
**BIRLA INSTITUTE OF TECHNOLOGY MESRA**

**RANCHI, INDIA**

**CHOICE BASED CURRICULUM**

**Under Graduate Programme**

# B.TECH. LAB MANUAL

**Department of Chemistry**

**Course code: CH 102**

## Syllabus

1. Gravimetric estimation of Nickel by Dimethylglyoxime.
2. Quantitative estimation of $Ca^{2+}$ and $Mg^{2+}$ ions by complexometric titration using $Na_2$-EDTA.
3. To verify Bears Law using $Fe^{3+}$ solution by spectrophotometer/colorimeter and to determine the concentration of a given unknown $Fe^{3+}$ solution.
4. Separation of binary organic mixture by acid-base extraction and analysis using given FTIR and NMR spectrum.
5. Preparation of Diazoamino Benzene and report the melting point and yield of product.
6. Draw melting point-mass percent composition diagram for two component mixture and determine the Eutectic Temperature.
7. To study the kinetics of acid-catalyzed hydrolysis of ethyl acetate and to evaluate the value of the rate constant.
8. To determine the rate law for the reaction between iodide and hydrogen peroxide in an acidic environment and to determine the effect of a catalyst on the rate of reaction.
9. To determine the strength of the given strong acid by strong base Potentiometrically.
10. To determine the transition temperature of the given salt hydrate.
11. Qualitative detection of special elements in organic compounds.
12. To draw the pH-titration curve of strong acid vs strong base.

**Reference book:**


1. Experimental Physical Chemistry, By B. Viswanathan, P. S. Raghavan, Narosa Publishing House (1997).
2. Vogels Textbook of Practical Organic Chemistry
3. Experiments in General chemistry, C. N. R. Rao and U. C. Agarwal

4. Experimental Organic Chemistry Vol 1 and 2, P R Singh, D S gupta, K S Bajpai, Tata McGraw Hill

**Lab Check-In:**

**General:**

- Laboratory apron and experimental notebook is mandatory to work in the laboratory.
- Be sure that all of your glassware, labwares, equipment etc. is present with you to conduct your experiment.
- Once you have checked-in, you will be responsible for missing labware items issued to you. Pay particular attention to the labwares, which is expensive and required for several students for their experiments, treat it with respect.
- It is your responsibility to clean all of the used labwares, glassware etc. and your work place after completion of your experiment before leaving lab.
- Learn the cleaning and drying technique for glassware's. Always use clean and dry glassware's for your experiment.
- Learn Good and Safe Laboratory Practice. Learn the safe handling of labwares, glassware's, chemicals, equipment, etc. Ask you lab instructor/Teacher for any queries.
- You need to maintain your lab record book updated as per instruction and be sure to get verified & signed by your teacher in every lab classes.
- Keep your personal safety googles, lab aprons etc. with you for your next time use.

## Experiment No: 1

**Aim: Gravimetric Estimation of Nickel by Dimethyl glyoxime**

**Theory:**

Gravimetric analysis is one of the most accurate analytical methods available. It is concerned with the determination of a substance by the process of weighing. The element or radical to be determined is converted into a stable compound of definite composition and the mass of the compound is determined accurately. From this, the mass of element or radical is calculated.

The gravimetric analysis involves a) precipitation b) filtration c) washing of the precipitate

d) drying e) weighing of the precipitate.

There are four types of gravimetric analysis:

1. Physical gravimetry
2. Thermogravimetry
3. Precipitative gravimetric analysis
4. Electrodeposition.

**Physical gravimetry:** Physical separation and classification of matter in environmental samples based on volatility and particle size (e.g., total suspended solids).

**Thermogravimetry:** Volatile solid samples are analyzed by this method. In this method the samples are heated and the changes in sample mass are recorded.

**Precipitative gravimetry:** The chemical precipitation of an analyte and weighing of the precipitate is done in the precipitative gravimetry.

**Electrodeposition:** It involves the electrochemical reduction of metal ions at a cathode and simultaneous deposition of the ions on the cathode.

**Pecipitative Gravimetric Analysis:**

Precipitative gravimetric analysis requires that the substance to be weighed be readily removed by filtration. In order for a non-filterable precipitate to form, it must be supersaturated with respect to its solubility product constant. However, if it is too far above the saturation limit, crystal nucleation may occur at a rate faster than crystal growth (the addition of molecules to a crystal nucleus, eventually forming a non-filterable crystal). When this occurs, numerous tiny micro-crystals are formed rather than a few large ones. In the extreme case, micro-crystals may behave as colloids and pass through a fibrous filter. To avoid this, precipitating solutions may be heated. Because the solubility of most salts increases with increasing temperature, this treatment will lower the relative degree of super saturation and slow the rate of nucleation. Also, one might

add the precipitant slowly with rapid mixing to avoid the occurrence of locally high concentrations.

**The Gravimetric Estimation of Nickel:**

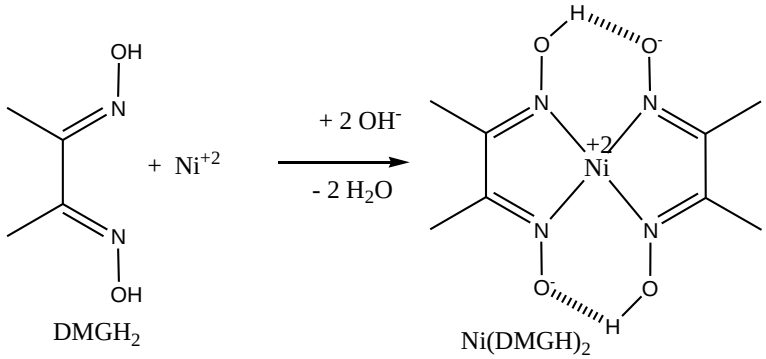
The nickel is precipitated as nickel dimethyl glyoxime by adding alcoholic solution of dimethyl glyoxime $C_4H_6(NOH)_2$ and then adding a slight excess of aqueous ammonia solution.

In the pH range 5 to 9, the formation of the red chelate complex occurs quantitatively in a solution. The chelation reaction occurs due to donation of the electron pairs on the four nitrogen atoms, not by electrons on the oxygen atoms. The reaction is performed in a solution buffered by either an ammonia or citrate buffer to prevent the pH of the solution from falling below 5. At very low pH reverse reaction takes place causing the hydrolysis of Ni $(DMGH)_2$ that leads to the formation of $Ni^{+2}$ in the mother liquor.

A slight excess of the reagent has no action on the precipitate, but a large excess should be avoided because of the possible precipitation of the reagent itself. It is therefore crucial to avoid the addition of too large and excess of the reagent because it may crystallize out with the chelate. The nickel dimethylglyoximate is a very bulky precipitate. Therefore, the sample weight used in the analysis must be carefully controlled to allow more convenient handling of the precipitate during the transfer to the filtering crucible. The compactness of the precipitate is improved by adjusting the pH to 3 or 4, followed by the addition of ammonia solution.

A slow increase in the concentration of ammonia in the solution causes a slight increase in the pH gradually and results in the precipitation of the complex. The result is the formation of a denser precipitate. Once the filtrate has been collected and dried, the nickel content of the solution is calculated stoichiometrically from the weight of the precipitate.

*The structure of DMG & the complex with nickel ions is given below;*




**Procedure:**

- The given nickel solution is made up to 100mL in a standard measuring flask.
- 20 mL of solution is pipetted into a 250 mL beaker.

- About 5 mL 1:1 HCl is added and diluted to 150 mL.
- The solution is heated to 70-80°C. 25 mL of 1% dimethyl glyoxime in alcohol is added, immediately followed by dilute ammonia solution drop wise until it strongly smells of ammonia.
- The solution containing the precipitate is heated in a water bath for 30 minutes.
- The precipitate is allowed to stand for an hour.
- Filter the solution through a previously weighed sintered glass crucible.
- The precipitate is washed with cold water to free chloride.
- The crucible is placed in a dry 100 mL beaker and heated in the air oven at 110-120°C for 1 hour.
- It is cooled in a dessicator and weighed. Repeat drying until constant weight is obtained.

**Calculation:**

Mass of sintered glass crucible = ***x*** g.

Mass of sintered glass crucible + nickel complex = ***y*** g.

Mass of dimethyl glyoxime nickel complex = ***(y-x)*** g.

