PREFACE

With its grounding in the "guiding pillars of Access, Equity, Equality, Affordability and Accountability," the New Education Policy (NEP 2020) envisions flexible curricular structures and creative combinations for studies across disciplines. Accordingly, the UGC has revised the CBCS with a new Curriculum and Credit Framework for Undergraduate Programmes (CCFUP) to further empower the flexible choice based credit system with a multidisciplinary approach and multiple/ lateral entry-exit options. It is held that this entire exercise shall leverage the potential of higher education in three-fold ways – learner's personal enlightenment; her/his constructive public engagement; productive social contribution. Cumulatively therefore, all academic endeavours taken up under the NEP 2020 framework are aimed at synergising individual attainments towards the enhancement of our national goals.

In this epochal moment of a paradigmatic transformation in the higher education scenario, the role of an Open University is crucial, not just in terms of improving the Gross Enrolment Ratio (GER) but also in upholding the qualitative parameters. It is time to acknowledge that the implementation of the National Higher Education Qualifications Framework (NHEQF) and its syncing with the National Skills Qualification Framework (NSQF) are best optimised in the arena of Open and Distance Learning that is truly seamless in its horizons. As one of the largest Open Universities in Eastern India that has been accredited with 'A' grade by NAAC in 2021, has ranked second among Open Universities in the NIRF in 2024, and attained the much required UGC 12B status, Netaji Subhas Open University is committed to both quantity and quality in its mission to spread higher education. It was therefore imperative upon us to embrace NEP 2020, bring in dynamic revisions to our Undergraduate syllabi, and formulate these Self Learning Materials anew. Our new offering is synchronised with the CCFUP in integrating domain specific knowledge with multidisciplinary fields, honing of skills that are relevant to each domain, enhancement of abilities, and of course deep-diving into Indian Knowledge Systems.

Self Learning Materials (SLM's) are the mainstay of Student Support Services (SSS) of an Open University. It is with a futuristic thought that we now offer our learners the choice of print or e-slm's. From our mandate of offering quality higher education in the mother tongue, and from the logistic viewpoint of balancing scholastic needs, we strive to bring out learning materials in Bengali and English. All our faculty members are constantly engaged in this academic exercise that combines subject specific academic research with educational pedagogy.We are privileged in that the expertise of academics across institutions on a national level also comes together to augment our own faculty strength in developing these learning materials. We look forward to proactive feedback from all stakeholders whose participatory zeal in the teaching-learning process based on these study materials will enable us to only get better. On the whole it has been a very challenging task, and I congratulate everyone in the preparation of these SLM's.

I wish the venture all success.

Professor Indrajit Lahiri
Vice Chancellor

NETAJI SUBHAS OPEN UNIVERSITY

Four Year Undergraduate Degree Programme
Under National Higher Education Qualifications Framework (NHEQF) &
Curriculum and Credit Framework for Undergraduate Programmes
Bachelor of Science (Honours) in Chemistry

Programme Code : NEP

Course Title: Practical Paper-III

Course Code: **6CC-CH-04**

First Print: February, 2025
Memo No. SC/DTP/25/019 Dated: 31-01-2025

Printed in accordance with the regulations of the University Grants
Commission — Distance Education Bureau.

NETAJI SUBHAS OPEN UNIVERSITY

Four Year Undergraduate Degree Programme

Under National Higher Education Qualifications Framework (NHEQF) & Curriculum and Credit Framework for Undergraduate Programmes

Bachelor of Science (Honours) in Chemistry

Programme Code : NEP

Course Title: Practical Paper-III

Course Code: **6CC-CH-04**

: Board of Studies:
Members

Prof. Bibhas Guha
(Chairperson)
Director, School of Sciences, NSOU

Prof. Chitta Ranjan Sinha
Department of Chemistry, Jadavpur University, Kolkata

Prof. Jayanta Maity
Department of Chemistry,
Diamond Harbour Women's University,
Sarisha, South 24-Pargana

Dr. Sukanya Chakraborty
Associate Professor,
Department of Chemistry,
Lady Brabourne College, Kolkata

Dr. Partha Sarathi Guin
Associate Professor,
Department of Chemistry,
Shibpur Dinobundhoo Institution (College),
Howrah

Dr. Paritosh Biswas
Associate Professor,
Department of Chemistry,
Chakdah College, Nadia

Prof. Sanjay Roy
HOD & Professor of Chemistry,
NSOU

Dr. Sintu Ganai
Assistant Professor of Chemistry,
Netaji Subhas Open University

Dr. Puspal Mukherjee
Assistant Professor of Chemistry,
Netaji Subhas Open University

Course Writer

Dr. Puspal Mukherjee
Assistant Professor
Department of Chemistry
School of Sciences,
Netaji Subhas Open University

Course Editor

Dr. Sintu Ganai
Assistant Professor
Department of Chemistry
School of Sciences,
Netaji Subhas Open University

Format Editor

Dr. Puspal Mukherjee
Assistant Professor
Department of Chemistry
School of Sciences,
Netaji Subhas Open University

Notification

All rights reserved. No part of this Self-Learning Material (SLM) may be reproduced in any form without permission in writing from Netaji Subhas Open University.

Ananya Mitra
Registrar (Additional Charge)

Netaji Subhas Open University

UG : Chemistry

Practical Paper – III

Course Code: 6CC-CH-04

Module-I : Kinetic Study of Physical Parameters

Module-2 : Study of Physical Parameters

Module-1

Kinetic Study of Physical Parameters

Basic Laboratory Knowledge

Laboratory Safety

The laboratory is a space dedicated to developing essential experimental skills in a controlled environment. To ensure a safe and productive experience, students must follow strict safety protocols. Wearing protective gear, such as an apron, is mandatory before entering the lab. Unauthorized experiments are prohibited, as they can compromise your safety and that of others. In the event of an accident, no matter how minor, it must be immediately reported to the lab supervisor. The following guidelines are designed to ensure a safe and efficient working environment for all.

Working in a laboratory requires strict adherence to safety protocols to ensure a safe and productive learning environment. The following safety guidelines are essential for minimizing risks during laboratory work:

1. Personal Protective Equipment (PPE)

- Always wear appropriate PPE, including a lab coat or apron, safety goggles, and gloves, as required.
- Footwear should be closed-toe and non-slip. Sandals or other open footwear are strictly prohibited.
- Long hair must be tied back, and loose clothing or accessories should be avoided to prevent accidents.

2. Access to the Laboratory

- No student is allowed to enter the laboratory without wearing the prescribed apron or protective gear.
- Unauthorized individuals or visitors are not allowed inside the lab during experiments.

3. Conduct in the Laboratory

- Follow the instructions provided by your instructor or lab supervisor carefully.
- Do not engage in horseplay, loud talking, or any other form of disruptive behavior that may endanger yourself or others.

- Eating, drinking, and smoking are strictly prohibited in the laboratory.

4. Handling Chemicals and Equipment

- Always label your chemicals and reagents, and never use unlabeled substances.
- Handle all chemicals, especially hazardous or volatile substances, with care.
- Use equipment only as instructed and report any damaged or malfunctioning equipment to the supervisor immediately.
- Never conduct unauthorized experiments. Stick to the experimental procedures provided in the manual.

5. Emergency Procedures

- Be aware of the locations of safety equipment such as fire extinguishers, first aid kits, safety showers, and eyewash stations.
- In case of a spill, chemical exposure, or accident, notify the supervisor immediately and follow emergency protocols.
- For any incident, even if it involves a minor injury, report it promptly to the supervisor.

6. Waste Disposal

- Dispose of chemical waste in designated containers as per the laboratory's waste disposal protocols.
- Never pour chemicals down the sink unless specifically instructed to do so by the supervisor.

7. Housekeeping

- Keep your workspace clean and organized. Always return equipment to its proper place after use.
- Clean up any spills immediately, and wash your hands thoroughly before leaving the lab.

8. Responsibility and Accountability

- Safety in the lab is a shared responsibility. By following these guidelines, you contribute to a safe and efficient environment.
- Failure to comply with these safety rules may result in removal from the laboratory and potential disciplinary action.

While working in a chemistry laboratory one should always follow the instructions mentioned below –

i. **Handle hot glassware with care** – It retains heat for a long time and may still be hot even if it does not appear so.

ii. **Protect your eyes** – In case of any acid or corrosive chemical splashes, wash your eyes immediately with plenty of water and seek medical attention.

iii. **Avoid reaching over burners** – This can lead to accidents, so exercise caution around open flames.

iv. **Thoroughly clean apparatus** – Use washing powder to clean all equipment after use.

v. **Heat substances safely** – Never point test tubes towards anyone while heating, as sudden ejection of contents can occur.

vi. **Handle dilute acids properly** – Always add acid to water with stirring, not water to acid, to avoid excessive heat generation.

vii. **Check chemical labels** – Read labels carefully and never return unused chemicals to their original containers.

viii. **Do not touch or taste chemicals** – Most chemicals are corrosive or poisonous.

ix. **Bring containers to the reagent shelf** – Avoid taking reagent bottles to your desk to prevent contamination.

x. **Avoid contamination** – Never insert pipettes or droppers into reagent bottles.

xi. **Do not heat graduated glassware** – Cylinders and bottles can easily break and their volume may change.

xii. **End of experiment protocol** – Clean and dry all glassware, wipe the workspace, and ensure gas and water taps are properly closed before leaving the lab.

Laboratory First-Aid

If a corrosive substance falls on your skin, immediately wash the spot with large quantities of water, followed by remedial action indicated below:

Acid spill: Treat with sodium bicarbonate or ammonium carbonate (2M) solution; then apply Vaseline or a soothing cream.

Base spill: Treat with acetic acid (1 M) followed by Vaseline or a soothing cream

Bromine:Treat with 2 M ammonia; keep the affected part dipped in dilute sodium bisulphite solution till bromine is washed off. Finally apply Vaseline.

Phenol:Wash with ethanol and then take hospital treatment.

The most common accidents in the chemistry laboratory involve cuts, burns or fire. The first-aid to be given in each case is below:

Cuts: If you have a cut, wash the wound well with cold water immediately. If bleeding is severe, apply pressure directly on to the wound to stop the bleeding. Then an antiseptic cream can be applied to the wound; it should be followed by proper dressing of the wound.

Burns: Wash the burnt part with cold water for some time and then apply Burnol to it.

Fire: A small fire in a beaker, caused by the vapours of an inflammable liquid can be extinguished by covering it with a watch glass. If the clothes catch fire, one should lie on the floor and, fire can be put off by wrapping a thick blanket around the body.

Specific Instructions for Physical Chemistry Experiments

Experiments in the physical chemistry laboratory are designed to provide insights into the properties of matter. To achieve accurate results, a solid theoretical understanding of the experiment's subject matter is essential. Success in the lab requires not only technical skills but also a thorough grasp of the underlying concepts.

Before starting any experiment, it is crucial to know exactly what needs to be done and how to do it. Systematic planning can save time and prevent unnecessary risks. Review the detailed procedure in advance and estimate the equipment you will need—such as flasks, beakers, reagent bottles, pipettes, and burettes—as well as the required quantities of chemicals and solutions. This preparation helps to avoid shortages during the experiment. Once you have made these estimations, organize the steps of the experiment to ensure it can be completed efficiently within the available time.

Two laboratory note books are essential; one is rough to be used in the laboratory and the other, the final report book having stiff cover. All measurements and observations should be recorded in the rough laboratory note book. Preliminary calculations and plots are also to be made here. All the results and information from this book should be finally arranged systematically in the final record book and signed daily by the subject counsellor. This description should consist of the following:

i. Writing the name of the experiment in bold letters at the top, with the date being indicated at left corner.

ii. Writing the theory in brief-you just mention the working formula, with proper explanation of the terms involved.

iii. Mentioning the apparatus and chemicals needed for your experiment;

iv. Meticulous and systematic representation of the data in TABULAR form. Write the temperature during experiment-because results of almost all experiments are temperature-dependent;

v. Calculations and graph (where necessary);

vi. Conclusion and

vii. Precautions.

In your laboratory note book you must maintain and index page where title of the experiment and its date of performance will be recorded. During recording of data and doing your calculations DON'T FORGET the following:

A) Temperature

Temperature during experiment in physical chemistry must be noted. Greater accuracy needs performance of the experiment in an electrically controlled thermostat. However, during ordinary experiment constancy in temperature can be kept by using large amount of water in a pneumatic trough as your thermostat. In absence of any such arrangement take room temperature as experimental temperature.

B) Units

Any number without unit is meaningless in physical chemistry. Very often a student forgets to write units while reporting the result. This is a gross mistake and marks are deducted for it.

C) Graph

During drawing a graph do not think that all points in your graph paper will lie in the curve, this never happens. Draw the best possible curve showing deviation of points on both sides. Thus, if the curve should be a straight line and all your points are not on the same line then pick those points only which give best possible straight line in this case. In doing so, some points will remain above this line and some points will also remain below this line.

Unit 1 ❑ Determination Of Heat Of Neutralization Of A Strong Acid By A Strong Base

1.1 Objectives

Upon completing this experiment, you will be able to:

- Define the enthalpy (heat) of neutralization and its significance in chemical reactions.
- Explain why the enthalpy of neutralization (ΔH_{neut}) for the reaction between a strong acid and a strong base is constant.
- Calculate the enthalpy of ionization for a weak acid or weak base using the enthalpy of neutralization.
- Understand and apply the principles of calorimetry to measure heat changes during a neutralization reaction.

1.2 Introduction

You may already have a basic understanding of enthalpy from your theory course. Enthalpy changes are named according to the type of transformation or reaction they accompany. Examples include the enthalpy of combustion, fusion, formation, hydration, neutralization, and ionization. In this experiment, we will focus on determining two specific enthalpies:(i) the enthalpy of neutralization, and(ii) the enthalpy of ionization, calculated using the enthalpy of neutralization.

1.3 Theory

The enthalpy of neutralization () of an acid is defined as the enthalpy change that occurs during the complete neutralization of its dilute aqueous solution, containing one mole of Hz ions, by a dilute aqueous solution of a base containing one mole of OH{ ions. For example, consider the neutralization of hydrochloric acid by sodium hydroxide. Since hydrochloric acid is a strong acid and sodium hydroxide is a strong base, both are fully dissociated in aqueous solution.

$$HCl \rightleftharpoons H^+ + Cl^-$$

$$NaOH \rightleftharpoons Na^+ + {}^-OH$$

The neutralisation reaction can be represented as

$$H^+ (aq) + Cl^- (aq) + Na^+ (aq) + {}^-OH (aq) \rightleftharpoons Cl^- (aq) + Na^+ (aq) + H_2O$$

When hydrochloric acid (HCl) and sodium hydroxide (NaOH) are mixed, they undergo a neutralization reaction that produces water and a salt, accompanied by a release of heat. This release of heat results in a rise in temperature of the reaction mixture. To quantify the heat evolved during this process, you need to measure the temperature increase.

The amount of heat released can be calculated using the following relationship:

$$q = C \times \Delta T$$

where q is the heat released, C is the heat capacity of the solution and the calorimeter, and is the change in temperature observed.

In this calculation, it is important to account for the heat capacities of both the solution and the calorimeter. The heat capacity of the solution includes the combined heat capacities of the reactants and the resulting products. The calorimeter itself, which absorbs some of the heat, also has a heat capacity that needs to be considered.

By accurately measuring the temperature rise and knowing the heat capacities, you can determine the total heat evolved during the neutralization reaction. This value, when divided by the number of moles of reactants, gives the enthalpy of neutralization.

1.4 Requirements

Apparatus

i. Calorimeter with stirrer
ii. 500 ml conical flask
iii. 250 ml conical flask
iv. Burette
v. Pipette
vi. Measuring cylinder
vii. thermometer

Chemicals

i. 500 ml N/4 HCl solution (Dilute 10.4 ml 12 (N) HCl to 500 ml with distilled water)
ii. 500 ml N/4 NaOH solution (Dissolve about 5 gm. of NaOH in 500 ml of distilled water)
iii. 250 ml N/4 oxalic acid solution
iv. Phenolphthalein indicator

1.5 Procedure

Preparation of 250 ml (N/4) oxalic acid solution

Dissolve near about 0.7879g oxalic acid (note accurate weight of taken amount) in 250mL volumetric flask, dilute up to the mark with distilled water and then shake to form a uniform solution.

☐ Strength of prepared oxalic acid solution

$$= \frac{\text{Actual weight of oxalic acid taken}}{0.7879} \quad (\frac{N}{20}) = S_1\ (N)$$

Table:-1.1

Initial weight (g)	Final weight (g)	Amount of oxalic acid taken (g)	Strength of the solution (N/20)
W_1	W_2	$W_1 - W_2 = W$	$S_1 = W/0.7879$

Standardization of NaOH solution

Pipette out of 25 mlof standard Oxalic Acidsolution in a 250 ml conical flask and add 1-2 drops of phenolphthalein indicator. Titrate with the NaOH solution with constant shaking until the pink colour just appeared. Record the burette reading (V_1). Repeat process three times.

Table: – 1.2

No. of obs.	Volm. of oxalic acid (ml)	Burette reading		Volume of NaOH (ml)	Concordant value (ml)
		Initial	Final		
1.	25	0	...	...	V_1
2.	25	...	...	...	
3.	25	...	...	...	

Standardisation of HCl Solution

Pipette out of 25 mlof HClsolution in a 250 ml conical flask and add 1-2 drops of phenolphthalein indicator. Titrate with the standard NaOH solution with constant shaking until the pink colour just appeared. Record the burette reading (V_2). Repeat process three times.

Table: – 1.3

No. of obs.	Volm. of oxalic acid (ml)	Burette reading		Volume of NaOH (ml)	Concordant value (ml)
		Initial	Final		
1.	25	0	...	...	V_2
2.	25	...	...	...	
3.	25	...	...	...	

Neutralisation of HCI with NaOH

a) Dilute the HCl or NaOH solution to make the equal strength.

b) Take 250 ml of the alkali solution in the previously weighed calorimeter.

c) Take 250 ml of the acid solution in a conical flask.

d) Place two thermometers in both the acid and alkali solution with occasional starring till temperature become equal.

e) Pour the acid solution as rapidly as possible into the alkali solution kept in calorimeter and note the time.

f) Mix the two solutions intimately with stirrer.

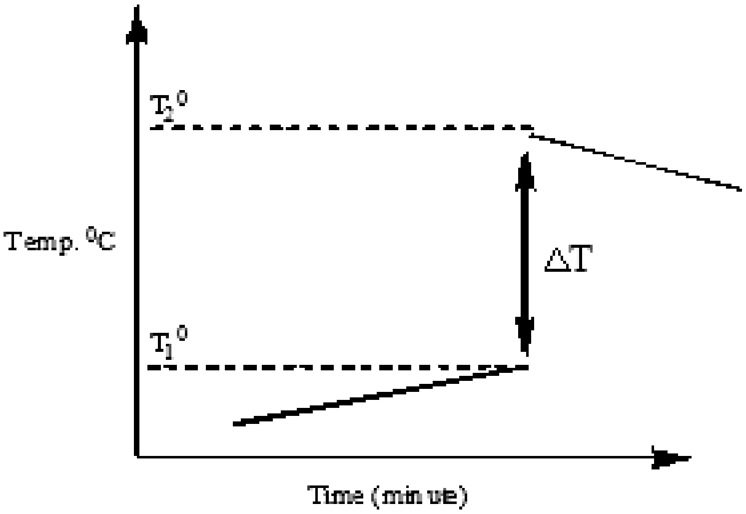
g) Note the temperature every half-minute for about 10 minutes after mixing, until it is found that the fall of temperature after initial rise becomes uniform.

h) At first the temperature rises rapidly, then more slowly, and then begins to fall.

Table: 1.4

Time (min)									
Temperature (^{0}C)									

Plot a graph of temperature against time, and obtain the temperature rise from extrapolation of the readings to the time of mixing. Let the temperature rise be $T_2\,^0C - T_1\,^0C = \Delta T\,^0C$.



Precautions

Ensure that the thermometer or temperature probe is properly calibrated before use. Prevent the thermometer from coming into direct contact with the reaction vessel walls or the stirrer, as this can affect the readings. Use a thermometer holder or clamp to position it correctly.Gently stir the reaction mixture to ensure uniform temperature distribution. This helps avoid localized hot or cold spots that could skew the measurements.Cover the calorimeter or vessel to reduce heat exchange with the surroundings.

1.6 Calculations

$\therefore$ Heat evolved = $(m_1s_1 + m_2s_2 + m_3s_3) \times \Delta T$

Where, m_1, m_2 and m_3 are the masses of the solution, calorimeter along with stirrer (if made of same element) and thermometer respectively, and s_1, s_2 and s_3 are their specific heats. As regards of specific heat of the solution, this will vary more or less from that of the pure water according to the concentration of the dissolved salt. It will be sufficiently accurate for this experiment to consider the water equivalent of the solution, i.e., mass x sp. heat, which is being equal to that of the water contained in it.

In this experiment, $m_1s_1 = 500$ cal. per degree.

Determination the water equivalent of thermometer (immersed portion):

Table: 1.5

Weight of thermometer (g)	Wt. of thermometer after immersing the bulb in water (g)	Weight of displaced water (g)	Water equivalent of thermometer
W_3	W_4	$W = W_3 - W_4$	$W \times 0.47$

[Water equivalent of 1 cc of glass = 2.5 × 0.19 = 0.47 and water equivalent of 1 cc of mercury = 13.6 × 0.034 = 0.46]

Since the specific heat of glass and mercury is practically same and equal to 0.47 / ml. Thus, multiplying the weight of the displaced water by 0.47 to obtain the water equivalent of the immersed portion of the thermometer.

