B.Sc.-III Practical Chemistry

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Practical Chemistry

Based on Syllabus of Sant Gadge Baba Amravati University, Amravati

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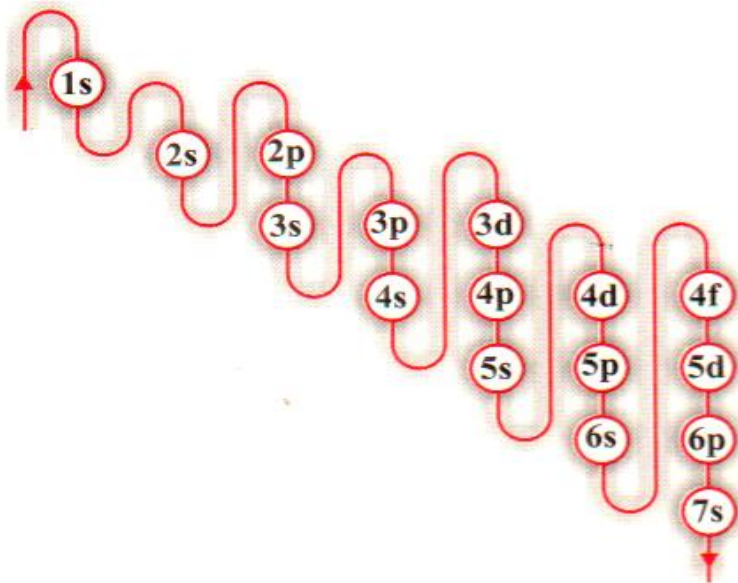
Every success that's worth framing is credited to my family members

Preface ...

I am extremely cheerful to introduce the book "B.Sc.-III Practical Chemistry". This book is strictly in accordance with the semester pattern of Sant Gadge Baba Amravati University, Amravati.

Chemistry is a practical science and an appropriate correlation between teaching theory and practical leads to a better understanding. The detailed study of theory, behind an experiment in practical enables the students to perform the experiment properly. So I have dealt with the theory of experiments in details. Throughout the book chemical reactions have been stressed wherever possible. The emphasis is on simplicity and clarity but not at the cost of logical scientific discussion. I sincerely hope that the method of presentation in the book will be helpful to the students and teachers in performing and demonstrating the experiments independently in laboratory.

In the present book of practical chemistry experiments of both Semester-V and Semester-VI are incorporated. In Semester-V, first part deals with the inorganic chemistry practicals and second part with physical chemistry practicals whereas in Semester-VI, first part deals with the organic chemistry practicals and second part with physical chemistry practicals. The procedure and formulae for the preparation of reagents and solutions required to carry out experiments are included in appendices along with other details.

I would like to put on record my deep sense of gratitude towards Hon'ble Adv. Motisingh G. Mohta, President, Hon'ble Shri Pavan N. Maheshwari, Honorary Secretary, The Berar General Education Society, Akola and Respected Dr. Vijay D. Nanoty, Principal, Shri R.L.T. College of Science, Akola for encouraging me to write the book. I acknowledge the support received from Prakash Printers, Akola in preparation of this book.

It gives me a great pleasure to acknowledge the love and support of my wife Harsha and sons Smit & Sparsh to finish this herculean task.

I believe that a man would do nothing if he waited until he could do it so well that no one would find fault with what he has done. Despite of my sincere efforts, there may have some errors in the book which might be escaped from my notice. Constructive suggestions regarding the improvement of contents of the book are most welcome.

Dr. Pradip P. Deohate

Contents ...

Semester-VI

Organic Chemistry Practicals

Semester-VI

Physical Chemistry Practicals

Semester-V

Inorganic Chemistry Practicals

A. Inorganic Synthesis (Preparation)

Inorganic synthesis or preparations gives us an insight in synthetic inorganic chemistry. As in organic preparations, in inorganic preparations also we have to consider the yield and purity of compounds formed. The theoretical yield of the product can be calculated from the stoichiometric equation for a particular reaction. The actual yield however depends upon the experimental conditions. Hence experiment should be performed in such a way that maximum yield is obtained.

The product can be purified by crystallization of the crude product. However it is time consuming process and hence not suggested in practical. Pure product can also be obtained by using the reactants in pure form and finally washing the product by suitable solvent. The purity is judged by observing the nature of the product.

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Experiment - 01

Preparation of tetraminecopper (II) sulphate

Theory

Tetraminecopper (II) sulphate is a complex salt of copper having the composition $[Cu(NH_3)_4]SO_4.H_2O$. It can be prepared by the action of excess of ammonia on a solution of copper sulphate as per the following reaction.

$$CuSO_4 \quad + \quad 4\ NH_3 \longrightarrow [Cu(NH_3)_4]SO_4$$
$$(CuSO_4.5H_2O)\ (4\ NH_4OH) \qquad ([Cu(NH_3)_4]SO_4.H_2O)$$
$$(MW : 249.5) \qquad\qquad (245.5)$$
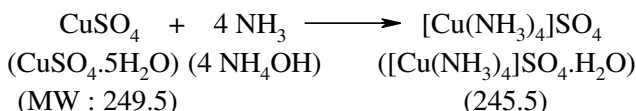
Initially copper sulphate is converted into copper hydroxide which further dissolves in excess of ammonia to form the complex.

Structure (Geometry) : Outer-orbital Square Planer (VBT)
Hybridization : sp^2d
Magnetic Property : Paramagnetic (One unpaired electron)
Colour : Blue
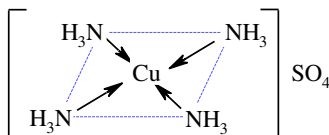
Note - *If the formation of tetraminecopper (II) sulphate complex is explained in terms of sp^3-hybridization then it has tetrahedral geometry while in terms of dsp^2-hybridization it has square planer geometry. Howerever, physical measurements indicated the non existance of tetrahedral geometry. Now, if square planer geometry corresponding to the dsp^2-hybridization is correct then electron in a higher energy level ($4p_z$ or $5s$) should be easily lost and convert Cu^{2+} into Cu^{3+}, but this is not so. Hence it is suggested by Huggin that it has square planer geometry but it corresponds to sp^2d-hybridization. According to CFT and MOT tetraminecopper (II) sulphate complex has distorted octahedral geometry.*

Facilities

Apparatus - Beaker (100 ml), Measuring cylinder, Funnel, Glass rod, Test tubes etc.
Chemicals - Crystalline copper sulphate, Liquor ammonia, Ethanol etc.

Procedure

1. Take 2 g of crystalline copper sulphate in a clean 100 ml beaker. Add about 5 ml of liquor ammonia solution in small installments with stirring so that the salt dissolves giving an intense blue solution and the solution smells strongly of ammonia.

2. Pour 5 ml of ethanol slowly down the side of beaker so as to cover the solution with alcohol. Keep it for half an hour, intense blue crystals of tetraminecopper (II) sulphate complex will appear in the solution.

3. Stir the solution slowly and gently to ensure complete precipitation. Filter the crystals of complex, dry them by pressing between the folds of filter papers and weigh it.

Result

Yield of tetraminecopper (II) sulphate is ……… g.

o-------------------------o

Experiment - 02

Preparation of hexaminenickel (II) chloride

Theory

Hexaminenickel (II) chloride is a complex salt of nickel having the composition $[Ni(NH_3)_6]Cl_2$. It can be prepared by the action of excess of ammonia with nickel chloride as per the following reaction.

$$NiCl_2 \quad + \quad 6\ NH_3 \quad \longrightarrow \quad [Ni(NH_3)_6]Cl_2$$
$$(NiCl_2.6H_2O)\ (6\ NH_4OH)$$
$$(MW : 237.6) \qquad\qquad\qquad (231.6)$$
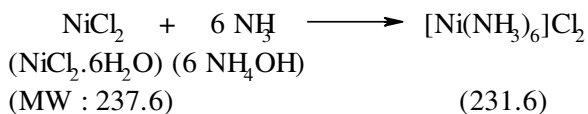
The reaction proceeds through the formation of hydroxide which is then converted into the complex.

Structure (Geometry) : Outer-orbital Octahedral
Hybridization   : sp^3d^2
Magnetic Property   : Paramagnetic (Two unpaired electrons)
Colour   : Violet
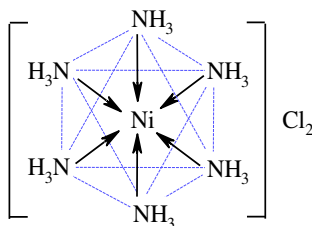
Facilities

Apparatus - Beaker (100 ml), Measuring cylinder, Funnel, Glass rod, Test tubes etc.
Chemicals - Nickel chloride, Liquor ammonia, Ammonium chloride etc.

Procedure

1. Take 1.5 g of nickel chloride in a clean 100 ml beaker. Add about 5 ml of liquor

ammonia solution in small installments with stirring so that the salt dissolves, giving an intense blue solution and the solution smells strongly of ammonia.

2. Add 5 ml of saturated ammonium chloride solution (*about 2 g ammonium chloride in 5 ml liquor ammonia*) to the reaction mixture and allow it to stand for half an hour, violet crystals of hexaminenickel (II) chloride complex will appear in the solution.

3. Stir the solution slowly and gently to ensure complete precipitation. Filter the crystals of complex, dry them by pressing between the folds of filter papers and weigh it.

Result

Yield of hexaminenickel (II) chloride is ……… g.

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Experiment - 03

Preparation of potassium trisoxalatoaluminate (III)

Theory

The complex potassium trisoxalatoaluminate (III) having the composition $K_3[Al(C_2O_4)_3].H_2O$, can be obtained by conversion of aluminum or aluminum hydroxide (hydrated alumina) into potassium aluminate and then reacting with oxalic acid as follows.

1. If aluminum metal is used -

$$Al + 3\ KOH \longrightarrow K_3AlO_3 + 3/2\ H_2$$

$$K_3AlO_3 + 3\ H_2C_2O_4 \longrightarrow K_3[Al(C_2O_4)_3].H_2O + 2\ H_2O$$

Thus, $\quad Al + 3\ KOH + 3\ H_2C_2O_4 \longrightarrow K_3[Al(C_2O_4)_3].H_2O + 2\ H_2O + 3/2\ H_2$

$$(3\ H_2C_2O_4.2H_2O)$$

(MW: 27)   (3 x 56)   (3 x 126)   (426)
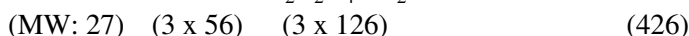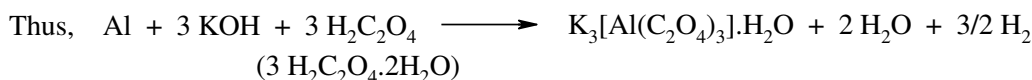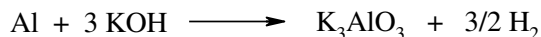
2. If aluminum hydroxide is used -
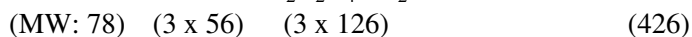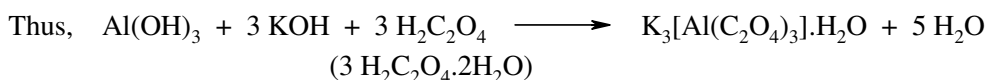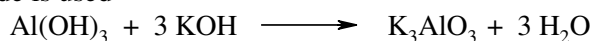
$$Al(OH)_3 + 3\ KOH \longrightarrow K_3AlO_3 + 3\ H_2O$$

$$K_3AlO_3 + 3\ H_2C_2O_4 \longrightarrow K_3[Al(C_2O_4)_3].H_2O + 2\ H_2O$$

Thus, $\quad Al(OH)_3 + 3\ KOH + 3\ H_2C_2O_4 \longrightarrow K_3[Al(C_2O_4)_3].H_2O + 5\ H_2O$

$$(3\ H_2C_2O_4.2H_2O)$$

(MW: 78)   (3 x 56)   (3 x 126)   (426)

Structure (Geometry) : Outer-orbital Octahedral
Hybridization   : sp^3d^2
Magnetic Property   : Diamagnetic (No unpaired electrons)
Colour   : Colourless
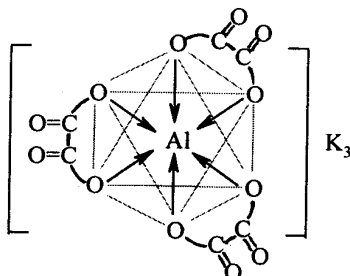
Facilities

Apparatus - Beaker (100 ml), Measuring cylinder, Funnel, Glass rod, Test tubes etc.
Chemicals - Aluminum metal or aluminum hydroxide, Potassium hydroxide, Oxalic acid, Ethanol etc.

Procedure

1. Weigh 1 g of aluminum hydroxide (hydrated alumina) or 0.35 g of aluminum metal and place it in a 100 ml beaker. Cover it with 5 ml of warm water.

2. Carefully add 15 ml of 15% KOH solution in small portions (*If aluminum metal is used, vigorous effervescence are produced because of evolution of hydrogen gas. Allow it to subside before subsequent addition*). Heat it to boiling so as to dissolve all aluminum and filter through glass wool to remove the solid. Add 5 ml of water to the filtrate and again heat it to boiling.

3. Weigh about 5 g of oxalic acid and add it in portions to the hot solution until the aluminum hydroxide first precipitated is redissolved just after boiling. Avoid adding excess of oxalic acid.

4. Filter the solution while hot. Cool the filtrate to room temperature, add 15 ml of ethanol and cool it in an ice bath. The product separates as small colourless prism (*sometimes after scratching the walls of beaker*). Filter it to separate the product, wash the crystals on filter paper with 50% ethanol, dry at room temperature and weigh it.

Result

Yield of potassium trisoxalatoaluminate (III) is ……… g.

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Experiment - 04

Preparation of prussian blue

Theory

The complex iron hexacyanoferrate is commonly called as prussian blue. It can be obtained by oxidation of iron to Fe^{3+}, followed by reaction with potassium ferrocyanide as follows.

$$Fe + H_2SO_4 \longrightarrow FeSO_4 + H_2$$
$$2\,FeSO_4 + H_2SO_4 + 2\,HNO_3 \longrightarrow Fe_2(SO_4)_3 + 2\,H_2O + 2\,NO_2$$
$$2\,Fe_2(SO_4)_3 + 3\,K_4[Fe(CN)_6] \longrightarrow Fe_4[Fe(CN)_6]_3 + 6\,K_2SO_4$$
$$\text{Thus, } 4\,Fe \longrightarrow Fe_4[Fe(CN)_6]_3$$
$$\text{(MW: 4 x 55.85)} \qquad \text{(859.25)}$$
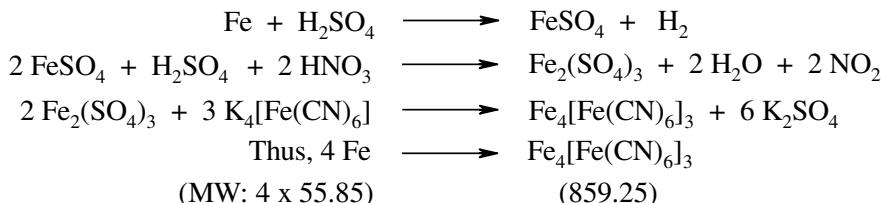
Structure (Geometry) : Inner-orbital Octahedral
Hybridization   : d^2sp^3
Magnetic Property   : Diamagnetic (No unpaired electrons)
Colour   : Deep Blue

$$\left[\ \begin{array}{c} NC \underset{\underset{\displaystyle CN}{\displaystyle NC}}{\overset{\overset{\displaystyle CN}{\displaystyle CN}}{Fe}}\ CN \end{array}\ \right]_3 Fe_4$$

Facilities

Apparatus - Beaker (100 ml), Measuring cylinder, Funnel, Glass rod, Test tubes etc.

Chemicals - Iron fillings, Potassium ferrocyanide, Dilute H_2SO_4, Conc. HNO_3, Ethanol etc.

Procedure

1. Weigh 0.5 g of iron fillings and place it in a 100 ml beaker. To this add 10 ml of dilute H_2SO_4 and heat it using wire gauze. Remove the burner as soon as the reaction becomes vigorous. When the reaction subsides, decant the supernatant liquid and repeat the procedure till whole iron fillings are dissolved.

2. Combine the solution of ferrous sulphate and heat it. Add 0.5 ml of conc. HNO_3 and boil to oxidize the iron to ferric state till solution becomes yellow. Continue boiling for 5 minutes to expel fumes of NO_2 gas and nitric acid.

3. Add the saturated solution of 4.5 g of potassium ferrocyanide and heat the solution until it acquires the uniform blue colour.

4. Filter the product and wash it with little quantity of ethanol. Dry it by pressing between the folds of filter papers and weigh it.

Result

Yield of prussian blue is ……… g.

o-------------------------o

Experiment - 05

Preparation of chrome alum

Theory

A double salt of the chromium and potassium i.e. chrome alum, $K_2SO_4.Cr_2(SO_4)_3.24H_2O$, can be prepared from potassium dichromate by reaction with alcohol or other oxidizable compound. The reaction can be given as follows.

$$K_2Cr_2O_7 + 4\ H_2SO_4 + 3\ C_2H_5OH \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 3\ CH_3CHO + 7\ H_2O$$
(MW: 294.22)   (98)

$$\downarrow$$

$$K_2SO_4.Cr_2(SO_4)_3.24\ H_2O$$
(998.8)

Structure : Double Salt
Colour   : Violet

$$\left[\text{KO}-\overset{\overset{\text{O}}{\|}}{\underset{\underset{\text{O}}{\|}}{\text{S}}}-\text{OK} \,.\, \text{O}=\overset{\overset{\text{O}}{\|}}{\underset{\underset{\text{O}}{|}}{\text{S}}}-\text{O}-\text{Cr}-\text{O}-\overset{\overset{\text{O}}{\|}}{\underset{\underset{\text{O}}{|}}{\text{S}}}=\text{O} \right] . 24\,H_2O$$

Facilities

Apparatus - Beaker (100 ml), Measuring cylinder, Glass rod, Thermometer, Test tubes, Funnel etc.

Chemicals - Potassium dichromate, Conc. H_2SO_4, Ethanol etc.

Procedure

1. Take 2 g of potassium dichromate in a 100 ml beaker and dissolve it by adding 10 ml of water. Add carefully 2 ml of concentrated sulphuric acid with constant stirring. Keep the solution for about 10 min. and then cool it in an ice bath.

2. Add 5 ml of ethanol with constant stirring and maintaining the temperature below 50^0C. Allow it to stand overnight. Violet crystals of chrome alum separate out.

3. Filter it, wash with little quantity of water. Dry the crystals in the folds of filter paper and weigh it.

Result

Yield of chrome alum is ……… g.

o-------------------------o

Experiment - 06

Preparation of sodium thiosulphate

Theory

Sodium thiosulphate ($Na_2S_2O_3.5H_2O$) can be prepared by reacting a mixture of sodium sulphite with sulphur. This reaction proceeds as follows.

$$Na_2SO_3 \ + \ S \ \longrightarrow \ Na_2S_2O_3$$
$$(Na_2SO_3.7H_2O) \qquad\qquad (Na_2S_2O_3.5H_2O)$$
$$(MW : 252) \quad (32) \qquad\qquad (248)$$
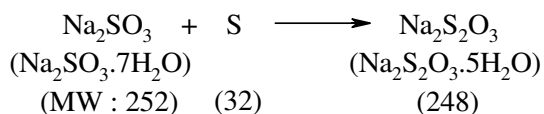
Structure (Geometry) : Tetrahedral
Colour : Colourless

6
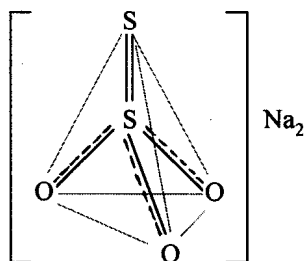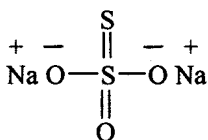
Facilities

Apparatus - Conical flask (100 ml), Air condenser, Porcelain dish, measuring cylinder, Funnel, Glass rod, Test tubes etc.

Chemicals - Sodium sulphite, Sulphur powder, Ethanol, Distilled water, Ice etc.

Procedure

1. Take 4 g of crystalline sodium sulphite in a clean 100 ml conical flask. Add 10 ml of distilled water and heat the flask until the salt dissolves.
2. Weigh 0.8 g of powdered sulphur, moist it with few drops of ethanol and add to the solution of sodium sulphite.
3. Attach an air condenser to the flask and boil the solution carefully till almost all sulphur dissolves.
4. Filter the solution through a filter paper, collect the filtrate in a porcelain dish and evaporate it till crystallization begins.
5. Cool the solution in an ice bath and filter the crystals of sodium thiosulphate. Dry the crystals by pressing them between folds of filter papers and weigh it.

Result

Yield of sodium thiosulphate is ……… g.

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Semester-V
Physical Chemistry Practicals

A. Conductometry

Like the metallic conductors, solutions of electrolytes (acids, bases and salts in water) conduct electricity. Electrolytic conductivity is a measure of the ability of a solution to carry an electric current. Solutions of electrolytes conduct an electric current by the migration of positively and negatively charged particles, known as cations and anions respectively, in opposite directions. The ions move at a rate dependent on their charge, size, microscopic viscosity of the medium and the magnitude of potential gradient.

Electrolytic solutions obey Ohm's law just as metallic conductors do. The reciprocal of resistance (1/R) is called as the conductance and is measured in reciprocal of ohms (ohms^{-1}) or mhos. In SI nomenclature the reciprocal of ohms takes the name Siemens (S).

Specific conductance

It is the conductance of a solution placed between two parallel plates of 1 cm^2 area and 1 cm apart. It is usually represented by kappa (κ or K) and its S.I. unit is siemens meter^{-1} (Sm^{-1}) but normally reported as siemens centimeter^{-1} (Scm^{-1}).

Equivalent conductance

It is the conductance of a solution containing 1 gram equivalent of an electrolyte placed between two parallel plates of 1 cm^2 area and 1 cm apart. It is usually represented by λ and reported as Scm^{-1}.g equi.$^{-1}$.

The equivalent conductance (λ) is related to the specific conductance (K or κ) by the equation,

$$\lambda = \frac{1000 \ K}{C}$$

The equivalent conductance for solution at particular dilution (λ_V) or at particular concentration (λ_C) is given by the equation,

$$\lambda_V \text{ or } \lambda_C = \frac{1000 \ K}{C}$$

Conductivity of a solution is influenced by the presence of traces of foreign electrolytic impurities. Ordinary water is not suitable for conductance measurements because it may contain dissolved CO_2 from air, ammonia etc. Hence the electrolytic solutions must be prepared in conductivity water.

For precise work, conductivity of the solution must be measured at constant temperature. An increase in temperature invariably results in an increase in ionic conductance. For most of the ions this amounts to 2 to 3 % per degree.

o-------------------------o

Experiment - 01

Study of conductometric titration of a strong acid (HCl) against a strong base (NaOH)

Problem - To determine the strength of a given strong acid (HCl) by titrating against a strong base (NaOH) using conductometer.

Theory

In conductometric titrations, the determination of equivalence point is based upon the variation of electrical conductivity of a solution during the course of titration. The electrical conductivity of a solution depends upon the number of ions present and their mobility which is different before and after the equivalence point.

When HCl solution is titrated with NaOH the following reaction takes place.

$$\overset{+}{H}\overset{-}{Cl} + \overset{+}{Na}\overset{-}{OH} \longrightarrow \overset{+}{Na}\overset{-}{Cl} + H_2O$$
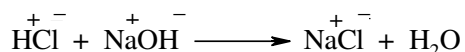
On addition of the NaOH, because of the replacement of highly mobile (conducting) H^+ ions ($\lambda_+ = 350$) of HCl by less mobile Na^+ ions ($\lambda_+ = 50$) of NaOH, conductance of the solution decreases linearly upto equivalence point (end point). When the neutralization of HCl is complete and NaOH is added in excess, the conductance starts increasing due to the addition of highly mobile OH^- ions ($\lambda_- = 200$) (*Note: all λ values are at 25^0C*).

The end point is found out from graph. It is obtained as an intercept of two straight lines. It is necessary to take 5-6 readings before and after the end point. The readings near the end point are not necessary, these deviate from the expected value.

Facilities

Apparatus - Conductometer, Conductivity cell, Magnetic stirrer or glass rod, Burette, Pipette, Conical flask, Volumetric flask, Beakers, Weighing bottle, Wash bottle, Funnel etc.
Chemicals - Oxalic acid (A.R.), NaOH solution (approx. 0.1 N), HCl solution (unknown), Phenolphthalein indicator, Conductivity water etc.

Procedure

1. Prepare approx. 0.1 N std. oxalic acid solution by dissolving accurately weighed 0.60 to 0.65 g of oxalic acid A.R. in distilled water in a 100 ml volumetric flask. Calculate the exact normality of prepared std. oxalic acid solution from the accurate weight of oxalic acid dissolved in 100 ml of solution.

2. Pipette out 10 ml of std. oxalic acid solution in a clean conical flask. Add 1-2 drops of phenolphthalein indicator and titrate it with NaOH solution (approx. 0.1 N) taken in a burette till colour changes from colourless to pink. Repeat the titration till you get two constant readings. Tabulate your readings (Table-A).

3. Understand the working of conductometer to be used for the experiment.

4. Pipette out 10 ml of given strong acid (HCl) solution in a clean 100 ml beaker and add about 25 ml of distilled water to it. Wash the conductivity cell with distilled water using a wash bottle. Place the cell in a beaker containing HCl solution and connect to conductivity meter.