288.69 of nickel complex contain 58.69 g of nickel.

Mass of nickel in ***(y-x)***g of complex = $\frac{(y-x) \times 58.69 \times 5}{288.69}$ g

Therefore, Mass of nickel in the whole of the given solution = $\frac{(y-x) \times 58.69}{288.69}$ g

**Result:**

Mass of Nickel in the given solution = .....g

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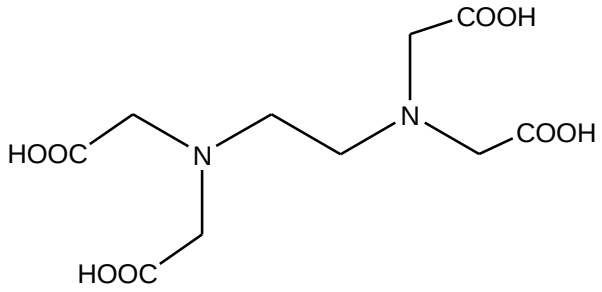
**Experiment No-2**

**Objective: Quantitative estimation of $Ca^{+2}$ and $Mg^{+2}$ ion by complexometric titration using $Na_2EDTA$**

Numerous methods are available for titrimetric determination of various cations with certain organic reagents called complexones. These complexones are imino-polycarboxylic acids, having excellent complex forming ability with a number of cations. The simplest of the complexones is iminodiacetic acid, HN(CH2COOH)z. Other complexones can be assumed to be higher derivatives of this family. The most important member of this family of reagents is ethylenediaminetetraacetic acid, abbreviated as EDTA The structure of EDTA is




In complexometric determination of magnesium and calcium ions in their mixture, EDTA is used as a titrant and Solochrome Black (Eriochrome Black **T)** as an indicator. EDTA is only slightly soluble in water. However, its disodium salt is freely soluble in water. EDTA, generally, forms **1:l** complexes with metal ions. In reactions, EDTA and its disodium salt are represented as H4Y and Na H Y, respectively.
2.2 Reaction of the dispdium salt with a bivadent cation can be written as follows:

$$Na_2H_2Y \longrightarrow 2\,Na^{+} + H_2Y^{-2}$$

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

It is apparent from the above equation that there is always a competition in solution between the metal ions and the hydrogen ions in seeking the negative sites on EDTA. The equilibrium condition is determined by the strength of the bond between the metal ion and the ligand, and the relative concentrations of metal ions versus hydrogen ions. In other words, we can say that the stability of the metal-EDTA complex will be governed by the hydrogen ion concentration or pH of the solution. Stability of $Ca^{+2}$ and $Mg^{+2}$ complex of EDTA is maximum at pH = 10. `

When indicator solution, which is blue in color, is added to the solution containing magnesium and calcium ions, wine red colored metal ion-indicator complexes of varying stability are formed. The magnesium-indicator complex is more stable than the calcium indicator complex but less stable than the magnesium-EDTA complex which in turn is less stable than the clacium-EDTA complex. Consequently, when EDTA solution is added, it reacts first with the free calcium ions, then with the free magnesium ions, then with the calcium indicator complex and finally with the magnesium-indicator complex. Since the magnesium-indicator complex is wine-red in color and the free indicator is blue between pH 7 and 11, the colour of the solution changes from wine-red to blue at the end point. In this experiment, we titrate one portion of the test solution containing both magnesium and calcium ions with EDTA using

Solochrome Black indicator at pH 10. Then another equal portion of test solution is titrated with EDTA under strongly alkaline condition using Patton-Reeder's indicator. in strong alkaline medium Mg is precipitated as $Mg(OH)_2$ leaving only $Ca^{+2}$ ion in solution. From the amount of EDTA consumed in the 1st titration total amount of $Ca^{+2}$ and $Mg^{+2}$ ions and from the 2nd titration amount of $Ca^{+2}$ ion present in the given unknown solution is obtained. From the difference in the EDTA titre value amount of $Mg^{+2}$ions in will be obtained.

**Preparation of solutions:**

1. 0.01 M $Zn(OAc)_2$. 2 $H_2O$ solution as primary standard: 0.5475 g of A.R. grade $Zn(OAc)_2$. 2 $H_2O$ is accurately weighed out in a 250 ml volumetric flask containing 2 g of $NH_4Cl$ dissolved in 10 ml deionised water, the volume is made upto the mark and made uniform by shaking.

2. $NH_3$-$NH_4Cl$ buffer (pH = 10) solution:
17.5 g of $NH_4Cl$ is mixed with 142 ml conc. $NH_3$ (Sp. Gravity 0.88-0.90) and the mixture is made upto 250 ml with deionised water.

3. 0.05 g EBT indicator and 4.9 g $KNO_3$ mixture is grinded in mortar.

4. Sample solution: It can be prepared by dissolving accurately 200-300 mg of calcium chloride and 100-200 mg of $MgSO_4$ into minimum quantity of dil. HCl and making up the volume to 250 ml with distilled water.

**Standardisation of EDTA solution:**

25 ml of the standard $Zn(OAc)_2$. 2 $H_2O$ solution is pipetted out into a 250 ml conical flask, 5 ml pH 10 buffer solution is added, diluted to 100 ml with deionised water, warmed to about 40° C; ~50 mg of EBT indicator are added and the mixture is shaken to obtain a wine-red color. The mixture is then titrated with standard EDTA solution till the color changes to blue. The titration is repeated to get concordant results.

**Estimation of total amount of $Ca^{+2}$ and $Mg^{+2}$**

25 ml of the sample solution (acidic in nature) is pipetted out into a 250 ml conical flask, 75 ml de-ionised water is added. Addition of 1-2 drops of methyl red indicator turns the solution red which is neutralised by drop wise addition of 1:1 ammonia until just yellow color develops. Then 5 ml of $NH_4Cl$-$NH_3$ (pH= 10) buffer solution and 30-40 mg of EBT indicator are added and the mixture is shaken to obtain a wine-red color. The mixture is then titrated with standard EDTA solution till the color changes to blue.

**Estimation of $Ca^{+2}$**

25 ml of the sample solution (acidic in nature) is pipetted out into a 250 ml conical flask, 75 ml de-ionized water is added. Addition of 1-2 drops of methyl red indicator turns the solution red which is neutralized by drop wise addition of 1:1 ammonia until just yellow color develops.10 ml 10% NaOH solution is added and the mixture is shaken to precipitate $Mg(OH)_2$ completely. 30-40 mg of Patton-Reeder's indicator is added. The mixture is shaken to obtain wine red color and titrated with standard EDTA until color changes to blue.

**Observations:**

**1. Standardisation of EDTA:**

| S.No. | Initial Reading(ml) | Final reading(ml) | Volume of 0.01 M Zinc acetate solution taken (ml) | Volume of E.D.T.A. Solution required (**V ml**) |
|---|---|---|---|---|
| 1 | | | 25 | |
| 2 | | | 25 | |
| 3 | | | 25 | |

**2. Determination of total amount of $Ca^{+2}$ and $Mg^{+2}$**

| S.No. | Initial Reading(ml) | Final reading(ml) | Volume of Unknown sample taken (ml) | Volume of E.D.T.A. Solution used up (**$V_1$ ml**) |
|---|---|---|---|---|
| 1 | | | 25 | |
| 2 | | | 25 | |
| 3 | | | 25 | |

**3. Determination of $Ca^{+2}$ only**

| S.No. | Initial Reading(ml) | Final reading(ml) | Volume of Unknown sample taken (ml) | Volume of E.D.T.A. Solution used up (**$V_2$ ml** ) |
|---|---|---|---|---|
| 1 | | | 25 | |
| 2 | | | 25 | |
| 3 | | | 25 | |

**Calculation:**
**Standardisation of EDTA:**

Let wt. of $Zn(OAc)_2$. 2 $H_2O$ in 250 ml water is W g.