Now, number of gram molecules of HCl = ——

Heat of neutralization per mole of HCl = —— Cal.

[Sp. heat of Copper = 0.092; Nickel = 0.109; Silver = 0.046; Platinum = 0.032]

1.7 Results

The heat of neutralisation of hydrochloric acid with sodium hydroxide is...... J mol^{-1}

1.8 Summary

In this unit, we discussed how to measure and calculate the enthalpy of neutralization which gave us insight into the heat released during the reaction between an acid and a base. We also applied the principles of calorimetry, including measuring temperature changes and accounting for the heat capacities of the solution and the calorimeter to determine the heat evolved. We practiced analyzing experimental data to calculate thermodynamic quantities, such as the enthalpy of neutralization and, by extension, the enthalpy of ionization for weak acids or bases.

1.9 Self-Assessment Questions

1. What is the enthalpy of neutralization, and how is it defined in terms of acid and base reactions?
2. Why is the enthalpy of neutralization for strong acids and strong bases typically constant?

3. How would you calculate the heat released during the neutralization reaction using temperature measurements?
4. Explain how you would account for the heat capacities of the solution and the calorimeter in your calculations.
5. Given a set of temperature measurements and heat capacities, describe the steps to determine the enthalpy of neutralization.
6. What precautions should you take to ensure accurate temperature measurements during the experiment?
7. How would you address potential sources of error in the measurement of temperature change?

Unit 2 ❑ Study of Kinetics of Acid-Catalyzed Hydrolysis of Methyl Acetate

2.1 Objectives

On completion of studying and performing this experiment, you should be able to:

- Explain the principle behind studying the kinetics of acid-catalyzed hydrolysis of methyl acetate using titrimetric procedure.
- Define and understand the concept of a 'pseudo-first-order reaction.'
- Conduct the acid-catalyzed hydrolysis of methyl acetate and monitor the reaction progress by titrating the reaction mixture with a standard NaOH solution.
- Analyse the experimental data to calculate the rate constant for the acid hydrolysis of methyl acetate.
- Determine the rate constant graphically using the collected data.
- Compare the strengths of two mineral acids by evaluating their effect on the rate of hydrolysis of methyl acetate.

2.2 Introduction

In this experiment, you will study the kinetics of the acid-catalysed hydrolysis of an ester, specifically methyl acetate. Chemical kinetics is the branch of chemistry that deals with the rates of chemical reactions and the factors that influence them. The rate of reaction refers to the speed at which reactants are converted into products, and it can be affected by various factors such as concentration, temperature, and catalysts.The progress of the reaction will be monitored using titrimetry, allowing you to track the changes in concentration over time.

2.3 Theory

A first-order reaction is defined as a reaction where the rate at any given instant is directly proportional to the concentration of one reactant raised to the first power. First order reaction can be represented as

$$A \rightarrow Products$$

$$Rate = k[A]$$

Rate is the rate of the reaction,5ØXÜis the rate constant, [A] is the concentration of the reactant.

A pseudo-first-order reaction is a reaction that, although involving more than one reactant, behaves kinetically as a first-order reaction under certain conditions. This occurs when the concentration of one reactant is much larger than that of the other(s) and remains approximately constant during the reaction.

In such cases, the rate law simplifies because the concentration of the excess reactant(s) doesn't change significantly, making the reaction rate effectively dependent on the concentration of only one reactant.

You may remember from your school chemistry that esters can be hydrolyzed by either mineral acids or bases. The hydrolysis of an ester on its own is typically slow and reversible. However, in the presence of acid or base catalysts, the reaction proceeds more rapidly and predominantly in the forward direction. In this experiment, you will investigate the hydrolysis of methyl acetate in the presence of hydrochloric acid.

$$CH_3COO.CH_3 + H_2O \xrightleftharpoons{H^+} CH_3COOH + CH_3OH$$

The rate of the reaction is expected to depend on the concentrations of methyl acetate, water, and the acid. However, this reaction is a pseudo-first order reaction. The change of concentration of water is negligible as it is present in large excess. HCl added to catalyse the reaction, is not used up during the reaction. So, the rate of reaction is written as

$$Rate = k[Ester][H_2O] = k'[Ester]$$

If we start with 'a' mole of ester and if 'x' moles be get decomposed in time t secs., then (a – x) remains undecomposed at that instant. The rate of reaction at at any instant, t, is directly proportional to the concentration of ester at that instant, i.e., $\propto$ (a – x).

Expressed mathematically,

$-\frac{d[ester]}{dt} \propto [ester]$ (= concentration at any instant, t)

Since [ester] is proportional to (a – x), thus, we have

$-\frac{d(a-x)}{} \propto (a - x)$

or, $\frac{d(a-x)}{} = - k (a - x)$

where k is the *rate constant*.

[Note the minus sign, which signifies the decrease of concentration with time]

Integrating, we have

$\int \frac{d(a-x)}{} = - k\int dt$

or, $\ln (a - x) = - k.t + \text{constant}$

The value of constant can be evaluated by substituting x = 0 and t = 0 in the above equation i.e., at the beginning. The equation then becomes, ln a = constant.

Substituting the value of constant, we have

$\ln (a - x) = - k.t + \ln a$

or, $\ln \frac{a}{(a-x)} = k.t$

or, $\frac{2.303}{t}\log_{10} = k$

The above reaction is slow and is efficiently catalysed by strong acids, say, HCl, H^+ being the active ion. The progress of catalysed reaction may be studied by withdrawing measured volumes of aliquot from the reaction mixture at different intervals of time and titrating with a standard alkali solution using phenolphthalein indicator. The volume of alkali required at any instant is equivalent to the sum of acetic acid (week acid) and the strong acid used as catalyst (HCl, a constant quantity).

Let V_0, V_t and $V\infty$ be the volume of alkali required for the same volume of aliquots – at the beginning, at time t and at the end of the reaction (infinite time) respectively.

Then we can write,

$a \propto (V - V_0)$ and $(a - x) \propto (V_\infty - V_t)$

$\therefore$ Amount of ester consumed = amount of week acid formed $\propto (V_t - V_0)$

Thus, amount of ester left = (initial – consumed) $\propto [(V - V_0) - (V_t - V_0)]$

$$\therefore\ k = \frac{2,303}{t}\log_{10}\frac{(V_\infty - V_0)}{(V_\infty - V_t)}$$

So, a graph may be obtained by plotting $\log_{10}\frac{(V_\infty - V_0)}{(V_\infty - V_t)}$ against t. A straight line passing through the origin is obtained. The value of k may be obtained from the slope of the line which is equal to $\frac{k}{2.303}$.

If a graph of log $(V_\infty - V_t)$ is plotted against t, a straight will be obtained with slope equal to $-\frac{k}{2.303}$.

2.4 Requirements

Apparatus

i) Burette
ii) Pipette
iii) Conical flask
iv) Volumetric flask
v) Stop watch

Chemicals

- i) Methyl acetate
- ii) 0.5 (N) Hydrochloric acid
- iii) 0.1 (N) Sodium hydroxide solution
- iv) 0.1 (N) Oxalic acid solution
- v) Phenolphthalein indicator.

2.5 Procedure

i. Take 100 ml of 0.5 (N) HCl solution in a 250 ml conical flask and keep the solution in a water bath for 10 – 15 min. at room temperature and note the temperature.

ii. Pipette out 5 ml of methyl acetate and add carefully to above mixture with constant swirling and start the stop watch at time of half discharged from the pipette. Shake the mixture.

iii. Pipette out 5 ml of the mixture immediately into a conical flask containing distilled water and crushed ice and titrate immediately with 0.1 (N) NaOH solution using phenolphthalein indicator. The volume of NaOH consumed in this titration is V_0.

iv. After 5 minutes, pipette out 5 ml of the reaction mixture and pour into the second conical flask containing distilled water and ice crushed. Titrate immediately with 0.1 (N) NaOH solution using phenolphthalein indicator. The volume of NaOH consumed in this titration is V_t.

v. Repeat the step (4) at least five times more at different time intervals (say, 10, 15, 20, 25 30 minutes) corresponds to volume V_t.

vi. Heat the rest of the solution at about 60-70^{0}C in a water bath for about 30 minutes fitting an air condenser to mouth of of the conical flask. Cool mixture, till it attain to room temperature. Pipette out 5 ml of the solution in ma conical flask containing distilled water and titrate with 0.1 (N) NaOH solution using phenolphthalein indicator. The volume of NaOH consumed in this titration is V.

Table 2.1

Temperature before experiment ^0C	**Temperature after experiment ^0C**	**Mean temperature ^0C**

Recording of data for hydrolysis of methyl acetate with 0.5 (N) HCl:

Table 2.2

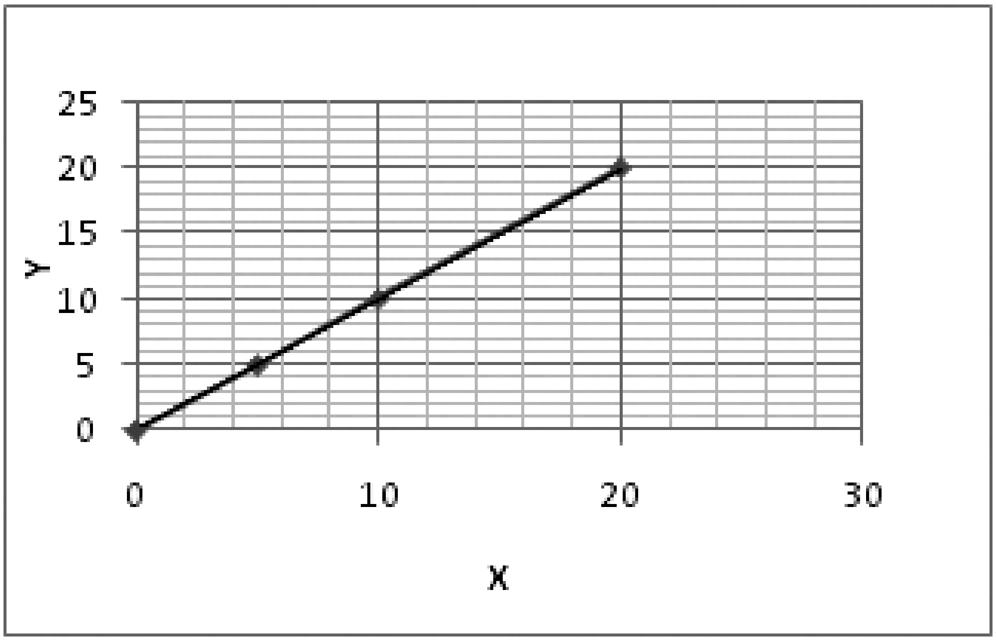
	Time in Mins. (t)	Vol. Of NaOH consumed (V_t) ml	($V_\infty - V_0$) ml	($V_\infty - V_t$) ml	Log ($V_\infty - V_t$)	$\log_{10}\frac{(V_\infty - V_0)}{(V_\infty - V_t)}$
1	0	V_0				
2	5					
3	10					
4	15					
5	20					
6	25					
7	infinity	V_∞				

2.6 Calculations

A graph, plotting $\log_{10}\frac{(V_\infty - V_0)}{(V_\infty - V_t)}$ against t, gives a straight line passing through the origin.

Its slope is = —

$\therefore$ k = slope × 2.303 = —— / min at...... ^0C



2.7 Results

The value of rate constant of acid catalysed hydrolysis of methyl acetate for 0.5 (N) HCl at ……… temperature is ……………

2.8 Summary

In this experiment, the kinetics of the acid-catalyzed hydrolysis of methyl acetate were studied. By monitoring the reaction progress through titrimetry, the concentration of the ester was tracked over time. The reaction was treated as a pseudo-first-order process, as the water concentration remained constant due to its large excess. Using the experimental data, the rate constant for the reaction was determined. Overall, this experiment demonstrated the principles of reaction kinetics and pseudo-first-order reactions in a practical context.

2.9 Self-Assessment Questions

1. Distinguish between order and molecularity
2. What is pseudo-first order reaction?
3. How rate constant varies with temperature?
4. The graph you draw, points corresponding to high ‘t; values being to show deviation, why?
5. Why NaOH is not necessary to standardize in this experiment?
6. What is the dimension of rate constant?
7. Why Baryta gives more accurate result compare to NaOH for this experiment?

Unit 3 ❑ Study of kinetics of decomposition of H_2O_2

3.1 Objectives

After studying and performing this experiment, you should be able to:

- Explain the mechanism and kinetics of the decomposition of hydrogen peroxide.
- Understand and apply the concept of a catalytic reaction in the decomposition of H_2O_2.
- Measure the rate of decomposition of H_2O_2 using titrimetric analysis or another suitable method.
- Analyse the data to determine the reaction order and calculate the rate constant for the decomposition reaction.
- Investigate the effect of a catalyst (such as manganese dioxide or potassium iodide) on the rate of decomposition.
- Graphically represent the reaction rate and calculate kinetic parameters from the experimental data.

3.2 Introduction

Chemical kinetics is essential for understanding the mechanisms and rates of chemical reactions that influence everything from living organisms to atmospheric processes. For example, chemists' model complex reactions in urban atmospheres, involving nearly two million elementary steps, to understand their impact on pollution and health. In this laboratory, you will explore these principles by studying the decomposition of hydrogen peroxide (H_2O_2), a common oxidant in the environment formed through atmospheric processes.

Hydrogen peroxide is known for its potential harm to cells, as it can damage unsaturated fatty acids in cell membranes. To counteract this, cells produce catalase, an enzyme that decomposes H_2O_2. Catalase serves as a biological catalyst, facilitating the decomposition of hydrogen peroxide by acting as both an electron donor and acceptor. This enzyme exemplifies the role of biological catalysts in accelerating reactions. Through this experiment, you will learn methods to analyse reaction rates and mechanisms, providing valuable insights into the factors affecting chemical reactions and the role of catalysts.

3.3 Theory

Hydrogen peroxide decomposes spontaneously to H_2O and O_2 as $H_2O_2 = H_2O + ½\ O_2$. It is observed that the decomposition rate of Hydrogen peroxide is very slow in absence of catalyst. However, reaction can be catalysed by many catalysts, such as Fe^{+3} ion and I^- ion. In presence of either of these catalysts the reaction behaves as a first order with respect to H_2O_2.

Decomposition of H_2O_2 catalysed by Fe^{+3} is believed to occur by the following paths. Here H_2O_2 decomposes by catalytic action of Fe^{+3} through the formation of Ferrate ion.

$$3H_2O_2 + 2Fe^{+3} + 2H_2O = 2FeO_4^{-2} + 10H^+$$

$$2FeO_4^{-2} + 10H^+ = 2Fe^{+3} + 5H_2O + \frac{3}{2}O_2$$

So, the overall reaction is

$$3H_2O_2 = 3H_2O + \frac{3}{2}O_2$$

Thus, the concentration of Fe^{+3}, which act as catalyst, remain constant

The course of reaction may be followed by titration with potassium permanganate solution.

$$2KMnO_4 + 3H_2SO_4 + 5H_2O_2 = K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2$$

As it is a first order reaction the expression for rate constant is

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

Here, 'a' is the initial concentration and '(a – x)' is the concentration at any time 't'. Since volume of $KMnO_4$ consumed is directly proportional to the concentration of H_2O_2 present. Thus, a $\propto V_0$ and (a – x) $\propto V_t$. Where, V_0 and V_t are volume of $KMnO_4$ consumed at the beginning and at time 't'. Thus,

$$k = \frac{2.303}{t}\log\frac{V_0}{V_t}$$

$$\log V_0 - \log V_t = \frac{k.t}{2.303}$$

$$\log V_t - \log V_0 = \frac{k.t}{2.303}$$

So, if we plot log V_t vs t, then the slope of the plot will be $\frac{k}{2.303}$ and we can find the value of rate constant.

3.4 Requirements

Apparatus

i. Burette

ii. Pipette

iii. Conical flask

iv. Glass trough

v. Stop watch

vi. Volumetric flask

vii. Thermometer

Chemicals

i. 1 vol. H_2O_2

ii. 1% $FeCl_3$ solution

iii. 2(N) H_2SO_4

iv. (N/50) $KMnO_4$ solution

3.5 Procedure

Preparation of Reagents

250 ml 1 vol. H_2O_2 : In laboratory available H_2O_2 is 30% which is equivalent to 98.8 vol. 2.53 ml (30% H_2O_2) should be diluted to 250 ml by adding distilled water.

1% $FeCl_3$ solution : Dissolve 1 gm. of $FeCl_3$ (using rough balance) in 100 ml of distilled water.

250 ml (N) H_2SO_4: 7 ml concentrated H_2SO_4 (36 N) to be diluted with distilled water to 250 ml.

500 ml N/50 $KMnO_4$ solution: Dissolve about 0.32 gm $KMnO_4$ in 500 ml of distilled water.

Experimental Method

- Take five or six 100 ml conical flask and transfer 25 ml (N) H_2SO_4 by pipette. Add some crush ice to make the solution ice cold.
- Take 100 ml of 1 vol. H_2O_2 in 250 ml conical flask and add 20 ml of 1% $FeCl_3$ solution by a pipette. When pipette was half-emptied time was noted. This is zero time.
- Pipette out 5 ml of the reaction mixture at an interval of 2to 3 mins. and pour into 25 ml ice cold (N) H_2SO_4 solution and then titrate with $KMnO_4$ solution taken in a burette. At the end point faint pink colour persists. Volume required is V_t. Repeat the experiment four to five or more different time intervals.

- To find the value of V_0, take 5 ml of 1 vol. H_2O_2 in a conical flask containing 25 ml (N) H_2SO_4 and titrate with $KMnO_4$ solution. However, in the reaction mixture 100 ml H_2O_2 solution was mixed with 20 ml $FeCl_3$ solution, so it was diluted by (120 100) = 1.2 times. If in this titration V is the burette reading then $V_0 = \frac{v}{1.2}$.

Recording of Data

Table 3.1: Recording of Room Temperature

Temperature before experiment ^{0}C	Temperature after experiment ^{0}C	Mean temperature ^{0}C

Determination of V_0

5 ml of original H_2O_2 solution ≡ —— ml $KMnO_4$ (say V)

$$V_0 = \frac{v}{1.2} = \text{—} \text{ ml}$$

Table 3.2: Titration with KMnO4 Solution

No. of obs.	Time (mins)	Volume of N/50 $KMnO_4$			$\log \frac{v_0}{v_t}$
		Burette Reading			
		Initial (ml)	Final (ml)	V_t ml	
1	2	0	V	V	...
2	4	V	...	...	...
3	6	...	...	...	...
4	8	...	...	...	...
5	10	...	...	...	...
6 etc.	...	...	...	...	...

3.6 Calculations

Now, plot a graph $\log\frac{v_0}{v_t}$ against time ‘t’; gives a straight line passing through the origin.

Its slope is = —

∴ k = slope × 2.303 = —— / min at..... ^{0}C

[Expected value of k =..... × 10^{-2} min^{-1} at 25^0C]

3.7 Results

The rate constant was found to be ………….

3.8 Summary

In this experiment, you studied the kinetics of hydrogen peroxide (H_2O_2) decomposition. The reaction was analyzed to understand the role of catalysts, that accelerates the breakdown of H_2O_2. By measuring the rate of decomposition and analyzing the data, you determined the reaction order and rate constant. This experiment provided insights into the principles of chemical kinetics, the effect of catalysts, and the practical application of these concepts in understanding reaction mechanisms.

3.9 Self-Assessment Questions

1. How do you determine the reaction order with respect to hydrogen peroxide from the experimental data?
2. Explain how you would calculate the rate constant for the decomposition reaction from the collected data.
3. Describe the method used to measure the rate of decomposition of hydrogen peroxide in this experiment.

4. What are the key factors that need to be controlled to ensure accurate measurement of the reaction rate?
5. How can you graphically determine the reaction rate and rate constant for the decomposition of hydrogen peroxide?
6. Why standardization of $KMnO_4$ is not necessary in this experiment?
7. How can the principles learned from this experiment be applied to other reactions involving biological or chemical catalysts? Provide an example.

Unit 4 ❑ Determination of partition coefficient for the distribution of I_2 between water and CCl_4

4.1 Objectives

After studying and performing this experiment, you should be able to:

- Understand the concept of the partition coefficient and its relation to Nernst's Distribution Law.
- Explain the principle of distribution of a solute between two immiscible solvents.
- Determine the partition coefficient of iodine between water and carbon tetrachloride experimentally.
- Analyze the equilibrium concentrations of iodine in both solvents using spectrophotometry or titration.
- Apply Nernst's Distribution Law to calculate the partition coefficient and verify the law's validity.
- Understand how factors like temperature or solvent properties can affect the partitioning behavior of a solute between two phases.

4.2 Introduction

The partition coefficient is a critical parameter in understanding how a solute distributes itself between two immiscible solvents. This experiment focuses on determining the partition coefficient of iodine (I,) between water and carbon tetrachloride (CCl,,) using Nernst's Distribution Law. The partition coefficient provides valuable insight into the solubility and distribution behavior of a substance, which has applications in various fields such as drug design, environmental science, and separation processes in chemistry.Understanding the partition coefficient is particularly useful in areas such as pharmacology, where it helps in predicting how drugs will distribute between aqueous and lipid environments in the body. It also plays a key role in solvent extraction techniques, where a solute needs to be separated from a mixture into a desired solvent.This experiment is closely linked to other physical chemistry experiments, as it demonstrates key principles of equilibrium, solubility, and the interactions between solutes and solvents. The concept of dynamic equilibrium, explored here, is foundational in understanding various chemical reactions and processes, such as chemical kinetics and thermodynamics. Additionally, the partitioning of solutes between phases connects to other experiments dealing with phase equilibria, such as the study of colligative properties and vapor-liquid equilibria.

