PRACTICAL MANUAL AND OBSERVATION RECORD
M.Sc., Chemistry, Final Year
Practical - I & II

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M.Sc., Chemistry(Final)   : PRACTICAL MANUAL AND OBSERVATIONS RECORD

PRACTICAL - I & PRACTICAL - II

This book is exclusively prepared for the use of students of
Second year M.Sc., Chemistry Courses, Centre for Distance Education,
Acharya Nagarjuna University
and this book is meant for limited circulation only.

FOREWORD

Acharya Nagarjuna University, since its establishment in 1976, has been moving ahead in the path of academic excellence, offering a variety of courses and research contributions. The University achieved recognition as one of the eminent universities in the country by gaining 'A' grade from the NAAC 2016. At present Acharya Nagarjuna University is offering educational opportunities at the UG, PG levels to students of 447 affiliated colleges spread over the two districts of Guntur and Prakasam.

The University had started the Centre for Distance Education in 2003-04 with the aim to bring Higher education within the reach of all. The Centre has been extending services to those who cannot join in colleges, cannot afford the exorbitant fees as regular students, and to housewives desirous of pursuing higher studies to study B.A., B.Com, and B.Sc., Courses at the Degree level and M.A., M.Com,, M.Sc, M.B.A. and LL.M. courses at the PG level.

For better understanding by students, self-instruction materials have been prepared by eminent and experienced teachers. The lessons have been prepared with care and expertise. However constructive ideas and scholarly suggestions are welcome from students and teachers. Such ideas will be incorporated for the greater efficacy of the distance mode of education. For clarification of doubts and feedback, Weekly classes and contact classes are arranged at UG and PG levels respectively.

I wish the students who pursue higher education through Centre for Distance Education will not only be personally benefited by improving their qualifications but also strive for nation's growth by being a member in Knowledge society I hope that in the years to come, the Centre for Distance Education will grow in strength by introducing new courses, catering to the needs of people. I congratulate all the Directors, Academic coordinators, Editors, Lesson - Writers, and Academic Counsellors and Non-teaching staff of the Centre who have been extending their services in these endeavours.

Prof. P. Rajasekhar, *M.A., M.Phil., Ph.D.*
Vice-Chancellor,
Acharya Nagarjuna University

M.Sc Chemistry (IInd year)
PRACTICAL –I

INORGANIC, ORGANIC, ENVIRONMENTAL CHEMICAL ANALYSIS

1. Analysis of synthetic mixture of copper & Nickel in live of an alloy.
   Copper by volumetry.
   Nickel by Gravimetry
2. Analysis of Tin & Lead from solder.
3. Quantitative Estimation of Glucose.
4. Quantitative Estimation of Aniline.
5. Quantitative Estimation of phenol
6. Determination of Dissolved oxygen in Water.

PRACTICAL –II
INSTUMENTAL METHODS FOR ANALYSIS

1. Estimation of Iron using Thiocyanate Colorimetrically
2. Estimation of Manganese (II) by periodate oxidation colorimetrically
3. Estimation of Vanadium and permanganate by Potentiometric Titration.
4. Estimation of Chloride and Lodide by Potentiometric Titration.
5. Estimation of mixture of strong acid and Weak acid with Strong base.
6. PH metric estimation of an Organic acid.

Equipment and items required for Instrumental Analysis

1.	Potentiometers	-	3
2.	Colorimeters	-	2
3.	Conductometers	-	3
4.	P^H meters	-	3
5.	Platinum electrodes	-	2
6.	Silver electrodes	-	2
7.	Reference electrodes like Calomel electrode	-	4
8.	Salt bridges	-	6
9.	Magnetic stirrers	-	4

CONTENTS

Note: The student is expected to practice all the experiments. *However the experiment-3 in Unit-II and experiment-3 in Unit-IV are not meant for examination.* The examination shall be conducted in both the practicals for a duration of six hours each and against maximum marks of 100 each.

PRACTICAL – I
(INORGANIC, ORGANIC, ENVIRONMENTAL CHEMICAL ANALYSIS)

UNIT – I

1. Quantitative estimation of glucose.

2. Quantitative estimation of aniline.

3. Quantitative estimation of phenol.

UNIT – II

1. Analysis of synthetic mixture of copper and nickel.

2. Analysis of tin and lead from solder.

3. Determination of dissolved oxygen in water.

QUANTITATIVE ESTIMATION OF GLUCOSE

AIM: To determine the amount of glucose present in the given solution.
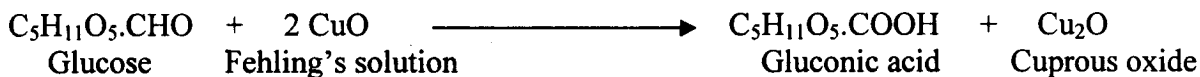
APPARATUS: Burette (50ml), pipettes (5ml) – 2, volumetric flasks (500ml) – 2, conical flasks

CHEMICALS REQUIRED: Glucose, copper sulphate pentahydrate, sodium potassium tartrate (Rochelle salt), sodium hydroxide, methylene blue indicator.

PRINCIPLE:

Alkaline solutions of copper salts, e.g., Fehling's solutions, are reduced by aldose sugars to cuprous oxide. The reduction is not stoichiometric, consequently all methods for the determination of reducing sugars are empirical and the results are affected by slight variations in procedure. Nevertheless the results are trust worthy if the experimental details are adhered to, or if standardisation is effected under identical conditions with solutions of the pure sugars.

The Fehling's solution is blue in colour because it is a solution of cupric ions and at the end point it changes its colour to red precipitate of cuprous oxide. As the supernatant liquid is blue and the precipitate red in colour, there may be some difficulty in the determination of end point accurately. Hence, methylene blue indicator is employed for accurate determination of the endpoint.

$$C_5H_{11}O_5.CHO \quad + \quad 2\,CuO \quad \xrightarrow{\hspace{3cm}} \quad C_5H_{11}O_5.COOH \quad + \quad Cu_2O$$

Glucose   Fehling's solution   Gluconic acid   Cuprous oxide

REAGENTS:

1. Fehling's Solution A :

34.639g of A.R. copper sulphate ($CuSO_4.5H_2O$) is dissolved in water and the volume is made up to the mark in 500 ml in volumetric flask (solution –I).

2. Fehling's solution B or Alkaline tartrate :

173g of Rochelle salt (Sodium potassium tartrate) and 50g of sodium hydroxide are dissolved in water and diluted to 500ml in volumetric flask (solution –II). The solution is allowed to stand for two days.

3. Preparation of standard glucose solution:

About 0.5180 g of glucose is weighed accurately. It is dissolved in water and made upto the mark in a 250 ml volumetric flask.

4. Methylene blue indicator (1%):

One gram of methylene blue indicator is dissolved in 100 ml distilled water.

PROCEDURE:

I. Standardisation of Fehling's solution with standard glucose solution:

5.0ml of Fehling's A and 5.0ml of Fehling's B are pipetted out into a clean 250ml conical flask. Then it is diluted with an equal volume of water and the solution is heated to boiling on a wire gauge with out bumping and titrated against standard glucose solution taken in a burette adding methylene blue as an indicator near the end point of the reaction. Glucose solution is added from the burette until the blue colour of the solution just disappears, this will give an approximate value of the volume of glucose solution required.

To obtain the exact value, the above procedure is repeated. Usually almost all sugar solution need to reduce total copper will be added so that not more than 0.5 to 1.0 ml is required later to complete the titration. The contents are heated to boiling, maintained the gentle boiling for 2 minutes, then without removing the flame beneath the flask, 3–5 drops of a methyleneblue are added. The titration is completed in one minute by adding the glucose solution drop wise until the colour of the methylene blue just disappears. The titration is repeated until concurrent values (i.e. values which do not differ by more than 0.1ml of glucose solution) are obtained.

Factor value is calculated using the formula:

Factor = Titre × mg of glucose per ml

II. Determination of glucose present in the given solution:

The given glucose solution is made up to the mark with distilled water and taken in burette. An aliquot of equal portions of Fehling A and B (5.0 ml each) are pipetted out and the titration is carried out in a similar way as discussed above. From the titre obtained and from the factor calculated previously, the amount of glucose present in the given solution can be calculated.

Precautions:

1. When Fehling solution is required, equal volumes of Fehling's A and Fehling's B are transferred to a dry flask and mixed thoroughly. Fehling's solution deteriorates slowly on keeping. Hence, only sufficient should be prepared to mee immediate requirements.
2. Exactly 5.0ml each of Fehling 'A' and 'B' are taken
3. The solution should be kept hot during the titration
4. The end point should be observed carefully.

Report: Amount of glucose present in 250ml of given solution is _____ mg.

Observations and Calculations:

w = Weight of glucose = g in 250ml

Amount of glucose per ml = $\dfrac{w \times 1000}{250}$ = mg (let us say z mg)

Standardisation of Fehling's Solution:

S. No	Volume (in ml) of		Burette Readings		Volume of glucose (ml)
	Fehling's A	Fehling's B	Initial	Final	
1.	5.0	5.0			
2.	5.0	5.0			
3.	5.0	5.0			

Factor = Titre value × (z) mg of glucose per ml

= volume of glucose × z

=

Estimation of Glucose:

S. No	Volume (in ml) of		Burette Readings		Volume of glucose (ml)
	Fehling's A	Fehling's B	Initial	Final	
1.	5.0	5.0			
2.	5.0	5.0			
3.	5.0	5.0			

Amount of glucose present = $\dfrac{\text{Factor} \times \text{Volume of the given solution}}{\text{Titre value}}$

= $\dfrac{\text{Factor} \times 250}{\text{Volume of given glucose solution run down}}$

=

Therefore, amount of glucose present in 250ml of given solution _____ mg.

AIM: To determine the amount of aniline present in the given solution by bromination process.

APPARATUS: Volumetric flasks, burette, pipettes, iodine flasks

CHEMICALS REQUIRED:

Potassium bromate, potassium bromide, hydrochloric acid, potassium iodide, sodium thiosulphate, starch.

THEORY:

Bromination of aniline by standard brominating mixture ($KBrO_3$ + KBr) in presence of HCl is the process.

$$KBrO_3 + 5\ KBr + 6HCl \rightleftharpoons 3Br_2 + 6\ KCl + 3H_2O$$
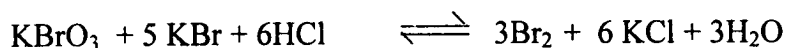
The bromine so liberated reacts quantitatively with aniline forming 2,4,6-tribromoaniline.

Aniline   2,4,6-tribromoaniline

Bromination is carried out with excess of standard bromate–bromide solution in presence of hydrochloric acid. The excess of bromine is made to react with potassium iodide solution, which in turn liberates iodine equivalent to the bromine present. The liberated iodine is titrated with standard thiosulphate solution using starch as indicator.

$$Br_2 + 2KI \longrightarrow I_2 + 2KBr$$

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

PREPARATION OF REAGENTS:

1. Potassium bromate-bromide solution:

0.1N bromate-bromide is prepared by dissolving 1.3916g of A.R potassium bromate and 18.75g of pure potassium bromide in water and made upto 500ml in a volumetric flask.

2. Sodium thiosulphate solution (0.1N):

12.5 g of AR grade sodium thiosulphate pentahydrate (hypo) is dissolved in 500ml with double distilled water.

3. Potassium dichromate solution (0.1N):

About 0.5 g of potassium dichromate is accurately weighed, dissolved in water and made upto 100ml in a volumetric flask. The normality is computed by weight.

4. Starch indicator Solution:

One gram of soluble starch is made into a paste with little amount of water and poured in to 100 ml of boiling water and the boiling is continued for a while and cooled and it can be used as an indicator.

5. 10% potassium iodide solution:

10g of potassium iodide is dissolved in 100ml of distilled water.

PROCEDURE:

Standardisation of hypo using standard potassium dichromate solution:

20.0 ml of potassium dichromate is pipetted out into an iodine flask and 10ml of 10% potassium iodide is added to the solution. 10 ml of 4N sulfuric acid is added and the flask is covered with a small watch glass, allowed to stand for five minutes inorder to complete the reaction. Then the watch glass is removed and vapours of iodine are condensed by flushing distilled water with a jet and titrated immediately with thiosulphate solution. 1–2 ml of starch solution is added when the solution shows a faint yellow colour of iodine. After the addition of starch indicator the contents turn into deep blue in colour. The end point is decolourisation of blue colour. The titration is repeated until consistent results are obtained.

Estimation of Aniline:

10.0 ml of the given aniline solution is pipetted out in to a 250 ml iodine flask. To this solution 20.0 ml of brominating mixture and 5 ml conc. HCl is added. The flask is stoppered immediately and shaken for about one minute for thorough mixing of reactants. The contents are allowed to stand for about 30 minutes with occasional swirling. The flask is cooled under the tap, 10 ml of 10 per cent potassium iodide solution is placed in the cup around the stopper. The stopper is slightly dislodged whereupon the iodide solution is drawn into the flask with no loss of bromine. The flask is shaken for 30 seconds and allowed to stand for 10 minutes. The stopper is removed, the neck of the flask and the stopper are washed with a little water. The liberated iodine is equivalent to the excess of bromine taken. The free iodine is titrated with standardised sodium thiosulphate using 1ml of starch solution near the end point.