Strength of $Zn(OAc)_2$. 2 $H_2O$ = $\frac{W}{0.5475}$ (0.01 M)

Let 25 ml of $\frac{W}{0.5475}$ (0.01 M) Zn-acetate solution ≡ V ml of EDTA

Strength of EDTA = $\frac{W \times 25}{0.5475 \times V}$ (0.01 M) = f (0.01 M)

**Determination of $Ca^{+2}$ and $Mg^{+2}$ ion in solution**

25 ml of $Ca^{+2}$ and $Mg^{+2}$ solution ≡ $V_1$ ml of **f** 0.01 M EDTA solution

25 ml of $Ca^{+2}$ solution ≡ $V_2$ ml of f 0.01 M EDTA solution

1000 ml of 0.01 M EDTA ≡ 1000 ml 0.01 M $Ca^{+2}$
≡ 0.40 g of $Ca^{+2}$

1 ml of 0.01 M EDTA ≡ 0.0004 g of $ca^{+2}$

Amount of $Ca^{+2}$ in 25 ml ≡ 0.0004 x $V_2$ x **f** g

**Amount of $Ca^{+2}$ in g $L^{-1}$ = 0.0004 x $V_2$ x f x 40**

Amount of $Mg^{+2}$ in 25 ml ≡ ( $V_1$ - $V_2$ ) ml of f 0.01 M EDTA solution

1000 ml of 0.01 M EDTA ≡ 1000 ml 0.01 M $Mg^{+2}$
≡ 0.2432 g of $Mg^{+2}$

Amount of $Mg^{+2}$ in 25 ml ≡ 0.0002432 x ( $V_1$ - $V_2$ ) x **f** g

**Amount of $Mg^{+2}$ in g $L^{-1}$ = 0.0002432 x ( $V_1$ - $V_2$ ) x f x 40**

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## Experiment No. - 3

**Aim: To verify Beer's Law using $Fe^{+3}$ solution by spectrophotometer/colorimeter and to determine the concentration of a given unknown $Fe^{+3}$ solution**

**Instrument required:** Colorimeter/ Spectrophotometer

**Glassware required:** Volumetric flask, Pipette

**Reagent required:**

1. Stock solution of ferrous ion
2. HCL
3. Potassium thiocyanate
4. Acetic acid
5. Conc. nitric acid.

**Theory:** Chemicals analysis through measurement of absorption of light radiation in visible region (400-700) of spectrum is known as spectrophotometry. A device which measure the percentage transmittance of light radiation when light of certain intensity and frequency range is passed through the sample is known as spectrophotometer. It compares the intensity of the transmitted light with that of the incident radiation.

Transmittance (T) of a solution is the fraction of incident light transmitted by solution mathematically: $T=I_t / l_0$, where $l_t$ is the intensity of transmitted light and $I_0$ is the intensity of a beam of monochromatic light.

Absorbance (A) or optical density (OD) is defined as $A=\log I_o / I_t$.

From the Lambert – beer's Law $A= \varepsilon Ct$

Where, $\varepsilon$ is molar extinction coefficient (or molar absorptivity),

C is concentration (in gms/L) of the absorbing medium,

T is thickness of the absorbing medium.

If same sample cell (t is constant) is used for measurement of absorbance by solutions of different concentration, then $A \alpha C$

i.e. the extent of absorbance (A) is directly proportional to the concentration (C) of the absorbing medium.

Thus if a graph is plotted between A and C we get a straight line for solution obeying Lambert-Beer's Law. This is known as calibration curve.

**Procedure:**

A. Preparation of stock solution (1000 ppm) of iron: Dissolve 4.836g of ferric chloride in 0.1 M HCl and dilute it to 1 litre.

B. Potassium thiocyanate solution: take 10g of potassium thiocyanate and dissolve it in distilled water, adjust the pH with the help of conc. nitric acid (4 ml) and acetic acid (10 ml), make the volume up to 1 litre.

C. Preparation of working standard:

100 ppm working standard solution: Take 10 ml of working stock solution (1000 ppm) and dilute it upto 100 ml by distilled water.

1. 2 ppm=Dilute 2 ml of working stock solution 100 ppm upto 100 ml with distilled water.
2. 4 ppm= Dilute 4 ml of working stock solution 100 ppm upto 100 ml with distilled water.
3. 6 ppm= Dilute 6 ml of working stock solution 100 ppm upto 100 ml with distilled water.
4. 8 ppm= Dilute 8 ml of working stock solution 100 ppm upto 100 ml with distilled water.
5. 10ppm= Dilute 10 ml of working stock solution 100 ppm upto 100 ml with distilled water.

D. Preparation of solution for calibration curve: Take 5 ml working standard (1-5) in 5 test tube, add 1 ml potassium thiocyanate in each test tube.

Observation Table:

| Sl.No. | Concentration in ppm | Absorbance |
|---|---|---|
| | | |
| | | |
| | | |
| | | |
| | | |
| | Unknown Sample | |

**Result:**

The conc. Of $Fe^{3+}$ ion in a given sample of water using colorimeter=……mg/l

**Precaution:**

1. Measure absorbance value only at 480 nm. Set absorbance zero for blank.
2. Cuvette is fragile and it should be used with great care.

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## Experiment No. 4

**AIM: Separation of binary organic mixture by acid-base extraction and analysis using given FTIR and NMR spectrum.**

**THEORY:**

The transfer of a solute from one phase to another is a very common technique in organic chemistry. It is called extraction, and it is also a common technique in everyday life. Extraction involves dissolving a compound or compounds either (1) from a solid into a solvent or (2) from a solution into another solvent.

Some organic molecules possess acidic or basic functional groups. These groups can be protonated or deprotonated in a solution given the right pH. When the organic molecule has undergone an acid-base reaction it becomes charged in the form of an ionic salt. In turn, this charge increases the solubility of the molecule in aqueous (or polar) solvents, and decreases the solubility of the molecule in nonpolar, organic/greasy solvents. This solubility difference allows the molecule to be selectively pulled out of the "soup" of other molecules. It might seem particularly daunting to try and selectively remove all of one molecule from a plant or animal while leaving the millions of other types of molecules behind. Nevertheless, extracting molecules from natural sources is a fairly common procedure and can be done on an industrial scale for a variety of biologically active molecules. Indeed, many important life-saving drugs on the market are originally isolated from natural sources.

| | |
|---|---|
| $RCO_2H + OH^- \rightarrow RCO_2^- + H_2O$ | $RNH_2 + H^+ \rightarrow RNH_3^+$ |
| Carboxylic acid carboxylate ion | Amine ammonium salt |

When infrared light is passed through a sample of an organic compound, some of the frequencies are absorbed and others are transmitted. The plot of absorbance or transmittance against the frequency represents the infrared spectrum. However, the convention is the absorbance or transmittance is plotted against the wavenumber (increasing order from right to left) to represent the Fourier transform infrared (FTIR) spectrum. Different types of chemical bods (like C-C, C=C, C-N, C-O, C=O, C=N, C-H, N-H etc.) in organic compound have different vibrational frequencies, and the presence of these bonds can be detected by identifying their characteristics frequencies as absorption bands in infrared spectrum.

**EQUIPMENT AND MATERIALS.**

Mixture of 500 mg each of benzoic acid and nitroaniline, HCl, NaOH, 2 Beakers 100 ml, 2 Conical Flask 100 ml, funnel, glass rod, 2 FTIR plots.

**PROCEDURE:**

1. Slowly adding 6 M NaOH and Swirl the solution frequently. Remember that the neutralization reaction of acids and bases is exothermic, so the flask should still be in an ice bath.
2. Check the pH with pH paper to make sure it's basic, adding more base if necessary.
3. When a precipitate forms in your extract, collect it by vacuum (suction) filtration on a piece of filter paper in a Büchner funnel.
4. Make the NaOH extract acidic with 6 M HCl, following the procedure outlined above. You should see a precipitate when the extract has been acidified.
5. When a precipitate forms in your extract, collect it by vacuum (suction) filtration on a piece of filter paper in a Büchner funnel.
6. Both the precipitate was dried well in a vacuum thermal chamber at 80 °C.
7. Record the melting point and explain the given FTIR spectra for the samples.

**OBSERVATION:**

1. Physical characteristics (Fill it according to the physical properties of the given mixture):
a. State:
b. Texture:
c. Color:
d. Order:

| Compound | Weight taken (g) | Weight recovered (g) | Melting point measured (ºC) | Melting point reported (ºC) |
|---|---|---|---|---|
| Benzoic acid | 0.5 | | | |
| Nitro aniline | 0.5 | | | |

**FTIR ANALYSIS:**

FTIR of Benzoic acid

(Explain the given spectrum in terms of delocalized ArC=C, ArC-H, carboxylic acid COO, hydrogen bonded acidic-OH)

FTIR of Nitro aniline

(Explain the given spectrum in terms of delocalized ArC=C, ArC-H, ArC-N, $NO_2$, hydrogen bonded acidic-$NH_2$)

**CALCULATION:**

Calculate the % recovery for Benzoic acid, Nitro aniline and for total mixture using the following equation;

$$\%\, Recovery = \frac{Weight\ recovered}{Weight\ taken} \times 100$$

**RESULT:**

The % recovery for Benzoic acid …. ……  with observed melting point of …. …..
The % recovery for Nitro aniline …. …. with observed melting point of …. …..