5. Wash the burette with distilled water, rinse it with NaOH solution and fill it with same NaOH solution upto the mark.

6. Stir the acid solution with a glass rod, switch on conductometer and note the conductance of acid solution. (*Allow the glass rod to remain in beaker throughout the experiment*)

7. Now go on adding 1 ml NaOH each time, stir the solution and note the conductance. The conductance will go on decreasing. The equivalence point (end point) will be crossed when the conductance starts increasing again. Take 5-6 more readings after the conductance is increased. Tabulate your readings (Table-B).

8. Plot a graph of observed conductance (y-axis) against volume of NaOH added (x-axis). Find out the end point from graph.

Graph

Observations

A. Preparation of std. oxalic acid solution

1. Weight of empty weighing bottle   = W_1 g
2. Weight of weighing bottle + oxalic acid   = W_2 g
3. Weight of weighing bottle + remaining particles of oxalic acid   = W_3 g

B. Standardization of NaOH solution (Titration of std. oxalic acid with NaOH)

Table-A

Sr. No.	Volume of oxalic acid (ml) V_1	Volume of NaOH (ml)	End Point (ml)
1.	10.0		
2.	10.0		V_2
3.	10.0		

C. Conductometric titration (Titration of HCl with NaOH)

Table-B

Sr. No.	Volume of NaOH (ml)	Observed conductance (mS)
1.	00	------
2.	01	------
3.	02	------
4.	03	------
.	.	.
.	.	.
.	.	.

Volume of NaOH required to neutralize HCl (End point from a graph) = V_2^1 ml

Calculations

A. Preparation of std. oxalic acid solution

1. Weight of oxalic acid transferred $\quad = \quad (W_2-W_3)$ g
2. Weight of oxalic acid dissolved in 100 ml $\quad = \quad (W_2-W_3)$ g

$$Normality = \frac{Weight / litre}{Equivalent\ weight}$$

Normality of std. oxalic acid solution $(N_1) = \dfrac{(W_2-W_3)\ x\ 10}{63}$

B. Standardization of NaOH solution (Titration of std. oxalic acid with NaOH)

(Oxalic acid) (NaOH)
$$N_1V_1 = N_2V_2$$

Normality of NaOH solution $(N_2) = \dfrac{N_1V_1}{V_2}$

N_1 = As calculated, V_1 = 10 ml, N_2 = Unknown, V_2 = End point (Table-A)

C. Conductometric titration (Titration of HCl with NaOH)

(NaOH) (HCl)
$$N_2V_2^1 = N_3V_3$$

Normality of HCl solution $(N_3) = \dfrac{N_2V_2^1}{V_3}$

N_2 = As calculated, N_3 = Normality of HCl (Unknown),
V_2^1 = Volume of NaOH (End point from a graph), V_3 = Volume of HCl (10 ml)

$\therefore$ Strength of HCl solution = (N_3) N

Result

The strength of a given strong acid (HCl) is found to be ……… N.

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Experiment - 02

Study of conductometric titration of a weak acid (CH₃COOH) against a strong base (NaOH)

Problem - To determine the strength of a given weak acid (CH_3COOH) by titrating against a strong base (NaOH) using conductometer.

Theory

In conductometric titrations, the determination of equivalence point is based upon the variation of electrical conductivity of a solution during the course of titration. The electrical conductivity of a solution depends upon the number of ions present and their mobility which is different before and after the equivalence point.

When CH_3COOH solution is titrated with NaOH following reaction takes place.

$$\overset{-}{C}H_3COO\overset{+}{H} + \overset{+}{N}a\overset{-}{O}H \longrightarrow CH_3COO\overset{-}{N}\overset{+}{a} + H_2O$$
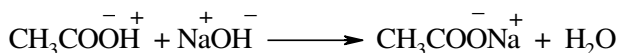
In the beginning on addition of the NaOH, conductance first decreases slightly owing to the formation of the salt which suppresses the ionization of CH_3COOH due to common ion effect (CH_3COOH-CH_3COONa), but soon the CH_3COO^- ions (λ-=40) and Na^+ ions (λ_+=50) are formed and hence the conductance begins to increase slowly upto equivalence point (end point). When the neutralization of CH_3COOH is complete and NaOH is added in excess, the conductance starts increasing rapidly due to the addition of highly mobile OH^- ions (λ-=200). In case of a very weak, there is no decrease in conductance in the beginning of titration. (*Note: all λ values are at 25^0C*)

The end point is found out from graph. It is obtained as an intercept of two straight lines. It is necessary to take 5-6 readings before and after the end point. The readings near the end point are not necessary, these deviate from the expected value.

Facilities

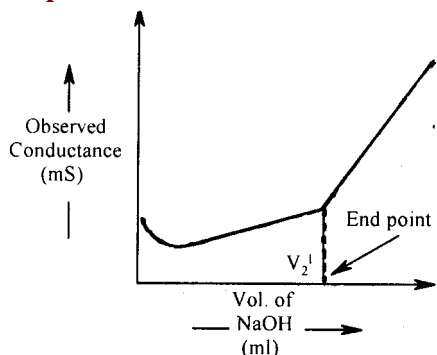**Apparatus** - Conductometer, Conductivity cell, Magnetic stirrer or glass rod, Burette, Pipette, Conical flask, Volumetric flask, Beakers, Weighing bottle, Wash bottle, Funnel etc.
Chemicals - Oxalic acid (A.R.), NaOH solution (approx. 0.1 N), CH_3COOH solution (unknown), Phenolphthalein indicator, Conductivity water etc.

Procedure

1. Prepare approx. 0.1 N std. oxalic acid solution by dissolving accurately weighed 0.60 to 0.65 g of oxalic acid A.R. in distilled water in a 100 ml volumetric flask. Calculate the exact normality of prepared std. oxalic acid solution from the accurate weight of oxalic acid dissolved in 100 ml of solution.

2. Pipette out 10 ml of std. oxalic acid solution in a clean conical flask. Add 1-2 drops of phenolphthalein indicator and titrate it with NaOH solution (approx. 0.1 N) taken in a burette till colour changes from colourless to pink. Repeat the titration till you get two constant readings. Tabulate your readings (Table-A).

3. Understand the working of conductometer to be used for the experiment.

4. Pipette out 10 ml of given weak acid (CH_3COOH) solution in a clean 100 ml beaker and add about 25 ml of distilled water to it. Wash the conductivity cell with distilled water using a wash bottle. Place the cell in a beaker containing CH_3COOH solution and connect to conductivity meter.

5. Wash the burette with distilled water, rinse it with NaOH solution and fill it with same NaOH solution upto the mark.

6. Stir the acid solution with a glass rod, switch on the conductometer and note the conductance of acid solution. (*Allow the glass rod to remain in the beaker throughout the experiment*)

7. Now go on adding 1 ml NaOH each time, stir the solution and note the conductance. In the beginning there will be slightly decrease in conductance and then conductance will go on increasing slowly. The equivalence point (end point) will be crossed when the conductance starts increasing rapidly. Take 5-6 more readings after the conductance is increased rapidly. Tabulate your readings (Table-B).

8. Plot a graph of observed conductance (y-axis) against volume of NaOH added (x-axis). Find out the end point from graph.

Graph

Observations

A. Preparation of std. oxalic acid solution

1. Weight of empty weighing bottle   = W_1 g
2. Weight of weighing bottle + oxalic acid   = W_2 g
3. Weight of weighing bottle + remaining particles of oxalic acid   = W_3 g

B. Standardization of NaOH solution (Titration of std. oxalic acid with NaOH)

Table-A

Sr. No.	Volume of oxalic acid (ml) V_1	Volume of NaOH (ml)	End Point (ml)
1.	10.0		
2.	10.0		V_2
3.	10.0		

C. Conductometric titration (Titration of CH₃COOH with NaOH)

Table-B

Sr. No.	Volume of NaOH (ml)	Observed conductance (mS)
1.	00	------
2.	01	------
3.	02	------
4.	03	------
.	.	.
.	.	.
.	.	.

Volume of NaOH required to neutralize CH_3COOH (End point from a graph) = V_2^1 ml
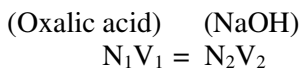
Calculations

A. Preparation of std. oxalic acid solution

1. Weight of oxalic acid transferred   = (W_2-W_3) g
2. Weight of oxalic acid dissolved in 100 ml   = (W_2-W_3) g

$$\text{Normality} = \frac{\text{Weight / litre}}{\text{Equivalent weight}}$$

Normality of std. oxalic acid solution $(N_1) = \dfrac{(W_2-W_3) \times 10}{63}$

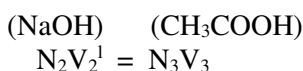## B. Standardization of NaOH solution (Titration of std. oxalic acid with NaOH)

(Oxalic acid)   (NaOH)

$\qquad N_1V_1 = N_2V_2$

Normality of NaOH solution $(N_2) = \dfrac{N_1V_1}{V_2}$

N_1 = As calculated, V_1 = 10 ml, N_2 = Unknown, V_2 = End point (Table-A)

C. Conductometric titration (Titration of CH₃COOH with NaOH)

(NaOH)   (CH₃COOH)

$\qquad N_2V_2^1 = N_3V_3$

Normality of CH$_3$COOH solution $(N_3) = \dfrac{N_2V_2^1}{V_3}$

N_2 = As calculated, N_3 = Normality of CH₃COOH (Unknown),

V_2^1 = Volume of NaOH (End point from a graph), V_3 = Volume of CH₃COOH (10 ml)

$\therefore$ Strength of CH₃COOH solution = (N_3) N

Result

The strength of a given weak acid (CH₃COOH) is found to be ……… N.

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Experiment - 03

Study of conductometric titration of a mixture of strong acid (HCl) and weak acid (CH₃COOH) against a strong base (NaOH)

Problem - To determine the strength of a strong acid (HCl) and a weak acid (CH₃COOH) in a given mixture by titrating against strong base (NaOH) using conductometer.

Theory

In conductometric titrations, the determination of equivalence point is based upon the variation of electrical conductivity of a solution during the course of titration. The electrical conductivity of a solution depends upon the number of ions present and their mobility which is different before and after the equivalence point.

When a mixture of HCl and CH₃COOH solution is titrated with NaOH the neutralization of strong acid (HCl) takes place first. The neutralization of weak acid (CH₃COOH) commences only after the complete neutralization of strong acid. During the titration following reactions takes place.
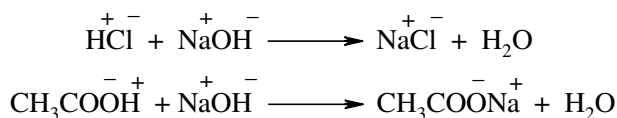
$$\overset{+}{H}\overset{-}{Cl} + \overset{+}{Na}\overset{-}{OH} \longrightarrow \overset{+}{Na}\overset{-}{Cl} + H_2O$$

$$CH_3\overset{-}{COO}\overset{+}{H} + \overset{+}{Na}\overset{-}{OH} \longrightarrow CH_3\overset{-}{COO}\overset{+}{Na} + H_2O$$

On addition of the NaOH, because of the replacement of highly mobile (conducting) H^+ ions (λ_+=350) of HCl by less mobile Na^+ ions (λ_+=50) of NaOH, conductance of the solution decreases linearly upto equivalence point (end point). When the neutralization of HCl is complete then neutralization of CH_3COOH commences. Initially conductance of the solution remains less on account of poor dissociation of CH_3COOH. On addition of the NaOH, the CH_3COO^- ions (λ_-=40) and Na^+ ions (λ_+=50) are formed and hence the conductance begins to increase slowly. When the neutralization of CH_3COOH is complete and NaOH is added in excess, the conductance starts increasing rapidly due to the addition of highly mobile OH^- ions (λ_-=200). (*Note: all λ values are at 25^0C*)

The end points are to be found out from graph. These are obtained as two intercepts of three straight lines. The first intercept corresponds to equivalence point (end point) of HCl and second to that of CH_3COOH. It is necessary to take 5-6 readings before and after the end points. The readings near the end point are not necessary, these deviate from the expected value.

Facilities

Apparatus - Conductometer, Conductivity cell, Magnetic stirrer or glass rod, Burette, Pipette, Conical flask, Volumetric flask, Beakers, Weighing bottle, Wash bottle, Funnel etc.
Chemicals - Oxalic acid (A.R.), NaOH solution (approx. 0.1 N), HCl solution (unknown), CH_3COOH solution (unknown), Phenolphthalein indicator, Conductivity water etc.
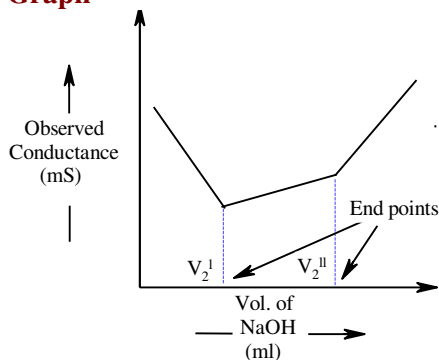
Procedure

1. Prepare approx. 0.1 N std. oxalic acid solution by dissolving accurately weighed 0.60 to 0.65 g of oxalic acid A.R. in distilled water in a 100 ml volumetric flask. Calculate the exact normality of prepared std. oxalic acid solution from the accurate weight of oxalic acid dissolved in 100 ml of solution.

2. Pipette out 10 ml of std. oxalic acid solution in a clean conical flask. Add 1-2 drops of phenolphthalein indicator and titrate it with NaOH solution (approx. 0.1 N) taken in a burette till colour changes from colourless to pink. Repeat the titration till you get two constant readings. Tabulate your readings (Table-A).

3. Understand the working of conductometer to be used for the experiment.

4. Pipette out separately 10 ml of given strong acid (HCl) and weak acid (CH_3COOH) solutions in a clean 100 ml beaker. Shake the mixture and add about 25 ml of distilled water to it. Wash the conductivity cell with distilled water using a wash bottle. Place the cell in a beaker containing mixture of HCl and CH_3COOH solution and connect to conductivity meter.

5. Wash the burette with distilled water, rinse it with NaOH solution and fill it with same NaOH solution upto the mark.

6. Stir the mixture of acid solution with a glass rod, switch on the conductometer and note the conductance of acid solution. (*Allow the glass rod to remain in the beaker throughout the experiment*)

7. Now go on adding 1 ml NaOH each time, stir the solution and note the conductance. Initially the conductance will go on decreasing. The first equivalence point (end point) will be crossed when the conductance starts increasing slowly and the second equivalence point (end point) will be crossed when the conductance starts increasing

very rapidly. Take 5-6 more readings after the conductance is increased rapidly. Tabulate your readings (Table-B).

8. Plot a graph of observed conductance (y-axis) against volume of NaOH added (x-axis). Find out the end point from graph.

Graph

Observations

A. Preparation of std. oxalic acid solution

1. Weight of empty weighing bottle   = W_1 g
2. Weight of weighing bottle + oxalic acid   = W_2 g
3. Weight of weighing bottle + remaining particles of oxalic acid   = W_3 g

B. Standardization of NaOH solution (Titration of std. oxalic acid with NaOH)

Table-A

Sr. No.	Volume of oxalic acid (ml) V_1	Volume of NaOH (ml)	End Point (ml)
1.	10.0		
2.	10.0		V_2
3.	10.0		

C. Conductometric titration (Titration of mixture of HCl and CH₃COOH with NaOH)

Table-B

Sr. No.	Volume of NaOH (ml)	Observed conductance (mS)
1.	00	------
2.	01	------
3.	02	------
4.	03	------
.	.	.
.	.	.
.	.	.

1. Volume of NaOH required to neutralize HCl (End point from a graph)   = V_2^I ml
2. Volume of NaOH required to neutralize CH₃COOH (End pt. from a graph) = V_2^{II} ml

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Calculations

A. Preparation of std. oxalic acid solution

1. Weight of oxalic acid transferred $= (W_2-W_3)$ g
2. Weight of oxalic acid dissolved in 100 ml $= (W_2-W_3)$ g

$$\text{Normality} = \frac{\text{Weight / litre}}{\text{Equivalent weight}}$$

Normality of std. oxalic acid solution $(N_1) = \dfrac{(W_2-W_3) \times 10}{63}$

B. Standardization of NaOH solution (Titration of std. oxalic acid with NaOH)

(Oxalic acid)   (NaOH)

$$N_1V_1 = N_2V_2$$

Normality of NaOH solution $(N_2) = \dfrac{N_1V_1}{V_2}$

$N_1 =$ As calculated, $V_1 = 10$ ml, $N_2 =$ Unknown, $V_2 =$ End point (Table-A)

C. Conductometric titration (Titration of mixture of HCl and CH₃COOH with NaOH)

(NaOH)   (HCl)

$$N_2V_2^{\,l} = N_3V_3$$

Normality of HCl solution $(N_3) = \dfrac{N_2V_2^{\,l}}{V_3}$

$N_2 =$ As calculated, $N_3 =$ Normality of HCl (Unknown),
$V_2^{\,l} =$ Volume of NaOH (End point from a graph), $V_3 =$ Volume of HCl (10 ml)

$\therefore$ Strength of HCl solution $= (N_3)$ N

(NaOH)   (CH₃COOH)

$$N_2V_2^{\,ll} = N_4V_4$$

Normality of CH_3COOH solution $(N_4) = \dfrac{N_2V_2^{\,ll}}{V_4}$

$N_2 =$ As calculated, $N_4 =$ Normality of CH_3COOH (Unknown)
$V_2^{\,ll} =$ Volume of NaOH (End point from a graph), $V_4 =$ Volume of CH_3COOH (10 ml)

$\therefore$ Strength of CH_3COOH solution $= (N_4)$ N

Result

The strengths of a given strong acid (HCl) and weak acid (CH₃COOH) are found to be
……… N and ……… N respectively.

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B. pH / Potentiometry

In Potentiometric experiments (titrations), there is change in potential of an electrode with the change in concentration of ions, with which it is in equilibrium. The change in potential may be used as an indicator in determining the end point. This method is applicable to wide range of titrations, provided an appropriate electrode (indicator electrode) is available. An indicator electrode is the one whose potential indicates the change in concentration of the ions to be titrated. As it is not possible to determine the electrode potential separately, the indicator electrode is used in conjunction with a reference electrode, the potential of which remains constant during the course of titration. Most commonly used reference electrode is the saturated calomel electrode (SCE). Some commonly used indicator electrodes are hydrogen electrode, quinhydrone electrode, glass electrode etc.
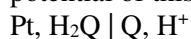
1. Calomel electrode (Saturated)

It consists of a glass tube immersed into another glass tube. Mercury of high degree of purity is placed at the bottom of inner glass tube, over which the calomel paste of mercury and mercurous chloride ($Hg + Hg_2Cl_2$) is placed. A platinum wire sealed in an inner glass tube helps in making the electrical contact. Saturated KCl solution is added from the inlet provided to the outer tube. Reduction potential of this electrode is +0.2415 V at 25^0C. Electrode is represented as below.

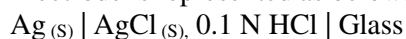Pt, $Hg_{(l)}$ | $Hg_2Cl_{2(S)}$ | $KCl_{(Sat)}$
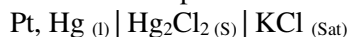
2. Quinhydrone electrode

It consists of shiny platinum electrode dipped in the test solution, which is saturated with quinhydrone (1:1 molecular compound of quinone and hydroquinone). Standard reduction potential of this electrode is +0.6994 V at 25^0C. Electrode is represented as below.
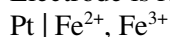
Pt, H_2Q | Q, H^+

3. Glass electrode

It consists of a thin bulb made up of a special soft glass of 50µm thickness with high electrical conductivity, blown at the end of a glass tubing. The bulb is filled with 0.1 N HCl or other suitable buffer solution and a silver wire coated with silver chloride is immersed in it. Standard reduction potential of this electrode is +0.225 V at 25^0C. Electrode is represented as below.

$Ag_{(S)}$ | $AgCl_{(S)}$, 0.1 N HCl | Glass

4. Oxidation - Reduction electrode (Redox electrode)

It consists of a platinum wire dipped in the solution of two salts of same metal having different valencies, e.g. Fe^{2+} and Fe^{3+}. The e.m.f. arises because of the tendency of metal ion in one oxidation state to pass into the second more stable state. The function of platinum wire is merely to pickup the electrons and to make an electrical contact to the electrode. Standard reduction potential of the Fe^{2+}/Fe^{3+} electrode is +0.771 V at 25^0C. Electrode is represented as below.

Pt | Fe^{2+}, Fe^{3+}

5. Metal - Insoluble salt anion electrode

It consists of a metal in contact with its sparingly soluble salt. This electrode is reversible with respect to anions, e.g. Ag-AgCl electrode. Standard reduction potential of the Ag/Ag^+ electrode is +0.799 V at 25^0C. Electrode is represented as Ag | $Ag^+_{(aq)}$.

Acid base titrations can be carried out potentiometrically by systematic measurement of e.m.f. of the following cells.

1. The cell formed when quinhydrone (indicator) electrode is coupled with calomel (reference) electrode.

(Calomel electrode) $\|$ (Quinhydrone electrode)

Pt, Hg $_{(l)}$ | Hg$_2$Cl$_{2\,(S)}$ | KCl $_{(Sat)}$ $\|$ H$^+$,Q | H$_2$Q, Pt

$E_{Cell} = E_{Quin} - E_{Cal}$
$E_{Cell} = (E^0_{Quin} - (2.303\ RT\ /\ F)\ pH) - E_{Cal}$
$E_{Cell} = E^0_{Quin} - E_{Cal} - (2.303\ RT\ /\ F)\ pH$
$E_{Cell} = 0.6994 - 0.2415 - 0.05916\ pH$ (at 25^{0}C)
$E_{Cell} = 0.4579 - 0.05916\ pH$
pH $= (0.4579 - E_{Cell})\ /\ 0.05916$

Where,
R is gas constant (8.3143 JK^{-1}.mol^{-1})
T is temperature (298 K)
F is Faraday constant (9.66 x 10^4 C.mol^{-1})

2. The cell formed when glass (indicator) electrode is coupled with calomel (reference) electrode.

(Glass electrode) $\|$ (Calomel electrode)

Ag $_{(S)}$ | AgCl $_{(S)}$ | 0.1 N HCl | Glass $\|$ KCl $_{(Sat)}$ | Hg$_2$Cl$_{2\,(S)}$ | Hg $_{(l)}$, Pt

$E_{Cell} = E_{Cal} - E_{Glass}$
$E_{Cell} = E_{Cal} - (E^0_{Glass} - (2.303\ RT\ /\ F)\ pH)$
$E_{Cell} = E_{Cal} - E^0_{Glass} + (2.303\ RT\ /\ F)\ pH)$
$E_{Cell} = 0.2415 - 0.225 + 0.05916\ pH$ (at 25^{0}C)
$E_{Cell} = 0.0165 + 0.05916\ pH$
pH $= (E_{Cell} - 0.0165)\ /\ 0.05916$

3. The cell formed when Fe^{2+}/Fe^{3+} (indicator) electrode is coupled with calomel (reference) electrode.

(Calomel electrode) $\|$ (Fe^{2+}/Fe^{3+} electrode)

Pt, Hg $_{(l)}$ | Hg$_2$Cl$_{2\,(S)}$ | KCl $_{(Sat)}$ $\|$ Fe^{3+}, Fe^{2+} | Pt

$E_{Cell} = E_{Fe^{2+}/Fe^{3+}} - E_{Cal}$
$E_{Cell} = (E^0_{Fe^{2+}/Fe^{3+}} - (2.303\ RT\ /\ F)\ pH) - E_{Cal}$
$E_{Cell} = E^0_{Fe^{2+}/Fe^{3+}} - E_{Cal} + (2.303\ RT\ /\ F)\ pH$
$E_{Cell} = 0.771 - 0.2415 - 0.05916\ pH$ (at 25^{0}C)
$E_{Cell} = 0.5295 - 0.05916\ pH$
pH $= (0.5295 - E_{Cell})\ /\ 0.05916$

4. The cell formed when Ag/Ag$^+$ (indicator) electrode is coupled with calomel (reference) electrode.

(Calomel electrode) $\|$ (Ag/Ag$^+$ electrode)

Pt, Hg $_{(l)}$ | Hg$_2$Cl$_{2\,(S)}$ | KCl $_{(Sat)}$ $\|$ Ag$^+_{(aq)}$ | Ag

$E_{Cell} = E_{Ag/Ag^+} - E_{Cal}$
$E_{Cell} = (E^0_{Ag/Ag^+} - (2.303\ RT\ /\ F)\ pH) - E_{Cal}$
$E_{Cell} = E^0_{Ag/Ag^+} - E_{Cal} - (2.303\ RT\ /\ F)\ pH$

E_{Cell} = 0.799 - 0.2415 - 0.05916 pH (at 25^{0}C)

E_{Cell} = 0.5575 - 0.05916 pH

pH = (0.5575 - E_{Cell}) / 0.05916

The instrument used for potentiometric titration is basically a millivoltmeter capable of measuring e.m.f. It is either potentiometer or pH-meter. pH-meter is designed to read both pH and e.m.f. (millivolts).
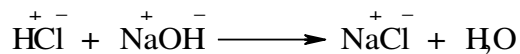
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Experiment - 04

Study of potentiometric titration of a strong acid (HCl) against a strong base (NaOH)

Problem - To determine the strength of a given strong acid (HCl) by titrating against a strong base (NaOH) using potentiometer.

