus always be absolutely clear before cooling is attempted. Therefore filter the hot solution into a clean tube through a very small fluted filter-paper contained in a correspondingly small glass funnel, which should have had its stem cut off.
- Unless the upper part of the filter is cut away to reduce its size to a minimum, a large proportion of the solution will remain held mechanically in the pores of the paper itself and only a few drops of clear filtrate will be obtained.

EXPERIMENT NO-2

PREPARATION OF ACETANILIDE FROM ANILINE

AIM: To prepare acetanilide from aniline using Zn/Acetic Acid

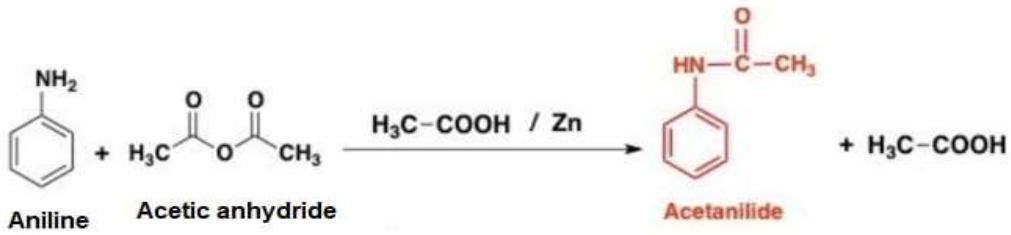
CHEMICALS REQUIRED: Aniline, Glacial acetic acid, Acetic anhydride, Zinc dust, Distilled water

APPARATUS: Round bottom flask, Beaker, Pipette, Reflux condenser, Funnel, Stirrer, Bunsen burner, Filter paper, Electronic balance

THEORY:

Acetanilide is prepared from aniline when it reacts with acetic anhydride/glacial acetic acid in the presence of zinc dust. A mixture of aniline, glacial acetic acid, acetic anhydride and zinc dust is refluxed under anhydrous condition and then poured the mixture into ice cold water to get acetic anhydride precipitate. The crude precipitate of acetic anhydride is recrystallized to get pure crystals of acetanilide.

The chemical reaction is given below



Zinc is used to prevent the oxidation of aniline during the chemical reaction. Acetanilide is medicinally important and it is used as febrifuge. Acetanilide cal also be prepared by acetylating aniline with acetic anhydride in the presence of concentrated hydrochloric acid. Dissolve aniline in hydrochloric acid and add acetic anhydride stir well. Pour the mixture to sodium acetate in water. Acetanilide is formed which can be separated and recrystallised by ethyl alcohol.

PROCEDURE:

1. Wash all the apparatus with distilled water before starting the experiment.
2. Take a round bottom flask in that add 10ml of aniline and 20ml of acetic anhydride and glacial acetic acid mixture and add zinc dust.
3. Fix the reflux condenser with the round bottom flask.
4. Heat the mixture gently for about 15-20 minutes on oil bath.
5. Pour the hot mixture in a beaker containing ice cold water with constant stirring.
6. Stir the mixture vigorously to hydrolyse excess of acetic anhydride.
7. Once all the acetanilide is precipitated collect and filter in Buchner funnel.
8. The precipitate obtained is a crude sample of acetanilide. To get the pure crystals crystallization should be carried out.

CRYSTALLIZATION:

Transfer the crude sample into a beaker containing 20ml water and heat gently. If the solution is coloured then add a small amount of activated carbon. Filter the hot solution with a funnel. Cool the mixture for 30 min so that white shiny crystals of acetanilide separate out. Filter off the crystals, wash them with water and dry in the folds of filter paper.

OBSERVATIONS:

Colour of the crystals	: Colourless crystals
Shape of the crystals	: Plate shaped
Melting point	: 114^{o}C

RESULT:

The yield of Acetanilide is ____g.

Precautions:

Do not inhale the fumes of acetic anhydride.

Always carry out experiments in fuming chamber or near the window.

Use the water condenser for refluxing the reaction mixture.

Dry the crystals of acetanilide before finding the weight and its melting point

EXPERIMENT NO-3

PREPARATION OF p-NITRO ACETANILIDE

AIM: To prepare P-nitro acetanilide from acetanilide

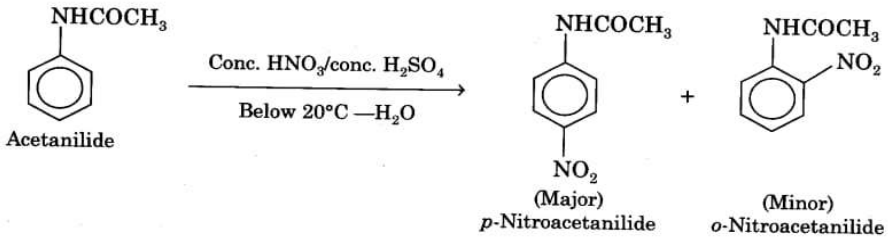
CHEMICALS REQUIRED: Acetanilide (5g), Glacial acetic acid(5 ml), Conc. H_2SO_4 (10 ml), Fuming HNO_3 (2 ml), Methylated spirit(20 ml)

APPARATUS: Conical flask (100 ml), beaker (250 ml), measuring cylinder (100 ml), funnel, glass-rod, test-tube, filter-papers, etc

THEORY :

The nitration of aniline is difficult to carry out with nitrating mixture (a mixture of cone. H_2SO_4, and conc. HNO_3) since —NH_2 group gets oxidised which is not required. So the amino group is first protected by acylation to form acetanilide which is then nitrated to give p-nitroacetanilide as a major product and o-nitro acetanilide as a minor product. Recrystallisation from ethanol readily removes the more soluble ortho-compound and the pure p-nitroacetanilide is obtained.

The chemical equation can be written as:



PROCEDURE:

1. Take a 100 ml conical flask and add 5 g of powdered acetanilide in it. Add 5 ml of glacial acetic acid and stir the mixture by the use of glass-rod.
2. Place 2 ml of fuming nitric acid in a clean test-tube and cool it in a freezing mixture (ice + salt) taken in a beaker. Carefully add drop by drop 2 ml of cone, sulphuric acid with constant shaking and cooling.
3. Add the remaining 8 ml of cone. H_2S0_4 drop by drop (with cooling under tap water) to the conical flask containing acetanilide and glacial acetic acid. Place the conical flask in a freezing mixture (Fig). Stir the contents and wait until the temperature becomes less than 5°C.
4. To the cooled contents in the flask add nitrating mixture prepared in step (2) drop by drop with constant stirring. During addition temperature of the mixture should not rise above 10°C. This operation should take about 15 minutes.
5. Remove the conical flask from the freezing mixture and allow it to stand for 30 minutes at room temperature.

6. Pour the contents of the flask on the crushed ice taken in a beaker. Stir it and filter the crude product. Wash thoroughly with cold water to remove acid.
7. Recrystallisation of p-nitroacetanilide. Dissolve the crude product obtained above in about 20 ml of methylated spirit. Warm to get a clear solution. Filter while hot and cool the filtrate in ice. o-Nitroacetanilide goes in the filtrate while p-nitroacetanilide is obtained as colourless crystals on the filter paper. Wash the solid on the filter paper with cold water. Dry the solid, weigh it and record its yield.

RESULT:

Weight of p-nitroacetanilide is obtained =……g
Melting point of the compound is =…….°C
Note: Approximate expected yield is 4 g.
The melting point of p-nitroacetanilide is 214°C.

Precautions

During addition of nitrating mixture, the temperature of the reaction mixture should not rise above 10°C.

Addition of fuming nitric acid should be done drop wise.

Do not inhale the vapours of nitric acid as they are very corrosive in nature. Addition of nitrating mixture may preferably be done in a fume-cupboard.

EXPERIMENT NO-4

PREPARATION OF DIAZOAMINOBENZENE

AIM: To prepare diazoaminobenzene from aniline (Conventional method)

CHEMICALS REQUIRED: Aniline, Conc. Sulphuric Acid, Sodium nitrite, Distilled water

APPARATUS: Round bottom flask, Beaker, Pipette, Reflux condenser, Funnel, Stirrer, Bunsen burner, Filter paper, Electronic balance

THEORY:

Diazonium salts couple readily with aromatic primary amines, giving diazoamino compounds. If for instance an aqueous solution of aniline sulphate is diazotised with a deficiency of nitrous acid, only part of it is converted into benzenediazonium sulphate and the latter then couples with the unchanged aniline to give diazoaminobenzene. The reaction is carried out at the optimum temperature of 30°, for at this temperature coupling takes place readily, and the diazonium sulphate is used up before it has time to decompose.

$$C_6H_5NH_2,H_2SO_4 + HONO \longrightarrow C_6H_6N_2HSO_4 + 2H_2O$$

$$C_6H_6N_2HSO_4 + HNHC_6H_5 \longrightarrow C_6H_5\text{-}N{:}N\text{-}NH\text{-}C_6H_5 + H_2SO_4$$

PROCEDURE:

Dissolve 2 ml (3.7 g) of concentrated sulphuric acid in 350 ml of water contained in a 600 ml. beaker, and then add with stirring 12 ml (12.3 g) of aniline. Place the beaker in a water bath and heat the latter gently until a thermometer in the solution records a temperature of 30 °C. Dissolve 4.5 g. of sodium nitrite in 15 ml of water, and add about 1 ml of this solution at half minute intervals to the solution of aniline sulphate, keeping the mixture well stirred meanwhile. When the addition of the nitrite is complete, keep the mixture at 30° C for a further 15 minutes: the diazo-aminobenzene rapidly begins to separate as a yellow crystalline mass. Then remove the beaker from the bath, and allow it to stand for 30 minutes, with occasional stirring. Filter off the solid material at the pump, using a Buchner funnel, wash repeatedly with water, and then drain thoroughly. Finally dry the diazoaminobenzene by pressing between several sheets of thick drying-paper.

RECRYSTALLIZATION:

Place 2 g. of the crude, freshly prepared, well-drained material in a boiling-tube, add about 15-20 ml. of ethanol and 1-2 drops of 10% aqueous sodium hydroxide solution, and then heat rapidly until boiling: if the solution should contain insoluble impurities, filter through a small fluted paper, and at once cool the filtrate in ice-water. The diazoaminobenzene should rapidly crystallise out from the cold and stirred solution: filter the crystals rapidly at the pump whilst the solution is still cold, as they tend to redissolve if the solution reaches room temperature. Diazoaminobenzene is thus obtained as yellow crystals, which melt at 98°, the molten material decomposing vigorously above this temperature: the crystalline material darkens on exposure to light and most specimens are therefore of a yellowish-brown colour.

OBSERVATIONS:

Colour of the crystals : Yellow crystals

Melting point : 98 ºC

RESULT:

The yield of diazoaminobenzene is ____g.

EXPERIMENT NO-5

PREPARATION OF DIBENZAL-ACETONE (Claisen Reaction)

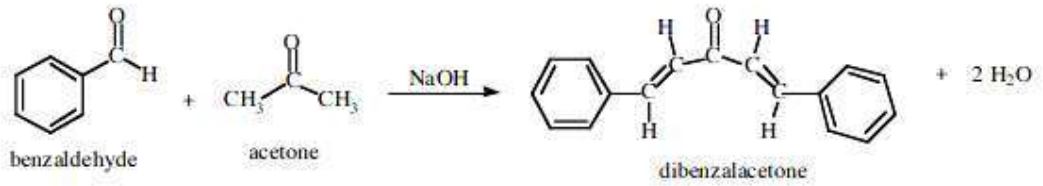
(Semi-micro Scale, green method)

CHEMICALS REQUIRED: Benzaldehyde (1 ml); acetone (0.4 ml); methylated spirit (10 ml)

APPARATUS: Round bottom flask, Beaker, Pipette, Reflux condenser, Funnel, Stirrer, Bunsen burner, Filter paper, Electronic balance

THEORY:

When an ethanolic solution containing both acetone and two equivalents of benzaldehyde is made alkaline with sodium hydroxide, rapid condensation occurs with the formation of dibenzal-acetone, or dibenzylidene-acetone.



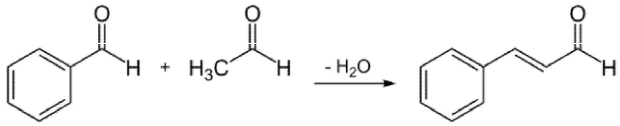
This is a particular example of the Claisen Reaction, for Claisen showed that aldehydes under the influence of sodium hydroxide will condense with

(i) Another aldehyde, or

(ii) a ketone, with the elimination of water.

Thus benzaldehyde will condense with (i) acetaldehyde to give cinnamic aldehyde, and with (ii) one equivalent of acetone to give (mono) benzal-acetone.

(i)



Cinnamic aldehyde

(ii)

Benzylidene-acetone.

In these reactions it is probable that an intermediate hydroxy-compound is formed ($C_6H_6CH(OH)CH_2CHO$ and $C_6H_6CH(OH)CH_2COCH_3$ respectively) and water is then lost from the unstable - $CH(OH)CH_2$ - group.

PROCEDURE:

Dissolve 1 ml of benzaldehyde and 0.4 ml of pure acetone in 10 ml of methylated spirit contained in a conical flask or wide mouthed bottle of about 50 ml capacity. Dilute 2 ml of 10% aqueous sodium hydroxide solution with 8 ml of water, and add this dilute alkali solution to the former solution. Shake the mixture vigorously in the securely corked flask for about 10 minutes (releasing the pressure from time to time if necessary) and then allow to stand for 30 minutes, with occasional shaking. Finally cool in ice-water for a few minutes. During the shaking, the dibenzal-acetone separates at first as a fine emulsion which then rapidly forms pale yellow crystals. Filter at the pump, wash well with water to eliminate traces of alkali, and then drain thoroughly.

Recrystallize from hot methylated or rectified spirit.

OBSERVATIONS:

Colour of the dibenzal-acetone crystals	: Pale Yellow crystals
Melting point	: 112 ºC

RESULT:

The yield of diazoaminobenzene is ____g.

B. L. D. E. ASSOCIATION'S

S. B. ARTS AND K. C. P. SCIENCE COLLEGE

Smt. Bangaramma Sajjan Campus, Shri B. M. Patil Road (Solapur Road), Vijayapur-586 103

Accredited with CGPA of 2.99 at 'B^{++}' Grade in 4th Cycle by NAAC

(Affiliated to Rani Channamma University, Belagavi)

DEPARTMENT OF CHEMISTRY

BSC II SEMESTER

CHEMISTRY LAB MANUAL

Name of the Student :_____

Reg. No. :_____

1. DETERMINATION OF SODIUM CARBONATE AND SODIUM HYDROXIDE FROM THE MIXTURE

Aim: To prepare the standard sodium carbonate solution, standardize hydrochloric acid solution and to determine sodium carbonate and sodium hydroxide from their mixture of the solution.

Apparatus: Burette, pipette, conical flask, volumetric flask, funnel, beaker etc.

Chemicals: Sodium carbonate, hydrochloric acid, phenolphthalein indicator and methyl orange, etc.

Theory: Sodium carbonate (Mol.wt. =106) is referred as the primary standard in the titrimetric analysis with the gram equivalent mass (E) of 53 and forms weakly basic solution in water. The amount of sodium carbonate to be weighed to prepare any volume (V) and any concentration (N) is calculated by using the equation NEV/1000. The standard solution of sodium carbonate is used to standardize the secondary standard solutions like hydrochloric acid.

The given hydrochloric acid solution is standardized by titrating against the standard solution of sodium carbonate using phenolphthalein as an indicator till the colour changes from pink to colourless.

$$Na_2CO_3 + 2HCl \longrightarrow NaCl + H_2O + CO_2\uparrow$$

The sodium carbonate and sodium hydroxide present in the given solution is determined by titrating against the standard solution of hydrochloric acid by the selective use of indicators. The sodium hydroxide undergoes complete neutralisation with HCl to form NaCl, where as sodium carbonate reacts with HCl to form first $NaHCO_3$ and then NaCl. The phenolphthalein is added as first indicator which decolorizes its pink colour in alkaline medium when NaOH and half Na_2CO_3 are neutralised (Na_2CO_3 turns to $NaHCO_3$). The $NaHCO_3$ is slightly acidic in nature (pH =4); hence phenolphthalein is not a suitable indicator for its determination. Therefore, methyl orange is used as the second indicator which shows the complete neutralisation ($NaHCO_3$ turns to NaCl) of solution of NaOH and Na_2CO_3 mixture

$$NaOH + HCl \longrightarrow NaCl + H_2O$$

$$Na_2CO_3 + HCl \longrightarrow NaCl + NaHCO_3$$

$$NaHCO_3 + HCl \longrightarrow NaCl + H_2O + CO_2\uparrow$$

Procedure:

A. Preparation of standard (0.1 N) Sodium carbonate solution:

Accurately weighed (1.325g) sodium carbonate is transferred to a beaker and is dissolved by adding distilled water. The solution is carefully transferred (along with washings) to a 250 cc volumetric flask and further diluted up to the mark using distilled water. It is shaken well to get homogeneous solution.

B. Standardization of hydrochloric acid solution:

The burette is washed with water, rinsed with the given hydrochloric acid solution and filled with the same solution up to the zero mark (Avoid air bubbles). The pipette is washed with distilled water and rinsed with sodium carbonate solution. The given conical flask is washed with distilled water. Exactly 25 cc of sodium carbonate solution is pipetted out into the clean conical flask. Two drops of phenolphthalein indicator is added and the solution is titrated against sodium carbonate solution till the colour changes from pink to colourless. The burette reading is noted. The titration is repeated to get concordant values and determined exact strengtg(normality) of hydrochloric acid solution.

C. Determination of sodium carbonate and sodium hydroxide from their mixture of the solution:

The mixture of sodium hydroxide and sodium carbonate solution supplied in the 250 cc volumetric flask is diluted up to the mark with distilled water or *ready mixture of the solution may be directly supplied*. 25 cc of this solution is pipetted out into a clean conical flask and 2 to 3 drops of phenolphthalein indicator is added and titrated against hydrochloric acid solution till the colour changes from pink to colourless. The burette reading is noted as V_1. The titration is further continued by adding 2-3 drops of methyl orange indicator till the colour changes from yellow to red. The burette reading is noted as V_2. The above procedure repeated to get concordant values.

Using appropriate formula sodium carbonate and sodium hydroxide from the given mixture is determined.

Observations and Calculation

A. Preparation of 250 cc of standard (0.1N) sodium carbonate solution

The amount of sodium carbonate required $= \frac{N \times E \times V}{1000} = \frac{0.1 \times 53 \times 250}{1000} = 1.325$ g

Mass of empty watch glass : m_1 =..... g

Mass of watch glass + sodium carbonate : m_2 =..... g

Mass of sodium carbonate : $(m_2 - m_1)$ = --------- g

If the value of mass of sodium carbonate weighed differs from 1.325 g then, normality of sodium carbonate solution is calculated by

$$\therefore \text{ Normality of sodium carbonate solution} = \frac{\text{Mass of sod . carbonate x 4}}{\text{Eq.mass of sod.carbonate}}$$

$$= \frac{(m_2 - m_1) \times 4}{53} = \text{.....} \quad \mathbf{N}$$

B. Standardization of hydrochloric acid:

Solution taken in the burette : HCl solution
Solution taken in the conical flask : 25 cc of sodium carbonate
Indicator used : Methyl red
Colour change at the end point : Yellow to orange red

Tabulations

Trial No	Burette readings (cc)		Volume of HCl added (B – A) (cc)	Concordant burette reading in cc (CBR)
	Initial reading (A)	Final reading (B)		
1	0.0			
2	0.0			
3	0.0			

Calculations: Equation used $N_1 V_1 = N_2 V_2$

N_1 =Normality of HCl V_1 = Volume of HCl (CBR)

N_2= Normality of sodium carbonate and V_2 = volume of sodium carbonate

Therefore, Normality of HCl, $N_1 = \frac{N_2 V_2}{V_1}$ = ... N

C. Determination of sodium carbonate and sodium hydroxide from their mixture of the solution:

Solution taken in the burette : HCl solution

Solution taken in the conical flask : 25 cc of mixture of NaOH and Na_2CO_3 solution

Indicator used : Phenolphthalein for first stage & methyl orange for second stage

Colour change at the end point : For first stage Pink to colourless for second stageyellow to red

Tabulations **I stage (with Phenolphthalein)** $NaOH + HCl \longrightarrow NaCl + H_2O$

$Na_2CO_3 + HCl \longrightarrow NaCl + NaH\,CO_3$

Trial No	Burette readings (cc)		Volume of HCl added (B – A) (cc)	Concordant burette reading in cc (CBR)
	Initial reading (A)	Final reading (B)		
1	0.0			CBR = V_1 cc
2	0.0			
3	0.0			

II stage (with Methyl red) $NaHCO_3 + HCl \longrightarrow NaCl + H_2O + CO_2\uparrow$

Trial No	Burette readings (cc)		Volume of HCl added (B – A) (cc)	Concordant burette reading in cc (CBR)
	Initial reading (A)	Final reading (B)		
1	Final Level of I stage			CBR = V_2 cc
2	,,			
3	,,			

Concordant burette reading for V_1 =.....cc & for V_2 =..... cc

Calculations :

Determination of amount of Na_2CO_3

V_1: Volume of HCl used for complete neutralization of NaOH and half neutralization of Na_2CO_3(conversion of Na_2CO_3 to $NaHCO_3$)

V_2 : Volume of HCl used for half neutralization of Na_2CO_3

∴ Volume of HCl required for half neutralization of Na_2CO_3 = $V_2 - V_1$ = ….c.c.

∴ Volume of HCl required for complete neutralization of Na_2CO_3 $2(V_2 - V_1)$ = ..c.c.

N = [illegible] = N [illegible] = [illegible] $\times$ [illegible] = [illegible] $\times 2(V_2 - V_1)$ [illegible] = .. [illegible]

∴ Grams per litre of sodium carbonate = $N_{Na_2CO_3}$ $\times$ [illegible] = [illegible] $\times$ [illegible] = [illegible]

∴ Amount of Na_2CO_3 present in the given 250 cc solution = [illegible] = .. [illegible] **= a**

Determination of amount of NaOH

∴ Volume of HCl required for complete neutralization of NaOH = total volume of HCl – volume of HCl required for neutralization of Na_2CO_3 = $V_2 - 2(V_2 - V_1)$ =…cc

Equation used N [illegible] = [illegible]

N [illegible] = [illegible] $\times$ [illegible] = [illegible] $\times V_2 - 2(V_2 - V_1)$ [illegible] **=..N**

∴ Grams per litre of NaOH= N [illegible] × equivalent mass of NaOH = [illegible] × [illegible] = [illegible]

∴ Amount of NaOH present in the given 250 cc solution = [illegible] =.. g = b

Percentage of Na_2CO_3 = [illegible] × 100 = [illegible] %

Percentage of NaOH = [illegible] × 100 = [illegible] %

Result:

1.	Normality of sodium carbonate solution	............N
2.	Normality of hydrochloric acid solution	............N
3.	Amount of NaOH present in 250 cc of the mixture	............g
4.	Amount of Na_2CO_3 present in 250 cc of the mixture	............g
5.	Percentage (%) of NaOH in the mixture	………..%
6.	Percentage (%) of Na_2CO_3 in the mixture	………..%

Note: NaOH & Na_2CO_3 solutions are prepared separately and added separately using two burettes in to the same volumetric flask to distribute to students.

Experiment no. 02

Determination of Total Alkalinity in Antacid

AIM: To determine the amount of acid neutralized by an antacid tablet using back titration

APPARATUS: Burette, 25 ml pipette, conical flask, beakers and funnel etc.

CHEMICALS REQUIRED: Standard (0.05 M) Na_2CO_3 solution, HCl solution, NaOH solution, Antacid, Methyl Orange and Phenolphthalein

PRINCIPLE:

Antacids are medicines that counteract (neutralize) the acid in your stomach to relieve indigestion and heartburn. Antacids are bases that react stoichiometrically with acid. The number of moles of acid that can be neutralized by a single tablet of a commercial antacid will be determined by back titration. An antacid tablet is dissolved in a known excess amount of acid. The resulting solution will be acidic because the tablet did not provide enough moles of base to completely neutralize the acid. The solution will be titrated with base of known concentration to determine the amount of acid not neutralized by the tablet. To find the number of moles of acid neutralized by the tablet, the number of molesof acid neutralized in the titration is subtracted from the moles of acid in the initial solution.

PROCEDURE:

1.<u>Preparation of Antacid Solution:</u>

Antacid tablet or 5 ml of antacid suspension is taken in to a 100 ml. standard flask and make it up to the mark with distilled water.

2. Preparation of standard (0.05 M) Na_2CO_3 solution :

Weigh accurately 1.325 g of crystalline Na_2CO_3 in a clean and dry watch glass and transfer it carefully into a beaker. Dissolve the crystals using distilled water. Transfer the dissolved Na_2CO_3 solution into 250 mL volumetric flask and dilute it up to the mark with distilled water. Shake well for uniform concentration.

3. <u>Standardization of HCl:</u>

- Rinse and Fill the burette with given HCl solution and adjust the solution level to zero mark.
- Pipette out 25 mL of Na_2CO_3 solution into a 250 mL conical flask and add 1-2 drops of methyl orange indicator.
- Titrate until the colour changes from yellow to faint pink or red
- Repeat the titration until concordant values are obtained.
- Calculate the normality of the HCl using the normality of standard sodium carbonate

4. <u>Standardization of NaOH solution (Blank titration):</u>

- Pipette out exactly 25 mL of given NaOH solution into a conical flask and add 2-3 drops of phenolphthalein indicator.
- Titrate NaOH solution with standardized HCl taken in the burette until the pink colour disappears.
- Repeat the titration to get concordant readings.

5. Determination of Alkali content in Antacid (Main Titration):

The burette is filled with standard NaOH solution and the initial reading is noted. 25 ml of antacid solution is pipette out into a conical flask and 25 ml of standard HCl is added. The conical flaskis covered and heated to 70^{o} C on a hot water bath for about 10 minutes and cool. Then the cooled solution (containing unreacted or excess HCl) is back titrated with standard NaOH solution using phenolphthalein as an indicator. At the end point the color of the solution is turned to light pink color. The final reading is noted and repeats the titration for concordant values. From the burette value the amount of alkali present in the given 100 ml ofantacid can be determined.

OBSERVATIONS AND CALACULATION:

2. Preparation of 250 cc of standard (M/20) sodium carbonate solution

Equivalent mass of crystalline Na_2CO_3 is 53

The amount of Na_2CO_3 crystals required to prepare M/20 solution is given by,

$$W = \frac{M \times E \times V}{1000} = \frac{0.05 \times 106 \times 250}{1000} = 1.325 \text{ g}$$

Mass of empty watch glass :W_1 =…….g

Mass of watch glass + Na_2CO_3 : W_2 = ……g

Mass of Na_2CO_3 : W= (W_2 - W_1) = ……..g

Note: If the value of mass of sodium carbonate weighed differs from 0.6625 g then, normality of sodium carbonate solution is calculated by

Molarity of Na_2CO_3 = $\frac{W \times 1000}{M\ W \times V}$

$= \frac{(W_2 - W_1) \times 1000}{106 \times 250}$

= …… M

3. Standardization of HCl solution

Solution taken in burette : M/20 HCl solution

Solution taken in conical flask : 25 mL of Na_2CO_3 solution

Indicator : Methyl orange

Colour change : Yellow to faint pink or red

Reaction: $Na_2CO_3 + 2HCl \longrightarrow 2NaCl + CO + H_2O$

Tabular Column

Burette Readings (mL)		I	II	Concordant Burette Reading (CBR)
Final B.R.				
Initial B.R.				
Difference				

Calculation

Equation used,

$$M_{(HCl)} \times V_{(HCl)} = M_{(Na2CO3)} \times V_{(Na2CO3)}$$

Where,

$M_{(HCl)}$ = Molarity of HCl, $V_{(HCl)}$ = Volume of HCl (CBR)

$M_{(Na2CO3)}$ = Molarity of Na_2CO_3, $V_{(Na2CO3)}$ = Volume of Na_2CO_3 (25 mL)

$$M_{HCl} = \frac{M(Na2CO3) \times V(Na2CO3)}{V(HCl)}$$

$$= \cdots \ldots \ldots M$$

4. Determination of NaOH solution (Back Titration):

Solution taken in burette : Standardized NaOH solution

Solution taken in titration flask : 25 mL of given HCl solution

Indicator : Phenolphthalein

Color change : Pale Pink to Colorless

Reaction: $NaOH + HCl \longrightarrow NaCl + H_2O$

Tabular Column

Burette Readings (mL)		I	II	Concordant Burette Reading (CBR_1)
Final B.R.				
Initial B.R.				
Difference				

Volume of NaOH consumed for 25 ml HCl solution = CBR_1 = V1 = ……ml

5. Determination of Alkali in Antacid solution (Main Titration):

Solution taken in burette : Standardized NaOH solution

Solution taken in titration flask : 25 mL of antacid solution + 25 ml of HCl solution

Indicator : Phenolphthalein

Color change : Pale Pink to Colorless

Reaction: $NaOH + HCl \longrightarrow NaCl + H_2O$

Tabular Column

Burette Readings (mL)		I	II	Concordant Burette Reading (CBR_2)
Final B.R.				
Initial B.R.				
Difference				

Volume of NaOH required for unreacted HCl in the Antacid solution = CBR_2=

V_2= …….ml

Volume of HCl required for complete neutralization of alkali present in antacid

= $(V_1 – V_2)$ = (Blank Titre Value - Main Titre Value)

= ……...mL

Calculation

Equation used, $M_{Antacid} \times V_{Antacid} = M_{(HCl)} \times V_{HCl}$

Molarity of antacid solution ($M_{Antacid}$) = $\frac{N\,(HCl) \times (V_1 - V_2)\,HCl}{25}$

= …….. M

The amount of alkali OH present in antacid = $M_{antacid}$ x Mol Wt of –OH group

= $M_{antacid}$ x 17

= …….. g / 1000ml

The amount of alkali OH present in 100 ml antacid solution = $\frac{\text{M antacid x 17}}{10}$

= …….. g / 100ml

RESULTS:

normality of given HCl solution .....N

the amount of alkali OH present in 100 ml antacid solution

.....g

Experiment 5

Estimation of oxalic acid and sodium oxalate in a given mixture.

Theory:

Molecular Equations

$$2\,KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]$$

$$\begin{matrix}COOH\\|\\COOH\end{matrix} . 2H_2O + [O] \longrightarrow 2CO_2 + 3H_2O$$

$$\begin{matrix}COONa\\|\\COONa\end{matrix} + H_2SO_4 + [O] \longrightarrow 2CO_2 + H_2O + Na_2SO_4$$

Ionic Equations

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O\ ] \times 2$$

$$C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-\ ] \times 5$$

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

Both oxalic acid and sodium oxalate can be titrated against N/20 $KMnO_4$ since both of them are reducing agents.

So normality (N/2) of the solution will be due to both of them. From the combined normality(N/2), the composition of each can be calculated.

Indicator

$KMnO_4$ is a self-indicator.

End Point

Colourless to permanent pink ($KMnO_4$ in burette).

Procedure

Rinse and fill the burette with the N/20 $KMnO_4$, solution.

Weigh exactly 1.0 g of the given mixture of oxalic acid and sodium oxalate and dissolve in water to prepare exactly 250 ml of solution using a 250 ml measuring flask. Rinse the pipette with the prepared oxalate solution and pipette out 20.0 ml of it in a washed titration flask.

Add one test-tube (~ 20 ml) full of dilute sulphuric acid (~ 4 N) to the solution in titration flask.Note the initial reading of the burette.

Heat the solution of titration flask to 60-70°C and run down KMnO4 solution from the burettetill a permanent

light pink colour is just imparted to the solution in the titration flask.

Note the final reading of the burette.

Repeat the above steps 4−5 times to get three concordant readings.

Observations

Normality of KMnO4 solution = 1/20
Volume of oxalate solution taken for each titration = 20.0 ml.

x ml of N/20 KMnO4 solution are equivalent to 20 ml of the given oxalate solution.

S. No.	Initial reading of the burette	Final reading of the burette	Volume of the $KMnO_4$ solution used
1.	—	—	— ml
2.	—	—	— ml
3.	—	—	— ml
4.	—	—	— ml

Concordant volume = x ml (say).

Calculations

$$\underset{KMnO_4}{N_1V_1} = \underset{\text{oxalate soln.}}{N_2V_2}$$

$$\frac{1}{20} \times x = N_2 \times 20$$

$\therefore$ Normality of oxalate solution, $N_2 = \frac{x}{400}$

$\frac{x}{400}$ is the total normality due to oxalic acid and sodium oxalate.

Suppose, strength of oxalic acid = a g/litre

$\therefore$ Strength of sodium oxalate = $(4 - a)$ g/litre

Normality due to oxalic acid, $N_{\text{oxalic acid}} = \frac{a}{\text{Eq. mass of oxalic acid}} = \frac{a}{63}$

Normality due to sod. oxalate, $N_{\text{sod. oxalate}} = \frac{4-a}{\text{Eq. mass of sod. oxalate}} = \frac{4-a}{67}$

$\therefore$ Total normality of the oxalate solution = $N_{\text{oxalic acid}} + N_{\text{sod. oxalate}}$

$$\frac{x}{400} = \frac{a}{63} + \frac{4-a}{67}$$

From this equation, 'a' can be calculated. Knowing 'a', the percentage composition of the mixture can be calculated.

% of oxalic acid $= \frac{a}{4} \times 100 = X$ (say)

% of sod. oxalate $= \frac{4-a}{4} \times 100 = Y$ (say).

Instructions for the Preparation of Solutions
Provide the following solutions :
1. $KMnO_4$ solution (1.58 g/litre)
2. A mixture of oxalic acid and sodium oxalate
3. 4N H_2SO_4.

Gravimetry

01 . Determination of Barium as BaSO4

Aim: To determine the amount of Barium as $BaSO_4$ present in a given solution.