4.3 Theory

The distribution law, also known as Nernst's Distribution Law, applies to systems composed of two or more homogeneous phases in equilibrium within a heterogeneous system. When a solute is soluble in both of two immiscible solvents and these solvents are brought into contact with each other, the solute will distribute itself between the two phases. At equilibrium, the ratio of the solute's concentrations in each solvent remains constant at a given temperature. This ratio is known as the partition coefficient.

For the distribution law to hold true, the solute must retain its molecular form and not undergo any chemical changes, such as dissociation or association, in either of the solvents. In cases where the solute does alter its molecular state, the observed distribution may deviate from the expected behaviour described by Nernst's law. This principle is widely applicable in various areas of chemistry, particularly when studying systems in equilibrium, and is essential for processes such as liquid-liquid extractions, environmental pollution analysis, and pharmacological studies of drug solubility.

For practical purposes, the concentrations of the solute in the two solvents are typically expressed in grams per liter (g/L). If C_1 and C_2 represent the concentrations of the solute in solvents A and B, respectively, then the following relationship is observed:

$$K = \frac{C_1}{C_2}$$

Here, K is a constant known as the partition coefficient, or distribution coefficient, which describes how the solute is distributed between the two immiscible solvents at equilibrium.When a solution containing a solute is shaken with a second solvent that is immiscible with the first, part of the solute will be transferred from the first solvent into the second. Typically, water is used as one solvent, while the other is an organic solvent that does not mix with water. The ratio of the solute's concentration in the organic solvent to its concentration in the aqueous phase is known as the partition coefficient. This coefficient provides a measure of how the solute distributes itself between the two immiscible solvents.

When iodine is added to water in presence of CCl_4 (organic solvent) which is immiscible with water then the following equilibrium is established,

$$I_2\,(aq) \rightleftharpoons I_2\,(CCl_4)$$

So, for this equilibrium we can write the Nernst Distribution law as

$$K = \frac{C_1}{C_2} = \frac{Concentration\ of\ I_2\ in\ CCl_4\ layer}{Concentration\ of\ I_2\ in\ Aqueous\ layer}$$

In this experiment I_2 in each layer is estimated by titrating against the standard $Na_2S_2O_3$ solution using starch as indicator.

$$I_2 + 2S_2O_3^{-2} = 2I^- + S_4O_6^{-2}$$

If V_1 ml of aqueous layer of iodine requires V_2 ml of S_1(N) thiosulphate solution, then

$$C_2 = \frac{V_2 S_1}{V_1}$$

[C_2 = Strength of I_2 in aqueous layer]

Similarly, if V_3 ml of CCl_4 layer of iodine requires V_4 ml of S_2(N) thiosulphate solution, then

$C_1 = V_4 \times S_2 / V_3$ [C_1 = Strength of I_2 in CCl_4 layer]

4.4 Requirements

Apparatus

i) Three clean and dry 500ml glass-stoppered bottles

ii) Volumetric flask (250 ml)

iii) Burette

iv) Pipette

v) Conical flask (250 ml)

vi) Mechanical shaker

Chemicals

i) Saturated solution of I_2 in CCl_4

ii) Pure CCl_4

iii) N/20 $K_2Cr_2O_7$

iv) N/20 $Na_2S_2O_3$

v) 10% KI solution

vi) 1% freshly prepared starch solution

4.5 Procedure

Recording of room temperature

Table 4.1: Recording of Room Temperature

Temperature before experiment ^{0}C	**Temperature after experiment ^{0}C**	**Mean temperature ^{0}C**

Preparation of standard 250 ml ~ (N/20) $K_2Cr_2O_7$ solution

Molecular Weight of Potassium Dichromate= 294.185 g/mol

Dissolve near about 0.6129 g $K_2Cr_2O_7$ (note accurate weight of taken amount) in 250mL volumetric flask, dilute up to the mark with distilled water and then shake to form a uniform solution.

Equivalent weight of $K_2Cr_2O_7$ = Mol. Wt./6 = 294.18/6 = 49.03

∴ 250 ml (N/20) $K_2Cr_2O_7$ solution ≡ $\frac{49.03\ x\ 250}{}$ ≡ 0.6129 g of $K_2Cr_2O_7$

Table-4.2

Initial weight (g)	Final weight (g)	Amount of $K_2Cr_2O_7$ taken (g)	Strength of the solution (N/20)
W_1	W_2	$W_1 - W_2 = W$	S = W/0.6129

Standardisation of ≡ (N/20) Sodium thiosulphate solution:

Pipette out 10 ml of standard $K_2Cr_2O_7$ solution in a 250 ml conical flask, add 15 ml of 4(N) H_2SO_4 and pinch of solid KI. Cover the flask with a watch glass and keep in a dark place for 3 minutes. Add 100 ml of distilled water, titrate the liberated I_2 with S (N/20) $Na_2S_2O_3$ solution till straw yellow colour appears. Add 2 ml of 1% starch solution then solution turns to blue and continue the titration until blue colour just changes to light green. Repeat the experiment thrice.

Table-4.3

No. of obs.	Volm. of $K_2Cr_2O_7$ (ml)	Burette reading		Volm. of $Na_2S_2O_3$ soln. (ml)	Concordant volm. of $Na_2S_2O_3$ soln. (ml)
		Initial	Final		
1.	10	0	...	...	V_1
2.	10	...	...	...	
3.	10	...	...	...	

Measurement of Distribution Coefficient

Prepare three sets of mixture in 500 ml glass-stoppered bottles as follows:

Bottle No.	Volume of saturated I_2 soln. In CCl_4 (ml)	Volume of pure CCl_4 added (ml)	Volume of water added (ml)
1	20	0	200
2	15	5	200
3	10	10	200

Stopper the bottles properly and shake for 30 to 45 mins. Allow to settle about 10-15 mins. To separate into two distinct layers.Pipette out 50 ml of aqueous layer into a 250 ml conical flask containing 10 ml of 10% KI solution and 1 ml 1% starch solution. Now titrate against N/100 $Na_2S_2O_3$ solution.Repeat the experiment 2-3 times for each separate bottles.Pipette out 5 ml of carbon tetrachloride layer into a 250 ml conical flask containing 10 ml of 10% KI solution and 1 ml 1% starch solution. Now titrate against N/20 $Na_2S_2O_3$ solution.Repeat the experiment 2-3 times for each separate bottles.

Table- 4.4

Bottle No.	Volm. of CCl_4 layer (ml)	**Carbon tetrachloride layer**				**Aqucous layer**				
		Burette reading		Volm. of N/20 $S_2O_3^=$ (ml)	Con-cordant volume (ml)	Volm. of aqueous layer (ml)	Burette reading		Volm. of N/100 $S_2O_3^=$ (ml)	Con-cordant volume (ml)
		Initial	Final				Initial	Final		
1	5	0	...	...		50	0	...	...	
	5	0	...	...		50	0	...	...	
	5	0	...	...		50	0	...	...	
2	5	0	...	...		50	0	...	...	
	5	0	...	...		50	0	...	...	
	5	0	...	...		50	0	...	...	
2	5	0	...	...		50	0	...	...	
	5	0	...	...		50	0	...	...	
	5	0	...	...		50	0	...	...	

4.6 Calculation

Determination of strength of $Na_2S_2O_3$ solution :

Volume of $K_2Cr_2O_7$ solution = 25 ml

Strength of $K_2Cr_2O_7$ solution = S (N)

Volume of $Na_2S_2O_3$ solution = V_1 ml

Strength of $Na_2S_2O_3$ solution = S_1 = ?

We know that, $25 \times S$ (N) = $V_1 \times S_1$; $\therefore S_1 = 25 \times S/V_1$ (N)

Determination of Partition co-efficient

Bottle – 1 :

CCl_4 layer : Volume of CCl_4 layer = 5 ml

Strength of CCl_4 layer = C_1 = ?

Volume $Na_2S_2O_3$ solution = V_1

Strength of $Na_2S_2O_3$ solution = S_1

$\therefore C_1 = V_1$ x S_1 / 5 (N)

Aqueous layer : Volume of aqueous layer = 50 ml

Strength of aqueous layer = C_2 = ?

Volume $Na_2S_2O_3$ solution = V_2

Strength of $Na_2S_2O_3$ solution = S_2

$\therefore\ C_2 = V_2 \times S_2 / 50$ (N)

$\therefore\ K_1 = C_1/C_2$

Similarly calculate the concentration of I_2 in aqueous and CCl_4 layers for two other bottles separately.

$\therefore$ Partition co-efficient = $K = (K_1 + K_2 + K_3)/3$

4.7 Results

The value of partition coefficient for the distribution of I_2 between water and CCl_4 at ………….. temperature is …………………..

4.8 Summary

In this experiment, you determined the partition coefficient of iodine (I,) between water and carbon tetrachloride (CCl,,) using Nernst's Distribution Law. The partition coefficient describes how a solute distributes itself between two immiscible solvents at equilibrium. By measuring the concentration of iodine in both the aqueous and organic phases, you calculated the partition coefficient and examined how it is affected by temperature and solvent properties. This experiment provided practical insights into the principles of solubility, equilibrium, and the application of distribution laws in chemical processes such as solvent extraction and purification techniques.

4.9 Self-Assessment Questions

1. What is a partition coefficient, and why is it important in this experiment?
2. Can you explain Nernst's Distribution Law and how it applies to this experiment?
3. Why are water and carbon tetrachloride used as the two solvents in this experiment? What properties make them suitable for studying partitioning?
4. How do you measure the concentration of iodine in both the aqueous and organic layers?
5. What conditions must be met for the solute to reach equilibrium between the two immiscible solvents?
6. How might changes in temperature affect the partition coefficient, and why?
7. Under what conditions might the partition coefficient deviate from the value predicted by Nernst's Distribution Law?
8. How could you modify this experiment to study the partitioning behavior of a different solute or solvent system? What factors would you need to consider?

Unit 5 ❑ Verification of Ostwald's dilution law and determination of Ka of weak acid by conductometry

5.1 Objectives

After studying and performing this experiment, you should be able to:

- Explain the principle behind Ostwald's dilution law and its application to weak electrolytes.
- Use conductometry to measure the electrical conductivity of a weak acid at different dilutions.
- Determine the dissociation constant (K_a) of a weak acid by analyzing the conductivity data.
- Understand the relationship between molar conductivity, concentration, and the degree of dissociation for weak acids.
- Verify Ostwald's dilution law experimentally by calculating the degree of dissociation of the weak acid at different concentrations.
- Apply the concept of limiting molar conductivity in the context of weak electrolytes.

5.2 Introduction

Ostwald’s dilution law is a fundamental principle in physical chemistry that explains the relationship between the dissociation of weak electrolytes and their concentration in solution. For weak acids and bases, which only partially dissociate in water, this law provides a way to calculate the degree of dissociation at varying concentrations. According to Ostwald’s dilution law, the degree of dissociation of a weak electrolyte increases as its concentration decreases, and this can be quantitatively related to the dissociation constant (Ka) of the electrolyte.

The importance of Ostwald’s dilution law lies in its ability to help us understand and predict the behaviour of weak electrolytes in dilute solutions. It is crucial for calculating the dissociation constant, which is an important parameter that reflects the strength of a weak acid or base. Verifying this law experimentally allows chemists to confirm the theoretical behavior of weak acids and to measure their dissociation constants with accuracy.

Conductometry, a method used to measure the electrical conductivity of solutions, plays an essential role in this experiment. Since the conductivity of a solution depends on the concentration and mobility of ions, it provides a powerful tool to study the dissociation of weak acids. As the concentration of a weak acid changes, its conductivity will vary due to the changing number of ions in the solution. By measuring the conductivity at different dilutions, the dissociation constant (Ka) of the weak acid can be determined.

5.3 Theory

A monobasic weak acid HA, is partially ionised in aqueous solution.

$$HA \rightleftharpoons H+ + A-$$

$$c(l-\alpha)\ c\alpha c\alpha$$

The ions are aquated and the degree of ionisation (a) increases with dilution.

The degree of ionization of a weak electrolyte, such as HA, at a particular concentration (c) can be approximated by the ratio $\frac{\lambda}{\lambda_0}$, where λ represents the equivalent conductance of HA at concentration c, and λ_0 is the equivalent conductance at infinite dilution. The ionization constant K_a for the weak acid HA is given by:

$$K_a = \frac{a^2[H^+][A^-]}{[HA]}$$

where a represents the activity of the respective species. Since activity a is the product of molar concentration and the activity coefficient f, we can modify the equation as

$$K_a = \frac{c\alpha^2}{(1-\alpha)}f$$

For dilute solutions of weak acids, the ionic strength is very low, making the activity coefficient f close to unity (as per Debye-Hückel limiting law). In such cases, the equation simplifies to

$$K_a = \frac{c\alpha^2}{(1-\alpha)}$$

By substituting $\alpha = \frac{\lambda}{\lambda_o}$

$$K_a = \frac{c(\frac{\lambda}{\lambda_o})^2}{(1-\frac{\lambda}{\lambda_o})}$$

Rearranging we get

$$\frac{1}{\lambda} = \frac{1}{\lambda_o} + \frac{c}{K_a{\lambda_o}^2}$$

If we prepare a series of solutions of the weak acid HA at different concentrations and determine their equivalent conductances using a conductometric cell with a known cell constant, we can plot $\frac{1}{\lambda}$ against c. This should yield a straight line with a positive intercept of $\frac{1}{\lambda_o}$ and a slope of $\frac{1}{K_a{\lambda_o}^2}$. So can be calculated as

$$K_a = \frac{intercept^2}{slope}$$

5.4 Requirements

Apparatus

- Conductivity meter
- Conductivity cell
- 100 ml beakers
- Volumetric flasks (100 ml, 250 ml)
- Pipettes (25 ml)
- Burettes (50 ml)

Chemicals

- Potassium chloride (KCl)
- Oxalic acid
- Sodium hydroxide (NaOH)
- Acetic acid (CHƒ COOH)
- Phenolphthalein indicator
- Distilled water

5.5 Procedure

Preparation of KCl Solutions

- Prepare 250 ml of a standard KCl solution (strength slightly higher than N/10) using conductivity water.
- Accurately dilute the standard KCl solution to prepare:
    - 100 ml of an exact N/10 KCl solution.
    - 100 ml of an exact N/100 KCl solution.

Determination of Cell Constant

- Rinse a 100 ml beaker and the conductivity cell thoroughly with the N/100 KCl solution.
- Pour enough N/100 KCl solution into the beaker to fully immerse the conductivity cell.
- Record the conductance.
- Repeat the procedure using the N/10 KCl solution.
- Calculate the cell constant using the measured conductance values and the literature values of the specific conductance for KCl at both concentrations.

Table 5.1: Determination of Cell Constant

KCl Solution	**Concentration (N)**	**Specific Conductance (S/m)**	**Measured Conductance (S)**	**Cell Constant (cm^{-1})**
KCl (N/100)				
KCl (N/10)				

Preparation of 250ml (N/10) oxalic acid and (N/100 acetic acid solution:

Dissolve near about 1.5758 g oxalic acid (note accurate weight of taken amount) in 250mL volumetric flask, dilute up to the mark with distilled water and then shake to form a uniform solution.

☐ Strength of prepared oxalic acid solution = $\frac{\textit{Actual weight of oxalic acid taken}}{1.5758}(\frac{N}{10}) = S_1(N)$

Table -1

Initial weight (g)	Final weight (g)	Amount of oxalic acid taken (g)	Strength of the solution (N/20)
W_1	W_2	$W_1 - W_2 = W$	$S_1 = W/1.5758$

- Prepare ~N/10 NaOH and standardize it against the oxalic acid using phenolphthalein as an indicator.
- Prepare a ~N/10 acetic acid solution and standardize it using the standardized NaOH solution.

- Accurately dilute the N/10 acetic acid solution to prepare100 ml of an exact N/50 acetic acid solution using a volumetric flask.

Conductance Measurements:

- Measure the conductance of the conductivity water and subtract it from all recorded values to correct for background conductance
- In a clean, dry 100 ml beaker, take 50 ml of the N/50 acetic acid solution using a 25 ml pipette.
- Immerse the conductivity cell into the solution, stir, and record the conductance.
- Pipette out 25 ml of the N/50 acetic acid solution and replace it with 25 ml of conductivity water, thoroughly washing the pipette between uses.
- Record the conductance of the resulting N/100 acetic acid solution.
- Repeat this process to progressively dilute the acetic acid to N/200, N/400, and N/800 concentrations, recording the conductance of each solution.

Table 5.2: Conductance of Diluted Acetic Acid Solutions

Acetic Acid Concentration (N)	Measured Conductance (S)	Corrected Conductance (S)
N/50		
N/100		
N/200		
N/400		
N/800		

5.6 Calculations

Calculate the equivalent conductance (Λ) of each acetic acid solution

Table 5.3: Calculation of Equivalent Conductance

Acetic Acid Concentration (N)	Corrected Conductance (S)	Specific Conductance (S/m)	Equivalent Conductance (Λ) (S cm²/mol)
N/50			
N/100			
N/200			
N/400			
N/800			

Plotting and Determining Constants:

- Plot 1/Λ against the concentration c.
- Determine the intercept $1/\Lambda_0$ and calculate Λ_0 (the equivalent conductance at infinite dilution).
- Estimate K_a using the slope and intercept based on the equation

$$K_a = \frac{intercept^2}{slope}$$

5.7 Results

The dissociation constant of acetic acid is …………

5.8 Summary

In this experiment, the conductometric method is used to verify Ostwald's Dilution Law and determine the dissociation constant (K_a) of a weak acid, such as acetic acid. By measuring the conductance of acetic acid solutions at various concentrations and applying corrections for the conductivity of water, the equivalent conductance at infinite dilution is obtained. Using the relationship between the degree of ionization and concentration, the dissociation constant is determined. The experiment provides valuable insights into the behavior of weak electrolytes and reinforces the practical applications of conductometry in studying ionization phenomena.

5.9 Self-Assessment Questions

1. What is Ostwald's Dilution Law, and how does it apply to weak electrolytes?
2. Why is conductometry suitable for studying the ionization of weak acids?
3. What is the significance of determining the Ka value of a weak acid?
4. How is the equivalent conductance related to the specific conductance of a solution?
5. What role does the conductance of distilled water play in the experiment, and how is it corrected?
6. Why is it important to measure the conductance of acetic acid at different concentrations?
7. How can you obtain, the equivalent conductance at infinite dilution, from your experimental data?
8. What is the relationship betweenand the degree of ionization (α) for a weak acid?
9. How can the Ka value be calculated from the slope and intercept of the graph plotted during the experiment?
10. What is the significance of the cell constant in conductometric measurements, and how is it determined?

Unit 6 ❑ Determination of solubility of sparingly soluble salt in water, in electrolyte with common ions and in neutral electrolyte (using common indicator)

6.1 Objectives

On completion of study and experiment of this unit the learner will be able to-

- Determine the solubility of a sparingly soluble salt in pure water using a common indicator.
- Assess the effect of a common ion on the solubility of the sparingly soluble salt in an electrolyte solution.
- Evaluate the solubility of the sparingly soluble salt in a neutral electrolyte solution.
- Understand the influence of ionic strength and common ion effect on the solubility of the sparingly soluble salt.
- Apply theoretical concepts related to solubility and common ion effect to practical measurements.

6.2 Introduction

Understanding the solubility of salts is fundamental in physical chemistry, as it provides insight into the behaviour of ionic compounds in various solutions. This experiment focuses on determining the solubility of a sparingly soluble salt in water, in an electrolyte with common ions, and in a neutral electrolyte, using a common indicator to facilitate the observation of equilibrium.The solubility product constant is a key concept in solubility chemistry. It represents the equilibrium constant for the dissolution of a sparingly soluble salt, indicating the extent to which the salt dissolves in a solution to form ions. This constant is crucial for predicting the solubility of salts under different conditions and for understanding the effects of common ions on solubility.

In real-life applications, the solubility product has significant implications in areas such as pharmaceuticals, where it influences the formulation of drugs; in environmental science, where it affects the behaviour of pollutants; and in industrial processes, where it impacts the efficiency of various chemical reactions and separations.

By performing this experiment, learners will gain hands-on experience with concepts such as equilibrium, ionic interactions, and the common ion effect. This practical understanding will enhance their grasp of physical chemistry principles and their applications, providing a foundation for analyzing and predicting the behavior of ionic compounds in different environments.

6.3 Theory

The product of the concentration of the ions of the salt in the saturated solution of that salt is called the solubility product of that salt.

Silver bromate (or Silver acetate) is sparingly soluble in water. It ionised as follows :

$$AgBrO_3\text{ (Solid)} \rightleftharpoons AgBrO_3\text{ (Solution)} \rightleftharpoons Ag^+ + BrO_3^-$$

Or,

$$AgOAc\text{ (Solid)} \rightleftharpoons AgOAc\text{ (Solution)} \rightleftharpoons Ag^+ + AcO^-$$

Thermodynamically it can be shown that the products of activities of Ag^+ and BrO_3^- (or AcO^-) ions is a constant at a given temperature.

$a_{Ag^+} . a_{BrO_3^-} = S_a$ where, S_a = Activity solubility of Silver bromate

Since activity of a substance is equal to the product of its concentration and activity coefficient.