Theory

In potentiometric titrations, the end point is determined by measuring the change in electrode potential with the addition of titrant i.e. with the change in concentration of ions. When HCl solution is titrated with NaOH the following reaction takes place.

$$\overset{+}{H}\overset{-}{Cl} \ + \ \overset{+}{Na}\overset{-}{OH} \longrightarrow \overset{+}{Na}\overset{-}{Cl} \ + \ H_2O$$

During the titration, when strong base (NaOH) is added to the strong acid (HCl), pH increases slowly upto the equivalence point (end point) because of the fraction of H^+ ions removed. As the equivalence point reaches, the fraction of H^+ ions removed by a constant volume of NaOH increases rapidly, thereby causing a sharp jump (increase) in pH just at the equivalence point. After the equivalence point, again pH increases slowly because of addition of excess of NaOH (excess of OH^- ions).

The change in pH reflects in the change in e.m.f. (E). So when the alkali (NaOH) is added to the acid (HCl) dropwise and measured the e.m.f after addition of each drop (or drops), e.m.f. decreases slowly upto the equivalence point because of a little change in electrode potential due to removal of fraction of H^+ ions. As the equivalence point reaches, the fraction of H^+ ions removed by a constant volume of the alkali increases rapidly which results in a rapid change in electrode potential, thereby causing a sharp drop (decrease) in e.m.f. just at the equivalence point. After the equivalence point, again e.m.f. decreases slowly because of addition of excess of alkali causing a little change in electrode potential.

The rate of change in e.m.f. is much more near the equivalence point (end point) than any other region of the titration before or after the equivalence point. The end point is to be found out by plotting a graph of E (e.m.f.) or $\Delta E/\Delta V$ against the volume of alkali added. The point of inflexion in the curve (the point where the curve changes its curvature) gives the end point.

Sharpness of the inflexion point and symmetry of the curve on its two sides depends on ionisability of the acid and base used.
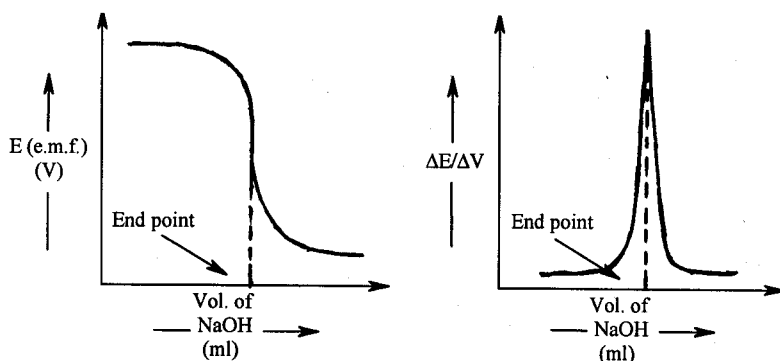
Facilities

Apparatus - Potentiometer, Calomel electrode, Platinum electrode, Magnetic stirrer or glass rod, Burette, Pipette, Conical flask, Volumetric flask, Beakers, Weighing bottle, Wash bottle, Funnel etc.

Chemicals - Oxalic acid (A.R.), NaOH solution (approx. 0.1 N), HCl solution (unknown), Quinhydrone, Phenolphthalein indicator, Distilled water etc.

Procedure

1. Prepare approx. 0.1 N std. oxalic acid solution by dissolving accurately weighed 0.60 to 0.65 g of oxalic acid A.R. in distilled water in a 100 ml volumetric flask. Calculate the exact normality of prepared std. oxalic acid solution from the accurate weight of oxalic acid dissolved in 100 ml of solution.

2. Pipette out 10 ml of std. oxalic acid solution in a clean conical flask. Add 1-2 drops of phenolphthalein indicator and titrate it with NaOH solution (approx. 0.1 N) taken in a burette till colour changes from colourless to pink. Repeat the titration till you get two constant readings. Tabulate your readings (Table-A).

3. Understand the working of potentiometer to be used for experiment and standardize it.

4. Pipette out 10 ml of given strong acid (HCl) solution in a clean 100 ml beaker and add about 25 ml of distilled water to it. Add about 0.2 g of quinhydrone. Wash the tips of calomel and platinum electrode with distilled water using wash bottle and place both the electrodes in a beaker containing HCl solution. Stir the acid solution with a glass rod and note the e.m.f. (*Allow the glass rod to remain in the beaker throughout the experiment*)

5. Wash the burette with distilled water and fill it with NaOH solution upto the mark.

6. Now go on adding 1 ml of NaOH solution at each time, stir well and note the e.m.f. Continue the addition, till there is sudden decrease in e.m.f. After this again take 4 to 5 readings. (*Near the end point take the reading at an interval of 0.2 ml*). Tabulate your readings (Table-B).

7. Plot a graph of E (e.m.f.) or $\Delta E/\Delta V$ (y-axis) against volume of NaOH added (x-axis). Find out the end point from inflexion in the curve.

Graphs

Observations

A. Preparation of std. oxalic acid solution

1. Weight of empty weighing bottle $= W_1$ g
2. Weight of weighing bottle + oxalic acid $= W_2$ g
3. Weight of weighing bottle + remaining particles of oxalic acid $= W_3$ g

B. Standardization of NaOH solution (Titration of std. oxalic acid with NaOH)

Table-A

Sr. No.	Volume of oxalic acid (ml) V_1	Volume of NaOH (ml)	End Point (ml)
1.	10.0		
2.	10.0		V_2
3.	10.0		

C. Potentiometric titration (Titration of HCl with NaOH)

Table-B

Sr. No.	Volume of NaOH (ml)	E (e.m.f.) (V)	$\Delta E/\Delta V$
1.	00	------	------
2.	01	------	------
3.	02	------	------
4.	03	------	------
.	.	.	.
.	.	.	.
.	.	.	.

Volume of NaOH (End point from a graph) = V_2^1 ml

Calculations

A. Preparation of std. oxalic acid solution

1. Weight of oxalic acid transferred = (W_2-W_3) g
2. Weight of oxalic acid dissolved in 100 ml = (W_2-W_3) g

$$\text{Normality} = \frac{\text{Weight / litre}}{\text{Equivalent weight}}$$

$$\text{Normality of std. oxalic acid solution } (N_1) = \frac{(W_2-W_3) \times 10}{63}$$

B. Standardization of NaOH solution (Titration of std. oxalic acid with NaOH)

(Oxalic acid)   (NaOH)

$$N_1V_1 = N_2V_2$$

$$\text{Normality of NaOH solution } (N_2) = \frac{N_1V_1}{V_2}$$

N_1 = As calculated, V_1 = 10 ml, N_2 = Unknown, V_2 = End point (Table-A)

C. Potentiometric titration (Titration of HCl with NaOH)

(NaOH)   (HCl)

$$N_2V_2^1 = N_3V_3$$

$$\text{Normality of HCl solution } (N_3) = \frac{N_2V_2^1}{V_3}$$

N_2 = As calculated, N_3 = Normality of HCl (Unknown),
V_2^1 = Volume of NaOH (End point from a graph), V_3 = Volume of HCl (10 ml)

$\therefore$ Strength of HCl solution = (N_3) N

Result

The strength of given strong acid (HCl) is found to be ……… N.

<div align="center">o------------------------o</div>

Experiment - 05

Study of potentiometric titration of ferrous ammonium sulphate (FAS) against potassium dichromate ($K_2Cr_2O_7$)

Problem - To perform the potentiometric titration of ferrous ammonium sulphate (FAS) against potassium dichromate ($K_2Cr_2O_7$) using potentiometer and determine the redox potential of Fe^{2+}/Fe^{3+} system.

Theory

The potentiometric titration can be easily carried out for any reversible redox reaction. These titrations involve transfer of electron from the substance being oxidized to the substance being reduced. The potential (e.m.f.) of any redox reaction can be given by the Nernst's equation as follows.

$$E = E^0 - \frac{2.303\ RT}{nF} \log_{10} \frac{[Product]}{[Reactant]}$$

When a platinum electrode is placed in the solution containing Fe^{2+} and Fe^{3+} ions, the potential developed across the electrode with respect to calomel electrode for the equilibrium $Fe^{2+} \rightleftharpoons Fe^{3+} + e^-$ is given by-

$$E_{Fe^{2+}/Fe^{3+}} = E^0_{Fe^{2+}/Fe^{3+}} - \frac{2.303\ RT}{nF} \log_{10} \frac{[Fe^{3+}]}{[Fe^{2+}]}$$

Where, E^0 is the standard potential of Fe^{2+}/Fe^{3+} system and is a measure of the tendency of the ion to pass from the lower oxidation state to the higher oxidation state.

For potentiometric titration of Fe^{2+}/Fe^{3+} system, this redox electrode is coupled with calomel electrode (reference electrode) and e.m.f. of the cell is measured. The complete cell is represented as below.

(Calomel electrode) $\|$ (Fe^{2+}/Fe^{3+} electrode)
Pt, Hg $_{(l)}$ | Hg$_2$Cl$_{2\ (S)}$ | KCl $_{(Sat)}$ $\|$ Fe^{3+}, Fe^{2+} | Pt
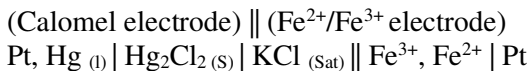
Initially Fe^{3+} is present in infinitesimal amount, its concentration increases when a solution is titrated with oxidizing agent. This results in rapid change in the ratio of concentration of Fe^{2+} and Fe^{3+} ions. Thus there is sharp rise in e.m.f. at equivalence point and beyond equivalence point the e.m.f. depends upon the behaviour of oxidizing agent.

$$E_{Cell} = E_{Fe^{2+}/Fe^{3+}} - E_{Cal}$$

$$E_{Fe^{2+}/Fe^{3+}} = \left[E^0_{Fe^{2+}/Fe^{3+}} - \frac{2.303\ RT}{nF} \log_{10} \frac{[Fe^{3+}]}{[Fe^{2+}]} \right]$$

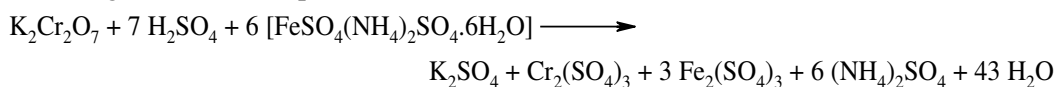$$\therefore E_{Cell} = \left[E^0_{Fe^{2+}/Fe^{3+}} - \frac{2.303\, RT}{nF}\, \log_{10} \frac{[Fe^{3+}]}{[Fe^{2+}]} \right] - E_{Cal}$$

At half equivalence point, $[Fe^{2+}] = [Fe^{3+}]$. So observed potential at half equivalence point,

$$E_{Cell} = E^0_{Fe^{2+}/Fe^{3+}} - E_{Cal} \quad \textbf{or} \quad E_{Cell} = E_{Fe^{2+}/Fe^{3+}} - E_{Cal}$$

$$\therefore E^0_{Fe^{2+}/Fe^{3+}} = E_{Cell} + E_{Cal} \quad \textbf{or} \quad E_{Fe^{2+}/Fe^{3+}} = E_{Cell} + E_{Cal}$$

This potential is called as redox potential of Fe^{2+}/Fe^{3+} system. It is obtained by taking concentration of Fe^{2+} and Fe^{3+} instead of activities (a=fc) in the Nernst's equation.

When ferrous ammonium sulphate solution is titrated with potassium dichromate the following reaction takes place.

$$K_2Cr_2O_7 + 7\, H_2SO_4 + 6\, [FeSO_4(NH_4)_2SO_4.6H_2O] \longrightarrow$$
$$K_2SO_4 + Cr_2(SO_4)_3 + 3\, Fe_2(SO_4)_3 + 6\, (NH_4)_2SO_4 + 43\, H_2O$$

The rate of change in e.m.f. is much more near the equivalence point (end point) than any other region of the titration before or after the equivalence point. The end point is to be found out by plotting a graph of E (e.m.f.) or $\Delta E/\Delta V$ against the volume of potassium dichromate added. The point of inflexion in the curve (the point where the curve changes its curvature) gives the end point.

Facilities

Apparatus - Potentiometer, Calomel electrode, Platinum electrode, Magnetic stirrer or glass rod, Burette, Pipette, Beakers, Wash bottle etc.

Chemicals - Ferrous ammonium sulphate (FAS) solution (0.1 N) in 2 N H_2SO_4, Potassium dichromate solution (0.1 N) in 2 N H_2SO_4, Distilled water etc.

Procedure

1. Understand the working of potentiometer to be used for experiment and standardize it. (*Connect platinum electrode to positive point*)

2. Pipette out 10 ml of ferrous ammonium sulphate solution in a clean 100 ml beaker and add about 25 ml of distilled water to it. Wash the tips of calomel and platinum electrode with distilled water using wash bottle and place both the electrodes in a beaker containing ferrous ammonium sulphate solution. Stir the solution with a glass rod and note the e.m.f. (*Allow the glass rod to remain in the beaker throughout the experiment*)

3. Wash the burette with distilled water and fill it with potassium dichromate solution upto the mark.

4. Go on adding 1 ml of potassium dichromate solution at each time, stir well and note the e.m.f. Continue the addition, till there is sudden increase in e.m.f. After this again take 4 to 5 readings. (*Near the end point take the reading at an interval of 0.2 ml*) Tabulate your readings (Table-A).

5. Plot a graph of E (e.m.f.) or $\Delta E/\Delta V$ (y-axis) against volume of potassium dichromate added (x-axis). Find out the end point from inflexion in the curve.

Graphs

Observations

Table-A
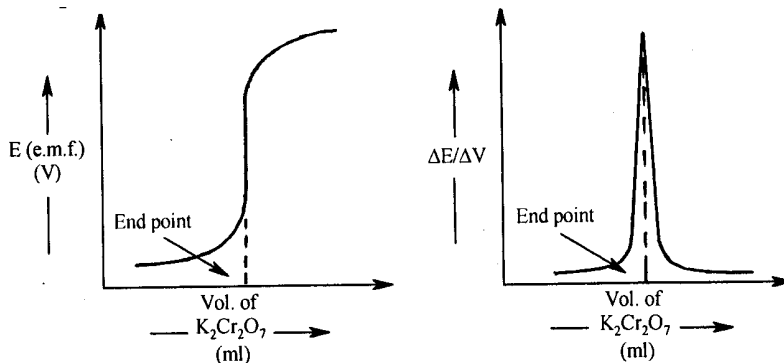
Sr. No.	Volume of $K_2Cr_2O_7$ (ml)	E (e.m.f.) (V)	$\Delta E/\Delta V$
1.	00	------	------
2.	01	------	------
3.	02	------	------
4.	03	------	------
.	.	.	.
.	.	.	.
.	.	.	.

Volume of $K_2Cr_2O_7$ solution (Equivalence point from a graph) = V ml

Calculations

Equivalence point (from a graph)   =   V   ml

∴ ½ equivalence point   =   ….. ml

e.m.f. at ½ equivalence point (from a graph)   =   ….. (E_{Cell})

At ½ equivalence point (½ neutralization point), $[Fe^{2+}] = [Fe^{3+}]$

$$\therefore E_{Cell} = E^0_{Fe^{2+}/Fe^{3+}} - E_{Cal} \quad \textbf{or} \quad E_{Cell} = E_{Fe^{2+}/Fe^{3+}} - E_{Cal}$$

$$\therefore E^0_{Fe^{2+}/Fe^{3+}} = E_{Cell} + E_{Cal} \quad \textbf{or} \quad E_{Fe^{2+}/Fe^{3+}} = E_{Cell} + E_{Cal}$$

$$\therefore E^0_{Fe^{2+}/Fe^{3+}} = E_{Cell} + 0.2415 \text{ V} \quad \textbf{or} \quad E_{Fe^{2+}/Fe^{3+}} = E_{Cell} + 0.2415 \text{ V}$$

Result

The redox potential of Fe^{2+}/Fe^{3+} system is found to be ……… V.

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C. Polarimetry

The waves constituting an ordinary beam of light vibrate or oscillate in all planes at right angle to the direction of propagation. When a beam of ordinary light is passed through a Nicol prism, the emergent beam of light vibrates in one plane. This light vibrating in one plane is called plane polarized light and the plane along which vibrations are taking place is known as plane of polarization.

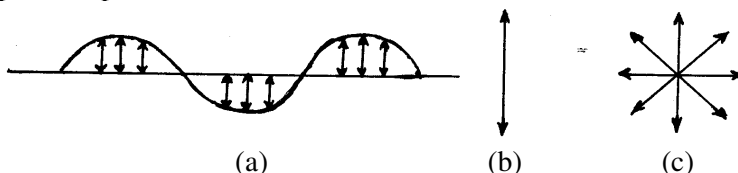(a)   (b)   (c)

Fig (a) (b): Plane polarized light (wave motion in a single plane only)
Fig (c): Ordinary light (wave motion in different planes)

When a beam of plane polarized light vibrating in one plane is passed through an optically active compound, it rotates the beam of plane polarized light through certain angle and the emergent beam of plane polarized light vibrates in another plane.

This optical rotation is caused by individual molecules of the optically active compound. The amount of rotation depends upon the number of molecules that is encountered by the light while passing through the polarimeter tube.

Optically active compounds which rotate the beam plane polarized light towards right (clockwise) are known as dextro (+) rotatory while those which rotate towards left (anticlockwise) are known as laevo (-) rotatory. An optically inactive mixture containing equal proportions of two is known as racemic mixture.

The angle of rotation of a beam of plane polarized light by a solution of an optically active compound depends on its nature, concentration, temperature, wavelength of the light used (shorter the wavelength, greater is the angle of rotation) and length of the layer through which light passes. The rotatory power of solution is generally expressed as specific rotation and represented by [α]. At a given temperature and for a given wavelength of the light used, specific rotation $[\alpha]^t_\lambda$, depends on concentration and length of the layer only.

Specific rotation is defined as the angle of rotation produced by a solution of optically active compound of concentration 1g/ml, when the length of the column (tube) through which light passes is 1 dm (decimeter).

It is given by the expression,

$$[\alpha]^t_\lambda = \frac{\alpha}{l \cdot C}$$

Where,
α is the observed angle of rotation.
l is the length of the column (tube) in dm.
C is the concentration of optically active compound in g/ml.

Working of polarimeter

In polarimeter, when a beam of ordinary light is passed through a Nicol prism (Diagonally cut calcite crystal into two halves and cemented using Canada balsam)

26

known as polarizer, the emergent beam is of plane polarized light. When this beam of plane polarized light is viewed through another Nicol prism known as analyzer, with its optical axis parallel to that of polarizer, the field of view appears bright. On rotating the analyzer the brightness decreases and field of view becomes perfectly dark when the axis of analyzer is perpendicular to that of polarizer (The field of view appears bright and dark alternately). If a tube containing solution of optically active compound (e.g. cane sugar) is placed between the two prisms, the field of view brightens (because of rotation of beam of plane polarized light from one plane to another). In order to get the darkness (remove brightness), the analyzer is to be rotated through certain angle called as angle of rotation of optically active compound.
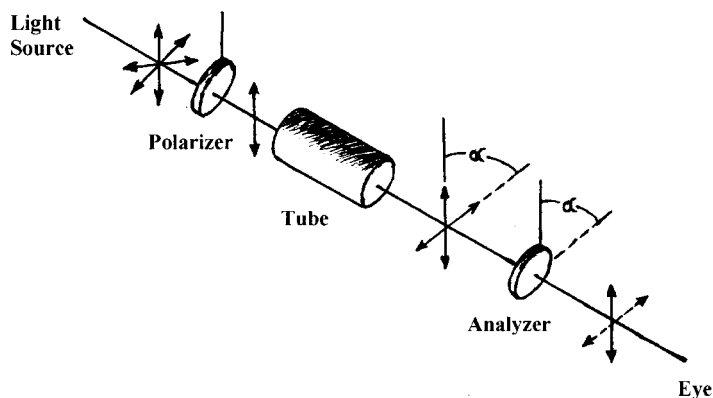
Fig: Schematic representation of a polarimeter.
(Solid lines: before rotation, doted lines: after rotation, α: angle of rotation)

o--------------------------o

Experiment - 06

Determination of specific rotation of optically active compound by polarimetry

Problem - To determine the specific rotation of a given optically active compound using polarimeter.

Theory

When beam of plane polarized light vibrating in one plane is passed through the solution of an optically active compound like cane sugar, it rotates the beam of plane polarized light through certain angle and the emergent beam of plane polarized light vibrates in another plane. The angle of rotation can be determined by using polarimeter.

The angle of rotation of a beam of plane polarized light at a given temperature and for a given wavelength of the light used, depends on concentration of the solution of an optically active compound and length of the layer through which light passes. It is generally expressed as specific rotation $[\alpha]^t_\lambda$ and is given by the expression,

$$[\alpha]^t_\lambda = \frac{\alpha}{l \, .C}$$

Where,
α is the observed angle of rotation.
l is the length of the column (tube) in dm.
C is the concentration of optically active compound in g/ml.

This experiment involves the determination specific rotation of cane sugar by measuring the angle of rotation of a beam of plane polarized light by the solution of cane sugar of different concentrations.

Facilities

Apparatus - Polarimeter, Sodium lamp, Pipette, Beakers, Wash bottle etc.
Chemicals - Cane sugar, Distilled water etc.

Procedure

1. Understand the working of polarimeter to be used for the experiment.
2. Prepare 4%, 6%, 8% and 10% solution of cane sugar by dissolving 4, 6, 8 and 10 g of cane sugar (previously dried and cooled to room temperature in a desicator) in distilled water and making up the volumes to100 ml.
3. Wash the polarimeter tube with distilled water. Fill it with distilled water and place in a polarimeter. Switch on the polarimeter. Observe the intensity of red colour through viewing window. Adjust it to minimum by rotating the analyzer and note the reading at minimum intensity. It should be zero (if not there is an error called zero error, if +ve it should be substracted and if –ve it should be added to observed rotation).
4. Remove the distilled water and place 4% cane sugar solution in polarimeter tube. Note the reading at minimum intensity of red colour.
5. Similarly note the reading for 6%, 8% and 10% solution. Tabulate your readings as shown below.

Observations

Concentration of cane sugar solution	(%)	4%	6%	8%	10%
	(g/ml)	0.04	0.06	0.08	0.1
Observed angle of rotation	(α)	------	------	------	------

Calculations

For each solution calculate the value of specific rotation [α] by using the formula,

$$[\alpha]_\lambda^t = \frac{\alpha}{l \cdot C}$$

Result

The average specific rotation of cane sugar is found to be .... at ... ^{0}C.

o------------------------o

D. Molecular Weight Determination

The addition of a non-volatile solute into a liquid lowers its freezing point and raises the boiling point. The depression in freezing point and elevation of boiling point of a solution is found to be proportional to the molal concentration of the solute, provided it does not undergo dissociation or association. Thus the measurement of depression in freezing point or elevation of boiling point of a solution may be used to determine the molecular weights of the non-volatile substances.

o------------------------o

Experiment - 07

Determination of molecular weight of non-volatile solute by Rast's method

Problem - To determine the molecular weight of a given non-volatile solute by Rast's method.

Theory

It is known that there is depression in freezing point (melting point) of a solvent when a non-volatile solute is dissolved in it. This depression is related to the molecular weight (molar mass) of a solute by following equation.

$$M = \frac{1000 \times K \times w}{\Delta T \times W}$$

Where,

M is molecular weight (molar mass) of non-volatile solute.

K is molal depression constant (39.7).

w is mass of non-volatile solute.

ΔT is depression in melting point.

W is mass of solvent (camphor).

Facilities

Apparatus - Rast tube.

Chemicals - Paraffin oil bath, Pure camphor (solvent), Non-volatile solute etc.

Procedure

1. Take a clean dry Rast tube and weigh it accurately. Separately weigh about 1 g of camphor, transfer it to the Rast tube and weigh the tube along with camphor. Now add 0.1 g of given non-volatile solute to this Rast tube and again weigh it accurately.

2. Seal the open end of Rast tube and heat the sealed tube in paraffin oil bath. During heating rotate the tube. The camphor and solute melts on heating and a homogenous mixture is formed *(Not to be heated more than 1 min.)*.

3. Allow the Rast tube to cool, the mixture becomes solid. Break the tube and find out the melting point of this solid mixture using melting point apparatus.

4. Separately determine the melting point of pure camphor.

Observations

1. Weight of empty Rast tube $= \quad W_1$ g
2. Weight of Rast tube + camphor $= \quad W_2$ g
3. Weight of Rast tube + camphor + non-volatile solute $= \quad W_3$ g
4. Melting point of mixture $= \quad T_1 \ {}^0C$
5. Melting point of pure camphor $= \quad T_2 \ {}^0C$

Calculations

1. Weight of camphor taken $= \quad W$ g. $(W_2 - W_1)$
2. Weight of non-volatile solute taken $= \quad w$ g. $(W_3 - W_2)$

$\Delta T = (T_2 - T_1)$

$$M = \frac{1000 \times K \times w}{\Delta T \times W}$$

Result

Molecular weight of given unknown non-volatile solute is found to be ………

o-------------------------o

Semester-VI

Organic Chemistry Practicals

A. Organic Estimation

**Experiment - 01**

Estimation of formaldehyde

Problem - To determine the amount of formaldehyde present in given solution.