Apparatus: Watch glass, Beaker, Funnel, silica crucible, desiccators etc.

Chemical: $BaCl_2$ solution, Conc. HCl, 5% H_2SO_4 Solution etc.

Outline: Barium from the solution is precipitated as barium sulphate by the addition of H_2SO_4 to the acidified hot solution. The precipitate is digested, filtered washed with water till it is free from sulphate and chloride ions. It is then dried, ignited and weighed as $BaSO_4$.

Procedure:

1. Dilute the given barium chloride solution up to the mark with distilled water in 250 cc volumetric flask.
2. Shake it well and pipette out 25 cc in to a clean 250 cc beaker with the help of a pipette.
3. Introduce a glass rod in to the beaker at this stage and it should not be taken out till the precipitate is completely transferred to filter paper.
4. Dilute it to about 100 cc with distilled water (Add about 75 cc distilled water) and 1-2cc conc. HCl. Heat the solution to boiling.
5. Heat about 20 cc of 5% solution of H_2SO_4 in a small beaker and add it to hot barium solution drop wise with constant stirring till the precipitation of **$BaSO_4$** is complete.
6. Cover the beaker partially with a watch glass and digest the precipitate on a sand bath for about 45 minutes for **Digestion** of the precipitate (i.e. heating the solution just short of boiling without actually boiling which granulates the precipitate).
7. Allow the precipitate to settle. Test the supernatant solution by adding a few drops of 5% sulphuric acid solution for complete precipitation.
8. Clean the crucible by heating the crucible with 1 cc conc.HNO_3 by placing on wire gauze and cool, wash with water, wipe out with clean cloth. Heat it by placing on pipe-clay triangle supported by tripod stand for 10 minutes with non-luminous (Blue)flame. Cool on tripod stand for 10 minutes and transfer it with a clean pair of tongs to desiccator. After thorough cooling weigh the crucible and note down the weight(W_1).
9. Take Whatman's filter paper no. 41 circle and fold it along a diameter to form a semicircle. Fold again symmetrically so as to form four folds. Open one fold on side & three on the other side to form a cone. Attach filter paper cone properly to the funnel in such a way that it touches the funnel only along its edges leaving the filter paper cone hanging & moisten it with few drops of distilled water.

10. Decant the supernatant solution carefully through Whatman's filter paper no. 41 without disturbing the precipitate.
11. Wash the precipitate with hot distilled water (100-120 ml) for several times in the beaker itself and then transfer it quantitatively to the filter paper, using the policeman to detach the particles from the sides of the beaker.
12. Wash the precipitate again with hot water till the filtrate is free from sulphate and chloride ions (test the filtrate with dil. $BaCl_2$ & $AgNO_3$ solutions which should not give white ppt. with both).
13. Drain the filter paper thoroughly. Dry the precipitate partially on a hot air cone and incinerate it along with the filter paper in a previously weighed crucible.
14. First heat slowly till the precipitate dries and filter paper gets charred then strongly till the residue becomes white. Then heat strongly either in a burner or electrical Incinerator or Muffle furnace. If the crucible is blackened due to preliminary heating, by turning the crucible repeatedly and carefully ignited by the flame until all the carbon has been burned off: the crucible becomes white as before. The white residue is $BaSO_4$.
15. Heat the crucible for another 10 minutes, cool, desiccate and weigh. Note down the weight of the residue. Again heat it for 10 minutes, cool, desiccate and weigh it again and note down the weight of the residue. (Heating, cooling and desiccating and weighing the crucible is repeated till a constant weight is obtained.)
16. From the weight of $BaSO_4$ obtained calculate the amount of barium present in the given solution.

Equatns :

$$\mathbf{BaCl_2 + H_2SO_4 \longrightarrow \underset{\text{barium sulphate}}{BaSO_4\downarrow} + 2HCl}$$

1 gram mole of $BaSO_4$ ≡ 1 gram mole of Ba

233.42 g $BaSO_4$ ≡ 137 gram mole of Ba

1 g. $BaSO_4$ ≡ 0.5887 g Ba

Observations: 1. Weight of the empty crucible = W_1 = ---- g
2. Weight of the crucible + residue = W_2 = ---- g
3. Weight of the residue ($BaSO_4$) = W_2 - W_1 = ---- g

Calculations

1. Weight of the residue ($BaSO_4$) = W_2 - W_1 = ----- g
2. Amount of Barium present in 25cc of the given solution = X = (W_2 - W_1) × 0.5887=… g
3. Amount of Barium present in 250 cc of the given solution = X × 10 = ..'a' ..g
4. Amount of Barium present in 1dm^3 of the given solution =X × 40 = **…**g Or 'a'× 4 = **...** g

Result:

1. Weight of the residue ($BaSO_4$)____g
2. Amount of Barium present in 25 cc of the given solution=
3 .Amount of Barium present in 250 cc of the given solution____g
3. Amount of Barium present in 1dm^3 of the given solution

EXPERIMENT 2

AIM : - Find out gravimetrically the percentage of Cu in given solution of$CuSo_4.5H_2O$, 20g of which has been dissolved per litre.

APPARALUS REQUIRED:-

Beaker, watch glass, pipette, glassrod.

CHEMICAL REQUIRED:-

1. Ammonium thiocyanate solution.
2. Saturated solution of NH_4HSO_3.
3. Solution of $CuSO_4.5H_2O$.

REACTIONS:-

$2CuSO_4 + H_2O + NH_4HSO_3 \rightarrow Cu_2SO_4 + NH_4HSO_3 + H_2SO_4$

$Cu_2SO_4 + 2NH_4SCN \rightarrow 2CuSCN + (NH_4)_2SO_4$

OBJECTIVE:-

In this experiment firstly, cupric salt is reduced to cuprous salt either by using sulphurous acid or ammonium bisulphate solution. Then cuprous ions are precipitated by ammonium thiocyanate (NH_4SCN). After then precipitates formed are filtered, washed dried and weighed using sintered glass crucible. From the weight of precipitates formed percentage of copper is determined.

PROCEDURE:-

1. Take 20 ml of given solution of copper sulphate in a clean 400 ml beaker.
2. Add few drops of HCl, followed by addition of 25 ml of 10% NH_4HSO_3Solution.
3. Dilute the above solution by adding 150 ml of distilled water. Boil thesolution.
4. Now put the beaker on an asbestos sheet, and then add drop wise 10% ammonium thiocyanate solution with constant stirring till the supernatantsolution becomes colourless. (To check for complete precipitation add few drops more of ammonium thiocyanate).
5. Cover the beaker and allow the contents to stand for 2-3 hours preferablyovernigh

6. Filter the precipitates using G-4 crucible, wash the precipitates using 1%cold dilute solution of NH_4HSO_3 till the filterate is free from SCN^- ions.
7. Finally wash the precipitates with 20% alcohol to remove NH_4SCN.
8. Heat the crucible in oven at 110^0 - 120^0C to constant weight.

OBSERVATIONS:-

Volume of given solution = 20ml

Strength of given Copper sulphate solution=20 g/litre

Weight of sintered glass crucible Before experiment i.e., empty=W_1gWeight of sintered glass crucible

and $Cu_2(SCN)_2$ = W_2g

Weight of $Cu_2(SCN)_2$ formed = $w_{2-W}1$ =Wg

CALCULATIONS:-

I. From 20 ml of given solution weight $Cu_2(SCN)_2$ formed = Wg

From 1 ml of given solution weight = $\frac{W}{20}$

From 1000 ml given solution weight = $\frac{W}{20} \times 1000 = 50$ Wgm

II. $Cu_2(SCN)_2 = 2$ cu

243 gm $Cu_2(SCN)_2$ is formed from copper =127 gm

1 gm $Cu_2(SCN)_2$ is formed from copper = $\frac{127}{243}$

50w gm of $Cu_2(SCN)_2$ is formed from copper =

$\frac{127}{243} \times 50\, w = a\ gm$ $\quad litre\ (say)$

III. In 20.0n gms of copper sulphate, actual amount of Cu present = a gmsIn 1 gms of copper sulphate,

Actual amount of Cu present = $\frac{a}{20}$

In 100 gms of copper sulphate,

Actual amount of Cu present + $\frac{a}{20} \times 100 + 5a$

RESULT:-

Percentage of Cu = 5a

PRECAUTIONS:-

1. Precipitate i.e. NH_4SCN should not added in excess to avoid solubility of $Cu_2(SCN_2$ as complex ion
2. Washing of the precipitates is to be done with dilute solution of NH_4HSO_3 to avoid oxidation of Cu(I) to Cu (II)

Part-B

Physical chemistry experiments

Experiment no. 01

Determination of surface tension and parachor of alcohol series.

Aim: To Determine the Surface Tension and Parachor of toluene, xylene and n-hexane.
Calculate the atomic Parachor of Carbon and Hydrogen.

Chemicals: Liquids: Toluene, Xylene and n-hexane.

Apparatus: Trauts Stalagmometer with pinchcock, beaker, etc.,

Theory: Surface tension is one of the physical properties of the liquid. It is defined as the force in dynes acting on a surface at right angles to any line of unit length. This can be determined by drop number method using Stalagmometer. The surface tension can be calculated according to the following expression:

$$\gamma_L = \frac{n_W}{d_L n_L} \times \gamma_W \times d_W$$

Where γ_W = surface tension of water (72 dyne/cm)
γ_L = surface tension of liquid
n_W = no. drops of water, n_L = no.of drops for liquid, d_W = density of water, d_L = density of liquid.

The magnitude of surface tension is used to calculate the parachor of liquid series, which are additive and constitutive properties. The parachor is calculated using the following equation.

$$P = \frac{M}{\gamma^{1/4}\, d}$$

Where, P = parachor, d = density
γ = surface tension of liquid & M= Mol.Wt. of liquid

When the parachor are calculated for the liquids of given homologous series, parachor values ofdifference in the atoms / group can be calculated.

Procedure:

1. Clean the Stalagmometer by ether / acetone. Dry it thoroughly by blowing hot air from rubber air blower and attach a clean and dry rubber with a screw clip in the middle to the upper end of Stalagmometer.
2. Clamp the apparatus exactly in a vertical position, lower end should be slightly inside the edge of the beaker to avoid disturbance while falling the drops by air.
3. Loosen the screw clip and suck the liquid taken in a small beaker, so that it is well above the upper round mark (care must taken to see the liquid does not enter the rubber tube). Close the tubes with the screw clips.
4. Adjust the flow of liquid using the screw clip, so that the number of drops falling from the flat end is between 20-25 drops per minute. Do not disturb this adjustment.
5. Suck the liquid again little above the upper mark and count the number of drops when the liquid flows from the upper round mark to the lower mark.
6. Repeat the same procedure for at least three times and calculate the average number of drops for the liquid.
7. Rinse the stalagmometer with ether / acetone and blow the air to dry before using for new liquid.
8. Take similar readings for other liquids under study and finally for distilled water.
9. Calculate the surface tension and parachor of each liquid by using the suitable formula and finally the parachor of CH_2 from the difference in the parachor of toluene and xylene.
10. From this, calculate the atomic parachor of 'H' and 'C'.

Observations:

Liquids	No. of drops of liquids	Mean(n)	Density g/cc	Surface tension (dyne/cm)	Molar. mass	Parachor (P)
Toluene	i ii iii		0.8660		92	P_T=
Xylene	i ii iii		0.8811		106	P_X=
Hexane	i ii iii		0.6548		86	P_{Hx} =

Water	i ii iii		1.0		18	

Calculation :

1) Surface tension of liquid : $\gamma_L = \frac{n_w \text{ x}}{d_L n_L \text{ x } d_w} \text{ x } \gamma_w$

1) Calculation of parachor:

$$P = \frac{M\,\gamma^{1/4}}{d}$$

2) achor of CH_2 group = $P_X - P_T = P(CH_2)$ =--------

3. Calculation of atomic parachor of hydrogen:

$P(C_6H_{14}) = 6\,P(CH_2) + 2P(H)$

$2P(H) = P(C_6H_{14}) - 6P(CH_2)$

$P(H) = \{ P(C_6H_{14}) - 6P(CH_2)\} / 2$ =--------

4. Calculation of atomic parachor of carbon:

$P(C) = P(CH_2) - 2 \times P(H)$ = ------

Results:

Surface Tension of (dyne/cm)	Toluene	Xylene	Hexane
Parachor of carbon		Parachor of hydrogen	

Theoretical Values

Surface Tension of (dyne/cm)	Toluene	Xylene	Hexane
Parachor of carbon	4.8	Parachor of hydrogen	17.1

Experiment no. 02

Determination of surface tension of soap solutions

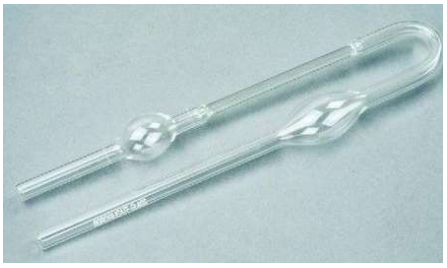
2. Determination of surface tension of soap solutions for various concentrations.

Aim: To determine the Surface tension of soap solutions for various concentrations by drop number method and calculate the Parachor of these liquid series.

Chemicals: Liquids- soap solutions for various concentrations i.e., 10% (A), 20% (B) & 30%(C)

Apparatus: Trauts Stalagmometer with pinchcock, beaker, etc.,

Theory: Surface tension is one of the physical properties of the liquid. It is defined as the force in dynesacting on a surface at right angles to any line of unit length. This can be determined by drop number method using Stalagmometer. The surface tension can be calculated according to the following expression.



Trauts Stalagmometer

$$\text{Surface tension of liquid} = (\gamma_l) = \frac{d_l \times n_w \times \gamma_w}{d_w \times n_l}$$

Where, Y_L &, Y_w are surface tension of liquid and water respectively

d_L & d_w are density of liquid & water respectively

n_L – number of drops of liquid

n_w – Number of drops of water

Procedure:

1. Determine the density of liquids A,B & C using Specific Gravity bottle
2. Clean the Stalagmometer by ether / acetone. Dry it thoroughly by blowing hot air from rubber airblower and attach a clean and dry rubber with a screw clip in the middle to the upper end of Stalagmometer.
3. Clamp the apparatus exactly in a vertical position, lower end should be slightly inside the edge ofthe beaker to avoid disturbance while falling the drops by air.
4. Loosen the screw clip and suck the liquid taken in a small beaker, so that it is well above the upper round mark (care must taken to see the liquid does not enter the rubber tube). Close the tubes with the screw clips.

5. Adjust the flow of liquid using the screw clip, so that the number of drops falling from the flat endis between 20-25 drops per minute. Do not disturb this adjustment.
6. Suck the liquid again little above the upper mark and count the number of drops when the liquid flows from the upper round mark to the lower mark.
7. Repeat the same procedure for at least three times and calculate the average number of drops for theliquid.
8. Rinse the stalagmometer with ether / acetone and blow the air to dry before using for new liquid.
9. Take similar readings for other liquids under study and finally for distilled water.
10. Calculate the surface tension

Observation and Calculation:

Calculation of density of liquids

1. Weight of empty specific gravity bottle $=W_1 =$_____ g
2. Weight of specific gravity bottle+ 5 mL liquid A $= W_2 =$ _____g
3. Weight of specific gravity bottle+ 5 mL liquid B $= W_3 =$ _____g
4. Weight of specific gravity bottle+ 5 mL liquid C $= W_4 =$ _____g
5. Weight of liquid A $=W_5 =$ _____g
6. Weight of liquid B $=W_6 =$ _____g
7. Weight of liquid C $=W_7 =$ _____g
8. Density of Liquid A = Weight of liquid A/ Volume(5 mL)

   =_____g/cc
9. Density of Liquid B = Weight of liquid B/ Volume (5 mL)

   = _____g/cc
10. Density of Liquid A = Weight of liquid A/ Volume(5 mL)

    = _____g/cc

Tabulation

Liquids	No. of drops of liquids	Mean(n)	Density g/cc	Surface tension(dyne/cm)
10% liquid (A)	a b c			

20% liquid (B)	a b c			
30% liquid (C)	a b c			
Water	a b c		1.00	72.00

Calculation:

Calculation of surface tension,

Formula used,

$$\text{Surface tension of liquid : } \gamma_L = \frac{n_w \times d_L}{n_L \times d_w} \times \gamma_w$$

LiquidA:

$$\text{Surface tension of liquid} = (\gamma_l) = \frac{d_l \times n_w \times \gamma_w}{d_w \times n_l}$$

Liquid = _____ dynes cm^{-1}. B:

$$\text{Surface tension of liquid} = (\gamma_l) = \frac{d_l \times n_w \times \gamma_w}{d_w \times n_l}$$

Liquid C:

= _____ dynes cm^{-1}.

$$\text{Surface tension of liquid} = (\gamma_l) = \frac{d_l \times n_w \times \gamma_w}{d_w \times n_l}$$

= _____ dynes cm^{-1}.

= _____ $\times 10^{-3}$ N m^{-1}.

Results:

Surface Tension of	liquid A - (10% soap solution)	liquid B – (20% soap solution)	Liquid C – (30% soap solution)
In SI unit dyne/cm			
In CGS unit N/m			

Experiment no. 03

Determination of the viscosity of liquids

Aim: To determine the coefficient of viscosity of liquids (ethylacetate& ethyl alcohol /toluene, & chlorobenzene or any other two non hazardous liquids) using Ostwald's Viscometer

Chemicals required: Ethyl acetate and ethyl alcohol

Apparatus: Ostwald's Viscometer, beaker, specific gravity bottle, weight box, etc.,

Theory: Viscosity is a resistance exerted by a liquid against the displacement of its own molecules. It is expressed in terms of coefficient of viscosity (η). It is defined as the force acting on unit area to maintain unit difference of velocity between two parallel layers of liquid 1 cm apart. It can be calculated using Poiseuille's equation when η of other liquid is known.

$$\eta_L = \frac{\eta_w \, x \, t_L d_L}{t_w \, d_w}$$

Where, t_L is time of flow of liquid,t_w is time of flow of water

d_L is density of liquid, d_w is density of water

Experimentally, this can be determined with the help of Ostwald's viscometer by taking water as a reference liquid having 'ηw' , the viscosity coefficient 0.0089 poise.

Procedure:

- Clean the Viscometer with acetone or ether and dry it thoroughly by blowing hot air from rubber air blower.
- Clamp the Viscometer in a perfectly vertical position.
- Attach a clean piece of rubber tube to the narrow arm of the viscometer.
- Take 10 mL of ethylacetate with the help of a pipette into the wider arm of viscometer.
- Suck the liquid by a rubber tube into the capillary side bulb up to a little above the upper mark. Allow the liquid to flow down through the capillary and at the same time record carefully the time required for the liquid to flow from upper mark to the lower mark on the capillary arm using stopwatch. Take at least three readings with each liquid and find the mean time in second (t_L).
- Rinse the Viscometer with ether / acetone and blow the air to dry before using for new liquid.
- Repeat the same procedure for ethyl alcohol and lastly find the time of flow for water (tw).
- Determine the density of ethylacetate and ethyl alcohol using a specific gravity bottle.
- Calculate the viscosity coefficient of each liquid using the suitable formula.

Record of Observations

1) Determination of Densities:

1. Weight of empty specific gravity bottle = W_1 = ----g
2. Weight of specific gravity bottle + ethyl acetate = W_2 = ------g
3. Weight of specific gravity bottle + ethyl alcohol = W_3 = ----g
4. Weight of specific gravity bottle + water = W_4 = -----g
5. Weight of ethyl acetate = $W_2 - W_1$ = -----g
6. Weight of ethyl alcohol = $W_3 - W_1$ = -----g
7. Weight of water = $W_4 - W1$ = -----g

$$\text{Density of ethyl acetate} = \frac{\text{Weight of ethyl acetate}}{\text{Volume of water}} = \frac{W_2 - W1}{W_4 - W_1} = \text{.....g/mL}$$

$$\text{Density of ethyl alcohol} = \frac{\text{Weight of ethyl alcohol}}{\text{Volume of water}} = \frac{W_3 - W1}{W_4 - W_1} = \text{.....g/mL}$$

2) Determination of coefficient of viscosity (η):

Liquids	Density (d) g/cc	Time of flow in second (t)	Mean(t)	Coefficient of viscosity in **poise** $\eta_L = \frac{\eta_w x\ t_L d_L}{t_w d_w}$
Ethyl acetate		i ii iii		
Ethyl alcohol		i ii iii		
Water		i ii iii		**η w** = 0.0089

Calculation:

Formula Used,

Result:

1.	Coefficient of viscosity of ethyl acetate	……..poise
2.	Coefficient of viscosity of ethyl alcohol	……..poise

Experiment no. 05

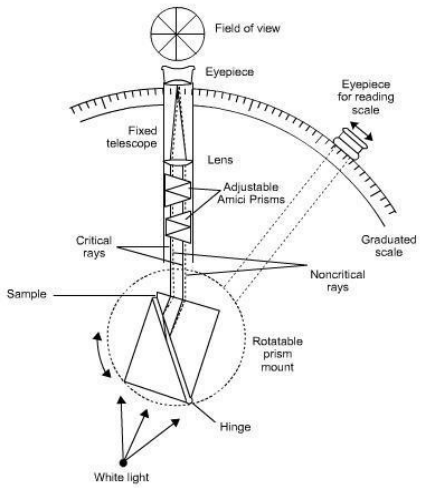
Determination of Specific Refraction and Molar Refraction

Aim: To find Refractive Index, Molar Refraction and Specific Refraction of the given liquid samples (ethyl acetate, methyl acetate and ethylene chloride) using Abbes refractrometer

Materials Required: Abbe's refractometer, temperature controller, lightsource and samples.
Chemicals Required: Ethyl acetate, Methyl acetate and Ethylene chloride

Theory:
Abbe's Refractometer:

The principle of an Abbe refractometer is based on the principle of total reflection. The Abbe instrument is the most convenient and widely used refractometer, Fig(1)shows a schematicdiagram of its opticalsystem. The sample iscontained as a thinlayer (~0.1mm)between two prisms. The upper prism is firmly mounted on a bearing that allows its rotation by means ofthe side arm shown indotted lines. Thelower prism is hingedt o the upper to permit separation for cleaning and for introduction of the sample. The lower prism face is rough-ground: when light is reflected into the prism, this surface effectively becomes the source for an infinite number of rays that pass through the sample at all angels. The radiation is refracted at the interface of the sample and the smooth-ground face of the upper prism. After this it passes into the fixed telescope. Two Amici prisms that can be rotated with respect to another serve to collect the divergent critical angle rays of different colors into a single white beam, that corresponds in path to that of the sodium D ray. The eyepiece of the telescope is provided with crosshairs: in making a measurement, the prism angle is changed until the light-dark interface just coincides with the cross hairs. The position of the prism is then established from the fixed scale (which is normally graduates in units of n_D). Thermosetting is accomplished by circulation of water through the jackets surrounding the prism.



The refractive index of a substance is ordinarily determined by measuring the change in direction of colliminated radiation as it passesfrom one medium to another.

$$\frac{n_2}{n_1} = \frac{v_1}{v_2} = \frac{\sin\theta_1}{\sin\theta_2} \qquad (1)$$

Where v_1 is the velocity of propagation in the less dense medium M_1 and v_2 is the velocity in medium M_2; n_1 and n_2 are the corresponding refractive indices and θ_1 and θ_2 are the angles of incidence and refraction, respectively Fig 2.

When M_1 is a vacuum, n_1 is unity because v_1 becomes equal to c inequation (1). Thus,

$$n_2 = n_{vac} = \frac{c}{v_2} = \frac{\sin \theta_1}{\sin \theta_2} \qquad (2)$$

Where n_{vac} is the absolute refractive index of M_2. Thus n_{vac} can be obtained by measuring the two angles θ_1 and θ_2Abbe's refractometeris used to measure the refractive index of the given organic liquid. Using a particular monochromatic light source, the apparatus is calibrated with water as the liquid. Adjust the micrometer screw to focus the boundary between the bright and dark regions. Adjust the refractometer scale to place the cross wire of the telescope exactly on the boundary between the bright and dark regions. Repeat the same process for different organic liquids after the equipment is calibrated.

Procedure:

1. Clean the surface of prism first with alcohol and then withacetone using cotton and allow it to dry.
2. Using a dropper put 2-3 drops of given liquid b/w prisms andpress them together
3. Allow the light to fall on mirror.
4. Adjust the mirror to reflect maximum light into the prism box
5. Rotate the prism box by moving lever until the boundary b/wshaded and bright parts appear in the field of view.
6. If a band of colors appear in the light shade boundary make itsharp by rotating the compensator.
7. Adjust the lever so that light shade boundary passes exactlythrough the centre of cross wire
8. Read the refractive index directly on the scale
9. Take 3 set of readings and find the average of all the readings.
10. Now calculate the specific refraction and molar refraction using formulae.

Observation/Tabulation:

Room temp. =…….degrees

Sr.No.	Liquid	Refractive index	Specific refraction $R = (n^2 - 1)/(n^2 + 2) \times 1/d$	Molar refraction $R_m = R \times M$
1.	Ethyl acetate			
2.	Methyl acetate			
3.	Ethylene chloride			

Calculation:

Formula used,

Specific refraction, $R = (n^2 - 1)/(n^2 + 2) \times 1/d$

Molar refraction, $R_m = R \times M$ (molecular mass of liquid)

Result:

Sl.No	Liquid	Specific refraction	Molar refraction
1.	Ethyl acetate		
2.	Methyl acetate		
3.	Ethylene chloride		

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QULITATIVE ANALYSIS OF ORGANIC COMPOUNDS

Name:_____

RCU No:_____

Department:_____

Mobile No: _____

QUALITATIVE ANALYSIS OF ORGANIC COMPOUND-SOLIDS

I. Preliminary Tests

S.N	TEST	OBSERVATION	INFERENCE
1.	**Appearance and Colour**	Colourless solid	Salicylic acid, Phthalic and, Anthranilic acid, Naphthalene, Acetanilide, Diphenyl, Benzamide, Benzophenone may be present.
		Coloured solids	
		Cream coloured solid Pink (or pale brown) Dark brown Pale yellow Turmeric or greenish yellow Black/dirty green shining crystals Cream coloured solid Pink (or pale brown)	Cinnamic acid *β*-Naphthol *α*-Naphthol *m*-dinitrobenzene *m*-nitroaniline or *p*-nitroaniline may be present *p*-toluidine may be present Cinnamic acid *β*-Naphthol
2.	**Odour**	Pleasant odour Moth ball smell Cinnamon like odour Phenolic odour Fishy odour Odour of bitter almonds No Characteristic odour	Diphenyl may be present Naphthalene Cinnamic acid Naphthols Amines (*p*-toluidine, *m*-nitro ar or *p*-nitroaniline)*m*-dinitrobenz Carboxylic acids (Except cinnamic acid)
3.	**<u>Beilstien's Test</u>** Heat a loop of copper wire till it does not impart green colour to the flame. Cool, and take substance on loop of copper wire and then heat it.	(a) Burns with sooty flame	Aromatic compounds present
		(b) Burns with non-sooty flame	Aliphatic compounds present
		(c) Green edged flame after the initial sooty flame has vanished	Halogenated compounds present ***Exception:*** Urea gives a green flame due to cyanide of copper formed and not due to halogen

Conclusion: The given compound_____(Aliphatic / Aromatic)

SOLUBILITY TEST (IDENTIFICATION OF NATURE OF THE COMPOUND)

II. Solubility Test		
Take a little compound in a test tube and test the solubility in the following solvents.		
a) Compound(0.5 g) + water (1ml) Shake well and test with litmus paper ***If insoluble*** **Compound** + water + heat Shake well and test with litmus paper	Soluble in cold water and solution is acidic to litmus. (blue to red) Sparingly soluble in cold but soluble in hot water and solution is acidic to litmus. (blue to red) Soluble and the solution is neutral to litmus.	Carboxylic acid (Anthranilic acid) may be present Carboxylic acids(Phthalic acid, Salicylic acid, Cinnamic acid etc.) may be present Acetanilide, Benzamide may be present
b) Compound (0.5 g) + $NaHCO_3$ (1 ml) and Shake well	Soluble with effervescence	Carboxylic acid is present
c) Compound (0.5 g) + NaOH (1ml) and shake well	*Dissolves in NaOH and $NaHCO_3$ and reprecipitated by adding conc. HCl Dissolves only in NaOH but not in $NaHCO_3$	Carboxylic acid is present Naphthols (phenol) present
d) Compound + 1:1 HCl and shake well	Soluble and reprecipitated by adding NaOH Soluble in water & dil HCl	Bases like amines, -p-toluidine) may be present Acidic (Anthranilic acid) or neutral(acetanilide)may be present
e) Compound + Conc. H_2SO_4	**Soluble** with colour (yellow) Soluble with red colour In soluble	Ketones may be present Cinnamic acid may be present Aromatic Hydrocarbons may be present

Note: If the given compound is soluble in H_2O & acidic to litmus, and it is soluble in $NaHCO_3$ & NaOH – Acidic

- If the given compound is soluble only in NaOH & insoluble in $NaHCO_3$ & reprecipitated by adding Con.HCl- Phenol
- If the given compound is soluble only in HCl & reprecipitated by adding NaOH & insoluble in NaOH & $NaHCO_3$ – Basic.
- If the given compound is soluble in H_2O & neutral to litmus, and it is insoluble in $NaHCO_3$, NaOH & HCl or soluble/ insoluble in all –Neutral(Aromatic Hydrocarbons, amides, Anilides etc.)
- *If substance gives test with both $NaHCO_3$ solution as well as NaOH, then report as Carboxylic acid. If fails to give test with $NaHCO_3$ solution but soluble only with NaOH, report it as* ***Phenol***

II. TEST FOR SATURATION AND UNSATURATION

i. Baeyer's reagent (Alkaline $KMnO_4$) 0.2 g comp. + 2cc Na_2CO_3 solution + 2-3 drops of very dilute $KMnO_4$ solution	Decolourisation of $KMnO_4$ No decolourisation of $KMnO_4$	*Unsaturated compoundsmay be present Saturated compounds may be present
ii. ii Bromine water or Bromine in Carbon tetra Chloride 0.2 g comp. + 2cc bromine water. (If compound is water insoluble perform the test with bromine in carbon tetra chloride).	Decolourisation of Br_2 No decolourisation of Br_2	Unsaturated compounds may be present Saturated compounds may be present

** Quickly oxidisable compounds like phenols, aromatic amines. Aldehydes & ketones change purple colour to brown or black at once.*

Conclusion: The given compound is_____(Saturated / Unsaturated)

III. DETERMINATION OF PHYSICAL CONSTANT:

Determine physical constant (melting point) M.P. using Thiele's Apparatus or Electric melting point instrument

The melting point of the given compound is_____ $^{\circ}C$ (Observed)

Literature value..... $^{\circ}C$

The melting point is represented in range by $\pm$ 0.2^0C. for example 156^0C - 158^0C or 157^0C - 159^0C

IV. DETECTION OF ELEMENTS:

Generally organic compounds contain Nitrogen(N), Halogen(X) and Sulphur(S) along with Carbon, Hydrogen and (Oxygen). For the detection of N, X, and S the **Lassaigne's** test is performed.

Preparation of Sodium fusion extract (S.E.)

Place a piece of dry sodium metal (*dried by pressing between folds of the filter paper*) in a fusion tube and heat till sodium melts to form shining globule. Add a pinch of an organic compound and heat slowly and then strongly until the tube becomes red hot. Plunge the tube at once in a china dish or 50 ccl beaker containing 5 cc. of distilled water. Boil the resulting contents to concentrate for about five minutes and filter the hot solution. The filtrate so obtained is called as ***Lassaigne's sodium fusion extract (S.E.).***

i. <u>Test for Nitrogen (N)</u> 1 ml of S.E. + 1ml of freshly prepared saturated $FeSO_4$ solution + 1or 2 drops NaOH, boil well, add 2 drops of $FeCl_3$, cool thoroughly and acidify with conc. HCl or dil. H_2SO_4.	Blue ppt or greenish blue coloured solution	Nitrogen present
ii. <u>Test for Sulphur (S)</u> **a) *<u>Nito prusside solution test</u>*** 1 ml of S.E. + 3-4 drops of fresh and very dilute sodium nitro prusside solution + 1or 2 drops NaOH solution. **b) *<u>Lead acetate solution test</u>*** 1 ml of S.E. is acidified with 1ml of dilute acetic acid + 2-3 drops of lead acetate solution.	Intense purple colour Black ppt of PbS	Sulphur present Sulphur present
iii. <u>Test for Halogens (X)</u> 2 ml of S.E. treated with dil HNO_3 till acidic boil well, cool and add few drops of Silver nitrate ($AgNO_3$) solution.	i. White curdy ppt. readily soluble in ammonia solution. ii. Pale yellow ppt. soluble in ammonia solution. iii. Yellow ppt. insoluble in ammonia solution	Chlorine present Bromine present Iodine present

Conclusion : The compound contains the elements : C, H, (O) and ……

V. DETECTION OF FUNCTIONAL GROUPS:

The functional groups are detected based on the elements present in the compound and categoried into the following division; **a]** C, H,(O) **b]** C, H, (O) and N **c]** C, H, (O), N and S **d]** C, H, (O), N , and X and **e]** C, H, (O), N, S, and X

Division: I : Compounds containing elements C, H, & (O). The compounds may be Acids / Phenols / Neutral.