We have,

$$S_a = a_{Ag^+} . a_{BrO_3^-} = C_{Ag^+} . C_{BrO_3^-} . f_{Ag^+} . f_{BrO_3^-} = C_{Ag^+} . C_{BrO_3^-} . (f_{\pm})^2$$

In very dilute solution,

$$f_{Ag^+} = f_{BrO_3^-} = 1$$

$\therefore S_a = C_{Ag^+} . C_{BrO3^-} = K_{sp}$ (concentration solubility product)

$= S \times S = S^2$ (S = molar solubility of ions)

$S = -\sqrt{S_a}$

So, the molar solubility 'S' of the salt in pure water is a constant at a given temperature.

Effect of Common Ion

The solubility of a sparingly soluble salt in water is much affected by the presence of other salts having a common ion, as contained by that sparingly soluble salt.

The product, $K_{sp} = C_{Ag^+} . C_{BrO3^-}$, does not remain constant when either C_{Ag^+} or C_{BrO3^-} is altered by the addition of common ion from another compound. But S_a remains constant.

When silver nitrate is added to a saturated solution of silver bromate, the activity or concentration of Ag^+ ions becomes large. So, to keep the 'S_a' constant, activity of BrO_3^- ions should decrease, with increase of concentration of Ag^+ ions. Thus, as C_{BrO3^-} decreases, this is reflected as a decrease in the solubility of silver bromate.

Addition of Neutral (Inert) electrolyte

The solubility of sparingly soluble salt is highly influence by the presence of other salts in solution. Which do have common ion with the saturating salt. So the solubility product, K_{sp}, will vary, when other salts are present in the solution.

The presence of other salts (neutral/ inert electrolytes) increase the ionic strength (*i*) of the solution. According to the Debye – Huckel Limiting Law, the increase ionic strength (*i*) reduce the activity coefficient (f) of the saturating salt, silver bromate (or silver acetate). So, in order to keep the activity product, S_a, constant, the concentration solubility product,K_{sp}, must increase. That is, the molar solubility (S) will increase. Thus, " Concentration solubility product" may vary but the " activity solubility product " remains constant.

6.4 Requirements

Apparatus

i) 250 ml volumetric flask

ii) Burette

iii) Pipette

iv) 250 ml conical flask

v) Bottles with stopper

Chemicals

a) Silver bromate (or Silver acetate)

b) Silver nitrate

c) KNO_3

d) NH_4CNS or KCNS

e) Ferric alum

f) Concentrated HNO_3

6.5 Procedure

Recording of room temperature

Table 6.1: Recording of Room Temperature

Temperature before experiment ^{0}C	Temperature after experiment ^{0}C	Mean temperature ^{0}C

Preparation of 250 ml of standard 0.01 (N) $AgNO_3$ solution

Prepare 250 ml of $AgNO_3$ solution of the order 0.01(N) (or slightly higher)

Table 6.2: Preparation of 250 ml of standard 0.01 (N) $AgNO_3$

Initial weight (g)	Final weight (g)	Weight taken (g)	Weight required (g)	Volume to be made (ml)	Strength of $AgNO_3$ solution
W_1	W_2	$W = W_1 - W_2$	0.4247	250	$W/0.4247 = S_1$ (N/100)

Preparation of 100 ml of standard 0.01 (N) KNO_3 solution

Prepare 100 ml of KNO_3 solution of the order 0.01(N)

Table 6.3: Preparation of 100 ml of standard 0.01 (N) KNO_3 solution

Initial weight (g)	Final weight (g)	Weight taken(g)	Weight required(g)	Volume to be made (ml)	Strength of KNO_3 solution (N/100)
W_3	W_4	$W = W_3 - W_4$	0.2528	100	W/0.2528

Standardisation of NH_4CNS (or KCNS) solution with 0.01 (N) AgNO3 solution

Prepare 250 ml of 0.05 (N) NH_4CNS or KCNS solution.Standardize NH_4CNS or KCNS solution against standard 0.01 (N) $AgNO_3$ solution, using ferric alum in conc. HNO_3, as indicator, till faint permanent pink colour appears.

Preparation of Ferric Alum indicator :

Dissolve about 8 g of Ferric ammonium sulphate in 20 ml of distilled water and then add 5 ml of conc. HNO_3. Use 1 ml of this indicator for each titration.

Pipette out 25 ml of silver nitrate solution in a 250 ml conical flask containing 20 ml of distilled water. Add 1 ml of ferric alum indicator. Titrate with ammonium thiocyanate (or potassium thiocyanate) solution from burette till permanent pink colour persists.

Table 6.4: Standardisation of NH_4CNS (or KCNS) solution with 0.01 (N) $AgNO_3$ solution

No. of obs.	Volm. of $AgNO_3$ (ml)	Burette reading		Volm. of NH_4CNS soln. (ml)	Concordant volm. of NH_4CNS soln. (ml)
		Initial	Final		
1.	25	0	...	...	V_2
2.	25	...	...	...	
3.	25	...	...	...	

Measurement of Solubility Product

Take three well-stoppered bottles and mark as I, II & III.

About 0.5 g of silver bromate (or silver acetate) [weighed approximately] in each bottle. Then make the following addition as follows:

Bottle No. I : 50 ml distilled water

Bottle no. II : 50 ml 0.01 (N) $AgNO_3$ solution

Bottle No. III : 50 ml 0.01 (N) KNO_3 solution.

The bottles are then stoppered well and shaken in a mechanical shaker for about 30 minutes.

Filter the contents of the Bottle No. I and collect the filtrate in a dry and clean beaker. 10 ml of the filtrate is then titrated with 0.05 (N) NH_4CNS or KCNS solution, using ferric alum as indicator. While pipetting out the sample solution, put cotton / glass wool in the tip of the pipette.

Repeat the procedure (vii) above for Bottle No. II & III.

Calculate the concentration of silver each bottle. Hence, the molar solubilites and "Concentration Solubility Products" of silver bromate (or Silver acetate) are found out.

6.6 Calculations

Strength of NH_4CNS solution = S_2

Volume of NH_4CNS solution = V_2

Strength of $AgNO_3$ solution = $S_1(N/100)$

Volume of $AgNO_3$ solution = V_1 = 25 ml $S_2 = (25.\ S_1 / V_2)\ N / 100$

Table – 6.5 : Contents of Three Bottles

Bottle No.	$AgBrO_3$ (or AgOAc) (g)	0.01 (N) $AgNO_3$ (ml)	0.01 (N) KNO_3 (ml)	Distilled water (ml)
I	1	Nil	Nil	50
II	1	50	Nil	Nil
III	1	Nil	50	Nil

Table – 6.6 : Estimation of Ag^+ in bottles by titration with standard NH_4CNS solution

Bottle No.	Volm. of aliquot taken (ml)	Burette reading		Volm. of NH_4CNS soln. (ml)	Concordant volume (ml)	Molar concentration of Ag^+
		Initial	Final			
I	10	0	...	...	X_1	$X_1 \times S_2 / 10 = y_1$ (M)
	10	...	...	...		
II	10	...	...	...	X_2	$X_2 \times S_2 / 10 = y_2$ (M)
	10	...	...	...		
III	10	...	...	...	X_3	$X_3 \times S_2 / 10 = y_3$ (M)
	10	...	...	...		

Table – 6.7 : Molar Solubility and Concentration Solubility Product of Silver Bromate (or Silver Acetate)

Bottle No.	Molar concentration of Ag^+	Molar concentration of BrO_3^- (or AcO^-)	Molar Solubility of $AgBrO_3$ (orAgOAc)	Solubility Product of $AgBrO_3$ (orAgOAc) (Ksp)
I	y_1 (M)	y_1 (M)	y_1 (M)	y_1^2
II	y_2 (M)	$y_2 - 0.01$ (M)	$y_2 - 0.01$ (M)	$y_2 (y_2 - 0.01)$
III	y_3 (M)	y_3 (M)	y_3 (M)	y_3^2

6.7 Results

The value of solubility product of silver chloride is ……………………..

6.8 Summary

In this experiment, learners determine the solubility of a sparingly soluble salt in pure water, an electrolyte solution with a common ion, and a neutral electrolyte solution. Using a common indicator, learners observe and measure the extent of dissolution and how it is influenced by the presence of common ions. The solubility product constant is calculated based on the experimental data, illustrating the impact of ionic strength and the common ion effect on solubility. This experiment provides practical insight into the concepts of solubility equilibrium and the common ion effect, reinforcing the theoretical understanding of these phenomena in physical chemistry.

6.9 Self-Assessment Questions

1. What is the solubility product constant, and how is it calculated?
2. How does the presence of a common ion affect the solubility of a sparingly soluble salt?

3. Why is a common indicator used in this experiment, and how does it aid in determining solubility?
4. What are the differences in solubility of a sparingly soluble salt in pure water versus an electrolyte solution with a common ion?
5. How can you determine the solubility of the salt in a neutral electrolyte solution from your experimental data?
6. What is the significance of the common ion effect in this experiment?
7. How does the ionic strength of a solution influence the solubility of a salt?
8. What steps are involved in preparing the solutions for this experiment, and why is accuracy important?
9. How do you interpret the results obtained from this experiment to determine the solubility product constant?
10. What are some real-life applications of the solubility product constant and the common ion effect?

Unit 7 ❑ Determination of K_{eq} for KI + I_2= KI_3, using partition coefficient between water and CCl_4

7.1 Objectives

On completion of this unit the learners will be able to-

- Understand the concept of equilibrium constant and how it relates to the distribution of species in a chemical reaction.
- Determine the equilibrium constant for the reaction KI+I2’!KI_3 using the partition coefficient of iodine between water and carbon tetrachloride
- Apply the Nernst distribution law to analyze the partitioning of iodine between two immiscible solvents
- Calculate the concentration of tri-iodide ion formed in the aqueous phase from experimental data.
- Learn the importance of partition coefficients in determining the equilibrium concentrations of reactants and products in heterogeneous systems.
- Enhance skills in titration and data analysis to calculate equilibrium constants

7.2 Introduction

In a previous experiment, we explored Nernst's Distribution Law by determining the partition coefficient of iodine between water and carbon tetrachloride. That experiment introduced the concept of how a solute distributes itself between two immiscible solvents, governed by the concentration ratio in each solvent at equilibrium. In this experiment, we build on that foundational knowledge by determining the equilibrium constant (K_{eq}) for the reaction between potassium iodide (KI) and iodine (I_2) to form triiodide ion (KI_3), using the partition coefficient. This experiment not only reinforces the principles of distribution laws but also provides insights into chemical equilibria and how equilibrium constants can be experimentally determined. By comparing the distribution of iodine between two phases before and after the reaction, learners will gain an advanced understanding of both partition behaviour and equilibrium chemistry, valuable in many areas of physical and analytical chemistry.

7.3 Theory

Iodine is more soluble in aqueous potassium iodide solution than in water because iodine reacts chemically with an aqueous solution of potassium iodide to produce potassium tri-iodide. The reaction can be expressed as

$$KI + I_2 \rightleftharpoons KI_3 \quad \text{or,} \quad I_2 + I^- \rightleftharpoons I_3^- \quad \text{(in aqueous solution)}$$

The equilibrium constant 'K' for this reaction may be expressed as –

$$K = \frac{a_{KI_3}}{a_{KI} \times a_{I_2}}$$

Where 'a' represents the activity of the species at equilibrium.

For dilute solution, a $\cong$ C, where 'C' represents the molar concentrations of the species at equilibrium, then, the equilibrium constant 'K' is given by,

$$K = \frac{C_{KI_3}}{C_{KI} \times C_{I_2}}$$

According to Nernst distribution law, when a solute is added to two immiscible liquids in contact with each other, the solute distributes itself between the solvents in such a way that at equilibrium the ratio of the activities (or the molar concentration, if the solutions are very dilute) of the solute in the two solvents is found to be a constant, at constant temperature, is known as partition or distribution coefficient. Applying this law to iodine for water and immiscible organic solvent (CCl_4), we have –

$$K_d = \frac{a_{I_2}\ (\text{org})}{a_{I_2}\ (\text{water})} = \frac{C_{I_2}\ (\text{org})}{C_{I_2}\ (\text{water})}$$

We now evaluate the quantities required for determination of the equilibrium constant, K.

$$K = \frac{[KI_3]_{aq}}{[KI]_{aq}\,[I_2]_{aq}}$$

For dilute solution activities are represented by the concentration terms (equilibrium value).

i) Let C = total initial concentration of KI, C_w = total iodine concentration in aqueous layer at equilibrium, C_0 = total iodine concentration in organic (CCl_4) layer at equilibrium.

ii) Concentration of free I_2 in aqueous layer = $[I_2]_{aq} = [I]_{org} / K_d = C_0 / K_d$ [from definition of K_d]

iii) $[KI_3]_{aq}$ = (total iodine conc. in aq. Layer) – (conc. of free iodine in aq. Layer) = $(C_w - C_0 / K_d)$

iv) $[KI]_{aq}$ = (Initial conc. of KI) – (amount consumed to form equivalent amount of KI_3)

$= C - (C_w - C_0 / K_d)$

Hence, $$K_{eqm} = \frac{C_w - \dfrac{C_0}{K_d}}{\{C - (C_w - \dfrac{C_0}{K_d})\}\,\dfrac{C_0}{K_d}}$$

Thus from the determination of C, C_w and C_0 experimentally and knowing the value of K_d (experimentally determined, or supplied or from literature) the value of the equilibrium constant 'K' may be calculated, at the temperature of the experiment.

7.4 Requirements

Apparatus

i. Three dry 250 ml glass- stoppered bottles

ii. Volumetric flask (250 ml)

iii. Burette

iv. Pipette

v. Conical flask (500 ml & 250 ml)

vi. Mechanical shaker

Chemicals

i. Saturated I_2 solution in CCl_4

ii. Pure CCl_4

iii. A.R KI

iv. A.R. $K_2Cr_2O_7$

v. (N/20) $Na_2S_2O_3$ solution [S 12.5 g in 1000 ml]

vi. 10% KI solution

vii. 1% freshly prepared starch solution.

7.5 Procedure

Recording of room temperature

Table 7.1: Recording of Room Temperature

Temperature before experiment ^{0}C	Temperature after experiment ^{0}C	Mean temperature ^{0}C

Preparation of 250 ml (N/20) $K_2Cr_2O_7$ solution

Weigh approximately 0.6128 gm $K_2Cr_2O_7$and transfer in a volumetric flask. Then fill up to the mark with 250 ml distilled water. Dissolve thoroughly.

Table – 7.2 : Preparation of 250 ml (N/20) $K_2Cr_2O_7$ solution

Initial weight (g)	Final weight (g)	Weight taken(g)	Weight required(g)	Volume to be made (ml)	Strength of $K_2Cr_2O_7$ solution
W_1	W_2	$W = W_1 - W_2$	0.6128	250	(W/0.6128) N/20

Preparation of 500 ml (N/20) KI solution

Follow similar procedure to prepare the solution.

Table – 7.3 : Preparation of 500 ml (N/20) KI solution

Initial weight (g)	Final weight (g)	Weight taken(g)	Weight required(g)	Volume to be made (ml)	Strength of KI solution
W_3	W_4	$W = W_3 - W_4$	4.15	250	(W/4.15) N/20

Standardisation of (N/20) Na2S2O3 solution with standard ~ (N/20) $K_2Cr_2O_7$ solution

First prepare 500 ml of approximately (N/20) $Na_2S_2O_3$ solution. Then pipette out 25 ml of standard ~ (N/20) $K_2Cr_2O_7$ solution into a 500 ml conical flask, add 25 ml of 4 (N) H_2SO_4 and 10 ml of 10% KI solution. Cover the mouth of the conical flask with a watch glass and keep in dark for about 5 minutes. Dilute to 200 ml by adding 165 ml of distilled water, titrate the liberated iodine with ~ (N/20) $Na_2S_2O_3$ solution till a straw yellow (pale yellow) colour appears. Add 2 ml of starch solution when it turns blue and continue the titration until the blue colour is just discharged.

Table – 7.4 : Standardisation of S (N/20) $Na_2S_2O_3$ solution against standard $K_2Cr_2O_7$ solution

No. of obs.	Volm. of $K_2Cr_2O_7$ (ml)	Burette reading		Volm. of $Na_2S_2O_3$ soln. (ml)	Concordant volm. of $Na_2S_2O_3$ soln. (ml)	Strength of $Na_2S_2O_3$ solution (N)
		Initial	Final			
1.	25	0	...	...		
2.	25	...	...	...		
3.	25	...	...	...		

Determination of Concentration in Aquoes and Organic Layer

Prepare the following mixtures in dry, clean, leak proof glass stoppered 250 ml bottles.

Table – 7.5 : preparation Mixture

Bottle No.	Vol. of (N/20) KI sol. (ml)	Vol. of water (ml)	Vol. of I_2 in CCl_4 (ml)	Concn. of KI sol. (M)
1	15	100	35	0.005
2	25	100	25	0.00833
3	35	100	15	0.01667

Shake the bottles for about 45 minutes and then allow to stand for 15 minutes for complete separation of layers.Pipette out 5 ml of organic layer from each bottle in a 250 ml conical flask. Add 10 ml of 10% KI solution and about 20 ml of distilled water. Shake the mixture thoroughly and titrate against standard S (N/20) $Na_2S_2O_3$ solution as usual following iodometric method. Then calculate C_0.Pipette out 10 ml of aqueous KI layer from each bottle in a 250 ml conical flask. Add 30 ml of distilled water and titrate against standard S (N/20) $Na_2S_2O_3$ solution as usual following iodometric method. Then calculate C_w.Determine partition coefficient (K_d) of iodine between CCl_4 and water.

Table – 7.6 : Titration of solvent layers

		CCl$_4$ layer						Aqueous KI layer								
			Burette reading						Burette reading							
Bottle Nos.	No. of obs.	Vol of aliquot (ml)	Initial	Final	Vol. of $Na_2S_2O_3$ (ml)	Concordant Vol. of $Na_2S_2O_3$ (ml)	Value of C_0	Vol of aliquot (ml)	Initial	Final	Vol. of $Na_2S_2O_3$ (ml)	Concordant Vol. of $Na_2S_2O_3$ (ml)	Value of C_w	Partition co-efficient $K_d = C_o/C_w$	Conc. of free I_2 in aq. layer (C_o / K_d)	Conc. of $[KI_3]_{aq} = C_w - C_0 / K_d$ (M)
1	1	5	0	...	...			10	0	...	...					
	2	5	...	...	...			10	...	...	...					
	3	5	...	...	...			10	...	...	...					
2	1	5	0	...	...			10	0	...	...					
	2	5	...	...	...			10	...	...	...					
	3	5	...	...	...			10	...	...	...					
3	1	5	0	...	...			10	0	...	...					
	2	5	...	...	...			10	...	...	...					
	3	5	...	...	...			10	...	...	...					

7.6 Calculations

Partition coefficient = $K_d = C_{(org)} / C_{(aq)} = C_0 / C_w = K_1$

$\therefore$ Partition coefficient = $K_d = (K_1 + K_2 + K_3) / 3$

$$K_{eqm} = \frac{C_w - \frac{C_0}{K_d}}{\{C - (C_w - \frac{C_0}{K_d})\}\frac{C_0}{K_d}}$$

$$\therefore\ K_{eqm} = (K^{'}_{eqm} + K^{''}_{eqm} + K^{'''}_{eqm})\ /\ 3 = K_{eqm}\ \text{at....}\ {}^{0}C$$

7.7 Results

The equilibrium constant of the reaction is

7.8 Summary

In this experiment, the equilibrium constant (K_{eq}) for the reaction between potassium iodide (KI) and iodine (I_2) to form triiodide (KI_3) is determined using the partition coefficient of iodine between water and carbon tetrachloride (CCl_4). The experiment involves several key steps. First, sodium thiosulphate ($Na_2S_2O_3$) is standardized using potassium dichromate ($K_2Cr_2O_7$) to ensure accurate titration results. Then, iodine is distributed between the aqueous and organic (CCl_4) phases, and samples from both layers are titrated with the standardized $Na_2S_2O_3$ solution to determine the concentration of iodine in each layer. The partition coefficient is calculated from the iodine concentrations in the two layers, and this information is used to determine the equilibrium constant for the reaction. This experiment enhances understanding of equilibrium constants, partition coefficients, and titrimetric analysis.

7.9 Self-Assessment Questions

1. What is the partition coefficient, and how is it relevant to this experiment?
2. Why is iodine more soluble in carbon tetrachloride than in water?
3. How do you calculate the equilibrium constant for the reaction $KI+I_2$’!?
4. Why do we use sodium thiosulphate to titrate iodine in this experiment?

5. What is the purpose of standardizing the sodium thiosulphate solution?
6. How does the presence of KI affect the distribution of iodine between the water and CCl_4 layers?
7. Can you explain the steps involved in calculating the partition coefficient from the titration data?
8. Why is the equilibrium constant important in understanding the formation of KI_3?
9. What role does the Nernst Distribution Law play in this experiment?
10. How does this experiment relate to real-life applications of partition coefficients in chemical processes?

Unit 8 ❑ Determination of Ksp for AgCl by potentiometric titration of AgNO3 solution against standard KCl solution

8.1 Objectives

After study and completion of this experiment, the learner will be able to:

- Understand the concept of solubility product (Ksp) and its significance in predicting the solubility of sparingly soluble salts.
- Explain the principle of potentiometric titration and its application in determining the Ksp of silver chloride (AgCl).
- Perform the potentiometric titration of silver nitrate ($AgNO_3$) solution against a standard potassium chloride (KCl) solution.
- Accurately measure and record potential changes using a potentiometer to identify the equivalence point.
- Calculate the solubility product (Ksp) of AgCl from the titration data collected.
- Interpret the results in terms of theoretical solubility of AgCl in aqueous solutions.