A blank analysis is carried out using 20.0 ml of the bromate – bromide reagent and 5 ml of concentrated HCl following the same procedure given above.

Precaution:

The flask must be stoppered every time after the addition of reagents to prevent loss of bromine.

Report: Amount of aniline present in 100ml of given solution _____ g.

OBSERVATIONS / CALCULATIONS:

Weight of potassium dichromate (w)   =   g in 100 ml

Normality of potassium dichromate solution (N_1)

$$= \frac{\text{Wt. of potassium dichromate} \times 1000}{\text{Eq. wt. of potassium dichromate} \times \text{volume}}$$

$$= \frac{w \times 1000}{49.032 \times 100}$$

$$= \underline{\qquad} N$$

Standardisation of sodium thiosulphate solution:

S. No.	Volume of dichromate solution (V_1 ml)	Burette Readings		Volume of hypo (V_2 ml)
		Initial	Final	
1.	20.0			
2.	20.0			
3.	20.0			

We know that $V_1 N_1 = V_2 N_2$

Where V_1 = volume of dichromate solution   = 20.0 ml

N_1 = normality of dichromate solution   N

V_2 = volume of hypo solution   =   ml

N_2 = normality of hypo solution $= \dfrac{V_1 N_1}{V_2} = \underline{\qquad} N$

QUANTITATIVE ESTIMATION OF ANILINE:

Unknown (Sample/ test) titration:

S.No.	Volume of aniline solution (V_3 ml)	Volume of brominating mixture	Burette Readings		Volume of Hypo (V_t ml)
			Initial	Final	
1.	10.0	20.0			
2.	10.0	20.0			
3.	10.0	20.0			

Blank titration:

S.No.	Volume of aniline solution	Volume of brominating mixture	Burette Readings		Volume of Hypo (V_b ml)
			Initial	Final	
1.	0	20.0			
2.	0	20.0			
3.	0	20.0			

Since the concentration of hypo used in both the solutions is one and the same whose normality is known to us, the normality of aniline can be calculated as follows:

Volume of hypo required for the 20ml of bromate-bromide mixture(blank) = V_b = ___ ml

Volume of hypo required for the left over bromate-bromide solution

after brominating 10.0ml of aniline test solution = V_t = ___ ml

Volume of hypo equivalent of bromate-bromide solution

required for bromination of aniline taken = $(V_b - V_t)$ = ___ ml

Since the concentration of hypo used in both the solutions is one and the same whose normality is known to us, the normality of aniline can be calculated as follows:

Volume of aniline (10.0 ml) (V_3) × normality of aniline (N_3) =

    Volume of hypo consumed by left over bromine after bromination ($V_b - V_t$) × normality of hypo(N_2)

In the above mathematical expression except normality of aniline all other entries are known to us and hence normality of the given aniline solution is obtained.

$$N_3 = \frac{(V_b - V_t) \times N_2}{V_3} = \underline{\hspace{1cm}} N$$

Amount of aniline = normality of aniline X $\dfrac{\text{molecular weight of aniline}}{3 \times 2}$

                                      (since 3 bromine molecules are involved in bromination)

$$= N_3 \times \frac{93.13}{3 \times 2} = \underline{\hspace{1cm}} \text{ g/lit}$$

If the unknown (test) solution is given in 100 ml volumetric flask, then the amount of aniline in the given solution will be 1/10th of the amount of aniline calculated above.

Therefore, amount of aniline present in 100ml of given solution _____ g.

AIM: To determine the amount of aniline present in the given solution by bromination process.
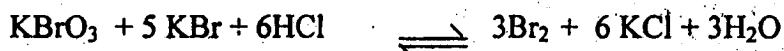
APPARATUS: Volumetric flasks, burette, pipettes, iodine flasks

CHEMICALS REQUIRED:

Potassium bromate, potassium bromide, hydrochloric acid, potassium iodide, sodium thiosulphate, starch.

THEORY:

Bromination of phenol by standard brominating mixture ($KBrO_3$ + KBr) in presence of HCl is the process.

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

The bromine so liberated reacts quantitatively with phenol forming 2,4,6-tribromophenol.
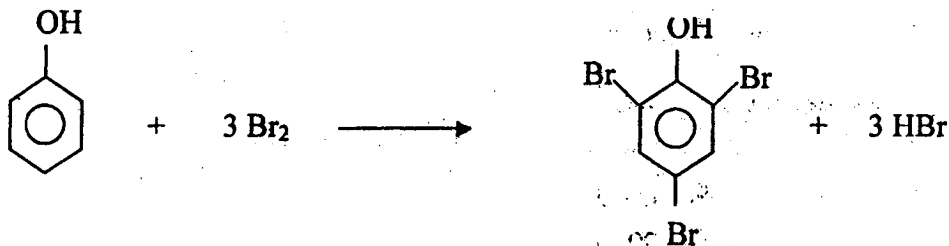
Phenol   2,4,6-tribromophenol

Bromination is carried out with excess of standard bromate–bromide solution in presence of hydrochloric acid. The excess of bromine is made to react with potassium iodide solution, which in turn liberates iodine equivalent to the bromine present. The liberated iodine is titrated with standard thiosulphate solution using starch as indicator.

$$Br_2 + 2KI \longrightarrow I_2 + 2KBr$$

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

PREPARATION OF REAGENTS:

1. Potassium bromate-bromide solution:

0.1N bromate-bromide is prepared by dissolving 1.3916g of A.R potassium bromate and 18.75g of pure potassium bromide in water and made upto 500ml in a volumetric flask.

2. Sodium thiosulphate solution (0.1N):

12.5 g of AR grade sodium thiosulphate pentahydrate (hypo) is dissolved in 500ml with double distilled water.

3. Potassium dichromate solution (0.1N):

About 0.5 g of potassium dichromate is accurately weighed, dissolved in water and made upto 100ml in a volumetric flask. The normality is computed by weight.

4. Starch indicator Solution:

One gram of soluble starch is made into a paste with little amount of water and poured in to 100 ml of boiling water and the boiling is continued for a while and cooled and it can be used as an indicator.

5. 10% potassium iodide solution:

10g of potassium iodide is dissolved in 100ml of distilled water.

PROCEDURE:

Standardisation of hypo using standard potassium dichromate solution:

20.0 ml of potassium dichromate is pipetted out into an iodine flask and 10ml of 10% potassium iodide is added to the solution. 10 ml of 4N sulfuric acid is added and the flask is covered with a small watch glass, allowed to stand for five minutes inorder to complete the reaction. Then the watch glass is removed and vapours of iodine are condensed by flushing distilled water with a jet and titrated immediately with thiosulphate solution. 1–2 ml of starch solution is added when the solution shows a faint yellow colour of iodine. After the addition of starch indicator the contents turn into deep blue in colour. The end point is decolourisation of blue colour. The titration is repeated until consistent results are obtained.

Estimation of Phenol:

10.0 ml of the given phenol solution is pipetted out in to a 250 ml iodine flask. To this solution 20.0 ml of brominating mixture and 5 ml conc. HCl is added. The flask is stoppered immediately and shaken for about one minute for thorough mixing of reactants. The contents are allowed to stand for about 30 minutes with occasional swirling. The flask is cooled under the tap, 10 ml of 10 per cent potassium iodide solution is placed in the cup around the stopper. The stopper is slightly dislodged whereupon the iodide solution is drawn into the flask with no loss of bromine. The flask is shaken for 30 seconds and allowed to stand for 10 minutes. The stopper is removed, the neck of the flask and the stopper are washed with a little water. The liberated iodine is equivalent to the excess of bromine taken. The free iodine is titrated with standardised sodium thiosulphate using 1ml of starch solution near the end point.

A blank analysis is carried out using 20.0 ml of the bromate – bromide reagent and 5 ml of concentrated HCl following the same procedure given above.

Precaution:

The flask must be stoppered every time after the addition of reagents to prevent loss of bromine.

Report: Amount of phenol present in 100ml of given solution _____ g.

OBSERVATIONS / CALCULATIONS:

Weight of potassium dichromate (w) $\qquad$ = $\qquad$ g in 100 ml

Normality of potassium dichromate solution (N_1)

$$= \frac{\text{Wt. of potassium dichromate} \times 1000}{\text{Eq. wt. of potassium dichromate} \times \text{volume}}$$

$$= \frac{w \times 1000}{49.032 \times 100}$$

$$= \underline{\qquad} N$$

Standardisation of sodium thiosulphate solution:

S. No.	Volume of dichromate solution (V_1 ml)	Burette Readings		Volume of hypo (V_2 ml)
		Initial	Final	
1.	20.0			
2.	20.0			
3.	20.0			

We know that $\qquad$ $V_1 N_1 = V_2 N_2$

Where V_1 = volume of dichromate solution $\qquad$ = 20.0 ml

N_1 = normality of dichromate solution $\qquad$ = $\qquad$ N

V_2 = volume of hypo solution $\qquad$ = $\qquad$ ml

N_2 = normality of hypo solution $\qquad$ = $\dfrac{V_1 N_1}{V_2}$ = $\underline{\qquad}$ N

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QUANTITATIVE ESTIMATION OF PHENOL:

Unknown (Sample/ test) titration:

S.No.	Volume of phenol solution (V_3 ml)	Volume of brominating mixture	Burette Readings		Volume of Hypo (V_t ml)
			Initial	Final	
1.	10.0	20.0			
2.	10.0	20.0			
3.	10.0	20.0			

Blank titration:

S.No.	Volume of phenol solution	Volume of brominating mixture	Burette Readings		Volume of Hypo (V_b ml)
			Initial	Final	
1.	0	20.0			
2.	0	20.0			
3.	0	20.0			

Since the concentration of hypo used in both the solutions is one and the same whose normality is known to us, the normality of phenol can be calculated as follows:

Volume of hypo required for the 20ml of bromate-bromide mixture(blank) = V_b = ___ ml

Volume of hypo required for the left over bromate-bromide solution

         after brominating 10.0ml of phenol test solution   = V_t = ___ ml

Volume of hypo equivalent of bromate-bromide solution

         required for bromination of phenol taken   = $(V_b - V_t)$ = ___ ml

Since the concentration of hypo used in both the solutions is one and the same whose normality is known to us, the normality of phenol can be calculated as follows:

Volume of phenol (10.0 ml) (V_3) × normality of phenol (N_3) =
    Volume of hypo consumed by left over bromine after bromination ($V_b - V_t$) × normality of hypo(N_2)

In the above mathematical expression except normality of phenol all other entries are known to us and hence normality of the given phenol solution is obtained.

$$N_3 = \frac{(V_b - V_t) \times N_2}{V_3} = \underline{\quad\quad} N$$

Amount of phenol = normality of phenol X $\dfrac{\text{molecular weight of phenol}}{3 \times 2}$

(since 3 bromine molecules are involved in bromination)

$$= N_3 \times \frac{94.114}{3 \times 2} = \underline{\quad\quad} \text{g/lit}$$

If the unknown (test) solution is given in 100 ml volumetric flask, then the amount of phenol in the given solution will be 1/10th of the amount of phenol calculated above.

Therefore, amount of phenol present in 100ml of given solution _____ g.

ANALYSIS OF SYNTHETIC MIXTURE OF COPPER AND NICKEL

AIM:
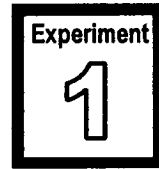
To estimate the amount of copper and nickel in the given solution (copper volumetrically and nickel gravimetrically).

APPARATUS:

Burette (50ml), pipette (20ml), volumetric flask (250ml), measuring cylinder (10ml), conical flask (250ml), beakers (500ml), sintered glass crucibles (SG_3).

CHEMICALS REQUIRED:

Analytical reagent grade copper sulphate penta hydrate ($CuSO_4.5H_2O$), sulphuric acid, sodium carbonate, glacial acetic acid, sodium thiosulphate, potassium iodide, ammonium thiocyanate, starch, nickel sulphate or nickel chloride (preferably nickel ammonium sulphate), hydrochloric acid, ethyl alcohol, dimethyl glyoxime, liquor ammonia.

PRINCIPLE:

When a solution of potassium iodide is added to a slightly acidic solution of copper sulphate, iodine is liberated and the liberated iodine is treated against standard solution of sodium thiosulphate (hypo). Potassium iodide reacts with copper sulphate as follows.

$$2CuSO_4 + 4KI \rightarrow 2CuI + I_2 + 2K_2SO_4$$

$$I_2 + 2Na_2S_2O_3 \rightarrow Na_2S_2O_3 + 2NaI$$
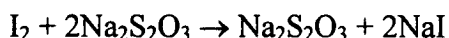
From the equation it follows that equivalent weight of copper sulphate is equal to its formula weight = 249.68gm.

$$\text{0.05N copper sulphate in 250 ml requires } \frac{249.68 \times 0.05}{4} = 3.121 \text{ g}$$

After precipitating and separating Cu^{2+} as CuS using hydrogen sulphide gas in presence of dilute hydrochloric acid, nickel is precipitated by the addition of the alcoholic solution of dimethyl glyoxime (DMG) (or by an aqueous solution of sodium salt of dimethyl glyoxime) to a hot solution of nickel and then slight excess of ammonia is added. The precipitate is washed with cold water, filtered through SG_3 crucible, weighed as nickel dimethyl glyoximate after drying in an oven at 100 to 110^{0}C.

$$Ni^{2+} + 2H_2DMG \rightarrow Ni(DMG)_2 + 2H^+$$
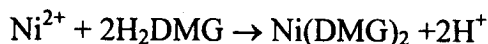
PROCEDURE:

(a) Standerdisation of sodium thiosulphate:

About 3.121g of $CuSO_4.5H_2O$ is weighed accurately and transferred into 250 ml. volumetric flask and made up to the mark with distilled water (Few drops of dilute sulphuric acid are added to suppress the hydrolysis of Cu^{2+}).