1. TEST FOR CARBOXYLIC ACIDS

DISTINGUISHING TESTS FOR ACIDS

<u>Neutral $FeCl_3$ Test :</u> Compound + 1 ml H_2O heat to dissolve + 3 drops of neutral $FeCl_3$ Solution and observe.	(a) Violet colour in cold disappearing by HCl (b) Buff coloured ppt (warm if you do not get in cold) dissolved by ammonia or HCl . (c) Reddish brown ppt or buff coloured ppt soluble in HCl.	Salicylic acid present Cinnamic acid present Phthalic acid present

Confirmatory Tests for Carboxylic Acids		
C.T. for Salicylic acid : compound + 5drops methyl alcohol + one drop of conc. H_2SO_4 warm cool and pour in cold water taken in a beaker.	Smell of oil of wintergreen (Iodex smell)	Salicylic acid is present and **confirmed**
C.T. for Cinnamic acid : To the aqueous solution of the acid + 2-4 drops of $CaCl_2$ Solution	White ppt. insoluble in acetic acid	Cinnamic acid is present and **confirmed**
C.T. for Phthalic acid : **(Flourescein test) :** Fuse a pinch of the compound with equal quantity of resorcinol, Cool + 2-3 drops of conc. H_2SO_4 warm, cool and pour in water containing 2-5 drops of NaOH taken in a beaker.	Reddish green fluorescence (red colour with a green fluorescence)	Phthalic acid is present and **confirmed**

2. TEST FOR PHENOLS

Distinguishing Tests for phenols (α – Naphthol & *β*-Naphthol)

i. Neutral $FeCl_3$ solution Test Sub + alcohol, shake well and add 1-2drops of neutral $FeCl_3$ solution	a) Green colour immediately changing to a white ppt. b) White ppt slowly changing to violet.	*β*-Naphthol present *α*-Naphthol present
C . T. for Naphthols **ii. Phthalein fusion Test** 0.2g sub + 0.2g Phthalic anhydride + 3drops of con. H_2SO_4 fuse the mixture in a dry test tube gently for about 5-10 minutes. Cooled and diluted with 2ml water and pour into beaker containing 10ml of 10% NaOH solution .	a) Very faint green colour with slight blue fluorescence b) Green colour	*β*-Naphthol present & Confirmed *α*-Naphthol present & Confirmed
C . T. for Naphthols 0.1 g. of substance + 5ml of 10% NaOH solution + Few drops chloroform + Copper turnings and warm gently	a) Blue colour to the solution b) Blue colour changes to green-brown on exposure	*β*-Naphthol present & Confirmed *α*-Naphthol present & Confirmed

3. TEST FOR NEUTRAL COMPOUNDS (KETONES AND AROMATICHYDROCARBONS) (Benzo phenone, *Naphthalene and Diphenyl*)

Test for Ketone (Benzo Phenone) (a) Sub + Conc. H_2SO_4. (b) Sub + Dry sodium metal (rice grain size) fuse on gentle heating	Yellow solution Deep blue colour	Benzophenone present Benzophenone present and confirmed
2,4 – DNP Test Take Compound in a TT, add ethyl alcohol + Brady's reagent (2,4,DNP) warm on water bath. (*take orange ppt. as derivative)	Orange ppt.	Benzophenone is confirmed
Test for Hydrocarbons 0.1 g. of substance + 0.5cc of Conc. H_2SO_4	Insoluble	Hydrocarbon Present (Naphthalene or Diphenyl may be present . confirmed on the basis of their M.P.s)
C.T. for Naphthalene Compound + benzene + Picric acid in benzene, mix & shake well	Yellow ppt.	**Naphthalene** is present and confirmed
C. T. Dipehenyl Compound (0.5g) + 2 ml of fuming HNO_3 (or 1 cc of con. H_2SO_4 + 1 cc of Con. HNO_3) in a conical flask. Heat for 5 minutes, cool and pour it into ice cold water. (* take white ppt. as derivative)	White ppt.	(Biphenyl) Diphenyl is present and confirmed

Division II: Compounds containing elements C, H, (O) & N. The compounds may be Acids/ Bases / Neutral.

Test for Acids (Anthranilic acid)

i. Sub + $NaHCO_3$ solution	Soluble with effervescence	Acid (-COOH) present
ii. Test for $-NH_2$ Group by Diazotisation: ***Diazotization test*** ***Diazotization:*** 0.1g Comp. + 3 times conc. HCl in a test tube and cool in ice cold water + add few drops of ice cold solution of sodium nitrite($NaNO_2$). Add an ice cold solution of β-Naphthol in NaOH to the above solution.	Orange dye stuff	'**$-NH_2$**' (primary amino) group present.
iii. Comp. + Alcohol	Soluble with blue fluorescence	Anthranilic acid present

iv. C.T. for Anthranilic acid Mix a small amount of substance with equal amount of $CaCl_2$ and heat gently. Dissolve the product in 2 ml. of alcohol.	Red coloured solution exhibiting violet fluorescence on standing	Anthranilic acid present and Confirmed
v. 0.1g Sub + $ZnCl_2$ fuse by gentle heating dissolve the product in alcohol	Yellow colour	Anthranilic acid present and Confirmed

TEST FOR BASES: (*p*- Toluidine or *p*-Nitroaniline or *m*-Nitro aniline)

Sub + 1:1 HCl	Soluble and re precipitation with NaOH	Base present
Test for $-NH_2$ Group by Diazotisation: ***Diazotization test*** ***Diazotization:*** 0.1g Comp. + 3 times conc. HCl in a test tube and cool in ice cold water + add few drops of ice cold solution of sodium nitrite ($NaNO_2$). Add an ice cold solution of *β*-Naphthol in NaOH to the above solution.	Orange Red dye	**$-NH_2$ group** is present Amine is present (p-Toluidine or Nitro aniline)
Test for $-NO_2$ group : Mulliken's Test (Neutral Reduction test) : Dissolve the Compound (0.3 g) in 0.5 ml of hot 50% aqueous alcohol + 5-6 drops of 10% $CaCl_2$ + pinch of Zn dust. Boil the mixture for a minute. Filter and test the filtrate with Tollen's reagent (To silver nitrate add NaOH. Then add NH_4OH till the ppt. first formed dissolves)	A black ppt. or grey ppt.	**$-NO_2$ group** is present (Nitro anilines present)
C.T. FOR NITRO ANILINES:		
Dissolve the Compound in (0.2 g) 0.5 ml acetone + titanous chloride reagent,(0.5 ml) warm the mixture very gently.	Discharge of Mauve colour of the titanous chloride	*m*- & *p*-Nitro aniline is present and confirmed
Further these m- & p-Nitro anilines are confirmed by their melting points.		
C.T. FOR NITRO *P*-TOLUIDENE		
0.5g sub + 3-4 drops of dilute HCl. +2 ml water + 2-3 drops of $FeCl_3$ solution.	A pale yellow colour changing to red	*p*- Toluidene present and confirmed

TEST FOR NEUTRAL COMPOUNDS

COLOURLESS (BENZAMIDE & ACETANILIDE), M-DINITROBENZENE (YELLOW)

Compound + Water warm	Soluble in hot water	-Anilides (Acetanilide) & (Benzamide) present
Compound + NaOH, Warm	Smell of NH_3 No smell of NH_3 *(Fishy odour of aniline)*	Amide is present **(Benzamide)** Anilides (Acetanilide) is present
Confirmatory tests for Benzamide, Acetanillide or m-dinitrobenzene		
C.T. for Benzamide Boil the compound with dilute NaOH for 5 minutes, cool and acidify with dilute H_2SO_4	White ppt. of benzoic acid	Benzamide is present and confirmed
C.T. for Acetanilide Compound + dilute HCl, heat to dissolve, then cool in ice + ice cold solution aq. $NaNO_2$ solution + ice cold solution β-Naphthol in excess NaOH.	Bright Red ppt.	Acetanilide present and confirmed

Division –III: Compounds containing elements C, H, (O) & Halogens.

i. Beilstien.s Test Heat a loop of copper wire till it does not impart green colour to the flame. Cool, and take substance on loop of copper wire and then heat it.	Green edged lame after the initial sooty flame has vanished	Halogen present
Test for Hydrocarbons 0.1 g. of substance + 0.5 cc of Conc. H_2SO_4	Insoluble	Halogenated hydrocarbon Present

VI. BROAD INFERENCE

S.N	Particulars	Inference
1.	Nature	:
2.	Aliphatic / Aromatic	:
3.	Saturated / Unsaturated	:
4.	Physical Consatant (Melting point)	M.P. =_____°C Literature_____°C
5	Elements present	
6	Functional group (s) present	:
7	Name of the compound	:
8	Molecular formula	:
9	Structural formula	:
10	Name of the Derivative	:
11	Structural formula of the Derivative	:
12	Physical Constant (Melting point) of the derivative	M.P. =_____°C Literature_____°C

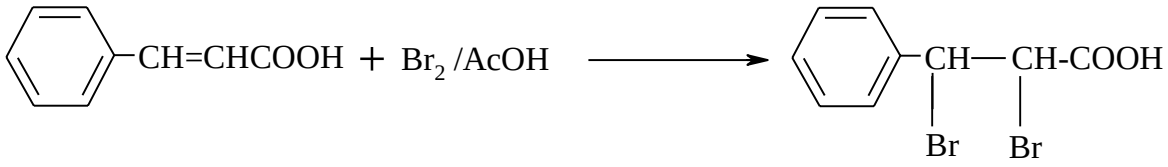
PREPARATION OF DERIVATIVES

A derivative may be defined as a chemical compound obtained by the chemical reaction of a substance, generally retaining the structure of parent substance.

Preparation of a derivative constitutes the last and of course confirmatory step in systematic identification of an organic compound since the identification of organic compound is said to be correct if the melting point of the derivative coincides with the melting point given in the literature for the same derivative of the same compound.

1. Dibromo derivative of Cinnamic Acid (2,3-Dibromo-2-phenyl propionic acid)

Dissolve about 0.5g of cinnamic acid in 5 ml. of glacial acetic acid in a 100 ml. beaker or conical flask and add excess (5-6ml) of solution of bromine in acetic acid in small lots with constant shaking. Allow the reaction mixture to stand for about 10 min. and dilute with water. Filter, and wash the product with water and dry. Recrystallise from hot water and determine its M.P.

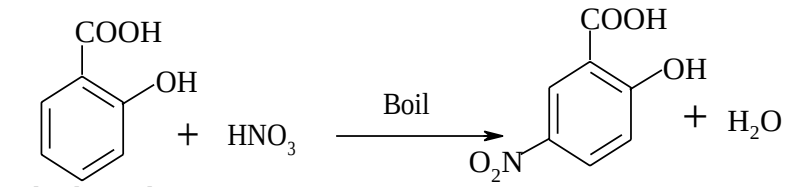


3-phenyl-prop-2-ene-1-oic acid
(Cinnamic acid)

2,3-Dibromo-3-phenylpropanoic acid

2. 5-Nitro Salicylic acid from Salicylic acid

Dissolve the compound (0.5 gm) in hot water and add 0.5 ml of dilute HNO_3 and boil for 5 minutes. Yellow solution is obtained Pour it into the ice – cold water taken in a beaker. Solid separates. Filter, and wash the product with water and dry. Recrystallise from hot water and determine its M.P.

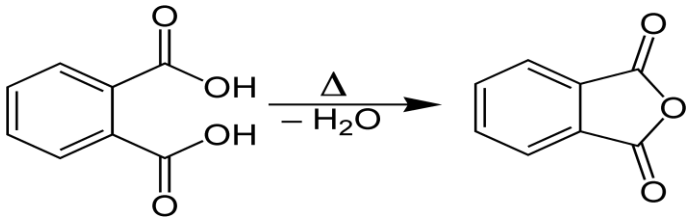


Salicylic acid

5-Nitro salicylic acid

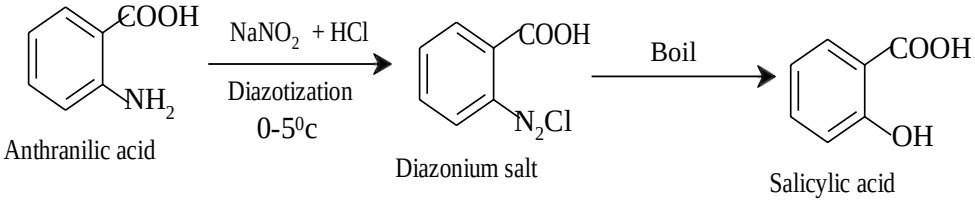
3. Phthalic acid to Phthalic anhydride

Take 0.5g Phthalic acid in a china dish covered with filter paper having a hole in the middle. Place aninverted funnel on the filter paper, lightly plug the nozzle with cotton or filter paper, and heat the dishon a sand bath. On sublimation the acid converts into Phthalic anhydride which collects on the inner side of the funnel. Collect the crystals of phthalic anhydride and determine its M.P.



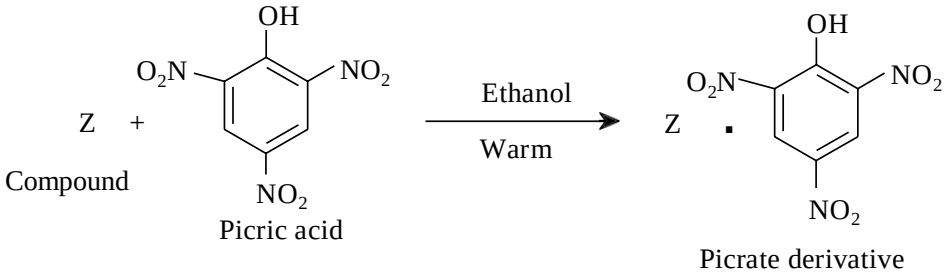
4. Anthranilic acid to Salicylic acid

Diazotise anthranilic acid as follows: Dissolve 0.5g of acid in about 4ml of 1:1 HCl and cool thoroughly. To this solution, add $NaNO_2$ solution drop by drop till a drop of the solution just tints the starch – iodide paper blue, showing a slight excess of HNO_2. Boilthe solution until the evolution of nitrogen ceases. Cool and shake thoroughly, Salicylic acid separates out easily. Dry and recrystallise from hot water, determine its the M.P.



5. Picrate derivative for α-Naphthol , β-Naphthol and Naphthalene

Dissolve 0.5 to 1 g of the given substance (α – naphthol or β – naphthol or naphthalene) in ethanol. Add 2-3 ml of saturated solution of picric acid in the ethanol. Picrate derivative separates out on mixing. In case no solid separates on mixing , heat the reaction mixture on hot water bath. Cool thoroughly. Filter the product, recrystallize from alcohol(if necessary), dry and determine its M.P.

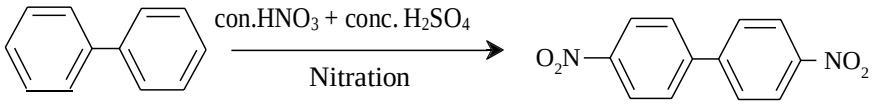


Z = α – Naphthol or β – Naphthol or Naphthalene whichever is given

6. *p,p'*- Dinitro diphenyl from Diphenyl

Dissolve 0.5g. substance in 3ml of conc H_2SO_4 add 2ml. conc HNO_3. Shake well and place the test tubein a gently boiling water bath for about 5-10 minutes with occasional shaking. Pour the reaction mixture

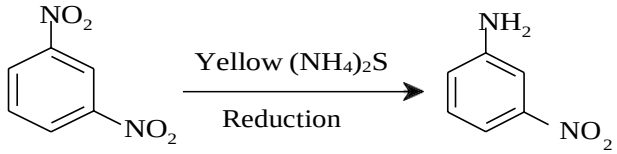
in 50ml, ice cold water with constant stirring. Filter, dry and recrystallise from aqueous alcohol anddetermine its M.P.



Diphenyl — *p,p'*-Dinitro diphenyl

7. *m*-Nitroaniline from *m*-Dinitrobenzene

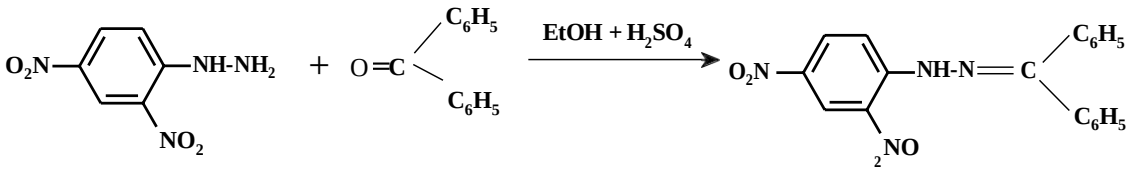
Dissolve 0.5g. of m-Dinitrobenzene in 25ml. of boiling water. To the boiling solution, add yellow ammonium sulphide till the yellow colour is persistent. Boil further for five minutes. Filter while hot. On cooling, yellow needles of *m*-Nitro aniline separates out. Recrystallise from hot water and determine its M.P.



m-Dinitro benzene — *m*-Nitro aniline

8. 2,4-Dinitrophenylhydrazone derivative from Benzophenone

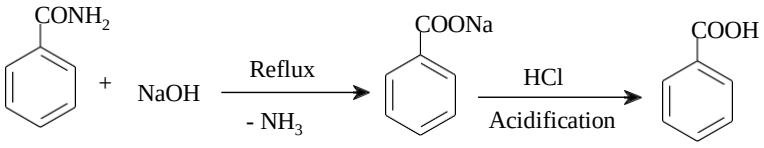
Take 0.5 g of benzophenone in a dry test tube and dissolve it in few drops of water or ethanol. Add 1cm^3 of 2,4 – DNP solution. Heat the mixture on water bath for few minutes and cool it in ice. Orange orred crystalline precipitate separates out. Filter, dry and take the melting point.



2,4-Dinitro phenyl hydrazine — Benzophenone — Benzophenone-2,4-Dinitro phenyl hydrazone

9. Benzoic acid from Benzamide

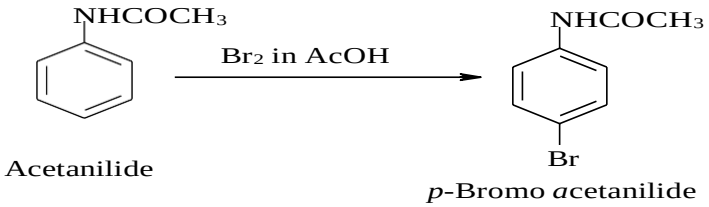
Take 0.5g. of benzamide in a 100ml. R.B. flask or conical flask and add 6-7ml. of 25% NaOH solution. The flask is fitted with reflux (air) condenser. Reflux the contents until all ammonia has been driven off (it takes about half an hour) and then cool. Add concentrated hydrochloric acid drop wise till the reaction mixture is strongly acidic and the benzoic acid separates out as a derivative. Filter and recrystallise from hot water. Determine melting point.



Benzamide — Sodium benzoate — Benzoic acid

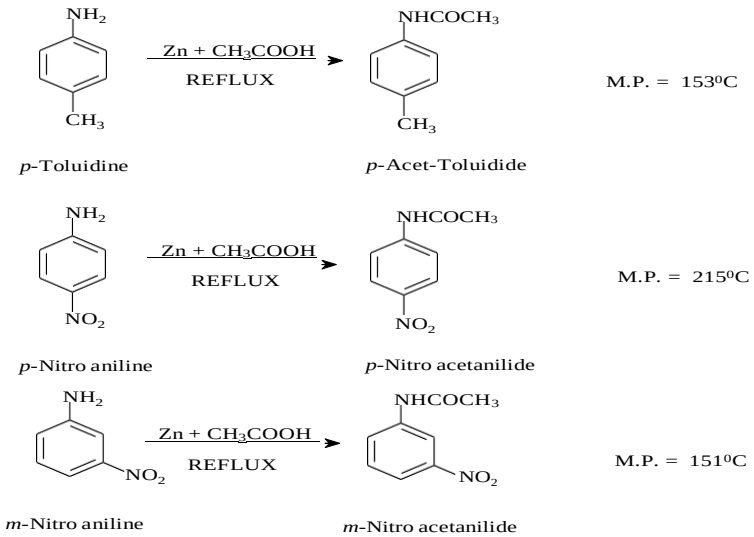
10. *p*-Bromo acetanilide from Acetanilide

1g. of acetanilide is dissolved in 5ml. glacial acetic acid in a 100 or 50ml. conical flask. To this add bromine in acetic acid in small quantities till colour of bromine persists to solution. The mixture is allowed to stand for 10-15 minutes and then poured into ice cold water with constant stirring and filter the product, wash with cold water and recrystallise from 25% ethanol. Determine the melting point.



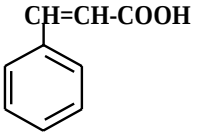
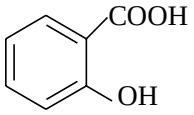
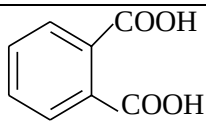
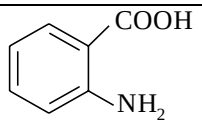
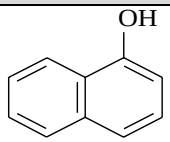
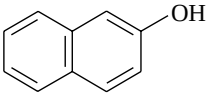
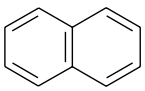
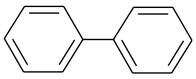
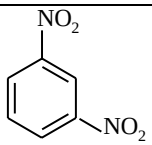
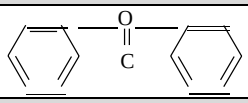
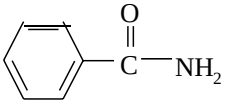
11. Acetyl derivative.

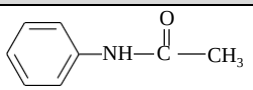
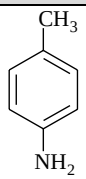
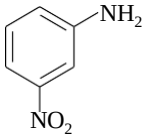
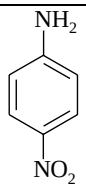
A mixture of *p*-toluidine or *m*-nitroaniline or *p*-nitroaniline (1g) and zinc dust (0.5 g) in acetic acid (5 ml) in a 100 ml round bottom flask was heated over a gentle flame using water condenser. Heating was continued for about 30min. The reaction mixture was then carefully poured in cold water (20 ml) in a 100 ml beaker with cooling and vigorous stirring. The shining crystals of respective anilides were separated slowly. After 15 min. the anilide crystals were collected by filtration. The solid crystals were washed over the Buchner funnel with water and the products driedand take melting point.



Picrate derivative can also be performed for nitro anilines. Procedure is remained same to that of Naphthols.

Name, Structure and M.P. of derivatives of Organic Compounds

Compound	Melting point range (^{0}C)	Molecular Formula	Structural formula	Derivative Melting point
1. Cinnamic acid	133 -134	$C_6H_5CH=CH-COOH$		2,3 – Dibromo-3- phenyl propionic acid (**194-195^{0}C**)
2. Salicylic acid	157 - 158	$C_6H_4(OH)COOH$		5-Nitro salicylic acid (**230-231^{0}C**)
3. Phthalic acid	193-213	$C_6H_4(COOH)_2$		Phthalic anhydride (**127-128^{0}C**)
4. Anthranilic acid	148-149	$C_6H_4(NH_2)COOH$		Salicylic acid **(157-158^{0}C)**
PHENOLS				
5. α-Naphthol	93 - 94	$C_{10}H_7OH$		Picrate derivative (**189-190^{0}C**)
6. β-Naphthol	121-122	$C_{10}H_7OH$		Picrate derivative (**156-158^{0}C**)
NEUTRALS **1. Hydrocarbons**				
7. Naphthalene	79-80	$C_{10}H_8$		Picrate derivative Naphthalene picrate (**149-151^{0}C**)
8. Diphenyl	70-72	$C_{12}H_{10}$		*p,p'*- Dinitro diphenyl (**233-234^{0}C**)
9. *m*-Dinitrobenzene	89-90	$C_6H_4(NO_2)_2$		*m*-Nitroaniline (**114-115^{0}C**)
2. KETONES				
10. Benzo phenone	48-49	C_6H_5-CO- C_6H_5		2,4 – Dinitrophenyl hydrazone (**238-239^{0}C**)
3. AMIDES				
11. Benzamide	128-129	C_6H_5-$CONH_2$		Benzoic acid (**122-123^{0}C**)

4. ANILIDES				
12. Acetanilide	114-115	$C_6H_5NHCOCH_3$		*p*-Bromoacetanilide **(166-167^{0}C)**
BASES				
13. *p*-Toluidine	43-44	$C_6H_4(CH_3)NH_2$		*p*-Acet-toluidide (**153-154^{0}C**)
14. *m*-Nitroaniline	113-114	*o*-$C_6H_4(NO_2)NH_2$		*m*-Nitroacetanilide (**154-155^{0}C**)
15. *p*-Nitroaniline	147-148	*p*-$C_6H_4(NO_2)NH_2$		*p*-Nitroacetanilide (**255-257^{0}C**)

References:

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2. Organic Experiments VIIth Edition Louis F. Fieser Late Professor Emeritus Harvard University Kenneth L Williamson Mount Holyoke College
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Qualitative analysis of Organic Compounds-Liquids

I) PRELIMINARY TESTS

S.N	Test	Observation	Inference
1.	State	Liquid	***Low boiling liquids***; Acetone, Ethyl acetate may be present. ***High boiling liquids***; Aniline, Phenol, Acetophenone, Nitrobenzene,Toluene, Benzaldehyde, bromobenzene, Chlorobenzene may be present.
2.	Colour	Colourless Yellow Reddish/Brown	Benzaldehyde, Acetone, Acetophenone, Ethyl acetate, Toluene, Chlorobenzene may be present. Nitrobenzene, bromobenzene may be present. Phenol,Aniline may be present
3.	Odour	Phenolic Fishy Pleasant /Fruity Bitter almond	Phenol Amines (Aniline) may be present. Acetone, Acetophenone, Ethyl acetate, Bromobenzene, Chlorobenzene Benzaldehyde, Nitrobenzene
4.	Beilstein's Test : Heat a loop of copper wire till it does not impart green colour to the flame. Cool, and dip in the liquid and then heat it.	Burns with non-sooty flame Burns with sooty flame Burns with sooty flame followed by green edged flame	Aliphatic compound Aromatic compound Halogenated aromatic compound
Therefore, the given compound is ----------			
5.	Solubility Test		
i	Liq. + Water	Miscible in cold solution acidic to litmus Miscible in cold and neutral to litmus Immiscible	Acetic acid may be present Acetone and ethylacetate may be present Phenol, aniline, toluene, chlorobenzene, benzaldehyde etc; may be present.
ii	Liq. + $NaHCO_3$ Solution	Miscible with effervescence	Acids present
	Above Sol. + dil HCl	Reappearance of oily drops or turbidity	Acid confirmed

iii	Liq. + NaOH	Miscible	Phenol present
	Above Sol. + dil HCl	Reappearance of oily drops or turbidity	Phenol confirmed
iv	Liq. + 1:1 HCl	Miscible	Base present
	Above Sol. + NaOH	Reappearance of oily drops or turbidity	Base confirmed

(if all the above tests are negative the nature of the given compound is NEUTRAL)

Note: A.S. = Above solution

Conclusion: The given compound is_____(Acid/Phenol/Base/Neutral)

6.	Test for Un-saturation.		
i	Br_2 water test: 2-3 drops of liquid + few drops of Br_2 water. If it doesn't give test treat with Bromine in carbon tetra chloride	Decolourisation of Br_2 water No decolourisation	Unsaturated compound Saturated compound
ii	Alkaline $KMnO_4$ test : Dissolve the compound in hot water + few drops of very dilute alkaline $KMnO_4$ solution	Decolourisation of $KMnO_4$ solution No decolourisation	Unsaturated compound present Saturated compound

Conclusion: The given compound is_____(Saturated/Unsaturated)

II. Determination of physical constant:

Using Thiel's tube the *boiling point* of given compound under investigation is determined.

Boiling point of the compound is..... ^0C

III. Detection of Elements:

Generally organic compounds contain Nitrogen (N), Halogen (X) and Sulphur (S) along with Carbon, Hydrogen and (Oxygen). For the detection of N, X, and S the Lassaigne's test is performed.

Lassaigne's Test :

Take a small piece of clean and dry Sodium metal in a fusion tube and heat it slowly till the metal fuses. Cool and add 2-3 drops of liquid under investigation. Heat continuously till the fusion tube becomes red hot. Plunge the red hot fusion tube into about10 ml of distilled water taken in an evaporating dish. Break the fusion tube with a glass rod and boil the mixture for about 5 min and filter. The filtrate is called Sodium Extract (S.E) and use it for the test for Nitrogen, Halogen/s and Sulphur.

Test for Nitrogen : 1 cm^3 of S.E. + 1 cm^3 of freshly prepared $FeSO_4$ + 1 drop of NaOH soln. Boil and cool. Add a few drops of $FeCl_3$ and acidify with Conc. H_2SO_4 or Conc. HCl.	Green or blue colouration. (Prussian blue colour)	Nitrogen present
Test for halogens : 1 cm^3 of S.E. + dil HNO_3 boil and cool + $AgNO_3$ solution.	a) Curdy white ppt. easily soluble in NH_4OH b) Pale yellow ppt. sparingly soluble in NH_4OH c)Yellow ppt insoluble in NH_4OH	Chlorine is present Bromine is present Iodine is present
Test for Sulphur : S.E. (2ml) + 2-3 drops of sodium nitroprusside solution.	Violet colouration	Sulphur present

Conclusion: The elements present in the compound are C, H, (O) and .....

IV. Detection of Functional Group

It can be done on the basis of elements present in the compound, its nature and they are divided into following divisions.

Division I - C, H, & (O) Division II – C, H, (O) & N

Division III – C, H, (O) and Halogen

The given compound contains the elements C,H (O) & … The compound belongs to the division ……

V) DETECTION OF FUNCTIONAL GROUPS

Division I - C, H, & (O)

[Phenols, Neutral (Aldehydes, Ketones, Esters & Aromatic Hydrocarbons)].

B) Test for Phenols

i)**Br_2 Water Test** : Dissolve the given Compound in water or in acetic acid + Bromine water and observe	White ppt	Phenol is present
ii) Alcoholic $FeCl_3$ Test : Dissolve the given Compound in water or in acetic acid + alcoholic $FeCl_3$ solution and observe.	Violet Colouration	Phenol is present

Confirmatory tests for Phenols)		
i)**PhthaleinFusionTest:** Compound (1-2 drops) + a pinch of phthalic anhydride + 2 drops of conc. H_2SO_4, heat gently, cool, pour it in a beaker containing water and NaOH (5 drops)	Red (Pink) Colour	Phenol is present and confirmed
ii) **Leiberman's Nitroso Test** Compound (2-3 drops) + $NaNO_2$, heat gently, cool + Con. H_2SO_4 (5 drops)	A deep green to blue solution is formed at first which turns red when poured in to water containing few drops of NaOH	Phenol is present & confirmed.
C) Test for neutral compounds containing C,H& (O) (Aldehydes, Ketones & Esters)		
Brady's reagent Test: Compound + 2,4:DNP	Yellow crystalline ppt.	Benzaldehyde or (Ketones) Acetone or Acetophenone present.
Schiff's reagent test: Compound(1 drop)+Schiff's reagent(2-3 drops) and shake the mixture well. Keep for a while.	Pink colouration	Benzaldehyde is present.
	No Pink colouration	Acetophenone is present.
C.T. for Benzaldehyde:		
Silver mirror test (*Tollen's reagent test) : Compound(1 drop) +Tollen's reagent. Warm the mixture on a water bath without disturbing.	Silver mirror or grey ppt.	Benzaldehyde is present & confirmed
*Preparation of Tollen's reagent : Mix equal volume of 10% aqueous $AgNO_3$ (1 ml) & dil NaOH (1 ml) Add dilute NH_4OH drop wise till the brown ppt. just dissolves to get a clear solution.		
Ketones – Acetone & Acetophenone		
Aliphatic compound-Acetone, Aromatic compound-Acetophenone		
Compound (1-2 drops) + Sodium Nitroprusside solution(5 drops) + few drops of NaOH.	Red colouration Red coluration changes to blue on adding acetic acid	Acetone is present Acetophenone is present
<u>C.T. for Acetophenone</u>		
Brady's reagent Test: Compound + 2,4:DNP	Yellow ppt.	Acetophenone is present and confirmed.

C.T. for Acetone		
ii) Iodoform test: Compound(3-4 drops) + I_2 in KI solution till yellow colour persists + NaOH, heat the solution gently.	Yellow ppt.	Acetone is present and confirmed.
Esters - Ethyl Acetate		
Compound (5drops) + 1-2 drops of phenolphthalein and one drop of very dil. NaOH (Diluted 10 times), heat	Pink colour is formed, which disappears on heating due to the free acid formed by the hydrolysis of esters.	Ethyl acetate is present
C.T. Ethyl Acetate		
Feigl Test : 1-2 drop of compound + Hydroxylamine hydrochloride Solution(5 drops) + 5 drops of KOH in methanol solution. Boil for a minute, cool & acidify with dil HCl. + 1-2 drops of $FeCl_3$	Violet colouration	Ethyl acetate is present and confirmed
Test for Neutral compounds containing C & H only (Aromatic Hydrocarbons)		
Hydrocarbons(Toluene)		
Compound + Conc.H_2SO_4	Insoluble	Toluene is present
C.T. for Toluene		
Compound + Picric acid in Benzene shake well.	Yellow ppt.*	Toluene is present & confirmed
*Take it as picrate derivative with M.P. = 88°C		
Division II - C, H, (O) & N (Bases & Neutral compounds)		
Base – Amines (Aniline)		
Compound + dil HCl	Dissolves completely and reprecipitated by NaOH	Base (Amine) is present
Compound (2-3 drops) + $K_2Cr_2O_7$ (pinch) + conc. H_2SO_4 (3-4 drops) shake well.	Blue or Black colour	Anilne is present.

