

মানুষের জ্ঞান ও ভাবকে বইয়ের মধ্যে সঞ্চিত করিবার যে একটা প্রচুর সুবিধা আছে, সে কথা কেহই অস্বীকার করিতে পারে না। কিন্তু সেই সুবিধার দ্বারা মনের স্বাভাবিক শক্তিকে একেবারে আচ্ছন্ন করিয়া ফেলিলে বুদ্ধিকে বাবু করিয়া তোলা হয়।

— রবীন্দ্রনাথ ঠাকুর

ভারতের একটা mission আছে, একটা গৌরবময় ভবিষ্যৎ আছে, সেই ভবিষ্যৎ ভারতের উত্তরাধিকারী আমরাই। নূতন ভারতের মুক্তির ইতিহাস আমরাই রচনা করছি এবং করব। এই বিশ্বাস আছে বলেই আমরা সব দুঃখ কষ্ট সহ্য করতে পারি, অন্ধকারময় বর্তমানকে অগ্রাহ্য করতে পারি, বাস্তবের নিষ্ঠুর সত্যগুলি আদর্শের কঠিন আঘাতে ধুলিসাৎ করতে পারি।

— সুভাষচন্দ্র বসু

Any system of education which ignores Indian conditions, requirements, history and sociology is too unscientific to commend itself to any rational support.

— Subhas Chandra Bose

Price : Rs. 250.00

(NSOU-র ছাত্রছাত্রীদের কাছে বিক্রয়ের জন্য নয়)



NETAJI SUBHAS OPEN UNIVERSITY

Choice Based Credit System
(CBCS)

SELF LEARNING MATERIAL

HCH
CHEMISTRY

Pactical Paper-III

CC-CH-05

CBGS • UG • HCH • CHEMISTRY • CC-CH-05

Under Graduate Degree Programme

PREFACE

In a bid to standardise higher education in the country, the University Grants Commission (UGC) has introduced Choice Based Credit System (CBCS) based on five types of courses viz. *core, discipline specific, generic elective, ability and skill enhancement* for graduate students of all programmes at Honours level. This brings in the semester pattern, which finds efficacy in sync with credit system, credit transfer, comprehensive continuous assessments and a graded pattern of evaluation. The objective is to offer learners ample flexibility to choose from a wide gamut of courses, as also to provide them lateral mobility between various educational institutions in the country where they can carry acquired credits. I am happy to note that the University has been accredited by NAAC with grade 'A'.

UGC (Open and Distance Learning Programmes and Online Learning Programmes) Regulations, 2020 have mandated compliance with CBCS for U.G. programmes for all the HEIs in this mode. Welcoming this paradigm shift in higher education, Netaji Subhas Open University (NSOU) has resolved to adopt CBCS from the academic session 2021-22 at the Under Graduate Degree Programme level. The present syllabus, framed in the spirit of syllabi recommended by UGC, lays due stress on all aspects envisaged in the curricular framework of the apex body on higher education. It will be imparted to learners over the *six* semesters of the Programme.

Self Learning Materials (SLMs) are the mainstay of Student Support Services (SSS) of an Open University. From a logistic point of view, NSOU has embarked upon CBCS presently with SLMs in English / Bengali. Eventually, the English version SLMs will be translated into Bengali too, for the benefit of learners. As always, all of our teaching faculties contributed in this process. In addition to this we have also requisitioned the services of best academics in each domain in preparation of the new SLMs. I am sure they will be of commendable academic support. We look forward to proactive feedback from all stakeholders who will participate in the teaching-learning based on these study materials. It has been a very challenging task well executed, and I congratulate all concerned in the preparation of these SLMs.

I wish the venture a grand success.