Theory

In this estimation, formaldehyde is oxidized to formic acid by means of known quantity of iodine dissolved in an excess of NaOH solution. Sodium hydroxide reacts with iodine to give sodium hypoiodite which acts as oxidizing agent.

$$I_2 + 2\,NaOH \longrightarrow NaOI + NaI + H_2O$$

$$HCHO + NaOI \longrightarrow HCOOH + NaI$$
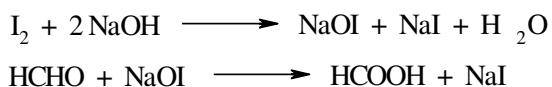
After the completion of oxidation, the unreacted sodium hypoiodite is acidified with HCl and the liberated iodine is titrated against standard sodium thiosulphate solution using starch as an indicator.
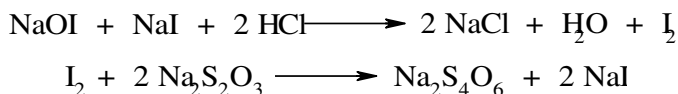
$$NaOI + NaI + 2\,HCl \longrightarrow 2\,NaCl + H_2O + I_2$$

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

Facilities

Apparatus - Burette, Pipette, Conical flasks, Volumetric flasks, Beakers, Weighing bottle, Funnel etc.

Chemicals - Sodium thiosulphate, Iodine solution (approx. 0.05 N), Unknown formaldehyde solution, NaOH solution (10%), Dilute HCl, Starch solution etc.

Procedure

1. Prepare approx. 0.05 N std. sodium thiosulphate solution by dissolving accurately weighed about 1.25 g of sodium thiosulphate (A.R.) in distilled water in a 100 ml volumetric flask. Calculate the exact normality of prepared std. sodium thiosulphate solution from the accurate weight of sodium thiosulphate dissolved in 100 ml of solution.

2. Pipette out 10 ml of iodine solution in a clean conical flask. Add 10% NaOH solution dropwise till the colour turns to pale yellow. Now add dilute HCl till the solution is acidic and colour of iodine persists back. Add 1-2 ml of HCl in excess. Titrate this solution with 0.05 N std. sodium thiosulphate solution taken in a burette, without adding indicator, till the dark brown colour changes to pale yellow. Now add 1 ml of starch solution and titrate till the blue colour just vanishes. Repeat the titration till you gets two constant readings (*This is blank titration*). Tabulate your readings (Table-A).

3. Pipette out same 10 ml of iodine solution in a clean conical flask. Add 10% NaOH solution dropwise till the colour turns to pale yellow. Now add 10 ml of unknown formaldehyde solution using a separate pipette. Immediately stopper the conical

flask. Stir it and wait for 10 minutes. Add dilute HCl till the solution is acidic and colour of iodine persists back. Add 1-2 ml of HCl in excess and titrate this solution with same 0.05 N std. sodium thiosulphate solution taken in a burette as described above till the blue colour just vanishes. Repeat the titration till you gets two constant readings (*This is experimental titration*). Tabulate your readings (Table-B).

Observations

A. Preparation of std. sodium thiosulphate solution

1. Weight of empty weighing bottle   = W_1 g
2. Weight of weighing bottle + sodium thiosulphate   = W_2 g
3. Weight of weighing bottle + remaining particles of sodium thiosulphate   = W_3 g

B. Blank titration (Titration of iodine with sodium thiosulphate)

Table-A

Sr. No.	Volume of iodine solution (ml)	Volume of sodium thiosulphate (ml)	End Point (ml)
1.	10.0		
2.	10.0		V_1
3.	10.0		

C. Experimental titration (Titration of iodine + formaldehyde with sodium thiosulphate)

Table-B

Sr. No.	Volume of iodine solution (ml)	Volume of formaldehyde solution (ml)	Volume of sodium thiosulphate (ml)	End Point (ml)
1.	10.0	10.0		
2.	10.0	10.0		V_2
3.	10.0	10.0		

Calculations

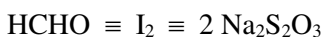1. Weight of sodium thiosulphate transferred   = (W_2-W_3) g
2. Weight of sodium thiosulphate dissolved in 100 ml   = (W_2-W_3) g

$$\text{Normality} = \frac{\text{Weight / litre}}{\text{Equivalent weight}}$$

Normality of std. sodium thiosulphate solution $(N_1) = \dfrac{(W_2-W_3) \times 10}{248}$

Amount of iodine required for oxidation of 10 ml of formaldehyde solution $\equiv (V_1-V_2)$ ml of sodium thiosulphate solution.

$\therefore$ Amount of sodium thiosulphate solution required for oxidation of 10 ml of formaldehyde solution $= (V_1-V_2)$ ml.

$HCHO \equiv I_2 \equiv 2\ Na_2S_2O_3$

Hence,

  2000 ml 1 M of $Na_2S_2O_3 \equiv$ 1000 ml 1 M of HCHO

$\therefore$ 2000 ml 1 N of $Na_2S_2O_3 \equiv$ 1000 ml 1 M of HCHO

$\therefore 2000$ ml 1 N of $Na_2S_2O_3$ $\equiv$ 30 g of HCHO

$\therefore 1000$ ml 1 N of $Na_2S_2O_3$ $\equiv$ 15 g of HCHO

$\therefore 1$ ml 1 N of $Na_2S_2O_3$ $\equiv$ 0.015 g of HCHO

$\therefore 1$ ml N_1 N of $Na_2S_2O_3$ $\equiv$ (0.015 x N_1) g of HCHO

For 10 ml of formaldehyde solution (V_1-V_2) ml of N_1 N of $Na_2S_2O_3$ required.

$\therefore (V_1-V_2)$ ml N_1 N of $Na_2S_2O_3$ $\equiv$ $[0.015 \times N_1 \times (V_1-V_2)]$ g of HCHO

$\therefore$ Amount of formaldehyde present in 10 ml of solution = $[0.015 \times N_1 \times (V_1-V_2)]$ g

$\therefore$ Amount of formaldehyde present per litre = $[0.015 \times N_1 \times (V_1-V_2) \times 100]$ g

N_1 = As calculated, V_1 = End point (Table-A), V_2 = End point (Table-B)

Result

The amount of formaldehyde present in given unknown solution is found to be ……… g / litre.
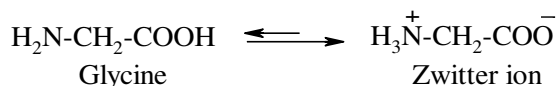
o--------------------------o

Experiment - 02

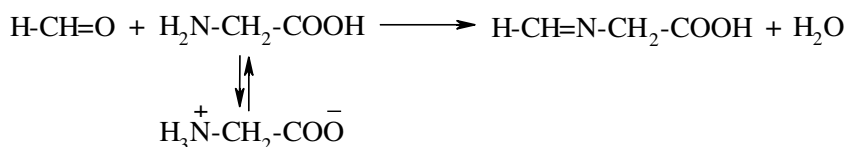## Estimation of glycine (Amino acid)

Problem - To determine the amount of glycine present in given solution.

Theory

Glycine is an amino acid and occurs as a zwitter ion in aqueous solution due to the presence of amino and carboxyl group in the same molecule.

$$H_2N\text{-}CH_2\text{-}COOH \; \rightleftharpoons \; H_3\overset{+}{N}\text{-}CH_2\text{-}CO\overset{-}{O}$$

Glycine   Zwitter ion

Glycine cannot be estimated directly by titration with standard alkali solution but treated with formaldehyde to block (protect) the $-NH_2$ group and makes $-COOH$ group free.

$$H\text{-}CH{=}O + H_2N\text{-}CH_2\text{-}COOH \longrightarrow H\text{-}CH{=}N\text{-}CH_2\text{-}COOH + H_2O$$

$$H_3\overset{+}{N}\text{-}CH_2\text{-}CO\overset{-}{O}$$

The free $-COOH$ group can now be titrated with alkali.

Facilities

Apparatus - Burette, Pipette, Conical flasks, Volumetric flasks, Beakers, Weighing bottle, Funnel etc.

Chemicals - Oxalic acid (A.R.), NaOH solution (approx. 0.1 N), Unknown glycine solution, Neutral formalin solution, Phenolphthalein indicator etc.

Procedure

1. Prepare approx. 0.1 N std. oxalic acid solution by dissolving accurately weighed 0.60 to 0.65 g of oxalic acid (A.R.) in distilled water in a 100 ml volumetric flask. Calculate the exact normality of prepared std. oxalic acid solution from the accurate weight of oxalic acid dissolved in 100 ml of solution.

2. Pipette out 10 ml of std. oxalic acid solution in a clean conical flask. Add 1-2 drops of phenolphthalein indicator and titrate it with 0.1 N NaOH solution taken in a

burette till colour changes from colourless to pink. Repeat the titration till you get two constant readings. Tabulate your readings (Table-A).

3. Pipette out 10 ml of given unknown glycine solution in a conical flask and titrate it with same 0.1 N NaOH solution taken in a burette, using phenolphthalein as an indicator till colour changes from colourless to faint pink *(Do not note the burette reading at this stage)*. Now add about 5 ml (1/3rd test tube) of neutral formalin solution to the same conical flask. Pink colour disappears. Continue the titration till pink colour is obtained. Repeat the titration till you get two constant readings. Tabulate your readings (Table-B).

Observations

A. Preparation of std. oxalic acid solution

1. Weight of empty weighing bottle   = W_1 g
2. Weight of weighing bottle + oxalic acid   = W_2 g
3. Weight of weighing bottle + remaining particles of oxalic acid   = W_3 g

B. Standardization of NaOH solution (Titration of std. oxalic acid with NaOH)

Table-A

Sr. No.	Volume of oxalic acid (ml) V_1	Volume of NaOH (ml)	End Point (ml)
1.	10.0		
2.	10.0		V_2
3.	10.0		

C. Determination of amount of glycine (Titration of glycine with NaOH)

Table-B

Sr. No.	Volume of glycine (ml)	Volume of NaOH (ml)	End Point (ml)
1.	10.0		
2.	10.0		V_2^1
3.	10.0		

Calculations

A. Preparation of std. oxalic acid solution

1. Weight of oxalic acid transferred   = (W_2-W_3) g
2. Weight of oxalic acid dissolved in 100 ml = (W_2-W_3) g

$$Normality = \frac{Weight \ / \ litre}{Equivalent \ weight}$$

$$Normality \ of \ std. \ oxalic \ acid \ solution \ (N_1) = \frac{(W_2-W_3) \ x \ 10}{63}$$

B. Standardization of NaOH solution (Titration of std. oxalic acid with NaOH)

(Oxalic acid)   (NaOH)

$$N_1V_1 = N_2V_2$$

33

Normality of NaOH solution (N_2) = $\dfrac{N_1 V_1}{V_2}$

N_1 = As calculated, V_1 = 10 ml, N_2 = Unknown, V_2 = End point (Table-A)

C. Determination of amount of glycine (Titration of glycine with NaOH)

Equivalent weight of glycine = 75

Hence,

1000 ml 1 N of NaOH	≡	75 g of glycine
∴1 ml 1 N of NaOH	≡	0.075 g of glycine
∴1 ml N_2 N of NaOH	≡	(0.075 x N_2) g of glycine

For 10 ml of glycine V_2^l ml of N_2 N of NaOH is required.

∴V_2^l ml N_2 N of NaOH ≡ (0.075 x N_2 x V_2^l) g of glycine

∴Amount of glycine present in 10 ml of solution = (0.075 x N_2 x V_2^l) g

∴Amount of glycine present per litre = (0.075 x N_2 x V_2^l x 100) g

N_2 = As calculated, V_2^l = End point (Table-B)

Result

The amount of glycine present in given unknown solution is found to be .... g / litre.

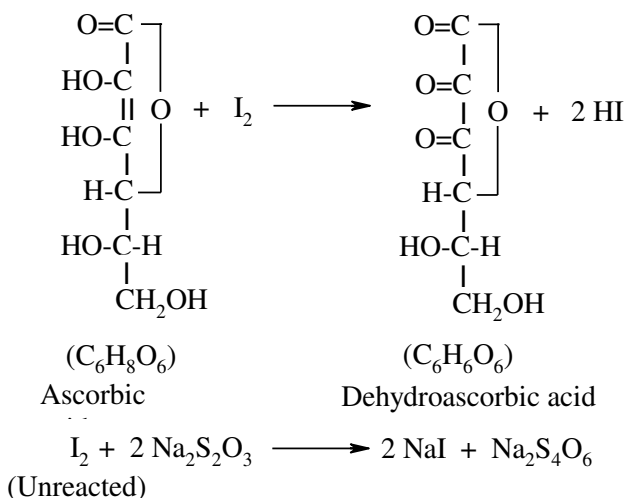o-------------------------o

Experiment - 03

Estimation of ascorbic acid (Vitamin C) by iodimetric method

Problem - To determine the amount of ascorbic acid (Vitamin C) present in given solution.

Theory

An aqueous solution of ascorbic acid (Vitamin C) is oxidized by iodine. To estimate the amount of ascorbic acid its solution is oxidized by known excess of iodine. Some iodine is required for oxidation of ascorbic acid and the unreacted excess of iodine is back titrated with standard sodium thiosulphate solution.

$(C_6H_8O_6)$
Ascorbic

$(C_6H_6O_6)$
Dehydroascorbic acid

$I_2 + 2\,Na_2S_2O_3 \longrightarrow 2\,NaI + Na_2S_4O_6$
(Unreacted)

34

Facilities

Apparatus - Burette, Pipette, Conical flasks, Volumetric flasks, Beakers, Weighing bottle, Funnel etc.

Chemicals - Sodium thiosulphate, Iodine solution (approx. 0.05 N), Unknown ascorbic acid solution, Starch solution etc.

Procedure

1. Prepare approx. 0.05 N std. sodium thiosulphate solution by dissolving accurately weighed about 1.25 g of sodium thiosulphate (A.R.) in distilled water in a 100 ml volumetric flask. Calculate the exact normality of prepared std. sodium thiosulphate solution from the accurate weight of sod. thiosulphate dissolved in 100 ml of solution.

2. Pipette out 10 ml of iodine solution in a clean conical flask and titrate it with 0.05 N sodium thiosulphate solution taken in a burette, without adding indicator, till the dark brown colour changes to pale yellow. Now add 1 ml of starch solution and titrate till the blue colour just vanishes. Repeat the titration till you gets two constant readings (*This is blank titration*). Tabulate your readings (Table-A).

3. Pipette out same 10 ml of iodine solution in a clean conical flask. Add 10 ml of ascorbic acid solution using a separate pipette. Shake the mixture and wait for 2-3 minutes. Now titrate it with same 0.05 N sodium thiosulphate solution taken in a burette as described above till the blue colour just vanishes. Repeat the titration till you gets two constant readings (*This is experimental titration*). Tabulate your readings (Table-B).

Observations

A. Preparation of std. sodium thiosulphate solution

1. Weight of empty weighing bottle   = W_1 g
2. Weight of weighing bottle + sodium thiosulphate   = W_2 g
3. Weight of weighing bottle + remaining particles of sodium thiosulphate   = W_3 g

B. Blank titration (Titration of iodine with sodium thiosulphate)

Table-A

Sr. No.	Volume of iodine solution (ml)	Volume of sodium thiosulphate (ml)	End Point (ml)
1.	10.0		
2.	10.0		V_1
3.	10.0		

C. Experimental titration using ascorbic acid (Titration of unreacted iodine with sodium thiosulphate)

Table-B

Sr. No.	Volume of iodine solution (ml)	Volume of ascorbic acid (ml)	Volume of sodium thiosulphate (ml)	End Point (ml)
1.	10.0	10.0		
2.	10.0	10.0		V_2
3.	10.0	10.0		

Calculations

1. Weight of sodium thiosulphate transferred $\quad\quad\quad = \quad (W_2-W_3)$ g
2. Weight of sodium thiosulphate dissolved in 100 ml $\quad = \quad (W_2-W_3)$ g

$$\text{Normality} = \frac{\text{Weight / litre}}{\text{Equivalent weight}}$$

Normality of std. sodium thiosulphate solution $(N_1) = \dfrac{(W_2-W_3) \times 10}{248}$

Amount of iodine required for oxidation of 10 ml of ascorbic acid solution $\equiv (V_1-V_2)$ ml of sodium thiosulphate solution.

$\therefore$ Amount of sodium thiosulphate solution required for oxidation of 10 ml of ascorbic acid solution $= (V_1-V_2)$ ml.

$C_6H_8O_6 \equiv I_2 \equiv 2\ Na_2S_2O_3$

Hence,

$\quad$ 2000 ml 1 M of $Na_2S_2O_3 \quad \equiv$ 1000 ml 1 M of $C_6H_8O_6$

$\therefore$ 2000 ml 1 N of $Na_2S_2O_3 \quad \equiv$ 1000 ml 1 M of $C_6H_8O_6$

$\therefore$ 2000 ml 1 N of $Na_2S_2O_3 \quad \equiv$ 176 g of $C_6H_8O_6$

$\therefore$ 1000 ml 1 N of $Na_2S_2O_3 \quad \equiv$ 88 g of $C_6H_8O_6$

$\therefore$ 1 ml 1 N of $Na_2S_2O_3 \quad\quad \equiv$ 0.088 g of $C_6H_8O_6$

$\therefore$ 1 ml N_1 N of $Na_2S_2O_3 \quad \equiv (0.088 \times N_1)$ g of $C_6H_8O_6$

For 10 ml of ascorbic acid solution (V_1-V_2) ml of N_1 N of $Na_2S_2O_3$ required.

$\therefore (V_1-V_2)$ ml N_1 N of $Na_2S_2O_3 \equiv [0.088 \times N_1 \times (V_1-V_2)]$ g of $C_6H_8O_6$

$\therefore$ Amount of ascorbic acid present in 10 ml of solution $= [0.088 \times N_1 \times (V_1-V_2)]$ g

$\therefore$ Amount of ascorbic acid present per litre $= [0.088 \times N_1 \times (V_1-V_2) \times 100]$ g

N_1 = As calculated, V_1 = End point (Table-A), V_2 = End point (Table-B)

Result

The amount of ascorbic acid present in given unknown solution is found to be ……… g / litre.
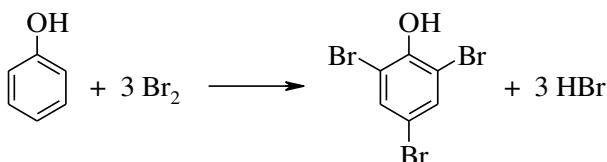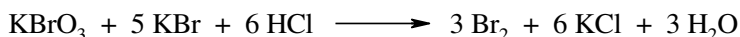
o--------------------------o

Experiment - 04

## Estimation of phenol by bromination method

Problem - To determine the amount of phenol present in given solution using potassium bromate-bromide mixture.

Theory

An aqueous solution of phenol gives 2,4,6-tribromophenol in quantitative yield when treated with excess of potassium bromate and potassium bromide solution in presence of hydrochloric acid.

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

The unreacted (excess) of bromine is treated with potassium iodide and the liberated iodine is then titrated against standard sodium thiosulphate solution using starch as an indicator.

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

$$I_2 + 2\,Na_2S_2O_3 \longrightarrow Na_2S_4O_6 + 2\,NaI$$
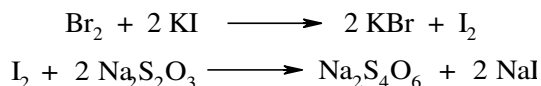
During bromination of phenol some 2,4,6-tribromophenol bromide may also formed, but it is converted to 2,4,6-tribromophenol on addition of potassium iodide during titration.
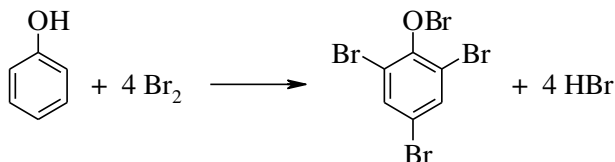
Facilities

Apparatus - Burette, Pipette, Conical flasks, Volumetric flasks, Beakers, Weighing bottle, Funnel etc.

Chemicals - Sodium thiosulphate, Potassium bromate-bromide solution (approx. 0.05 N), Unknown phenol solution, Conc. HCl, 10% KI solution, Starch solution etc.

Procedure

1. Prepare approx. 0.05 N std. sodium thiosulphate solution by dissolving accurately weighed about 1.25 g of sodium thiosulphate (A.R.) in distilled water in a 100 ml volumetric flask. Calculate the exact normality of prepared std. sodium thiosulphate solution from the accurate weight of sod. thiosulphate dissolved in 100 ml of solution.

2. Pipette out 10 ml of distilled water in a clean conical flask. To this add 15 ml of potassium bromate-bromide solution and 2.5 ml of conc. HCl. Immediately stoppered the flask, shake it for 2 minutes and allow the flask to stand at room temperature for 15 minutes with occasional shaking. Add 10 ml of 10 % KI solution and again stoppered the flask. Shake the flask well and allow to stand at room temperature for 5 minutes. Titrate the contents in the flask with 0.05 N std. sodium thiosulphate solution taken in a burette, without adding indicator, till the dark brown colour changes to pale yellow. Now add 1 ml of starch solution and titrate till the blue colour just vanishes. Note the end point (*This is blank titration*).

3. Separately pipette out 10 ml of unknown phenol solution in a clean conical flask, perform similarly and titrate the contents in the flask with 0.05 N std. sodium thiosulphate solution as described above (*This is experimental titration*).

    Preparation of potassium bromate-bromide solution (0.05 N): *Dissolve 1.392 g of anhydrous potassium bromate and 15 g of potassium bromide in 1 litre of distilled water in volumetric flask.*

Observations

1. Weight of empty weighing bottle   = W_1 g
2. Weight of weighing bottle + sodium thiosulphate   = W_2 g
3. Weight of weighing bottle + remaining particles of sodium thiosulphate   = W_3 g
4. Volume of std. sodium thiosulphate solution required for blank titration   = V_1 ml
5. Volume of std. sodium thiosulphate solution required for exp. titration   = V_2 ml

Calculations

1. Weight of sodium thiosulphate transferred $\quad = \quad (W_2-W_3)$ g
2. Weight of sodium thiosulphate dissolved in 100 ml $= \quad (W_2-W_3)$ g
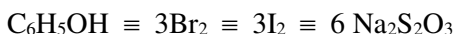
$$\text{Normality} = \frac{\text{Weight / litre}}{\text{Equivalent weight}}$$

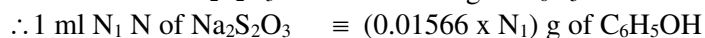Normality of std. sodium thiosulphate solution $(N_1) = \dfrac{(W_2-W_3) \times 10}{248}$

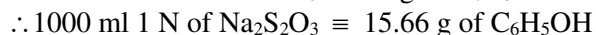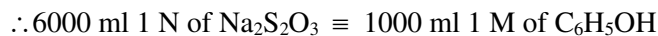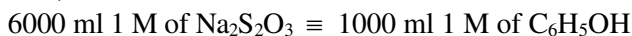Amount of sodium thiosulphate required for total bromine solution $\qquad = \ V_1$ ml

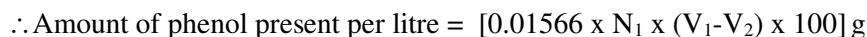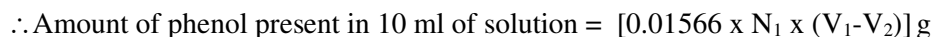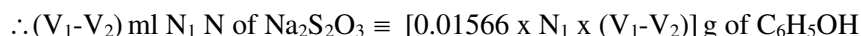Amount of sodium thiosulphate required for unreacted (excess) bromine soln. $= \ V_2$ ml

$\therefore$ Amount of sodium thiosulphate solution equivalent to bromine solution consumed by 10 ml of phenol solution $= (V_1-V_2)$ ml.

$C_6H_5OH \equiv 3Br_2 \equiv 3I_2 \equiv 6\ Na_2S_2O_3$

Hence,

$\quad$ 6000 ml 1 M of $Na_2S_2O_3 \equiv$ 1000 ml 1 M of C_6H_5OH

$\therefore$ 6000 ml 1 N of $Na_2S_2O_3 \equiv$ 1000 ml 1 M of C_6H_5OH

$\therefore$ 6000 ml 1 N of $Na_2S_2O_3 \equiv$ 94 g of C_6H_5OH

$\therefore$ 1000 ml 1 N of $Na_2S_2O_3 \equiv$ 15.66 g of C_6H_5OH

$\therefore$ 1 ml 1 N of $Na_2S_2O_3 \quad \equiv$ 0.01566 g of C_6H_5OH

$\therefore$ 1 ml N_1 N of $Na_2S_2O_3 \quad \equiv$ (0.01566 x N_1) g of C_6H_5OH

For 10 ml of phenol solution (V_1-V_2) ml of N_1 N of $Na_2S_2O_3$ required.

$\therefore (V_1-V_2)$ ml N_1 N of $Na_2S_2O_3 \equiv$ [0.01566 x N_1 x (V_1-V_2)] g of C_6H_5OH

$\therefore$ Amount of phenol present in 10 ml of solution = [0.01566 x N_1 x (V_1-V_2)] g

$\therefore$ Amount of phenol present per litre = [0.01566 x N_1 x (V_1-V_2) x 100] g

Result

The amount of phenol present in given unknown solution is found to be ……… g / litre.

o--------------------------o

Experiment - 05

Estimation of amine by bromination method

Problem - To determine the amount of aniline present in given solution using potassium bromate-bromide mixture.

Theory

An aqueous solution of aniline gives 2,4,6-tribromoaniline in quantitative yield when treated with excess of potassium bromate and potassium bromide solution in presence of hydrochloric acid.

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

The unreacted (excess) of bromine is treated with potassium iodide and the liberated iodine is then titrated against standard sodium thiosulphate solution using starch as an indicator.