C T. for Aniline (Test for -NH_2 group)		
Azo-dye test: Compound + con. HCl (1:1) cool in ice + 10% ice cold $NaNO_2$ solution + 2-naphthol in NaOH.	Orange Red dye	Aniline present and confirmed (-NH_2 group is present)
Neutral -- Nitro Benzene		
Mulliken's Test (Neutral reduction test : Dissolve the Compound (4 drops) in a hot 50% aqueous alcohol + 5-6 drops of 10 % $CaCl_2$ + pinch of Zn dust Boil the mixture for a minute. Filter and test the filtrate with Tollen's reagent.	A black ppt.or grey ppt.	Nitro(-NO_2) group (Nitro benzene) is present.
C.T. for Nitro Benzene		
Compound(5 drops) + Glacial acetic acid(1 ml) + pinch of Zn dust, Boil cool, & add water(1 ml) +NaOH till alkaline + Sodium nitroprusside (2-3 drops)	Violet colouration	Nitro benzene is present and confirmed
DIVISION – III (C, H and Halogens(Br or Cl) (Bromobenzene or Chlorobenzene)		
Test for Bromobenzene		
Beilstein's Test: (Test for aliphatic or aromatic) Heat a small piece of copper foil in a non-luminous flame using pair of tongs until it imparts no colour to the flame. Cool, dip into the given organic compound and again hold it to the flame and observe	Burns with Sooty(smokey) flame followed by green edged flame	Bromobenzene or Chlorobenzene present
Compound + Alcoholic $AgNO_3$ & mix & warm	Pale yellow ppt. A white curdy ppt.	Bromobenzene is present Chlorobenzene is present
C.T. for Bromobenzene		
Compound (4 drops) + 2 ml of fuming HNO_3 (or 1 ml of con. H_2SO_4 + 1 ml of Con. HNO_3) Heat for 5 minutes, cool and pour it into water.	Yellow solid	Bromobenzene is present and confirmed

C.T. for Chlorobenzene		
Compound (4 drops) + 2 ml of fuming HNO_3 (or 1 ml of con. H_2SO_4 + 1 ml of Con. HNO_3) Heat for 5 minutes, cool and pour it into water containing ice pieces.	*Yellow solid	Chlorobenzene is present and confirmed
*Take it as derivative p-nitro-chlorobenzene with M.P.=83 ^oC		

VI. BROAD INFERENCE

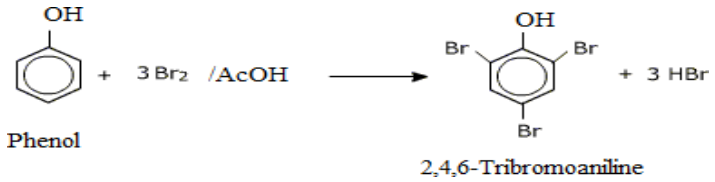
S.N	**Particulars**	**Inference**
1.	Nature (Acid/ base/phenol/Neutral)	
2.	Aliphatic / Aromatic	
3.	Saturated or Unsaturated	
4.	Physical constant of compound	Observed B.P = …^{0}C Literature B.P =…. ^{0}C
5.	Elements present	
6.	Functional group	
7.	Molecular formula of the compound	
8.	Structural formula of the compound	
9.	Name of the compound	
10.	Name of the derivative	
11.	Structure of the derivative	
12.	Physical constant of the derivative	Observed MP = …^{0}C Literature MP =…. ^{0}C

PREPARATION OF DERIVATIVES

1. Bromo derivative for Phenol and Aniline

Dissolve about 1ml of aniline or phenol in acetic acid and take this content in 100 c.c. conical flask. Add strong bromine solution (bromine in acetic acid) until, after shaking, the liquid is pale yellow. Add 50 c.c. water, cool and shake vigorously. Filter and wash the bromo-derivative with water. Recrystallise the product from alcohol.

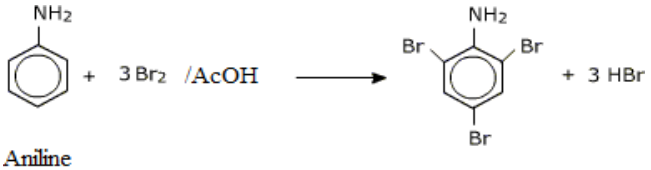
For Phenol



Phenol

2,4,6-Tribromoaniline

For Aniline

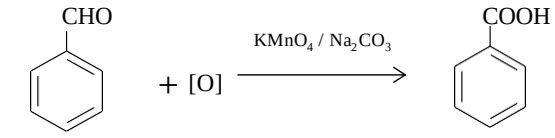


Aniline

2,4,6-Tribromoaniline

2. Benzoic acid from Benzaldehyde

Take 1ml of benzaldehyde in a 100ml. conical flask and add about 10ml. of 10% Na_2CO_3 and boil the solution by placing boiling chips. To, the boiling solutions add about 15ml of $KMnO_4$ gradually till the solution contains a little excess of potassium permanganate. Filter of the precipitated hydrated MnO_2 and few drops of SO_2 water to remove excess of $KMnO_4$. Filter and acidify the filterate, on cooling, the acid precipitates. Recrystallise from hot water.

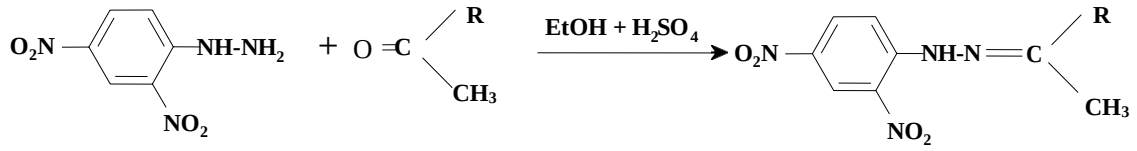


BENZALDEHYDE

BENZOIC ACID

3. 2,4-D.N.P – derivative for Acetone and acetophenone

Take about 5 ml of 2,4-DNP solution in a test tube. Add 5-6 drops of the given liquid (acetone or Acetophenone) shake well and warm it for few minutes. Cool and filter the precipitate thus formed. Recrystallise it from alcohol.

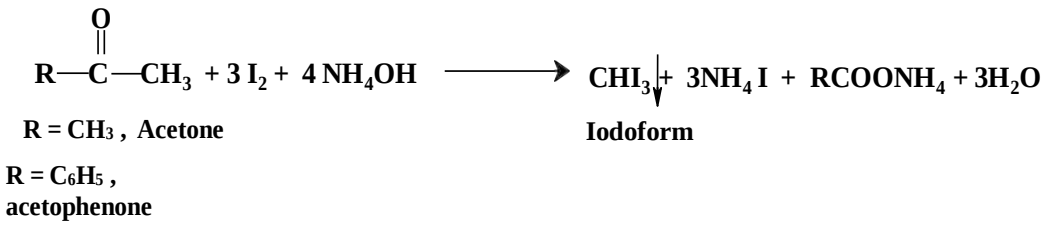


2,4-Dinitro phenyl hydrazine Ketone Ketone-2,4-Dinitro phenyl hydrazone

If R = CH_3 ; Acetone and R = C_6H_5 Acetophenone

4. Iodoform derivative for Acetone and Acetophenone

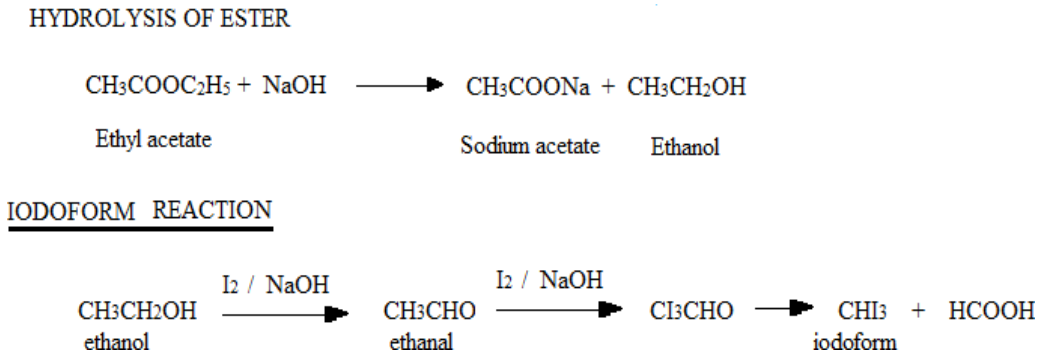
To about 5-6 drops of the liquid add 10ml NH_4OH. Add iodine solution drop by drop till the solution is distinctly yellow. Warm gently on water bath. When iodoform a yellow crystalline solid , separates in short time. Filter, dry and take M.P.



5. Iodoform derivative for Ethyl acetate

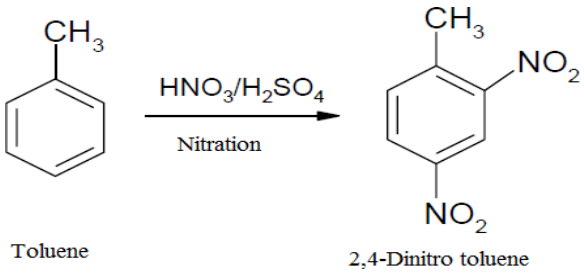
Hydrolyse 1ml of ethyl acetate with 50 ml of 10% NaOH by gently boiling under reflux for 1 hour. A mixture of ethyl alcohol and sodium acetate are formed. Completion of hydrolysis is indicated by the formation of a homogeneous solution.

Take about 1 ml of above hydrolysed solution, add 10% of potassium iodide solution and 5ml of freshly prepared sodium chlorite solution. Warm for few minutes and cool. Yellow crystals of iodoform are produced. Filter and collect it as derivative.



6. 2,4-Dinitrotoluene from toluene

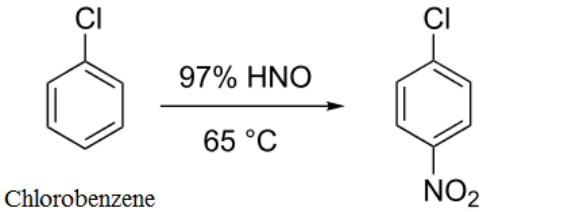
To 5ml of nitrating mixture (1:1 Conc. H_2SO_4 + Fuming Nitric acid), add 1ml of toluene in small lots with shaking after each addition. Cool in ice –water, by maintaining temperature 10^0C. Heat for two minutes and pour into about 50 ml. of cold water. Filter, wash and crystallise from alcohol.



Toluene — 2,4-Dinitro toluene

7. *p*-Nitrochlorobenzene from Chlorobenzene

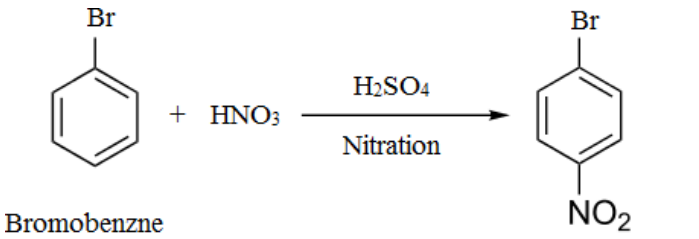
4-5 drops of chlorobenzne + 2ml of fuming nitric acid. Heat for 5-10 minutes on water bath and pour into 10 ml. water. Separated solid is Filter and dry. Recrystallise from ethanol.



Chlorobenzene — *p*-Nitro chlorobenzne

8. *p*-Nitrobromobenzene from Bromobenzene

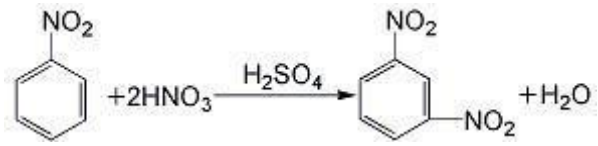
4-5 drops of Bromobenzne + 2ml of Conc. HNO_3 and Conc. H_2SO_4 shake well, and Heat for 2 minutes on water bath and pour into 10 ml. water. Separated solid is Filter and dry. Recrystallise from ethanol.



Bromobenzne — p - Nitro bromobenzne

9. *m*-Dinitrobenzene from Nitrobenzene

4-5 drops of nitrobenzene dissolved in 1 ml of Conc. H_2SO_4 in a dry test tube and add a mixture of 1ml of Conc. HNO_3 and 1ml of Conc. H_2SO_4 and add few drops of fuming nitric acid shake well. Heat for 2 minutes at 100^0C and pour into finely crushed ice in a beaker. Cool thoroughly and scratch by means of a glass rod when the oily suspension solidifies. Filter and recrystallise from alcohol.



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2. Organic Experiments VIIth Edition Louis F. Fieser Late Professor Emeritus Harvard University Kenneth L Williamson Mount Holyoke College

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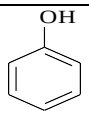
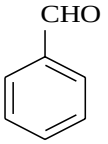
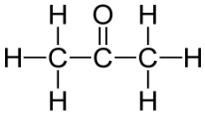
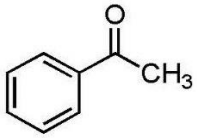
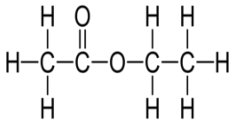
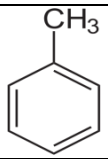
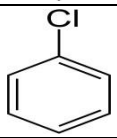
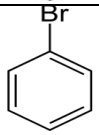
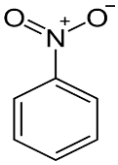
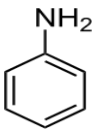
6. Practical Chemistry -.O.P.Pandey,D.N.Bajpai & S.Giri
7. A hand book of Analytical Chemistry– Subhash & Satish

Name, Structure and M.P. of derivatives of Organic Compounds

Substance	B.P. (^{0}C)	Mol. Formula	Str. Formula	Derivative (in M.P.)
1. Phenol	183-184	C_6H_5OH		2,4,6-Tribromo phenol (**95-97^{0}C**)
2. Benzaldehyde	179-180	C_6H_5CHO		Benzoic acid (**120-122^{0}C**) Or 2,4-D.N.P derivative (**237-239^{0}C**)
3. Acetone	56-58	CH_3-CO-CH_3		Iodoform (**119-121^{0}C**) or 2,4-D.N.P derivative (**126-128^{0}C**)
4. Acetophenone	202-204	C_6H_5-CO-CH_3		Benzoic acid (**120-122^{0}C**) or 2,4-D.N.P derivative (**249^{0}C**)
5. Ethyl acetate	77-79	$CH_3COOC_2H_5$		Iodoform (**119-120^{0}C**)
6. Toluene	110-112	C_6H_5-CH_3		2,4-Dinitrotoluene (**70-72^{0}C**)
7. Chlorobenzne	132-134	C_6H_5-Cl		*p*-Nitrochlorobenzne (**83-84^{0}C**)
8. Bromobenzne	155-157	C_6H_5-Br		*p*-Nitrobromobenzne (**126-127^{0}C**)
9. Nitrobenzene	209	C_6H_5-NO_2		*m*-Dinitrobenzne (**90-92^{0}C**)
10. Aniline	184	C_6H_5-NH_2		2,4,6-Tribromoaniline (**119-121^{0}C**)

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QULITATIVE ANALYSIS OF SOLID-SOLID ORGANIC BINARY MIXTURE

B. Sc.

V SEMESTER

PAPER-1

Name:_____

RCU No:_____

Department:_____

Mobile No: _____

B. Sc. V Sem: Paper - I

QULITATIVE ANALYSIS OF SOLID-SOLID ORGANIC BINARY MIXTURE

Total No of Hours/Week : 03 Hours — Practical: 40 Marks

Total No of Hours : 45 Hours — IA :10 Marks

CONTENTS
Qualitative analysis of solid – solid organic mixtures: Identification of nature and separation of mixture (in semi micro scale). Characterization of any one separated compound through Preliminary tests, Element test, Physical constant, Functional Group test and preparation of suitable derivative and its physical constant.
Acids: Salicylic, Cinnamic, Phthalic and Anthranilic acid.
Phenol: α –naphthol, β–naphthol.
Base: p-toluidine, m-nitroaniline and p-nitroaniline.
Neutral: Naphthalene, Acetanilide, Diphenyl, Benzamide, Benzophenone and m-dinitrobenzene.

Instructions

In a batch of ten students, not more than two students should get the same mixture in the practical examination. Viva questions may be asked on any of the experiments prescribed in the practical syllabus. During practical examination chart may be referred whenever necessary.

DISTRIBUTION OF MARKS	
Nature and separation	2 +3
Prelimanary tests	02
Element test	04
Physical constant	03
Functional Group test	04
Identification and Structure	03
Preparation of derivative	03
Physical constant of derivative	03
Systematic Presentation	03
Journal	05
Viva voce	05
TOTAL	**40**

SEPARATION OF SOLID-SOLID BINARY ORGANIC MIXTURE AND SPOTTING (QULITATIVE ANALYSIS) OF ORGANIC COMPOUND

INTRODUCTION

The purpose of organic qualitative analysis is to spot a given organic substance and to substantiate its nature by performing a set of reaction/s with it. The whole process of this analysis is based on the two important concepts, namely, Homologous series and Functional group. A compound belonging to a particular class will exhibit characteristic reactions of the atoms or group of atoms present in it. Compounds of a particular homologous series show a similarity in chemical reactions and gradation in physical properties.

The process of identifying unknown compound/s is analogous to solving a puzzle. An organic chemist can often identify a sample in a very short time by performing solubility tests and some simple tests of functional group/s. Millions of known organic compounds are easily and effectively classified into a limited number of groups based on their functional group. Part of the challenge of organic qualitative analysis lays in borderline cases and possible exceptions to the general rules for many of the tests. One must work with an open, unprejudiced mind, ready to make, and test, preparing derivatives this lead to success in finding the identities of unknown compound under investigation. Thus obtained information will help to determine the structure of an unknown compound. This is the way things were done prior to the advancement of modern instrumentation like Spectroscopic methods advanced chemical technique/s using sophisticated equipments.

Five basic areas of experimental inquiry are useful for identifying an unknown compound. One must develop an understanding for what information can be obtained from each of them.

The five areas of inquiry are;

(I) Physical properties (II) Classification by solubility (III) Elemental analysis by sodium fusion (IV) Classification tests for functional groups (V) Synthesis of solid derivative, and authentication by its M.P.

All the areas of experimental inquiry just listed depend on what can be called the structural theory of organic chemistry. By discovering how compounds act under certain conditions, a chemist can deduce what their structures are. Once you have a large number of characteristics in hand, you can deduce the structure of a compound.

I. Physical properties

The physical appearance of an unknown will be our first information in the search to discover its identity. Simply knowing that the compound is a solid rather than a liquid at room temperature narrows the search considerably. A few solids have characteristic bright colors that may be of great significance in reaching a final answer. The physical properties of a compound that are of interest in qualitative analysis are its appearance and its melting point or boiling point etc.

II. Solubility

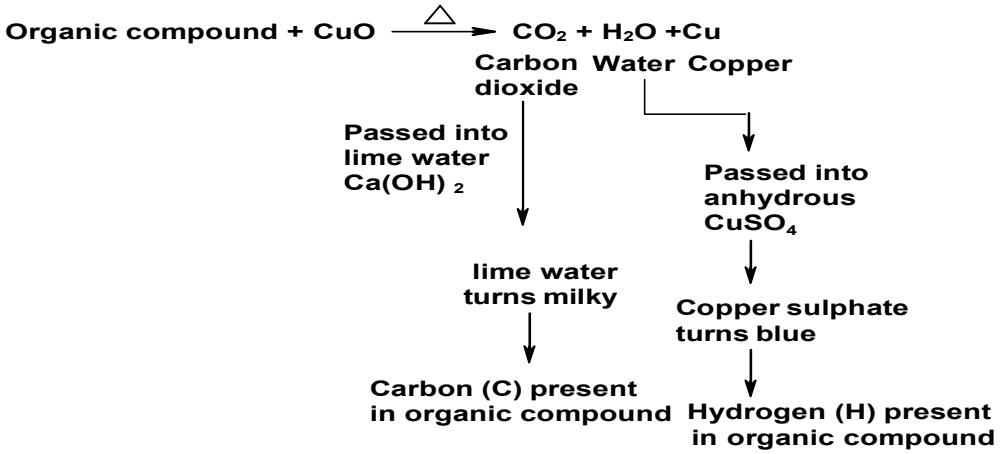
Solubility tests should be performed on every general unknown because they are quick and reliable and use only a small amount of sample. One can gather valuable information about possible functional groups through the use of the solubility classifications. Five common reagents are used for solubility tests are (1) Water (2) $NaHCO_3$ (3) NaOH (4) HCl, and (5) Concentrated H_2SO_4. Except in the case of water, solubility experiments probe the acid-base properties of organic compounds.

If a compound is an acid, you can obtain a relative measure of its acid strength by testing it against the weak base sodium bicarbonate and the stronger base sodium hydroxide. Naturally, *any organic compound that is soluble in water is also likely to be soluble in $NaHCO_3$, NaOH, HCl, and H_2SO_4 solutions* because these solutions are composed largely of water.

III. Elemental analysis

Presence of oxygen in organic compound is detected by testing for functional group containing oxygen eg- alcohol (–OH), aldehyde (–CHO), ketone (RCOR), carboxylic acid (–COOH), ester (– COOR) and nitro ($–NO_2$) etc.

Detection of Carbon and Hydrogen is generally carried in the following way**.**



Lassaigne's Test:

Sodium fusion converts halogens to corresponding sodium halides, which are easily detected by silver nitrate. A knowledge of the elemental composition of a substance is useful in planning the identification procedure.

C, H, S, N, X (covalent forms) + Na $\longrightarrow$ **$NaCN$, Na_2S, NaX (ionic)**
Organic compound X= halogen/s

- **Halogen test:** Sodium extract is treated with $AgNO_3$ following reactions takes place.

$$NaX + AgNO_3 \longrightarrow AgX + NaNO_3$$

$$\text{ppt} \downarrow 2NH_4OH$$

$$[Ag(NH_3)_2]X + 2H_2O$$

- **Sulphur test:** $Na_2S + Pb(CH_3COO)_2 \longrightarrow PbS + 2CH_3COONa$

- **Nitrogen test:** On treatment sodium extract with freshly prepared $FeSO_4$, $FeCl_3$ in presence of H_2SO_4 a prussian blue or greenish blue coloration is observed.

$$Fe(NH_4)_2(SO_4)_2 \rightarrow Na_4Fe(CN)_6 + Na_2SO_4\ 6NaCN + (NH_4)_2SO_4$$

Ferrous amm. Sulphate — sodium ferrocyanide

$$Na_4Fe(CN)_6 + Fe^{+3} \longrightarrow NaFe[Fe(CN)_6] + 3Na^+$$

Sodium ferriferrocyanide(Prussian blue)

IV. Functional Groups

The functional groups are detected based on the elements present in the compound. These are categorized as follows;

C, H, and **(O)** : This category includes Alcohols, phenols, aldehydes, ketones, carboxylic acids, esters and even hydrocarbons.

C, H, (O) and **N** : This category includes Amines, amides, annilides nitro compounds and even bi-functional compounds containing nitro and amino groups of Alcohols, phenols, aldehydes, ketones,carboxylic acids, esters etc.

C, H, (O), N and **S** : This category includes thio compounds containing amino, amido, annilido and nitro groups.

C, H, (O), N , and **X** : This category includes halogen compounds containing amino, amido, annilido and nitro groups.

C, H, (O), N , S, and **X:** This category includes thio and halogen compounds containing amino, amido, annilido and nitro groups.

V. Derivative:

After detecting the functional group/s by carrying out confirmative tests, finally the compound under investigation is confirmed by preparing its solid state derivative. Thus formed derivative isconfirmed by finding its melting point.

Solid – Solid type of mixtures

The organic compounds are classified in to the four groups viz., acid, phenol, base and neutral. Organic acids contain carboxylic acid group. Phenols are the class of organic compound where –OH group is directly attached to the benzene nucleus. Organic compounds containing amino ($–NH_2$) group are the bases. The rest of the organic compounds containing various functional groups are neutral in nature**.** Usually the following combination of mixtures of organic compounds is given for the separation. 1] Acid + Base 2] Acid + Neutral 3] Phenol + Base 4] Phenol + Neutral 5] Base + Neutral 6] Neutral + Neutral (Acid + Phenol combination is usually not given)

After separation of the organic compound from the mixture, the individual compound is systematically analyzed. The process of analysis / identification of an organic compound is called **"organic spotting".**

Principles of separation: Solid Mixture:

Generally two components present in the mixture are of different nature. They may differ in their solubility in water, acids, and alkalies or in some common solvents. The separation of two components of the solid mixture is achieved by dissolution of one component in a solvent or a reagent leaving behind the insoluble component which is collected by filtration.

Separation of organic mixture is based on the chemical nature of components like difference in polarities, acidic or basic strength. General method developed for the separation is based on the concept of converting one of the components in to salt which being polar becomes soluble in water. For example, an acid dissolves in sodium bicarbonate solution as it forms its salt sodium benzoate and can be regenerated by neutralization of the solution with hydrochloric acid. Aniline (or bases) forms its salt aniline-hydrochloride & goes into aqueous solution when treated dilute HCl or dilute sulphuric acid. Acetanilide dissolves in hot water and can be obtained back by evaporation of the solvent.

Compounds differing in acidic strength can be separated by extraction methods. Strong acids form salts with sodium bicarbonate solution whereas the weaker acids do not react with this weak base. So, weakly acidic Phenols dissolve in sodium hydroxide solution but not in sodium bicarbonate. So it is necessary, at the beginning itself, to find out the nature of the components

of a solid-solid binarymixture before starting the actual separation.

Sl.No.	Test	Observation	Inference
1	Mixture + $NaHCO_3$	Partially soluble with effervescence	One component is Carboxylic acid.
2.	Mixture + NaOH	Partially Soluble in NaOH	One component is Phenol / acid.
3.	Mixture + HCl	Partially Soluble in HCl	One component is base (an amine).

Note: If only one component is detected then the remaining component is **neutral.**

Systematic analysis of the individual compounds: The two components in their pure forms are now analysed in the following systematic manner.

1. Preliminary tests
2. Identification of nature of the compound
3. Determination of melting point or boiling point.
4. Detection of Elements
5. Detection of functional groups
6. Identification of the compound
7. Confirmation of the compound through preparation of derivative.

IDENTIFICATION OF NATURE OF SOLID-SOLID BINARY MIXTURES

Take 5 mg of solid mixture in a test tube, add reagents as given below and observe.

Sl. No	Test	Observation	Inference
1	Mixture + 1cc $NaHCO_3$ solution. Shake well & filter the above solution, (if soluble)- Residue* Filtrate + Conc. HCl, cool (add ice)	Effervescence & Partially soluble Precipitate	One component is **Carboxylic acid.** **Carboxylic acid** is present.
	If above test is negative, perform the following tests.		
2.	***Residue** from above solution or **Mixture +** 1cc NaOH solution. Shake well & filter the above solution, Filtrate + Conc. HCl, cool (add ice)	Partially Soluble in NaOH Precipitate	One component is **Phenol**. **Phenol** is present.
3.	Mixture + 1cc HCl (1:1), Shake well & add H_2O filter the above solution, Filtrate + NaOH cool. (add ice pieces)	Partially Soluble in HCl Precipitate	One component is **base** (an amine). **Base** (an amine) is present.

If only one component is detected then the remaining component is **neutral.**

Conclusion: Nature / type of the given binary mixture is_____

Note: If one component of mixture is soluble both in $NaHCO_3$ and NaOH solutions gives ppt with Conc.HCl, nature of the component is **ACID.** If it is insoluble in $NaHCO_3$ but soluble only in NaOH and gives ppt with Conc. HCl then nature of the component is **PHENOL**

1. SEPARATION OF THE COMPONENTS OF A BINARY MIXTURE

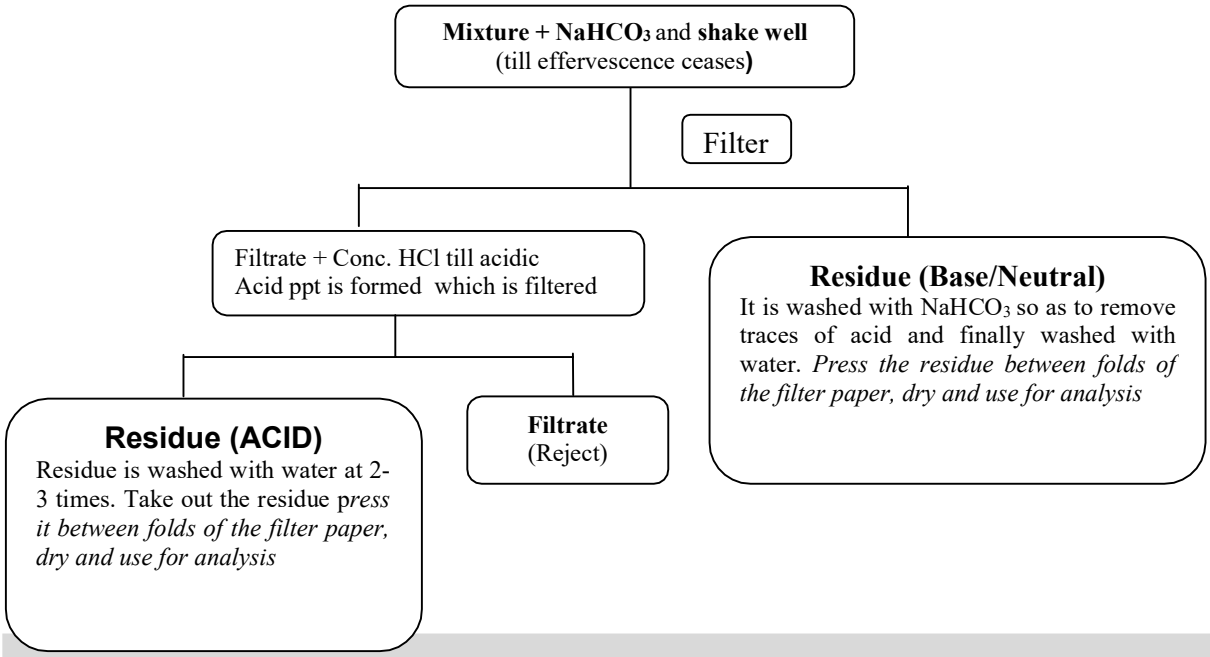
Follow the scheme according to the type of binary mixture

SCHEME - I

(ACID + BASE or ACID + NEUTRAL MIXTURE)

Separation of two components when one of the component is acid i.e., given mixture is of the type Acid + Base or Acid + Neutral

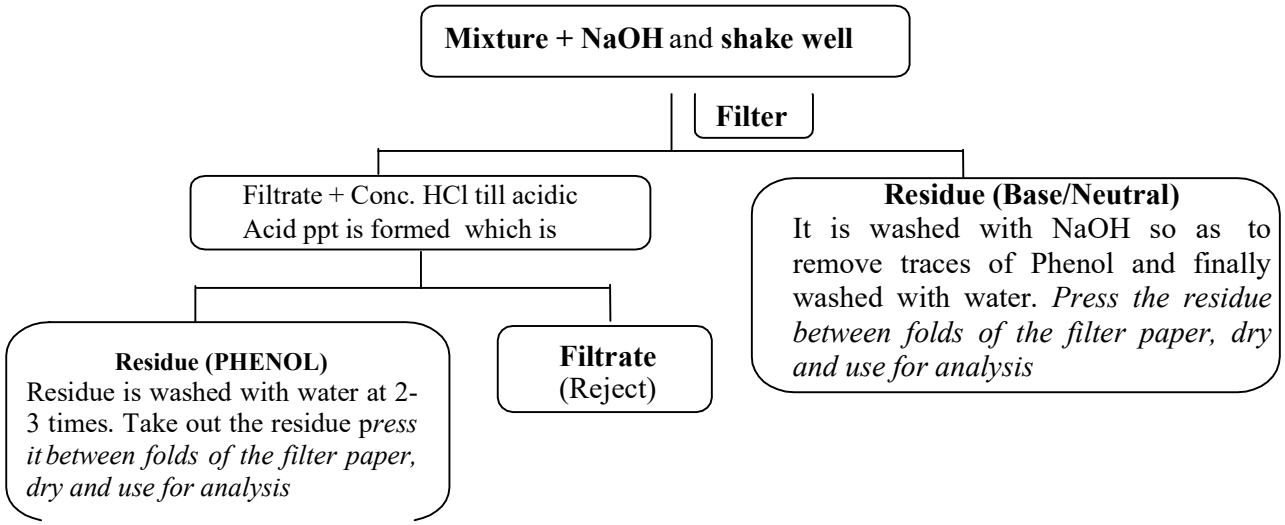
Take about 85% given mixture in a beaker. Add 10% sodium bicarbonate solution till there is no effervescence. Stir thoroughly with a glass rod and filter. Acidify the filtrate with conc. HCl. Follow below mentioned scheme.



SCHEME - II

PHENOL + BASE or PHENOL + NEUTRAL MIXTURE

Take the mixture in a beaker. Add 10% NaOH solution till alkaline . Stir thoroughly with a glass rod andfilter. Acidify the filtrate with conc. HCl. Follow below mentioned scheme.