The burette is filled with hypo solution to be standardized and initial reading is noted.

20.0 ml. of standard solution of copper is transferred into a conical flask. To this sodium carbonate solution (1%) is added drop wise till the appearance of the slight turbidity. Then about 5ml of acetic acid and 10ml of 10% solution of potassium iodide are added and diluted to 100ml. The contents are allowed to stand for about 10 minutes, placing a watch glass on the top of the flask in order to arrest liberated iodine vapours. There after, vapours are condensed by flushing distilled water with the jet of the wash bottle. Hypo is rundown from the burette until the colour of the solution turns to straw yellow. To this 1-2ml of starch solution is added and again hypo is rundown until the solution turns to pale blue. To this about 2 g of ammonium thiocyanate salt is added. Then the solution turns deep blue. Again hypo is run down until the blue colour just disappears to give a fleshy white precipitate. The final reading of the burette is noted. The difference between initial and final readings of hypo gives the volume of hypo rundown. The titrations are repeated until concurrent values are obtained.

Knowing the normality and volume of copper solution taken and the volume of hypo run down , the normality of hypo can be calculated using the formula $V_1N_1 = V_2N_2$.

The given solution (Cu^{2+} and Ni^{2+}) is made up to the mark in 250 CC volumetric flask and this is used for determination of amounts of Cu^{2+} and Ni^{2+}.

ESTIMATION OF COPPER:

20.0 ml. of the given solution of mixture of copper and nickel is transferred into a conical flask. To this sodium carbonate solution (1%) is added drop wise till the appearance of the slight turbidity. Then about 5ml of acetic acid and 10ml of 10% solution of potassium iodide are added and diluted to 100ml. The contents are allowed to stand for about 10 minutes, placing a watch glass on the top of the flask in order to arrest liberated iodine vapours. There after, vapours are condensed by flushing distilled water with the jet of the wash bottle. Hypo is rundown from the burette until the colour of the solution turns to straw yellow. To this 1-2ml of starch solution is added and again hypo is rundown until the solution turns to pale blue. To this about 2 g of ammonium thiocyanate salt is added. Then the solution turns deep blue. Again hypo is run down until the blue colour just disappears to give a fleshy white precipitate. The final reading of the burette is noted. The difference between initial and final readings of hypo gives the volume of hypo rundown. The titrations are repeated until concurrent values are obtained.

From the normality and volume of hypo run down and the volume of the given solution, the normality of copper in the given mixture can be calculated using the formula $V_2 N_2 = V_3 N_3$. Thus, from the normality of the given Cu^{+2} solution, the amount of copper present in the given solution can be calculated.

ESTIMATION OF NICKEL:

50.0ml of the solution Cu^{2+} and Ni^{2+} is transferred into a 500ml beaker. 3 to 4ml of 1:1 dilute HCl and 50ml of water are added. The solution is warmed to 40^0C. H_2S gas is passed through the solution for about 15 minutes for complete precipitation of Cu^{+2} as a black CuS precipitate. The solution is filtered through Whatmann '40' filter paper. The precipitate is washed with cold water, acidified with a little dilute HCl and saturated with H_2S. (The filtrate is tested for complete precipitation with H_2S). As the precipitate is 'CuS', thus copper is rejected.

The filterate now contains only nickel. Excess H_2S gas is boiled off from the filtrate for one hour with precautions to arrest the bumping. To the solution 0.5ml of dilute. HNO_3 is added and the solution is again boiled. To the hot nickel solution of 30 ml of 1% alcoholic solution of dimethylglyoxime is added and then slight excess of aqueous ammonia solution is added to precipitate nickel as nickel dimethylglyoximate. The beaker containing precipitate and contents are heated on a steam bath for about one hour to coagulate the precipitate so as to filter easily. Then the solution is transferred through a previously weighed sintered glass crucible dried at (100 to 120^0C). The precipitate is washed with cold water until the washings do not give test for chloride. The precipitate is dried in an oven at $100–110^0C$, cooled and weighed. From the weight of nickel dimethyl glyoximate obtained, the amount of nickel is calculated.

The same experiment is repeated with another 50.0ml of the given mixture.

Report: The amount of copper present in the given 250 ml solution is _____ g

The amount of nickel present in the given 250 ml solution is _____ g (original)

The amount of nickel present in the given 250 ml solution is _____ g (duplicate)

Precautions:

1. For the gravimetric determination of nickel, the experiment shall be conducted in duplicate.

2. The crucibles shall be preheated and weighed.

OBSERVATIONS AND CALCULATIONS

Preparation of standard copper sulphate solution:

Weight of the bottle + $CuSO_4. 5H_2O$ = _____ W_1

Weight of weighing bottle   = _____ W_2

W_3 = Weight of $CuSO_4. 5H_2O$ transferred into 250ml volumetric flask = (W_1-W_2)=_____ g

N_1= Normality of standard copper sulphate solution

$$= \frac{Weight\ of\ copper\ sulphate\ taken \times 1000}{Equivalent\ weight\ of\ copper\ sulphate \times volume\ of\ copper\ solution}$$

$$= \frac{W_3 \times 1000}{249.68 \times 250} = _____ N$$

Stadardisation of Hypo:

S.No.	Vol. of standard copper sol. transferred (V_1 ml)	Burette Readings		Volume of hypo rundown (V_2 ml)
		Initial	Final	
1	20.0			
2	20.0			
3	20.0			

We know that $V_1N_1= V_2N_2$

Where V_1 = Volume of standard copper sulphate solution = 20ml

N_1 = Normality of standard copper sulphate solution =

V_2 = Volume of hypo = _____ml

N_2 = Normality of hypo = ?

Therefore, $N_2 = \dfrac{V_1N_1}{V_2} = _____ N$

Determination of Cu^{2+} in the given Solution:

S.No.	Vol. of standard copper sol. transferred (V_3 ml)	Burette Readings		Volume of hypo rundown (V_2 ml)
		Initial	Final	
1	20.0			
2	20.0			
3	20.0			

We know that $\qquad V_2N_2 = V_3N_3$

Where $\qquad V_2 =$ Volume of hypo = _____ ml

$\qquad N_2 =$ Normality of hypo = _____ N

$\qquad V_3 =$ Volume of given copper solution = 20ml

$\qquad N_3 =$ Normality of given copper solution = _?

Therefore, $N_3 = \dfrac{V_2 N_2}{V_3} =$ _____ N

Amount of copper present in the given 250 ml solution =

$$\frac{\text{Normality of the given copper solution} \times \text{Atomic wt. of copper} \times \text{Volume of the given solution}}{1000}$$

$$= \frac{N_3 \times 63.54 \times 250}{1000} = \underline{\quad\quad} \text{ g}$$

Determination of nickel present in the given Solution:

Crucible – I: (Original)

W_1 = Weight of empty sintered Crucible ____ = _____ g

W_2 = Weight of the crucible + nickel dimethyl glyoximate = _____ g

W_3 = Weight of nickel dimethyl glyoximate = $W_2 - W_1$ = _____ g

288.942g of nickel dimethyl glyoximate contains 58.71g of nickel.

Therefore, W_3 g of nickel dimethyl glyoximate (or 50 ml of the given solution) contains =

$$\frac{58.71}{288.942} \times W_3 \text{ g of nickel}$$

Amount of nickel present in the given 250 ml solution = $\frac{58.71}{288.942} \times W_3 \times \frac{250}{50}$ = _____ g

Crucible – II: (Duplicate)

W_4 = Weight of empty sintered Crucible ____ = _____ g

W_5 = Weight of the crucible + nickel dimethyl glyoximate = _____ g

W_6 = Weight of nickel dimethyl glyoximate = $W_5 - W_4$ = _____ g

288.942g of nickel dimethyl glyoximate contains 58.71g of nickel.

Therefore, W_6 g of nickel dimethyl glyoximate (or 50 ml of the given solution) contains =

$$\frac{58.71}{288.942} \times W_6 \text{ g of nickel}$$

Amount of nickel present in the given 250 ml solution = $\frac{58.71}{288.942} \times W_6 \times \frac{250}{50}$ = _____ g

ANALYSIS OF TIN AND LEAD FROM SOLDER

AIM:

To determine the percentage and composition of solder.

APPARATUS:

Beaker (250ml), watch glass, silica crucible, sintered glass crucible (SG$_3$)

CHEMICALS REQUIRED:

Nitric acid, Whatmann–42 filter paper, sulphuric acid, ammonium iodide.

PRINCIPLE:

The method of determination of tin depends upon the oxidation of the tin to the quadrivalent state, precipitation with aqueous ammonia, followed by ignition to stannic oxide, SnO$_2$. The alloy is treated with nitric acid, when a precipitate of hydrous stannic oxide is formed; the formula for this may be written, for simplicity, as H$_2$SnO$_3$, metastannic acid:

$$3Sn + H_2O + 4HNO_3 = 3H_2SnO_3 + 4NO$$
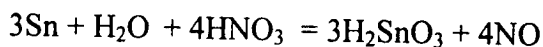
The precipitate possesses colloidal character and exhibits powerful adsorption properties for certain ions, for example, iron, lead, copper, nickel and zinc. It is advisable to use ashless filter paper in the subsequent filtration and also to wash the precipitate with dilute nitric acid in order to avoid peptisation. The precipitate is ignited at the highest temperature to stannic oxide:

$$H_2SnO_3 = SnO_2 + H_2O$$
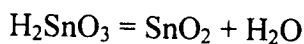
Owing to the ready reduction of the oxide to the metal, the carbon of the filter paper must be burnt off at as low as possible and the flame gases excluded from the crucible.

The precipitate should be white, but rarely it will be so because of the presence of impurities. The amount of impurity may be determined by adding to the impure weighed oxide fifteen times its weight of pure ammonium iodide and heating for 15 minutes in an electric crucible or muffle furnace at 425–475^{0}C., or until no further fumes are evolved. The tin is volatilized quantitatively as stannic iodide.

$$SnO_2 + 4NH_4I = SnI_4 + 4NH_3 + 2H_2O$$
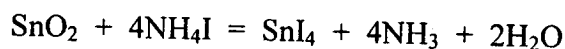
The residue is treated with 2-3 ml of concentrated nitric acid, cautiously evaporated, ignited, and the residual metallic oxides weighed; the loss in weight gives the weight of pure

stannic oxide present in the precipitate. The treatment with nitric acid is necessary, for the other metals are converted into iodides and/or oxyiodides, which are only slowly converted into the oxides by heating in air.

Determination of lead by lead sulphate method provides a separation from the numerous elements which form soluble sulphates. HCl and HNO_3 exert a solvent action upon lead sulphate, hence if these are present, the solution must be evaporated twice with sulphuric acid until dense white fumes are evolved.

PROCEDURE:

About 0.5g of alloy is correctly weighed in to a 250ml beaker. Then 5ml of water and 15ml of concentrated HNO_3 is added. It is covered with a watch glass till the reaction ceases. When the reaction is over it is evaporated to 5ml. It is then diluted to 50ml and heated on a water bath for 15minutes and then filtered through Whatmann–42. The filtrate is collected in a 400ml beaker and the precipitate is washed several times with $1:100HNO_3$. The filtrate and washings are used to determine lead.

Determination of Tin:

The filter paper is dried and placed in a previously weighed porcelain crucible. It is gently heated first and finally ignited for 30 minutes. It is allowed to cool and weighed. The above procedure is repeated until constant weight is obtained. The difference in weight is noted. Then NH_4I is added in excess (about 15 times of the weight of precipitate). The contents are mixed well. It is heated till no fumes are evolved and then for some more time. It is cooled, 2–3ml of concentrated HNO_3 is added and gently evaporated to dryness and cautiously decomposing the residual nitrate over a small flame. It is then ignited and the crucible is cooled and weighed. The loss in weight gives the amount of pure tin present from which the percentage of tin is calculated.

Determination of Lead:

To the filtrate obtained above 4ml of concentrated H_2SO_4 are added and evaporated carefully until free from HNO_3. The solution is allowed to cool, 20ml of water is added and again evaporated until the completion of expulsion of HNO_3. The solution is cooled. 25ml of water are added stirred well and the contents are allowed to stand for an hour. Then filtered through a previously weighed sintered glass crucible, washed with $1:50$ H_2SO_4. It is then dried in an oven cooled and weighed. From the difference of weight the percentage of lead is calculated.