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

$$I_2 + 2\,Na_2S_2O_3 \longrightarrow Na_2S_4O_6 + 2\,NaI$$
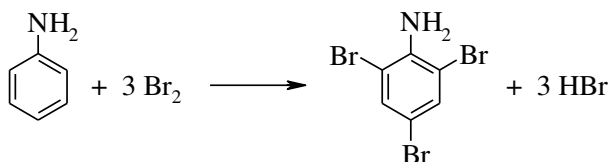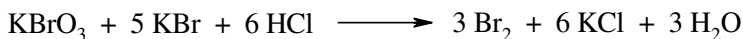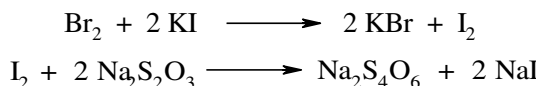
During bromination of aniline some 2,4,6-tribromoaniline bromide may also formed, but it is converted to 2,4,6-tribromoaniline on addition of potassium iodide during titration.
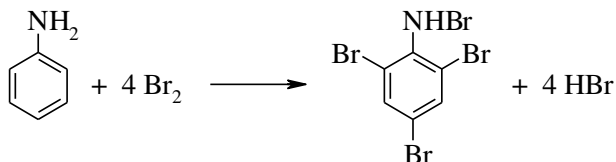
Facilities

Apparatus - Burette, Pipette, Conical flasks, Volumetric flasks, Beakers, Weighing bottle, Funnel etc.

Chemicals - Sodium thiosulphate, Potassium bromate-bromide solution (approx. 0.05 N), Unknown aniline solution, Conc. HCl, 10% KI solution, Starch solution etc.

Procedure

1. Prepare approx. 0.05 N std. sodium thiosulphate solution by dissolving accurately weighed about 1.25 g of sodium thiosulphate (A.R.) in distilled water in a 100 ml volumetric flask. Calculate the exact normality of prepared std. sodium thiosulphate solution from the accurate weight of sod. thiosulphate dissolved in 100 ml of solution.

2. Pipette out 10 ml of distilled water in a clean conical flask. To this add 15 ml of potassium bromate-bromide solution and 2.5 ml of conc. HCl. Immediately stoppered the flask, shake it for 2 minutes and allow the flask to stand at room temperature for 15 minutes with occasional shaking. Add 10 ml of 10 % KI solution and again stoppered the flask. Shake the flask well and allow to stand at room temperature for 5 minutes. Titrate the contents in the flask with 0.05 N std. sodium thiosulphate solution taken in a burette, without adding indicator, till the dark brown colour changes to pale yellow. Now add 1 ml of starch solution and titrate till the blue colour just vanishes. Note the end point (*This is blank titration*).

3. Separately pipette out 10 ml of unknown aniline solution in a clean conical flask, perform similarly and titrate the contents in the flask with 0.05 N std. sodium thiosulphate solution as described above (*This is experimental titration*).

   Preparation of potassium bromate-bromide solution (0.05 N): *Dissolve 1.392 g of anhydrous potassium bromate and 15 g of potassium bromide in 1 litre of distilled water in volumetric flask.*

Observations

1. Weight of empty weighing bottle = W_1 g
2. Weight of weighing bottle + sodium thiosulphate = W_2 g
3. Weight of weighing bottle + remaining particles of sodium thiosulphate = W_3 g
4. Volume of std. sodium thiosulphate solution required for blank titration = V_1 ml
5. Volume of std. sodium thiosulphate solution required for exp. titration = V_2 ml

Calculations

1. Weight of sodium thiosulphate transferred $= (W_2-W_3)$ g
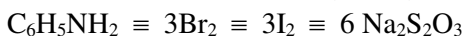2. Weight of sodium thiosulphate dissolved in 100 ml $= (W_2-W_3)$ g

$$\text{Normality} = \frac{\text{Weight / litre}}{\text{Equivalent weight}}$$

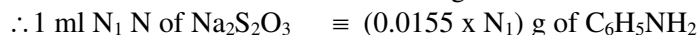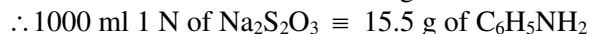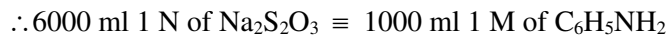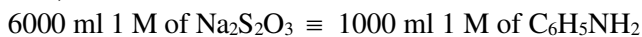Normality of std. sodium thiosulphate solution $(N_1) = \dfrac{(W_2-W_3) \times 10}{248}$

Amount of sodium thiosulphate required for total bromine solution $= V_1$ ml

Amount of sodium thiosulphate required for unreacted (excess) bromine soln. $= V_2$ ml
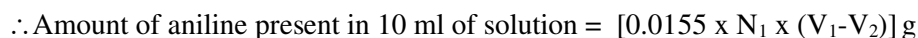
$\therefore$ Amount of sodium thiosulphate solution equivalent to bromine solution consumed by 10 ml of aniline solution $= (V_1-V_2)$ ml.

$C_6H_5NH_2 \equiv 3Br_2 \equiv 3I_2 \equiv 6 Na_2S_2O_3$

Hence,

6000 ml 1 M of $Na_2S_2O_3 \equiv$ 1000 ml 1 M of $C_6H_5NH_2$

$\therefore$ 6000 ml 1 N of $Na_2S_2O_3 \equiv$ 1000 ml 1 M of $C_6H_5NH_2$

$\therefore$ 6000 ml 1 N of $Na_2S_2O_3 \equiv$ 93 g of $C_6H_5NH_2$

$\therefore$ 1000 ml 1 N of $Na_2S_2O_3 \equiv$ 15.5 g of $C_6H_5NH_2$

$\therefore$ 1 ml 1 N of $Na_2S_2O_3 \equiv$ 0.0155 g of $C_6H_5NH_2$

$\therefore$ 1 ml N_1 N of $Na_2S_2O_3 \equiv$ (0.0155 x N_1) g of $C_6H_5NH_2$

For 10 ml of aniline solution (V_1-V_2) ml of N_1 N of $Na_2S_2O_3$ required.

$\therefore (V_1-V_2)$ ml N_1 N of $Na_2S_2O_3 \equiv [0.0155 \times N_1 \times (V_1-V_2)]$ g of $C_6H_5NH_2$

$\therefore$ Amount of aniline present in 10 ml of solution $= [0.0155 \times N_1 \times (V_1-V_2)]$ g

$\therefore$ Amount of aniline present per litre $= [0.0155 \times N_1 \times (V_1-V_2) \times 100]$ g

Result

The amount of aniline present in given unknown solution is found to be ……… g / litre.

o-------------------------o

Experiment - 06

Determination of unsaturation by bromination method

Problem - To determine the unsaturation (bromine / iodine value) of given oil or fat.

Theory

The olefinic unsaturation or number of double bonds in a compound can be determined by catalytic hydrogenation i.e. H_2 with Pt or Raney Ni as catalyst. The volume of hydrogen gas absorbed is measured and number of double bonds can be estimated.

$$\begin{array}{ccc} \diagdown \!\!\!\!\diagup \\ C\!=\!C \\ \diagup \quad \diagdown \end{array} + H_2 \longrightarrow \begin{array}{c} | \quad | \\ -C-C- \\ | \quad | \\ H \quad H \end{array}$$
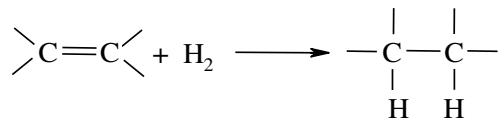
Most of the classical methods for the determination of unsaturation are concerned primarily for the analysis of animal and vegetable oils or fats. Oil or fat contains both saturated and unsaturated fatty acids. Halogens add across the double bonds of unsaturated fatty acids to form dihalogen compounds and from the amount of halogen atoms absorbed, the unsaturation is estimated. The unsaturation values so determined are

expressed as bromine / iodine number. This value represents the number of grams of halogens taken up (absorbed) by 100 g of oil or fat completely. Each double bond absorbs two halogen atoms.

To determine the unsaturation, a known amount of oil or fat is reacted with excess amount of standard solution of iodine monobromide in acetic acid (Hanus's solution) in dark (*The reaction mixture is kept in dark and the titration is carried out as quickly as possible since the halogens are oxidized in presence of light*).

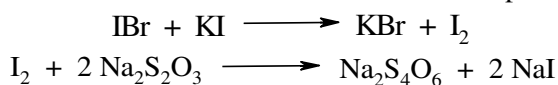$$\text{>C=C<} + IBr \longrightarrow \overset{\mid}{\underset{\mid}{-C}}\overset{\mid}{\underset{\mid}{-C-}}$$
$$\hspace{5cm} I \quad Br$$
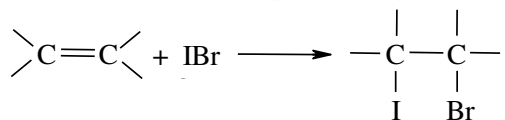
The amount of iodine monobromide consumed is then determined by titrating iodine released from unused iodine monobromide with sodium thiosulphate solution.

$$IBr + KI \longrightarrow KBr + I_2$$
$$I_2 + 2\,Na_2S_2O_3 \longrightarrow Na_2S_4O_6 + 2\,NaI$$

Facilities

Apparatus - Burette, Pipette, Conical flasks, Beakers, Weighing bottle, Funnel etc.
Chemicals - Oil or fat sample, Sodium thiosulphate, Hanus's solution (iodine monobromide in acetic acid), 10% KI solution, Starch solution etc.

Procedure

1. Prepare approx. 0.05 N std. sodium thiosulphate solution by dissolving accurately weighed about 1.25 g of sodium thiosulphate (A.R.) in distilled water in a 100 ml volumetric flask. Calculate the exact normality of prepared std. sodium thiosulphate solution from the accurate weight of sod. thiosulphate dissolved in 100 ml of solution.

2. Weigh accurately about 0.2 g of given oil or fat in a 250 ml glass stoppered iodine flask and dissolve it in 10 ml of chloroform or carbon tetrachloride. Add 25 ml of Hanus's solution and stoppered the flask. Shake the flask and allow it to stand in the dark for about 1 hour with occasional shaking. Rinse the stopper and neck of the flask with about 50 ml of water. Add 10 ml of 10% KI solution and titrate it immediately with 0.05 N sodium thiosulphate solution taken in a burette, without adding indicator with vigorous shaking, till the dark brown colour changes to pale yellow. Now add 1 ml of starch solution and titrate till the blue colour just vanishes. Note the end point (*This is experimental titration*).

3. Simultaneously carry out the titration without adding oil or fat in another iodine flask in a similar manner (*This is blank titration*).

Observations

1. Weight of empty weighing bottle = W_1 g
2. Weight of weighing bottle + sodium thiosulphate = W_2 g
3. Weight of weighing bottle + remaining particles of sodium thiosulphate = W_3 g
4. Weight of oil or fat taken = W_4 g
5. Volume of std. sodium thiosulphate solution required for blank titration = V_1 ml
6. Volume of std. sodium thiosulphate solution required for exp. titration = V_2 ml

Calculations

1. Weight of sodium thiosulphate transferred = (W_2-W_3) g
2. Weight of sodium thiosulphate dissolved in 100 ml = (W_2-W_3) g

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$$\text{Normality} = \frac{\text{Weight / litre}}{\text{Equivalent weight}}$$

Normality of std. sodium thiosulphate solution $(N_1) = \dfrac{(W_2\text{-}W_3) \ \times \ 10}{248}$

Weight of the fat or oil taken = W_4 g

Volume of 0.05 N std. sodium thiosulphate solution required for amount of iodine released from un-utilized iodine monobromide by oil or fat = V_2 ml.

$\therefore$ Volume of 0.05 N std. sodium thiosulphate solution required for amount of iodine released from utilized iodine monobromide by oil or fat = $(V_1\text{-}V_2)$ ml.

$2\,Na_2S_2O_3 \equiv I_2$

Hence,

   2000 ml 1 M of $Na_2S_2O_3 \equiv 1000$ ml 1 M of I_2

$\therefore 2000$ ml 1 N of $Na_2S_2O_3 \equiv 1000$ ml 1 M of I_2

$\therefore 2000$ ml 1 N of $Na_2S_2O_3 \equiv 254$ g of I_2

$\therefore 1000$ ml 1 N of $Na_2S_2O_3 \equiv 127$ g of I_2

$\therefore 1$ ml 1 N of $Na_2S_2O_3 \quad \equiv 0.127$ g of I_2

$\therefore 1$ ml N_1 N of $Na_2S_2O_3 \quad \equiv (0.127 \times N_1)$ g of I_2

For iodine released from utilized iodine monobromide by oil or fat $(V_1\text{-}V_2)$ ml of N_1 N of $Na_2S_2O_3$ is required.

$\therefore (V_1\text{-}V_2)$ ml N_1 N of $Na_2S_2O_3 \equiv [0.127 \times N_1 \times (V_1\text{-}V_2)]$ g of I_2

$(V_1\text{-}V_2)$ ml of N_1 N of $Na_2S_2O_3$ is required for W_4 g of oil or fat.

$\therefore$ Iodine taken up (absorbed) by W_4 g of oil or fat $= [0.127 \times N_1 \times (V_1\text{-}V_2)]$

$\therefore$ Iodine taken up (absorbed) by 100 g of oil or fat $= \dfrac{[0.127 \times N_1 \times (V_1\text{-}V_2) \times 100]}{W_4}$

$\therefore$ Unsaturation (bromine/iodine value) of oil or fat $= \dfrac{[0.127 \times N_1 \times (V_1\text{-}V_2) \times 100]}{W_4}$

Result

The unsaturation (bromine / iodine value) of given oil or fat is found to be ………

o-------------------------o

Experiment - 07

Determination of iodine value of an oil or fat

Problem - To determine the iodine value of given oil or fat.

Theory

Iodine value of an oil or fat is defined as the number of grams of iodine taken up (absorbed) by 100 g of oil or fat completely.

Oil or fat contains both saturated and unsaturated fatty acids. Halogens add across the double bonds of unsaturated fatty acids to form dihalogen compounds and from the amount of halogen atoms absorbed, the number of double bonds is estimated. This is usually expressed as the iodine number or iodine value. Each double bond absorbs two halogen atoms.

To determine the iodine value, a known amount of oil or fat is reacted with excess amount of standard solution of iodine monochloride in acetic acid (Wij's solution) or iodine monobromide in acetic acid (Hanus's solution) in dark (*The reaction mixture is kept in dark and the titration is carried out as quickly as possible since the halogens are oxidized in presence of light*).

$$>C=C< + ICl \longrightarrow \underset{I\quad Cl}{-C-C-} \quad \textbf{or} \quad >C=C< + IBr \longrightarrow \underset{I\quad Br}{-C-C-}$$
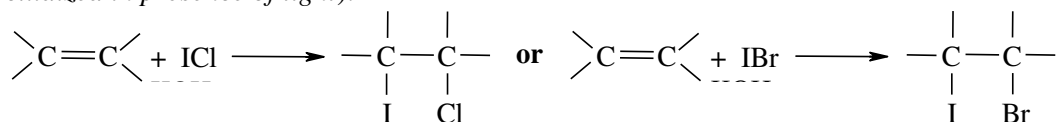
The amount of iodine monochloride or iodine monobromide consumed is then determined by titrating iodine released from unused iodine monochloride or iodine monobromide with sodium thiosulphate solution.
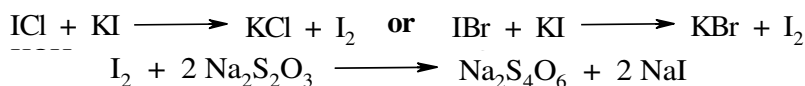
$$ICl + KI \longrightarrow KCl + I_2 \quad \textbf{or} \quad IBr + KI \longrightarrow KBr + I_2$$

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

Facilities

Apparatus - Burette, Pipette, Conical flasks, Beakers, Weighing bottle, Funnel etc.
Chemicals - Oil or fat sample, Sodium thiosulphate, Wij's solution (iodine monochloride in acetic acid) or Hanus's solution (iodine monobromide in acetic acid), 10% KI solution, Starch solution etc.

Procedure

1. Prepare approx. 0.05 N std. sodium thiosulphate solution by dissolving accurately weighed about 1.25 g of sodium thiosulphate (A.R.) in distilled water in a 100 ml volumetric flask. Calculate the exact normality of prepared std. sodium thiosulphate solution from the accurate weight of sod. thiosulphate dissolved in 100 ml of solution.

2. Weigh accurately about 0.2 g of given oil or fat in a 250 ml glass stoppered iodine flask and dissolve it in 10 ml of chloroform or carbon tetrachloride. Add 25 ml of Wij's solution or Hanus's solution and stoppered the flask. Shake the flask and allow it to stand in the dark for about 1 hour with occasional shaking. Rinse the stopper and neck of the flask with about 50 ml of water. Add 10 ml of 10% KI solution and titrate it immediately with 0.05 N sodium thiosulphate solution taken in a burette, without adding indicator with vigorous shaking, till the dark brown colour changes to pale yellow. Now add 1 ml of starch solution and titrate till the blue colour just vanishes. Note the end point (*This is experimental titration*).

3. Simultaneously carry out the titration without adding oil or fat in another iodine flask in a similar manner (*This is blank titration*).

Observations

1. Weight of empty weighing bottle = W_1 g
2. Weight of weighing bottle + sodium thiosulphate = W_2 g
3. Weight of weighing bottle + remaining particles of sodium thiosulphate = W_3 g
4. Weight of oil or fat taken = W_4 g
5. Volume of std. sodium thiosulphate solution required for blank titration = V_1 ml
6. Volume of std. sodium thiosulphate solution required for exp. titration = V_2 ml

Calculations

1. Weight of sodium thiosulphate transferred = (W_2-W_3) g
2. Weight of sodium thiosulphate dissolved in 100 ml = (W_2-W_3) g

$$\text{Normality} = \frac{\text{Weight / litre}}{\text{Equivalent weight}}$$

Normality of std. sodium thiosulphate solution $(N_1) = \dfrac{(W_2-W_3) \times 10}{248}$

Weight of the fat or oil taken = W_4 g

Volume of 0.05 N std. sodium thiosulphate solution required for amount of iodine released from unutilized iodine monochloride or monobromide by oil or fat $= V_2$ ml.

$\therefore$ Volume of 0.05 N std. sodium thiosulphate solution required for amount of iodine released from utilized iodine monochloride or monobromide by oil or fat $= (V_1-V_2)$ ml.

$2\ Na_2S_2O_3 \equiv I_2$

Hence,

2000 ml 1 M of $Na_2S_2O_3$ $\equiv$ 1000 ml 1 M of I_2

$\therefore$ 2000 ml 1 N of $Na_2S_2O_3$ $\equiv$ 1000 ml 1 M of I_2

$\therefore$ 2000 ml 1 N of $Na_2S_2O_3$ $\equiv$ 254 g of I_2

$\therefore$ 1000 ml 1 N of $Na_2S_2O_3$ $\equiv$ 127 g of I_2

$\therefore$ 1 ml 1 N of $Na_2S_2O_3$ $\equiv$ 0.127 g of I_2

$\therefore$ 1 ml N_1 N of $Na_2S_2O_3$ $\equiv$ $(0.127 \times N_1)$ g of I_2

For iodine released from utilized iodine monochloride or iodine monobromide by oil or fat (V_1-V_2) ml of N_1 N of $Na_2S_2O_3$ is required.

$\therefore (V_1-V_2)$ ml N_1 N of $Na_2S_2O_3$ $\equiv [0.127 \times N_1 \times (V_1-V_2)]$ g of I_2

(V_1-V_2) ml of N_1 N of $Na_2S_2O_3$ is required for W_4 g of oil or fat.

$\therefore$ Iodine taken up (absorbed) by W_4 g of oil or fat $= [0.127 \times N_1 \times (V_1-V_2)]$

$\therefore$ Iodine taken up (absorbed) by 100 g of oil or fat $= \dfrac{[0.127 \times N_1 \times (V_1-V_2) \times 100]}{W_4}$

$\therefore$ Iodine value or iodine number of oil or fat $= \dfrac{[0.127 \times N_1 \times (V_1-V_2) \times 100]}{W_4}$

Result

The iodine value of given oil or fat is found to be ………

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Experiment - 08

Determination of equivalent weight of an ester

Problem - To determine the equivalent weight of given ester by saponification method.

Theory

The equivalent weight of an ester is the weight of ester in grams, which reacts with one gram equivalent of a strong base.

The common method for determination of equivalent weight of water soluble ester is saponification of ester with aqueous solution of sodium or potassium hydroxide. In this method weighed amount of an ester is heated with a known excess volume of the standard alkali hydroxide solution and after hydrolysis, the excess of alkali is determined by titration with standard acid.
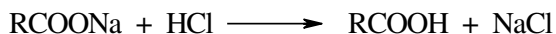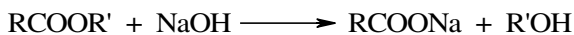
44

$$RCOOR' + NaOH \longrightarrow RCOONa + R'OH$$

$$RCOONa + HCl \longrightarrow RCOOH + NaCl$$

Facilities

Apparatus - Burette, Pipette, Conical flasks, Volumetric flasks, Beakers, Weighing bottle, Funnel etc.

Chemicals - Unknown ester, NaOH solution (0.5 N), HCl solution (0.1 N), Phenolphthalein indicator etc.

Procedure

1. Weigh accurately about 0.5 to 0.8 g of given unknown ester and transfer that in a 250 ml conical flask or R.B. flask. Add 50 ml of 0.5 N NaOH solution by using a pipette. Add few pieces of broken porcelain, connect the flask to reflux condenser and boil the contents very gently for 1½ hours using sand bath. Stop heating and pour 10 to 15 ml of distilled water down the condenser. Remove the flask and cool it in cold water.

2. Transfer the contents of flask and washings in a 250 ml volumetric flask and make up the volume to the mark with distilled water. Mix it well and titrate 25 ml of this solution with 0.1 N HCl solution using phenolphthalein as an indicator till colour changes from pink to colourless. Repeat the titration till you get two constant readings. Tabulate your readings (Table-A).

3. Separately, using pipette transfer 50 ml of 0.5 N NaOH solution in a 250 ml volumetric flask and make up the volume to the mark with distilled water. Mix it well and titrate 25 ml of this diluted NaOH solution with same 0.1 N HCl solution using phenolphthalein as an indicator till colour changes from pink to colourless. Repeat the titration till you get two constant readings. Tabulate your readings (Table-B).

Observations

1. Weight of empty weighing bottle   = W_1 g
2. Weight of weighing bottle + ester   = W_2 g
3. Weight of weighing bottle + remaining ester = W_3 g

A. Experimental titration (Titration of ester and NaOH mixture with HCl)

Table-A

Sr. No.	Volume of ester and NaOH mixture (ml)	Volume of HCl (ml)	End Point (ml)
1.	25.0		
2.	25.0		V_1
3.	25.0		

B. Blank titration (Titration of NaOH with HCl)

Table-B

Sr. No.	Volume of NaOH (ml)	Volume of HCl (ml)	End Point (ml)
1.	25.0		
2.	25.0		V_2
3.	25.0		

Calculations

1. Weight of ester transferred and hydrolysed $\qquad = (W_2-W_3)$ g
2. Volume of acid equivalent to ester (for 25 ml solution) $\qquad = (V_2 -V_1)$ ml
3. Volume of acid equivalent to ester (for 250 ml solution) $\qquad = (V_2 -V_1)$ x 10 ml
4. Normality of HCl solution $\qquad = \dots\dots$ N (Standard)

$$\text{Equivalent weight of unknown ester} = \frac{(W_2-W_3) \text{ x } 1000}{(V_2-V_1) \text{ x } 10 \text{ x } N}$$

Result

The equivalent weight of given unknown ester is found to be $\dots\dots$

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B. Chromatography

Chromatography is a technique of separation of mixture into individual components. It was first invented by M. T. Swett and since then it has undergone tremendous modifications. At present various types of chromatography are available to separate the mixture. Basically chromatography consists of two main branches.

Adsorption chromatography - It depends on the components of a mixture having different adsorbing capacities on the adsorbent. The more adsorbable components are adsorbed faster than others and can be desorbed or eluted by a suitable solvent more slowly.

Partition chromatography - It depends on the distribution of one or more solutes between two immiscible solvents. The one solvent is kept stationary while the other one is mobile.

Depending upon the mobile and stationary phase the chromatography may be classified into liquid-solid, liquid-liquid, gas-liquid or gas-solid type of chromatography. On the basis of the techniques used for the separation, chromatography can be further differentiate into paper chromatography, thin layer chromatography, column chromatography, gas chromatography, high pressure liquid chromatography etc. Paper chromatography is a partition chromatography. Depending upon the stationary phase used, thin layer chromatography is called as adsorption or partition chromatography.

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Experiment - 09

Chromatographic separation of a mixture of dyes methyl orange and methylene blue by thin layer chromatography (using benzene) and determination of R_f values

Problem - To separate the mixture of dyes methyl orange and methylene blue by thin layer chromatography (using benzene) and determine R_f values.

Theory

Thin layer chromatography is also known as adsorption or partition chromatography depending upon the stationary phase used. It depends on the distribution of one or more solutes between two immiscible solvents. When alumina or silica gel is used as a stationary phase then it is liquid-solid type of chromatography whereas when cellulose is used as a stationary phase then it is liquid-liquid type of chromatography. Thin layer chromatography involves the separation of components using a glass slide or plate covered with thin layer of adsorbent like alumina or silica gel. In this technique a drop of

test solution is applied as a small spot on a glass slide covered with thin layer of adsorbent. The spot is allowed to dry. The spotted glass slide is kept in a closed chamber and the edge of the slide is dipped in a solvent, called developing solvent. The solvent rises in the adsorbent through capillary action and carries along with it the components at different speeds. When the solvent has moved through a suitable distance, the glass slide is taken out, dried and the various spots (*if not visible*) are made visible by suitable reagent, called visualizing reagent.