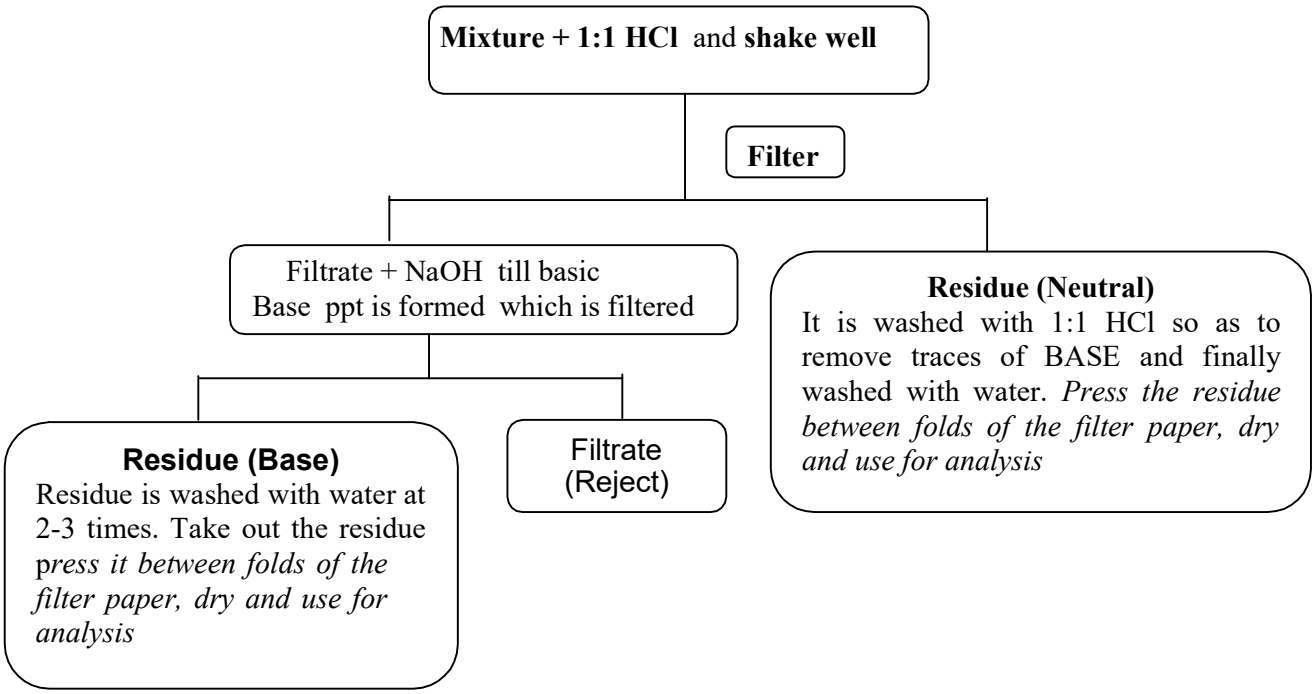


SCHEME - *III*

(BASE + NEUTRAL MIXTURE)

Separation of two components when one of the component is Base i.e., given mixture is of the type *Base + Neutral*

Take the mixture in a beaker. Add 1:1 HCl . Stir thoroughly with a glass rod and filter. Add NaOHsolution to the filtrate till alkaline and filter. Follow below mentioned scheme.



QUALITATIVE ANALYSIS OF ORGANIC COMPOUND

I. Preliminary Tests

S.N	TEST	OBSERVATION	INFERENCE
1.	**Appearance and Colour**	Colourless solids	**<u>Acids</u>** Salicylic acid, Phthalic and, Anthranilic acid may be present **<u>Neutral Compounds</u>** Naphthalene, Acetanilide, Diphenyl, Benzamide, Benzophenone
		Coloured solids	
		Cream coloured solid Pink (or pale brown) Dark brown Pale yellow Turmeric or greenish yellow Black/dirty green shining crystals Cream coloured solid Pink (or pale brown)	Cinnamic acid *β*-Naphthol *α*-Naphthol *m*-dinitrobenzene *m*-nitroaniline or *p*-nitroaniline may be present *p*-toluidine may be present Cinnamic acid *β*-Naphthol
2.	**Odour**	Pleasant odour Moth ball smell Cinnamon like odour Phenolic odour Fishy odour Odour of bitter almonds No Characteristic odour	Diphenyl may be present Naphthalene Cinnamic acid Naphthols Amines (*p*-toluidine, *m*-nitro ar or *p*-nitroaniline)*m*-dinitrobenz Carboxylic acids (Except cinnamic acid)
3.	**<u>Beilstien's Test</u>** Heat a loop of copper wire till it does not impart green colour to the flame. Cool, and take substance on loop of copper wire and then heat it.	(a) Burns with sooty flame	Aromatic compounds present
		(b) Burns with non-sooty flame	Aliphatic compounds present
		(c) Green edged flame after the initial sooty flame has vanished	Halogenated compounds present ***Exception:*** Urea gives a green flame due to cyanide of copper formed and not due to halogen

Conclusion: The given compound_____(Aliphatic / Aromatic)

SOLUBILITY TEST (IDENTIFICATION OF NATURE OF THE COMPOUND)

II. Solubility Test		
Take a little compound in a test tube and test the solubility in the following solvents.		
a) Compound(0.5 g) + water (1ml) Shake well and test with litmus paper ***If insoluble*** **Compound** + water + heat Shake well and test with litmus paper	Soluble in cold water and solution is acidic to litmus. (blue to red) Sparingly soluble in cold but soluble in hot water and solution is acidic to litmus. (blue to red) Soluble and the solution is neutral to litmus.	Carboxylic acid (Anthranilic acid) may be present Carboxylic acids(Phthalic acid, Salicylic acid, Cinnamic acid etc.) may be present Acetanilide, Benzamide may be present
b) Compound (0.5 g) + $NaHCO_3$ (1 ml) and Shake well	Soluble with effervescence	Carboxylic acid is present
c) Compound (0.5 g) + NaOH (1ml) and shake well	*Dissolves in NaOH and $NaHCO_3$ and reprecipitated by adding conc. HCl Dissolves only in NaOH but not in $NaHCO_3$	Carboxylic acid is present Naphthols (phenol) present
d) Compound + 1:1 HCl and shake well	Soluble and reprecipitated by adding NaOH Soluble in water & dil HCl	Bases like amines, -p-toluidine) may be present Acidic (Anthranilic acid) or neutral(acetanilide)may be present
e) Compound + Conc. H_2SO_4	**Soluble** with colour (yellow) Soluble with red colour In soluble	Ketones may be present Cinnamic acid may be present Aromatic Hydrocarbons may be present

Note: If the given compound is soluble in H_2O & acidic to litmus, and it is soluble in $NaHCO_3$ & NaOH – Acidic

- If the given compound is soluble only in NaOH & insoluble in $NaHCO_3$ & reprecipitated by adding Con.HCl- Phenol
- If the given compound is soluble only in HCl & reprecipitated by adding NaOH & insoluble in NaOH & $NaHCO_3$ – Basic.
- If the given compound is soluble in H_2O & neutral to litmus, and it is insoluble in $NaHCO_3$, NaOH & HCl or soluble/ insoluble in all –Neutral(Aromatic Hydrocarbons,amides, Anilides etc.)
- *If substance gives test with both $NaHCO_3$ solution as well as NaOH, then report as Carboxylic acid. If fails to give test with $NaHCO_3$ solution but soluble only with NaOH, report it as* ***Phenol***

II. TEST FOR SATURATION AND UNSATURATION

i. Baeyer's reagent (Alkaline $KMnO_4$) 0.2 g comp. + 2cc Na_2CO_3 solution + 2-3 drops of very dilute $KMnO_4$ solution	Decolourisation of $KMnO_4$ No decolourisation of $KMnO_4$	*Unsaturated compounds may be present Saturated compounds may be present
ii. ii Bromine water or Bromine in Carbon tetra Chloride 0.2 g comp. + 2cc bromine water. (If compound is water insoluble perform the test with bromine in carbon tetra chloride).	Decolourisation of Br_2 No decolourisation of Br_2	Unsaturated compounds may be present Saturated compounds may be present

** Quickly oxidisable compounds like phenols, aromatic amines. Aldehydes & ketones change purple colour to brown or black at once.*

Conclusion: The given compound is_____(Saturated / Unsaturated)

III. DETERMINATION OF PHYSICAL CONSTANT

Determine physical constant (melting point) M.P. using Thiele's Apparatus or Electric melting point instrument

The melting point of the given compound is_____$^{\circ}$C(Observed)

Literature value..... $^{\circ}$C

The melting point is represented in range by $\pm$ 0.2^0C. for example 156^0C - 158^0C or 157^0C - 159^0C

IV. DETECTION OF ELEMENTS:

Generally organic compounds contain Nitrogen(N), Halogen(X) and Sulphur(S) along with Carbon, Hydrogen and (Oxygen). For the detection of N, X, and S the **Lassaigne's** test is performed.

Preparation of Sodium fusion extract (S.E.)

Place a piece of dry sodium metal (*dried by pressing between folds of the filter paper*) in a fusion tube and heat till sodium melts to form shining globule. Add a pinch of an organic compound and heat slowly and then strongly until the tube becomes red hot. Plunge the tube at once in a china dish or 50 ccl beaker containing 5 cc. of distilled water. Boil the resulting contents to concentrate for about five minutes and filter the hot solution. The filtrate so obtained is called as ***Lassaigne's sodium fusion extract (S.E.).***

i. <u>Test for Nitrogen (N)</u> 1 ml of S.E. + 1ml of freshly prepared saturated $FeSO_4$ solution + 1or 2 drops NaOH, boil well, add 2 drops of $FeCl_3$, cool thoroughly and acidify with conc. HCl or dil. H_2SO_4.	Blue ppt or greenish blue coloured solution	Nitrogen present
ii. <u>Test for Sulphur (S)</u> **a) *<u>Nito prusside solution test</u>*** 1 ml of S.E. + 3-4 drops of fresh and very dilute sodium nitro prusside solution + 1or 2 drops NaOH solution. **b) *<u>Lead acetate solution test</u>*** 1 ml of S.E. is acidified with 1ml of dilute acetic acid + 2-3 drops of lead acetate solution.	Intense purple colour Black ppt of PbS	Sulphur present Sulphur present
iii. <u>Test for Halogens (X)</u> 2 ml of S.E. treated with dil HNO_3 till acidic boil well, cool and add few drops of Silver nitrate ($AgNO_3$) solution.	i. White curdy ppt. readily soluble in ammonia solution. ii. Pale yellow ppt. soluble in ammonia solution. iii. Yellow ppt. insoluble in ammonia solution	Chlorine present Bromine present Iodine present

Conclusion : The compound contains the elements : C, H, (O) and ……

V. DETECTION OF FUNCTIONAL GROUPS:

The functional groups are detected based on the elements present in the compound and categoried into the following division; **a]** C, H,(O) **b]** C, H, (O) and N **c]** C, H, (O), N and S **d]** C, H, (O), N , and X and **e]** C, H, (O), N, S, and X

Division: I : Compounds containing elements C, H, & (O). The compounds may be Acids / Phenols / Neutral.

1. TEST FOR CARBOXYLIC ACIDS

DISTINGUISHING TESTS FOR ACIDS

<u>Neutral $FeCl_3$ Test :</u> Compound + 1 ml H_2O heat to dissolve + 3 drops of neutral $FeCl_3$ Solution and observe.	(a) Violet colour in cold disappearing by HCl (b) Buff coloured ppt (warm if you do not get in cold) dissolved by ammonia or HCl . (c) Reddish brown ppt or buff coloured ppt soluble in HCl.	Salicylic acid present Cinnamic acid present Phthalic acid present

Confirmatory Tests for Carboxylic Acids		
C.T. for Salicylic acid : compound + 5drops methyl alcohol + one drop of conc. H_2SO_4 warm cool and pour in cold water taken in a beaker.	Smell of oil of wintergreen (Iodex smell)	Salicylic acid is present and **confirmed**
C.T. for Cinnamic acid : To the aqueous solution of the acid + 2-4 drops of $CaCl_2$ Solution	White ppt. insoluble in acetic acid	Cinnamic acid is present and **confirmed**
C.T. for Phthalic acid : (Flourescein test) : Fuse a pinch of the compound with equal quantity of resorcinol, Cool + 2-3 drops of conc. H_2SO_4 warm, cool and pour in water containing 2-5 drops of NaOH taken in a beaker.	Reddish green fluorescence (red colour with a green fluorescence)	Phthalic acid is present and **confirmed**

2. TEST FOR PHENOLS

Distinguishing Tests for phenols (α – Naphthol & *β*-Naphthol)

i. Neutral $FeCl_3$ solution Test Sub + alcohol, shake well and add 1-2drops of neutral $FeCl_3$ solution	a) Green colour immediately changing to a white ppt. b) White ppt slowly changing to violet.	*β*-Naphthol present *α*-Naphthol present
C . T. for Naphthols **ii. Phthalein fusion Test** 0.2g sub + 0.2g Phthalic anhydride + 3drops of con. H_2SO_4 fuse the mixture in a dry test tube gently for about 5-10 minutes. Cooled and diluted with 2ml water and pour into beaker containing 10ml of 10% NaOH solution .	a) Very faint green colour with slight blue fluorescence b) Green colour	*β*-Naphthol present & Confirmed *α*-Naphthol present & Confirmed
C . T. for Naphthols 0.1 g. of substance + 5ml of 10% NaOH solution + Few drops chloroform + Copper turnings and warm gently	a) Blue colour to the solution b) Blue colour changes to green-brown on exposure	*β*-Naphthol present & Confirmed *α*-Naphthol present & Confirmed

3. TEST FOR NEUTRAL COMPOUNDS (KETONES AND AROMATICHYDROCARBONS)
(Benzo phenone, *Naphthalene and Diphenyl*)

Test for Ketone (Benzo Phenone) (a) Sub + Conc. H_2SO_4. (b) Sub + Dry sodium metal (rice grain size) fuse on gentle heating	Yellow solution Deep blue colour	Benzophenone present Benzophenone present and confirmed
2,4 – DNP Test Take Compound in a TT, add ethyl alcohol + Brady's reagent (2,4,DNP) warm on water bath. (*take orange ppt. as derivative)	Orange ppt.	Benzophenone is confirmed
Test for Hydrocarbons 0.1 g. of substance + 0.5cc of Conc. H_2SO_4	Insoluble	Hydrocarbon Present (Naphthalene or Diphenyl may be present . confirmedon the basis of their M.P.s)
C.T. for Naphthalene Compound + benzene + Picric acid in benzene, mix & shake well	Yellow ppt.	**Naphthalene** is present and confirmed
C. T. Dipehenyl Compound (0.5g) + 2 ml of fuming HNO_3 (or 1 cc of con. H_2SO_4 + 1 cc of Con. HNO_3) in a conical flask. Heat for 5 minutes, cool and pour it into ice cold water. (* take white ppt. as derivative)	White ppt.	(Biphenyl) Diphenyl is present and confirmed

Division II: Compounds containing elements C, H, (O) & N. The compounds may be Acids/ Bases / Neutral.

Test for Acids (Anthranilic acid)

i. Sub + $NaHCO_3$ solution	Soluble with effervescence	Acid (-COOH) present
ii. Test for $-NH_2$ Group by Diazotisation: ***Diazotization test*** ***Diazotization:*** 0.1g Comp. + 3 times conc. HCl in a test tube and cool in ice cold water + add few drops of ice cold solution of sodium nitrite($NaNO_2$). Add an ice cold solution of β-Naphthol in NaOH to the above solution.	Orange dye stuff	'**$-NH_2$**' (primary amino) group present.
iii. Comp. + Alcohol	Soluble with blue fluorescence	Anthranilic acid present

iv. C.T. for Anthranilic acid Mix a small amount of substance with equal amount of $CaCl_2$ and heat gently. Dissolve the product in 2 ml. of alcohol.	Red coloured solution exhibiting violet fluorescence on standing	Anthranilic acid present and Confirmed
v. 0.1g Sub + $ZnCl_2$ fuse by gentle heating dissolve the product in alcohol	Yellow colour	Anthranilic acid present and Confirmed

TEST FOR BASES: (*p*- Toluidine or *p*-Nitroaniline or *m*-Nitro aniline)

Sub + 1:1 HCl	Soluble and re precipitation with NaOH	Base present
Test for $-NH_2$ Group by Diazotisation: ***Diazotization test*** ***Diazotization:*** 0.1g Comp. + 3 times conc. HCl in a test tube and cool in ice cold water + add few drops of ice cold solution of sodium nitrite ($NaNO_2$). Add an ice cold solution of *β*-Naphthol in NaOH to the above solution.	Orange Red dye	**$-NH_2$ group** is present Amine is present (p-Toluidine or Nitro aniline)
Test for $-NO_2$ group : Mulliken's Test (Neutral Reduction test) : Dissolve the Compound (0.3 g) in 0.5 ml of hot 50% aqueous alcohol + 5-6 drops of 10% $CaCl_2$ + pinch of Zn dust. Boil the mixture for a minute. Filter and test the filtrate with Tollen's reagent (To silver nitrate add NaOH. Then add NH_4OH till the ppt. first formed dissolves)	A black ppt. or grey ppt.	**$-NO_2$ group** is present (Nitro anilines present)
C.T. FOR NITRO ANILINES:		
Dissolve the Compound in (0.2 g) 0.5 ml acetone + titanous chloride reagent,(0.5 ml) warm the mixture very gently.	Discharge of Mauve colour of the titanous chloride	*m*- & *p*-Nitro aniline is present and confirmed
Further these m- & p-Nitro anilines are confirmed by their melting points.		
C.T. FOR NITRO *P*-TOLUIDENE		
0.5g sub + 3-4 drops of dilute HCl. +2 ml water + 2-3 drops of $FeCl_3$ solution.	A pale yellow colour changing to red	*p*- Toluidene present and confirmed

TEST FOR NEUTRAL COMPOUNDS

COLOURLESS (BENZAMIDE & ACETANILIDE), M-DINITROBENZENE (YELLOW)

Compound + Water warm	Soluble in hot water	-Anilides(Acetanilide) &(Benzamide) present
Compound + NaOH, Warm	Smell of NH_3 No smell of NH_3 *(Fishy odour of aniline)*	Amide is present **(Benzamide)** Anilides(Acetanilide) is present
Confirmatory tests for Benzamide, Acetanillide or m-dinitrobenzene		
C.T. for Benzamide Boil the compound with dilute NaOH for 5 minutes, cool and acidify with dilute H_2SO_4	White ppt. of benzoic acid	Benzamide is present and confirmed
C.T. for Acetanilide Compound + dilute HCl, heat to dissolve, then cool in ice + ice cold solution aq. $NaNO_2$ solution + ice cold solution β-Naphthol in excess NaOH.	Bright Red ppt.	Acetanilide present and confirmed

Division –III: Compounds containing elements C, H, (O) & Halogens.

i. Beilstien,s Test Heat a loop of copper wire till it does not impart green colour to the flame. Cool, and take substance on loop of copper wire and then heat it.	Green edged lame after the initial sooty flame has vanished	Halogen present
Test for Hydrocarbons 0.1 g. of substance + 0.5 cc of Conc. H_2SO_4	Insoluble	Halogenated hydrocarbon Present

Note: as per the syllabus halogen compounds are not included

VI. BROAD INFERENCE

S.N	Particulars	Inference
1.	Nature	:
2.	Aliphatic / Aromatic	:
3.	Saturated / Unsaturated	:
4.	Physical Consatant (Melting point)	M.P. =_____°C Literature_____°C
5	Elements present	
6	Functional group (s) present	:
7	Name of the compound	:
8	Molecular formula	:
9	Structural formula	:
10	Name of the Derivative	:
11	Structural formula of the Derivative	:
12	Physical Constant (Melting point) of the derivative	M.P. =_____°C Literature_____°C

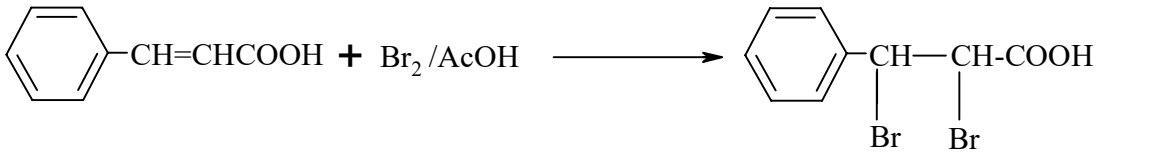
PREPARATION OF DERIVATIVES

A derivative may be defined as a chemical compound obtained by the chemical reaction of a substance, generally retaining the structure of parent substance.

Preparation of a derivative constitutes the last and of course confirmatory step in systematic identification of an organic compound since the identification of organic compound is said to be correct if the melting point of the derivative coincides with the melting point given in the literature for the same derivative of the same compound.

1. **Dibromo derivative of Cinnamic Acid (2,3-Dibromo-2-phenyl propionic acid)**

   Dissolve about 0.5g of cinnamic acid in 5 ml. of glacial acetic acid in a 100 ml. beaker or conical flask and add excess (5-6ml) of solution of bromine in acetic acid in small lots with constant shaking. Allow the reaction mixture to stand for about 10 min. and dilute with water. Filter, and wash the product with water and dry. Recrystallise from hot water and determine its M.P.

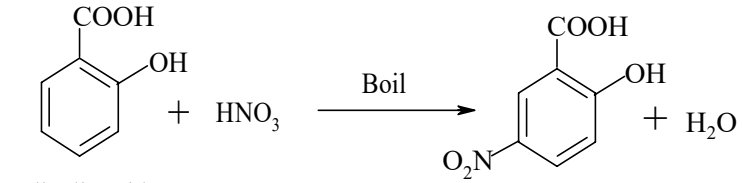


3-phenyl-prop-2-ene-1-oic acid (Cinnamic acid)

2,3-Dibromo-3-phenylpropanoic acid

2. **5-Nitro Salicylic acid from Salicylic acid**

   Dissolve the compound (0.5 gm) in hot water and add 0.5 ml of dilute HNO_3 and boil for 5 minutes. Yellow solution is obtained Pour it into the ice – cold water taken in a beaker. Solid separates. Filter, and wash the product with water and dry. Recrystallise from hot water and determine its M.P.

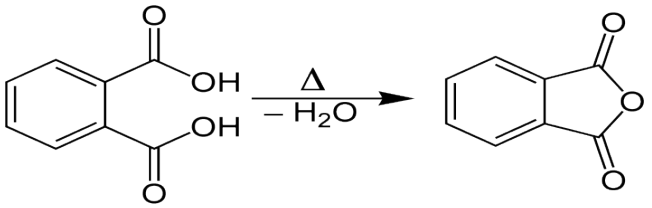


Salicylic acid

5-Nitro salicylic acid

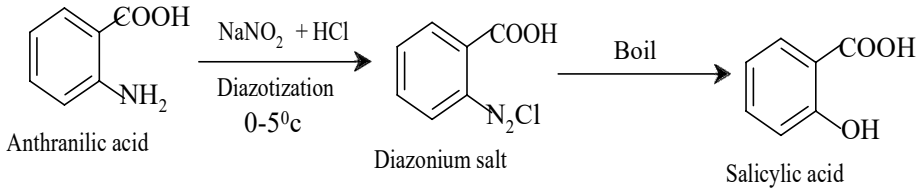
3. **Phthalic acid to Phthalic anhydride**

   Take 0.5g Phthalic acid in a china dish covered with filter paper having a hole in the middle. Place an inverted funnel on the filter paper, lightly plug the nozzle with cotton or filter paper, and heat the dish on a sand bath. On sublimation the acid converts into Phthalic anhydride which collects on the inner side of the funnel. Collect the crystals of phthalic anhydride and determine its M.P.



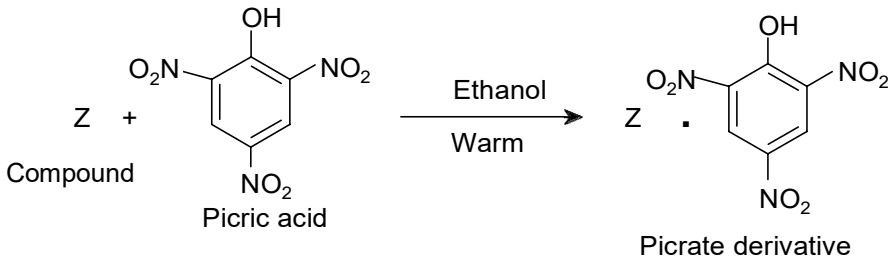
4. Anthranilic acid to Salicylic acid

Diazotise anthranilic acid as follows: Dissolve 0.5g of acid in about 4ml of 1:1 HCl and cool thoroughly. To this solution, add $NaNO_2$ solution drop by drop till a drop of the solution just tints the starch – iodide paper blue, showing a slight excess of HNO_2. Boilthe solution until the evolution of nitrogen ceases. Cool and shake thoroughly, Salicylic acid separates out easily. Dry and recrystallise from hot water, determine its the M.P.



5. Picrate derivative for α-Naphthol , β-Naphthol and Naphthalene

Dissolve 0.5 to 1 g of the given substance (α – naphthol or β – naphthol or naphthalene) in ethanol. Add 2-3 ml of saturated solution of picric acid in the ethanol. Picrate derivative separates out on mixing. In case no solid separates on mixing , heat the reaction mixture on hot water bath. Cool thoroughly. Filter the product, recrystallize from alcohol(if necessary), dry and determine its M.P.

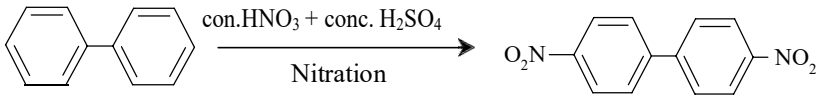


Z = α – Naphthol or β – Naphthol or Naphthalene whichever is given

6. *p,p'*- Dinitro diphenyl from Diphenyl

Dissolve 0.5g. substance in 3ml of conc H_2SO_4 add 2ml. conc HNO_3. Shake well and place the test tubein a gently boiling water bath for about 5-10 minutes with occasional shaking. Pour the reaction mixture

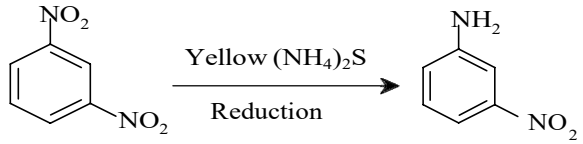
in 50ml, ice cold water with constant stirring. Filter, dry and recrystallise from aqueous alcohol anddetermine its M.P.



Diphenyl *p,p'*-Dinitro diphenyl

7. *m*-Nitroaniline from *m*-Dinitrobenzene

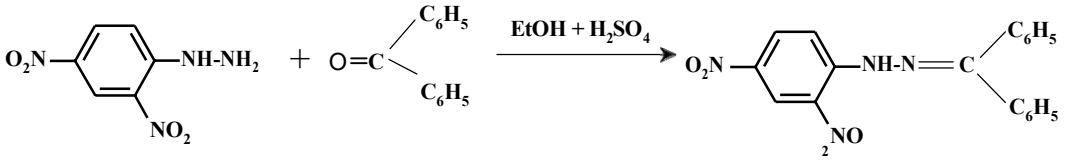
Dissolve 0.5g. of m-Dinitrobenzene in 25ml. of boiling water. To the boiling solution, add yellow ammonium sulphide till the yellow colour is persistent. Boil further for five minutes. Filter while hot. On cooling, yellow needles of *m*-Nitro aniline separates out. Recrystallise from hot water and determine its M.P.



m-Dinitro benzene *m*-Nitro aniline

8. 2,4-Dinitrophenylhydrazone derivative from Benzophenone

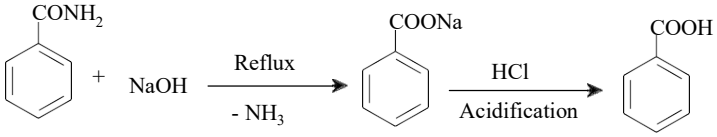
Take 0.5 g of benzophenone in a dry test tube and dissolve it in few drops of water or ethanol. Add 1cm^3 of 2,4 – DNP solution. Heat the mixture on water bath for few minutes and cool it in ice. Orange orred crystalline precipitate separates out. Filter, dry and take the melting point.



2,4-Dinitro phenyl hydrazine Benzophenone Benzophenone-2,4-Dinitro phenyl hydrazone

9. Benzoic acid from Benzamide

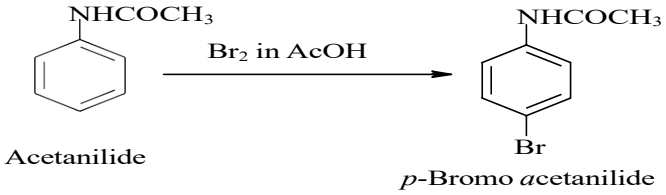
Take 0.5g. of benzamide in a 100ml. R.B. flask or conical flask and add 6-7ml. of 25% NaOH solution. The flask is fitted with reflux (air) condenser. Reflux the contents until all ammonia has been driven off (it takes about half an hour) and then cool. Add concentrated hydrochloric acid drop wise till the reaction mixture is strongly acidic and the benzoic acid separates out as a derivative. Filter and recrystallise from hot water. Determine melting point.



Benzamide Sodium benzoate Benzoic acid

10. *p*-Bromo acetanilide from Acetanilide

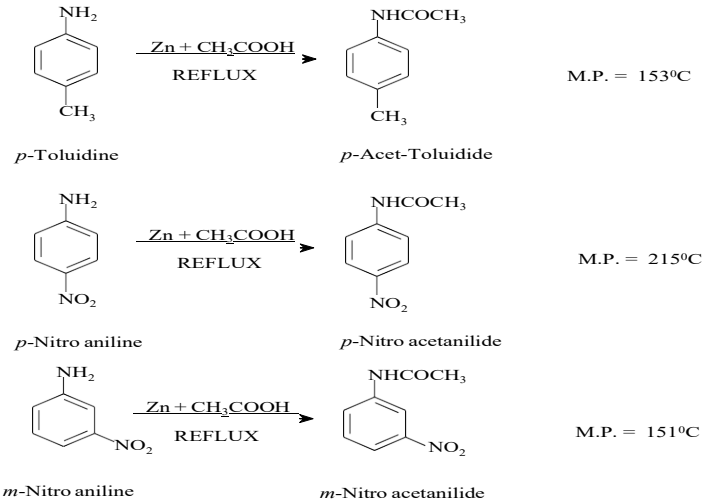
1g. of acetanilide is dissolved in 5ml. glacial acetic acid in a 100 or 50ml. conical flask. To this add bromine in acetic acid in small quantities till colour of bromine persists to solution. The mixture is allowed to stand for 10-15 minutes and then poured into ice cold water with constant stirring and filter the product, wash with cold water and recrystallise from 25% ethanol. Determine the melting point.



Acetanilide — *p*-Bromo *a*cetanilide

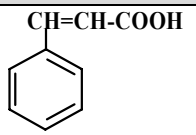
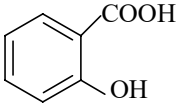
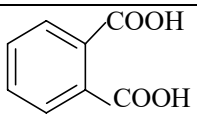
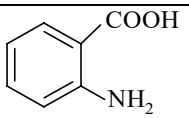
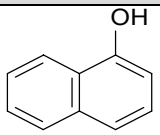
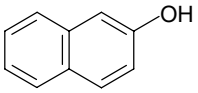
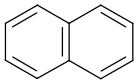
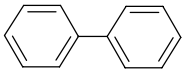
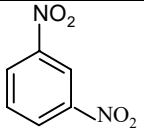
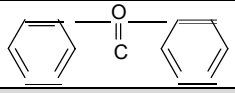
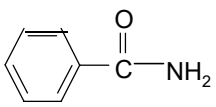
11. Acetyl derivative.

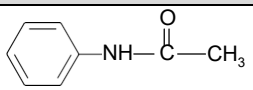
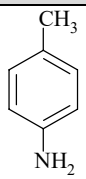
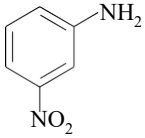
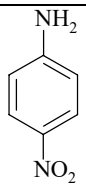
A mixture of *p*-toluidine or *m*-nitroaniline or *p*-nitroaniline (1g) and zinc dust (0.5 g) in acetic acid (5 ml) in a 100 ml round bottom flask was heated over a gentle flame using water condenser. Heating was continued for about 30min. The reaction mixture was then carefully poured in cold water (20 ml) in a 100 ml beaker with cooling and vigorous stirring. The shining crystals of respective anilides were separated slowly. After 15 min. the anilide crystals were collected by filtration. The solid crystals were washed over the Buchner funnel with water and the products driedand take melting point.



Picrate derivative can also be performed for nitro anilines. Procedure is remained same to that of Naphthols.

Name, Structure and M.P. of derivatives of Organic Compounds

Compound	Melting point range (^{0}C)	Molecular Formula	Structural formula	Derivative Melting point
1. Cinnamic acid	133 -134	$C_6H_5CH=CH-COOH$		2,3 – Dibromo-3- phenyl propionic acid (**194-195^{0}C**)
2. Salicylic acid	157 - 158	$C_6H_4(OH)COOH$		5-Nitro salicylic acid (**230-231^{0}C**)
3. Phthalic acid	193-213	$C_6H_4(COOH)_2$		Phthalic anhydride (**127-128^{0}C**)
4. Anthranilic acid	148-149	$C_6H_4(NH_2)COOH$		Salicylic acid **(157-158^{0}C)**
PHENOLS				
5. α-Naphthol	93 - 94	$C_{10}H_7OH$		Picrate derivative (**189-190^{0}C**)
6. β-Naphthol	121-122	$C_{10}H_7OH$		Picrate derivative (**156-158^{0}C**)
NEUTRALS **1. Hydrocarbons**				
7. Naphthalene	79-80	$C_{10}H_8$		Picrate derivative Naphthalene picrate (**149-151^{0}C**)
8. Diphenyl	70-72	$C_{12}H_{10}$		*p,p'*- Dinitro diphenyl (**233-234^{0}C**)
9. *m*-Dinitrobenzene	89-90	$C_6H_4(NO_2)_2$		*m*-Nitroaniline (**114-115^{0}C**)
2. KETONES				
10. Benzo phenone	48-49	C_6H_5-CO- C_6H_5		2,4 – Dinitrophenyl hydrazone (**238-239^{0}C**)
3. AMIDES				
11. Benzamide	128-129	C_6H_5-$CONH_2$		Benzoic acid (**122-123^{0}C**)

4. ANILIDES				
12. Acetanilide	114-115	$C_6H_5NHCOCH_3$		*p*-Bromoacetanilide **(166-167^{0}C)**
BASES				
13. *p*-Toluidine	43-44	$C_6H_4(CH_3)NH_2$		*p*-Acet-toluidide **(153-154^{0}C)**
14. *m*-Nitroaniline	113-114	*o*-$C_6H_4(NO_2)NH_2$		*m*-Nitroacetanilide **(154-155^{0}C)**
15. *p*-Nitroaniline	147-148	*p*-$C_6H_4(NO_2)NH_2$		*p*-Nitroacetanilide **(255-257^{0}C)**

References:

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2. Organic Experiments VIIth Edition Louis F. Fieser Late Professor Emeritus Harvard University Kenneth L Williamson Mount Holyoke College
3. Systematic Lab experiments in Organic Chemistry- ArunSethi
4. Practical Organic Chemistry – Nadkarni and Kulkarni
5. Advanced Practical Organic Chemistry – N.K.Vishnoi
6. Practical Chemistry -.O.P.Pandey,D.N.Bajpai & S.Giri
7. A hand book of Analytical Chemistry– Subhash & Satish
8. Elementary Practical Chemistry–G.D.Sharma, Arun Bahl
9. Practical Organic Chemistry – V. K. Ahluvalia, Dhingra & Gulati

DISTRIBUTION OF MARKS	
Nature and separation	2 +3
Prelimanary tests	02
Element test	04
Physical constant	03
Functional Group test	04
Identification and Structure	03
Preparation of derivative	03
Physical constant of derivative	03
Systematic Presentation	03
Journal	05
Viva voce	05
TOTAL	**40**

SEPARATION AND QULITATIVE ANALYSIS OF LIQUID-LIQUID ORGANIC BINARY MIXTURES

Total No of hours/week : 3Hrs
Total No. of Hours : 45 Hrs

Total No of hours/week : 3Hrs
Total No. of Hours : 45 Hrs

CONTENTS
Separation of organic liquid binary mixture by distillation. Characterization of any one separated compound through preliminary tests, element test, physical constant, functional group test and preparation of suitable derivative and its physical constant. Low Boiling Liquids : Ethyl acetate, Acetone, Toluene, Chlorobenzene. High Boiling Liquids: Phenol, Aniline, Nitrobenzene, Benzaldehyde, Acetophenone, Bromobenzene.