Report: The given solder sample is analysed and its various constituents are found to have the following percentages:

Tin   :

Lead   :

OBSERVATIONS AND CALCULATIONS:

TIN:

w_1 = Weight of solder　　　　　　　=

w_2 = Weight of crucible + Lid　　　　=

w_3 = Weight of crucible after ignition　=

w_4 = Weight of crucible after adding NH_4I　=

w = Weight of SnO_2　　　　　= $w_4 - w_3$ = _____ g

$$\% \text{ of Tin} = \frac{Weight \text{ of } SnO_2(w) \times At.\,Wt.\,of\,tin \times 100}{Mol.\,Wt.\,of\,SnO_2 \times weight\,of\,solder(w_1)} = \frac{w \times 118.7 \times 100}{150.7 \times w_1}$$

$$= \underline{\hspace{1.5cm}} \%$$

LEAD:

w_5 = Weight of empty sintered glass crucible　= _____ g

w_6 = Weight of sintered glass crucible with precipitate　= _____ g

w_7 = Weight of lead sulphate　　= $w_6 - w_5$ = _____ g

$$\% \text{ of Lead} = \frac{weight\,of\,lead\,sulphate\,(w_7) \times Atomic\,weight\,of\,lead \times 100}{molecular\,weight\,of\,lead\,sulphate \times weight\,of\,solder\,(w_1)}$$

$$= \frac{w_7 \times 207.21 \times 100}{303.276 \times w_1} = \underline{\hspace{1.5cm}} \%$$

DETERMINATION OF DISSOLVED OXYGEN IN WATER

AIM:
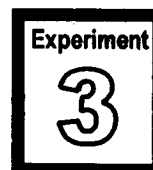
To estimate the amount of dissolved oxygen (D.O.) present in water.

APPARATUS:

Burette, B.O.D. bottle, pipette (2ml), glass bottles, glass rod, conical flask, measuring flask

CHEMICALS REQUIRED:

Potassium hydroxide, sodium thiosulphate, sodium azide, potassium permanganate, potassium oxalate, manganous sulphate, sodium hydroxide, potassium iodide, concentrated sulphuric acid, starch solution.

THEORY:

In natural and waste water dissolved oxygen level depend on the physical, chemical and biological activities in water body. Solubility of oxygen depends on temperature, pressure and salinity of water. The solubility of oxygen decreases with increase in concentration of the salt under a pressure of one atmosphere, the solubility of oxygen of air in distilled or fresh waters with low solid concentrations varies from 14.5 mg/lit at 0^0C to about 7.5 mg/lit at 30^0C.

Dissolved oxygen is needed for living organism to maintain their biological processes. It is essential to the life of fish and other aquatic organisms. Determination of dissolved oxygen (D.O.) is important for industrial purposes. In industrial waters, dissolved oxygen is a nuisance as it induces corrosion reactions. D.O. test is used to monitor the amount of oxygen in boiler feed water by mechanical, physical and chemical methods. D.O. is also important in precipitation and dissolution of inorganic substances in water. This test helps to assess raw water quality and to keep a check on stream pollution. D.O. test is the basis of B.O.D. (biological test which is an important parameter in evaluating the pollution potential of domestic wastes).

The analysis of dissolved oxygen plays a key role in water pollution control activities and waste- water treatment process control. Three methods are used.
   a. Winklers method (or) iodometric method
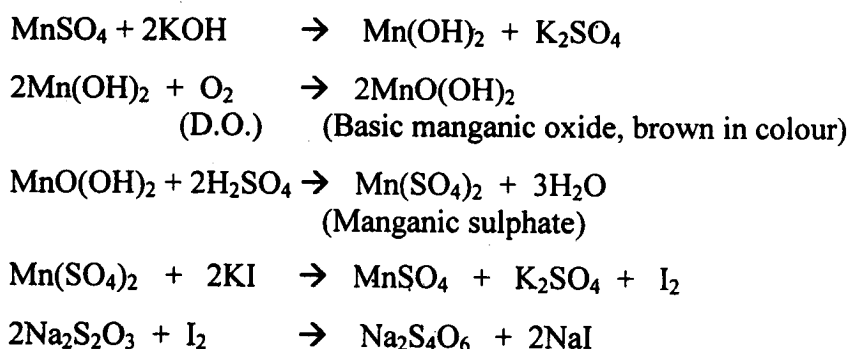   b. Electrometric method using membrane electrode
   c. Polarographic method

Winklers method:

The basic Winkler method is used to determine D.O. It has been modified however to remove the most common interferences. Among the modifications, the Alsterberg's modification

of adding sodium azide to remove nitrate and Rideal–Stewart's modification of adding permanganate to eliminate the interference of ferrous iron are important.

The samples were collected in clean 250ml glass ground joint reagent bottles. At the time of collecting sample 2ml of manganous sulphate solution and 2ml of alkaline-iodie reagent solution were added in quick succession and then bottle was stoppered immediately without entrainment of any air and mixed thoroughly by inverting the bottle atleast ten times.

When manganous sulphate is added to the sample containing alkaline potassium iodide, manganous hydroxide is formed which is oxidized by the dissolved oxygen of the sample to basic manganic oxide. On addition of sulphuric acid, the basic manganic oxide liberates iodine equivalent to that of dissolved oxygen originally present in the sample. The liberated iodine is titrated with a standard solution of sodium thiosulphate using starch as the indicator.

$$MnSO_4 + 2KOH \rightarrow Mn(OH)_2 + K_2SO_4$$

$$2Mn(OH)_2 + O_2 \rightarrow 2MnO(OH)_2$$
$$\quad\quad\quad (D.O.) \quad (\text{Basic manganic oxide, brown in colour})$$

$$MnO(OH)_2 + 2H_2SO_4 \rightarrow Mn(SO_4)_2 + 3H_2O$$
$$\quad\quad\quad\quad (\text{Manganic sulphate})$$

$$Mn(SO_4)_2 + 2KI \rightarrow MnSO_4 + K_2SO_4 + I_2$$

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

Interferences:

Nitrite is the major interfering ion. Ferrous and ferric iron, residual chlorine, oxidisable sulphur compounds such as sulphide, sulphites, thiourea and its derivatives, organic matter and suspended matter also interfere.

Removal of nitrites (Alsterberg modification):

Nitrites interfere during acidification with sulphuric acid. They react with potassium iodide and liberate iodine.

$$2KI + H_2SO_4 \rightarrow 2HI + K_2SO_4$$

$$2HNO_2 + 2HI \rightarrow 2H_2O + N_2O_2 + I_2$$
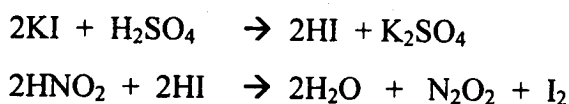
If a longer duration is allowed, the D.O. of the sample reacts with N_2O_2 liberating more iodine and a cyclic reaction occurs.

$$2N_2O_2 + 2H_2O + O_2 \rightarrow 4HNO_2$$
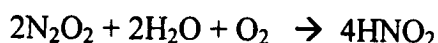
However, nitrites are eliminated by the addition of sodium azide (incorporated in the alkaline iodine reagent) in the presence of sulphuric acid as follows:

$$2NaN_3 + H_2SO_4 \rightarrow 2HN_3 + Na_2SO_4$$

$$HNO_2 + HN_3 \rightarrow N_2O + H_2O + N_2$$

Removal of ferrous salts, sulphides and nitrites (Rideal–Stewart modification):

Addition of potassium permanganate in presence of acid suppresses the interference due to ferrous salts, sulphides and nitrites. Excess of permanganate is removed by reaction with potassium oxalate. However sulphides and organic mater are not oxidized by this method. Hence Rideal–Stewart modification is not used as a general procedure. If it is necessary, electrometric method may be applied to remove such interferences in preference to Ridel–Stewart modification.
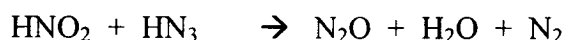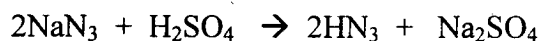
Interference by ferric compounds are suppressed by the addition of phosphoric acid, in place of sulphuric acid. Samples containing suspended solids absorb appreciable quantities of iodine in acid solution. Suspended matter can be flocculated by the use of alum solution and the supernatant liquid may be used for D.O. determination.

When sulphites, thiosulphates and polythionates are present, a preliminary oxidation with alkaline sodium hypochlorite is necessary.

If the sample contains any residual chlorine, it has to be removed by reaction with potassium iodide solution.

PREPARATION OF REAGENTS:

Preparation of standard potassium dichromate solution (0.05N):

About 0.613g of potassium dichromate is accurately weighed and transferred quantitatively to a 250ml volumetric flask. The substance is dissolved in small amount of water and then made up to the mark.

Manganous sulphate solution (36%): 91.0g of manganous sulphate monohydrate ($MnSO_4.H_2O$) is dissolved in water, filtered and diluted to 250ml. (This solution should not liberate iodine when treated with acidified potassium iodide).

Alkali – iodide – azide reagent:

(i) 50 g of sodium hydroxide and 13.5 g of sodium iodide are dissolved in distilled water and diluted to 250ml.
(ii) 1.0 g of sodium azide is dissolved in 10 ml of distilled water.

The azide solution is poured in to the alkali – iodide solution and mixed well and diluted to one liter. This solution should not give colour with starch solution when diluted and acidified.

Dilute sulphuric acid solution (12N):

33ml of concentrated sulphuric acid is added slowly to 67 ml of water while stirring.

KF solution (40%):

40 gm of potassium fluoride is dissolved in 100 ml of distilled water.

Sodium thiosulphate solution (0.02N):

4.96 g of sodium thiosulphate is dissolved in distilled water and made up to one litre in a volumetric flask. It is standardized against standard potassium dichromate solution.

Starch solution:

About one gram of soluble starch is made into a paste with a small amount of water and poured while stirring into 100ml of boiling water, allowed for boiling for two to three minutes more and cooled.

PROCEDURE:

Standardisation of sodium thiosulphate solution:

A 10.0 ml of standard dichromate solution is pipetted out into 10ml of 10% potassium iodide solution acidified with 5ml of dilute sulphuric acid. The liberated iodine is titrated with hypo solution taken in a burette. The titration is continued till the brown solution turns to pale yellow. Then 2ml of starch solution is added and titration is continued till disappearance of the blue colour. The normality of sodium thiosulphate is determined from the volume of hypo consumed.

Determination of dissolved oxygen:

1. A 100ml of water sample is taken in a 250ml B.O.D. bottle, to it 2ml of 40% KF (to mask Fe^{3+}), 2ml of manganous sulphate solution and 2ml of alkaline iodide, azide solution are added while keeping the tip of the pipette below the surface of water. The bottle is stoppered without entrainment of air and mixed by inverting the bottle atleast about ten times. The formation of a brown precipitate of basic manganic oxide indicates presence of D.O. (while the formation of a white precipitate indicates that the sample is devoid of D.O.).

2. Allowed the precipitate to settle completely leaving a clear supernatant liquid. Then stopper is removed carefully and 6ml of 12N H_2SO_4 is added along the sides of the bottle. The bottle is stoppered and the contents are mixed thoroughly till the precipitate dissolved.

3. The liberated iodine is titrated immediately with standardized sodium thiosulphate solution using starch as an indicator.

4. The experiment is repeated until concurrent readings are obtained.

5. From the volume of sodium thiosulphate consumed, D.O. is calculated.

Precautions:

1. Before transporting the samples to the laboratory, the first step to be followed is to fix the oxygen.

2. The solutions are added while keeping the tip of the pipette below the surface of water to avoid more air contact.

3. As far as possible the sample should not be allowed to come in contact with air.

Report: Dissolved oxygen present in the given water sample is _____ mg/lit.

OBSERVATIONS AND CALCULATIONS:

Weight of potassium dichromate (w)   = _____ g in 250 ml

Normality of potassium dichromate solution (N_1)

$$= \frac{\text{Wt. of potassium dichromate} \times 1000}{\text{Eq. wt. of potassium dichromate} \times \text{volume}}$$

$$= \frac{w \times 1000}{49.03 \times 250} = \text{_____ N}$$

Stadardisation of Hypo:

S.No.	Vol. of standard dichromate sol. transferred (V_1 ml)	Burette Readings		Volume of hypo rundown (V_2 ml)
		Initial	Final	
1	20.0			
2	20.0			
3	20.0			

We know that $V_1N_1 = V_2N_2$

Where V_1 = Volume of standard dichromate solution   = 20ml

N_1 = Normality of standard dichromate solution = _____

V_2 = Volume of hypo   = _____ ml

N_2 = Normality of hypo   = ?

Therefore, $N_2 = \dfrac{V_1N_1}{V_2}$ = _____ N

Determination of D.O:

S. No.	Vol. of water sample transferred (V_3 ml)	Burette Readings		Volume of hypo rundown (V_2 ml)
		Initial	Final	
1	100.0			
2	100.0			
3	100.0			

We know that $V_2N_2 = V_3N_3$

Where V_2 = Volume of hypo $\qquad$ = _____ ml

$\qquad$ N_2 = Normality of hypo $\qquad$ = _____ N

$\qquad$ V_3 = Volume of water sample taken $\qquad$ = 100 ml

$\qquad$ N_3 = Normality of water sample with respect to D.O = ?