- Analyze the effect of ionic strength on the solubility product and apply this understanding to other chemical systems.

8.2 Introduction

In this experiment, the determination of the solubility product (Ksp) of silver chloride (AgCl) will be carried out using potentiometric titration. The solubility product is a fundamental concept in chemistry that helps in understanding the solubility of sparingly soluble salts. It provides a quantitative measure of how much a salt can dissolve in a solvent before reaching saturation. The Ksp is particularly useful in predicting the formation of precipitates, determining the conditions for precipitation reactions, and understanding equilibrium in ionic solutions.The significance of this experiment lies in its practical application for accurately determining the solubility of a compound like AgCl. This information can be used in areas such as analytical chemistry, geochemistry, and environmental science where solubility controls various natural and industrial processes.Potentiometric titration offers distinct advantages over conventional titration methods. Instead of relying on a visual indicator to detect the equivalence point, potentiometric titration uses an electrode to measure the change in potential of the solution as the titration proceeds. This provides higher precision and is particularly useful for reactions where there is no sharp colour change or where the endpoint is not easily observable. The potentiometric method is more sensitive and accurate, especially in cases involving complex mixtures or low concentrations of ions, making it an ideal technique for determining the Ksp of AgCl in this experiment.

8.3 Theory

When a solution of $AgNO_3$ is taken in a beaker and clean Ag wire is inserted in it to act as an electrode the Ag^+/Ag (s) half-cell is produced, which is reversible with respect to Ag^+ ions. If this electrode is coupled with a reference electrode, such as saturated calomel electrode (SCE), (Pt) Hg (l) | Hg_2Cl_2 (s) | KCl (sat, aq), the following electrochemical cell is produced :

Saturated Calomel Electrode (SCE) || Ag^+ (aq) | Ag (s)

Where, || represents salt bridge (agar-agar, KNO_3 or NH_4NO_3), which eliminates the liquid junction potential.

The half – cell reactions occurring at the electrodes are as follows :

At Left hand electrode,

$$2Hg\,(l) + 2Cl^- \rightleftharpoons Hg_2Cl_2\,(s) + 2e$$

At Right electrode,

$$Ag^+\,(aq) + e \rightleftharpoons Ag\,(s)$$

The cell reaction is,

$$2Hg\,(l) + 2Cl^- + 2Ag^+\,(aq) \rightleftharpoons Hg_2Cl_2\,(s) + 2Ag\,(s)$$

The *emf* of the cell at 25 ^{0}C is given by,

$$E_{cell} = E_R - E_L = E_{Ag^+/Ag} - E_{SCE}$$

$$= E^0_{Ag^+/Ag} + 0.059 \log \frac{a_{Ag^+(aq)}}{a_{Ag\,(s)}} - E_{SCE} \quad \ldots \quad \ldots \quad (i)$$

Where 'a' is represented as the activity of the species, E^0 is the standard electrode potential (means when all species being at the standard state of unit activity).

Since Ag (s) is in the standard state, its activity is unity. When the solution is dilute, the activity comes numerically equal to the molar concentration as activity coefficient (f) tends to unity. Thus for dilute solution, the equation (i) at 25^{0}C becomes,

$$E_{cell} = E^0_{Ag^+/Ag} + 0.059 \log [Ag^+] - E_{SCE} \quad \ldots \quad \ldots \quad (ii)$$

The *emf* of the cell varies with the change of $[Ag^+]$, as E_{SCE} remains unchanged at a given temperature and $E^0_{Ag+/Ag}$ is constant.

When a solution of KCl is added to the $AgNO_3$ solution, AgCl will be precipitate out and the concentration of Ag^+ will decrease as AgCl is a sparingly soluble salt.

$$Ag^+\,(aq) + Cl^-\,(aq) = AgCl\,(s)$$

As a consequence the value of E_{cell} decreases. A sharp drop in the value of E_{cell} occurs on adding a small amount (~1 drop) of KCl solution near the equivalence point.

Ag^+ ions present at the equivalence point come the dissociation of sparingly soluble salt AgCl.

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$

The activity of Ag^+ and Cl^- are identical and the activity solubility product of AgCl is given by –

$$K_s = a_{Ag^+} \times a_{Cl^-}$$

As the solution is dilute, so the activity may be replaced by the numerical value of the molar concentrations of the species and the solubility product of AgCl can be represented as

$$K_s = a_{Ag^+} \times a_{Cl^-} = [\overset{+}{Ag}][\overset{-}{Cl}] = [\overset{+}{Ag}]^2 \text{5″} [Ag^+] = [Cl^-]$$

$$\therefore [Ag^+] = K_s^{1/2}$$

The E_{cell} at equivalence point is given by ;

$$E_{cell}\,(eqv.) = E^0_{Ag^+/Ag} + (0.059/2) \log K_s - E_{SCE} \quad \ldots \quad \ldots \quad (iii)$$

So, K_s can be determined by measuring E_{cell} (eqv.), knowing the value of $E^0_{Ag^+/Ag}$ and E_{SCE}.

If the room temperature is T° K then the factor 0.059 is to be modified to (0.059 T/298).

Beyond the equivalence point, further addition of KCl solution will further decrease the {Ag^+] due to the common ion effect of Cl^- ions. Hence E_{cell} will gradually decrease with increase of [Cl^-].

The volume of KCl solution required to completely precipitate Ag^+ ions as AgCl may be obtained from inflection of the graph plotted E_{cell} Vs. n (number of drops of KCl solution) and E_{cell} at equivalence point.

8.4 Requirements

Apparatus

i) Potentiometer

ii) Silver electrode

iii) Saturated calomel electrode

iv) Beaker

v) Pipette

vi) Burette

vii) ~2(M) KNO_3 (or NH_4NO_3) – Agar-Agar salt bridge

Chemicals

i) Standard S (M/10) KCl solution

ii) Standard S (M/100) $AgNO_3$ solution

8.5 Procedure

Recording of room temperature

Table 8.1: Recording of Room Temperature

Temperature before experiment ^0C	Temperature after experiment ^0C	Mean temperature ^0C

Preparation of 100 ml of (M/100) AgNO3 solution

To prepare 100ml (M/100) $AgNO_3$ solution, weigh accurately ~0.17 silver nitrate, take in 100ml volumetric flask and dissolve in distilled water. Then make up the volume upto the mark. Keep the flask wrapped in aluminium foil or keep in a dark place since silver nitrate dissociates in presence of light.

Table – 8.2 : Preparation of 100 ml of (M/100) $AgNO_3$ solution

Initial wt. (g)	Final wt. (g)	Wt. of $AgNO_3$ taken (g)	Weight required (g)	Concentration of $AgNO_3$ soln.
W_1	W_2	$W_1 - W_2 = W$	0.1699	W / 0.1699 = f

Potentiometric Titration

Take 10 ml ~(M/100) $AgNO_3$ solution in a 100 ml beaker and add sufficient amount of distilled water so that the Ag- electrode can be properly dipped.Connect this half – cell with the SCE through the prepared salt bridge.Connect the experimental cell with the potentiometer.Standardise the potentiometer against the standard cell (most cases it is inbuilt). Then measure the *emf* of the experimental cell.Now add two drops of standard KCl solution into $AgNO_3$ solution from a burette, stir well and measure the *emf*. Repeat the process for number of times until a sharp change in *emf* attained (near the equivalence point, add only 1 – 2 drops of KCl from the burette). Take at least 6 readings before and after the end point.Plot the observed *emf* Vs. n (number of drops of KCl added.Determine the end point from the graph. Calculate the solubility product from the known value of $E^0_{Ag^+/Ag}$ and $E_{SCE.}$

Table – 8.4 : Potentiometric Titration of $AgNO_3$ solution against KCl solution

No. of obs.	Volume of $AgNO_3$ (ml)	No. of drops of KCl soln. Added	Observed emf (Volt)
1	10		
2			
12			

8.6 Calculation

Calculate K_s using the relation :

$$E_{cell}\,(eqv.) = E^0_{Ag^+/Ag} + (0.059/2)\log K_s - E_{SCE}$$

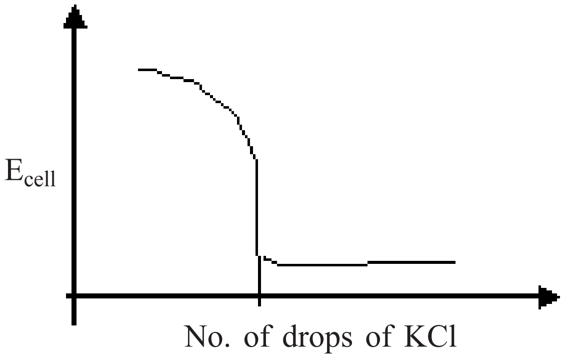
If the room temperature is T Kelvin then the factor 0.059 is to be modified to (0.059 T/298).

Literature values of $E^0_{Ag^+/Ag} = +\,0.779$ V and E_{SCE} at room temperature (t ^{0}C) is,

$$E_{SCE}\,(saturated) = 0.2415 - 7.6 \times 10^{-4}\,(t - 25) \text{ in Volt.}$$

8.7 Result

Plot E_{cell} Vs. n (number of drops of KCl solution added) and note the equivalence point.



Report the value of K_s.

8.8 Summary

In this experiment, the solubility product (Ksp) of silver chloride (AgCl) is determined using potentiometric titration. The titration involves gradually adding a standard potassium chloride (KCl) solution to a silver nitrate ($AgNO_2$) solution while monitoring the potential change with a silver electrode. The potential difference, which corresponds to the concentration of free silver ions in the solution, is recorded throughout the titration. By analyzing the titration curve, the point at which precipitation of AgCl occurs is identified. Using this data, the solubility product of AgCl is calculated.

8.9 Self-Assessment Questions

1. What is the solubility product (Ksp) and why is it important in chemistry?
2. Why is silver chloride (AgCl) chosen for this type of experiment?
3. What role does the potentiometric method play in this titration, and how is it better than using visual indicators?

4. What is the function of the silver electrode in this experiment?
5. How does the potential change during the titration of AgNO*f* with KCl, and what does it signify?
6. How is the equivalence point determined in potentiometric titration?
7. What factors can affect the accuracy of the Ksp value obtained in this experiment?
8. Can you explain the principle of potentiometry and how it is applied in this experiment?

Module-2

Study of Physical Parameters

Unit 9 ❑ Study of Viscosity of Unknown Liquid (Glycerol, Sugar) With Respect to Water

9.1 Objectives

After study and completion of this experiment, the learner will be able to:

1. Understand the concept of viscosity and its dependence on molecular interactions.
2. Measure the viscosity of unknown liquids such as glycerol or sugar solutions with respect to water using a viscometer.
3. Calculate the relative viscosity and compare it with the theoretical value.
4. Correlate the viscosity of the liquids with their molecular structure and concentration.
5. Analyze the effect of temperature on the viscosity of liquids.

9.2 Introduction

Viscosity is a measure of a fluid's resistance to flow and plays a crucial role in various physical, chemical, and biological processes. It determines how liquids move under different conditions and is important in industries ranging from pharmaceuticals to petrochemicals. Common methods for measuring viscosity include capillary viscometers, rotational viscometers, and falling sphere viscometers. In this experiment, you will use a viscometer to measure the viscosity of an unknown liquid relative to water, gaining hands-on experience in the technique and its applications. This experiment will provide a foundational understanding of viscosity, helping to interpret fluid dynamics in other areas of physical chemistry.

9.3 Theory

When a liquid flows each portion of the liquid experiences a resistance to flow when flowing another portion. The amount of this internal friction is measured in terms of coefficient of viscosity which is defined as the tangential force per unit area required to keep unit difference of velocity between two layers which are unit distance apart, the space being filled with the viscous liquid. It is denoted generally by the symbolη(called as 'eta') whose unit is thus dyne-second/sq.cm which is generally known as poise after the name of Poiseuille.

According to Poiseulle if 'V' be the volume of a liquid flows in time 't' (second) through a capillary of length '1' and radius 'r', the driving force being 'P', then the viscosity η of the given liquid will be

$$\eta = \frac{\pi P r^4 t}{8Vl}$$

The determination of absolute viscosity is a difficult task. But the measurement of relative viscosity i.e., the ratio of viscosity of a liquid to that of another reference liquid, usually water is simple and adequate for many purposes.

In a simple Ostwald-viscometer the force driving a liquid of viscosity η_1, through a capillary. depends on the difference in liquid level 'h', the density 'ρ_1' and the acceleration due to gravity 'g', and is given by the above expression. Ifthe same volume of a liquid of viscosity η_2 is introduced into the same tube, the driving force is equal to $\rho_2$hg where 'ρ_2' is the density of the second liquid.

Now from Poiseuille's equation $\eta = \frac{\pi P r^4 t}{8Vl}$ i.e., for a given apparatus (constant 'r' and 'l') same volume V, η is Proportional to the driving force and the time of out flow. Hence-

$$\frac{\eta_1}{\eta_2} = \frac{hg\rho_1}{hg\rho_2} \cdot \frac{t_1}{t_2} = \frac{\rho_1 t_1}{\rho_2 t_2}$$

$$\square\eta_1 = \frac{\rho_1 t_1}{\rho_2 t_2} \times \eta_2$$

The expression gives the viscosity of the first liquid relative to the second (Usually water).

9.4 Requirements

Apparatus

i) Ostwald viscometer fitted with rubber tube and pinch cork

ii) Specific gravity bottle/Pycnometer;

iii) Chemical Balance and weight box

iv) Stopwatch

v) Beaker

Chemicals

i) Supplied 'standard 'solution (let 20% glycerine);

ii) Supplied solution of unknown strength for same thing (let glycerine)

9.5 Procedure

Recording of room temperature

Table 9.1: Recording of Room Temperature

Temperature before experiment ^{0}C	Temperature after experiment ^{0}C	Mean temperature ^{0}C

Viscosity of water at this-temperature =... poise (η_2)

Density of water at the experimental temperature (ρ_{H_2O}) =

Measurement of Density

- The specific gravity bottle is thoroughly washed and dried and then weighed accurately.
- It is next filled with water and weighed again.
- It is dried and filled with the supplied standard solution (let 20% glycerine) and weighed again.
- It is next dried and filled with the supplied solution of unknown strength and then weighed. From the above weights specific gravities of the supplied standard solution and solution of unknown, strength are determined. These are their density values in the c.g.s system, when multiplied by ρ_{H_2O} at this temperature.
- Now from the supplied standard solution of known strength (let 20%) two other standard solution (let 10% and 5%) are prepared by method of dilution.
- The densities of these two solutions are then determined either graphically or by means of calculation, from the densities of the supplied standard solution and water.

Table 9.2:Measurement of density

Name of the Solution	Weight of empty sp. gravity bottle W_1	Weight of sp. gravity bottle filled with water W_2	Weight of sp. gravity bottle filled with liquid W_3	Density= $\frac{W_3-W_1}{W_2-W_1} x \rho_{H_2O}$ gm/cc
Standard solution (let 20%)				
Solution of unknown strength				

From the graph (or calculation):

Density of diluted (let 5%) solution =... gm/c.c.

Density of diluted (let 10 %) solution =... gm/c.c.

Measurement of Viscosity

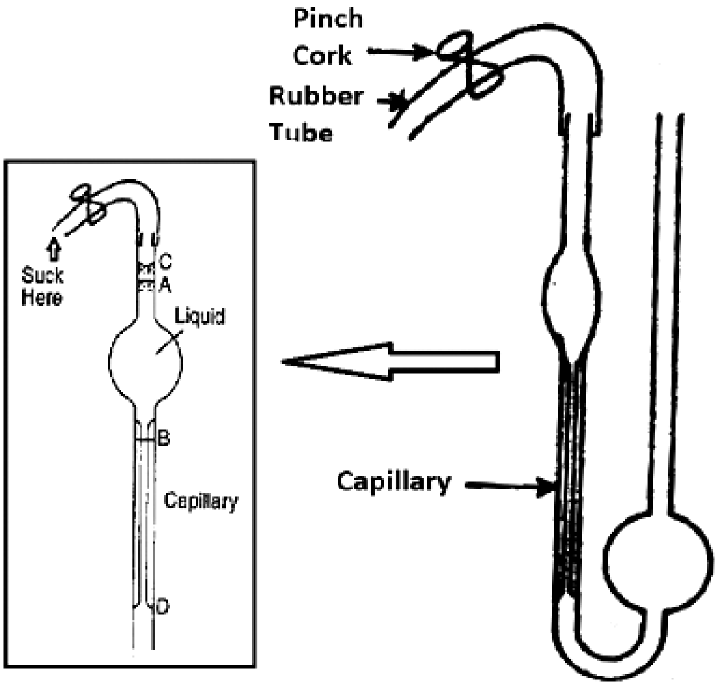


Fig. 1: Ostwald's Viscometer

The Ostwald', Viscometer (see fig.1) is a U-tube one limb of which consists of a fine capillary tube through which definite volume of a liquid (contained in between two marks A, B of the small bulb above the capillary) is allowed to flow under gravity. The other limb consists of a tube of wider-bore having a large bulb at the bottom. Liquids are generally introduced to this bulb from outside and it is sucked to the capillary during experiment.

During experiment the viscometer is washed with chromic acid solution followed by distilled water. Next 10 to 15 c.c. of distilled water is introduced in the larger bulb of the viscometer, thevolume should be such that when the liquid is sucked on the other side above the upper mark over the bulb the liquid level in the other limb remains just below the bulb in this limb.

With the help of the attached rubber-tube at the limb, having the capillary, water is sucked from the larger bulb so that it rises above the upper mark in the viscometer and pinch cock is closed. Next making the stop-watch ready the pinch-cock is opened and when the liquid level just crosses the upper mark the stop-watch is started. It is stopped at the moment of crossing the lower mark by the liquid level. Thus the time required for the falling of water level from the upper to the lower level is noted. This observation is repeated twice.

Next water is thrown away-Viscometer is washed with little amount of alcohol and then dried by blowing hot air. Next it is filled with the supplied solution of known strength (let 20% sol”) and here also the time of fall is noted as above. This observation is repeated twice.

It is again dried and similar experiments are carried out with other two solutions of known strength and the solution of unknown strength. In every case, the volume of the liquid introduced in the viscometer must be the same and the observation is repeated twice.

From the above data viscosities of all solutions are determined. Next a graph is drawn by plotting viscosities against concentrations, from which the concentration of the unknown solution is determined.

Table 9.3:Measurement of flow time

No of observation	Time taken by water	Mean Time taken by water	Time taken by 1st Standard (20%)	Mean Time taken by 1st Standard (20%)	Time taken by 2nd Standard (10%)	Mean Time taken by 2nd Standard (10%)	Time taken by 3rd Standard (5%)	Mean Time taken by 3rd Standard (5%)	Time taken by unknown solution	Mean Time taken by unknown solution
1										
2										
3										
4										

Precaution

1. The flow time of a liquid filled in viscometer should be between 1-10 minutes.
2. The viscometer and sp. gravity bottle should be thoroughly cleaned.
3. The viscometer should be adjusted in an accurately vertical position.
4. The volume of liquid introduced should be the same in each time
5. The temperature should be controlled within ±0.1 ^{o}.

9.6 Calculations

Table 9.4: Determination of viscosity

Solution	**Time taken by the liquid (t_1 Sec)**	**Time taken by water (t_2 Sec)**	**Density of liquid (ρ_1) (gm/cc)**	**Density of water (ρ_2) (gm/cc)**	**Viscosity $\eta_1 = \eta_2 \cdot \frac{\rho_1 t_1}{\rho_2 t_2}$ (poise)**
1st standard (20%)					
2nd standard (10%)					
3rd standard (5%)					
Solution of unknown strength					

9.7 Result

From the above data plot a graph by plotting viscosity against concentration and obtain a straight line. From the graph obtained, the concentration of the solution supplied was found to be... % at... °C.

9.8 Summary

In this experiment, the viscosity of an unknown liquid (such as glycerol or a sugar solution) will be measured relative to water using a viscometer. The experiment involves determining the flow time of the liquid through a capillary tube and comparing it to the flow time of water. From this data, the relative viscosity can be calculated. The experiment helps in understanding how molecular interactions and composition affect the flow behavior of liquids, providing insights into the concept of viscosity and its importance in both theoretical and applied physical chemistry contexts.

9.9 Self-Assessment Questions

1. What do you mean by viscosity?
2. What are the factors responsible for the property of viscosity?
3. What is the unit of co-efficient of viscosity?
4. What is the effect of temperature on viscosity of liquids?
5. Do you determine the absolute or relative viscosity?
6. What is the Poiseuille equation?
7. Can Poiseuille equation be applied in case of a liquid flowing through a pipette or a burette?
8. What is fluidity-how is it related with viscosity?
9. What is intrinsic viscosity? How molecular weights of high polymer can be determined?
10. How does viscosity of a fluid change with temperature?
11. What will happen if the capillary part of the viscometer is replaced by a tube of wider bore?
12. Why it is necessary to take exactly same volume of liquid in each case?

Unit 10 ❑ Determination of Ph of Unknown Solution (Buffer), By Colour Matching Method

10.1 Objectives

After completing this experiment, the learner will be able to:

- Understand the principle of color matching for pH determination.
- Identify suitable indicators for different pH ranges.
- Perform a pH measurement of an unknown buffer solution using the color matching method.
- Compare and interpret the pH results with standard pH values.
- Develop the ability to choose appropriate indicators for unknown solutions.