Instructions:

In a batch of ten students, in the practical examination, five students may be given experiment number 1-6 (binary mixture) and remaining five students may be given physical experiments. In a batch of five students in the practical examination, not more than two students should get the same experiment.

SCHEME FOR PRACTICAL EXAMINATION

DISTRIBUTION OF MARKS	
Separation	03
Preliminary tests	02
Nature	02
Element test	04
Physical constant	03
Functional Group test	04
Identification and Structure	03
Preparation of derivative	03
Physical constant of derivative	03
Systematic Presentation	03
Journal	05
Viva voce	05
TOTAL	40

NOTE: In a batch of ten students, not more than two students should get the same mixture in the practical examination. Viva questions may be asked on any of the experiments prescribed in the practical syllabus. During practical examination chart may be referred whenever necessary.

SEPARATION OF ORGANIC LIQUID BINARY MIXTURE BY DISTILLATION

Principles of separation:

Liquid-Liquid binary mixture: If mixture is a given is homogeneous, it is possible that both componentsare liquids or one liquid and other solid that has dissolved in the liquid on mixing.

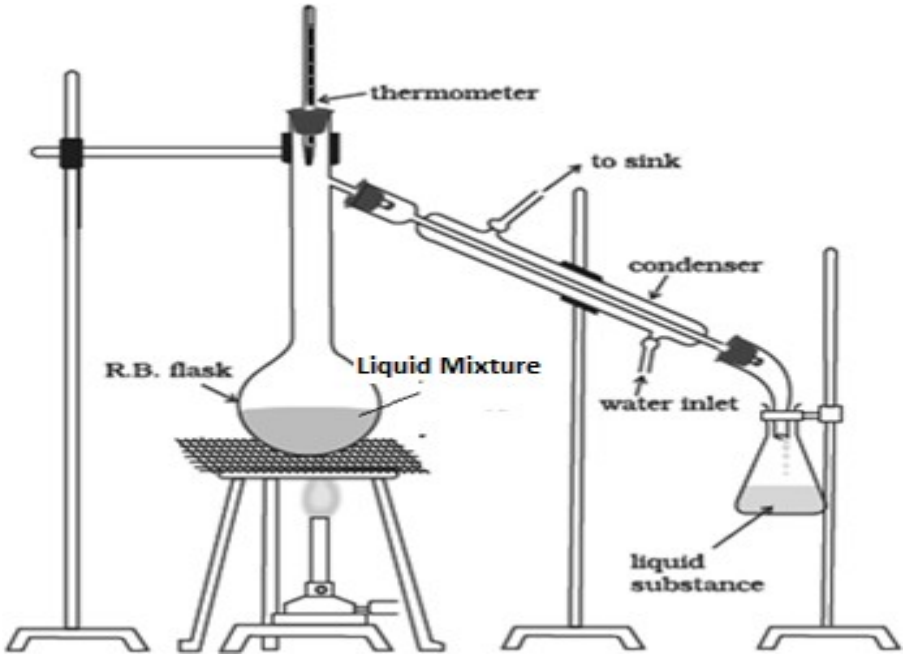
When both components are liquid, the mixture is separated by fractional distillation. The distillationshould be carried out slowly and carefully.

Scheme for actual separation of organic liquid- liquid mixture:

DISTILLATION OF A LIQUID MIXTURE

Place 15-20 cc of an unknown liquid mixture (say *10cc P + 10 cc Q*) that is to be purified by simple distillation and for which the boiling point range is to be determined.

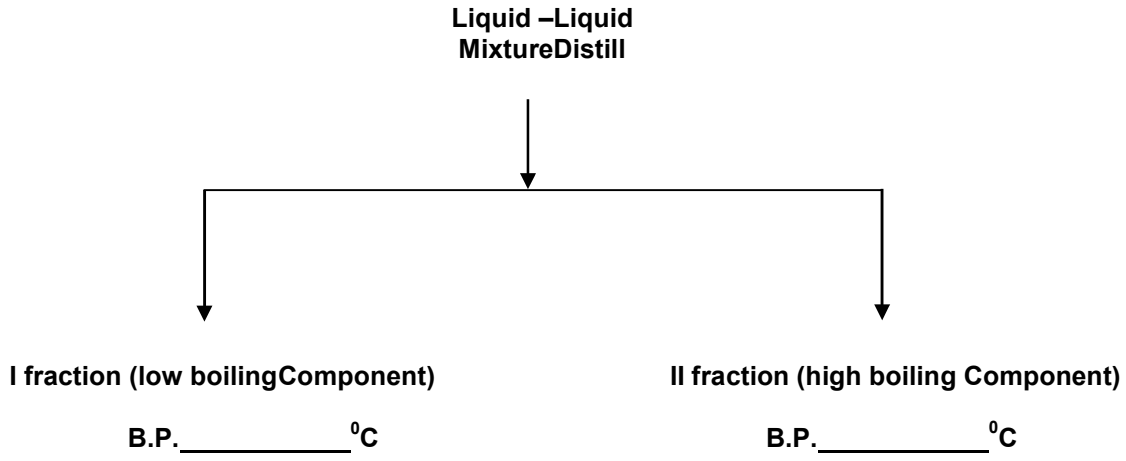
Step 1: Assemble the distillation apparatus (simple or fractional). Transfer the unknown liquid to a 50 cc round bottom flask (*this will be the distilling pot*). Add one boiling chip, and proceed to distill the liquid into a 10 cc graduated cylinder (*this will be the receiver*). Check the position of the thermometer (*the bulb of the thermometer must be below the arm of the distillation head*) and make sure that the bottom of the distillation pot touching the heating surface of the heating set. Now fix the condenser along with rubber tubes for water circulation. As shown in figure.



Step-2: Slowly turn on the water for condenser, and begin heating. Adjust the heating set to maintain a distillation rate of one drop per second. As the lower boiling component is distilled, the boiling point of the mixture in the distillation flask will increase. *Record the temperature after the first drop is collected and again after every 2 ml of distillate is collected. Collect at least 10 ml of distillate in a separate test tube labelled as Low boiling fraction* (component P). PRESERVE IT.

Step 3: Collect the next 10 ml of distillate, again recording the temperature after every 1 ml of distillate. Collection of last portion of distillate should continue until the temperature remains constant. If the distillation flask is approaching dryness, remove the heat source immediately and after cooling, transfer the distillate and any remaining liquid from the flask to the third test tube (component Q). KEEP IT.

Determine the boiling point range of the first fraction of the collected liquid and the third portion of the collected liquid. Identify the unknowns by their boiling points using the possible boiling points of compounds by referring the literature.



Qualitative analysis of Organic Compounds

After separation (distillation) of the organic compound from the binary mixture, the individual compound is systematically analyzed. The process of analysis / identification of an organic compound is called "organic spotting". The purpose of organic qualitative analysis is to spot a given organic substance and to substantiate its nature by performing a set of reaction/s with it. The frame work for qualitative analysis of the given organic compound will proceeds follows.

I) PRELIMINARY TESTS

S.N	Test	Observation	Inference
1.	State	Liquid	*Low boiling liquids*; Acetone, Ethyl acetate may be present. *High boiling liquids*; Aniline, Phenol,Acetophenone, Nitrobenzene,Toluene, Benzaldehyde, bromobenzene, Chlorobenzene may be present.
2.	Colour	Colourless Yellow Reddish/Brown	Benzaldehyde, Acetone, Acetophenone, Ethyl acetate, Toluene, Chlorobenzene may be present. Nitrobenzene, bromobenzene may be present. Phenol,Aniline may be present
3.	Odour	Phenolic Fishy Pleasant /Fruity Bitter almond	Phenol Amines (Aniline) may be present. Acetone, Acetophenone, Ethyl acetate, Bromobenzene, Chlorobenzene Benzaldehyde, Nitrobenzene
4.	Beilstein's Test : Heat a loop of copper wire till it does not impart green colour to the flame. Cool, and dip in the liquid and then heat it.	Burns with non-sooty flame Burns with sooty flame Burns with sooty flame followed by green edged flame	Aliphatic compound Aromatic compound Halogenated aromatic compound
Therefore, the given compound is ----------			
5.	Solubility Test		
i	Liq. + Water	Miscible in cold solution acidic to litmus	Acetic acid may be present

		Miscible in cold and neutral to litmus Immiscible	Acetone and ethylacetate may be present Phenol, aniline, toluene, chlorobenzene, benzaldehyde etc; may be present.
ii	Liq. + $NaHCO_3$ Solution	Miscible with effervescence	Acids present
	Above Sol. + dil HCl	Reappearance of oily drops or turbidity	Acid confirmed
iii	Liq. + NaOH	Miscible	Phenol present
	Above Sol. + dil HCl	Reappearance of oily drops or turbidity	Phenol confirmed
iv	Liq. + 1:1 HCl	Miscible	Base present
	Above Sol. + NaOH	Reappearance of oily drops or turbidity	Base confirmed

(if all the above tests are negative the nature of the given compound is NEUTRAL)

Note: A.S. = Above solution

Conclusion: The given compound is_____(Acid/Phenol/Base/Neutral)

6.	Test for Un-saturation.		
i	Br_2 water test: 2-3 drops of liquid + few drops of Br_2 water. If it doesn't give test treat with Bromine in carbon tetra chloride	Decolourisation of Br_2 water No decolourisation	Unsaturated compound Saturated compound
ii	Alkaline $KMnO_4$ test : Dissolve the compound in hot water + few drops of very dilute alkaline $KMnO_4$ solution	Decolourisation of $KMnO_4$ solution No decolourisation	Unsaturated compound present Saturated compound

Conclusion: The given compound is_____(Saturated/Unsaturated)

II. Determination of physical constant:

Using Thiel's tube the *boiling point* of given compound under investigation is determined.

Boiling point of the compound is....."C

III. Detection of Elements:

Generally organic compounds contain Nitrogen (N), Halogen (X) and Sulphur (S) along with Carbon, Hydrogen and (Oxygen). For the detection of N, X, and S the Lassaigne's test is performed.

Lassaigne's Test :

Take a small piece of clean and dry Sodium metal in a fusion tube and heat it slowly till the metal fuses. Cool and add 2-3 drops of liquid under investigation. Heat continuously till the fusion tube becomes red hot. Plunge the red hot fusion tube into about10 ml of distilled water taken in an evaporating dish. Break the fusion tube with a glass rod and boil the mixture for about 5 min and filter. The filtrate is called Sodium Extract (S.E) and use it for the test for Nitrogen, Halogen/s and Sulphur.

Test for Nitrogen : 1 cm^3 of S.E. + 1 cm^3 of freshly prepared $FeSO_4$ + 1 drop of NaOH soln. Boil and cool. Add a few drops of $FeCl_3$ and acidify with Conc. H_2SO_4 or Conc. HCl.	Green or blue colouration. (Prussian blue colour)	Nitrogen present
Test for halogens : 1 cm^3 of S.E. + dil HNO_3 boil and cool + $AgNO_3$ solution.	a) Curdy white ppt. easily soluble in NH_4OH b) Pale yellow ppt. sparingly soluble in NH_4OH c)Yellow ppt insoluble in NH_4OH	Chlorine is present Bromine is present Iodine is present
Test for Sulphur : S.E. (2ml) + 2-3 drops of sodium nitroprusside solution.	Violet colouration	Sulphur present

Conclusion: The elements present in the compound are C, H, (O) and .....

IV. Detection of Functional Group

It can be done on the basis of elements present in the compound, its nature and they are divided into following divisions.

Division I - C, H, & (O) Division II – C, H, (O) & N

Division III – C, H, (O) and Halogen

The given compound contains the elements C,H (O) & … The compound belongs to the division ……

V) DETECTION OF FUNCTIONAL GROUPS

Division I - C, H, & (O)

[Phenols, Neutral (Aldehydes, Ketones, Esters & Aromatic Hydrocarbons)].

B) Test for Phenols

i) **Br_2 Water Test** : Dissolve the given Compound in water or in acetic acid + Bromine water and observe	White ppt	Phenol is present
ii) Alcoholic $FeCl_3$ Test : Dissolve the given Compound in water or in acetic acid + alcoholic $FeCl_3$ solution and observe.	Violet Colouration	Phenol is present

Confirmatory tests for Phenols)		
i)**PhthaleinFusionTest:** Compound (1-2 drops) + a pinch of phthalic anhydride + 2 drops of conc. H_2SO_4, heat gently, cool, pour it in a beaker containing water and NaOH (5 drops)	Red (Pink) Colour	Phenol is present and confirmed
ii) **Leiberman's Nitroso Test** Compound (2-3 drops) + $NaNO_2$, heat gently, cool + Con. H_2SO_4 (5 drops)	A deep green to blue solution is formed at first which turns red when poured in to water containing few drops of NaOH	Phenol is present & confirmed.
C) Test for neutral compounds containing C,H& (O) (Aldehydes, Ketones & Esters)		
Brady's reagent Test: Compound + 2,4:DNP	Yellow crystalline ppt.	Benzaldehyde or (Ketones) Acetone or Acetophenone present.
Schiff's reagent test: Compound(1 drop)+Schiff's reagent(2-3 drops) and shake the mixture well. Keep for a while.	Pink colouration	Benzaldehyde is present.
	No Pink colouration	Acetophenone is present.
C.T. for Benzaldehyde:		
Silver mirror test (*Tollen's reagent test) : Compound(1 drop) +Tollen's reagent. Warm the mixture on a water bath without disturbing.	Silver mirror or grey ppt.	Benzaldehyde is present & confirmed
*Preparation of Tollen's reagent : Mix equal volume of 10% aqueous $AgNO_3$ (1 ml) & dil NaOH (1 ml) Add dilute NH_4OH drop wise till the brown ppt. just dissolves to get a clear solution.		
Ketones – Acetone & Acetophenone		
Aliphatic compound-Acetone, Aromatic compound-Acetophenone		
Compound (1-2 drops) + Sodium Nitroprusside solution(5 drops) + few drops of NaOH.	Red colouration Red coluration changes to blue on adding acetic acid	Acetone is present Acetophenone is present
C.T. for Acetophenone		
Brady's reagent Test: Compound + 2,4:DNP	Yellow ppt.	Acetophenone is present and confirmed.

C.T. for Acetone		
ii) Iodoform test: Compound(3-4 drops) + I_2 in KI solution till yellow colour persists + NaOH, heat the solution gently.	Yellow ppt.	Acetone is present and confirmed.
Esters - Ethyl Acetate		
Compound (5drops) + 1-2 drops of phenolphthalein and one drop of very dil. NaOH (Diluted 10 times), heat	Pink colour is formed, which disappears on heating due to the free acid formed by the hydrolysis of esters.	Ethyl acetate is present
C.T. Ethyl Acetate		
Feigl Test : 1-2 drop of compound + Hydroxylamine hydrochloride Solution(5 drops) + 5 drops of KOH in methanol solution. Boil for a minute, cool & acidify with dil HCl. + 1-2 drops of $FeCl_3$	Violet colouration	Ethyl acetate is present and confirmed
Test for Neutral compounds containing C & H only (Aromatic Hydrocarbons)		
Hydrocarbons(Toluene)		
Compound + Conc.H_2SO_4	Insoluble	Toluene is present
C.T. for Toluene		
Compound + Picric acid in Benzene shake well.	Yellow ppt.*	Toluene is present & confirmed
*Take it as picrate derivative with M.P. = 88°C		
Division II - C, H, (O) & N (Bases & Neutral compounds)		
Base – Amines (Aniline)		
Compound + dil HCl	Dissolves completely and reprecipitated by NaOH	Base (Amine) is present
Compound (2-3 drops) + $K_2Cr_2O_7$ (pinch) + conc. H_2SO_4 (3-4 drops) shake well.	Blue or Black colour	Anilne is present.

C T. for Aniline (Test for -NH_2 group)		
Azo-dye test: Compound + con. HCl (1:1) cool in ice + 10% ice cold $NaNO_2$ solution + 2-naphthol in NaOH.	Orange Red dye	Aniline present and confirmed (-NH_2 group is present)
Neutral -- Nitro Benzene		
Mulliken's Test (Neutral reduction test : Dissolve the Compound (4 drops) in a hot 50% aqueous alcohol + 5-6 drops of 10 % $CaCl_2$ + pinch of Zn dust Boil the mixture for a minute. Filter and test the filtrate with Tollen's reagent.	A black ppt.or grey ppt.	Nitro(-NO_2) group (Nitro benzene) is present.
C.T. for Nitro Benzene		
Compound(5 drops) + Glacial acetic acid(1 ml) + pinch of Zn dust, Boil cool, & add water(1 ml) +NaOH till alkaline + Sodium nitroprusside (2-3 drops)	Violet colouration	Nitro benzene is present and confirmed
DIVISION – III (C, H and Halogens(Br or Cl) (Bromobenzene or Chlorobenzene)		
Test for Bromobenzene		
Beilstein's Test: (Test for aliphatic or aromatic) Heat a small piece of copper foil in a non-luminous flame using pair of tongs until it imparts no colour to the flame. Cool, dip into the given organic compound and again hold it to the flame and observe	Burns with Sooty(smokey) flame followed by green edged flame	Bromobenzene or Chlorobenzene present
Compound + Alcoholic $AgNO_3$ & mix & warm	Pale yellow ppt. A white curdy ppt.	Bromobenzene is present Chlorobenzene is present
C.T. for Bromobenzene		
Compound (4 drops) + 2 ml of fuming HNO_3 (or 1 ml of con. H_2SO_4 + 1 ml of Con. HNO_3) Heat for 5 minutes, cool and pour it into water.	Yellow solid	Bromobenzene is present and confirmed

C.T. for Chlorobenzene		
Compound (4 drops) + 2 ml of fuming HNO_3 (or 1 ml of con. H_2SO_4 + 1 ml of Con. HNO_3) Heat for 5 minutes, cool and pour it into water containing ice pieces.	*Yellow solid	Chlorobenzene is present and confirmed
*Take it as derivative p-nitro-chlorobenzene with M.P.=83 ^oC		

VI. BROAD INFERENCE

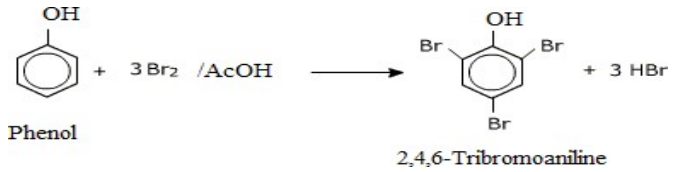
S.N	**Particulars**	**Inference**
1.	Nature (Acid/ base/phenol/Neutral)	
2.	Aliphatic / Aromatic	
3.	Saturated or Unsaturated	
4.	Physical constant of compound	Observed B.P = … ^0C Literature B.P =…. ^0C
5.	Elements present	
6.	Functional group	
7.	Molecular formula of the compound	
8.	Structural formula of the compound	
9.	Name of the compound	
10.	Name of the derivative	
11.	Structure of the derivative	
12.	Physical constant of the derivative	Observed MP = … ^0C Literature MP =…. ^0C

PREPARATION OF DERIVATIVES

1. Bromo derivative for Phenol and Aniline

Dissolve about 1ml of aniline or phenol in acetic acid and take this content in 100 c.c. conical flask. Add strong bromine solution (bromine in acetic acid) until, after shaking, the liquid is pale yellow. Add 50 c.c. water, cool and shake vigorously. Filter and wash the bromo-derivative with water. Recrystallise the product from alcohol.

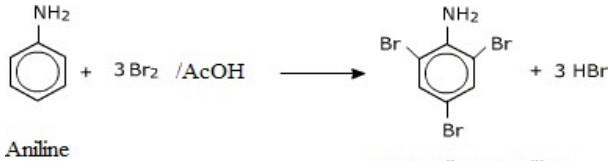
For Phenol



Phenol

2,4,6-Tribromoaniline

For Aniline

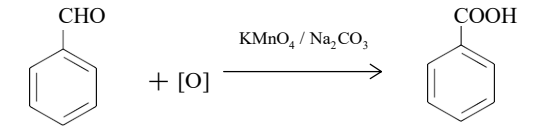


Aniline

2,4,6-Tribromoaniline

2. Benzoic acid from Benzaldehyde

Take 1ml of benzaldehyde in a 100ml. conical flask and add about 10ml. of 10% Na_2CO_3 and boil the solution by placing boiling chips. To, the boiling solutions add about 15ml of $KMnO_4$ gradually till the solution contains a little excess of potassium permanganate. Filter of the precipitated hydrated MnO_2 and few drops of SO_2 water to remove excess of $KMnO_4$. Filter and acidify the filterate, on cooling, the acid precipitates. Recrystallise from hot water.

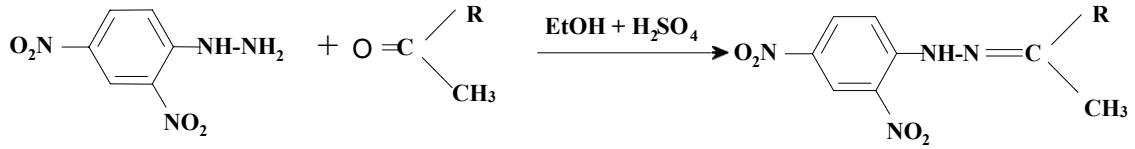


BENZALDEHYDE

BENZOIC ACID

3. 2,4-D.N.P – derivative for Acetone and acetophenone

Take about 5 ml of 2,4-DNP solution in a test tube. Add 5-6 drops of the given liquid (acetone or Acetophenone) shake well and warm it for few minutes. Cool and filter the precipitate thus formed. Recrystallise it from alcohol.

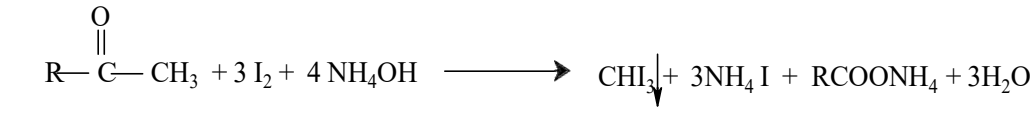


2,4-Dinitro phenyl hydrazine Ketone Ketone-2,4-Dinitro phenyl hydrazone

If R = CH_3 ; Acetone and R = C_6H_5 Acetophenone

4. Iodoform derivative for Acetone and Acetophenone

To about 5-6 drops of the liquid add 10ml NH_4OH. Add iodine solution drop by drop till the solution is distinctly yellow. Warm gently on water bath. When iodoform a yellow crystalline solid , separates in short time. Filter, dry and take M.P.



R = CH_3 , Acetone Iodoform

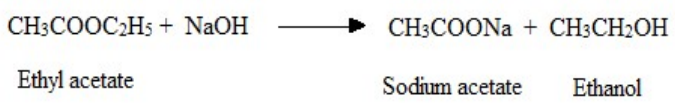
R = C_6H_5 , acetophenone

5. Iodoform derivative for Ethyl acetate

Hydrolyse 1ml of ethyl acetate with 50 ml of 10% NaOH by gently boiling under reflux for 1 hour. A mixture of ethyl alcohol and sodium acetate are formed. Completion of hydrolysis is indicated by the formation of a homogeneous solution.

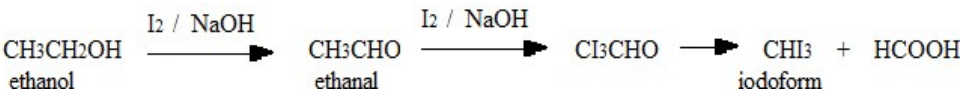
Take about 1 ml of above hydrolysed solution, add 10% of potassium iodide solution and 5ml of freshly prepared sodium chlorite solution. Warm for few minutes and cool. Yellow crystals of iodoform are produced. Filter and collect it as derivative.

HYDROLYSIS OF ESTER



Ethyl acetate Sodium acetate Ethanol

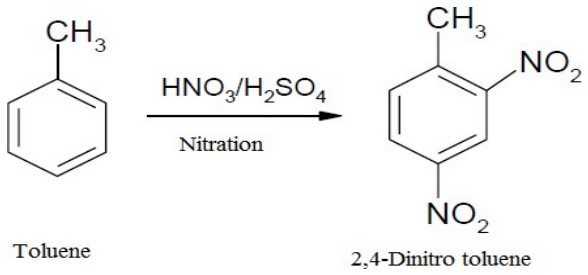
IODOFORM REACTION



ethanol ethanal iodoform

6. 2,4-Dinitrotoluene from toluene

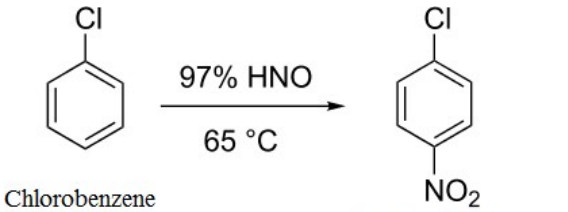
To 5ml of nitrating mixture (1:1 Conc. H_2SO_4 + Fuming Nitric acid), add 1ml of toluene in small lots with shaking after each addition. Cool in ice –water, by maintaining temperature 10^0C. Heat for two minutes and pour into about 50 ml. of cold water. Filter, wash and crystallise from alcohol.



Toluene — 2,4-Dinitro toluene

7. *p*-Nitrochlorobenzene from Chlorobenzene

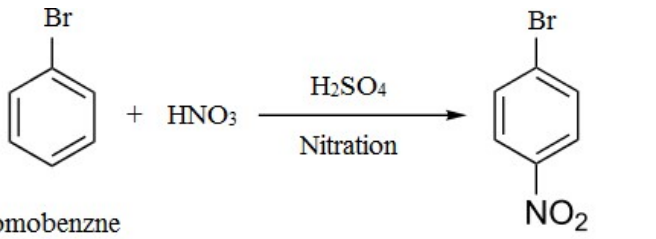
4-5 drops of chlorobenzne + 2ml of fuming nitric acid. Heat for 5-10 minutes on water bath and pour into 10 ml. water. Separated solid is Filter and dry. Recrystallise from ethanol.



Chlorobenzene — *p*-Nitro chlorobenzne

8. *p*-Nitrobromobenzene from Bromobenzene

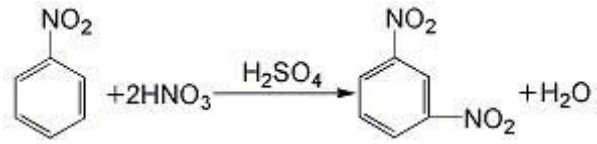
4-5 drops of Bromobenzne + 2ml of Conc. HNO_3 and Conc. H_2SO_4 shake well, and Heat for 2 minutes on water bath and pour into 10 ml. water. Separated solid is Filter and dry. Recrystallise from ethanol.



Bromobenzne — p - Nitro bromobenzne

9. *m*-Dinitrobenzene from Nitrobenzene

4-5 drops of nitrobenzene dissolved in 1 ml of Conc. H_2SO_4 in a dry test tube and add a mixture of 1ml of Conc. HNO_3 and 1ml of Conc. H_2SO_4 and add few drops of fuming nitric acid shake well. Heat for 2 minutes at 100^0C and pour into finely crushed ice in a beaker. Cool thoroughly and scratch by means of a glass rod when the oily suspension solidifies. Filter and recrystallise from alcohol.

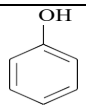
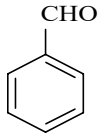
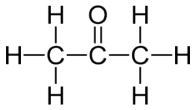
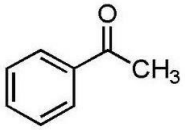
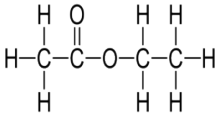
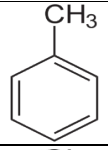
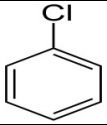
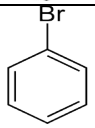
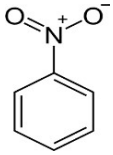
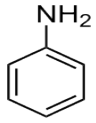


References:

1. A Text book of Practical Organic Chemistry- By Arthur I .Vogel, IVth Edn. ELBS, 1978 Longman Group Ltd.
2. Organic Experiments VIIth Edition Louis F. Fieser Late Professor Emeritus Harvard University Kenneth L Williamson Mount Holyoke College

   D. C.HEATH AND COMPANY Lexington, Massachusetts Toronto
3. Systematic Lab experiments in Organic Chemistry- ArunSethi
4. Practical Organic Chemistry – Nadkarni and Kulkarni
5. Advanced Practical Organic Chemistry – N.K.Vishnoi
6. Practical Chemistry -.O.P.Pandey,D.N.Bajpai & S.Giri
7. A hand book of Analytical Chemistry– Subhash & Satish

Name, Structure and M.P. of derivatives of Organic Compounds

Substance	B.P. (^{0}C)	Mol. Formula	Str. Formula	Derivative (in M.P.)
1. Phenol	183-184	C_6H_5OH		2,4,6-Tribromo phenol (**95-97^{0}C**)
2. Benzaldehyde	179-180	C_6H_5 CHO		Benzoic acid (**120-122^{0}C**) Or 2,4-D.N.P derivative (**237-239^{0}C**)
3. Acetone	56-58	CH_3-CO-CH_3		Iodoform (**119-121^{0}C**) or 2,4-D.N.P derivative (**126-128^{0}C**)
4. Acetophenone	202-204	C_6H_5-CO-CH_3		Benzoic acid (**120-122^{0}C**) or 2,4-D.N.P derivative (**249^{0}C**)
5. Ethyl acetate	77-79	CH_3-$COOC_2H_5$		Iodoform (**119-120^{0}C**)
6. Toluene	110-112	C_6H_5-CH_3		2,4-Dinitrotoluene (**70-72^{0}C**)
7. Chlorobenzne	132-134	C_6H_5-Cl		*p*-Nitrochlorobenzne (**83-84^{0}C**)
8. Bromobenzne	155-157	C_6H_5-Br		*p*-Nitrobromobenzne (**126-127^{0}C**)
9. Nitrobenzene	209	C_6H_5-NO_2		*m*-Dinitrobenzne (**90-92^{0}C**)
10. Aniline	184	C_6H_5-NH_2		2,4,6-Tribromoaniline (**119-121^{0}C**)

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(Affiliated to Rani Channamma University, Belagavi)

CHEMISTRY LABORATORY MANUAL

B. Sc. V SEMESTER

PAPER-II

Name:_____

RCU No:_____

Department:_____

Mobile No: _____

B.Sc V Semester: Paper-II

EXPERIMENTS IN PHYSICAL CHEMISTRY

Total No of Hours/Week : 04 Hours Practical: 40 Marks

Total No of Hours : 52 Hours IA : 10 Marks

Expt. No	Experiments	Page No.
	PART-A	
1	Determination of concentration of HCl by conductometric titration using the standard NaOH.	1
2	Determination of concentration of CH_3COOH by conductometric titration using the standard NaOH.	4
3	Verification of the Beer Lambert's Law by colorimetric method and calculation of molar extinction coefficient of $FeCl_3$.	6
4	Determination of dissociation constant of (Weak acid) acetic acid conductometrically.	8
5	Determination of concentration of strong acid HC1 by potentiometric titration against strong solution of NaOH.	10
6	Determination of heat of neutralization of strong acid by strong base by water equivalent calorimetric method	12
7	Determination of solubility of sparingly soluble salt ($BaSO_4$) Conductometrically	16
	PART-B	
1	Determination of pH of the following biological Juices. (i) Milk (ii) Orange Juice (iii) Lime water (iv) citrus acid solutions (vi) $NaHCO_3$.	18

Scheme of Marking:

Accuracy = 18

Proper Technique and Presentation = 03 Calculation (Calculation + Graph) = 09 (5+4)Viva voce

Journal = 05

Total = 40 Marks

NB: 1. Scientific calculators are not allowed.

2. Use A4 size graph sheets.

Expt No 1: CONDUCTOMETTIC TITARATION (Acid-Base)

Aim: To titrate conductometrically the given solution of HCl (approx 0.1 N) against standard NaOH solution and determine the strength and amount of the acid solution.

Chemicals: 0.5N NaOH and approx 0.1N HCl solution.

Apparatus: Conductivity meter, conductivity cell (1.0 or 0.5 cm) , Micro burette, Pipette etc.

Theory: Conductivity of a solution depends on the mobility as well as number of ions. The H^+ ions have greater mobility than any other ions. When a strong acid is titrated against NaOH, the $[H^+]$ decreases there by conductance decreases till all the H^+ ions are neutralized. Further, addition of NaOH increases the conductance due to a second highest mobile ion, OH^- that is not consumed after neutralization. Hence, for any strong acid against strong base titration, a plot of conductance against volume of alkali gives two straight lines. Intersection of these lines will be the end point or neutralization point.