Therefore, $\quad N_2 = \dfrac{V_1 N_1}{V_2}$ $\qquad$ = _____ N

Dissolved oxygen of the given water sample

$\qquad$ = Normality of water sample w.r.t. D.O. × Eq.Wt. of oxygen × 1000 mg/lit

$\qquad$ = $N_3 \times 8 \times 1000$ $\qquad$ = _____ mg/lit

Amount of dissolved oxygen in the given water sample = _____ mg / lit

PRACTICAL – II
INSTRUMENTAL METHODS OF ANALYSIS

UNIT – III

1. Estimation of iron using thiocyanate colorimetrically.

2. Estimation of Mn(II) by periodate oxidation colorimetrically.

3. Estimation of manganese(VII) and vanadium(V) by potentiometric titration.

UNIT – IV

1. Estimation of chloride and iodide by potentiometric titration.

2. Estimation of mixture of strong acid and weak acid with strong base conductometrically.

3. Estimation of an organic acid by pH metry.

AIM:

To determine the amount of iron(III) present in the given solution colorimetrically.

APPARATUS:

Burettes – 4, volumetric flasks (50ml)–16

CHEMICALS REQUIRED:

Ferric alum (Ferric ammonium sulphate), hydrochloric acid, nitric acid, potassium thiocyanate.

PRINCIPLE:

Ferric iron reacts with thiocyanate to give a series of intensely red - coloured compounds, which remain in true solution. Ferrous iron does not react. Depending upon the thiocyanate concentration, a series of complexes can be formulated as $[Fe(SCN)_n]^{3-n}$ where n = 1,2,3--6.

At low thiocyanate concentration the predominant coloured species is $[Fe(SCN)]^{2+}$,
($Fe^{3+} + SCN^- = [Fe(SCN)]^{2+}$),

at 0.1M thiocyanate concentration $[Fe(SCN)_2]^+$ and

at very high thiocyanate concentration it is largely $[Fe(SCN)_6]^{3-}$.

In the colorimetric determination a large excess of thiocyanate should be used, since this increases the intensity and also the stability of the colour. Strong acids (HCl or HNO_3, 0.05 - 0.5M) should be present to suppress hydrolysis. Sulphuric acid is not recommended because it has a tendency to form complexes with ferric ions.

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+$$
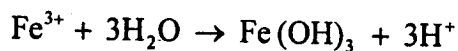
PREPARATION OF REAGENTS:

Preparation of standard iron(III) solution:

About 0.864 g of ferric ammonium sulphate is accurately weighed and dissolved in distilled water. To it 10 ml of concentrated hydrochloric acid is added and the volume is made to one litre in a volumetric flask. One ml of this solution consists 0.1 mg of iron.

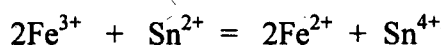The solution can be standardized by reducing Fe(III) to Fe(II) using stannous chloride. Since it is very convenient to standardize iron(II) in presence of hydrochloric acid with dichromate solution.

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

To 25.0ml of hot ferric solution $(70 - 90^0C)$ containing $5 - 6$ N hydrochloric acid is reduced by adding concentrated stannous chloride solution dropwise from a burette with stirring until the yellow colour of the solution has disappeared. The reduction is then completed by diluting the concentrated solution of stannous chloride with two volumes of dilute hydrochloric acid and adding the dilute solution dropwise, with agitation after each addition, until the liquid has a faint green colour, quite free from any tinge of yellow. The solution is then rapidly cooled under the tap to about 20^0C with protection from the air and the slight excess of stannous chloride present is removed by adding 10ml of saturated solution of (5%) mercuric chloride rapidly in one portion and with through mixing. A silky white precipitate of mercurous chloride should be obtained.

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

The oxidizing agent has no appreciable effect upon the small amount of mercurous chloride in suspension. Thus obtained iron(II) solution by reduction is standardized using standard potassium dichromate solution.

Preparation of potassium thiocyanate solution (20%):

About 20 g of potassium thiocyanate is dissolved in 100 ml of water, the solution is 2M.

Preparation of 4N nitric acid:

125 ml of concentrated nitric acid is diluted to 500 ml using distilled water.

PROCEDURE:

A standard series of different concentrations of iron (III) solutions are required for the preparation of calibration curve. About 10 to 12, 50ml standard volumetric flask numbered in a serial order are taken. To each flask 5ml of potassium thiocyanate (2M) and 4ml of nitric acid (4N) are added. Then about 25ml of distilled water is added to all the flasks such that the total volume in each flask ranges from 30 to 35ml. Then iron (III) solution is added to each one of the flasks staring from 0.5ml. Then immediately the contents are made upto the mark, thoroughly mixed and the optical density is measured at 480nm (λ_{max}) against the reagent blank. A reagent blank is one in which both 4ml of nitric acid (4N), 5ml of potassium thiocyanate (2M) are taken and the flask is made upto the mark with distilled water. The successive measurements are done with incremental additions of different concentrations of iron(III) solution to the rest of the flasks. The optical densities are found against the blank solution for each concentration at λ_{max} (480mm). This must be done as soon as after preparation, since there will be variations in colour intensities owing to the formation of different complexes of iron – thiocyanate based on the ratios of iron and thiocyanate at each concentration of iron taken for the colour development..

A calibration curve is constructed taking amount of iron(III) on x axis and corresponding optical densities on y-axis and the curve is checked whether the Beer's law is obeyed or not. The unknown solutions are similarly taken and the colour intensity (optical density is measured) from which the concentration of iron(III) present in unknown solutions are computed.

Precautions:

1. Sulphuric acid should not be used to suppress the hydrolysis of ferric ions.
2. The optical densities must be taken as soon as after preparation (i.e., after colour development)
3. There should not be any time lag after the addition of iron(III) solution in colour development process.

Report: The amount of iron(III) present in the given 100 ml solution is _____ mg.

OBSERVATIONS AND CALCULATIONS:

For drawing Beers law plot:

S. No	Volume of KSCN ml	Volume of 4N HNO₃ (ml)	Volume of Fe(III) solution	Amount of iron (mg)	Optical Density
1	5.0	4.0	0.5		
2	5.0	4.0	1.0		
3	5.0	4.0	1.5		
4	5.0	4.0	2.0		
5	5.0	4.0	2.5		
6	5.0	4.0	3.0		
7	5.0	4.0	3.5		
8	5.0	4.0	4.0		
9	5.0	4.0	4.5		
10	5.0	4.0	5.0		

For the determination of amounts from Beers law plot:

S. No	Volume of KSCN ml	Volume of 4N HNO₃ (ml)	Volume of Fe(III) solution	Amount of iron (mg)	Optical Density
11	5.0	4.0	x_1	-	ODx_1
12	5.0	4.0	x_2	-	ODx_2
13	5.0	4.0	y_1	-	ODy_1
14	5.0	4.0	y_2	-	ODy_1
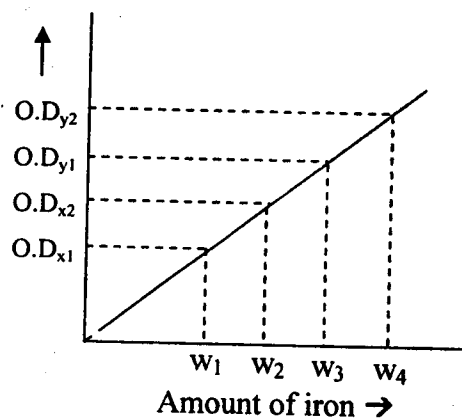
Amount of iron →

From graph:

A_1 x_1 ml of the given solution contains w_1 mg of iron(III).

   Then 100 ml of the given solution contains $\dfrac{w_1}{x_1} \times 100$ mg of iron(III)

A_2 x_2 ml of the given solution contains w_1 mg of iron(III).

   Then 100 ml of the given solution contains $\dfrac{w_2}{x_2} \times 100$ mg of iron(III)

B_1 y_1 ml of the given solution contains w_3 mg of iron(III).

   Then 100 ml of the given solution contains $\dfrac{w_3}{y_1} \times 100$ mg of iron(III).

B_2 y_2 ml of the given solution contains w_4 mg of iron(III).

   Then 100 ml of the given solution contains $\dfrac{w_4}{y_2} \times 100$ mg of iron(III).

Report:

The amount of the iron(III) present in the given 100ml of unknown solution is as follows:

A_1 = Amount of iron(III) present in unknown solution A (original) = _____ mg

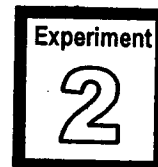A_2 = Amount of iron(III) present in unknown solution A (duplicate) = _____ mg

B_1 = Amount of iron(III) present in unknown solution B (original) = _____ mg

B_2 = Amount of iron(III) present in unknown solution B (duplicate) = _____ mg

ESTIMATION OF MANGANESE (II) BY PERIODATE OXIDATION COLORIMETRICALLY

AIM:

To determine the amount of manganese(II) present in the given solution colorimetrically.

APPARATUS:

Burettes–2, graduated pipette (5ml)-1, volumetric flasks (50ml)–12, volumetric flasks (500ml), volumetric flasks (250ml), volumetric flasks (100ml)

CHEMICALS REQUIRED:

Potassium permanganate, oxalic acid, sodium sulphite, potassium periodate, phosphoric acid (manganese free), sulphuric aicd.

PRINCIPLE:

Manganese in small quantities can be estimated by oxidation to permanganic acid. The oxidizing agent is potassium periodate. In hot acid solution periodate oxidises manganese ion quantitatively to permanganic acid.

$$2\,Mn^{2+} + 5IO_4^- + 3H_2O \rightarrow 2MnO_4^- + 5\,IO_3^- + 6H^+$$
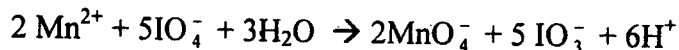
Permanganic acid is pink coloured and the colour produced is proportional to the Mn^{2+} present.

PREPARATION OF REAGENTS:

Preparation of Mn^{2+} solution:

A standard $KMnO_4$ is prepared by dissolving 0.8 g of $KMnO_4$ in 500 ml water and its normality is found by titrating with standard 0.05N oxalic acid solution. 100ml of this solution is quantiatatively transferred into 1000ml beaker and 20ml of 10N H_2SO_4 is added to maintain 2N acidity. To this solution saturated sodium sulphite solution is added until the contents are colourless and boiled to evaporate excess sodium sulphite until no SO_2 fumes are evolved. The solution is colourless and it is quantitatively transferred to 250ml volumetric flask and made up to the mark. This is the stock solution.

Working solution:

50ml of stock solution is diluted to 100ml in a volumetric flask using distilled water.

Note: Alternatively suitable dilutions are advised depending upon the colour intensity that is measured by trail and error method

PROCEDURE:

Standardization of KMnO₄ solution:

20.0 ml of standard oxalic acid solution is transferred to a 250 ml conical flask and it is titrated against $KMnO_4$ solution by maintaining 2N H_2SO_4 acidity at 60^0C temperature. The end point is colourless to pale pink.

Determination of λ_{max} for maximum absorbance:

Note: This is given only for training the student in getting absorption spectrum and hence locating the maximum absorbance (λ_{max}) for the coloured system.

1ml of 1N H_2SO_4, 5ml of orthophosphoric acid (manganese free), 2mg of potassium periodate are added to 'x'ml (where x is any volume between 1 to 10ml) of Mn^{2+} solution and made about 40 ml in a 50ml volumetric flask in order to keep room for expansion during heating. The solution is heated by keeping the flask in a water bath for 10 minutes and suddenly cooled. The solution is made upto the mark with distilled water. The absorbances are noted at various wavelengths between 450–570nm and graph is drawn between wavelength and optical density. The graph shows maximum absorbance (λ_{max}) at 545nm.

Estimation of Mn(II) present in the given solution:

1 to 10 ml of Mn^{2+} solution is taken in 50 ml volumetric flasks. Then to each flask 1ml of sulphuric acid (1N) and 5ml of phosphoric acid (manganese free) are added. 2mg of potassium periodate is added to each of them. A blank solution is also made in a similar manner without Mn^{2+} solution. The contents of the flasks are made approximately say to 40ml. They are heated in a water bath for 10min and suddenly cooled and made upto the mark. The wave length is set at 545nm and optical densities are measured for different concentrations to draw a Beer's law plot.

A graph is drawn by taking amount of Mn^{2+} present on X-axis and optical density on Y-axis. A straight line is obtained. Same procedure is adopted for the given unknown samples also and the amount of Mn^{2+} in unknown samples is computed from the graph.

PRECAUTIONS:

1. The amount of manganese should not exceed 2mg per 100ml, otherwise the colour will be too dark and hence will be out of range of determination.
2. Before periodate oxidation, excess sodium sulphite solution should be removed by expelling SO_2 completely.
3. Phosphoric acid should be added to the test solution, which prevent the precipitation of ferric iodate and also decolourises ferric iron by complex formation.

Report: The amount of manganese(II) present in the given 100 ml solution is _____ mg.

OBSERVATIONS AND CALCULATIONS:

N_1 = Normality of oxalic acid solution = $\dfrac{\textit{Amount of oxalic acid}}{63.035} \times \dfrac{1000}{100}$

= _____ N .