10.2 Introduction

The determination of pH is a fundamental concept in chemistry, particularly for understanding the acidity or basicity of solutions. pH plays a crucial role in biological systems, where even slight changes can have significant effects on enzyme activity, metabolic processes, and the overall function of living organisms. Buffers are solutions that resist changes in pH, making them essential for maintaining stable environments in biological and chemical systems, such as blood pH in organisms or in industrial processes.The colour matching method provides a simple and efficient way to determine the pH of an unknown buffer solution. By comparing the colour of a pH indicator in the solution to a standard colour chart, students can easily approximate the pH without needing sophisticated instruments. This experiment gives learners practical experience with an important chemical analysis technique and emphasizes the importance of pH control in various real-world applications.

10.3 Theory

The pH of an aqueous solution is the negative of logarithm to base 10 ($\log_{10}$) of hydrogen ion activity (a_{H+})

$$pH = -\log_{10} a_{H+} \quad \text{..............................(1)}$$

For dilute solutions, activity coefficients (f) are nearly unity, and so the activity may be replaced by the numerical value of the molar concentration (c) (since a = c.f; as $f \rightarrow 1, a \rightarrow c$). For such a dilute solution,

$$pH = -\log_{10} c_{H+} \quad \text{..............................(2)}$$

Buffer solution is a solution whose pH doesn't change on addition of a little quantity of acid or alkali. The resistance offered by the solution to change the pH of the solution is known as buffer action.Generally buffer solution is a mixture of a weak acid and its salt or a weak base and its salt.pH of buffer solutions have definite values depending upon the ionization constants (pK's) of the constituent acids or bases and the ratios of acid: salt or base: salt as the casemay be. pH of a buffer solution consisting of a weak acid and its salt with a strong base is expressed by the Henderson equation:

$$pH = pK_a + \log_{10}\frac{[Salt]}{[Acid]} \quad \text{...........................(3)}$$

where, K_a is the ionisation constant of the weak acid and [ ]'s represent the molar concentrations. Thus, a series of buffer solutions of known pH values may be obtained by mixing known amounts of a weak acid with known amounts of its salt.

Acid base indicators are generally weak acids or weak bases. Acid-base indicators exhibit distinguishable colours in distinctly acidic and distinctly alkaline solutions, the actual shade of colour, of course, depends up on the ratio of the concentrations of the acidic and basic forms, of the indicator, which in turn depends upon the pH of the solution. An acid-base indicator (HIn) ionises according to,

$$\mathrm{HIn} \rightleftharpoons \mathrm{H^+} + \mathrm{In^-} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(4)$$

for which the ionisation constant, $K_{in}$is given by

$$K_{in} = \frac{[\mathrm{H^+}][\mathrm{In^-}]}{[\mathrm{HIn}]} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(5)$$

since, HIn and In^- have distinctly different colours depending upon their concentrations and pH of the solution, the ionisation constant, K_{in} of the indicator may be expressed according to,

$$K_{in} = \frac{[\mathrm{H^+}][\mathrm{In^-}]_{colour}}{[\mathrm{HIn}]_{colour}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(6)$$

$$+\cdot pH = pK_{in} + \log_{10}\frac{[\mathrm{In^-}]_{colour}}{[\mathrm{HIn}]_{colour}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(7)$$

Since, human eye can recognise one colour distinctly when-its intensity is 10 times higher than that of other colours, the indicator will show the colour of its acid form (Hln) when$[\mathrm{Hln}] \geq 10\,[\mathrm{In^-}]$ and it will show the colour of its basic form (In^-) when $[\mathrm{In^-}] \geq 10\,[\mathrm{Hln}]$.That is, the colour change interval of the indicator will be :

$[\mathrm{Hln}] \geq 10\,[\mathrm{In^-}]$ pH =$pK_{in} - 1$ colour of HIn

$[\mathrm{In^-}] \geq 10\,[\mathrm{Hln}]$ pH =$pK_{in} + 1$ colour of In^-

When the pH of the buffer solution is in range: $(pK_{in} - 1) < pH < (pK_{in} + 1)$, the indicator will show a mixed colour depending upon the pH of the buffer solution as determined by the ratio of concentrations of the weak acid to that of its salt, ([acid] / [salt]). Therefore, the unknown pH of a buffer solution can be determined by developing colours by adding 3-4 drops of an indicator to a series of the buffer solutions of known pH prepared by adding a weak acid solution of known concentration and an alkali of known concentration. And the same amount of indicator is added to the solution of unknown pH. Then the pH of unknown solution is determined by matching the colour with the colour of the solutions of known pH's.It should be noted that the pH of the unknown solution falls within the range: $(pK_{in} - 1) < pH < (pK_{in} + 1)$ and pK_a of the weak acid falls within pH ± 1 of the unknown solution.

10.4 Requirements

Apparatus

i) Hard glass test-tubes

ii) Burette

iii) Beaker

iv) Volumetric flask

Chemicals

i) (N/10) oxalic acid solution

ii) ~0.5 (N) NaOH solution

iii) 0.4 (N) acetic acid solution

iv) phenolphthalein indicator

v) Supplied Unknown buffer solution of unknown pH

10.5 Procedure

Preparation of 100 ml Standard ~ (N/10) oxalic acid solution

Prepare 100 ml Standard ~ (N/10) oxalic acid solution by exact weighing and dissolving it in appropriate amount of water

Table-10.1: Preparation of 100 ml Standard ~ (N/10) oxalic acid solution

Initial weight (W_1)	Second Weight (W_2)	Weight of oxalic acid taken ($W = W_2 - W_1$)	Strength of oxalic acid solution prepared

Standardisation of Sodium Hydroxide

Approximately ~0.5 (N) NaOH solution is prepared by weighing about 5-6 g of NaOH beads in a rough balance followed by dilution to 250 ml with distilled water. This is then titrated against standard (N/10) oxalic acid solution using phenolphthalein indicator as usual. Find the strength of the alkali solution and prepare 100 ml of accurate 0.4(N) NaOH solution by exact dilution of the ~0.5(N) solution using a burette.

Table - 10.3: Standardisation of ~0.5 (N) NaOH solution against Standard oxalic acid solution

No. of obs.	Volume of oxalic acid solution taken (ml)	Burette reading. of NaOH solution		Volume of NaOH solution required (ml)	Concordant Volume of NaOH solution required (ml)	Strength of NaOH solution
		Initial	Final			

Standardisation of Acetic Acid

Approximately 0.5(N) of acetic acid is made by dissolving 8 ml of glacial acetic acid in water and the volume is made upto 250 ml. Standardize the prepared acetic acid solution, taking 10 ml of the acid as aliquot and titrating with the NaOH solution of known strength using phenolphthalein as indicator. Find the strength of the acetic acid solution and prepare 100 ml exact 0.4 (N) acetic acid solution by dilution using a burette.

Table-10.4: Standardisation of ~0.5 (N) acetic acidsolution against Standard NaOH solution

No. of obs.	Volume of acetic acid solution taken (ml)	Burette reading. of NaOH solution		Volume of NaOH solution required (ml)	Concordant Volume of NaOH solution required (ml)	Strength of acetic acid solution
		Initial	Final			

Determination of pH

9 test tubes of almost equal size are taken and marked serially 0.4 (N) acetic acid and 0.4 (N) NaOH solutions are mixed according to the following table. pH of each set is determined from Henderson equation. Take 10 hard glass test-tubes (20 ml) of approximately equal diameter, label them with 1 to 9 and prepare the buffer solutions of following compositions according to the following table (**Table-10.5**) and mix uniformly. pH of each set is determined from Henderson equation.viii)
2-3 drops of bromocresol green indicator (pKin close to pKa. of the acid) is added to each test tube (1 to 9) and mixed well. In the remaining test-tube marked 10 pipette out exactly 10 ml of the unknown solution. Add 2-3 drops of bromocresol green indicator to the unknown solution and mix well. Match the colour of the unknown solution (10) with the colours of the series of buffer solutions (1 to 9) and hence find the pH of the unknown solution.

Table-10.5: Preparation of different standard buffer solution

Test-tube No.	Volume of 0.4(N) CH_3COOH (ml)	Vol. of 0.4(N) NaOH (ml)	Vol. of H_2O (ml)	Total Volume (ml)	pH (experimental) (ml)
1	5.0	0.5	4.5	10.0	3.72
2	5.0	1.0	4.0	10.0	4.05

Test-tube No.	Volume of 0.4(N) CH_3COOH (ml)	Vol. of 0.4(N) NaOH (ml)	Vol. of H_2O (ml)	Total Volume (ml)	pH (experimental) (ml)
3	5.0	1.5	3.5	10.0	4.27
4	5.0	2.0	3.0	10.0	4.45
5	5.0	2.5	2.5	10.0	4.63
6	5.0	3.0	2.0	10.0	4.80
7	5.0	3.5	1.5	10.0	4.99
8	5.0	4.0	1.0	10.0	5.23
9	5.0	4.5	0.5	10.0	5.57
10	Unknown buffer solution			10.0	Match

10.6 Results

The colour of the unknown solution is found to match with the test tube number X i.e. one of 1 to 9, hence the pH of the unknown solution would be as per pH against the X mark test tube. So, the pH of the unknown solutionis …………………

10.7 Summary

In this experiment, the pH of an unknown buffer solution is determined using the colour matching method. This technique involves adding a pH indicator to the solution and comparing the resulting colour to a standard pH chart to estimate the pH value. The experiment provides a hands-on understanding of pH measurement and reinforces the importance of pH control in various chemical and biological systems. It also highlights the simplicity and practicality of the colour matching method as a useful tool for quick and approximate pH determination in situations where precise instruments may not be available.

10.8 Self-Assessment Question

1. Why a buffer solution has reserved acidity and alkalinity? Or explain the buffer action?
2. When the buffer action is optimum?
3. Give the pH range of the buffer action?
4. What do you mean by sensitiveness of an indicator?
5. What do you mean universal indicator?

Unit 11 ❑ Conductometric Titration of An Acid (Strong, Weak/ Monobasic, Dibasic) Against Strong Base

11.1 Objectives

After the study and completion of this experiment, the learner will be able to:

- Understand the principle and procedure of conductometric titration.
- Differentiate between the conductometric titration curves of strong acids, weak acids, and polybasic acids against a strong base.
- Perform the conductometric titration of strong and weak acids (monobasic and dibasic) against a strong base, such as NaOH.
- Interpret the changes in conductivity during titration and use the data to determine the equivalence point accurately.
- Calculate the concentration of acid in the solution based on the titration data.
- Apply the method to study ionization and conductance behaviour of acids and bases in solution.

11.2 Introduction

Conductometric titration is a vital analytical technique used to measure the electrical conductance of a solution during a titration. Conductance, which reflects the ability of ions to carry an electrical current, changes as ions are introduced or neutralized in the reaction. By monitoring these changes, one can accurately determine the endpoint of a titration, even when visual indicators are ineffective. This method is particularly valuable when dealing with solutions that are turbid or colored, making it difficult to observe colour changes typically used in titrations.

In conductometric titration, the principle relies on the movement of ions. When an acid reacts with a base, for instance, hydrogen ions (Hz) are replaced by less conductive ions such as sodium (Naz) during the neutralization process, leading to changes in conductance. This method is used not only for strong acids but also for weak acids and polybasic acids, offering insight into their ionization properties and behaviour in aqueous solutions.

Conductometric titration is important because it allows for precise determination of equivalence points without relying on indicators, which can sometimes provide misleading results. It also provides valuable data on the strength and ionization characteristics of acids and bases. This experiment is being studied to give learners a practical understanding of how conductometric titration can be applied to analyze different types of acids, and how conductance measurements can lead to a deeper understanding of chemical reactions

11.3 Theory

Solution of electrolytes normally obey Ohm's law, i.e. $R = \frac{E}{I}$ where R = resistance of the solution, E = e.m.f. applied, I = current flow.

The conductance 'G' of a solution is related to the resistance as follows -

$$G = \frac{1}{R} = \frac{K.a}{l}$$

Where, K = Specific conductance

a = Cross-sectional area

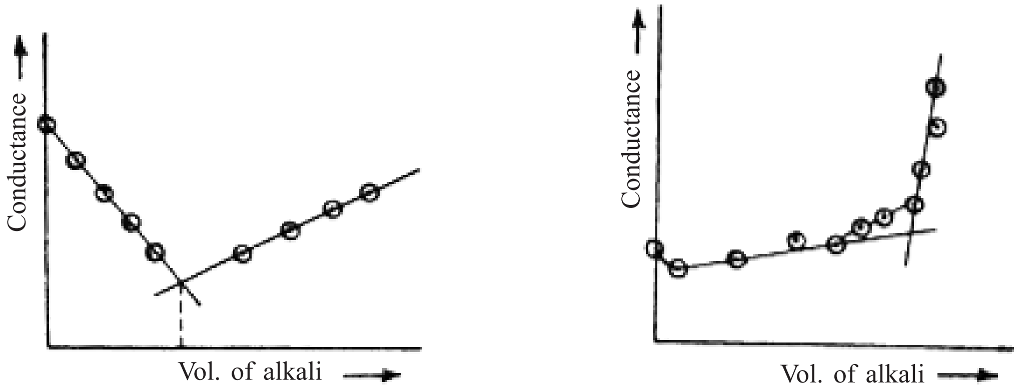
l = length of the Conductor

The conductance of a solution is dependent on: (i) Ionic mobility, (ii) no. of ions and, (iii) dilution.

In conductivity experiments it is important to control the temperature because the ionic mobility of most ions is increased at least 2% per degree rise in temperature.

If during titration, nature of variation of conductance of titrant up to end point, is different from its nature of variation after end point then conductometric titration can be carried out. Thus when a strong acid e.g. HCl is titrated by a strong base e.g. NaOH then up to end point high conducting H^+ ions are replaced by low conducting Na^+ ions and so overall conductance of the titrant steadily decreases. It reaches its minimum value at end point when all H^+ions are removed. If addition of NaOH is still continued then overall conductance will rise steadily due to high conductance value of OH^- ion and also excess Na^+ ions. A plot of conductance Vs volume of alkali added will be a V-shaped curve (fig.1); volume corresponding to the lowest conductance value is the volume required for exact neutralisation.

When a weak acid e.g. CH_3COOH is titrated by a strong base e.g. NaOH then at the beginning there is a momentary drop in conductance due to replacement of high conducting $H^+$by low conducting CH_3COO^-; but almost immediately the dissociation equilibrium $CH_3COOH= H^+ + CH_3COO^-$ shift's towards right compensating the loss of H+ ion. The result is accumulation of some excess Na^+ ion and CH_3COO^-. Due to this conductance slowly rises up to end point. After end point if addition of base is continued conductance will increase sharply due to Na^+ion and high conducting OH^- ion (fig.1).



(1) (2)

Fig. 1&2 : Conductometric titration curves for strong acid strong base and strong acid week base

[N.B.: The stronger the solution used the sharp and more definite is the appearance of the end point. During conductometric titration concentration of the titre should be approximately ten times more than the titrant; this is to minimise dilution error. Also during conductometric titration of a weak acid by a strong base the points in the graph near end point do not fall in the straight line but makes a curve (dotted portion of fig.2). This is due to hydrolysis of the salt, which produces some OH^- ion and raises the conductance value from expected value.]

11.4 Requirements

Apparatus

i) Conductivity bridge

ii) Conductivity cell

iii) Microburette or ordinary burette

iv) Pipette

v) Volumetric flask

Chemicals

i) Hydrochloric acid

ii) Acetic acid of (N/10) order

iii) Sodium hydroxide solution of (N) order

iv) (N/10) Oxalic acid

11.5 Procedure

Recording of room temperature

Table 11.1: Recording of Room Temperature

Temperature before experiment ^0C	Temperature after experiment ^0C	Mean temperature ^0C

Preparation of 250 ml Standard ~ (N/10) oxalic acid solution

Prepare 250 ml Standard ~ (N/10) oxalic acid solution by exact weighing and dissolving it in appropriate amount of water[1.575 gm oxalic acid dissolved in 250 ml. water gives a N/10 solution]

Table-11.2: Preparation of 100 ml Standard ~ (N/10) oxalic acid solution

Initial weight (W_1)	Second Weight (W_2)	Weight of oxalic acid taken ($W= W_2 - W_1$)	Strength of oxalic acid solution prepared

Standardisation of NaOH solution against standard oxalic acid solution

250 ml sodium hydroxide solution of (N) order is prepared. [10 gms of NaOH (weighed in rough balance) when dissolved in 250 ml water gives a (N) solution]. Exact strength of NaOH is determined by titrating with standard N/10 oxalic acid as usual procedure.

Table-11.3: Standardisation of ~(N/10) NaOH solution against Standard oxalic acid solution

No. of obs.	Volume of oxalic acid solution taken (ml)	Burette reading. of NaOH solution		Volume of NaOH solution required (ml)	Concordant Volume of NaOH solution required (ml)	Strength of NaOH solution
		Initial	Final			

Standardisation of Acetic Acid Solution by Standard NaOH Solution

Table - 11.4: Standardisation of ~ (N/10) acetic acidsolution against Standard NaOH solution

No. of obs.	Volume of acetic acid solution taken (ml)	Burette reading. of NaOH solution		Volume of NaOH solution required (ml)	Mean Volume of NaOH solution required (ml)	Strength of acetic acid solution
		Initial	Final			

Measurement of Conductance

1. The conductivity cell is thoroughly washed with deionised water and is kept in a 100 ml beaker. 25 ml of the supplied HCI solution is pipetted out and is added to this beaker. If the electrodes are not completely dipped then sufficient deionised water can be added so that the electrodes are completely dipped. The cell is now connected to the conductivity bridge and conductance of the solution in the cell is measured.

2. The microburette is washed with water; rinsed with NaOH and then it is filled with NaOH. [when microburette is not available, then ordinary burette can be used. In this case number of drops coming out of the burette during exit of 1 ml NaOH is to be counted from where drop-value can be known.]
3. From the burette 3 to 4 drops of NaOH is added to the HCI solution in the conductivity cell. The solution is stirred thoroughly and its conductance is measured. Again another 3 to 4 dropsof NaOH is added and conductance is again measured after thorough stirring. This measurement should be repeated until the break in the curve is obtained i.e. conductance is increased on further addition of 2-3 drops of alkali (noted by a sharp rise in conductance value).
4. A graph is now drawn by plotting conductance Vs no. of drops (or volume) of alkali and from the graph volume of alkali corresponding to the end point is determined.
5. For titration of a weak acid e.g. CH_3COOH Vs NaOH process is exactly same. However, here initial momentary drop in conductance can be found if at the beginning conductance is measured adding ONLY ONE drop of alkali and without making much delay in measurement. Otherwise this initial drop in conductance may not be found.

Table - 11.5: Measurement of conductance

No. of observations	Volume (or Drops) of alkali added	Conductance of solution
1		
2		
3		
4		

11.6 Calculations

From the graph the volume of NaOH at the equivalence point = V ml

- $10 \times S = V \times f\ (N)$ [where f(N) is the strength of alkali & S= Strength of HCl]
- $S = \frac{Vx\ f}{25}\ (N)$
- Strength of HCl = ...(N)

From the graph the volume of NaOH at the equivalence point = V ml

- $10 \times S = V \times f\ (N)$ [where f(N) is the strength of alkali & S= Strength of Acetic Acid]
- $S = \frac{Vx\ f}{25}\ (N)$
- Strength of Acetic Acid = ...(N)

11.7 Results

The strength of HCl and Acetic Acid solution is ....

11.8 Summary

In this experiment, conductometric titration is used to analyze the titration of different types of acids—strong, weak (monobasic), and dibasic—against a strong base, such as NaOH. The key objective is to monitor changes in the electrical conductance of the solution as the titration progresses, which provides insights into the equivalence point of the reaction. By measuring the conductivity before, during, and after the addition of the base, students can determine the endpoint of the titration and calculate the concentration of the acid. This experiment emphasizes the importance of conductance measurement as a tool for accurate titration and offers practical experience in interpreting conductometric data for various types of acids.

11.9 Self-Assessment Questions

i) What is conductometric titration, and how does it differ from traditional titration methods?

ii) Why is conductivity a useful property to monitor during a titration?

iii) How does the conductance of a solution change as an acid is titrated with a strong base?

iv) What information can be obtained from the conductometric titration curve of a strong acid versus a strong base?

v) Describe the changes in conductivity that occur during the titration of a weak acid with a strong base. How does this differ from the titration of a strong acid?

vi) Explain the concept of equivalence point in the context of conductometric titration. How is it determined from the conductance data?

vii) How would the conductometric titration curve differ when titrating a dibasic acid compared to a monobasic acid?

viii) What are the advantages of using conductometric titration for analyzing acids and bases compared to visual indicators?

ix) Discuss the role of ionic mobility in determining the conductance of a solution during titration.

x) How can you ensure accurate measurement of conductance during the titration process? What potential sources of error should be considered?

Unit 12 ❑ Study of saponification reaction conductometrically

12.1 Objectives

After studying and performing this experiment, the learner will be able to

- explain the principle of saponification and how it can be monitored conductometrically.
- describe the changes in conductance that occur during the saponification reaction between an ester and a base.
- perform a conductometric titration to determine the progress and endpoint of the saponification reaction.
- calculate the rate of the saponification reaction from the conductometric data obtained.
- interpret conductometric titration curves and correlate them with the reaction mechanism of saponification.
- compare the conductometric data for saponification under different experimental conditions, such as varying concentrations or temperatures.