Reaction: $HCl + NaOH \longrightarrow NaCl + H_2O$

Procedure:

1. Switch on the conductivity meter for stabilization.
2. Calibrate the conductivity meter if necessary.
3. Wash the electrode of the conductivity cell with distilled water.
4. Pipette out 25cc of given HCl solution into a 100 cc beaker.
5. Place the conductivity cell and connect to the terminals of the conductivity meter.
6. Add about 20 cc distilled water to the beaker (if the electrodes are not completely immersed) andstir well with glass rod. Note down the conductance of solution in mS.
7. Rise up the electrodes and add 0.5cc of the NaOH solution from micro burette carefully and stir the solution. There may be a slight heating effect due to neutralization and hence, wait for 30 seconds to cool. Note down the conductance.
8. Continue the titration by adding 0.5cc at a lot up to 10cc and record the conductance for every addition.
9. Plot a graph of conductance against volume of NaOH added. Find out the end point from the intersection of two lines. Calculate the normality and amount of HCl.

Observations:

Volume of HCl solution taken =25.0cc

Volume of NaOH added	Observed conductance (mS)
0.0 cc	
0.5 cc	
1.0 cc	
..	
..	
10.0 cc	

Calculations:

i. Normality of acid solution : $N_1 V_1 = N_2 V_2$

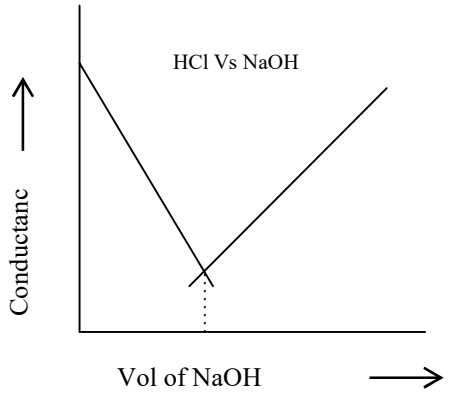
$$N_{HCl} = \frac{N_{NaOH} \times \text{End point from graph}}{V_{HCl}}$$

$$= \ldots\ldots\ldots\ldots\ldots N$$

ii. Amount of HCl = N_{HCl} x equivalent mass of HCl

= ……g/dm^3

Nature of the Graph



Results:-

1. Normality of HCl =.....N
2. Amount of HCl =… ..... g/dm^3

Note: 1. Preserve the conductivity cell always in distilled water

Expt No 2: CONDUCTOMETTIC TITARATION (Acid-Base)

Aim: To titrate conductometrically the given solution of CH_3COOH (approx 0.1 N) against standard NaOH solution and determine the strength and amount of the acid solution.

Chemicals: 0.5N NaOH, approx. 0.1N CH_3COOH solution.

Apparatus: Conductivity meter, conductivity cell (1.0 or 0.5 cm) , Micro burette, Pipette etc.

Theory: Conductivity of a solution depends on the mobility as well as number of ions. The H^+ ions have greater mobility than any other ions. When a strong acid is titrated against NaOH, the $[H^+]$ decreases there by conductance decreases till all the H^+ ions are neutralized. Further addition of NaOH increases the conductance due to a second highest mobile ion, OH^- that is not consumed after neutralization.

In case of weak acid like CH_3COOH, the free H^+ ions are not there in sufficient numbers. Hence, the addition of NaOH increases the conductance gradually due to formation of CH_3COONa till neutralization and further addition of NaOH leads to a rapid increase in conductance due to unused OH^- ions

Hence, for any weak acid against strong base titration, a plot of conductance against volume of alkali gives two straight lines. Intersection of these lines will be the end point or neutralization point.

Reaction: $CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$

Procedure:

1. Switch on the conductivity meter for stabilization.
2. Calibrate the conductivity meter if necessary.
3. Wash the electrode of the conductivity cell with distilled water.
4. Pipette out 25cc of given CH_3COOH solution into a 100 cc beaker.
5. Place the conductivity cell and connect to the terminals of the conductivity meter.
6. Add about 20 cc distilled water to the beaker (if the electrodes are not completely immersed) and stir well with glass rod. Note down the conductance of solution in mS.
7. Rise up the electrodes and add 0.5cc of the NaOH solution from micro burette carefully and stir the solution. There may be a slight heating effect due to neutralization and hence, wait for 30 seconds to cool. Note down the conductance.
8. Continue the titration by adding 0.5cc at a lot up to 10cc and record the conductance for every addition.
9. Plot a graph of conductance against volume of NaOH added. Find out the end point from the

intersection of two lines. Calculate the normality and amount of acid.

Observations:

Volume of CH_3COOH solution taken =25.0cc

Volume of NaOH added	Observed conductance (mS)
0.0 cc	
0.5cc	
1.0 cc	
..	
..	
10.0 cc	

Calculation:

i. Normality of acid solution: $N_1 V_1 = N_2 V_2$

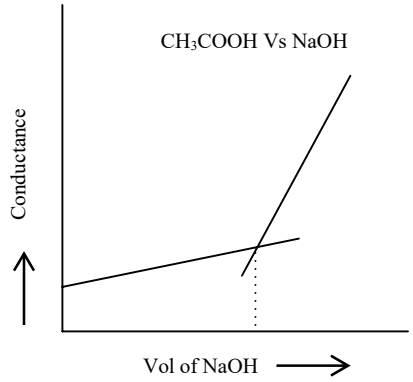
$$N_{CH3COOH} = \frac{N_{NaOH} \times \text{End point from graph}}{V_{CH3COOH}}$$

=..... N

ii. Amount of CH_3COOH = $N_{CH3COOH}$ x equivalent mass of CH_3COOH

=.....g /dm^3

Nature of the Graph



Results:-

1. Normality of CH_3COOH =.....N
2. Amount of CH_3COOH =..... g /dm^3

Note: 1. Preserve the conductivity cell always in distilled water

Expt No.3 COLORIMETRY

Aim: Verification of the Beer Lambert's Law by colorimetric method and determination of unknown concentration of ferric (Fe^{3+}) ions.

Chemicals: 0.001M $Fe_2(SO_4)_3$ $(NH_4)_2 SO_4.24H_2O$(Ferric alum) and 2% KCNS,

Apparatus: Colorimeter, cells, test tubes, test tube stand etc.

Theory: Suppose an intensity of light absorption of a colored solution at a suitable wavelength for various known concentration is determined, using Beer-Lambert's law the unknown concentration of same solution can be determined by measuring absorption at the same wavelength.

Beer-Lambert's states that when beam of light is passed through a coloured solution, decrease in intensity of transmitted light is directly proportional to thickness as well as path length of the solution

Mathematically, Beer-Lambert's law can be written as

$I = I_o.e^{-kCd}$ where, I_o = Intensity of the incident light

$\ln I_o/I = k C d$ I = Intensity of transmitted light

C= concentration of a solution

d = thickness of a solution

k = absorption coefficient

or $\log I_o/I = \frac{k.\ C.d}{2.303}$ or $OD = \frac{k.\ C.d}{2.303}$ = Optical Density

or $OD = \varepsilon Cd$ where, OD = Optical Density, i.e., amount of light absorbed by solution of known concentration& known thickness.

$\varepsilon = \frac{k.}{2.303}$ = molar extinction coefficient (constant) when 'C' in mol dm^3

This principle is extensively used in colorimetric estimation. When the thickness of a solution is 1 cm, a slope from the plot of OD Vs Concentration gives ε. The $[Fe^{3+}]$ in a colored complex can be estimated colorimetrically.

Reaction: The complex between Fe^{3+} & CNS^- ions are formed as follows:

$$Fe^{3+} + nCNS^- \rightleftharpoons [Fe(CNS)]^{(3-n)+}$$

Ferric thiocyanate complex ion

Procedure:

1. Prepare a stock solution of 0.0001M ferric alum solution by diluting10 cc of given 0.001M Ferric alum solution in to 100 cc.
2. Prepare ferric thiocyanate complex solutions of different concentrations in 08 separate test tubes by adding required volume of 0.0001M ferric alum solution , 2% KCNS solution and distilled water as given in table 2.
3. **Selection of suitable filter**: Inserting the cell containing solution No.1 in the colorimeter, adjust the OD to zero. Now using solution No. 5 of moderate concentration, observe the OD for a filter having a lower wave length.

4. Similarly, observe the OD of the same solution for remaining filters of higher wave lengths by setting OD zero to solution No. 1 for every filter. The filter which gives the maximum OD is suitable one.
5. **Determination of OD of solutions**: Using the suitable filter selected, find out the OD for all the prepared solutions.
6. Plot a graph of OD against concentration of Fe^{3+}, which gives a straight line passing through the origin. This is the verification of Beer-Lambert's law.
7. Determine the concentration of Fe^{3+} in unknown composition.
8. From the slope of graph, calculate the molar extinction coefficient of complex.

Observations:

Table No.1 Selection of filter using solution no 4

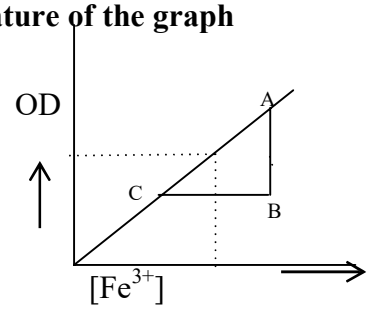
Filter No							
OD							

Remarks: The Filter no------ nm gives maximum OD. Hence it is selected as suitable filter.

Table No.2 Determination of OD of Solutions

Sl.No.	0.0001M Ferric alum (cc)	Distilled water (cc)	2% KCNS	Concentration of Fe^{3+} in mol/dm^3	OD
1	0.0	8.0	2.0	0.00000	
2	1.0	7.0	2.0	0.00001	
3	2.0	6.0	2.0	0.00002	
4	3.0	5.0	2.0	0.00003	
5	4.0	4.0	2.0	0.00004	
6	5.0	3.0	2.0	0.00005	
7	6.0	2.0	2.0	0.00006	
8	7.0	1.0	2.0	0.00007	
9	8.0	0.0	2.0	0.00008	
10	Unknown composition				

Nature of the graph



Calculation of Molar extinction coefficient:

$\varepsilon = \frac{\text{Slope}}{\text{length}} = \frac{\text{Slope}}{1} = \frac{AB}{BC} = \ldots\ldots\ldots$ dm^3 mol^{-1} cm^{-1}

Because, l (length) = 1 cm

Result: Concentration of Fe^{3+}= ---------- mol/dm^3

Expt No. 4 CONDUCTOMETERY (Ka HAC)

Aim: To determine the dissociation constant K_a of acetic acid conductometrically.

Chemicals: 0.1N KCl, 0.1N CH_3COOH solution

Apparatus: Conductivity meter, conductivity cell (1.0 cm), beaker, glass rod etc.

Theory: Since acetic acid is weak electrolyte, it partially ionizes in aqueous solution. Hence, acetic acid solution shows a low conductance. As dilution increases, specific conductance of CH_3COOH decreases, but both equivalent conductance and degree of dissociation (α) will increase with dilution. According to Ostwald's dilution law, the degree of dissociation (α) of weak electrolyte is inversely proportional to square root of initial molar concentration of electrolyte. For strong electrolytes, α is almost equal to 1, but in case of weak electrolytes α is less than 1. However, dissociation constant of CH_3COOH (K_a) always remains constant for any dilution.

Procedure:

A) Determination of cell constant :

1. Switch on the conductivity meter for stabilization.
2. Calibrate the conductivity meter if necessary.
3. Wash the electrode of the conductivity cell with distilled water.
4. Pipette out 50cc of 0.1N KCl solution in to 100cc beaker.
5. Place the conductivity cell in the beaker and connect it to the terminals of conductivity meter.
6. Note down the conductance of the solution in mS.
7. Calculate the cell constant.

B) Determination of equivalent conductivities:

1. Pipette out 50cc of 0.1N CH_3COOH solution into 100cc clean beaker containing the conductivity cell and note down the conductance in mS.

2. Dilute this solution to 0.05N by withdrawing 25 cc of the above solution and adding 25cc distilled water with pipette, stir well and note down the conductance in mS.

3. Similarly, dilute the above solution to 0.025 N and 0.0125N, and record the conductance for every dilution.

4. Calculate the specific conductance, equivalent conductance, degree of ionization and dissociation constant K_a.

Observations:

A) Determination of cell constant :

1. Observed conductance of 0.1N KCl soln. = ……x 10^{-3} S.

2. Specific conductance of 0.1N KCl soln. at room temperature = 0.01288 S cm^{-1}

3. Determination of cell constant:

$$\text{Cell constant} = \frac{\text{Specific conductance of 0.1N KCl}}{\text{Observed conductance}}$$

$$= \frac{0.01288}{\text{Observed conductance}}$$

$$= \text{----------} \text{cm}^{-1}$$

B) Determination of equivalent conductivities:

The equivalent conductance of CH_3COOH at infinite dilution ie λ_∞ **$= 387 Scm^2eqv^{-1}$**

Concentration of solution (C)	Observed conductance (S)	Specific conductance, κ = Cell constant × Observed conductance (Scm^{-1})	Equivalent conductance $\lambda_c = \frac{1000 \times \kappa}{C}$ (Scm^2eqv^{-1})	Degree of dissociation $\alpha = \lambda_c / \lambda_\infty$	$K_a = \frac{C.\alpha^2}{(1-\alpha)}$
0.1 N	x 10^{-3}				
0.05N	x 10^{-3}				
0.025N	x 10^{-3}				
0.0125N	x 10^{-3}				
				Average of K_a	

Result:

The average value of Ka of CH_3COOH =……

Conclusion

1. As dilution increases equivalent conductance increases.
2. As dilution increases degree of dissociation increases.
3. As dilution increases magnitude of dissociation constant remains same.

Note: 1. The theoretical value of $Ka_{CH3COOH}$ = 1.8 x 10^{-5} mol /dm^3

2. Preserve the conductivity cell always in distilled water

Expt. No.5 POTENTIOMETRIC TITRATION (Acid-Base)

Aim: To determine the concentration of strong acid (HCl) by potentiometric titration against standard solution of 0.1N NaOH solution.

Chemicals: 0.1N NaOH, approx 0.1N HCl, Quinhydrone. Saturated solution of KCl etc.

Apparatus: Potentiometer, calomel electrode, platinum electrode etc.

Theory: If HCl is titrated against NaOH potentiometrically, one should select an electrode reversible to hydrogen ions. Quinhydrone is one such electrode and when an inert electrode like platinum is inserted in its solution, a potential develops. It can be given as:

$E_{Qin} = E^o + 0.0591 \log [H^+]$ at 25^oC.

When this is connected to reference electrode like calomel, a cell is set up. The EMF of the cell depends on $[H^+]$. On adding small quantities of NaOH, the EMF will change slowly first and rapidly at the end point and again becomes slow after crossing the end point. The graph of EMF v/s volume of NaOH added gives a reverse sigmoid curve passing through X-axis, which is the equivalence point. The differential plot of $\Delta E/\Delta V$ vs. volume of NaOH added also gives a sharp end point

Procedure:

1. Pipette out 25cc of given HCl solution in 100cc beaker and add a pinch of solid quinhydrone and stir the solution with a glass rod. Keep it for a while.
2. Fill the burette with exact 0.1N NaOH solution.
3. Switch on the potentiometer and standardize the potentiometer by inserting two banana plugs into the sockets at channel I or II and adjust the EMF to 1.018V with the calibration screw. Remove these plugs after standardization.
4. Place the platinum electrode in the above quinhydrone solution and calomel electrode in another beaker having about 50 cc saturated KCl solution. Connect the solutions internally through KCl salt bridge and electrodes externally to the terminals of Potentiometers at either channel I or II at which it is standardized i.e., calomel electrode to negative and platinum electrode to positive terminals of the potentiometer. Record the EMF at 0.0 volume.
5. Start titration by adding 1.0cc of 0.1N NaOH at a lot with constant stirring and record the EMF every addition. Meanwhile, observe the rapid change in EMF at certain volume of NaOH where there will be an equivalence point (approximate) and EMF will be in –ve value. Continue the additions for another 04 readings after –ve EMF are obtained.
6. Plot a graph of EMF v/s volume of NaOH added which gives a reverse sigmoid curve and $\Delta E/\Delta V$ v/s volume of NaOH added gives a peak which is the exact point of equivalence.

Observations

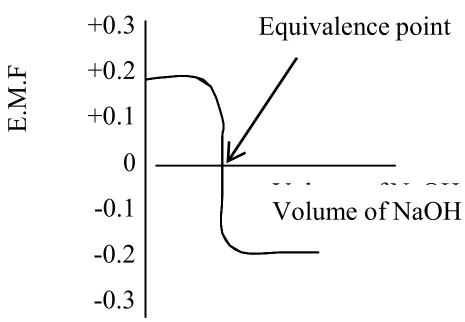
a) Representation of cell

$\overset{-}{Hg} \;/\; Hg^{+} \;//\; H^{+} \;/\; Quinhydrone \;/\; \overset{+}{Pt}$

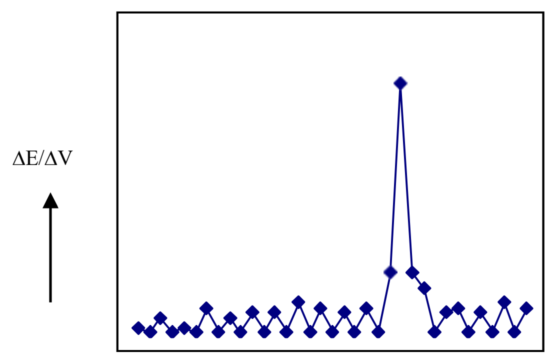
Table: Volume of HCl taken =25.0cc

Volume of 0.1N NaOH (V cc)	EMF (E) in Volts	ΔV	ΔE	ΔE/ΔV
0.0				
1.0				
2.0				
.				
.				
.				

Nature of the graph (graph-I)



Differential curve (graph-II)



Volume of NaOH ⟶

Calculation

From graph-I

1. $N_{HCl} = \dfrac{N_{NaOH} \text{ X equivalence point from graph}}{V_{HCl}} = \dfrac{0.1 \text{ x equivalence point}}{25}$

2. Amount of HCl = N_{HCl} x equivalent mass of HCl=………. g / dm^3

From graph-II

1. $N_{HCl} = \dfrac{N_{NaOH} \text{X equivalence point from graph}}{V_{HCl}} = \dfrac{\text{ x equivalence point}}{25}$

2. Amount of HCl =N_{HCl} x equivalent mass of HCl=............ g / dm^3

Result:

1. The concentration of the given HCl solution = graph-I………& graph-II ……N
2. Amount of HCl = graph-I………& graph-II..........g / dm^3

Expt. No.6 HEAT OF NEUTRALISATION

Aim : Determination water equivalent of the calorimeter and heat the naturalization of a strong acid by a strong base

Apparatus : Calorimeter, thermometer, beakers, measuring cylinder, stop watch, distilled water, lid, etc.

Chemicals : 0.5N HCI and 0.5N NaOH

Theory:

Heat of neutralization of an acid by a base is the change in enthalpy when one gram equivalent mass of the acid is neutralized by one gram equivalent mass of base when both acid and base are in dilute solution.

When the reaction is conducted in a calorimeter, a part of the heat evolved in a reaction is absorbed by the calorimeter . Heat capacity of calorimeter is expressed in terms water equivalent of calorimeter(W) which is the mass of water the mass of water with heat capacity is equal to heat capacity of calorimeter. i.e. If W is the water equivalent of a calorimeter, it indicates that heat capacity of calorimeter is equal to heat capacity of W_g of water.

When 100 ml of hot water is added to 100ml of cold water in the calorimeter, hot water loses heat and cold water & the calorimeter absorb the same quantity of heat. Specific heat of water is 4.2 J/oC (1cal/0 C). Mass of 100ml of water is taken equal to 100g .If ΔT_1 is decreased in temperature of hot water and ΔT_2 is the a increase in temp of cold water, then heat gained by water and calorimeter is equal to heat lost by hot water .

i.e. $(100+W) \times 4.2 \times \Delta T_2 = 100 \times 4.2 \times \Delta T_1$

$$W = \frac{(100 \times 4.2 \times \Delta T_1) - (100 \times 4.2 \times \Delta T_2)}{4.2 \times \Delta T_2} = \frac{100 \times (\Delta T_1 - \Delta T_2)}{\Delta T_2}$$

When known quantities of acid & base are mixed, heat is evolved & temp of mixture rises knowing the water equivalent of calorimeter , the mass if solution specific heat of solution & rise in temp. Heat evolved is calculated. Then the heat of evolved for 1g equivalent mass of acid & base is calculated which gives the heat of neutralization.

Procedure :

Part I : <u>Determination of water equivalent of the calorimeter</u>

100 ml of distilled water is taken in a calorimeter fitted with $1/10^0$C thermometer and its temperature is recorded for 5min. 100cc of hot water is taken in another beaker and heated to about to 45^{o}C. The exact temperature of hot water is recorded for 5 min. Exactly at 6th min all the 100ml of Hot water is added to 100ml cold water in calorimeter & mixture stirred, temp of mixture is noted at 7th min, 8thmin

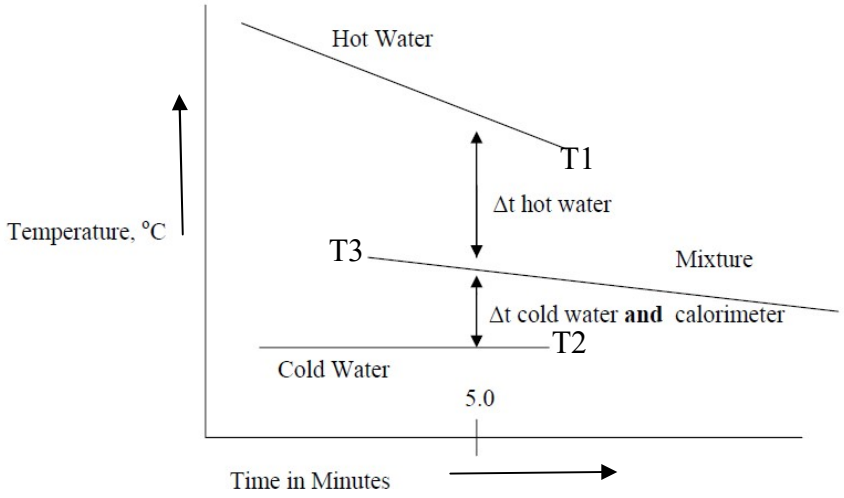
etc for 15min. A graph of temp of hot water, cold water & there mixture, is plotted against time in the same graph. From the graph temp of hot water, temp of cold water and temp of mixture at the time of mixing (6^{th} min) are noted as T1, T2 and T3 respectively. Water equivalent of calorimeter is calculated by using above equation.

Part II : Determination heat of neutralization ΔH

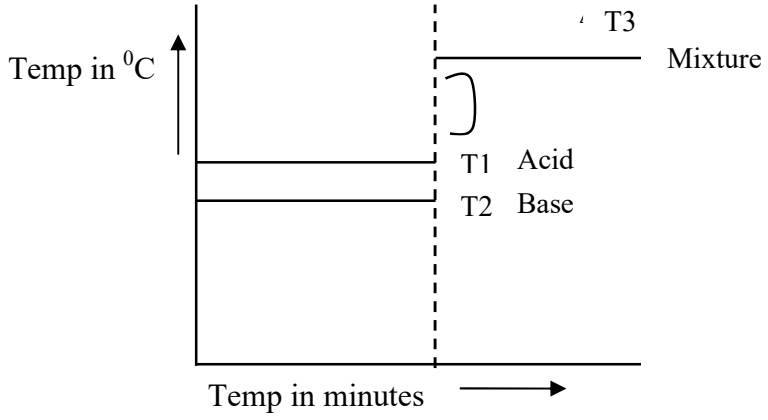
100 cc of 0.5 N NaOH is taken in a calorimeter and its temperature is recorded for 5min. 100cc of 0.5 N HCl is taken in another beaker and its temperature is recorded for 5min. Exactly at 6^{th} min all the 100ml 0.5 N of HCI is poured into 100ml 0.5 N of NaOH taken in calorimeter . The mixture is stirred gently and the temperature is recorded at 7^{th} min, 8^{th} min etc up to the interval of 15 minutes. A graph of temp of acid, base & their mixture against time is plotted. From the graph temp of acid (T1) , temp of base (T2) and temperature of their mixture (T3) at the time of mixing (6^{th} min) are noted. Knowing the water equivalent of calorimeter (W), heat evolved (Q) is calculated and then heat of neutralization (ΔH) is calculated.

Record of observation:

Part I : A graph of temperature against time is plotted as



Part II :A graph of temperature against time is plotted as



Part-I: Determination of water equivalent of calorimeter					**Part-II: Determination of enthalpy of neutralization**			
Time in min	Temperature of				Time in min	Temperature of		
	Cold water	Hot water	mixture			Base	Acid	mixture
1			--------		1			--------
2			--------		2			--------
3			--------		3			--------
4			--------		4			--------
5			--------		5			--------
6	--------	--------			6	--------	--------	
7	--------	--------			7	--------	--------	
8	--------	--------			8	--------	--------	
9	--------	--------			9	--------	--------	
10	--------	--------			10	--------	--------	
11	--------	--------			11	--------	--------	
12	--------	--------			12	--------	--------	
13	--------	--------			13	--------	--------	
14	--------	--------			14	--------	--------	
15	--------	--------			15	--------	--------	

Part I : <u>Determination of water equivalent of the calorimeter</u>

Record of observations:

1. Temperature of the hot water T_1 = -------- ^0C
2. Temperature of the cold water T_2 = -------- ^0C
3. Temperature of Mixture T3 = -------- ^0C
4. Fall in temp of hot water = $\Delta T1 = T1 - T3$ = -------- ^0C
5. Rise in temp of cold water = $\Delta T2 = T3 - T2$ = -------- ^0C
6. Water equivalent of calorimeter = $W = \dfrac{100 \times (\Delta T_1 - \Delta T_2)}{\Delta T_2}$

Part II : <u>Determination of Heat of Neutralisation</u>

1. Temperature of Acid T_1 = -------- ^0C
2. Temperature of Base T_2 = -------- ^0C
3. Temperature of Mixture T3 = -------- ^0C

$$T1 + T2$$

4. Mean temp of acid and base before mixing = $\frac{(T1 + T2)}{2}$ ^{0}C

5. Rise in temp $\Delta T = T3 - \frac{(T1 + T2)}{2}$ ^{0}C

6. Total volume of the Solution = 200 ml = 200g

7. Enthalpy change in when 100 ml of 0.5N HCl is neutralized by 100 ml of 0.5N NaOH = (Mass of solution + W) x sp. Heat x Rise in temp = (200 + W) x 4.2 x ΔT = Q = _____

8. Enthalpy change in when 1000 ml of 1N HCl (1 gr. Eq. mass) is neutralized by 1000 ml of 1N NaOH (1 gr. Eq. mass) = ΔH = - Q x 20 = _____ J

Result : The heat of neutralization of HCI by NaOH is Δ H = -------- K cals

Expt. No. 7: CONDUCTOMETERY (Solubilty-$BaSO_4$)

Aim:- To determine the solubility and solubility product of Sparingly soluble salt (BaSO4) conductometrically.

Chemicals: - $BaSO_4$ powder, distilled water and 0.1N KCl.

Apparatus: Conductometer, conductivity cell, glass rod, beaker etc.

Theory: The solubility of sparingly soluble salts like AgCl, $BaSO_4$, $PbSO_4$ etc can be determined by conductometric measurements. As the solubility of the sparingly soluble salt is extremely low, a small quantity that is dissolved in saturated solution may be regarded as present at infinite dilution. Thus, its equivalent conductance λ_v may be taken as the equivalent conductance at infinite dilution λ_∞.

Thus, $\lambda_v = \lambda_\infty = \lambda_+ + \lambda_-$

Knowing the specific conductance, the solubility of sparingly soluble salt i.e $BaSO_4$ can be calculated.

Concentration of sparingly soluble salt = Solubility, $S = \frac{1000K}{\lambda^0_m}$

Where, 'λ^0_m' is molar conductance at infinite dilution.

Procedure:

A) Determination of cell constant :

1. Switch on the conductivity meter for stabilization.
2. Calibrate the conductivity meter if necessary.
3. Wash the electrode of the conductivity cell with distilled water.
4. Pipette out 50cc of 0.1N KCl solution to 100cc beaker.
5. Place the conductivity cell in the beaker and connect it to the terminals of conductivity meter.
6. Note down the conductance of the solution in mS.
7. Calculate the cell constant.

B). Determination of Solubility of $BaSO_4$

1. Measure the conductance of conductivity water (distilled water).
2. Grind 2 g of $BaSO_4$ to fine powder. Add conductivity water. Stir well and allow the solid to settle down. Decant the supernatant liquid and reject it.
3. Wash the $BaSO_4$ paste three to four times with fresh distilled water to dissolve out all the soluble impurities.
4. Add about 50cc of conductivity water to the above paste; warm the solution gently with stirring for about 5 minutes (solution becomes saturated).
5. Allow the heavier particles to settle down by cooling to room temperature. Decant the solution

and determine the conductance.

6. Repeat the same procedure for two more times for the same paste and record the conductance of the solution as above.

Observations:

A) **Determination of cell constant :**

1. Observed conductance of 0.1N KCl soln. = ……x 10^{-3} S.

2. Specific conductance of 0.1N KCl soln. at room temperature = 0.01288 S cm^{-1}

3. Determination of cell constant:

$$\text{Cell constant} = \frac{\text{Specific conductance of 0.1N KCl}}{\text{Observed conductance}}$$

$$= \frac{0.01288}{\text{Observed conductance}}$$

$$= \text{----------}\ cm^{-1}$$

B). Determination of Solubility of $BaSO_4$

1. Observed conductance of conductivity water, C_1=……x 10^{-6} S
2. Equivalent conductance of $BaSO_4$ at infinite dilution

$$\lambda_\infty = \lambda_{Ba^{2+}} + \lambda_{SO4^{2-}}$$

$$= 64.3 + 80.0$$

$$= 144.3$$

3. Molar Conductance of $BaSO_4$ at infinite dilution

$$\lambda^0_m = \lambda_\infty \times 2 = 144.3 \times 2 = 288.6$$

Sl.No	Observed Conductance of solution (C_2)	Actual conductance = C_2-C_1	Specific Cond (**κ**) = Cell const × Actual Conductance	Solubility, S = $\frac{1000\ \kappa}{\lambda^0_m}$ (mol / dm^3)
1				
2				
3				
Average value of S				

Calculations:

1. Solubility product (K_{sp}) of $BaSO_4$ = (Solubility)^2 =.....mol^2/ dm^6
2. The solubility of $BaSO_4$ in g/ dm^3 = solubility x molar mass of $BaSO_4$
   = _____ x 233.3

Result:

1. Solubility of $BaSO_4$ = _____g/ dm^3
2. Solubility product (K_{sp}) of $BaSO_4$ = ... ……..mol^2 / dm^6

Note: Expected value of solubility of $BaSO_4$ = 2.5×10^{-4} mol / dm^3

Expt. 1 pH metry (pH of biological juice)

Aim: To determine the pH of the following biological juices

i) Milk ii) Orange juice iii) Lime water iv) Citric acid v) $NaHCO_3$

Chemicals: Raw milk, Orange fruits, Lime, Citrus fruits, Baking soda

Apparatus: pH meter, glass electrode etc.

Theory: Biological juices like milk and fruit juices will be in good quality only when they have desirable pH values. They may spoil due to change in their pH values. Milk is one of the deliberately flavored, easily changed foods. It is an excellent culture medium for many kinds of microorganisms, being high in moisture nearly neutral in pH. When milk sours, it is usually considered to be as spoiled. On proteolysis (hydrolysis of proteins) milk may turn up into acidic or alkaline in nature. The spoilage of milk and thus change in its pH value occurs due to the microbial action of bacteria like lactostreptococci and micrococci, thermodurics etc. Low temperature always favors to maintain good quality of milk i.e below 7.2^{o}C.

Further, in fruit juices under normal course of changes an alcoholic fermentation occurs at ordinary temperature. It leads to change in their pH value followed by spoilage. Low temperatures help to maintain the desirable pH and thus minimize the spoilage.

The dissolution of **Quick lime** or Lime (CaO) in water is regarded as highly exothermic in nature. Its cold and filtered clear solution [$Ca(OH)_2$] i.e lime water shows alkalinilty.

Similarly, the **Baking soda** ($NaHCO_3$) is lass soluble in water. Its solution shows the alkalinity. pH of all such solutions can be ascertained before usage using pH meter.

Procedure:

1. Standardize the pH meter as mentioned on the instrument. (May be using the standard solutions of known (minimum) pH=4.0 and known (maximum) pH=9.2 with the help of glass electrode or with the adjustment by screw driver).
2. Collect the raw milk (not dairy milk), filtered orange juice, citrus fruit, supernatant solution of lime, baking soda, etc
3. Take 25 cc of each juice or solution into a beaker. Dip the glass electrode into it.
4. Connect the glass electrode to the terminals of pH meter and record the pH and then tabulate.
5. Write the nature of the solution or the juice (Acidic/Alkaline)

Observations:

Biological juices or solutions	pH	Acidic/Alkaline
Raw milk		
Orange juice		
Lemon juice		
Lime water		
Baking soda		

Result:

1. Raw milk is found to be slightly acidic, where as orange juice and Lemon juice are highly acidic.
2. Lime water and Baking soda are found to basic in nature.