Standardisation of KMnO$_4$ solution:

S.No	Volume of oxalic acid (v$_1$ ml)	Burette readings		Volume of KMnO$_4$ solution (v$_2$ ml)
		Initial	Final	
1.	20.0			
2.	20.0			
3.	20.0			

We know that $V_1N_1 = V_2N_2$

where V_1 = Volume of oxalic acid solution   = _____ ml

N_1 = Normality of oxalic acid solution   = _____ N

V_2 = Volume of permanganate solution   = _____ ml

N_2 = Normality of permanganate solution   =   ?

Therefore, $N_2 = \dfrac{V_1 N_1}{V_2}$ =   = _____ N

Amount of manganese present in the 500 ml solution = w_1

$\dfrac{\text{Normality of permanganate solution} \times \text{Eq. wt. of manganese} \times \text{Volume of solution}}{1000}$

$= \dfrac{N_1 \times 10.988 \times 500}{1000}$ = _____ g

Since 250 ml of stock solution is prepared from 100 ml of permanganate solution,

Amount of manganese present in the 250 ml of stock solution = Amount of manganese present in

$$100 \text{ ml of permanganate solution} = w_2 = \frac{w_1 \times 100}{500} = \_\_\_\_ g$$

Since 100 ml of working solution is prepared by diluting 50 ml of stock solution,

Amount of manganese present in the 100 ml working solution = Amount of manganese present

$$\text{in the 50 ml of stock solution} = w_3 = \frac{w_2 \times 50}{250} = \_\_\_\_ g$$

Therefore, amount of manganese(II) present in 1 ml of working solution = $\dfrac{w_3}{100}$ = ____ g

Determination of λ_{max}:

Wavelength (λ)	O.D.
400	
410	
420	
430	
440	
450	
460	
470	
480	
490	
500	
510	
520	
530	
540	
550	
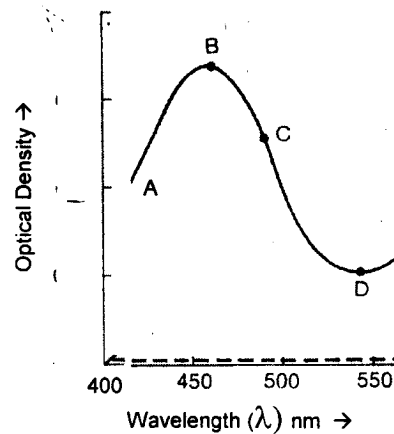
The λ_{max} in this figure lies around 460 nm

Determination of manganese(II):

For drawing Beers law plot:

S. No	Volume of 1N H_2SO_4 (ml)	Volume of H_3PO_4 (ml)	Wt. of periodate (mg)	Volume of working Mn(II) solution (ml)	Amount of Manganese(II) (mg)	Optical Density
1	1.0	5.0	2.0	1.0		
2	1.0	5.0	2.0	2.0		
3	1.0	5.0	2.0	3.0		
4	1.0	5.0	2.0	4.0		
5	1.0	5.0	2.0	5.0		
6	1.0	5.0	2.0	6.0		
7	1.0	5.0	2.0	7.0		
8	1.0	5.0	2.0	8.0		
9	1.0	5.0	2.0	9.0		
10	1.0	5.0	2.0	10.0		

For the determination of amounts from Beers law plot:

S. No	Volume of 1N H_2SO_4 (ml)	Volume of H_3PO_4 (ml)	Wt. of periodate (mg)	Volume of working Mn(II) solution (ml)	Amount of Manganese(II) (mg)	Optical Density
11	1.0	5.0	2.0	x_1	-	
12	1.0	5.0	2.0	x_2	-	
13	1.0	5.0	2.0	y_1	-	
14	1.0	5.0	2.0	y_2	-	
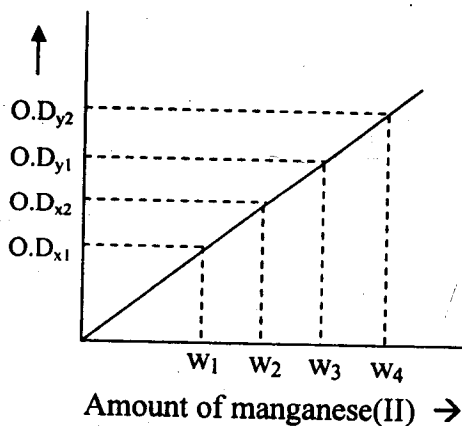
Amount of manganese(II) →

From graph:

A_1 x_1 ml of the given solution contains w_1 mg of manganese(II).

Then 100 ml of the given solution contains $\dfrac{w_1}{x_1}$ x 100 mg of manganese(II).

A_2 x_2 ml of the given solution contains w_1 mg of manganese(II).

Then 100 ml of the given solution contains $\dfrac{w_2}{x_2}$ x 100 mg of manganese(II).

B_1 y_1 ml of the given solution contains w_3 mg of manganese(II).

Then 100 ml of the given solution contains $\dfrac{w_3}{y_1}$ x 100 mg of manganese(II).

B_2 y_2 ml of the given solution contains w_4 mg of manganese(II).

Then 100 ml of the given solution contains $\dfrac{w_4}{y_2}$ x 100 mg of manganese(II).

Report:

The amount of the manganese(II) present in the given 100ml of unknown solution is as follows:

A_1 = Amount of manganese(II) present in unknown solution A (original) = _____ mg

A_2 = Amount of manganese(II) present in unknown solution A (duplicate) = _____ mg

B_1 = Amount of manganese(II) present in unknown solution B (original) = _____ mg

B_2 = Amount of manganese(II) present in unknown solution B (duplicate) = _____ mg

ESTIMATION OF MANGANESE(VII) AND VANADIUM(V) BY POTENTIOMETRIC TITRATION

AIM:

To determine the amount of manganese(VII) and vanadium(V) present in the given solution.

APPARATUS:

Burette, volumetric flasks (250ml), beaker(250ml), salt bridge closed with sintered disks.

CHEMICALS REQUIRED:

Potassium permanganate, ammonium meta vanadate, sodium carbonate, potassium dichromate, ferrous ammonium sulphate, sulphuric acid, phosphoric acid.

PRINCIPLE:

The standard oxidation potentials of permanganate[Mn(VII) – Mn(II)] and vanadate [(V(V)- V(IV)] are 1.51V and 1.0V respectively. Ferrous/Ferric system has a potential of 0.76V. So, when a mixture of permanganate[Mn(VII)] and vanadate [V(V)] is titrated with ferrous solution at an overall acidity of 2N with respect to sulphuric acid, permanganate[Mn(VII)] reacts first, since it has a high oxidation potential than vanadate – vanadyl system. That means the first equivalence point corresponds to the complete reduction of permanganate leading to the formation of Mn(II). Then ferrous system reacts with vanadate. After first equivalence point, addition of phosphoric acid is desirable to reduce or lower the potential of ferrous-ferric system. A second potential jump indicates the equivalence point corresponding to the completion of reduction of [V(V)] to [V(IV)] .

PREPARATION OF REAGENTS:

Preparation of standard potassium dichromate solution (0.05N):

About 0.613g of potassium dichromate is accurately weighed and transferred quantitatively to a 250ml volumetric flask. The substance is dissolved in small amount of water and then made up to the mark.

Preparation of sodium vanadate

Sodium vanadate can be obtained by treating ammonium meta vanadate with a slight excess of sodium carbonate and boiling the solutions until all the ammonia is expelled.

$$2NH_4VO_3 + Na_2CO_3 \longrightarrow 2NaVO_3 + H_2O + CO_2\uparrow + 2NH_3\uparrow$$
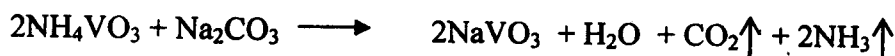
From the above equation it is evident that one mole of sodium carbonate is required for two moles of ammonium vanadate to give two moles of sodium vanadate. This must be kept in mind during the conversion of ammonium vanadate to sodium vanadate.

About 1.5 g of ammonium metavanadate and 1.6g ol sodium carbonate are taken into a 500ml beaker and 150ml of distilled water are added. The mixture is heated well until all the ammonia goes off. The solution is cooled, filtered and made upto 250ml in a volumetric flask.

The sodium vanadate solution so prepared can be standardized with ferrous ammonium sulphate which in turn should be standardized with standard potassium dichromate solution.

Preparation of iron(II) solution (0.05N):

About 5.0 g of ferrous ammonium sulphate is dissolved in small amount of distilled water and 50 ml of 10N H_2SO_4 is added to maintain overall acidity of the solution 2N. Then the contents are made upto the mark in a 250ml volumetric flask with distilled water.

Salt Bridge: 2N sulphuric acid

PROCEDURE:

Standardisation of iron(II) solution:

The cell is

$$Pt \mid Fe^{2+} - Fe^{3+} \mid salt\ bridge \mid KCl(satd); \quad Hg_2Cl_2 \mid Hg$$
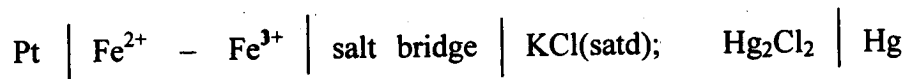
10.0ml of iron(II) solution is pipetted out into to a 250 ml beaker, 10 ml of 10N sulphuric acid is added to maintain the overall acidity 2N. The solution is diluted to about 50ml by adding 30 ml of water. A bright platinum electrode is dipped into the solution which is connected to the positive terminal of potentiometer. The experimental solution is connected to reference electrode through salt bridge. Potassium dichromate is added in equal increments. The solution in beaker being uniformly agitated by the magnetic stirrer. The corresponding potential of the solution after each addition of dichromate is noted. Near the equivalence point which is approximately determined by means of a pilot titration, the titrant is added dropwise. The equivalence point is detected by the sudden jump in potential by the addition of one drop of potassium dichromate solution. To get a neat curve titration continued to a few more incremental additions of potassium dichromate.

A graph is drawn by taking volume of potassium dichromate on x-axis and the corresponding potential on y-axis. The end point is detected by a clear sudden jump. The normality of iron(II) solution is determined using the formula $V_1N_1 = V_2N_2$.

Determination of manganese(II) and vanadium(V):

10.0 ml of the mixture of permanganate and vanadate solution is pipetted out into a 250 ml beaker. 10 ml of 10N sulphuric acid are added to maintain the overall acidity 2N. The solution is diluted to 50ml by adding 30 ml of water. A bright platinum electrode is dipped into the solution which is connected to the positive terminal of potentiometer. The experimental solution is connected to reference electrode through salt bridge.

Standardised iron(II) solution is added in equal increments. The solution in beaker being uniformly agitated by the magnetic stirrer. The corresponding potential of the solution after each increment is noted. Near the equivalence point which is approximately determined by means of a pilot titration, the titrant is added dropwise. The equivalence point is detected by the sudden jump in potential by the addition of one drop of iron(II) solution. The first jump indicates the completion of reaction between permanganate and iron(II) leading to the reduction of Mn(VII) to Mn(II). After the first equivalence point, 5ml of syrupy phosphoric acid is added. Titration is carried out until the second equivalence point is obtained. The second equivalence point indicates the completion of reaction between vanadate and iron indicating the complete reduction of V(V) to V(IV). To get a neat curve titration continued with a few more increments of iron(II) solution.

A graph is drawn by taking volume of iron(II) {preferably amount of Fe(II) } on x-axis and the potential (in mv) on y-axis. The end points are detected by clear sudden jumps. The normality of permanganate and vanadate solutions are determined from first and second equivalence points respectively.

Precautions:

1. It is necessary to clean the platinum electrode wire from time to time. This can be done by dipping the platinum wire in 1N HCl and heating over a spirit lamp (alcohol flame).
2. The stirring should be vigorous after each addition of the titrant.

Report:

The amounts of manganese (VII) and vanadium (V) present in the given 100 ml solution are _____ g and _____ g respectively.

The report can be made as amount of permanganate (MnO_4^-) and vanadate (VO_3^+) also.