The movement of substance (component) relative to the solvent is expressed in terms of R_f value i.e. migration parameter and is given by the equation,

$$R_f = \frac{\text{Distance travelled by the solute (component) from base (original) line}}{\text{Distance travelled by the solvent from base (original) line}}$$

The glass slide on which different spots are seen after their separation is called as thin layer chromatogram. A typical thin layer chromatogram is as below.
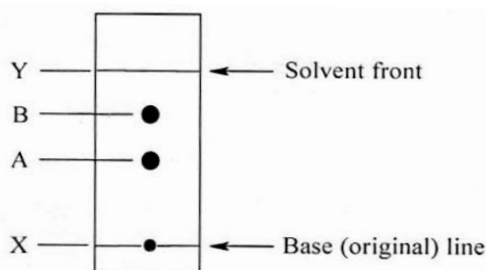
Where,
XY is distance travelled by solvent.
XA is distance travelled by component A.
XB is distance travelled by component B.

Hence,
R_f of component A = XA / XY
R_f of component B = XB / XY

Since the R_f value of a component is constant under given conditions, thin layer chromatography is useful both for separation and identification of components from a mixture.

Facilities

Apparatus - Chromatographic chamber, TLC plates or glass slides, Beakers, Capillary tubes, Glass rod, Hot air oven, Drier etc.

Chemicals - Solution of dyes (2.5 mg methyl orange and 2.5 mg methylene blue in 10 ml of ethanol), Solvent (benzene), Alumina or silica gel, Calcium sulphate etc.

Procedure

A. Preparation of TLC plates or slides

1. Prepare 1:1 slurry of adsorbent by mixing the adsorbent with distilled water or solvent and store it in a well stoppered bottle. Before use, stir the slurry well with glass rod to make the suspension uniform (*Adsorbents used are generally alumina or silica gel containing little calcium sulphate to increase the strength of coating*).

2. Glass slides can be coated by dipping them in pairs, held back-to-back in the slurry and withdrawing slowly and steadily to let the solvent drain away. Then evaporate the solvent, separate the two glass slides and activate them by drying in hot air oven.

B. Development of chromatogram

1. Place an activated glass slide on a clean table over white paper. Draw a base line with pencil, about 6-10 mm from one end of the glass slide.
2. Dip a clean capillary tube in the given solution of dyes. Keep the tube exactly vertical at the centre point of base line drawn on the glass slide. A small drop will fall on the glass slide, dry it, apply one more drop on the same point in the same manner and again dry it (*Drop must be a small with diameter not more than 2 mm*). Similarly apply the drops of individual dye(s) on same glass slide for comparison.
3. Place the glass slide in chromatographic chamber in such a way that its lower end dips in the solvent benzene. The solvent will rise through thin layer coated on glass slide. Allow the solvent front to travel about ¾th of the length of glass slide.
4. After this take out the glass slide and mark the solvent front with pencil. Dry the glass slide and mark the centre of two separate spots of dyes methyl orange and methylene blue, so as to calculate the R_f values.

Observations

1. Distance travelled by solvent front   =   …… cm
2. Distance travelled by methyl orange   =   …… cm
3. Distance travelled by methylene blue   =   …… cm

Calculations

1. R_f value of methyl orange $= \dfrac{\text{Distance travelled by methyl orange from base (original) line}}{\text{Distance travelled by the solvent from base (original) line}}$

   $= \text{......}$

2. R_f value of methylene blue $= \dfrac{\text{Distance travelled by methylene blue from base (original) line}}{\text{Distance travelled by the solvent from base (original) line}}$

   $= \text{......}$

Result

The R_f values of dyes methyl orange and methylene blue are found to be ……… and ……… respectively.

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Experiment - 10

Chromatographic separation of a mixture of 2,4-dinitrophenylhydrazones of acetaldehyde and benzaldehyde by thin layer chromatography (using 3:1 v/v mixture of benzene and petroleum ether) and determination of R_f values

Problem - To separate the mixture of 2,4-dinitrophenylhydrazones of acetaldehyde and benzaldehyde by thin layer chromatography (using 3:1 v/v mixture of benzene and petroleum ether) and determine R_f values.

Theory

Same as in Experiment No. 09

Facilities

Apparatus - Chromatographic chamber, TLC plates or glass slides, Beakers, Capillary tubes, Glass rod, Hot air oven, Drier etc.

Chemicals - Solution of 2,4-dinitrophenylhydrazones of acetaldehyde and benzaldehyde in ethanol or ethyl acetate, Solvent mixture (3:1 v/v mixture of benzene and petroleum ether), Alumina or silica gel, Calcium sulphate etc.

Procedure

Same as in Experiment No. 09, with following exceptions.

a. Use the solvent mixture of benzene and petroleum ether.
b. Use the solution of 2,4-dinitrophenylhydrazones of acetaldehyde and benzaldehyde.

   (*If it is difficult to locate the spots of 2,4-dinitrophenylhydrazones of acetaldehyde and benzaldehyde on glass slide, hence spray the 5% aqueous-ethanolic KOH solution to develop intense colour spots*).

Observations

1. Distance travelled by solvent front   =   …… cm
2. Distance travelled by 2,4-DNP hydrazone of acetaldehyde   =   …… cm
3. Distance travelled by 2,4-DNP hydrazone of benzaldehyde   =   …… cm

Calculations

1. R_f value of 2,4-DNP hydrazone of acetaldehyde $= \dfrac{\text{Distance travelled by 2,4-DNP hydrazone of acetaldehyde from base (original) line}}{\text{Distance travelled by the solvent from base (original) line}}$

   $= \text{......}$

2. R_f value of 2,4-DNP hydrazone of benzaldehyde $= \dfrac{\text{Distance travelled by 2,4-DNP hydrazone of benzaldehyde from base (original) line}}{\text{Distance travelled by the solvent from base (original) line}}$

   $= \text{......}$

Result

The R_f values of 2,4-dinitrophenylhydrazones of acetaldehyde and benzaldehyde are found to be ……… and ……… respectively.

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Experiment - 11

Chromatographic separation of a mixture of dyes methyl red and methylene blue by thin layer chromatography (using 8.5:1.5 v/v mixture of cyclohexane and ethyl acetate) and determination of R_f values

Problem - To separate the mixture of dyes methyl red and methylene blue by thin layer chromatography (using 8.5:1.5 v/v mixture of cyclohexane and ethyl acetate) and determine R_f values.

Theory

Same as in Experiment No. 09

Facilities

Apparatus - Chromatographic chamber, TLC plates or glass slides, Beakers, Capillary tubes, Glass rod, Hot air oven, Drier etc.

Chemicals - Solution of dyes (2.5 mg methyl red and 2.5 mg methylene blue in 10 ml of ethanol), Solvent mixture (8.5:1.5 v/v mixture of cyclohexane and ethyl acetate), Alumina or silica gel, Calcium sulphate etc.

Procedure

Same as in Experiment No. 09, with following exceptions.

a. Use the solvent mixture of cyclohexane and ethyl acetate.
b. Use the solution of methyl red and methylene blue.

Observations

1. Distance travelled by solvent front   =   …… cm
2. Distance travelled by methyl red   =   …… cm
3. Distance travelled by methylene blue   =   …… cm

Calculations

1. R_f value of methyl red $= \dfrac{\text{Distance travelled by methyl red from base (original) line}}{\text{Distance travelled by the solvent from base (original) line}}$

    $= \ldots$

2. R_f value of methylene blue $= \dfrac{\text{Distance travelled by methylene blue from base (original) line}}{\text{Distance travelled by the solvent from base (original) line}}$

    $= \ldots$

Result

The R_f values of dyes methyl red and methylene blue are found to be ……… and ……… respectively.

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Experiment - 12

Chromatographic separation of a mixture of 2,4-dinitrophenylhydrazones of acetaldehyde and benzaldehyde by thin layer chromatography (using 2:3 v/v mixture of toluene and petroleum ether) and determination of R_f values

Problem - To separate the mixture of 2,4-dinitrophenylhydrazones of acetaldehyde and benzaldehyde by thin layer chromatography (using 2:3 v/v mixture of toluene and petroleum ether) and determine R_f values.

Theory

Same as in Experiment No. 09

Facilities

Apparatus - Chromatographic chamber, TLC plates or glass slides, Beakers, Capillary tubes, Glass rod, Hot air oven, Drier etc.

Chemicals - Solution of 2,4-dinitrophenylhydrazones of acetaldehyde and benzaldehyde in ethanol or ethyl acetate, Solvent mixture (2:3 v/v mixture of toluene and petroleum ether), Alumina or silica gel, Calcium sulphate etc.

Procedure

Same as in Experiment No. 09, with following exceptions.

a. Use the solvent mixture of toluene and petroleum ether.
b. Use the solution of 2,4-dinitrophenylhydrazones of acetaldehyde and benzaldehyde.

(If it is difficult to locate the spots of 2,4-dinitrophenylhydrazones of acetaldehyde and benzaldehyde on glass slide, hence spray the 5% aqueous-ethanolic KOH solution to develop intense colour spots).

Observations

1. Distance travelled by solvent front   =   …… cm
2. Distance travelled by 2,4-DNP hydrazone of acetaldehyde   =   …… cm
3. Distance travelled by 2,4-DNP hydrazone of benzaldehyde   =   …… cm

Calculations

1. R_f value of 2,4-DNP hydrazone of acetaldehyde $= \dfrac{\text{Distance travelled by 2,4-DNP hydrazone of acetaldehyde from base (original) line}}{\text{Distance travelled by the solvent from base (original) line}}$

   $= \dots$

2. R_f value of 2,4-DNP hydrazone of benzaldehyde $= \dfrac{\text{Distance travelled by 2,4-DNP hydrazone of benzaldehyde from base (original) line}}{\text{Distance travelled by the solvent from base (original) line}}$

   $= \dots$

Result

The R_f values of 2,4-dinitrophenylhydrazones of acetaldehyde and benzaldehyde are found to be ……… and ……… respectively.

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Semester-VI

Physical Chemistry Practicals

A. Conductometry

Like the metallic conductors, solutions of electrolytes (acids, bases and salts in water) conduct electricity. Electrolytic conductivity is a measure of the ability of a solution to carry an electric current. Solutions of electrolytes conduct an electric current by the migration of positively and negatively charged particles, known as cations and anions respectively, in opposite directions. The ions move at a rate dependent on their charge, size, microscopic viscosity of the medium and the magnitude of potential gradient.

Electrolytic solutions obey Ohm's law just as metallic conductors do. The reciprocal of resistance (1/R) is called as the conductance and is measured in reciprocal of ohms (ohms^{-1}) or mhos. In SI nomenclature the reciprocal of ohms takes the name siemens (S).

Specific conductance

It is the conductance of a solution placed between two parallel plates of 1 cm^2 area and 1 cm apart. It is usually represented by kappa (κ or K) and its S.I. unit is siemens meter^{-1} (Sm^{-1}) but normally reported as siemens centimeter^{-1} (Scm^{-1}).

Equivalent conductance

It is the conductance of a solution containing 1 gram equivalent of an electrolyte placed between two parallel plates of 1 cm^2 area and 1 cm apart. It is usually represented by λ and reported as Scm^{-1}.g equi.$^{-1}$.

The equivalent conductance (λ) is related to the specific conductance (K or κ) by the equation,

$$\lambda = \frac{1000 \text{ K}}{C}$$

The equivalent conductance for solution at particular dilution (λ_V) or at particular concentration (λ_C) is given by the equation,

$$\lambda_V \text{ or } \lambda_C = \frac{1000 \text{ K}}{C}$$

Conductivity of a solution is influenced by the presence of traces of foreign electrolytic impurities. Ordinary water is not suitable for conductance measurements because it may contain dissolved CO_2 from air, ammonia etc. Hence the electrolytic solutions must be prepared in conductivity water.

For precise work, conductivity of the solution must be measured at constant temperature. An increase in temperature invariably results in an increase in ionic conductance. For most of the ions this amounts to 2 to 3 % per degree.

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Experiment - 01

Determination of dissociation constant (Ka) of a weak acid by conductometry

Problem - To determine the dissociation constant (Ka) of an acetic acid using conductometer.

Theory

Acetic acid is a weak acid and it undergoes dissociation to a very small extent. The dissociation of acetic acid is represented by the following equation.

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

If one mole of acetic acid is dissolved in V litre of solution and α is the degree of dissociation, then dissociation constant (Ka) of acetic acid by Ostwald's dilution law is given by the formula,

$$Ka = \frac{[H^+] \ [CH_3COO^-]}{[CH_3COOH]} = \frac{\frac{\alpha}{V} \times \frac{\alpha}{V}}{\frac{(1-\alpha)}{V}} = \frac{\alpha^2}{(1-\alpha) \times V} = \frac{\alpha^2 C}{(1-\alpha)}$$

Where, C is the concentration of acetic acid in mol/litre.

In case of weak acid α is very small as compare to unity. So (1-α) may be taken equal to 1 and the above formula becomes,

$$Ka = \alpha^2 C$$

The degree of dissociation (α) is given by the expression,

$$\alpha = \frac{\lambda_V}{\lambda_\infty} \ \text{or} \ \frac{\lambda_C}{\lambda_0}$$

So, dissociation constant (Ka) is given by the formula,

$$Ka = (\lambda_V / \lambda_\infty)^2 C \quad \text{or} \quad (\lambda_C / \lambda_0)^2 C$$

Where,

λ_V is equivalent conductance of acetic acid at particular dilution.

λ_∞ is equivalent conductance of acetic acid at infinite dilution.

or,

λ_C is equivalent conductance of acetic acid at particular concentration.

λ_0 is equivalent conductance of acetic acid at zero concentration.

The equivalent conductance for solution at particular dilution (λ_V) or at particular concentration (λ_C) is given by the equation,

$$\lambda_V \ \text{or} \ \lambda_C = \frac{1000 \ K}{C}$$

Where, K is specific conductance of acetic acid.

In this experiment equivalent conductance of acetic acid solutions at different concentration (or dilution) is determined using conductometer and then degree of dissociation (α) is calculated. Using the value of α and knowing the concentration, dissociation constant (Ka) is determined.

Facilities

Apparatus - Conductometer, Conductivity cell, Magnetic stirrer or glass rod, Burette, Beakers, Wash bottle etc.

Chemicals - KCl solution (0.1 N), Acetic acid solution (0.1 N), Conductivity water etc.

Procedure

1. Understand the working of conductometer to be used for the experiment.
2. Wash the conductivity cell thoroughly with distilled water and then rinse it first with conductivity water and then with 0.1 N KCl solution. Take 0.1 N KCl solution in a clean glass beaker and dip the cell in it. Stir the solution well and measure the conductance using conductometer.
3. From given 0.1 N acetic acid solution, prepare 0.02, 0.04, 0.06 and 0.08 N acetic acid solution by adding 40, 30, 20 and 10 ml of conductivity water in 10, 20, 30 and 40 ml of 0.1 N acetic acid solution respectively using standard burette.
4. Now measure the conductance of each of above prepared solution as well as given 0.1 N acetic acid solution. Wash the cell each time with conductivity water and also rinse with the solution, of which conductance is to be determined. (*Note : Perform the experiment at constant temperature*).

Observations

1. Observed conductance of 0.1 N KCl   =   A μS
2. Observed conductance of 0.02 N acetic acid   = B_1 μS
3. Observed conductance of 0.04 N acetic acid   = B_2 μS
4. Observed conductance of 0.06 N acetic acid   = B_3 μS
5. Observed conductance of 0.08 N acetic acid   = B_4 μS
6. Observed conductance of 0.1 N acetic acid   = B_5 μS
7. Temperature   =   --- ^{0}C

Calculations

1. Cell constant $(X) = \dfrac{\text{Specific conductance of 0.1 N KCl } (1.3 \times 10^4)}{\text{Observed conductance of 0.1 N KCl}}$

2. Specific conductance of acetic acid (K) = Observed conductance x Cell constant
                                                 $(B_1, B_2, B_3, B_4, B_5)$ (X)

3. Equivalent conductance of acetic acid $(\lambda_V) = \dfrac{1000 \text{ K}}{C}$

Where, C is concentration of acetic acid (Normality).

4. Degree of dissociation $(\alpha) = \dfrac{\lambda_V}{\lambda_{00}}$

Where, λ_∞ for acetic acid is 390×10^6 μS

5. Dissociation constant $(Ka) = \alpha^2 C$

6. pKa = -log Ka

Tabulate your readings as shown below.

Sr. No.	Concentration (Normality)	Observed conductance	Specific conductance	Equivalent conductance	Degree of dissociation	Dissociation constant	
	(C)	(B$_1$ to B$_5$)	(K)	(λ_V)	(α)	(Ka)	(pKa)
1.	0.02						
2.	0.04						
3.	0.06						
4.	0.08						
5.	0.10						
6.	Mean (Ka) and (pKa) ⟶						

Result

The dissociation constant of acetic acid is found to be ……… at ….. ^{0}C.
(*The values of Ka and pKa are found to be constant within experimental limits*).

o--------------------------o

Experiment - 02

Determination of solubility and solubility product of a sparingly soluble salt BaSO$_4$ by conductometry

Problem - To determine the solubility and solubility product of a sparingly soluble salt BaSO$_4$ using conductometer.

Theory

Electrolytes either strong or weak, these are considerably soluble in water but there are some which are soluble in water to a very small extent and are called as sparingly soluble salt.

The saturated solution of sparingly soluble salt is so dilute that the electrolyte in it may be regarded as completely ionized (dissociated). If saturated solution of BaSO$_4$ in water is filter, very less amount of BaSO$_4$ is dissolved in water and gives a very dilute solution. Further addition of water in it does not change the conductance value of solution and it is particularly taken as at infinite dilute solution. BaSO$_4$ dissociates in water as below.

$$BaSO_4 \rightleftharpoons Ba^{++} + SO_4^{--}$$
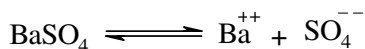
The solubility of such salts can not be determined by ordinary methods. Hence it is determined by conductometric method.

The equivalent conductance (λ) is related to the specific conductance (K or κ) by the equation,

$$\lambda = \frac{1000\ K}{C}$$

The equivalent conductance for solution at particular dilution (λ_V) or at particular concentration (λ_C) is given by the equation,

$$\lambda_V \text{ or } \lambda_C = \frac{1000\,K}{C}$$

In the solution of sparingly soluble salts, there are negligible interionic attractions. Hence equivalent conductance for such solution can be considered to be equivalent conductance at infinite dilution (λ_∞) or at zero concentration (λ_0) and is given by the equation,

$$\lambda_{\infty} \text{ or } \lambda_0 = \frac{1000\,K}{C}$$
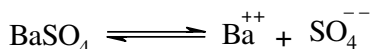
As the solution being saturated, concentration (C) represents the solubility (S) of sparingly soluble salt in gram equivalent per litre.

$$\lambda_{\infty} \text{ or } \lambda_0 = \frac{1000\,K}{S}$$

So, Solubility (S) in gram equivalent / litre $= \dfrac{1000\,K}{\lambda_{\infty}}$

Equivalent conductance of sparingly soluble salt is taken particularly as the sum of conductance of ionic product.

For $BaSO_4$,

$$BaSO_4 \rightleftharpoons Ba^{++} + SO_4^{--}$$

$\lambda_\infty = \lambda_C(Ba^{++}) + \lambda a(SO_4^{--})$
$\lambda_\infty = 63.65 + 79.80$
$\lambda_\infty = 143.45$ S (siemens) or mhos
$\lambda_\infty = 143.45 \times 10^6$ μS (microsiemens) or micromhos

Specific conductance (K) = Observed conductance x Cell constant

$$
\begin{aligned}
\text{Solubility product } (K_{sp}) &= [Ba^{++}] \times [SO_4^{--}] \\
&= S \times S \\
&= S^2
\end{aligned}
$$

Solubility (S) in grams/litre = S x Equivalent weight of $BaSO_4$

(Equivalent weight of $BaSO_4 = \dfrac{\text{Molecular weight}}{2} = \dfrac{233}{2} = 116.5$)

Facilities

Apparatus - Conductometer, Conductivity cell, Magnetic stirrer or glass rod, Beakers, Wash bottle etc.
Chemicals - KCl solution (0.1 N), $BaSO_4$ (A.R.), Conductivity water etc.

Procedure

1. Understand the working of conductometer to be used for the experiment.
2. Wash the conductivity cell thoroughly with distilled water and then rinse it with

conductivity water. Take conductivity water in a clean glass beaker. Dip the cell in it and measure the conductance using conductometer.

3. Remove the conductivity cell from a beaker containing conductivity water and rinse it with 0.1 N KCl solution. Take 0.1 N KCl solution in another clean glass beaker. Dip the cell in it and measure the conductance.

4. Prepare saturated solution of $BaSO_4$ by adding about 0.1 g of $BaSO_4$ to about 50 ml conductivity water in a clean glass beaker. Stir it vigorously for 5 minutes and allow to stand for 10 minutes. Stir again for 5 minutes and keep it for 5 minutes.

5. Wash the conductivity cell thoroughly with distilled water and then with conductivity water. Immerse the cell in a beaker containing saturated solution of $BaSO_4$ and measure its conductance (*Note : Perform the experiment at constant temperature*).

Observations

1. Observed conductance of conductivity water   =   A μS
2. Observed conductance of 0.1 N KCl   =   B μS (mS x 10^3)
3. Observed conductance of $BaSO_4$-Water solution   =   C μS
4. Temperature   =   --- ^0C

Calculations

1. Observed conductance of $BaSO_4$ alone   =   C-A μS

2. Cell constant $= \dfrac{\text{Specific conductance of 0.1 N KCl } (1.3 \times 10^4)}{\text{Observed conductance of 0.1 N KCl}}$

3. Sp. conductance of $BaSO_4$ (K) = Observed conductance of $BaSO_4$ alone x Cell const.

4. Solubility (S) in g eq./ litre $= \dfrac{1000 \text{ K}}{\lambda_{oo}}$

$$= \dfrac{1000 \text{ K}}{143.45 \times 10^6}$$

$\therefore$ Solubility (S) in g /litre = Solubility in g eq./litre x Equivalent weight of $BaSO_4$
        = (S) in g eq./litre x 116.5

5. Solubility product of $BaSO_4$ (K_{sp})   =   (S) in g/litre x (S) in g/litre
           =   (S^2)

Result

The solubility (S) and solubility product (K_{sp}) of sparingly soluble salt $BaSO_4$ are found to be ……… g / litre and ……… at ….. ^0C.

o-------------------------o

B. pH / Potentiometry

In Potentiometric experiments (titrations), there is change in potential of an electrode with the change in concentration of ions, with which it is in equilibrium. The change in potential may be used as an indicator in determining the end point. This method is applicable to wide range of titrations, provided an appropriate electrode (indicator electrode) is available. An indicator electrode is the one whose potential indicates the change in concentration of the ions to be titrated. As it is not possible to determine the electrode potential separately, the indicator electrode is used in conjunction with a reference electrode, the potential of which remains constant during the course of titration. Most commonly used reference electrode is the saturated calomel electrode (SCE). Some commonly used indicator electrodes are hydrogen electrode, quinhydrone electrode, glass electrode etc.

1. Calomel electrode (Saturated)

It consists of a glass tube immersed into another glass tube. Mercury of high degree of purity is placed at the bottom of inner glass tube, over which the calomel paste of mercury and mercurous chloride ($Hg + Hg_2Cl_2$) is placed. A platinum wire sealed in a inner glass tube helps in making the electrical contact. Saturated KCl solution is added from the inlet provided to the outer tube. Reduction potential of this electrode is +0.2415 V at 25^0C. Electrode is represented as below.

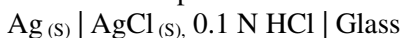Pt, Hg $_{(l)}$ | Hg$_2$Cl$_{2 (S)}$ | KCl $_{(Sat)}$

2. Quinhydrone electrode

It consists of shiny platinum electrode dipped in the test solution, which is saturated with quinhydrone (1:1 molecular compound of quinine and hydroquinone). Standard reduction potential of this electrode is +0.6994 V at 25^0C. Electrode is represented as below.
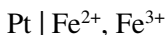
Pt, H$_2$Q | Q, H$^+$

3. Glass electrode

It consists of a thin bulb made up of a special soft glass of 50µm thickness with high electrical conductivity, blown at the end of a glass tubing. The bulb is filled with 0.1 N HCl or other suitable buffer solution and a silver wire coated with silver chloride is immersed in it. Standard reduction potential of this electrode is +0.225 V at 25^0C. Electrode is represented as below.

Ag $_{(S)}$ | AgCl $_{(S)}$, 0.1 N HCl | Glass

4. Oxidation - Reduction electrode (Redox electrode)

It consists of a platinum wire dipped in the solution of two salts of same metal having different valencies, e.g. Fe^{2+} and Fe^{3+}. The e.m.f. arises because of the tendency of metal ion in one oxidation state to pass into the second more stable state. The function of platinum wire is merely to pickup the electrons and to make an electrical contact to the electrode. Standard reduction potential of the Fe^{2+}/Fe^{3+} electrode is +0.771 V at 25^0C. Electrode is represented as below.

Pt | Fe^{2+}, Fe^{3+}

5. Metal - Insoluble salt anion electrode

It consists of a metal in contact with its sparingly soluble salt. This electrode is reversible with respect to anions, e.g. Ag-AgCl electrode. Standard reduction potential of the Ag/Ag$^+$ electrode is +0.799 V at 25^0C. Electrode is represented as Ag | Ag$^+_{(aq)}$.