- explain the significance of conductometric measurements in studying reaction kinetics and equilibrium.
- apply the knowledge of conductometric methods to other chemical reactions and practical applications.

12.2 Introduction

In the previous experiment, we explored conductometric titration as a method for analyzing acid-base reactions. Building on that foundation, this experiment focuses on the conductometric study of the saponification reaction. Conductometry, as a technique, provides a valuable tool for understanding various chemical processes due to its ability to measure changes in solution conductivity, which can offer insights into reaction progress and kinetics.

The saponification reaction, which involves the hydrolysis of esters in the presence of a base to produce soap and alcohol, is a classic example of a chemical reaction with significant industrial and practical relevance. This reaction is widely applied in the production of soaps and detergents, and understanding its kinetics is crucial for optimizing industrial processes.

In this experiment, you will use conductometric methods to monitor the saponification reaction, observing how the conductance of the solution changes as the reaction proceeds. By analyzing the conductometric data, you will gain insights into the reaction mechanism, the rate of the reaction, and how various factors influence the saponification process. This experiment highlights the utility of conductometry in studying complex chemical reactions and provides practical experience in applying this technique to real-world chemical processes.

12.3 Theory

When an ester, RCOOR’, derived from a monocarboxylic acid, RCOOH, and a monohydric alcohol R’OH, is treated with a caustic alkali (NaOH), the ester is hydrolysed to produce the alcohol and sodium salt of the acid. The hydrolysis reaction of an ester is given by the following equation,

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

Or, $RCOOR' + OH^- \rightleftharpoons R'OH + RCOO^-$

Such alkaline hydrolysis of an ester is called saponification.Ethyl acetate ($CH_3COOC_2H_5$) on alkaline hydrolysis produces ethanol (C_2H_5OH) and acetate ion (CH_3COO^-):

$CH_3COOC_2H_5 + OH^- \rightleftharpoons C_2H_5OH + CH_3COO^-$

t = 0	a	a	0	0
t = t	a – x	a – x	x	x
t = ∞	0	0	a	a

It is a second order reaction. So the rate equation is

$$\frac{dx}{dt} = k[CH_3COOC_2H_5].[OH^-] = k.(a-x)^2$$

The solution of the differential equation is $\int \frac{dx}{(a-x)^2} = \int kdt \ or \ \frac{1}{(a-x)} = kt + C$

where a = initial concentration of both the reactants;

x = moles of each reactant consumed at time ‘t’;

k = rate constant for second order reaction in $mole^{-1}.litre.second^{-1}$.

When t = 0, x = 0 we get $C = \frac{1}{a}$

So, the equation becomes $\frac{1}{a-x} = kt + \frac{1}{a}$

Or, $kt = \frac{1}{a-x} - \frac{1}{a} = \frac{x}{a(a-x)}$

☐ $a.k.t = \frac{x}{(a-x)}$

This is the equation for a second order reaction.

The progress of the reaction can be monitored by measuring the electrolytic conductance of the reaction mixture, since the highly conducting OH^- ions (λ_0=198.5 $ohm^{-1}cm^2.mol^{-1}$) are replaced by weakly conducting CH_3COO^- ions (λ_0= 40.9 $ohm^{-1}cm^2.mol^{-1}$). If C_0,C_t and C” be the conductances of the reaction mixture at the times t = 0, t, and at the completion of the reaction (infinite time, t = “)

respectively then, total change of conductivity is proportional to total concentration of ethyl acetate. Then we may write

$$a \propto (C_0 - C_\infty)$$

$$x \propto (C_0 - C_t)$$

□ $(a - x) \propto (C_t - C_\infty)$

:. Now, we have, $a.k.t = \frac{C_0 - C_t}{C_t - C_\infty}$

A plot of $\frac{C_0 - C_t}{C_t - C_\infty}$ versus '*t*' will be a straight line passing through the origin and possessing a positive slope = k.a Thus, k may be evaluated from the relation

$$k = \frac{Slope}{a}$$

Since '*a*' is known. Here, a is calculated by diluting a known amount of the ester to a definite volume with water. $C\infty$ may be indirectly determined by measuring the conductance of a solution of sodium acetate, $CH_3COO^-Na^+$, of the same concentration, '*a*', i.e., exactly equal tothe initial concentration, '*a*', of the ester and the alkali (NaOH). The conductances C_0,C_t and C" of the reaction mixture are measured at times t = 0, t and " respectively.

12.4 Requirements

Apparatus

- i) Conductometer with dip type cell.
- ii) 100 ml dry and clean beakers to be used as reaction vessel.
- iii) Volumetric Flask (100ml & 250 ml)
- iv) Pipette
- v) Burette etc.

Chemicals

- i) (N/25) NaOH solution,

ii) Oxalic acid solution ~(N/25) for standardising NaOH solution,

iii) KCl solutionexact (N/25) for standardising the conductometer,

12.5 Procedure

Recording of room temperature

Table 12.1: Recording of Room Temperature

Temperature before experiment ^0C	Temperature after experiment ^0C	Mean temperature ^0C

Preparation of 100 ml Standard ~ (N/25) oxalic acid solution

100 ml (N/25) oxalic acid solution is prepared by accurate weighing followed by dilution with distilled water

Table-12.2: Preparation of 100 ml Standard ~ (N/25) oxalic acid solution

Initial weight (W_1)	Second Weight (W_2)	Weight of oxalic acid taken ($W= W_2 - W_1$)	Strength of oxalic acid solution prepared

Preparation of exact (N/50) NaOH solution

At first 250 ml NaOH solution having concentration slightly higher than (N/25) is made. [0.16 gm in 250 cc. water will make (N/25) solution. Here ~0.2 gm is dissolved in 250 cc.] Its exact concentration is determined by titrating with standard oxalic acid solution using phenolphthalein indicator. When concentration is known, then Prepare 250 ml of exact (N/50) NaOH solution by accurate dilution of the standard ~(N/25) NaOH solution in a 250 ml volumetric flask.

Table-12.3: Standardisation of ~(N/25) NaOH solution against Standard oxalic acid solution

No. of obs.	Volume of oxalic acid solution taken (ml)	Burette reading. of NaOH solution (ml)		Volume of NaOH solution required (ml)	Concordant Volume of NaOH solution required (ml)	Strength of NaOH solution
		Initial	Final			

Preparation of exact (N/50) acetic acid solution

Prepare 250 ml of ~(N/25) acetic acid and standardise the same against standard (N/25) NaOH solution using phenolphthalein indictor. Prepare 100 ml of exact (N/50) acetic acid solution by accurate dilution of the standard ~(N/25) solution using the formula $V_1S_1 = V_2S_2$.

Table-12.4: Standardisation of ~(N/25) acetic acid solution against standard NaOH solution

No. of obs.	Volume of acetic acid solution taken (ml)	Burette reading. of NaOH solution (ml)		Volume of NaOH solution required (ml)	Concordant Volume of NaOH solution required (ml)	Strength of acetic acid solution
		Initial	Final			

Preparation of exact (N/50) acetic acid solution by dilution [Calculation: $V_1S_1 = V_2S_2$]

Preparation of exact (N/50) ethyl acetate solution by dilution [Calculation: $V_1S_1 = V_2S_2$]

Preparation of exact (N/50) ethyl acetate solution

At first prepare 250 ml standard (N/25) ethyl acetate solution by following method. Find the amount in gm of the ester required for 250 ml of (N/25) solution using the relation, density = mass/volume, and calculate the amount of the liquid ester required for 250 ml of (N/25) solution. Transfer the calculated amount of the pure ester into a 250 ml volumetric flask, make up to the mark with distilled water and mix uniformly. Then from the prepared standard (N/25) solution, prepare an exact (N/50) ethyl acetate solution by exact dilution. [N.B. For more accuracy double dilution method is referred for the preparation of exact (N/50) acetate solution]

Measurement of Conductance

Measurements of Conductance C_∞ : Prepare 50 ml exact (N/100) solution of sodium acetate, $CH_3COO^-Na^+$, by mixing 25 ml of prepared (N/50) CH_3COOH and 25 ml (N/50) NaOH solutions. Measure the conductance of this solution that will give the value of C∞.

Measurements of Conductance (C_t): In a dry 100 ml beaker, take 25 ml of (N/50) ethyl acetate, and add 25 ml of (N/50) NaOH to it from a pipette and note the time of half-discharge. The time of half discharge of NaOH solution is the starting time of the reaction. The conductivity cell is dipped in it and measure the conductance (C_t) of the reaction mixture at different time intervals, approximately 2, 4, 6, 8, 10, 12, 14, 16, 18, 20, 22, 24 ….minutes till the conductance remains practically unchanged with time. Record the conductance vs. time data in a tabular form. At least 10 to 12 readings are to be taken. Record the temperature of the experiment.Such reactions are reversible. Effect of reversibility becomes significant after some time. So, readings of first fifteen minutes are to be considered.

Now, $\frac{C_0 - C_t}{C_t - C_\infty}$ values are plotted against '*t*'. A straight line is obtained. Its slope is 'k.a'. Since here the initial concentration 'a' = N/100 moles/litre of the ester. Therefore the value of rate constant 'k' can be known. Its unit is mole^{-1}.litre.second^{-1}.

Table-12.5: Measurements of Conductance C_0 & $C\infty$

Solution taken	Conductance in mho (C_0)	Conductance in mho (C_∞)
(N/100) NaOH		————
(N/100) sodium acetate	————	

Table-12.6: Conductance (C_t) measurement at different time intervals of the reaction:

Time (min)	Conductance in mho (C_t)	$C_0 - C_t$ (in mho)	$C_t - C_\infty$ (in mho)	$\frac{C_0 - C_t}{C_t - C_\infty}$

12.6 Calculation

Plotting $\frac{C_0 - C_t}{C_t - C_\infty}$ values against time (*t*) which will give a straight line passing through the origin.

12.7 Results

From the slope of the curve we can determine k as follows.

Slope = k.a. :. k = Slope/a [a = initial concentration to be supplied solution i.e. 0.01 (N)]

12.8 Summary

In this experiment, the saponification reaction is studied using conductometric methods to understand how conductance changes throughout the reaction.

Saponification involves the hydrolysis of an ester with a base to produce soap and alcohol. By measuring the conductance of the reaction mixture at various stages, you can track the progress of the reaction and determine key parameters such as the rate of reaction and the endpoint. The experiment involves preparing a solution of the ester and base, conducting the saponification reaction, and recording changes in conductance using a conductometer. The data collected will be analyzed to gain insights into the reaction kinetics and mechanism, demonstrating the effectiveness of conductometry in studying chemical reactions. This practical experience emphasizes the application of conductometric techniques in analyzing and optimizing industrial and laboratory processes.

12.9 Self-Assessment Questions

1. What are conductometric titrations?
2. How in conductometric titration the end point is determined? (b) What is ionic mobility?
3. What is the main principle of conductometric titration?
4. On what factor conductivity depends?
5. What is molar conductivity?
6. When does the conductivity of weak electrolyte reaches its maximum value?
7. How the Kinetics of an ester hydrolysis reaction is studied conductometrically?
8. What are the advantages of a conductometric titration?
9. What precautions are to be taken for conductometric titrations?
10. What are order and molecularity?
11. What is half-life?
12. What is the difference between half-life of first and second order reaction?

Unit 13 ❑ Potentiometric titration of Mohr's salt solution against standard K2Cr2O7-solution

13.1 Objectives

After studying and performing this experiment, the learner will be able to

- explain the principle of potentiometric titration and how it is used to determine the endpoint of a redox reaction.
- describe the reaction between Mohr's salt and potassium dichromate, including the oxidation and reduction processes involved.
- perform a potentiometric titration to accurately determine the concentration of Mohr's salt using a standard K, Cr, O‡ solution.
- interpret the potentiometric titration curve to identify the equivalence point of the titration.
- calculate the concentration of Mohr's salt solution from the volume of K, Cr, O‡ solution used at the equivalence point.
- discuss the advantages of potentiometric titration over other titration methods, particularly in terms of accuracy and precision.

- understand and apply the principles of electrochemical cells and their role in potentiometric measurements.
- identify and troubleshoot common issues encountered during potentiometric titration, such as electrode calibration and solution preparation.

13.2 Introduction

Potentiometric titration is a precise and sensitive analytical method used to determine the endpoint of a chemical reaction, particularly redox reactions, by measuring the potential (voltage) difference between two electrodes as titrant is added. This method is especially useful when traditional indicators may not provide a clear or reliable endpoint, as is often the case in reactions involving colored species, such as the redox titration between Mohr's salt (ferrous ammonium sulfate) and potassium dichromate ($K_2Cr_2O_7$).

In this experiment, the reaction between Mohr's salt, which contains Fe^{2}z ions, and potassium dichromate, a strong oxidizing agent, will be studied. Potentiometric titration offers the advantage of a clear, sharp determination of the equivalence point through a potential change, without the interference of subjective color changes or complex indicator reactions.

The use of potentiometric titration in this experiment provides a reliable method to determine the concentration of Mohr's salt solution. This technique also demonstrates the significance of electrochemical cells in determining the progress of a reaction by measuring the potential difference between two electrodes, which can be used in a wide range of industrial, biochemical, and environmental applications. Through this experiment, learners gain hands-on experience in applying electrochemical principles to accurately determine reaction endpoints, improving their understanding of redox reactions and potentiometric analysis.

13.3 Theory

A titration in which the end point or equivalence point of a reaction is detected by measuring the potentials of the reaction mixture is known as potentiometric titration. The principle of the experiment is to develop a cell, half cell of which is a redox system and the Pt electrode and the other half cell is standard calomel electrode in the present titration, the following, cell is constructed.

$$\mathrm{Pt \mid Hg(l) \mid Hg_2Cl_2(s) \mid KCl(aq)(saturated) \parallel Fe^{+2}(aq), Fe^{+3}(aq) \mid Pt}$$

The cell reaction is :

$$2Hg + 2Cl^- + 2Fe^{+3} \rightleftharpoons Hg_2Cl_2 + 2Fe^{+2}$$

$$E_{cell} = E_R - E_L = E_{Fe^{+3}/Fe^{+2}} - E_{sat.cal}$$

E_{Cell} increases as $[Fe^{+3}]/[Fe^{+2}]$ varies during titration of Fe^{+2} with $Cr_2O_7^{-2}$and at the half equivalence point the ratio $[Fe^{+3}]/[Fe^{+2}]$ becomes unity

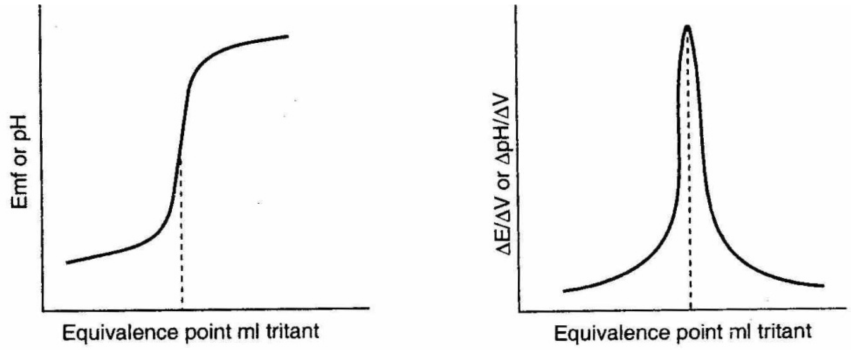
At this point,

$$E_{cell} = E_{1/2} = E^0_{Fe^{+3}/Fe^{+2}} - E_{sat.cal}$$

$$E^0_{Fe^{+3}/Fe^{+2}} = E_{1/2} + E_{sat.cal} \quad \ldots\ldots\ldots\ldots\ldots\ldots(1)$$

$E_{sat.cal}$ is obtainable from the literature. Thus, $E^0_{Fe^{+3}/Fe^{+2}}$ may be obtained with the $E_{1/2}$ determined at room temperature.

At the equivalence point, a sudden jump of E_{Cell} is observed. Further addition of $Cr_2O_7^{-2}$causes a minor increase of E_{Cell}. The volumes of titrant added are plotted against the measured e.m.f. values (or pH). From the smooth curve, the volume, or, the number of drops of the titrant required to completely oxidise Fe^{+2} to Fe^{+3} may be determined by extrapolation. Hence the amount of oxidant required to oxidise the Fe^{+2} ions originally present may be calculated and the corresponding value of E_{cell} ($=E_{1/2}$) may be evaluated graphically.The sets of the curves and the end point is shown in the following graph.



(a) (b)

Fig. 1 : (a) Typical titration curve, (b) Typical first derivative titation curve

In this experiment a known volume of ferrous salt is placed in the beaker and diluted with water. A clean Pt electrode is dipped into the solution and connected with a saturated calomel electrode by means of a salt bridge. Connect the Pt-electrode and the calomel electrode to the terminals of the potentiometer. A definite volume of $K_2Cr_2O_7$ solution is added from a burette each time and e.m.f. is recorded. The observed e.m.f. values are plotted against the volume or drops of titrantadded.

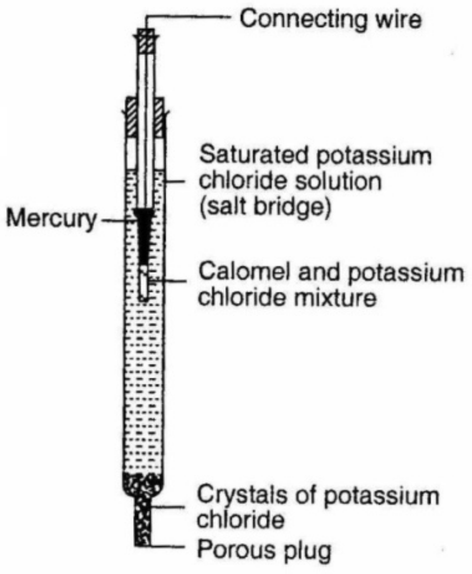


Fig. 2 : Saturated calomel electrode

13.4 Requirements

Apparatus

i. A digital potentiometer with saturated calomel electrode (Fig. 2) fitted with salt bridge.

ii. Standard cell

iii. Platinum electrode

iv. Volumetric flask, pipette, burette etc.

Chemicals

i. $K_2Cr_2O_7$ solution – (N/2)

ii. Mohr's salts – (N/10) [Add 9.8 gm Mohr's salt in 250 ml distilled waterand dissolve to make Fe^{+2} solution]

iii. H_2SO_4 – 2(N)

13.5 Procedure

Recording of room temperature

Table 13.1: Recording of Room Temperature

Temperature before experiment ^0C	Temperature after experiment ^0C	Mean temperature ^0C

Preparation of 250 ml standard (N/2) K2Cr2O7 solution

Prepare 250 ml standard (N/2) $K_2Cr_2O_7$ solution by accurately weighing required amount and dissolving it in distilled water in a volumetric flask. [6.125 gm $K_2Cr_2O_7$ when dissolved in 250 ml water produces a (N/2) solution.]

Table-13.2: Preparation of 250 ml standard (N/2) $K_2Cr_2O_7$ solution

Initial weight (W_1)	Second Weight (W_2)	Weight of $K_2Cr_2O_7$ taken ($W= W_2 – W_1$)	Strength of $K_2Cr_2O_7$ solution prepared
			$\frac{W}{6.125}\left(\frac{N}{2}\right)$

Potentiometric titration of Mohr's salt solution against K2Cr2O7 solution

A 2(N) H_2SO_4 solution is made and cooled. [10 ml of conc. H_2SO_4 is cautiously added to 170 ml of water to get 2(N) H_2SO_4]

25 ml. of the supplied Fe^{+2} solution is pipetted out and taken in a 100 ml beaker. An equal volume of 2(N) H_2SO_4 is now added. A cleaned Platinum electrode is

now dipped into it. With the help of a salt bridge this solution is now connected with a saturated calomel electrode. These two half cells i.e. Platinum electrode and calomel electrode are connected to the two terminals of a potentiometer properly.

Potentiometer is now standardised against a standard cell (e.g. with a Weston cadmium cell)

Then e.m.f. of the experimental cell is measured. $K_2Cr_2O_7$ solution is now added from a burette drop-wise. After addition of few drops (5 drops) the solution is stirred well with a glass-rod, allowed to stand for 1 minute and then e.m.f. is measured. Each time note the volume of $K_2Cr_2O_7$ added from burette (at the beginning calculate the number of drops in 1 ml of $K_2Cr_2O_7$ and calculate the volume accordingly). Repeat this procedure till the equivalence point is reached, which is indicated by a sharp increase of E_{cell}. Take a few more readings beyond the equivalence point. [At the beginning and after end point readings may be taken after adding large amount of $K_2Cr_2O_7$ (say 1 cc. at a time) but near end point readings should be taken frequently (say after 0.1 cc. has been added)].

Plot (a) E_{cell} versus number of drops (x) of $K_2Cr_2O_7$ solution, (b) plot $\Delta E/\Delta V$ or $\Delta E/\Delta x$ (number of drops). From this curve find the equivalence point, hence the value of E_{cell} corresponding to the half-neutralization point (i.e., $E_{1/2}$) accordingly and find the concentration of Fe^{+2} solutions and hence amount of Fe^{+2} ion in gms/litre can be calculated. Also calculate $E^0_{Fe^{+3}/Fe^{+2}}$ system with the aid of the relation (1) using the literature value of $E_{sat.cal.}$

Table-13.3: Potentiometric titration of Mohr's salt solution against $K_2Cr_2O_7$ solution

No. of observation	Volume of Mohr's salt taken	No. of drops of $K_2Cr_2O_7$	Observed e.m.f.	$\Delta E/\Delta V$
1.	25 ml			
2.				
3.				