The % recovery for Total mixture …. ….

**PRECAUTIONS:**
Write 3/4 points about the precautions that you have taken during your experiment.

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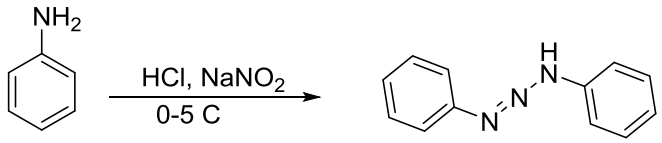
**Experiment-5:**

**Aim: Preparation of Diazoamino Benzene and report the melting point and yield of the product.**

**Reaction:**




Aniline Diazoaminobenzene

**1. Chemical/Materials**:

| | |
|---|---|
| Aniline | 9 mL |
| Conc. HCl: | 14 mL |
| Sodium Nitrite | 3.5 gm |
| Sodium Acetate: | 14 gm |
| Distilled Water: | 250 mL |

**2. Apparatus Required:**

1. Beaker 250 mL (No: 2).
2. Conical Flask 100 mL & 250 mL
3. Small Glass Stirring Rod: (No: 1)
4. Spatula
5. Magnetic Stirrer with stir bar
6. Thermometer
7. Measuring Cylinder: 100 mL and 10 mL
8. 10 mL Glass Pipette with Suction Bulb
9. Buchner Funnel/ or Glass Stemless Funnel
10. Filter Paper

**Procedure:** Take 50 mL distilled water in a 250 mL Beaker. Stir (use stir bar and magnetic stirrer) it on water-ice bath and add 16 mL of Conc. HCl (0.2 moles) portion wise (2 – 3 mL at a time). Allow the solution to cool to 0-5 ºC and then add 9.3 mL (0.1 moles) aniline using glass pipette & suction bulb. Add approx. 50g crushed ice into the reaction mixture with stirring. Add 0.05 moles of $NaNO_2$ solution (3.5 gm / 15 mL $H_2O$) dropwise into the reaction mixture with continuous stirring. Allow the reaction mixture to stirr for another 15 minutes at 0-5 ºC. Add 0.25 moles of sodium acetate solution (20 gm / 50 mL $H_2O$) slowly with stirring. Yellow precipitate will form, continue stirring for another 15 minutes. Then filter the yellow solid using buckner funnel with filter paper and wash the solid with distilled water. Dry the solid on

whatmann filter paper in a petri dish in a Hot-Air Oven at 45-50 ºC. Report the yield and melting point of dried solid of diazoamino benzene.

**Result:**

Yield, Melting Point [96-98 ºC]

Precautions:

Apron, Safety Googles and Gloves must wear during Experiment. Manual Stirring can be done with Glass Rod in place of magnetic stirrer. Recommended to conduct this experiment in chemical fume hood.

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# Experiment 6

## Aim: Draw melting point-mass percent composition diagram for two component mixtures and determine the Eutectic Temperature.

**List of Chemicals, Labwares and Equipment:**

a) Graph Paper, ruler scale (mm), butter paper (small pieces: 2 x2 )
b) Small spatula
c) 2 Watch glasses
d) 6-8 Melting point capillary tubes
e) Trans-Cinnamic Acid: 50 mg [133-134 °C]
f) Urea: 50 mg [133-134 °C]
g) Melting Point Apparatus
h) Analytical Balance

**Theory**

In the majority of cases the presence of a foreign substance will lower the melting point of a pure organic compound. This fact is utilized in the so-called mixed melting point test for the identification of organic compounds.

The melting point of a compound is the temperature at which the solid phase is in equilibrium with the liquid phase. A solid compound changes to a liquid when the molecules acquire enough energy to overcome the forces holding them together in an orderly crystalline lattice. For most organic compounds, these intermolecular forces are relatively weak. The melting point range is defined as the span of temperature from the point at which the crystals first begin to liquefy to the point at which the entire sample is liquid. Most pure organic compounds melt over a narrow temperature range of 1-2 °C. The presence of a soluble impurity almost always causes a decrease in the melting point expected for the pure compound and a broadening of the melting point range. In order to understand the effects of impurities on melting point behavior, consider the melting point-mass percent composition diagram for two different fictitious organic compounds, X and Y, shown in Figure 1. The vertical axis represents temperature and the horizontal axis represents varying mass percent compositions of X and Y.

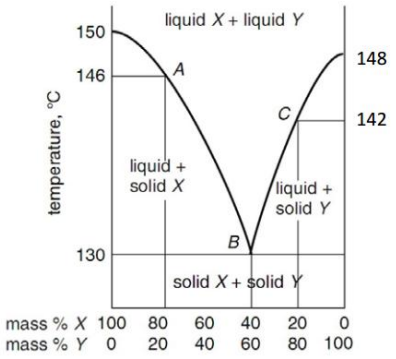



**Figure 1**. Melting point-mass percent composition diagram

Cases may arise in which the melting point of certain mixtures are higher than the individual components, e.g., if an addition compound of higher melting point is formed or if the two compounds are completely soluble in the solid state forming solid solutions. Furthermore, for certain optical isomers, e.g., d- and Z-camphoroximes and for d and Z-borneol, there is no depression in the melting point, the freezing or melting points of all mixtures being the same as the pure components. It will be seen, therefore, that the mixed melting point test, although of great practical value, is not infallible and should accordingly be used with reasonable regard to these possibilities.

## ii) Procedure

1. Determine the melting point of pure cinnamic acid (133°) and pure urea (133°).
2. Intimately mix equal weights (ca. 20 mg.) of the two finely-powdered compounds and determine the melting point; a considerable depression of melting point will be observed. It is instructive to construct a melting point diagram for mixtures of cinnamic acid and urea. Mix 80 mg of cinnamic acid (X) with 20 mg of urea (Y) intimately with the aid of a spatula on a glass slide, and determine the melting point (the temperature at which the mixture just becomes completely fluid is noted). Similarly prepare another three set of a mixed sample (in mg) for 60-40, 40-60, and 20-80. Plot temperatures as ordinates, and, concentration as abscissae, the percentage of urea from left to right (0-100 per cent.) and of cinnamic acid from right to left (0-100 per cent.).

## 3. Observation

Tabulate your results as follows:—

| CINNAMIC ACID | UREA | M.P. |
|---|---|---|
| 100 % | 0 % | 133° |
| 80 % | 20 % | — |
| 60 % | 40 % | — |
| 50 % | 50 % | — |
| 40 % | 60 % | — |
| 20 % | 80 % | — |
| 0 % | 100 % | 133° |

**4. Results:** Write the conclusion.

**5. Precautions:**

1. Mixed the samples homogeneously
2. Fill the capillary carefully without breaking the bottom
3. Observe carefully the complete malting of the mass inside the capillary during heating

**********

## Experiment No. 7

**AIM: To study the kinetics of acid-catalyzed hydrolysis of ethyl acetate and to evaluate the value of the rate constant.**

**THEORY:**

A first order reaction is one in which the rate depends on concentration of only one of the reactants. Methyl acetate hydrolyses, in the presence of an acid, which acts as a catalyst, to give acetic acid and methyl alcohol.

$$CH_3COOCH_3 + H_2O \xrightarrow{\text{acid}} CH_3COOH + CH_3OH \qquad \text{Rate} = k'[CH_3COOCH_3][H_2O],$$

Where k' is the specific reaction rate constant. Since water is present in large excess, its concentration remains practically constant throughout the reaction. As a result of this assumption, the above equation reduces to

$$\text{Rate} = k'[CH_3COOCH_3] \text{ where } k' = k[H_2O] = \text{constant}$$

Hence, the rate of reaction is determined by the first power of the concentration of the ester and so the reaction is of the first order. It is however, a pseudo first order reaction which is not first order but is forced to obey the first order rate expression. Such reactions involve more than one molecule in the chemical reaction. As acetic acid is produced during the hydrolysis of methyl acetate, the reaction can be followed by titrating the reaction mixture with standard solution of an alkali.