Acid base titrations can be carried out potentiometrically by systematic measurement of e.m.f. of the following cells.

1. The cell formed when quinhydrone (indicator) electrode is coupled with calomel (reference) electrode.

(Calomel electrode) ‖ (Quinhydrone electrode)

Pt, $Hg_{(l)}$ | $Hg_2Cl_{2(S)}$ | $KCl_{(Sat)}$ ‖ H^+, Q | H_2Q, Pt

$E_{Cell} = E_{Quin} - E_{Cal}$
$E_{Cell} = (E^0_{Quin} - (2.303\ RT / F)\ pH) - E_{Cal}$
$E_{Cell} = E^0_{Quin} - E_{Cal} - (2.303\ RT / F)\ pH$
$E_{Cell} = 0.6994 - 0.2415 - 0.05916\ pH$ (at 25^0C)
$E_{Cell} = 0.4579 - 0.05916\ pH$
$pH = (0.4579 - E_{Cell}) / 0.05916$

Where,
R is gas constant ($8.3143\ JK^{-1}.mol^{-1}$)
T is temperature (298 K)
F is Faraday constant ($9.66 \times 10^4\ C.mol^{-1}$)

2. The cell formed when glass (indicator) electrode is coupled with calomel (reference) electrode.

(Glass electrode) ‖ (Calomel electrode)

$Ag_{(S)}$ | $AgCl_{(S)}$ | 0.1 N HCl | Glass ‖ $KCl_{(Sat)}$ | $Hg_2Cl_{2(S)}$ | $Hg_{(l)}$, Pt

$E_{Cell} = E_{Cal} - E_{Glass}$
$E_{Cell} = E_{Cal} - (E^0_{Glass} - (2.303\ RT / F)\ pH)$
$E_{Cell} = E_{Cal} - E^0_{Glass} + (2.303\ RT / F)\ pH)$
$E_{Cell} = 0.2415 - 0.225 + 0.05916\ pH$ (at 25^0C)
$E_{Cell} = 0.0165 + 0.05916\ pH$
$pH = (E_{Cell} - 0.0165) / 0.05916$

3. The cell formed when Fe^{2+}/Fe^{3+} (indicator) electrode is coupled with calomel (reference) electrode.

(Calomel electrode) ‖ (Fe^{2+}/Fe^{3+} electrode)

Pt, $Hg_{(l)}$ | $Hg_2Cl_{2(S)}$ | $KCl_{(Sat)}$ ‖ Fe^{3+}, Fe^{2+} | Pt

$E_{Cell} = E_{Fe^{2+}/Fe^{3+}} - E_{Cal}$
$E_{Cell} = (E^0_{Fe^{2+}/Fe^{3+}} - (2.303\ RT / F)\ pH) - E_{Cal}$
$E_{Cell} = E^0_{Fe^{2+}/Fe^{3+}} - E_{Cal} + (2.303\ RT / F)\ pH$
$E_{Cell} = 0.771 - 0.2415 - 0.05916\ pH$ (at 25^0C)
$E_{Cell} = 0.5295 - 0.05916\ pH$
$pH = (0.5295 - E_{Cell}) / 0.05916$

4. The cell formed when Ag/Ag^+ (indicator) electrode is coupled with calomel (reference) electrode.

(Calomel electrode) ‖ (Ag/Ag^+ electrode)

Pt, $Hg_{(l)}$ | $Hg_2Cl_{2(S)}$ | $KCl_{(Sat)}$ ‖ $Ag^+_{(aq)}$ | Ag

$E_{Cell} = E_{Ag/Ag^+} - E_{Cal}$
$E_{Cell} = (E^0_{Ag/Ag^+} - (2.303\ RT / F)\ pH) - E_{Cal}$
$E_{Cell} = E^0_{Ag/Ag^+} - E_{Cal} - (2.303\ RT / F)\ pH$

E_{Cell} = 0.799 - 0.2415 - 0.05916 pH (at 25^0C)

E_{Cell} = 0.5575 - 0.05916 pH

pH   = (0.5575 - E_{Cell}) / 0.05916

The instrument used for potentiometric titration is basically a millivoltmeter capable of measuring e.m.f. It is either potentiometer or pH-meter. pH-meter is designed to read both pH and e.m.f. (millivolts).

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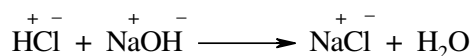
Experiment - 03

Study of pH-metric titration of a strong acid (HCl) against a strong base (NaOH)

Problem - To determine the strength of a given strong acid (HCl) by titrating against a strong base (NaOH) using pH-meter.

Theory

In pH-metric titrations, the end point is determined by measuring the change in pH with the addition of titrant i.e. with the change in concentration of ions.

When HCl solution is titrated with NaOH the following reaction takes place.

$$\overset{+}{H}\overset{-}{Cl} + \overset{+}{Na}\overset{-}{OH} \longrightarrow \overset{+}{Na}\overset{-}{Cl} + H_2O$$

During the titration, when strong base (NaOH) is added to the strong acid (HCl), pH increases slowly upto the equivalence point (end point) because of the fraction of H^+ ions removed. As the equivalence point reaches, the fraction of H^+ ions removed by a constant volume of NaOH increases rapidly, thereby causing a sharp jump (increase) in pH just at the equivalence point. After the equivalence point, again pH increases slowly because of addition of excess of NaOH (excess of OH^- ions).

The rate of change in pH is much more near the equivalence point (end point) than any other region of the titration before or after the equivalence point. The end point is to be found out by plotting a graph of pH or $\Delta pH/\Delta V$ against the volume of alkali added. The point of inflexion in the curve (the point where the curve changes its curvature) gives the end point.

Sharpness of the inflexion point and symmetry of the curve on its two sides depends on ionisability of the acid and base used.

Facilities

Apparatus - pH-meter, Calomel electrode, Glass electrode, Magnetic stirrer or glass rod, Burette, Pipette, Conical flask, Volumetric flask, Beakers, Weighing bottle, Wash bottle, Funnel etc.

Chemicals - Oxalic acid (A.R.), NaOH solution (approx. 0.1 N), HCl solution (unknown), Phenolphthalein indicator, Distilled water etc.

Procedure

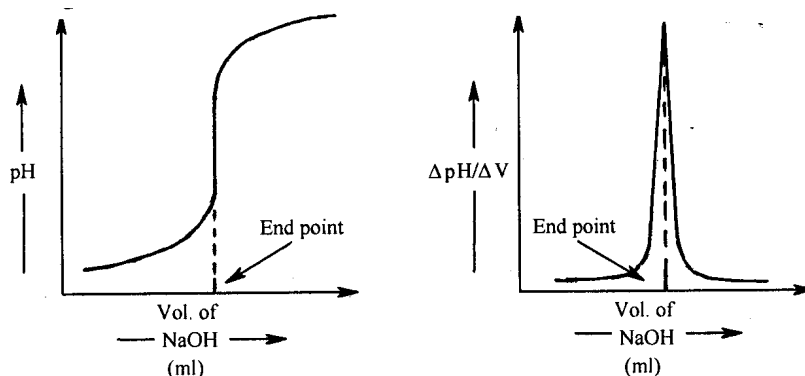1. Prepare approx. 0.1 N std. oxalic acid solution by dissolving accurately weighed 0.60 to 0.65 g of oxalic acid A.R. in distilled water in a 100 ml volumetric flask. Calculate the exact normality of prepared std. oxalic acid solution from the accurate weight of oxalic acid dissolved in 100 ml of solution.

2. Pipette out 10 ml of std. oxalic acid solution in a clean conical flask. Add 1-2 drops

of phenolphthalein indicator and titrate it with NaOH solution (approx. 0.1 N) taken in a burette till colour changes from colourless to pink. Repeat the titration till you get two constant readings. Tabulate your readings (Table-A).

3. Understand the working of pH-meter to be used for the experiment and standardize it by using buffer solution.

4. Pipette out 10 ml of given strong acid (HCl) solution in a clean 100 ml beaker and add about 25 ml of distilled water to it. Wash the tips of calomel and glass electrode with distilled water using wash bottle and place both the electrodes in a beaker containing HCl solution. Stir the acid solution with a glass rod and note the pH. (*Allow the glass rod to remain in the beaker throughout the experiment*)

5. Wash the burette with distilled water and fill it with NaOH solution upto the mark.

6. Now go on adding 1 ml of NaOH solution at each time, stir well and note the pH. Continue the addition, till there is sudden increase in pH. After this again take 4 to 5 readings. (*Near the end point take the reading at an interval of 0.2 ml*). Tabulate your readings (Table-B).

7. Plot a graph of pH or $\Delta pH/\Delta V$ (y-axis) against volume of NaOH added (x-axis). Find out the end point from inflexion in the curve.

Graphs

Observations

A. Preparation of std. oxalic acid solution

1. Weight of empty weighing bottle = W_1 g
2. Weight of weighing bottle + oxalic acid = W_2 g
3. Weight of weighing bottle + remaining particles of oxalic acid = W_3 g

B. Standardization of NaOH solution (Titration of std. oxalic acid with NaOH)

Table-A

Sr. No.	Volume of oxalic acid (ml) V_1	Volume of NaOH (ml)	End Point (ml)
1.	10.0		
2.	10.0		V_2
3.	10.0		

C. pH-metric titration (Titration of HCl with NaOH)

Table-B			
Sr. No.	Volume of NaOH (ml)	pH	$\Delta pH/\Delta V$
1.	00	------	------
2.	01	------	------
3.	02	------	------
4.	03	------	------
.	.	.	.
.	.	.	.
.	.	.	.

Volume of NaOH (End point from a graph) = V_2^1 ml

Calculations

A. Preparation of std. oxalic acid solution

1. Weight of oxalic acid transferred $\quad = \quad (W_2-W_3)$ g
2. Weight of oxalic acid dissolved in 100 ml $\quad = \quad (W_2-W_3)$ g

$$\text{Normality} = \frac{\text{Weight / litre}}{\text{Equivalent weight}}$$

$$\text{Normality of std. oxalic acid solution } (N_1) = \frac{(W_2-W_3) \times 10}{63}$$

B. Standardization of NaOH solution (Titration of std. oxalic acid with NaOH)

(Oxalic acid)　　(NaOH)

$$N_1V_1 = N_2V_2$$

$$\text{Normality of NaOH solution } (N_2) = \frac{N_1V_1}{V_2}$$

N_1 = As calculated, V_1 = 10 ml, N_2 = Unknown, V_2 = End point (Table-A)

C. pH-metric titration (Titration of HCl with NaOH)

(NaOH)　　(HCl)

$$N_2V_2^1 = N_3V_3$$

$$\text{Normality of HCl solution } (N_3) = \frac{N_2V_2^1}{V_3}$$

N_2 = As calculated, N_3 = Normality of HCl (Unknown),
V_2^1= Volume of NaOH (End point from a graph), V_3 = Volume of HCl (10 ml)

$\therefore$ Strength of HCl solution = (N_3) N

Result

The strength of given strong acid (HCl) is found to be ……… N.

o-------------------------o
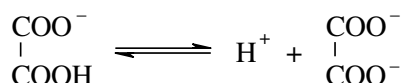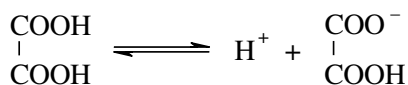
Experiment - 04

Determination of dissociation constants (Ka) of a dibasic acid (oxalic acid) by pH-metry

Problem - To determine the dissociation constants (Ka) of a dibasic acid (oxalic acid) using pH-meter.

Theory

Dissociation constants of oxalic acid can be determined by measuring the pH of a solution containing known amount of the acid and its salt with a strong base.

Oxalic acid is a dibasic acid having well separated dissociation constants. The first dissociation is complete before the second commences. The dissociation of oxalic acid is represented by the equations.

$$
\begin{array}{c} COOH \\ | \\ COOH \end{array} \rightleftharpoons H^+ + \begin{array}{c} COO^- \\ | \\ COOH \end{array}
$$

$$
\begin{array}{c} COO^- \\ | \\ COOH \end{array} \rightleftharpoons H^+ + \begin{array}{c} COO^- \\ | \\ COO^- \end{array}
$$

The dissociation constants (Ka_1, Ka_2) of oxalic acid are given by,

$$
Ka_1 = \frac{[H^+]\ [HC_2O_4^-]}{[H_2C_2O_4]} \quad , \quad Ka_2 = \frac{[H^+]\ [C_2O_4^{2-}]}{[HC_2O_4^-]}
$$

Hence as per the Henderson's equation,

$$
pH = pKa_1 + \log \frac{[HC_2O_4^-]}{[H_2C_2O_4]} \quad , \quad pH = pKa_2 + \log \frac{[C_2O_4^{2-}]}{[HC_2O_4^-]}
$$

At ½ equivalence point (½ neutralization point), $[HC_2O_4^-] = [H_2C_2O_4]$

At 1½ equivalence point (1½ neutralization point), $[C_2O_4^{2-}] = [HC_2O_4^-]$

Hence the above expressions for oxalic acid becomes,

$pH = pKa_1$

(when ½ equivalent of alkali corresponding to 1st equivalence point is added)

$pH = pKa_2$

(when 1½ equivalent of alkali corresponding to 2nd equivalence point is added)

In titrations using pH-meter, the end point is determined by measuring the change in pH with the addition of titrant i.e. with the change in concentration of ions.

When oxalic acid solution is titrated with NaOH it neutralizes in two steps and following reactions take place.

$$
\begin{array}{c} COOH \\ | \\ COOH \end{array} + NaOH \rightleftharpoons \begin{array}{c} COONa \\ | \\ COOH \end{array} + H_2O
$$

$$
\begin{array}{c} COONa \\ | \\ COOH \end{array} + NaOH \rightleftharpoons \begin{array}{c} COONa \\ | \\ COONa \end{array} + H_2O
$$
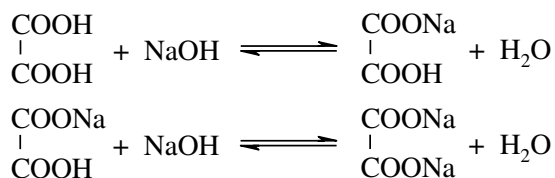
The solution remains acidic after the 1st neutralization step but owing to the salt hydrolysis it becomes mildly alkaline. After the 2nd neutralization step it becomes strongly alkaline.

63

During the titration, when strong base (NaOH) is added to the oxalic acid, pH increases slowly upto the 1st equivalence point because of the fraction of H^+ ions removed. As the equivalence point reaches, the fraction of H^+ ions removed by a constant volume of NaOH increases rapidly, thereby causing a sharp jump (increase) in pH just at the 1st equivalence point. Similarly pH increases for 2nd equivalence point. After the 2nd equivalence point, again pH increases slowly because of addition of excess of NaOH (excess of OH^- ions).

The rate of change in pH is much more near the 1st and 2nd equivalence points than any other region of the titration before or after these equivalence points. The end point is to be found out by plotting a graph of pH or $\Delta pH/\Delta V$ against the volume of alkali added. The two points of inflexion in the curve (the points where the curve changes its curvature) gives the 1st and 2nd equivalence points.

Facilities

Apparatus - pH-meter, Calomel electrode, Glass electrode, Magnetic stirrer or glass rod, Burette, Pipette, Beakers, Wash bottle etc.
Chemicals - Standard NaOH solution (0.05 N), oxalic acid solution (0.1 N), Distilled water etc.

Procedure

1. Understand the working of pH-meter to be used for the experiment and standardize it by using buffer solution.
2. Pipette out 10 ml of oxalic acid solution (0.1 N) in a clean 100 ml beaker and add about 25 ml of distilled water to it. Wash the tips of calomel and glass electrode with distilled water using wash bottle and place both the electrodes in a beaker containing oxalic acid solution. Stir the acid solution with a glass rod and note the pH. (*Allow the glass rod to remain in the beaker throughout the experiment*)
3. Wash the burette with distilled water and fill it with NaOH solution upto the mark.
4. Now go on adding 1 ml of NaOH solution at each time, stir well and note the pH. Continue the addition, till there is sudden increase in pH at two different points. After this again take 4 to 5 readings. Tabulate your readings (Table-A). (*Note : Perform the experiment at constant temperature*).
5. Plot a graph of pH or $\Delta pH/\Delta V$ (y-axis) against volume of NaOH added (x-axis). Find out the 1st and 2nd equivalence point from the two different inflexions in the curve.

Graphs
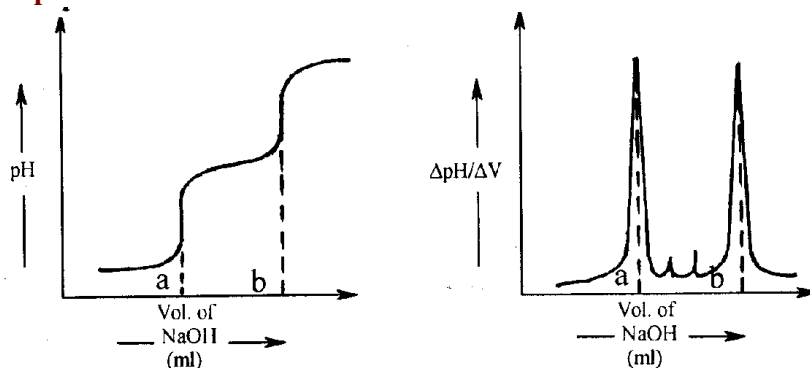
Where, a and b are 1st and 2nd equivalence points respectively.

Observations

Temperature = --- ^{0}C

Table-A

Sr. No.	Volume of NaOH (ml)	pH	$\Delta pH/\Delta V$
1.	00	------	------
2.	01	------	------
3.	02	------	------
4.	03	------	------
.	.	.	.
.	.	.	.

1st and 2nd equivalence points from a graph   = V_1, V_2 ml

Calculations

1.   1st equivalence point (from a graph)   = V_1 ml
∴   ½ equivalence point   =   ….. ml
     pH at ½ equivalence point (from a graph)   =   ….. pH

2.   2nd equivalence point (from a graph)   = V_2 ml
∴   1½ equivalence point   =   ….. ml
     pH at 1½ equivalence point (from a graph)   =   ….. pH

At ½ and 1½ equivalence point (neutralization point), pH = pKa

∴ pKa_1 = ……, pKa_2 = ……

pKa = -log Ka   or   log Ka = -pKa   or   Ka = antilog –pKa   or   Ka = 1 / antilog pKa

∴ Ka_1 = ……, Ka_2 = ……

Result

The 1st and 2nd dissociation constants of oxalic acid are found to be ……… and ……… at …. ^{0}C.

o-------------------------o

Experiment - 05

Determination of pH of soil samples

Problem - To determine the pH of given soil samples using pH-meter.

Theory

The degree of acidity or alkalinity of soil is expressed by the pH scale which is a series of numbers between 0 to 14.

pH of soil is the measure of "Hydrogen ion activity" and depends largely on relative amount of the adsorbed hydrogen and metallic ions. It is essential to determine the pH of soil for its different purposes like domestic, irrigation, industry, agriculture etc. Acidity and alkalinity provides a good identification of the soil chemical nature.

pH of soil suspension highly depends on the soil-water ratio and increases with dilution. The pH determination of soil is commonly carried out at moisture saturation level and in 1:5 soil suspension ratio.

Facilities

Apparatus - pH-meter, Calomel electrode, Glass electrode, Glass rod, Beakers, Wash bottle etc.

Chemicals - Soil samples, Distilled water etc.

Procedure

1. Understand the working of pH-meter to be used for the experiment and standardize it by using buffer solution.

2. To determine the pH at moisture saturation percentage of soil, take 50 g of soil having 2-4 mm size in a clean glass beaker. (To get soil of 2-4 mm size, pass it through 2-4 mm pore sieve). Add small increments of distilled water without stirring the soil, till a glistening layer appears on the surface of soil. Now stir the soil with the help of a glass rod to make uniform paste.

<div align="center">OR</div>

To determine the pH in 1:5 soil suspensions (1 part soil and 5 part water), take 20 g of soil in a clean glass beaker and add 100 ml distilled water to it. Stir for about 30 minutes at regular intervals.

3. Wash the tips of calomel and glass electrode with distilled water using wash bottle. Place both the electrodes in a beaker containing paste of soil and note the pH of soil.

4. Similarly measure the pH of other samples of soil. Tabulate your readings (Table-A). (*Soil samples can be collected at rooting depth (10-15 cm) with the help of borer or augers. These samples can be collected in polythene bags and transported to laboratory as early as possible*)

Observations

Table-A

Sr. No.	Soil sample	pH
1.	Soil sample - S1	------
2.	Soil sample - S2	------
3.	Soil sample - S3	------

Result

The pH of soil samples S1, S2 and S3 are found to be ……… , ……… and ……… respectively.

<div align="center">o--------------------------o</div>

Experiment - 06

Determination of dissociation constant (Ka) of weak acid by potentiometry

Problem - To determine the dissociation constant (Ka) of an acetic acid using potentiometer.

Theory

Dissociation constant of weak acid can be determined by measuring the potential of a solution containing known amount of the acid and its salt with a strong base.

Acetic acid is a weak acid and it undergoes dissociation to a very small extent. The dissociation of acetic acid is represented by the following equation.
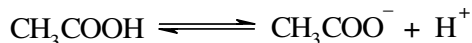
$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

The dissociation constant (Ka) of acetic acid is given by,

$$Ka = \frac{[H^+] \ [CH_3COO^-]}{[CH_3COOH]}$$

Taking logarithm on both sides and rearranging the terms we get,

$$-\log [H^+] = -\log Ka + \log \frac{[CH_3COO^-]}{[CH_3COOH]}$$

$$pH = pKa + \log \frac{[CH_3COO^-]}{[CH_3COOH]} \quad \text{(Henderson's equation)}$$

At ½ equivalence point (½ neutralization point), $[CH_3COO^-] = [CH_3COOH]$ hence the above expression becomes,

pH = pKa

(when ½ equivalent of alkali corresponding to equivalence point is added)

In titrations using potentiometer, the end point is determined by measuring the change in potential with addition of titrant i.e. with the change in concentration of ions.

When CH_3COOH solution is titrated with NaOH following reaction takes place.

$$CH_3COOH^- \overset{+}{} + Na^+OH^- \longrightarrow CH_3COO^-Na^+ + H_2O$$
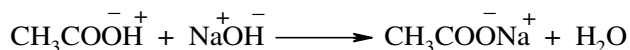
During the titration, when strong base (NaOH) is added to the weak acid (CH_3COOH), pH increases slowly upto the equivalence point (end point) because of the fraction of H^+ ions removed. As the equivalence point reaches, the fraction of H^+ ions removed by a constant volume of NaOH increases rapidly, there by causing a sharp jump (increase) in pH just at the equivalence point. After the equivalence point, again pH increases slowly because of addition of excess of NaOH (excess of OH^- ions).

The change in pH reflects in the change in e.m.f. (E). So when the alkali (NaOH)   is added to the acid (CH_3COOH) dropwise and measured the e.m.f after addition of each drop (or drops), e.m.f. decreases slowly upto the equivalence point because of a little change in electrode potential due to removal of fraction of H^+ ions. As the equivalence point reaches, the fraction of H^+ ions removed by a constant volume of the alkali increases rapidly which results in a rapid change in electrode potential, thereby causing a sharp drop (decrease) in e.m.f. just at the equivalence point. After the equivalence point, again e.m.f. decreases slowly because of addition of excess of alkali causing a little change in electrode potential.

The rate of change in e.m.f. is much more near the equivalence point (end point) than any other region of the titration before or after the equivalence point. The end point is to be found out by plotting a graph of E (e.m.f.) or $\Delta E/\Delta V$ against the volume of alkali added. The point of inflexion in the curve (the point where the curve changes its curvature) gives the end point.

Sharpness of the inflexion point and symmetry of the curve on its two sides depends on ionisability of the acid and base used.
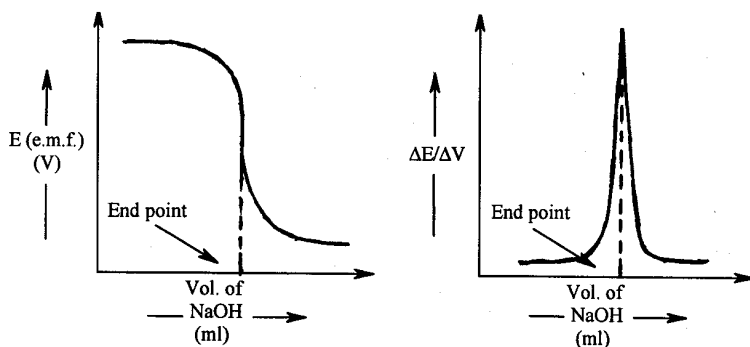
Facilities

Apparatus - Potentiometer, Calomel electrode, Platinum electrode, Magnetic stirrer or glass rod, Burette, Pipette, Beakers, Wash bottle etc.

Chemicals - Standard NaOH solution (0.1 N), Acetic acid solution (0.1 N), Quinhydrone, Distilled water etc.