Note:

1. Raw milk should be used for the test but not dairy milk.
2. Fruits should be squashed, juice should be filtered and pure juice may be used for the test.
3. For lime water , 56 gm of Lime (CaO) should be dissolved in one litre of water. It gives milk of lime. Cool and filter it to get clear solution of lime water. Take this lime water solution for the test.
4. For baking soda , 84 gm of baking soda ($NaHCO_3$) should be dissolved in one litre of water. Filter itto get a clear solution. Take this solution for the test.
5. Preserve the glass electrode always in wet condition by keeping it in sat. KCl. Solution.

B. L. D. E. ASSOCIATION'S

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(Affiliated to Rani Channamma University, Belagavi)

DEPARTMENT OF CHEMISTRY

VI SEMESTER CHEMISTRY LAB MANUAL PAPER-II

PART-A

Name of the Student :_____

Reg. No. :_____

Prepared by:

Dr. K. Mahesh Kumar

Department of Chemistry

S B Arts and K C P Science College, Vijayapur

(Source: Vogel Book and Google)

Experiment-1

Aim: To prepare 2,4-Dinitrophenylhydrazine from chloronitrobenzene

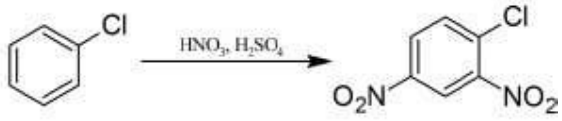
Step-I:

Aim: Preparation of 1-chloro-2,4-dinitrobenzene

Requirement: chlorobenzene, nitric acid, sulfuric acid

Process:

4.0 g of chlorobenzene are added drop by drop to a mixture of 6.4 g of nitric acid (d=1.50 g/ml) and 13.6 g of sulfuric acid(d=1.84 g/ml) while the mixture is stirred mechanically. The temperature rises because of the heat of the reaction, but is not allowed to go above 50-55° C. After all the chlorobenzene has been added, the temperature is raised slowly to 95° C and is kept there for 2 hours longer while the stirring is continued. The upper layer of light yellow liquid solidifies when cold. It is removed, broken up under water, and rinsed. The spent acid, on dilution with water, precipitates an additional quantity of 1-chloro-2,4-dinitrobenzene. All the product is brought together, washed with cold water, then several times with hot water while it is melted, and finally once more with coldwater under which it is crushed. Then it is drained and allowed to dry at ordinary temperature. The product, melting at about 50° C, consists largely of 1-chloro-2,4-dinitrobenzene, m.p. 53.4° C, along with a small quantity of the 2,6-dinitro compound, m.p. 87-88° C.



Result:

1. Theoretical Yield = _____
2. Practical Yield = _____
3. % of yield = _____
4. Melting point of the Compound = _____

Step-II:

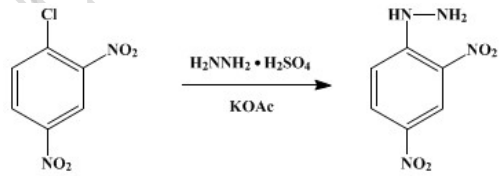
Aim: Preparation of 2, 4-Dinitrophenylhydrazine

Requirement: hydrazine sulfate, potassium/Sodium acetate, alcohol, 2,4-dinitrochlorobenzene

Process:

3.5 g. of hydrazine sulfate is suspended in 15 cc. of hot water in a 400-cc. beaker and stirred by hand during the addition of 8.5 g. of potassium/Sodium acetate. The mixture is boiled five minutes and then cooled to about 70°; 7.5 cc. of alcohol is added, and the solid is filtered with suction and washed with 10 cc. of hot alcohol. The filtered hydrazine solution is saved for the next step.

In a 1-l. flask fitted with a stirrer and reflux condenser, 5.05 g. of technical 2,4-dinitrochlorobenzene is dissolved in 15 cc. of alcohol; the hydrazine solution is added, and the mixture is refluxed with stirring for an hour. Most of the product separates during the first ten minutes; it is cooled well, filtered, and washed, once with 5 cc. of warm alcohol (60°) to remove unchanged halide and then with 10 cc. of hot water. The solid weighs 3 g. and melts at 190–192° with evolution of gas; it is pure enough for most purposes. By distilling half the alcohol from the filtrate a less pure second crop is obtained; this is recrystallized from *n*-butyl alcohol (10 cc. per g.). The total yield is 40–42 g.



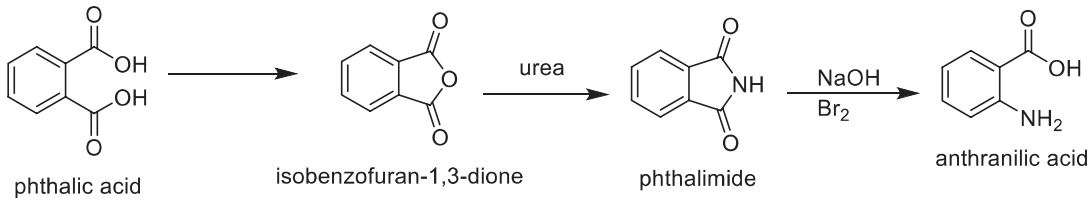
Result:

1. Theoretical Yield = _____
2. Practical Yield = _____
3. % of yield = _____
4. Melting point of the Compound = _____

Experiment-2

Aim: To prepare anthranilic acid from phthalic acid.

Reaction:



phthalic acid — isobenzofuran-1,3-dione — phthalimide — anthranilic acid

Step-1

Aim: To prepare phthalic anhydride from phthalic acid.

Requirement: phthalic acid, Whatman filter paper, crucible, funnel

Procedure:

- Take 15 gm phthalic acid in evaporating dish.
- Cover it with funnel & filter paper, Heat on burner.
- Collect phthalic anhydride with adjust of surface of filter paper.
- Dry it, weight it, check M.P & calculate % of yield.

Result :

(A) Theoretical Yield = …….

(B) Practical Yield = …….

(C) % Yield= …….. %

(D) M. P.=…….^{0}C

Step-2

Aim: To prepare phthalimide from phthalic anhydride.

Requirement: phthalic anhydride, urea.

Procedure:

- Take 0.033 M phthalic anhydride & 0.0231 M urea in RBF.
- Mix well & heat the reaction mixture on oil bath at 130-140ºC for 30 minute.
- Then raise the temperature upto 150-160ºC for 1 hour.
- Cool the reaction mixture at a room temperature.
- Pour it into ice cold water, filter out.
- Dry it, weight it, check M.P & calculate % of yield.

Result :

(A) Theoretical Yield = …….

(B) Practical Yield = …….

(C) % Yield= …….. %

(D) M.P ……^{0}C

Step-3

Aim: To prepare anthranilic acid from phthalimide. (Hoffman reaction)

Requirement: phthalimide, NaOH, Br2, con.HCl, glacial acetic acid.

Procedure:

- Dissolve 7.5 gm NaOH in 30ml of H_2O, cool it in ice bath at 0-5ºC.
- Add 2.1 ml bromine solution carefully, thus NaOBr is generated.
- Maintain the temperature at 0-5ºC then add 7.5 gm phthalamide in one portion with constant sturring to this solution.
- Add freshly prepared NaOH(5 gm in 25ml H_2O), so temperature will be raised about 70ºC, stand it for 20 minute.
- Heat on waterbath for 20 minute at 80-85ºC.
- Cool the reaction mixture filtered out & collect the filtrate, neutralized it with con. HCl at 5ºC & add glacial acetic acid till precipitate obtained.
- Maintain 4 pH filter precipitate & wash with water.
- Dry it, weight it, check M.P & calculate % of yield.

Result :

(A) Theoretical Yield = …….

(B) Practical Yield = …….

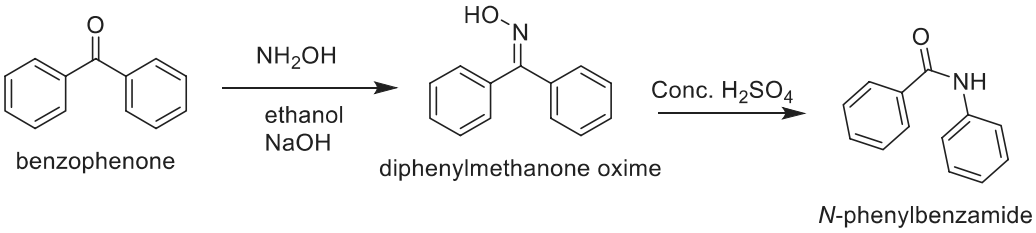
(C) % Yield= …….. %

(D) M. P.=…….^{0}C

Experiment-3

Aim: To prepare benzanilide from benzophenone.

Reaction:



Step-1

Aim: To prepare benzophenone oxime from benzophenone.

Requirement: Benzophenone, hydroxyl amine hydrochloride, ethanol, sodium hydroxide, dil.HCl.

Procedure:

- Dissolve 4 gm benzophenone & 2.5 gm hydroxyl amine hydrochloride in ethanol in RBF.
- Shake the mixture very well & add previously prepared solution of NaOH (4.8 gm NaOH in 5 ml water).
- After the complete addition of NaOH solution reflux the reaction mixture on boiling water bath for 45 min.
- Cool the reaction mixture & add 40 ml water & filter unreacted benzophenone then cool the filtrate.
- In filtrate add a solution of dilute HCl (12 ml Con.HCl + 75 ml water) sture the reaction mixture.
- Filter the separated solid, wash with ice water.
- Dry it, weight it, check M.P & calculate % of yield.

Result :

(A) Theoretical Yield = …….

(B) Practical Yield = …….

(C) % Yield= …….. %

(D) M. P.=…….^{0}C

Step-2

Aim: To prepare benzanilide from benzophenone oxime.

(Beckmann Rearrangement)

Requirement: Benzophenone oxime, Conc. H_2SO_4, diethyl ether.

Procedure:

- Take 20 ml diethyl ether in a conical flask & add 1 gm of benzophenone oxime & dissolve it.
- Cool the reaction mix. In ice-bath & add Conc. H_2SO_4 in drop-wise manner with constant sturring.
- Sture the reaction mixture for 20-25 min. & removed remaining solvent on water-bath.
- Pour the reaction mix. Into ice, filter the separated product & wash with cold water.
- Dry it, weight it, check M.P & calculate % of yield.

Result:

(A) Theoretical Yield = …….

(B) Practical Yield = …….

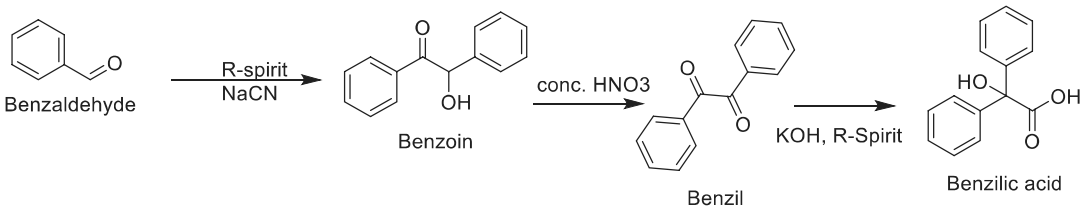
(C) % Yield= …….. %

(D) M. P.=…….^{0}C

Experiment-4

Aim: To prepare Benzylic Acid from Benzaldehyde

Reaction:



Step – I

Aim: To prepare Benzoic from Benzaldehyde

Requirement: Benzaldehyde, R-spirit and Sodium Cynide (NaCN)

Process :

In RBF place 6.5 ml of R-spirit, 4.8 ml of pure Benzaldehyde and 5.0 ml of solution of sodium cynide (NaCN) (Take 0.5 gm NaCN in 5 ml dis. Water) attached the RBF in condenser with reflux and boil the mixture for 30 min. Cool the solution. Poured in ice water bath. Recrystallize with hot R-spirit.

Result:

1. Theoretical yield = _____
2. Practical yield =_____
3. % of yield = _____
4. Melting point of the compound = _____

Step – II

Aim : To prepare Benzil from Benzoin.

Requirement : Benzoin and HNO_3

Process :

Place 2 gm of crude Benzoin and 10ml conc. HNO_3 in 250ml RBF. Heat on water bath with conc. shaking until the evolution of oxide of Nitrogen for 1.5 hour. Pour the mix in cold water. Stir well until the crystalize completely as yellow solid. Filter the product and wash with the water to remove the nitric acid and recrystallize and check M.P.

Result :

1. Theoretical yield = _____
2. Practical yield =_____
3. % of yield = _____
4. Melting point of the compound = _____

Step – III

Aim : To prepare Benzylic acid from Benzil.

Requirement : KOH, R-Spirit and Benzil

Process :

In 500ml RBF placed a solution of 35gm of KOH in 70 ml of water, then 90 ml of R-Spirit and 35gm of recrystallize Benzil. A deep bluish black solution is produce. Fit a reflex condenser to flask and heat the mixture on boiling water bath for 10 to 15 minute. Pour the contain of the flask into a porcelain dish and allow to cool overnight. Take the crystal and soluble in dis. water filter it and add dil. HCL in filtrate, PPT comes out filter it and recrystallize and check M.P.

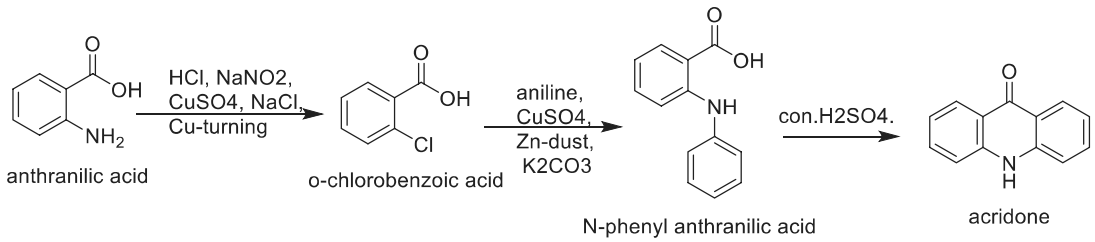
Result :

1. Theoritical yield = _____
2. Practical yield =_____
3. % of yield = _____
4. Melting point of the compound = _____

Experiment-5

Aim: To prepare acridone from anthranilic acid.

Reaction:



Step-1

Aim: To prepare o-chloro benzoic acid from anthranilic acid.

Requirement: anthranilic acid, HCl, $NaNO_2$, $CuSO_4$, NaCl, Cu-turning

Procedure:

- In a conical flask take 7 ml con. HCl & 35 ml of H_2O to this dissolve 5 gm of anthranilic acid & cool the reaction mixture at 0-5ºC.
- In another beaker prepare a solution of the $NaNO_2$ (2.5 gm $NaNO_2$ + 10 ml H_2O), add this solution to a hydrochloric salt of anthranilic acid with sturring by maintaining the temperature 0-5ºC.
- After addition of $NaNO_2$ solution keep it at 0-5ºC for 20 minute.
- In a beaker take 9.3 gm $CuSO_4$ & 8.6 gm of NaCl in a 20 ml distill water.
- In this solution add 30 ml HCl & 5 ml of Cu-turning & boil the mixture till solution become colourless & filter the solution & cool it at 0-5ºC then add previously prepared diazonium salt to the $CuCl_2$.
- Dry it, weight it, check M.P & calculate % of yield.

Result :

(A) Theoretical Yield = …….

(B) Practical Yield = …….

(C) % Yield= …….. %

(D) M. P.=…….^{0}C

Step-2

Aim : To prepare N-phenyl anthranilic acid from o-chlorobenzoic acid.

(Ullmann Reaction)

Requirement : o-chloro benzoic acid, aniline, $CuSO_4$, Zn-dust, K_2CO_3.

Procedure :

1) Preparation of Cu (fresh) :

- Take 5 gm $CuSO_4$ & dissolve in 50 ml H_2O.
- Then slowly add Zn-dust until Cu-metal deposite in the solution, sturr well, filter the fresh Cu & wash with acetone.

2) Preparation of N-phenyl anthranilic acid :

- Take 0.03 M of o-chlorobenzoic acid & 5 gm of K_2CO_3 in RBF.
- Then add 12 ml aniline & previously prepared fresh Cu.
- Reflux reaction mixture on oil-bath at 140-160ºC for 2 hour.
- Pour the reaction mixture into cold water, filter the separated product.
- Dry it, weight it, check M.P & calculate % of yield.

Result :

(A) Theoretical Yield = …….

(B) Practical Yield = …….

(C) % Yield= …….. %

(D) M. P.=…….^{0}C

Step-3

Aim : To prepare acridone from N-phenyl anthranilic acid.

Requirement : N-phenyl anthranilic acid, con.H_2SO_4.

Procedure :

- Take 0.005 M N-phenyl anthranilic acid in RBF.
- Add 3.5 ml con. H_2SO_4 & reflux the reaction mixture on boiling water-bath for 2 hour.
- Cool the reaction mixture & pour it into ice cold water.
- Filter the separated product.
- Dry it, weight it, check M.P & calculate % of yield.

Result:

(A) Theoretical Yield = …….

(B) Practical Yield = …….

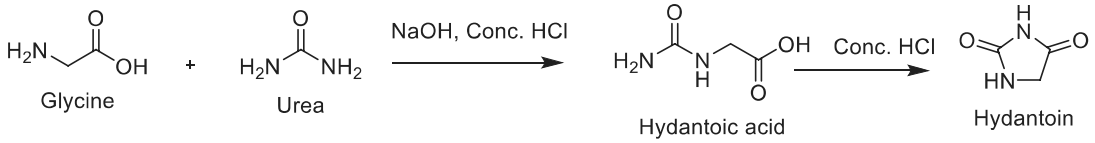
(C) % Yield= …….. %

(D) M. P.=…….^{0}C

Experiment-6

Aim: To prepare Hydantoin from Glycine

Reaction:



Step – I

Aim: To prepare Hydantoic acid from Glycine

Requirement: Glycine, Urea, NaOH, Conc. HCl

Process:

An aq. solution of 4 gm of NaOH in 6 ml of water is added to a mixture of 7.6 gm of glycine and 12.0 gm of urea in RBF. The mixture is shaken well and heated at the 110-115° C in oil bath by reflux for 1 hour. Cool the reaction mixture at 60° C and acidify with conc. HCl (when acidify the solution maintain the temp. at 60°C) then allow to cool the reaction mix in Ice bath filter the separated product crystallize with hot water. Calculate % of yield and check M.P.

Result:

1. Theoretical yield = _____
2. Practical yield =_____
3. % of yield = _____
4. Melting point of the compound = _____

Step – II

Aim :- To prepare Hydantoin from Hydantoic acid.

Requirement :- Hydantoic acid, Conc. HCl

Process :-

A mixture of 3 gm of Hydantoic acid, 5 ml of conc. HCl and 2 ml of H_2O is mixed and reflux on oil bath at 110°-115°C for 15-20 min. The reaction mixture is cooled in ice water bath. Filter the separated solid crystallize from hot water. Calculate the % of yield and check melting point.

Result:-

1. Theoretical yield = _____
2. Practical yield =_____
3. % of yield = _____
4. Melting point of the compound = _____

PART-B: Qualitative Analysis

Experiment-9: Estimation of phenols

Aim:

To estimate the amount of phenol present in whole of the given solution by bromination method.

Required: 0.1 N $Na_2S_2O_3.5H_2O$ solution, 0.1 N Brominating solution, 10% KI solution, con. HCl

Principle:

Phenol and some of the derivatives having the free *ortho* and *para* position can be estimated by bromination method. The method involves the following steps,

(a) Bromination of phenol by bromination mixture:

Phenol reacts with bromine to form 2,4,6- tribromophenol. Since the yield is quantitative, it is used for the estimation of phenol. The bromine required is obtained by treating a mixture of potassium bromide and potassium bromate with dilute hydrochloric acid. The bromine so liberated reacts with phenol to produce tribromophenol while excess of bromine remains unreacted.

$$5\ KBr + KBrO_3 + 6\ HCl \longrightarrow 3\ Br_2 + 3\ H_2O + 6\ KCl$$

(b) Determination of unreacted bromine:

The unreactive bromine is treated with potassium iodide, the equivalent iodine thus liberated is determined iodometrically with sodium thiosulphate solution using starch as indicator.

$$Br_2 + 2\ KI \longrightarrow 2\ KBr + I_2$$

$$2\ Na_2S_2O_3 + I_2 \longrightarrow 2\ NaI + Na_2S_4O_6$$

Sodium tetrathionate

Procedure:

Preparation of standard potassium dichromate solution

The standard potassium dichromate solution can be prepared by weighing accurately about 1.2260 g (0.016 M) of potassium dichromate, dissolving in water and making up to 250

ml in a standard measuring flask.

Standardization of sodium thiosulphate solution

Into a 250 ml iodine flask, pipette 20 ml of standard potassium dichromate solution. Add 10 ml of 1 M sulphuric acid and 1 g of sodium hydrogen carbonate into the iodine flask with gentle swirling. Then add 0.5 g of potassium iodide and swirl the flask and closed the flask, allow the solution to stand for 5 minutes in a dark place. Titrate against sodium thiosulphate solution taken in the burette, until a light pale yellow color is obtained. Add 1 ml of starch solution and continue the titration till the blue color of starch-iodide complex disappears. Repeat the titration to get at least two concordant readings.

Blank titration

Pipette out 20 ml of brominating solution in a 250 ml iodine flask and 5 ml of concentrated hydrochloric acid and add 0.5 g of KI and immediately insert the stopper. Keep the solution in dark 10 – 15 minutes. Wash the stopper and walls of the flask with 5 ml of water. Titrate this with sodium thiosulphate solution until the solution acquires light yellow color and then add 5 – 6 drops of starch solution and continue the titration with sodium thiosulphate solution. At the end point blue color disappears. Note the reading of thiosulphate solution required (A). Repeat the titration to get at least two concordant readings.

Estimation of Phenol:

The given solution dissolve in water and made up the volume to 100 ml. 20 ml of this solution was pipetted out into a 250 ml iodine flask and add 5 ml of concentrated hydrochloric acid. Brominating mixture is now added to this solution till it achieves light yellow color and then 0.5 g of KI is added and immediately insert the stopper. Keep the solution in dark 10 – 15 minutes. Wash the stopper and walls of the flask with 5 ml of water. Add 10 ml of chloroform shakes vigorously and titrate the liberated iodine with sodium thiosulphate using starch solution as indicator. The end point is blue color of starch-iodine complex disappears. Note the reading of thiosulphate solution required (B). Repeat the titration to get at least two concordant readings.

Result:

1. The amount of phenol present in the whole of the given solution = g.
2. % of purity of phenol =

Calculation:

Preparation of standard potassium dichromate solution

Mass of weighing bottle + $K_2Cr_2O_7$ = g

Mass of empty weighing bottle (after transferring) = g

Mass of $K_2Cr_2O_7$ = g

=

Strength of $K_2Cr_2O_7$ (in 250 ml) = M

Table: 1

Standard $K_2Cr_2O_7$ solution vs. Sodium thiosulphate solution

S. No.	Volume of $K_2Cr_2O_7$ solution (ml)	Burette Readings (ml)		Volume of sodium thiosulphate (ml)	Indicator
		Initial	Final		
1.					
2.					

Strength of $K_2Cr_2O_7$ = M

Volume of $K_2Cr_2O_7$ solution = ml.

Volume of sodium thiosulphate = ml.

=

Strength of sodium thiosulphate = M

Table: 2

Brominating solution vs. Sodium thiosulphate solution (Blank Titration)

S. No.	Volume of brominating solution (ml)	Burette Readings (ml)		Volume of sodium thiosulphate (ml)	Indicator
		Initial	Final		
1.					
2.					

Volume of sodium thiosulphate (A) = ml.

Table: 3

Sodium thiosulphate solution vs. Given phenol solution

S. No.	Volume of given solution (ml)	Burette Readings (ml)		Volume of sodium thiosulphate (ml)	Indicator
		Initial	Final		
1.					
2.					

Strength of sodium thiosulphate	=	M
Volume of given solution	=	ml.
Volume of sodium thiosulphate (B)	=	ml.
Therefore, A – B (C)	=	ml

The weight of phenol can be calculated by the formula given below,

$$weight\ of\ Phenol\ in\ 100\ ml = \frac{C\ \times Normality\ of\ Thio \times Eq.Wt.of\ Phenol}{20\ \times 10}$$

The weight of phenol = g.

The percentage of phenol can be calculated by the formula given below,

$$\%\ of\ Phenol = \frac{0.003138\ \times (A - B) \times N\ \times 100}{w\ \times 0.2}$$

Where,

A = ml of thiosulphate required for blank.

B = ml of thiosulphate required for sample.

N = Normality of thiosulphate used.

W = weight in grams of phenol.

(0.2 N brominating solution is equivalent to 0.003138 g of phenol)

Note:

Sodium thiosulphate solution 0.1 M:

It is prepared by dissolving 2.48 g of sodium thiosulphate pentahydrate (M.W = 248.18 g/mol) in 100 ml distilled water in a volumetric flask.

Starch indicator solution:

Make a paste of 1 g of starch with a little water and pour the suspension, with constant stirring into 100 ml of boiling water.

Potassium bromate ($KBrO_3$) 0.1 M:

It is prepared by dissolving 1.67 g $KBrO_3$ (M.W = 167 g/mol) in 100 ml distilled water and make up the volume in a volumetric flask.

Potassium bromide (KBr) 0.1 M:

It is prepared by dissolving 1.19 g KBr (M.W = 119.002 g/mol) in 100 ml distilled water and make up the volume in a volumetric flask.

Potassium dichromate 0.016 M:

It is prepared by dissolving 1.2260 g $K_2Cr_2O_7$ (M.W = 294.19 g/mol) in 250 ml distilled water in a volumetric flask.

Brominating solution (0.2 M)

Weigh 1.4 g $KBrO_3$ (M.W = 167 g/mol) and 9 g KBr (M.W = 119.002 g/mol) in distilled water and make up the volume to 250 ml in a volumetric flask.

Sulphuric acid (1 M):

It is prepared by dissolving 14 ml of sulphuric acid in 250 ml of distilled water.

Experiment-10: Iodine Value of Oil by Chloramine-T method

Aim:

To estimate the Iodine value of Oil by Chloramine-T method.

Required: Oil (any), Chloramine-T, iodine, carbon tetrachloride, potassium iodide, 0.04 M sodium thiosulfate solution, 0.05 N potassium dichromate solution

Procedure:

Preparation of standard potassium dichromate solution

The standard potassium dichromate solution can be prepared by weighing accurately about 0.05 M of potassium dichromate, dissolving in water and making up to 250 ml in a standard measuring flask.

Standardization of sodium thiosulphate solution

Into a 250 ml iodine flask, pipette 20 ml of standard potassium dichromate solution. Add 10 ml of 1 M sulphuric acid and 1 g of sodium hydrogen carbonate into the iodine flask with gentle swirling. Then add 0.5 g of potassium iodide and swirl the flask and closed the flask, allow the solution to stand for 5 minutes in a dark place. Titrate against sodium thiosulphate solution taken in the burette, until a light pale yellow color is obtained. Add 1 ml of starch solution and continue the titration till the blue color of starch-iodide complex disappears. Repeat the titration to get at least two concordant readings.

Preparation of reagent (I). Chloramine-T (2.5 g) was dis-solved in 75 mL of acetic acid taken in a dry beaker, and 1.25g of iodine was dissolved separately in 75 mL of carbon tetra-chloride. Both solutions were transferred to a 250-mL volumetric flask. The solution was diluted to the mark with carbon tetrachloride and acetic acid (1:1, vol/vol). The flask was stoppered and shaken well. The resulting nearly homogeneous brown solution was kept at room temparature for about 1 h. During that period there was a small amount of white precipitate formed, most of which settled at the bottom of the flask. The solution was filtered through a quantitative or an ordinary filter paper. The clear brown filtrate, reagent (I), was found to be stable for a week and satisfactory to determine the iodine value of the oils.

Determination of iodine value by the proposed method. A known weight of the oil (30–140 mg) was transferred into each of five clean and dry iodine flasks. A sixth flask, containing no oil, served as a control. 25 mL of reagent (I) was pipetted into each of the flasks. The flasks were stoppered and mixed well by shaking and then kept at room temperature under diffused light. After 20–25 min, 5 mL of 10% potassium iodide solution was added to each flask via a measuring cylinder (10 mL capacity). The flasks were

stoppered and mixed well by hand shaking, and each one was titrated separately against 0.04 M sodium thiosulfate solution, which had previously been standardized with 0.05 N potassium dichromate solution. The titration was continued with frequent shaking until the pale yellow color produced toward the end point just disappeared.

Result:

1. Iodine value of an oil =

Calculation:

The iodine value of an oil was calculated based on the following relations:

One mole of chloramine T + 1⁄ 2 mole I_2 produces 1 mole ICl, which adds to 1 mole of double bonds.

One mole of double bonds consumes 1 mole of I_2 , which would react with 2 moles of sodium thiosulfate.

Therefore, 1 mL of 0.1 M sodium thiosulfate solution = 0.05 mole, or 12.69 mg, of, I_2,

Iodine value of an oil = $[(V_1 - V_2) \times 12.69 \times 1000 \times M]/W$

where V_1 and V_2 are volumes in mL of sodium thiosulfate solution of molarity M consumed by a known volume of reagent (I) (25 mL) without and with W mg of the oil.

Experiment-8: Titrimetric Estimation of amino acids

Structure

1 INTRODUCTION

There are many titrimetric methods available for the determination of amino acids. Here we will estimate glycine by formal titration method (Soronsen's method).

Objectives

After studying and performing this experiment, you should be able to

- determine the amount of glycine in the given sample,
- describe formylation reaction, and
- perform acid–base titration using standard alkali

2 PRINCIPLE

Amino acids like glycine, alanine, etc. contain one amino group and one carboxylic group as part of their structures. These groups being of opposite nature neutralise one another intramolecularly and form internal salts called zwitter ions or dipolar ions. These ions are held together by electrostatic attraction. They are neutral but in presence of alkalies the dissociation favours formation of acid ion.

$$H_2N - CH_2COOH \rightleftharpoons N^+H_3 - CH_2COO^-$$

$$N^+H_3CH_2COO^- + OH^- \rightleftharpoons NH_2CH_2COO^- + H_2O$$

The free amino group then undergoes condensation with formaldehyde to form mono and dimethyl derivatives. Thus, the formation of these condensation products greatly reduces the basic character of amino group and the carboxylic group can readily be titrated with standard alkali.

$$CH_2 = O + H_2NCH_2COO^- \longrightarrow CH_2 = NCH_2COO^- + H_2O +$$

$$CH_2\,OHNHCH_2COO^- + (CH_2OH)_2NCH_2COO^- + \text{etc.}$$

3 REQUIREMENTS

Apparatus		Chemicals
Burette (50 cm^3)	- 1	Glycine

Pipette (25 cm^3)	- 1	Sodium hydroxide	
Vol. flasks (250 cm sup 3)	- 1	Formalin solution	
Conical flask (250 cm sup 3)	- 1	Phenolphthalein indicator	
Weighing bottle	- 1		
Funnel (small)	- 1		
Wash-bottle for distilled water	- 1		
Test-tube	- 1		
Burette stand	- 1		

Solutions Provided

ii) **Sodium hydroxide solution. O.1*M*:** Dissolve 2 g of sodium hydroxide in a 250 cm^3 volumetric flask and make up to the mark with distilled water.

iii) **Neutral 40% formalen solution:** Take 50 cm^3 of 40% formalin solution in a 250 cm^3 conical flask and add 8-10 drops of phenolphthalein indicator. To it add carefully from a burette a dilute solution of sodium hydroxide (0.1*M*), till the solution is just faintly pink.

iv) **Phenolpthalein indicator:** Dissolve 1.0 g of phenolphthalein in 100 cm^3 of ethanol and then dilute with 100 cm^3 of Water.

4 PROCEDURE

i) **Preparation of Standard solution of glycine:** Weigh accurately 2 g of glycine and transfer to a 250 cm^3 volumetric flask and make up to the mark with distilled water.

ii) **Titration with standard solution:** Take 25 cm^3 of standard glycine solution in a 250 cm^3 conical flask and add 3-4 drops of phenolphthalein indicator. Add dilute sodium hydroxide solution (0.1 *M*) taken in burette drop by drop to it until a pink colour is just obtained. Now add 10 cm^3 of neutral formalin solution to it. The pink colour of the solution immediately disappears. Continue adding sodium hydroxide slowly till pink colour is restored. Note the volume of sodium hydroxide used and repeat the experiment until two concordant readings are obtained. Records the observations in Observation Table I.

iii) **Titration with unknown glycine solution:** Perform the titration as described above for 20 cm^3 unknown glycine solution and note the volume of sodium hydroxide used in this titration. Record the observations in Observation Table II

5 Observations

Mass of the weighing bottle	$= m_1$	=..... g
Mass of the bottle + glycine	$= m_2$	=..... g
Mass of the bottle (after transferring the compound)	$= m_3$	=..... g

Mass of glucose transferred $= m_2 - m_3 = m$ =..... g

Observation Table I
Standard Glycine Solution Vs. Sodium Hydroxide Solution

Sl. No.	Volume of glycine solution in cm^3	Burette reading		Volume of sodium hydroxide solution in cm^3 (Final–Initial)
		Initial	Final	
1	25			
2	25			
3	25			

Observation Table II
Unknown Glycine Solution Vs. Sodium Hydroxide Solution

Sl. No.	Volume of glycine solution in cm^3	Burette reading		Volume of sodium hydroxide solution in cm^3 (Final–Initial)
		Initial	Final	
1	25			
2	25			
3	25			

6 Calculations

The volume of sodium hydroxide solution used for 25 cm^3 of standard glycine solution $= V_1$ cm^3

The volume of sodium hydroxide solution used for 25 cm^3 of unknown glycine solution $= V_2$ cm^3

The amount of glycine in given solution $= \frac{m \times V_2}{V_1}$ = ... g

The strength of the unknown glycine solution $= \frac{4 \times m \times V_2}{V_1}$ = ...g dm^{-3}

$$= \frac{\text{Strength of the standard glycine solution} \times V_2}{V_1}$$

7 Result

The amount of glycine in the given solution = ... g

The strength of the unknown glycine solution = ... g dm^{-3}