OBSERVATIONS AND CALCULATIONS:

Standardisation of iron(II) solution:

V_1 = Volume of standard potassium dichromate solution = 10.0 ml

PILOT TITRATION	
Volume of dichromate solution (ml)	Potential (mv)

REGULAR TITRATION	
Volume of dichromate solution (ml)	Potential (mv)

Volume of
dichromate sol. →
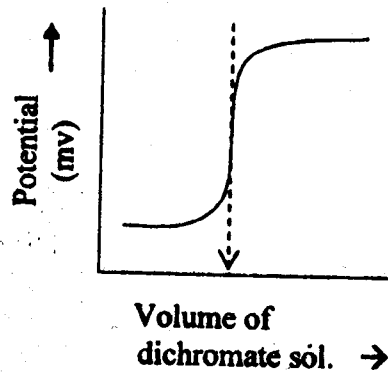
N_1 = Normality of standard potassium dichromate solution

$$= \frac{Weight\ of\ potassium\ dichromate\ taken \times 1000}{Equivalent\ weight\ of\ potassium\ dichromate \times volume\ of\ dichromate\ solution}$$

$$= \frac{W \times 1000}{49.03 \times 250} = \underline{\hspace{2cm}} N$$

We know that $\quad V_1N_1 = V_2N_2$

Where $\quad V_1 =$ Volume of standard potassium dichromate solution $\qquad = \underline{\hspace{1.5cm}}$ ml

$N_1 =$ Normality of standard potassium dichromate solution $\qquad = \underline{\hspace{1.5cm}} N$

$V_2 =$ Volume of iron(II) solution $\qquad = 10.0$ ml

$N_2 =$ Normality of iron(II) solution $\qquad = \ ?$

Therefore, $N_2 = \dfrac{V_1N_1}{V_2} = \underline{\hspace{1.5cm}} N$

Estimation of amount of manganese(VII) / permanganate and vanadium (V) / vanadate:

V_1 = Volume of mixture of permanganate and vanadate solution taken = 10.0 ml

PILOT TITRATION	
Volume of iron(II) solution (ml)	Potential (mv)

REGULAR TITRATION	
Volume of iron(II) solution (ml)	Potential (mv)
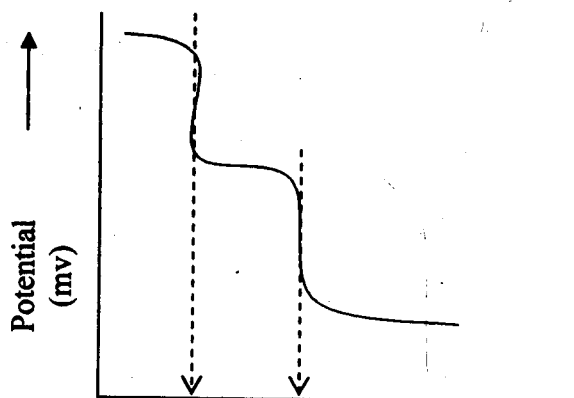
Volume of iron(II) against mixture
of permanganate and vanadate
solution →

We know that $V_2N_2 = V_3N_3$

Where V_2 = Volume of iron(II) solution (from first end point)   = _____ ml

N_2 = Normality of iron(II) solution   = _____ N

V_3 = Volume of permanganate solution (mixture)   = 10.0 ml

N_3 = Normality of permanganate in the mixture   = ?

Therefore, $N_3 = \dfrac{V_2 N_2}{V_3} =$ = _____ N

Amount of manganese present in the given 100 ml solution =

$$\frac{\text{Normality of the given Mn(VII) ion solution} \times \text{Eq. wt. of manganese} \times \text{Volume of the given solution}}{1000}$$

$$= \frac{N_3 \times 10.988 \times 100}{1000} = _____ \text{ g}$$

We know that $V_2 N_2 = V_4 N_4$

Where $V_2 =$ Volume of iron(II) solution (from second end point) = _____ml

$N_2 =$ Normality of iron(II) solution = _____ N

$V_4 =$ Volume of vanadate solution (mixture) = 10.0 ml

$N_4 =$ Normality of vanadate in the mixture = ?

Therefore, $N_4 = \dfrac{V_2 N_2}{V_4} =$ = _____ N

Amount of vanadium(V) present in the given 100 ml solution

$$= \frac{\text{Normality of the given vanadate ion solution} \times \text{Eq. wt. of vanadium} \times \text{Volume of the given solution}}{1000}$$

$$= \frac{N_4 \times 50.95 \times 100}{1000} = \text{_____} \text{ g}$$

ESTIMATION OF CHLORIDE AND IODIDE BY POTENTIOMETRIC TITRATION

AIM:

To determine the amounts of chloride and iodide present in the given solution with silver nitrate solution potentiometrically.

APPARATUS:

Burette, volumetric flasks (250ml), beaker(250ml), salt bridge.

CHEMICALS REQUIRED:

Potassium chloride, potassium iodide, silver nitrate, ammonium nitrate, agar-agar.

PRINCIPLE:

When two ions A^-, A'^- are present in a solution and if both form sparingly soluble salts BA and BA', then salt which has less solubility will be precipitated first.

The solubility product of AgCl, $S_{AgCl} = 1.2 \times 10^{-10}$ and AgI, $S_{AgI} = 1.7 \times 10^{-16}$. Since the solubility product of AgI is less than that of AgCl, AgI will get precipitated first and after the first equivalence point AgCl begins to get precipitated.

$5 \cdot 1$

REAGENTS:

Stock potassium chloride Solution:

A 0.2N solution of potassium chloride is prepared by dissolving 1.491g of potassium chloride in 100ml distilled water.

Stock potassium iodide solution:

A 0.2N solution of potassium iodide is prepared by dissolving 3.32g of potassium iodide in 100ml of distilled water.

From these two stock solutions, 0.01N potassium chloride and 0.01N potassium iodide solutions are prepared.

Working potassium iodide solution:

A 0.01N solution of potassium iodide is prepared by diluting 25 ml of stock potassium iodide solution to 500ml in a volumetric flask.

Silver nitrate solution:

To prepare 0.01N $AgNO_3$ solution 0.8495 g of $AgNO_3$ is dissolved in 500ml of distilled water and is standardized against standard potassium iodide solution.

Salt Bridge: Ammonium nitrate in agar-agar.

Preparation salt bridge:

It is usually more convenient to employ a gel formed from 3% agar in saturated ammonium nitrate solution, the so called agar – ammonium nitrate bridge. The gel is prepared by heating 3g of agar in 100ml of water saturated with ammonium nitrate until all has dissolved and the solution is clear. The narrow U shaped tubes are filled by suction with the warm solution. Upon the cooling the solution sets to a gel. The open ends of U tube shall be kept in a saturated ammonium nitrate solution when not in use for prolonged periods.

Note: Alternatively saturated ammonium nitrate solution may be filled in sintered disk salt bridge.

PROCEDURE:

Standardisation of silver nitrate solution:

10.0 ml of standard iodide ions solution is pipetted out in to a 250ml beaker, and the solution is diluted to about 50ml with distilled water. A bright 'Ag' electrode is used as an indicator electrode here which is connected to the negative terminal of potentiometer, through salt bridge, calomel electrode is connected to the positive terminal of the potentiometer. The beaker is wrapped with a black paper. Standardised silver nitrate is added from a burette. As the titration proceeds the potential changes from negative to positive values. Then the connections are reversed. Near the equivalence point silver nitrate is added dropwise. The jump corresponds to the complete precipitation of silver iodide.

Even other wise in the recent electronic potentiometers supplied by the commercial agencies LCD display is there and hence it depicts –ve values of potentials during iodide precipitation and jumps on to the positive side where + ve potenitials are depicted.

Note: in such case the terminals can be connected as usual i.e. silver electrode to the positive terminal and calomel electrode to the negative terminal of the potentiometer.

A graph is drawn by taking the volume(preferably amount) of silver nitrate on x-axis and corresponding potential on y-axis. The sudden jump in potential gives the end point from which the concentration of silver nitrate is calculated.

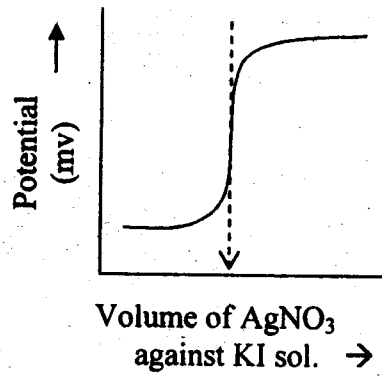### Determination of chloride and iodide:

10.0 ml of chloride and iodide ions mixture is pipetted out in to a 250ml beaker and the solution is diluted to about 50ml with distilled water. A bright 'Ag' electrode is used as an indicator electrode here which is connected to the negative terminal of potentiometer, through salt bridge, calomel electrode is connected which is connected to the positive terminal of the potentiometer. The beaker is wrapped with a black paper. Standardised silver nitrate is added from a burette. As the titration proceeds the potential change from negative to positive values. Then the connections are reversed. Near the equivalence point silver nitrate is added dropwise. The first jump corresponds to the complete precipitation of silver iodide. Then as the titration proceeds silver chloride precipitates and again with one drop of silver nitrate a second jump in potential is obtained which corresponds to precipitation of silver chloride.

A graph is drawn by taking the volume of silver nitrate on x-axis and corresponding potentials on y-axis. The sudden jumps in potential gives the end points.

Report:

The amounts of chloride and iodide present in the given 100 ml solution are _____ and _____ g respectively.

OBSERVATIONS AND CALCULATIONS:

Standardisation of silver nitrate solution:

V_1 = Volume of standard potassium iodide solution = 10.0 ml

PILOT TITRATION	
Volume of AgNO₃ (ml)	Potential (mv)

REGULAR TITRATION	
Volume of AgNO₃ (ml)	Potential (mv)

Volume of $AgNO_3$
against KI sol. →

We know that $V_1N_1 = V_2N_2$

Where V_1 = Volume of standard potassium iodide solution   = 10.0 ml

N_1 = Normality of standard potassium iodide solution   = 0.01 N

V_2 = Volume of silver nitrate solution   = _____ ml

N_2 = Normality of silver nitrate solution   =   ?

Therefore, $N_2 = \dfrac{V_1 N_1}{V_2} =$ = _____ N

Standardisation of silver nitrate solution:

V_3 = Volume of mixture of chloride and iodide solution = 10.0 ml

PILOT TITRATION		REGULAR TITRATION	
Volume of AgNO$_3$ (ml)	Potential (mv)	Volume of AgNO$_3$ (ml)	Potential (mv)

Volume of $AgNO_3$ against mixture of
chloride and iodide sol →
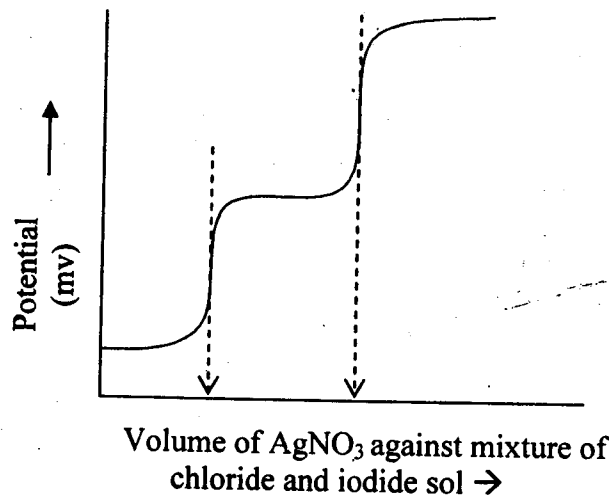
Estimation of amount of iodide present in the given solution:

We know that $\qquad$ $V_2N_2 = V_3N_3$.

Where $\qquad$ V_2 = Volume of silver nitrate solution (from first end point)= _____ ml

N_2 = Normality of silver nitrate solution $\qquad$ = _____ N

V_3 = Volume of iodide ions solution (mixture) $\qquad$ = 10.0 ml

N_3 = Normality of iodide ions in the mixture $\qquad$ = ?

Therefore, $N_3 = \dfrac{V_2 N_2}{V_3} =$ $\qquad$ = _____ N

Amount of iodide present in the given 100 ml solution =

$$\frac{\text{Normality of the given iodide ion solution} \times \text{Eq. wt. of iodine} \times \text{Volume of the given solution}}{1000}$$

$$= \frac{N_3 \times 126.91 \times 100}{1000} = \underline{\qquad} \ g$$

Estimation of amount of chloride present in the given solution:

We know that $\qquad V_2N_2 = V_4N_4$

Where $\qquad V_2 =$ Volume of silver nitrate solution (from second end point) $\quad =$ _____ ml

$\qquad\qquad N_2 =$ Normality of silver nitrate solution $\qquad\qquad\qquad\qquad\quad =$ _____ N

$\qquad\qquad V_4 =$ Volume of chloride ions solution (mixture) $\qquad\qquad\quad = 10.0$ ml

$\qquad\qquad N_4 =$ Normality of chloride ions in the mixture $\qquad\qquad\quad =\quad$?

$\qquad\qquad$ Therefore, $N_4 = \dfrac{V_2N_2}{V_4} = \qquad\qquad\qquad\qquad\qquad\qquad =$ _____ N

Amount of chloride present in the given 100 ml solution =

$$\frac{\text{Normality of the given chloride ion solution} \times \text{Eq. wt. of iodine} \times \text{Volume of the given solution}}{1000}$$

$$= \frac{N_4 \times 35.457 \times 100}{1000} = \text{\underline{\qquad}} \; g$$

Report:

Amount of chloride present in the given solution $\quad =$ _____ g

Amount of iodide present in the given solution $\quad =$ _____ g

AIM:

To determine the strength of a strong acid (hydrochloric acid) and a weak acid (acetic acid) in the given mixture.

APPARATUS:

Burette, volumetric flasks (250ml), beaker(250 ml)

CHEMICALS REQUIRED:

Sodium hydroxide, oxalic acid, hydrochloric acid, acetic acid, phenolphthalein indicator.

THEORY:

This type of titration is just a combination of two separate titrations viz., HCl against NaOH and CH_3COOH against NaOH. By adding alkali to the mixture, the conductivity of the solution decreases due to the replacement of H^+ ions from the strong acid. It then increases as the weak acid is converted into salt and finally rises more steeply as excess of alkali is added.

A curve is plotted with conductivity as ordinate(y-axis) against volume of alkali added as abscissa (x-axis). It is observed that there is a rounding off at both the end points. Usually extrapolation of the straight lines of the three branches would lead to a definite location of the end points. It must be noted that the first end point will be that of hydrochloric acid (strong) while the second is for that of acetic acid (weak).