The value of k can be calculated according to the first order rate expression which is given by

$$k = \frac{2.303}{t} \times \log \frac{a}{a - x} \quad \text{[or]}$$

$$k = \frac{2.303}{t} \times \log \frac{V_\infty - V_o}{V_\infty - V_t}$$

Where,
$V_o$ = Volume of alkali used at t = 0 min,
$V_t$ = Volume of alkali used at any time of reaction,
$V_\infty$ = Volume of alkali used at the end of the reaction.

The values of rate constant can be calculated at different intervals of time t. It is independent of the initial concentration of the ester. It has the dimensions of time$^{-1}$. Calculate the $k_t$ for each reading with respect to time and determine the calculated average k of the reaction. Plot a graph (straight line through origin) of $\log \frac{V_\infty - V_o}{V_\infty - V_t}$ against (t) and from the slope determine the rate constant k = slope x 2.303.

**EQUIPMENT AND MATERIALS.**

A. Measuring cylinder
B. Pipette
C. Burette
D. Conical Flask

E. Stop watch
F. N/10 NaOH
G. N/20 HCL
H. Phenolphthalein indicator etc.

**PROCEDURE:**

1. Take 25ml of cold water in a 250 ml conical flask. Add 4-5 drops of phenolphthalein indicator to it.
2. Take 50ml of N/20 HCL in a separate 100 ml conical flask. Add 5ml of ethyl acetate to it. Quickly shake the reaction mixture for few seconds and note the time because reaction starts. Immediately pipette out exact 5ml of reaction mixture take in the conical flask containing cold water and indicator.
3. Immediately titrate the mixture against N/10 NaOH solution in burette up to end point (pink colour) persisting for 20-30 seconds. Note down the titre value Vo.
4. Repeat the same operation and titration at every 10 minutes until 50th minute of the reaction. The titre value in such cases will be Vt.
5. Finally, heat the reaction mixture at $70^0$-$80^0$C for 10-15 minutes to complete the reaction. And then once again take 5ml of the reaction mixture and titrate it to get $\boldsymbol{V_\infty}$.

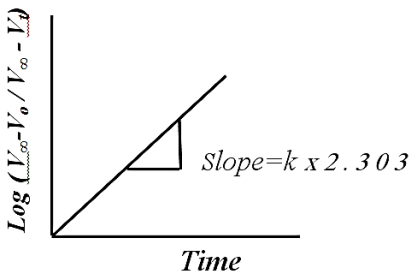
**OBSERVATION:**

Temperature: …. …. …..

| **Sl. No.** | **Time (min)** | **Burette Reading (ml)** | | **Vol. of NaOH (ml)** | $\log\frac{V_\infty - V_o}{V_\infty - V_t}$ | **k ($min^{-1}$)** |
|---|---|---|---|---|---|---|
| | | **Final** | **Final** | | | |
| 1 | 0 | | | (value =$V_0$) | | |
| 2 | 10 | | | | | |
| 3 | 20 | | | | | |
| 4 | 30 | | | | | |
| 5 | 40 | | | | | |
| 6 | 50 | | | | | |
| 7 | 60 | | | | | |
| 8 | ∞ | | | (value =$V_\infty$) | | |
| **Calculated average rate constant ($k_{av}$)=** | | | | | | |

**CALCULATION:**

1. Complete the calculation as per table.
2. Draw the plot and calculate $k_{plot}$




**RESULT:**

From the linear nature of the plot, the order of the reaction was confirmed as 1 (pseudo first order). For the reaction the $k_{av}$=…… and $k_{plot}$=…….

**PRECAUTIONS:**

Write 3/4 points about the precautions that you have taken during your experiment.

**********

## Experiment No. 8

**AIM: To determine the rate law for the reaction between iodide and hydrogen peroxide in an acidic environment and to determine the effect of a catalyst on the rate of reaction.**

**THEORY:**

When hydrogen peroxide is added to a solution of potassium iodide, the iodide ions are slowly oxidized according to the equation:

Molecular equation: $\underset{\text{potassium iodide}\\\text{colorless}}{2KI(aq)} + \underset{\text{hydrochloric acid}\\\text{colorless}}{2HCl(aq)} + \underset{\text{hydrogen peroxide}\\\text{coloroless}}{H_2O_2(aq)} \rightarrow \underset{\text{iodine}\\\text{yellow}}{I_2(s)} + 2H_2O(l)$

Net ionic equation: $\underset{\text{iodide}}{2I^-(aq)} + 2H^+(aq) + \underset{\text{hydrogen peroxide}}{H_2O_2(aq)} \rightarrow \underset{\text{iodine}}{I_2(s)} + 2H_2O(l)$

In this reaction, however, we can ignore the reverse reaction because the equilibrium position is so far on the I2 side that the reaction above does not take place to any appreciable extent. The rate law for this reaction should include the concentrations of iodide, hydrogen ion, and hydrogen perioxide. However, if the concentration of $H^+$ is held constant then its effect will not appear in the rate law. This results in a relatively simple rate law:

$$\text{rate} = k[I^-]^n[H_2O_2]^m[H^+]^p \text{ simplifies to: } \text{rate} = k'[I^-]^n[H_2O_2]^m \text{ where } k' = k[H^+]^p$$

The addition of thiosulfate ions ($S_2O_3^{2-}$) allows an accurate measurement of the rate at which the peroxide-iodide reaction is taking place. Suppose that you add a small and known amount of thiosulfate ion to the original mixture of peroxide and iodide. Iodine is produced slowly by the reaction between peroxide and iodide ions and the thiosulfate ions immediately react with the iodine as it is produced:

$$\underset{\text{iodine}\\\text{yellow}}{I_2} + \underset{\text{thiosulfate}\\\text{colorless}}{2S_2O_3^{2-}} \rightarrow \underset{\text{iodide}\\\text{colorless}}{2I^-} + \underset{\text{dithionate}\\\text{colorless}}{S_4O_6^{2-}} \quad \text{fast reaction}$$

The thiosulfate ions are the limiting reagent. So once all the thiosulfate ions are consumed, iodine starts to form in the solution. Iodine is a pale yellow. If starch is added to the solution then a more dramatic blue solution is formed by the complex of starch–iodine. The color change is sharp, and the time elapsed to this point is determined simply by use of a timer. The time from the addition of the peroxide solution to the appearance of the blue color is Δt for the reaction. Since the stoichiometry of the thiosulfate–iodine and the peroxide–iodide reactions is known, it is not difficult to calculate how many moles of peroxide were reduced in the known interval of time. Consequently, the average rate (moles of hydrogen peroxide consumed per liter per second) of the reaction during this period can be calculated.

$$\text{Rate} = -\frac{\Delta[H_2O_2]}{\Delta t}$$

$\Delta[H_2O_2]$ ← change in peroxide concentration, calculated from known amounts of reactants

$\Delta t$ ← change in time, measured with a stopwatch

If the amount of $H_2O_2$ which reacts during the period taken for the measurement is sufficiently small, no significant change in concentration of the $H_2O_2$ will occur. Under these conditions, the average rate of the reaction determined for this period will be a close approximation of the reaction rate corresponding to the initial concentration of reactants which is the initial rate of the reaction and by taking the log of the equation:

$$\text{Initial rate} = k'[I^-]_0^n[H_2O_2]_0^m$$

where $[I^-]_0$ = initial concentration of iodide
$[H_2O_2]_0$ = initial concentration of hydrogen peroxide

$$\log(\text{Initial rate}) = \log(k') + m\log[H_2O_2]_0 + n\log[I^-]_0$$

If we make two plots of log (Rate) versus log $[H_2O_2]_0$ (where concentration changes) and versus $[I^-]_0$ then the slope of the graph gives us the order of the reactant. Using the values of m and n to 2 significant figures (from the graphs), the initial rate, and the initial concentrations of the peroxide and iodide, calculate the rate constant k for each of the five runs. The values should be the same because k is only a function of temperature for a given reaction. However, due to experimental error the five values of k that you calculate will probably be somewhat different. The equation to calculate k is:

$$k = \frac{\text{initail rate}}{[H_2O_2]^m[I^-]^n}$$

Catalysts operate by decreasing the value of the activation energy for the reaction. An effective catalyst exists for the reaction of iodide with hydrogen peroxide. The catalyst is iron (II) ions dissolved in the reaction mixture. By adding these ions to the reaction mixture we can increase the rate of the reaction.