13.6 Calculation

Graph: Plot e.m.f. Vs x (number of drops of $K_2Cr_2O_7$ solution) and find the value of $E_{1/2}$ and the volume of $K_2Cr_2O_7$ solution added to reach the equivalence point.

1 ml of $K_2Cr_2O_7$ solution = x drops

Number of dropsof $K_2Cr_2O_7$ added at equivalence point = n

Strength of Mohr's salt solution $= \dfrac{V_{K_2Cr_2O_7} \times S_{K_2Cr_2O_7}}{V_{Mohr}}$

So, concentration of Fe^{+2} is ………..Hence amount of Fe^{+2} is …… gms/litre

The $E_{1/2}$ value is calculated

The $E_{1/2}$ value gives $E^0_{Fe^{+3}/Fe^{+2}}$ from the equation (1)

13.7 Results

The concentration of Fe^{+2} in the supplied solution is …………………………..

13.8 Summary

In this experiment, the potentiometric titration method is employed to determine the concentration of Mohr's salt (ferrous ammonium sulfate) by titrating it against a standard solution of potassium dichromate ($K_2Cr_2O_7$). Unlike traditional titrations, where visual indicators are used to detect the endpoint, potentiometric titration measures the change in electrical potential (voltage) between two electrodes as the titration progresses. The potential change helps accurately detect the equivalence point without relying on colour changes.

The experiment provides an opportunity to understand the redox reaction between Fe²z ions in Mohr's salt and the dichromate ions in $K_2Cr_2O_7$. The method is particularly useful when the reaction mixture involves coloured substances or when the endpoint is difficult to observe with traditional indicators. By plotting a graph of potential against the volume of titrant added, the endpoint of the reaction is precisely determined. This potentiometric approach enhances accuracy and reliability in redox titrations, making it a valuable tool in both academic and industrial chemistry applications.

13.9 Self-Assessment Questions

i. What is Mohr's salt, and what are its key components?

ii. What is the principle of potentiometric titration?

iii. How does potentiometric titration differ from a standard titration?

iv. Why is potassium dichromate ($K_2Cr_2O_7$) used as the titrant in this experiment?

v. Explain the redox reaction that occurs between Mohr's salt and $K_2Cr_2O_7$ during the titration.

vi. Why is Mohr's salt preferred over ferrous sulfate in this titration?

vii. What is the role of the electrodes in potentiometric titration, and why are they essential?

viii. What is the significance of the equivalence point in potentiometric titration?

ix. Why do we use a graph of potential vs. volume of titrant added in this experiment?

x. What are some advantages of potentiometric titration over traditional titration methods?

Unit 14 ❑ Study of phenol-water phase diagram

14.1 Objectives

After studying and performing this experiment, the learner will be able to

- Understand the concept of phase diagrams and their significance in physical chemistry.
- Explain the miscibility behavior of phenol and water at different temperatures.
- Identify the critical solution temperature (CST) and its importance in determining phase separation.
- Analyze the effect of composition and temperature on the phase behavior of a binary system.
- Plot the phase diagram of the phenol-water system based on experimental data.
- Interpret the results in terms of phase equilibria and thermodynamic principles.

14.2 Introduction

The study of phase diagrams is essential in understanding the behavior of components in a mixture as temperature and composition vary. A phase diagram provides crucial insights into the different states or phases a system can exist in, such as solid, liquid, or gas, and how they transition from one to another under different conditions. The phenol-water system, in particular, presents a two-component system that forms distinct phases due to the partial miscibility of phenol and water.

In this experiment, students will examine how temperature influences the solubility of phenol in water and vice versa. This type of study is valuable in physical chemistry as it offers a practical understanding of critical phenomena such as miscibility gaps, which have applications in industries like pharmaceuticals, food processing, and chemical engineering. Understanding this phase behavior helps to design separation processes and optimize product formulations where partial miscibility plays a crucial role.

14.3 Theory

A diagram representing the conditions of equilibrium among different forms or phases of a substance or of a mixture of substances is called a phase diagram. The phase rule is a relation between the number of components (C) and number of phases (P) and the variable parameters or the number of degree of freedom (F) of a heterogeneous system in equilibrium. Mathematically it is expressed as –

$$F = C - P + 2$$

In a binary mixture of two partially miscible liquids e.g., phenol and water, two phases are formed. When phenol is gradually added to water, phenol passes into solution until a saturated solution of phenol in water is obtained. A new phase of higher density, consisting of a saturated solution of water in phenol appears on addition of further quantities of phenol. Increase in the concentration of phenol increases the volume of the second phase (i.e., water in phenol) and decreases the volume of the first phase (i.e., phenol in water), but the relative concentrations of the components in either phase remain constant. Such mutually saturated liquid pairs in contact with the vapour phase constitutes an *invariant system*, the only variable being the temperature. Rise of temperature brings about a change in the mutual solubilities of the two liquids, which can be measured by placing known weights of the two liquids instoppered tubes and observing the temperature at which the boundary between the two liquid phases disappears. The solubility curve of phenol water system (Fig. 1) shows that the mutual solubilities increase with increase of temperature.

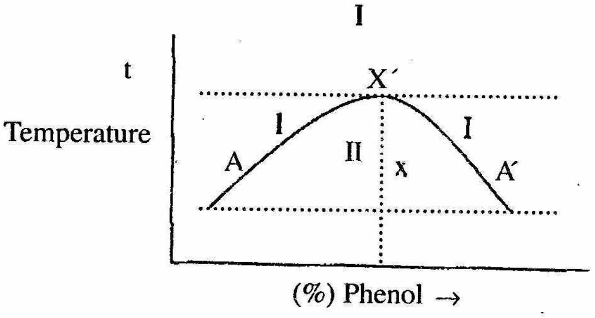


Fig. 1. Solubility curve of phenol-water system

The two phases has an uniquecomposition called *consolute composition* at a certain temperature (t_c) called *critical solution temperature* (CST), or, *consolute temperature* (CT), at which they form a single phase. For phenol water system t_c = 65.9°C is specifically the upper critical solution temperature (UCST) and the *consolute compositions* is, phenol = 34% and water = 66%. Above this temperature the two liquids are completely miscible. Compositions of the liquid pair indicated by any point (x) in between the two solubility curves will separate into two phases (II) indicated by two points A and A', while any composition represented by the points out side the area under the curves will form a single phase (I). Lines (such as A A') joining the two mutual solubilities at any given temperature are called tie-lines and the two solutions represented by the compositions A and A are called *conjugate solutions*.

Since the regions (1) out side the solubility curves consist of only one liquid phase, so. $P = 1$, $C = 2$ (water and phenol), hence, $F = C - P + 2 = 2 - 1 + 2$

= 3. That is, such a system a will be trivariant, Since, pressure is fixed (i.e., 1 atmos.), only two degrees of freedom remain, i.e., temperature and concentration, which should be specified in order to define the system completely. In the regions (II) under the solubility curves, there are two phases, i.e., P = 2, C = 2 (as before), hence, F = C – P + 2 = 2 – 2 + 2 = 2. That is, such systems will be *bivariant*. So if the pressure is fixed (i.e., 1 atmos.), the temperature alone will define the system completely. Therefore, the two phases at any given temperature will have definite compositions, irrespective of their amounts.

At any point on the solubility curves, say at A or A', only a saturated solution of fixed composition is present i.e., C = 1 and P = 1, hence, F = C – P + 2 = 1–1 + 2 = 2, i.e.,if the pressure is fixed (l atmos.), solubility has a definite value at a particular temperature.

At the point x' on this curve, the two liquids have identical composition i.e., saturated solution of phenol in water = saturated solution of water in phenol at temperature t_ci.e., C = 1, P = 2, hence, F = C – P + 2 = 1–2 + 2 = 1. The pressure being kept fixed (i.e., 1 atmos.), the system represented by this point x ' is invariant, since temperature (t_c> and compositions are automatically fixed.

When a third substance, such as, NaCl is added to a binary mixture of two partially miscible liquids (e.g., phenol-water), the 2-component system (C = 2) changes to a 3 component system (C = 3), in which the mutual solubility of the liquids will depend upon the chemical nature and quantity of the third substance. Mutual solubilities generally decrease when the third substance is soluble only in one ofthe two liquids, and consequently *consolute temperature* rises. When the third substance dissolves in both the liquids *consolute temperature* is generally lowered.

14.4 Requirements

Apparatus

i. Hard glass test tube.

ii. Stirrer

iii. Beaker

iv. Burette

v. Thermometer etc.

Chemicals

i. Distilled water (or 0.5% NaCl solution)

ii. Phenol

14.5 Procedure

Table 14.1: Recording of Room Temperature

Temperature before experiment ^{0}C	Temperature after experiment ^{0}C	Mean temperature ^{0}C

1. Weigh out accurately 2-3 g of phenol (Caution, Corrosive) from a weighing bottleinto a hard glass test tube.
2. Add 1 ml of water (or 0.5% NaCl solution as the case may be) to it from a burette. Clamp the test tube inside a large beaker fitted with a glass stirrer. Insert a thermometer into the test tube fitted with a cork. Pour sufficient amount of water in the beaker.
3. Heat the water in the beaker uniformly, while stirring it all the time. The mixture in the test tube which was initially turbid, becomes suddenly clear at a particular temperature. Note the temperature. Allow the whole system to cool. Record the temperature at which turbidity again reappears. Take the mean of these two temperatures (disappearance and reappearance).
4. Go on adding 1 ml portions of water (or 0.5% NaCl solution as the case may be) and at each step note the temperature for disappearance and reappearance of turbidity, until about 16 ml of water (or 0.5% NaCl solution) has been added.At least six readings are taken for before and after the C.S.T.
5. Find the weight percentages of phenol in the mixture from the known weights of phenol and water [density of water (or solution) – 1 g/ml].

6. Draw the solubility curve by plotting the mean of the temperature for the appearance and disappearance of turbidity against weight percentage of phenol. Determine the upper critical solution temperature and the consolute composition for the system and interpret your results.

Table-14.2: Weighing of Phenol

Initial weight (W_1)	**Final Weight (W_2)**	**Weight of Phenoltaken W= (W_2 –W_1) gm**

Table-14.3: Recording of miscibility temperature

No of obs.	**Volume of water added in mL**	**Percent of phenol**	**Miscibility Temperature ^{o}C**		**Mean Temperature ^{o}C**
			Turbidity disappearance	**Turbidity reappearance**	

14.6 Calculation

Draw the solubility curve by plotting the mean of the temperature for the appearance and disappearance of turbidity against weight percentage of phenol.

14.7 Results

Critical solute temperature = …………..

Criticalcomposition for the system= …………..

14.8 Summary

In this experiment, students studied the phase behavior of the phenol-water system to construct its phase diagram. By gradually increasing the temperature and observing the separation of phenol and water into distinct layers, they identified the temperature at which the two components become completely miscible. The experiment helped determine the miscibility limits and identify the critical solution temperature (CST). Understanding the phase diagram of the phenol-water system reinforces key concepts of phase equilibria and miscibility in binary mixtures, providing practical insights into the physical chemistry of two-component systems.

14.9 Self-Assessment Questions

1. What is a phase diagram, and why is it important in physical chemistry?
2. What do you understand by the term "critical solution temperature" (CST)?
3. How is the phenol-water system an example of a partially miscible binary system?
4. What are the phases involved in the phenol-water system at room temperature?
5. Why do phenol and water form two layers at lower temperatures?
6. What happens to the phenol-water system when it reaches the critical solution temperature?
7. How do you determine the composition of the phases in a two-component system using the phase diagram?
8. What is the significance of studying the miscibility of liquids in industrial or biological systems?
9. How does temperature affect the solubility of phenol in water?
10. What is the tie line, and how is it used in interpreting phase diagrams of binary systems?

Unit 15 ❑ Study of phase equilibrium of a ternary system (Toluene – Acetic Acid – Water)

15.1 Objectives

After studying and completing this experiment, the learner will be able to:

- Understand phase equilibrium in a ternary system and apply the concept to practical scenarios.
- Determine and interpret the phase composition in a system involving toluene, acetic acid, and water at equilibrium.
- Construct a ternary phase diagram based on experimental data.
- Analyze the tie-lines and solubility regions in the phase diagram for the system.
- Investigate the partitioning behavior of the components across different phases.
- Apply the lever rule to calculate the amounts of different phases in equilibrium.
- Understand the practical importance of ternary systems in separation processes in industrial applications.

15.2 Introduction

In the previous experiment, the study of the phenol-water phase diagram introduced you to the concept of phase equilibrium in a two-component system. Understanding such equilibrium helps in predicting how substances interact and form phases at different concentrations and temperatures. Building upon this knowledge, we now explore a more complex system involving three components: toluene, acetic acid, and water.

A ternary system involves three components that may form multiple phases depending on their concentrations and interactions. The construction of a ternary phase diagram provides a visual representation of the equilibrium relationships between these components. This experiment will allow you to investigate how the components distribute between different phases and understand the solubility limits and phase separation behaviour. Such diagrams are significant in industries for separation processes, extraction techniques, and other chemical engineering applications.

By expanding from a two-component system to a ternary system, this experiment deepens your understanding of phase equilibria and introduces you to the complexities involved when multiple substances are present in a mixture.

15.3 Theory

A ternary system consists of three components, and its phase behavior can be represented graphically using a triangular diagram, known as a ternary phase diagram. This experiment focuses on studying the phase equilibrium of a ternary system composed of toluene, acetic acid, and water. Understanding the phase equilibrium is essential for various industrial applications, including solvent extraction, chemical separations, and purification processes.

According to Gibbs' phase rule, the number of degrees of freedom (variance, f) of a system in equilibrium is given by the equation:

$$f = c - p + 2$$

where c is the number of components and p is the number of phases. This rule assumes that the equilibrium is influenced solely by temperature, pressure, and concentration.Since it is challenging to construct and visualize plots involving four variables, a common approach is to keep one or more variables constant and plot the remaining ones. In the case of a ternary system, temperature and pressure are typically held constant, while the composition of the components is plotted on triangular graph paper. The pure components are positioned at the corners of the triangle. Lines drawn parallel to the edge opposite each corner represent the total percentage of the component located at that corner within the system.

In the context of this experiment, which is conducted at constant temperature and pressure, these variables are not considered independent. Therefore, the equation simplifies to:

$$f = c - p$$

For a system with three components (c=3), the variance f is:

$$f = 3 - p$$

Thus, if only one phase is present, the variance is 2. If two phases are present, the variance is 1.

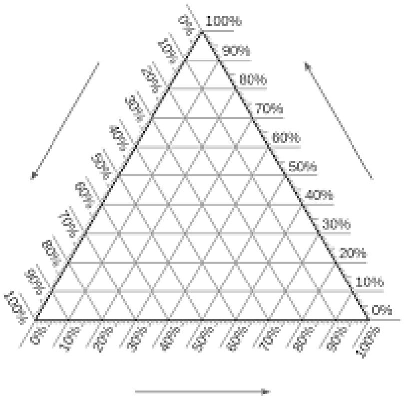


Figure 1: Triangular Plot for Ternary Phase Diagram

When all three pure components are liquids at the temperature and pressure where the phase diagram is constructed, there may be compositions where two immiscible liquid phases form. If we begin with a system that contains only one phase and add a component that shifts the composition into a region where two phases are stable, the phase transition can be observed as cloudiness or turbidity when the system is shaken. This cloudiness results from the scattering of light by the numerous tiny droplets of the second phase that form upon shaking.

For a mixture of components A, B, and C with an overall composition in the two-phase region, the system will separate into two phases—one rich in component B and the other rich in component A. The compositions of these two phases can be determined by the intersections of a tie-line with the phase boundary. The tie-line must also pass through the point representing the overall system composition. The exact location of the tie-lines cannot be predicted in advance and must be determined experimentally, but they all converge at a point on the phase boundary known as the plait point.

15.4 Requirements

Apparatus

- Erlenmeyer flasks
- Pipettes
- Burette
- separating funnels
- funnels

Chemicals

- Toluene;
- glacial acetic acid; 1N NaOH;
- Oxalic Acid
- Phenolphthalein
- Distilled Water

15.5 Procedure

Recording of room temperature

Table 15.1: Recording of Room Temperature

Temperature before experiment ^0C	Temperature after experiment ^0C	Mean temperature ^0C

Preparation of 250 ml Standard ~ (N/10) oxalic acid solution

Prepare 250 ml Standard ~ (N/10) oxalic acid solution by exact weighing and dissolving it in appropriate amount of water[1.575 gm oxalic acid dissolved in 250 ml. water gives a N/10 solution]

Table-15.2: Preparation of 100 ml Standard ~ (N/10) oxalic acid solution

nitial weight (W_1)	Second Weight (W_2)	Weight of oxalic acid taken ($W= W_2 – W_1$)	Strength of oxalic acid solution prepared

Standardisation of NaOH solution against standard oxalic acid solution

250 ml sodium hydroxide solution of (N) order is prepared. [10 gms of NaOH (weighed in rough balance) when dissolved in 250 ml water gives a (N) solution]. Exact strength of NaOH is determined by titrating with standard N/10 oxalic acid as usual procedure.

Table-15.3: Standardisation of ~(N/10) NaOH solution against Standard oxalic acid solution

No. of obs.	Volume of oxalic acid solution taken (ml)	Burette reading. of NaOH solution		Volume of NaOH solution required (ml)	Concordant Volume of NaOH solution required (ml)	Strength of NaOH solution
		Initial	Final			

Preparation of solutions of acetic acid dissolved in water:

In 125 mL conical flasks prepare four solutions of acetic acid in water that are ~ 10%, 25%, 40%, and 60% by weight acetic acid. The total mass of each solution should be ~20 g. For each solution record the mass of acetic acid and the mass of water as shown below. Titrate each of the acetic acid water solutions with toluene. After each addition of toluene, shake the flask. Record the initial and final volumes of toluene added upon the first appearance of cloudiness or turbidity.

Table-15.4: Mixing of Acetic Acid-Water-Toluene

	mass of acetic acid	**mass of water**	**Initial volume of Toluene**	**Final volume of Toluene**
Solution 1				
Solution 2				
Solution 3				
Solution 4				

Preparation of solutions of acetic acid dissolved in toluene

In 125 mL conical flasks prepare four solutions of acetic acid in toluene that are ~ 10%, 25%, 40%, and 60% by weight acetic acid. The total mass of each solution should be ~20 g. For each solution record the mass of acetic acid and the mass of toluene as shown. Titrate each of the acetic acid toluene solutions with water. After each addition of water, shake the flask. Re-cord the initial and final volumes of water added upon the first appearance of cloudiness or turbidity.

Table-15.5: Mixing of Acetic Acid-Water-Toluene

	mass of acetic acid	**mass of toluene**	**Initial volume of water**	**Final volume of water**
Solution 5				
Solution 6				
Solution 7				
Solution 8				

Preparation of solutions of acetic acid, toluene and water

In 125 mL conical flasks prepare four solutions that are approximately 45% by weight toluene and approximately 10%, 20%, 30%, and 40% by weight acetic acid in water. The total mass of each solution should be ~50 g. For each solution record the following data:

Table-15.6: Mixing of Acetic Acid-Water-Toluene

	mass of acetic acid	**mass of toluene**	**Mass of water**
Solution 9			
Solution 10			
Solution 11			
Solution 12			

15.6 Calculations

Calculate the weight percent composition of the initial acetic acid water solutions 1 – 4 and plot these compositions on triangular graph paper.

Place pure acetic acid at the apex of the triangular graph paper.

Calculate the mass of toluene required to just induce phase separation in the acetic acid water solutions 1 – 4.

- Calculate the weight percent composition of the initial acetic acid toluene solutions 5 – 8 and plot these compositions on triangular graph paper.
- Calculate the mass of water required to just induce phase separation in the acetic acid tolu-ene solutions 5 – 8.
- Calculate the weight percent compositions of the boundary separating the 1-phase and 2- phase regions and plot these compositions on triangular graph paper.

- For each of the acetic acid - toluene - water solutions 9 – 12:
- Plot the overall weight percent composition of these solutions on triangular graph paper.
- Calculate the moles of acetic acid in both the upper and lower phases.

Calculate the weight percent acetic acid in each phase.

- On triangular graph paper plot the intersections of the tie lines for these solutions with the boundary separating the 1-phase and 2-phase regions. To plot these tie line intersections, you will have to decide whether the upper or lower phase is the chloroform rich phase.
- Completely label the ternary phase diagram with the number of phases present in each re-gion, the identity of the pure components, present at the corners of the diagram, the plait point, the units on the axes.

15.7 Results

Determine the critical point on the curve

15.8 Summary

In this experiment, the phase equilibrium of a ternary system consisting of toluene, acetic acid, and water is studied. A ternary phase diagram is used to visualize the distribution of these components across different phases. By preparing and analyzing mixtures of the three components, the phase boundaries and compositions of each phase in equilibrium are deter-mined. The results illustrate the interactions between the components and their effects on phase separation. Understanding these interactions is crucial for applications in industrial processes such as solvent extraction, chemical separations, and purification, where managing phase behavior is essential for optimizing efficiency and product purity.

15.9 Self-Assessment Questions

1. What is the purpose of studying the phase equilibrium of a ternary system?
2. How does a ternary phase diagram differ from a binary phase diagram?
3. Describe the role of each component in the ternary system: toluene, acetic acid, and water.
4. What information can be obtained from the phase diagram of a ternary system?
5. Explain the significance of tie lines in a ternary phase diagram.
6. How are the compositions of the phases determined using a ternary phase diagram?