Procedure

1. Understand the working of potentiometer to be used for experiment and standardize it.
2. Pipette out 10 ml of acetic acid solution (0.1 N) in a clean 100 ml beaker and add about 25 ml of distilled water to it. Add about 0.2 g of quinhydrone. Wash the tips of calomel and platinum electrode with distilled water using wash bottle and place both the electrodes in a beaker containing acetic acid solution. Stir the acid solution with a glass rod and note the e.m.f. (*Allow the glass rod to remain in the beaker throughout the experiment*)
3. Wash the burette with distilled water and fill it with NaOH solution upto the mark.
4. Now go on adding 1 ml of NaOH solution at each time, stir well and note the e.m.f. Continue the addition, till there is sudden decrease in e.m.f. After this again take 4 to 5 readings. (*Near the end point take the reading at an interval of 0.2 ml*). Tabulate your readings (Table-A). (*Note : Perform the experiment at constant temperature*)
5. Plot a graph of E (e.m.f.) or $\Delta E/\Delta V$ (y-axis) against volume of NaOH added (x-axis). Find out the end point (equivalence point) from inflexion in the curve.

Graphs

Observations

Temperature = --- ^0C

Table-A			
Sr. No.	Volume of NaOH (ml)	E (e.m.f.) (V)	$\Delta E/\Delta V$
1.	00	------	------
2.	01	------	------
3.	02	------	------
4.	03	------	------
.	.	.	.
.	.	.	.
.	.	.	.

Equivalence point (End point) from a graph $\quad\quad = \quad V_1 \quad$ ml

Calculations

1. Equivalence point (from a graph) $\quad\quad\quad = \quad V_1 \quad$ ml

∴ ½ equivalence point $\quad\quad\quad\quad\quad\quad\quad = \quad$ ….. ml

e.m.f. at ½ equivalence point (from a graph) $\quad = \quad$ ….. V

When the cell is formed by quinhydrone electrode coupled with calomel electrode, according to Nernst's equation, pH = (0.4579 - E_{Cell}) / 0.05916

∴ pH = (0.4579 - V) / 0.05916

At ½ equivalence point (neutralization point), pH = pKa

∴ pKa = ……….

pKa = -log Ka $\quad$ or $\quad$ log Ka = -pKa $\quad$ or $\quad$ Ka = antilog –pKa $\quad$ or $\quad$ Ka = 1 / antilog pKa

∴ Ka = ……….

Result

The dissociation constant of acetic acid is found to be ……… at …. ^{0}C.

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Experiment - 07

Study of potentiometric titration of KCl solution against AgNO₃ solution

Problem - To determine the strength of a given KCl solution by titrating against AgNO$_3$ solution using potentiometer.

Theory

In potentiometric titrations, the end point is determined by measuring the change in electrode potential with the addition of titrant i.e. with the change in concentration of ions. Potentiometric titrations may also be used to determine the end point of a precipitation reaction, provided one of the ions takes part in the reversible reaction.

The potentiometric titration can be easily carried out for any reversible redox reaction. These titrations involve transfer of electron from the substance being oxidized to the substance being reduced. The potential (e.m.f.) of any redox reaction can be given by the Nernst's equation as below.

$$E = E^0 - \frac{2.303\ RT}{nF}\ \log_{10} \frac{[Product]}{[Reactant]}$$

When a silver electrode is placed in the solution containing Ag$^+$ ions, the potential developed across the electrode for the equilibrium Ag $\rightleftharpoons$ Ag$^+$ + e$^-$ is given by-

$$E_{Ag/Ag^+} = E^0_{Ag/Ag^+} - \frac{2.303\ RT}{nF}\ \log_{10} \frac{[Ag^+]}{[Ag]}$$

Where, E^0 is the standard potential of Ag/Ag$^+$ system and is a measure of the tendency of the ion to pass from the lower oxidation state to the higher oxidation state.

For potentiometric titration of Ag/Ag$^+$ system, this redox electrode is coupled with calomel electrode (reference electrode) and e.m.f. of the cell is measured. The complete cell is represented as below.
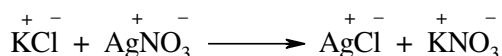
(Calomel electrode) $\|$ (Ag/Ag$^+$ electrode)

Pt, Hg $_{(l)}$ | Hg$_2$Cl$_{2\,(S)}$ | KCl $_{(Sat)}$ $\|$ Ag$^+_{(aq)}$ | Ag

$$E_{Cell} = E_{Ag/Ag^+} - E_{Cal}$$

$$E_{Ag/Ag^+} = \left[E^0_{Ag/Ag^+} - \frac{2.303\ RT}{nF}\ \log_{10} \frac{[Ag^+]}{[Ag]} \right]$$

$$\therefore\ E_{Cell} = \left[E^0_{Ag/Ag^+} - \frac{2.303\ RT}{nF}\ \log_{10} \frac{[Ag^+]}{[Ag]} \right] - E_{Cal}$$

When KCl solution is titrated with AgNO$_3$ the following reaction takes place.

$$\overset{+}{K}\overset{-}{Cl}\ +\ \overset{+}{Ag}\overset{-}{NO_3}\ \longrightarrow\ \overset{+}{Ag}\overset{-}{Cl}\ +\ \overset{+}{K}\overset{-}{NO_3}$$

The rate of change in e.m.f. is much more near the equivalence point (end point) than any other region of the titration before or after the equivalence point. The end point is to be found out by plotting a graph of E (e.m.f.) or $\Delta E/\Delta V$ against the volume of AgNO$_3$ added. The point of inflexion in the curve (the point where the curve changes its curvature) gives the end point.

Facilities

Apparatus - Potentiometer, Calomel electrode, Silver electrode, Magnetic stirrer or glass rod, Burette, Pipette, Conical flask, Volumetric flask, Beakers, Weighing bottle, Wash bottle, Funnel etc.

Chemicals - Standard AgNO$_3$ solution (0.1 N), KCl solution (unknown), Saturated KCl solution, 2 N HNO$_3$ solution, Distilled water etc.

Procedure

1. Understand the working of potentiometer to be used for experiment and standardize it.

2. Pipette out 10 ml of given KCl solution in a clean 100 ml beaker and add about 25 ml of distilled water and 2 ml of 2 N HNO$_3$ solution to it. Stir the solution with a glass rod. Wash the tip of silver electrode with distilled water using wash bottle and place the electrode and one end of KNO$_3$ salt bridge in a beaker containing KCl solution. Wash the calomel electrode and place the electrode and other end of KNO$_3$ salt bridge in a beaker containing saturated KCl solution. Note the e.m.f. of solution. (*Allow the glass rod to remain in the beaker throughout the experiment*)

3. Wash the burette with distilled water and fill it with AgNO$_3$ solution upto the mark.

4. Now go on adding 1 ml of AgNO$_3$ solution at each time, stir well and note the e.m.f. Continue the addition, till there is sudden increase in e.m.f. After this again take 4 to 5 readings. (*Near the end point take the reading at an interval of 0.2 ml*). Tabulate your readings (Table-A).

5. Plot a graph of E (e.m.f.) or $\Delta E/\Delta V$ (y-axis) against volume of AgNO$_3$ solution added (x-axis). Find out the end point from inflexion in the curve.
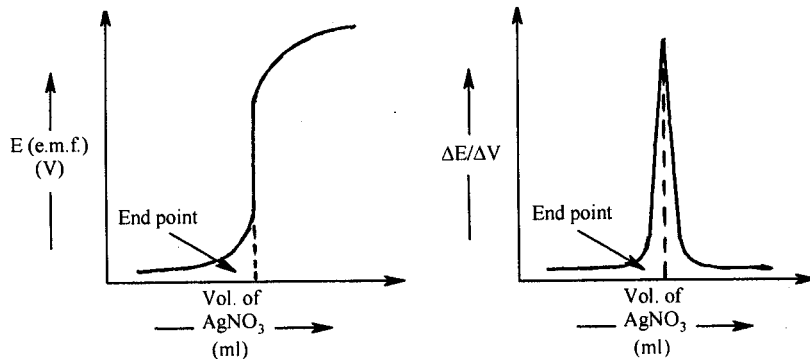
Graphs

Observations

Table-A			
Sr. No.	Volume of AgNO$_3$ (ml)	e.m.f. (V)	$\Delta E/\Delta V$
1.	00	------	------
2.	01	------	------
3.	02	------	------
4.	03	------	------
.	.	.	.
.	.	.	.
.	.	.	.

Volume of AgNO$_3$ solution (End point from a graph) = V$_1$ ml

Calculations

(AgNO$_3$)   (KCl)

$$N_1V_1 \ = \ N_2V_2$$

Normality of KCl solution (N$_2$) = $\dfrac{N_1V_1}{V_2}$

N$_1$ = Normality of AgNO$_3$ (0.1 N), N$_2$ = Normality of KCl (Unknown),
V$_1$ = Volume of AgNO$_3$ (End point from a graph), V$_2$ = Volume of KCl (10 ml)

$\therefore$ Strength of KCl solution = (N$_2$) N

Result

The strength of given KCl solution is found to be ……… N.

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C. Colorimetry / Spectrophotometry

When a beam of monochromatic radiation is passed through a sample (solid, liquid or gas), some of the radiation is absorbed by it, some is reflected and some is transmitted.

Lambert-Beer law tells about the relation between the amount of radiations absorbed and the thickness of the medium as well as the concentration of solution.

Lambert law states that, "When a beam of monochromatic light is passed through a homogeneous absorbing medium, the intensity of light decreases exponentially with the increase in thickness of absorbing medium".

Lambert law is again called as Bouguer law, since Bouguer really established a relationship between intensity of transmitted light with the thickness of medium several years before Lambert, but Bouguer publication was not generally known.

Beer law states that, "When a beam of monochromatic light is passed through a solution of an absorbing substance, the intensity of light decreases exponentially with the increase in concentration of solution".

Combination of these two laws gives the Lambert-Beer law.

Lambert-Beer law states that, "When a beam of monochromatic light is passed through a solution of an absorbing substance, the intensity of light decreases exponentially with the increase in thickness of absorbing solution and concentration of solution".

Lambert-Beer law, may called as Bouguer-Beer law or commonly Beer law.

If I_0 is the intensity of incident light and I_t is the intensity of transmitted light, then it can be shown from Lambert-Beer law that,

$$\log \frac{I_0}{I_t} = \varepsilon \, C \, x$$

Where,
ε is molar extinction coefficient.
C is concentration in mole/litre.
x is thickness in cm.

$\log \dfrac{I_0}{I_t}$ is called optical density (OD) or absorbance (A

$\therefore$ OD or A $= \varepsilon \, C \, x$

In colorimetric or spectrophotometric experiments, the absorbances of sample solution are directly measured on colorimeter or spectrophotometer. From the absorbances, the concentration of given solution is calculated. A plot of absorbance versus concentration should be a straight line passing through origin.

Deviation in Beer law falls into three categories; real, instrumental and chemical.

Beer law fails if -
1. Solution is concentrated
2. Monochromatic light is not used
3. Absorbing species associates or dissociates
4. Ionic strength and pH are not kept constant.

Important terms

1. **Colorimeter** - It is an instrument which makes the use of a narrow band of radiations of different wavelength for absorption. It uses suitable filters.
2. **Spectrophotometer** - It is an instrument which makes the use of only one wavelength for absorption. It uses monochromator like prism or grating.
3. **λ_{max}** - It is the wavelength at which the absorption is maximum.
4. **Calibration curve** - It is the curve obtained by plotting absorbances of different solutions against their concentration.
5. **Monochromatic light** - It is the light consisting of only one wavelength.
6. **Units of wavelength** - nanometer (nm), $1nm = 10^{-9}m = 10^{-7}cm = 10A$

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Experiment - 08

Verification of Lambert-Beer law

Problem - To verify Lambert-Beer law using colorimeter or spectrophotometer.

Theory

Lambert-Beer law states that, "When a beam of monochromatic light is passed through a solution of an absorbing substance, the intensity of light decreases exponentially with the increase in thickness of absorbing solution and concentration of solution".

Lambert-Beer law, may called as Bouguer-Beer law or commonly Beer law.

If I_0 is the intensity of incident light and I_t is the intensity of transmitted light, then it can be shown from Lambert-Beer law that,

$$\log \frac{I_0}{I_t} = \varepsilon\, C\, x$$

Where,
ε is molar extinction coefficient.
C is concentration in mole/litre.
x is thickness in cm.

$\log \dfrac{I_0}{I_t}$ is called optical density (OD) or absorbance (A)

$\therefore$ OD or A $= \varepsilon\, C\, x$

This experiment involves the measurement of absorbance of solutions of different concentrations. When absorbance of different solutions is plotted against their concentrations, a straight line passing through origin is obtained.

Facilities

Apparatus - Colorimeter or Spectrophotometer, Burette, Graduated pipette, Test tubes, Beakers, Wash bottle etc.

**Chemicals** - Potassium permanganate ($KMnO_4$) or Potassium dichromate ($K_2Cr_2O_7$), Distilled water etc.

Procedure

1. Understand the working of colorimeter or spectrophotometer to be used for the experiment.

2. Prepare a stock solution of $KMnO_4$ or $K_2Cr_2O_7$ by dissolving 1 g of it in 1 litre of water. Dilute 10 ml of this solution to 100 ml by distilled water. The strength of solution is 100 ppm.

3. Take 10 clean test tubes, number them from 1 to 10. Place the following quantities of stock solution of $KMnO_4$ or $K_2Cr_2O_7$ and water in them to get the solutions of different concentrations.

Test tube No.	1	2	3	4	5	6	7	8	9	10
Concentration (ppm)	10	20	30	40	50	60	70	80	90	100
Stock solution (ml)	1	2	3	4	5	6	7	8	9	10
Water (ml)	9	8	7	6	5	4	3	2	1	0

4. Determination of λ_{max}

   i) Clean the absorption cell. Fill it with solvent (water). Place it in a cell holder of colorimeter or spectrophotometer. Select the lowest wavelength (or filter) and set zero absorbance or 100%T (transmittance) for water.

   ii) Remove the cell containing water. Replace it by the cell containing any one of the above prepared solution (*preferably dark coloured solution*) and record the absorbance at this wavelength.

   iii) Repeat the above procedure and record the absorbances at an interval of 10 nm wavelength range (or at all filters). Tabulate your readings (Table-A).

   (*Before recording the absorbance for a given solution at any particular wavelength it is necessary to set 100%T for water each time*)

   iv) Plot a graph of absorbance (y-axis) against the wavelength in nm (or filters) (x-axis). The maximum of the curve gives the λ_{max}. The wave length (or filter) showing the maximum absorbance is λ_{max} (For $KMnO_4$ λ_{max} = 520 nm).

5. Set 100%T for water at λ_{max} and record the absorbance of each solution at λ_{max}. Tabulate your readings (Table-B).

6. Plot a graph of absorbance (A) (y-axis) against the concentration of solution in ppm. (x-axis). Straight line passing through origin will be obtained.

Graphs

74
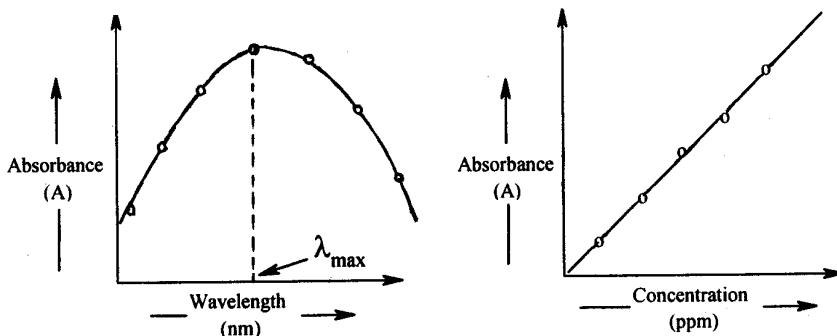
Observations

A. Determination of λ_{max}

Table-A

Filter No.	Wavelength (nm)	Absorbance (A)
1	------	------
2	------	------
3	------	------
.	.	.
.	.	.

λ_{max} = ……… nm.

B. Verification of Lambert-Beer law

Table-B

T.T. No.	Concentration (ppm)	Absorbance(A)
1	10	------
2	20	------
.	.	.
.	.	.
.	.	.
10	100	------

Result

Since the graph of absorbance against the concentration is straight line passing through origin, Lambert-Beer law is verified.

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Appendix-I

Preparation of solutions / reagents

1. **Acetic acid (CH₃COOH) solution (0.1 N)** - Dilute 5.8 ml of glacial acetic acid by distilled water in a 1 litre volumetric flask and make up the volume up to the mark with distilled water.

2. **Ferrous ammonium sulphate (FAS) solution (0.1 N)** - Dissolve 39.2 g of ferrous ammonium sulphate in 2 N sulphuric acid solution in a 1 litre volumetric flask and make up the volume up to the mark with same 2 N sulphuric acid solution.

3. **Hanus's / iodine monobromide (IBr) solution** - Dissolve 13 g of iodine crystals in about 500 ml of glacial acetic acid in a 1 litre volumetric flask. Add 3 ml of liquid bromine to it dropwise with constant stirring and make up the volume up to the mark with glacial acetic acid. Store the solution in a well stoppered amber colour bottle.

4. **Hydrochloric acid (HCl) solution (0.1 N)** - Dilute 9 ml of conc. hydrochloric acid by distilled water in a 1 litre volumetric flask and make up the volume up to the mark with distilled water.

5. **Iodine (I₂) solution (0.05 N)** - Dissolve 6.35 g of iodine crystals and 20 g of potassium iodide (KI) in about 25 ml distilled water in a 1 litre volumetric flask and after 20 to 30 minute make up the volume up to the mark with distilled water.

6. **Neutral formalin solution** - Dilute 100 ml of commercial formalin (38% formaldehyde) to 250 ml by distilled water in a beaker. Add 2-3 drops of phenolphthalein indicator to it and then 10% sodium hydroxide solution dropwise till it becomes faint pink. Now add dilute acetic acid till it becomes colourless.

7. **Nitric acid (HNO₃) solution (2 N)** - Dilute 126 ml of conc. nitric acid by distilled water in a 1 litre volumetric flask and make up the volume up to the mark with distilled water.

8. **Oxalic acid (HOOC-COOH) solution (0.1 N)** - Dissolve 6.3 g of oxalic acid in distilled water in a 1 litre volumetric flask and make up the volume up to the mark with distilled water.

9. **Phenolphthalein indicator** - Dissolve 1 g of phenolphthalein in 100 ml of ethanol.

10. **Potassium bromate-bromide (KBrO₃-KBr) solution (0.05 N)** - Dissolve 1.392 g of anhydrous potassium bromate and 15 g of potassium bromide in distilled water in a 1 litre volumetric flask and make up the volume up to the mark with distilled water.

11. **Potassium chloride (KCl) solution (0.1 N)** - Dissolve 7.45 g of potassium chloride in distilled water in a 1 litre volumetric flask and make up the volume up to the mark with distilled water.

12. **Potassium dichromate (K₂Cr₂O₇) solution (0.1 N)** - Dissolve 4.9 g of potassium dichromate in 2 N sulphuric acid solution in a 1 litre volumetric flask and make up the volume up to the mark with same 2 N sulphuric acid solution.

13. **Potassium dichromate (K₂Cr₂O₇) solution (100 ppm)** - Dissolve 1 g of potassium dichromate in distilled water in a 1 litre volumetric flask and make up the volume up to the mark with distilled water. Now dilute 100 ml of it by distilled water in another 1 litre volumetric flask and make up the volume up to the mark with distilled water.

14. **Potassium iodide (KI) solution (10%)** - Dissolve 100 g of potassium iodide in 1 litre distilled water in a beaker.

15. **Potassium permanganate (KMnO₄) solution (100 ppm)** - Dissolve 1 g of potassium permanganate in distilled water in a 1 litre volumetric flask and make up the volume up to the mark with distilled water. Now dilute 100 ml of it by distilled water in another 1 litre volumetric flask and make up the volume up to the mark with distilled water.

16. **Silver nitrate (AgNO₃) solution (0.1 N)** - Dissolve 1.7 g of silver nitrate in distilled water in a 100 ml amber colour volumetric flask and make up the volume up to the mark with distilled water.

17. **Sodium hydroxide (NaOH) solution (10%)** - Dissolve 100 g of sodium hydroxide in 1 litre distilled water in a beaker.

18. **Sodium hydroxide (NaOH) solution (0.5 N)** - Dissolve 20 g of sodium hydroxide in distilled water in a 1 litre volumetric flask and make up the volume up to the mark with distilled water.

19 **Sodium hydroxide (NaOH) solution (0.1 N)** - Dissolve 4 g of sodium hydroxide in distilled water in a 1 litre volumetric flask and make up the volume up to the mark with distilled water.

20. **Sodium hydroxide (NaOH) solution (0.05 N)** - Dissolve 2 g of sodium hydroxide in distilled water in a 1 litre volumetric flask and make up the volume up to the mark with distilled water.

21. **Starch solution (5%)** - Prepare a paste of 5 g of soluble starch in about 10 ml distilled water and add it to 100 ml of boiling water with stirring. Then add few crystals of potassium iodide and mix well.

22. **Sulphuric acid (H₂SO₄) solution (2 N)** - Dilute 56 ml of conc. sulphuric acid by distilled water in a 1 litre volumetric flask and make up the volume up to the mark with distilled water.

23. **Wij's / iodine monochloride (ICl) solution** - Dissolve 13 g of iodine crystals in about 500 ml of glacial acetic acid in a 1 litre volumetric flask. Pass dry chlorine gas into it till colour changes from dark brown to orange yellow and make up the volume up to the mark with glacial acetic acid. Store the solution in a well stoppered amber colour bottle.

24. **Wij's / iodine monochloride (ICl) solution** - Separately dissolve 7.9 g of iodine trichloride and 8.7 g of resublimed iodine crystals in about 100 ml of glacial acetic acid in a beaker by warming in water bath. Transfer both the solutions in a 1 litre volumetric flask, mix well and make up the volume up to the mark with glacial acetic acid. Store the solution in a well stoppered amber colour bottle.

Appendix-II

Concentration of solution - Concentration of solution refers to the relative amount of the solute and the solvent present in the solution. A common method is the percentage method which refers to the percentage of solute by weight or by volume. However this method is not precise and so concentration of solution is expressed in terms of the relative number of moles of solute.

A. **Normality** - Number of gram equivalents (equivalent weight in grams) of solute present per litre of the solution.

1. $\text{Normality} = \dfrac{\text{Weight of solute per litre of solution}}{\text{Equivalent weight of solute}}$ **(for solids)**

2. $\text{Normality} = \dfrac{10 \text{ x Specific gravity of the solution x Weight \% of the solute}}{\text{Equivalent weight of solute}}$ **(for liquids)**

   Use the formula $N_1V_1 = N_2V_2$ to calculate normality's of other solutions.

3. $\text{Normality} = \text{Molarity x } \dfrac{\text{Molecular weight}}{\text{Equivalent weight}}$

B. **Molarity** - Number of moles of solute present per litre of the solution.

1. $\text{Molarity} = \dfrac{\text{Weight of solute per litre of solution}}{\text{Molecular weight of solute}}$ **(for solids)**

2. $\text{Molarity} = \dfrac{10 \text{ x Specific gravity of the solution x Weight \% of the solute}}{\text{Molecular weight of solute}}$ **(for liquids)**

   Use the formula $M_1V_1 = M_2V_2$ to calculate molarity's of other solutions.

3. $\text{Molarity} = \text{Normality x } \dfrac{\text{Equivalent weight}}{\text{Molecular weight}}$

C. Weight of the solute to be taken for preparing the standard solution is depends on normality or molarity, volume of the solution and equivalent weight or molecular weight of the solute.

1. $\text{Weight of solute to be taken} = \dfrac{\text{Normality x Equivalent weight x Vol.of solution (ml)}}{1000}$

2. $\text{Weight of solute to be taken} = \dfrac{\text{Molarity x Molecular weight x Vol.of solution (ml)}}{1000}$

D. Strength of aqueous solutions of common acids

Types of acids	Weight % (approx.)	Specific gravity (approx.)	Normality (approx.)	Molarity (approx.)	Volume required to make 1 litre of 1 N (approx.) solution (ml)
1. Hydrochloric acid	35.0	1.18	11.3	11.3	89
2. Nitric acid	70.0	1.42	16.0	16.0	63
3. Sulphuric acid	96.0	1.84	36.0	18.0	28
4. Perchloric acid	70.0	1.66	11.6	11.6	86
5. Phosphoric acid	85.0	1.69	41.1	13.7	23
6. Acetic acid	99.5	1.05	17.4	17.4	58

E. Atomic weights of different elements

Name of element	Symbol	Atomic weight	Name of element	Symbol	Atomic weight
Aluminium	Al	26.982	Magnesium	Mg	24.305
Antimony	Sb	121.75	Manganese	Mn	54.938
Arsenic	As	74.922	Mercury	Hg	200.59
Barium	Ba	137.33	Molybdenum	Mo	95.941
Bismuth	Bi	208.98	Nickel	Ni	58.692
Boron	B	10.811	Nitrogen	N	14.007
Bromine	Br	79.904	Osmium	Os	190.23
Cadmium	Cd	112.41	Oxygen	O	15.999
Calcium	Ca	40.078	Phosphorous	P	30.973
Carbon	C	12.011	Platinum	Pt	195.08
Cerium	Ce	140.12	Potassium	K	39.098
Chlorine	Cl	35.453	Selenium	Se	78.963
Chromium	Cr	51.996	Silicon	Si	28.085
Cobalt	Co	58.933	Silver	Ag	107.87
Copper	Cu	63.546	Sodium	Na	22.990
Fluorine	F	18.998	Sulphur	S	32.066
Helium	He	4.0026	Tin	Sn	118.70
Hydrogen	H	1.0079	Titanium	Ti	47.880
Iodine	I	126.90	Tungsten	W	183.85
Iron	Fe	55.847	Vanadium	V	90.942
Lead	Pb	207.19	Zinc	Zn	65.390
Lithium	Li	6.9412	Zirconium	Zr	91.224

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