**EQUIPMENT AND MATERIALS.**

Beakers–250 mL, 100 mL. Graduated cylinders–100 mL, 10 mL. Electric timer, hot plate, 1 M HCl, 1 M KI, 0.04 M $Na_2S_2O_3$, 0.2 M $H_2O_2$, $FeSO_4$ solution, starch solution, and deionized water.

**PROCEDURE:**

1. The volumes of each solution that should be added to the reaction mixture according to the following chart. These mixtures possess varying amounts of hydrogen peroxide and potassium iodide but the amounts of hydrochloric acid and sodium thiosulfate are constant.

| Expt # | Deionized Water (mL) | HCl (mL) | KI (mL) | Starch (mL) | $Na_2S_2O_3$ (mL) | $H_2O_2$ (mL) |
|---|---|---|---|---|---|---|
| 1 | 170 | 4 | 4.0 | 2 | 10.0 | 10.0 |
| 2 | 166 | 4 | 8.0 | 2 | 10.0 | 10.0 |
| 3 | 162 | 4 | 12.0 | 2 | 10.0 | 10.0 |
| 4 | 152 | 4 | 12.0 | 2 | 10.0 | 20.0 |
| 5 | 132 | 4 | 12.0 | 2 | 10.0 | 40.0 |

2. Perform experiment according to mixture 1 to 5 following the following procedure.
3. Add the solutions, except for the peroxide, and place the beaker on a piece of white paper so that the color change may be observed as easily as possible. Start stirring before the addition of

the peroxide, rapidly pour in the peroxide while stirring, and start the time. Continue stirring for about 10 seconds and once the solution is well-mixed, further stirring is unnecessary.

4. Watch the mixture attentively for the first appearance of a blue coloration and stop the timer and the time required should be measured to the nearest second.

5. Clean and rinse the beaker to run the reaction for the next mixture in a similar manner.

6. Prepare any mixture as per table (e.g., 3), without peroxide. Add the peroxide to the mixture at the same time as you add 2 mL of iron (II) ions to the mixture. Measure and record the time of reaction as described earlier.

**OBSERVATION:**

Solution temperature: …. …. …..

$[H_2O_2]$ used in mol/L (M): … …. …. (*2 mole $Na_2S_2O_3$ consumes 1 mole $H_2O_2$)

| Exp. | Time (s) | Rate (M/s) | Log Rate | $[KI]_0$ mol/L | Log $[KI]_0$ | $[H_2O_2]_0$ mol/L | Log $[H_2O_2]_0$ |
|---|---|---|---|---|---|---|---|
| 1 | | | | | | | |
| 2 | | | | | | | |
| 3 | | | | | | | |
| 4 | | | | | | | |
| 5 | | | | | | | |

| **Reaction of Expt #3 solution** | **Solution temperature (°C)** | **Time with catalyst (s)*** | **Time without catalyst (s)**** |
|---|---|---|---|
| Reaction with catalyst of 1 mL iron (II) solution | | | |

**CALCULATION:**

1. From the plot calculate slope for two lines.
2. Calculate K for the 5 reaction mixtures.

**RESULT:**

The rate law for the reaction between iodide and hydrogen peroxide in an acidic environment was determined as…….

The reaction was completed ….. s with $FeSO_4$ catalyst and …..s without catalyst for a particular reaction mixture. The rate of a reaction was increased in presence of catalyst and therefore it was taken less time to complete.

**PRECAUTIONS:**

Write 3/4 points about the precautions that you have taken during your experiment.

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# Experiment No. 9

**Aim: To determine the strength of the given strong acid by strong base potentiometrically.**

**Apparatus:** Burette, pipette, volumetric flasks, beakers, potentiometer, saturated calomel reference electrode (SCE), platinum indicator electrode.

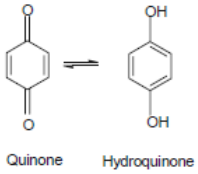
**Chemicals Required:** Hydrochloric acid (0.1 N approx.), sodium hydroxide (0.1 N approx.) and quinhydrone.

**Principle:** When an electrode is dipped in an electrolyte solution, its potential depends on the concentration of the ions to which the electrode is reversible. In the acid–base titration, quinhydrone which is an equimolar mixture of quinone and hydroquinone is employed as $H^+$ reversible system.

Quinone - hydroquinone system involves the equilibrium:

$$C_6H_4O_2 + 2H^+ + 2e^- \rightleftharpoons C_6H_6O_2$$

(Quinone, Q) (Hydroquinone, $QH_2$)




For this reduction reaction, the potential developed on the platinum electrode immersed in this system is given by Nernst equation.

$$E_{cell} = E^{o} + \frac{0.0591}{2}\log\frac{[H^+]^2[Q]}{[QH_2]}$$

$QH_2$ is a weak acid; its ionisation is very small particularly if the pH of the solution is less than 7. Therefore, the concentration of hydroquinone, $QH_2$ is same as that of quinone, Q i.e.

$[Q]/[QH_2]$ = unity

and hence the Nernst equation may be written as,

$E = E^o + 0.0591 \log [H^+]$ at $25^oC$

$E = E^o - 0.0591$ pH

The standard electrode potential of quinhydrone electrode

$E^o$ = + 0.6996 V (From the standard reduction potential table)

$E = 0.6996 - 0.0591$ pH

Thus the potential of quinhydrone electrode is dependent on pH of the solution i.e. quinhydrone electrode behaves as a reversible hydrogen electrode. This is less expensive than hydrogen

electrode since it can be set up easily simply by adding a pinch of quinhydrone to the solution and inserting a Pt electrode for making electrode connections.

The basic reaction involved in the neutralisation of an acid with a base is:

$H^+ (aq) + OH^- (aq) \rightleftharpoons H_2O$ ...(1)

Therefore, the indicator electrode to be selected is obviously an electrode reversible to $H^+$ ions e.g. Hydrogen electrode, glass electrode or quinhydrone electrode. For better results and simple experimentation the latter electrode is commonly used. The cell setup using quinhydrone electrode is:

SCE | quinhydrone (acid solution) | Pt ... (2)

The reduction potential of quinhydrone and the cell EMF will depend on the pH of the solution. On adding small aliquots of a base the EMF of the cell increases gradually; but, near the equivalence point a steep rise in the curve occurs (as shown in Fig. 1).

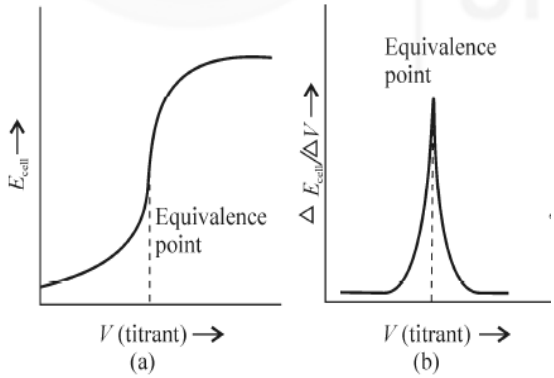



**Fig. 1:** Titration curves: (a) typical plot of EMF vs. volume; (b) typical first derivative titration curve.

**Procedure:**

(i) Take 20 ml of the given acid in a 100 ml beaker (or any other measured volume enough to allow the indicator and reference electrodes to dip into solution).

(ii) Add a pinch of quinhydrone to saturate the solution. Dip the indicator (Pt) and reference (SCE) electrodes in the above acid solution.

(iii) Add 1 ml of 0.1 N NaOH solution from the burette, stirrer for 2 minutes, stop it, wait for 1 minute and measure the EMF.

(iv) Repeat the above step, and go on noting the EMF after each addition.

(v) When the volume reached near about 1 ml of the expected equivalence point. Add the solution from the burette in 0.5 ml instalments and note the potential each time.

(vi) Continue adding these instalments even after the equivalence point (This can be easily observed from the change in the measured potentials). The change becomes very small. Continue for another 3-4 additions & note the potential readings.

(vii) Record the observations in the observation Table.