PREPARATION OF REAGENTS:

Preparation of double distilled water (conductivity water):

Ordinary distilled water possess large conductance due to materials dissolved from the container and also due to the presence of carbondioxide and ammonia dissolved from the air. So it is quite unsuitable for conductivity measurements. Hence conductivity water must be used. It can be prepared by the distillation of about 2 liters of distilled water in which about 8 to 10 crystals of potassium permanganate and 2 to 3 crystals of sodium hydroxide are added. The contents are boiled for about 10 to 15 minutes and the distillation is carried out. Discarding the head and tail portions the water vapour (steam) coming out of the outlet of flask are condensed and collected into ground joint bottles. It should not be preserved more than a week and hence a freshly prepared conductivity water has to be used.

Preparation of standard oxalic acid solution (0.1N):

About 3.15 g of oxalic acid dihydrate { $(COOH)_2.2H_2O$ } is weighed accurately and dissolved in small amount of distilled water and made upto the mark in a 250 ml volumetric flask.

Preparation of sodium hydroxide (0.1N):

About one gram of sodium hydroxide is dissolved in small amount of water and diluted to 250ml and it is standardized against standard oxalic acid solution.

PROCEDURE:

Standardisation of sodium hydroxide solution:

10.0 ml of oxalic acid is pipetted out into a conical flask and it is diluted to 30ml with distilled water. To the solution two or three drops of phenolphthalein indicator is added and then titrated against sodium hydroxide taken in a burette. The end point is colourless to pale pink. The experiment is repeated until concurrent readings are obtained.

Determination of strength of hydrochloric acid and acetic acid:

10.0 ml of the given mixture of hydrochloric acid and acetic acid is pipetted out into a 400ml beaker and about 100 ml of distilled water is added. The electrode of the cell is dipped in the solution of mixture. The beaker is placed in a water bath to maintain constant temperature.

The conductivity of the solution is noted before adding the alkali. Then standardized sodium hydroxide is added from a burette with 1ml increment and the conductivities are noted while shaking thoroughly the contents of the beaker during the addition. Near the equivalence sodium hydroxide is added dropwise. To get a neat curve the titration is continued with a few more increments.

The values of observed conductivity are plotted as ordinate against volume of sodium hydroxide added as abscissa. The concentrations of hydrochloric acid and acetic acid are determined using the end points from the graph.

Precautions:
1. After each addition of the titrant from the burette, the solution should be thoroughly stirred for about a minute and then the reading should be taken.
2. Just before and after the end point, the addition of titrant should be in as small fractions as possible.

Report: The strength of each acid in the give mixture is:
      (i)   hydrochloric acid   = _____ g/lit
      (ii)   acetic acid   = _____ g/lit.

Observations and calculations:

N_1 = Normality of oxalic acid solution = $\dfrac{\text{Amount of oxalic acid}}{63.035} \times \dfrac{1000}{250}$

$$= \underline{\hspace{2cm}} N$$

Standardisation of sodium hydroxide solution:

S. No.	Volume of oxalic acid (v₁ ml)	Burette readings		Volume of NaOH solution (v₂ ml)
		Initial	Final	
1.	20.0			
2.	20.0			
3.	20.0			

We know that $V_1 N_1 = V_2 N_2$

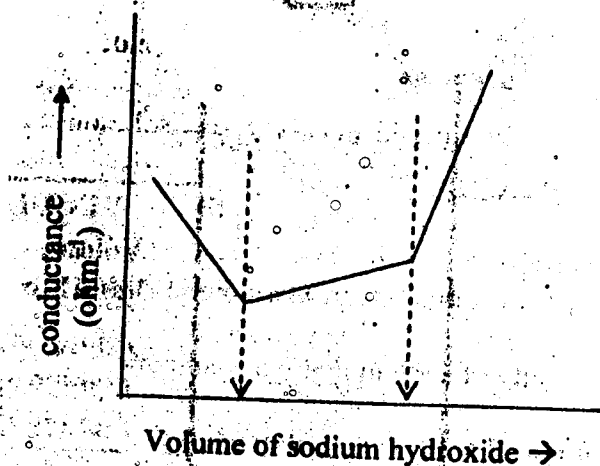where V_1 = Volume of oxalic acid solution   = 20.0 ml

N_1 = Normality of oxalic acid solution   = $\underline{\hspace{2cm}}$ N

V_2 = Volume of sodium hydroxide solution   = $\underline{\hspace{2cm}}$ ml

N_2 = Normality of sodium hydroxide solution   =   ?

Therefore, $N_2 = \dfrac{V_1 N_1}{V_2} =$ = $\underline{\hspace{2cm}}$ N

Determination of strength of hydrochloric acid and acetic acid:

V_3 = Volume of mixture of hydrochloric acid and acetic acid solution = 10.0 ml

PILOT TITRATION	
Volume of NaOH (ml)	Conductivity (ohm^{-1})

REGULAR TITRATION	
Volume of NaOH (ml)	Conductivity (ohm^{-1})

Volume of sodium hydroxide →

Determination of amount of hydrochloric acid

We know that $V_2 N_2 = V_3 N_3$

Where

V_2 = Volume of sodium hydroxide solution (from first end point) = _____ ml

N_2 = Normality of sodium hydroxide solution = _____ N

V_3 = Volume of hydrochloric acid solution (mixture) = 10.0 ml

N_3 = Normality of hydrochloric acid in the mixture = ?

Therefore, $N_3 = \dfrac{V_2 N_2}{V_3}$ = _____ N

Strength of hydrochloric acid = Normality of hydrochloric acid solution x Eq.Wt. of HCl

= N_3 x 36.5 = _____ g/lit

Determination of amount of acetic acid:

We know that $V_2N_2 = V_4N_4$

Where V_2 = Volume of sodium hydroxide solution (from second equivalence point) = _____ ml

N_2 = Normality of sodium hydroxide solution = _____ N

V_4 = Volume of acetic acid solution (mixture) = 10.0 ml

N_4 = Normality of acetic acid in the mixture = ?

Therefore, $N_4 = \dfrac{V_2 N_2}{V_4} =$ = _____ N

Strength of acetic acid = Normality of acetic acid solution x Eq.Wt. of acetic acid

$= N_4 \times 60 =$ _____ g/lit

Note: The mixture of HCl and CH$_3$COOH shall be prepared in such a way that the first equivalence point will lie near about the addition of 5ml, while the second equivalence point will be near about addition of another 5ml (10ml) of sodium hydroxide.

pH METRIC DETERMINATION OF AN ORGANIC ACID

AIM:
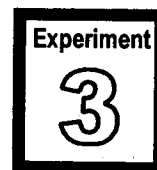
To determine the strength of an organic acid (acetic acid) using pH meter .

APPARATUS:

Burette, volumetric flasks (250ml), beaker(250 ml)

CHEMICALS REQUIRED:

Sodium hydroxide, oxalic acid, acetic acid, phenolphthalein indicator.

THEORY:

When an alkali is added to an acid solution, the pH of the solution increases slowly, but at the vicinity of the equivalence point, the rate of change of pH of the solution is very rapid. From the sharp break in the curve, we can find the equivalence point, from which the strength can be calculated by usual mathematical relation $V_1 N_1 = V_2 N_2$.

Preparation of standard oxalic acid solution (0.1N):

About 1.5759 g of oxalic acid dihydrate [(COOH)$_2$.2H$_2$O] is weighed accurately and dissolved in small amount of distilled water and made upto the mark in a 250 ml volumetric flask.

Preparation of sodium hydroxide (0.1N):

About one gram of sodium hydroxide is dissolved in small amount of water and diluted to 250ml and it is standardized against standard oxalic acid solution.

PROCEDURE:

Standardisation of sodium hydroxide solution:

10.0 ml of oxalic acid is pipetted out into a conical flask and it is diluted to 30ml with distilled water. To the solution two or three drops of phenolphthalein indicator are added and then titrated against sodium hydroxide taken in a burette. The end point is colourless to pale pink. The experiment is repeated until concurrent readings are obtained.

Determination of strength of acetic acid:

The pH meter is standardized first against a buffer of known pH. The glass electrode and reference electrodes are washed with distilled water.

10.0 ml of the given acetic acid solution is pipetted out into a 100ml beaker and about 40 ml of distilled water is added so that the tips of glass electrode as well as the reference electrode are completely immersed in solution. The pH of the solution is noted before adding the alkali. Then standardized sodium hydroxide is added from a burette with 1ml increment and the readings (pH) are noted while shaking thoroughly the contents of the beaker during the addition. Near the equivalence point sodium hydroxide is added dropwise. To get a neat curve titration is continued with a few more increments.

A curve is plotted with pH values as ordinate and the volume of alkali added as abscissa The concentrations of acetic acid is determined using the end point from the graph.

Precautions:
1. After the each addition of the titrant from the burette, the solution should be thoroughly stirred for about a minute and then the reading should be taken.
2. Just before and after the end point, the addition of titrant should be of as small fractions as possible.
3. The temperature control knob of the pH meter should be adjusted to the room temperature.
4. The pH meter should be first standardized by taking a buffer solution of known pH.

Report: The strength of acetic acid is : _____ g/lit

OBSERVATIONS AND CALCULATIONS:

N_1 = Normality of oxalic acid solution = $\dfrac{Amount\ of\ oxalic\ acid}{Eq.\ wt.\ of\ oxalic\ acid} \times \dfrac{1000}{250}$

$$= \dfrac{Amount\ of\ oxalic\ acid}{63.035} \times \dfrac{1000}{250}$$

$$= \underline{\hspace{2cm}} N$$

Standardisation of sodium hydroxide solution:

S. No.	Volume of oxalic acid (v$_1$ ml)	Burette readings		Volume of NaOH solution (v$_2$ ml)
		Initial	Final	
1.	20.0			
2.	20.0			
3.	20.0			

We know that $V_1 N_1 = V_2 N_2$

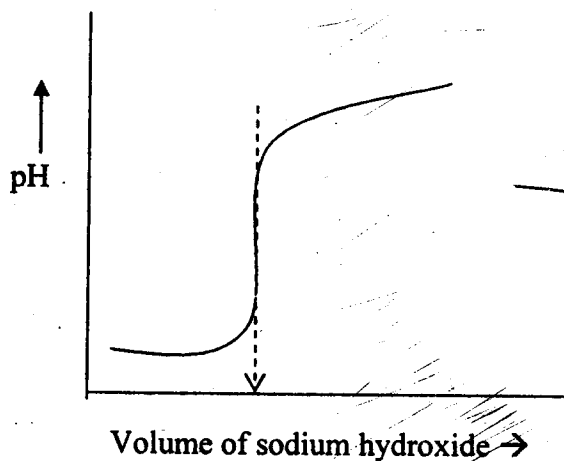where V_1 = Volume of oxalic acid solution = 20.0 ml

N_1 = Normality of oxalic acid solution = $\underline{\hspace{2cm}}$ N

V_2 = Volume of sodium hydroxide solution = $\underline{\hspace{2cm}}$ ml

N_2 = Normality of sodium hydroxide solution = ?

Therefore, $N_2 = \dfrac{V_1 N_1}{V_2} = $ = $\underline{\hspace{2cm}}$ N

Determination of strength of acetic acid:

V_3 = Volume of acetic acid solution = 10.0 ml

PILOT TITRATION	
Volume of NaOH (ml)	pH

REGULAR TITRATION	
Volume of NaOH (ml)	pH

Volume of sodium hydroxide →

We know that $\qquad V_2N_2 = V_3N_3$

Where $\qquad V_2 =$ Volume of sodium hydroxide solution $\qquad = \underline{\hspace{1cm}}$ ml

$\qquad N_2 =$ Normality of sodium hydroxide solution $\qquad = \underline{\hspace{1cm}}$ N

$\qquad V_3 =$ Volume of acetic acid solution (mixture) $\qquad = 10.0$ ml

$\qquad N_3 =$ Normality of acetic acid in the mixture $\qquad = $?

$\qquad$ Therefore, $N_3 = \dfrac{V_2N_2}{V_3} = \qquad\qquad = \underline{\hspace{1cm}}$ N

Strength of acetic acid $\qquad =$ Normality of acetic acid solution x Eq.Wt. of acetic acid

$\qquad = N_3 \times 60 = \underline{\hspace{1cm}}$ g/lit

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5. Environmental Chemistry, by A.K.De, 4th Edition, New Age International Publishers, India.

Acknowledgements

<u>అధ్యాపకుల, విద్యార్థుల సలహాలు, సూచనలు :</u>

అధ్యాపకులు, విద్యార్థులు ఈ స్టడీ మెటీరియల్కు సంబంధించిన సలహాలు, సూచనలు, ముద్రణ దోషాలు తెలియపరచినచో, పునర్ముద్రణలో తగు చర్యలు తీసుకొనగలము. తెలియపరచవలసిన చిరునామా : డిప్యూటీ డైరెక్టర్, దూరవిద్యా కేంద్రం, ఆచార్య నాగార్జున విశ్వవిద్యాలయం, నాగార్జున నగర్ – 522 510.

Course	**Year**	**Title**
M.Sc. Chemistry	Final Year	Practical Manual and Observations Record
		Practical - I & II