(viii) Plot the following graphs from the data obtained in the observation table:.

(a) Plot the graph by taking the EMF on the y-axis and volume of NaOH added on the x-axis. The graph will look like the Fig. 1 (a). The volume corresponding to steep rise in the potential is the equivalence point.

(b) Locate the exact end point of the titration by plotting $\Delta E/\Delta V$ along y-axis and average volume ($V^{/}$) on the x-axis. There is a maximum in the plot at the equivalence point Fig. 1 (b).

[$\Delta E = E_1-E_0, E_2-E_1, E_3-E_2, \ldots$ ; $\Delta V = V_1-V_0, V_2-V_1, V_3-V_1, \ldots$ & $V^{/}$ is the average of two consecutive volumes i.e. $V^{/} = (V_1+V_2) / 2$]

**Observations:**

**Observation Table:** Titration of HCl vs. NaOH

| **Vol. of NaOH added (V in ml)** | **EMF (mV)** | **ΔV** | **ΔE** | **ΔE/ΔV** | **Average Vol. of NaOH added ($V^{/}$ in ml)** |
|---|---|---|---|---|---|
| 0 | | $V_1-V_0$ | $E_1-E_0$ | | $(V_0 + V_1) / 2$ |
| 1 | | $V_2-V_1$ | $E_2-E_1$ | | $(V_1 + V_2) / 2$ |
| 2 contd…. | | contd…. | contd…. | | contd…. |

Plot a graph between EMF and Volume of NaOH added and a differential titration curve $\Delta E/\Delta V$ vs Average volume. From these two graphs, determine the volume of NaOH required for the complete neutralization of HCl.

**Calculation:**

Volume of NaOH required for complete neutralization of HCl ($V_1$) = ------ (ml) from graph

Strength of NaOH ($N_1$) = ---------- N

Volume of HCl ($V_2$) = ---------- (ml)

Strength of HCl ($N_2$) = ? (N)

Therefore Strength of HCl ($N_2$) = $V_1N_1 / V_2$

Amount = Normality x Equivalent Weight (HCl)

Amount of HCl present in the whole of the given solution = [$N_2$ x (Eq.wt) x 20] /1000 in gm

(Equivalent Weight of HCl = 36.5)

**Result:**

(i) Strength of the given HCl solution = ---------- N

(ii) The amount of HCl present in the whole of the given solution = --------- gm

**********

# Experiment No. 10

**Aim: To determine the transition temperature of the given salt hydrate.**

**Apparatus:** Melting point capillary tube, Melting point determination apparatus.

**Chemicals Required:** Hydrated salts (Sodium sulphate or sodium thiosulphate)

**Principle:** There are many substances which are capable of existing in more than one crystalline form. These different polymorphous form are not equally stable at a given temperature. However, at a particular temperature, two different forms of substance exist in equilibrium. This temperature is known as the transition temperature of that substance. Not only are transition points associated with polymorphous substances but also with the salt hydrates. When a salt combines with water to form one or more different hydrates, it is found that under a set of given conditions, only one of the hydtrates of the salt is stable. Thus when sodium sulphate decahydrate is heated above $33^0$C, it decomposes into anhydrous sodium sulphate and a saturated solution of this salt. On the other hand, when a saturated salt of sodium sulphate is cooled below $33^0$C, the anhydrous salt takes up water and forms crystals of decahydrate. Similar relationship is observed with other salt hydrate also.

**Procedure:**

(i) Take a small amount of salt hydrate in the melting point capillary
(ii) Insert the capillary into the melting point apparatus
(iii) Start heating the sample at very slow rate
(iv) Record the rise of temperature for every minutes
(v) Record the temperature of the mixture while cooling at regular interval of time

**Observation Table:**

| Time (min) | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 ... | 15 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Temp. on heating ($^0$C) | | | | | | | | | | | |
| Temp. on cooling ($^0$C) | | | | | | | | | | | |

Plot the temperature versus time graph. Two curves (Fig. 1) with common horizontal portions will be obtained. The horizontal portion corresponds to the transition temperature ($T_t$) of the given salt hydrate.

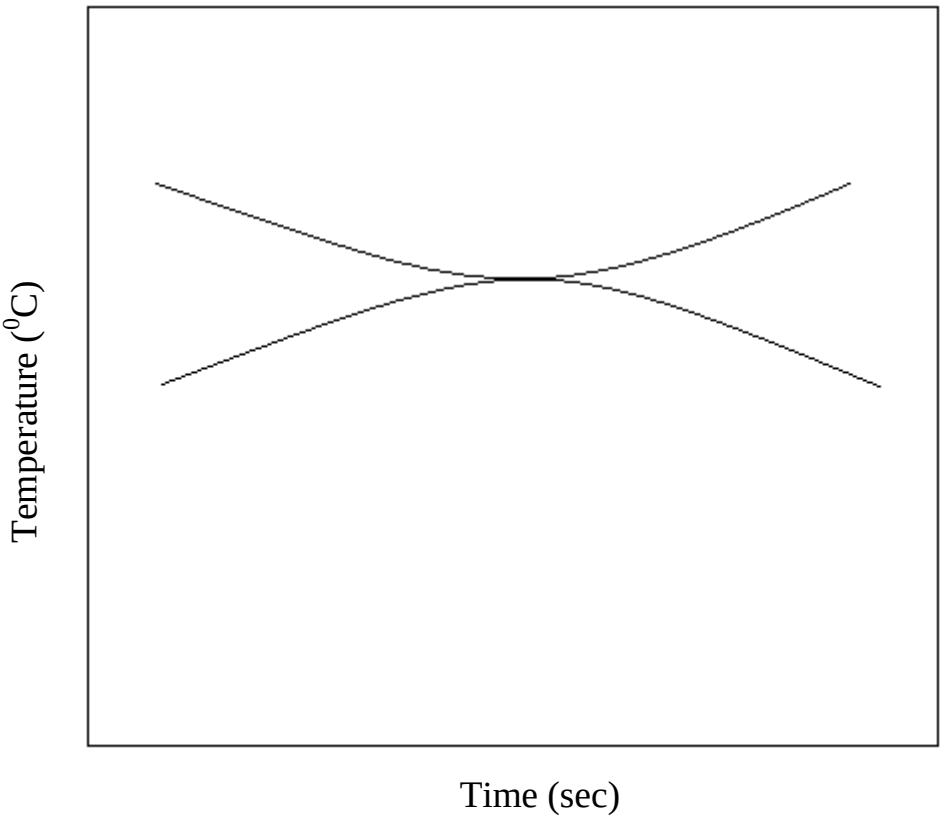



Fig. 1. Temperature-Time graph

**Result:** The transition temperature of the given substance = ……$^0$C.

**********

## Experiment No. 11

**AIM: Qualitative detection of special elements in organic compound (Nitrogen, sulphur and halogens are usually detected by Lassaigne's test)**

**PHYSICAL CHARACTERIZATION:**

a) State:
b) Texture:
c) Color:
d) Ordor:
e) Melting or Boiling point:

**SODIUM EXTRACT PREPARATION:**

Take a small pea size freshly cut and dried Na metal and place in a fusion tube. Heat the fusion tube (holding with a tongue) gently, so that Na melts. Add about 0.2 gm of the compound to be tested in it and heat the mixture to redness. Plungs the fusion tube immediately into about 8-10 ml of distilled water kept in small clean mortar. Grind the whole mass thoroughly with the help of pestle and filter it. The filtrate is called sodium extract, which is being used to detect nitrogen, sulphur & halogens.

**TEST FOR SPECIAL ELEMENTS (NITROGEN, SULPHUR & HALOGENS):**

| Experiment | Observation | Inference |
|---|---|---|
| 1. Take about 5ml of Na extract in a test tube. Add 5ml of freshly prepared dilute ferrous sulphate solution boil it for a few minute, Add two – three drops of dil. $FeCl_3$ solution and then excess sulfuric acid into the mixture. | A blue or green coloration or prussion blue precipitate.<br>OR<br>If red coloration is produced. | Nitrogen is present.<br><br>N & S both Present. |
| 2a) Take a few ml. of Na- extract in a test tube. Add a few ml of freshly prepared very dilute solution of Na nitroprusside to it. | Brillient purple colours appear and slowly vanish on standing. | Sulphur is present. |
| 3. Beilstein test for Halogen:<br>Heat a piece of cu- foil in non- luminous Bunsen flames till it ceases to produce green colour to the flame. Take a little of the organic substance on the burnt cu-foil non-luminous flame | The flame is again colored green.<br><br>If the compound burns with sooty flame. | Halogens present<br><br>Aromatic compound is present. |
| 4. Take a 5ml of Na-extract solu. In a test tube. Acidify the solution with dil. $HNO_3$ Boil for about 5 min. (Boiling is essential to drive out HCN. So if 'N'& 'S' are absent, boiling May be | a) curdy white ppt. Is obtained which is soluble in dil. $NH_4$ OH solu. | a) Chlorine is present. |

| | | |
|---|---|---|
| eliminated). After this add a few ml. of $AgNo_3$ solu. to mixture. | b) A pale yellow ppt.is obtained which dissolves in dil. $NH_4$ OH with difficulty but dissolves easily in conc. $NH_4$ OH<br>c) YelloW ppt. Obtained and is insoluble in $NH_4OH$ solu. | b) Bromine present.<br><br>Iodine present. |
| 5 a) Take about 5ml of solu. In a test tube. Acidify with acetic acid. Treat the solu. With dil. $CCL_4$ and $NaNO_3$ shake the mixture thoroughly.<br><br>b) Acidify the Na extract solu. With dil. $HNO_3$ boil for some time, cool and then add a few ml of $CCL_4$ to it. After this add an excess of $Cl_2$ water and shake. | a) $CCL_4$ layer becomes violet.<br>b) $CCL_4$ layer becomes brown.<br><br>1) $CCL_4$ layer becomes violet.<br>2) $CCL_4$ layer becomes violet. | Iodine present.<br><br>Bromine present.<br><br>Iodine present.<br><br>Bromine present. |

**RESULT:**

The result of the special element detection of given unknown sample was tabulated as below;

| Nitrogen | Sulfur | Halogens |
|---|---|---|
| (write '+' if present and '–' if absent) | (write '+' if present and '–' if absent) | (write '–' if absent and 'X+' if present) |

**PRECAUTIONS:**

Write 3/4 points about the precautions that you have taken during your experiment.

**********

## Experiment No. 12:

**Aim: To draw the pH-titration curve of strong acid vs strong base and to find out the strength of given acid solution.**

**Apparatus:** Burette, pipette, pH meter, glass electrode

**Chemicals Required:** HCl (Approx. 0.1 N), NaOH (Approx. 0.1 N), oxalic acid (0.1 N)

**Principle:** When an alkali is added to an acid solution, the pH of the solution increases slowly, but at vicinity of the end point, the rate of change of pH of the solution is very rapid. From the sharp break in the curve, we can find out the end point, from which the strength of HCl can be calculated.

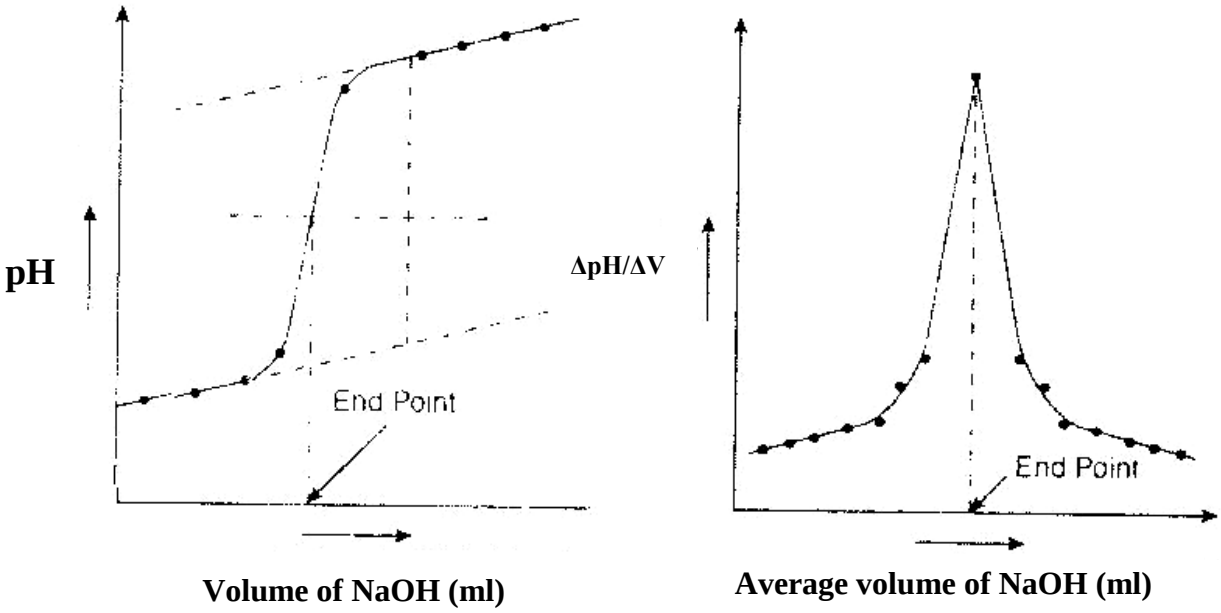



Fig. 1. Equivalence point and titration curve

**Procedure:**

(i) Standardize NaOH solution against 0.1 N oxalic acid solution using phenolphthalein as indicator. [ Equiv. wt. of oxalic acid: 63]

(ii) Wash the glass electrode with distilled water.

(iii) Take 20 ml of HCl solution in a 250 ml beaker. Add sufficient distilled water (100 ml) so that the glass electrode is completely dipped.

(iv) Note the pH of the pure acid solution.

(v) Now add 1 mL of 0.1 N NaOH from the burette in the beaker. Stir the contents well. Note the pH of the solution. Now keep on adding NaOH solution from the burette and note the pH of the solution, up to 9- 10 mL of the NaOH.

(vi) Near the end point add very small amount of sodium hydroxide, because change in pH will be very much appreciable when the acid is neutralized, further addition of such a small amount as 0.01 ml raises the pH about 9 to 10.

(vii) Plot titration curve (pH vs V) and differential titration curve $\Delta pH/\Delta V$ vs Average volume ($V^{/}$) and locate the end point to record the volume of the base required for neutralization of the acid of unknown strength taken into a beaker. [$\Delta pH = pH_2-pH_1$; $\Delta V = V_2-V_1$ & $V^{/}$ is the average of two consecutive volumes i.e. $V^{/}= (V_1+V_2) / 2$]

**Observations:**

| **Vol. of NaOH added (V in ml)** | **pH** | **ΔV** | **ΔpH** | **ΔpH/ΔV** | **Average Vol. of NaOH added ($V^{/}$ in ml)** |
|---|---|---|---|---|---|
| 0 | | $V_1-V_0$ | $pH_1-pH_0$ | | $(V_0 + V_1) / 2$ |
| 1 | | $V_2-V_1$ | $pH_2-pH_1$ | | $(V_1 + V_2) / 2$ |
| 2 contd…. | | contd…. | contd…. | | contd…. |

Plot a graph between pH and Volume of NaOH added and a differential titration curve $\Delta pH/\Delta V$ vs Average volume. From these two graphs, determine the volume of NaOH required for the complete neutralization of HCl.

**Calculation:**

*For standardization of NaOH solution:*

Volume of oxalic acid taken ($V_1$) = … ml

Strength of oxalic acid ($N_1$) = …. N

Volume of NaOH required ($V_2$) = … ml

Strength of NaOH ($N_2$) = ? (N)

$V_1N_1 = V_2N_2$ or $N_2 = V_1N_1 / V_2$

*For calculation of the strength HCl solution:*

Volume of NaOH required for complete neutralization of HCl ($V_1$) = -------- (ml) from graph

Strength of NaOH ($N_1$) = ---------- N

Volume of HCl ($V_2$) = ---------- (ml)

Strength of HCl ($N_2$) = ? (N)

Therefore Strength of HCl ($N_2$) = $V_1N_1 /V_2$

Amount = Normality x Equivalent Weight (HCl)

Amount of HCl present in the whole of the given solution = [$N_2$ x (Eq.wt) x 20] /1000 in gm

(Equivalent Weight of HCl = 36.5)

**Result:**

(i) Strength of the given HCl solution = ---------- N

(ii) The amount of HCl present in the whole of the given solution = --------- gm

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