Professor (Dr.) Subha Sankar Sarkar
Vice-Chancellor

Netaji Subhas Open University
Under Graduate Degree Programme
Choice Based Credit System (CBCS)
Subject: Honours in Chemistry (HCH)
Course : Practical Paper - III
Course Code : CC - CH - 05

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Netaji Subhas Open University

Under Graduate Degree Programme

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Course Code - CC-CH-05

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**Netaji Subhas
Open University**

**UG : Chemistry
(HCH)**

**Course : Practical Paper - III
Course Code - CC - CH - 05**

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Unit 1 □ Kinetic Study of Physical Parameter

Structure

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- 1.8 Determination of Partition Coefficient for the distribution of I_2 between Water**
- 1.9 Determination of solubility of sparingly soluble salt in water, in electrolyte with common ions and in neutral electrolyte (using common indicator)**
- 1.10 Determination of K_{eq} for $\text{KI} + \text{I}_2 = \text{KI}_3$, using partition coefficient between water and CCl_4**
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- 1.12 Determination of K_{sp} for AgCl by potentiometric titration of AgNO_3 solution against standard KCl solution**
- 1.13 Summary**
- 1.14 Questions and Answers**

1.1 Objective

On completion of this unit and performing the experiments, the learner will be able to-

- Explain the basic principles involved in physical chemistry experiments.
- Select and use proper apparatus, instruments and chemicals related to the experiments.
- Explain the concept of thermochemistry and estimate heat of neutralisation and heat of solution.
- Get a generalised idea about kinetics studies and estimate the rate constants of acid-catalysed hydrolysis and decomposition reactions.

- Understand partition co-efficient and use it .
- Measure solubility product of sparingly soluble salts.

1.2 Introduction

In this unit we will study different physical parameters. The first two experiments involves heat changes during chemical and physical processes. The study of heat evolved or absorbed (enthalpy change) during a chemical process is known as thermochemistry. The next few experiments are focused on chemical kinetics. We know that rate constant and order of a chemical reaction are experimentally estimated quantities. Here, we will determine those two quantities for acid-catalysed hydrolysis of ester and decomposition of H_2O_2 titrimetrically. The last part of the unit is focused on chemical equilibrium and measurement of equilibrium constants. There are several kinds of equilibrium possible. However, here we will learn about distribution equilibrium based on Nernst distribution law and solubility product of sparingly soluble salts. These quantities are highly useful in all the areas of chemistry and related subjects.

1.3 Basic Laboratory Knowledge

1.3.1 Laboratory Safety

Laboratory is a place for learning the experimental skills. You are strongly advised to be careful at all times. Without any apron students must not enter into the laboratory. It is recommended not to perform unauthorized experiments. This will ensure your safety as well as the safety of your fellow-students. Even a small accident involving minor injury must be reported to the counsellor. The following instructions should be observed during the laboratory work.

You must wear a laboratory coat or apron over your clothes while working in the chemistry laboratory. This will save you from injury and protect your clothes from damage.

- Handle the hot glass carefully; it cools very slowly and may be very hot without appearing so.
- Protect your eyes from any spurting of acid or a corrosive chemical. In case of such spurting into the eyes, immediately wash with lot of water and go to a doctor.
- You must not reach across lighted burners as it may result in an accident.
- Wash your apparatus thoroughly with a washing powder.
- While heating substances, do not point the tube towards your neighbour or

to yourself. A suddenly formed bubble may eject the contents violently and dangerously.

- (vi) When diluting sulphuric acid, pour the acid slowly and carefully into the water with constant stirring. Never add water to the acid as it may result in the liberation of a lot of heat.
- (vii) Read the label on the bottle carefully before using the required chemical. Never pour back the unused reagent into the bottle.
- (viii) Never touch or taste a chemical or solution as most of chemicals are either corrosive or poisonous.
- (ix) Always bring your container to the reagent shelf and do not take the bottles to your desk.
- (x) Do not insert the pipette or dropper into the reagent bottles; this helps in avoiding any possible contamination.
- (xi) Graduated cylinders and bottles are not to be heated because these break very easily and their volume also changes.
- (xii) At the end of the experiment, clean and dry the glass apparatus and wipe off the top of the working table. Ensure that the gas and water taps are closed before you leave the laboratory.

1.3.2 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 flammable 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

1.3.3 Study of physical parameter

Experiments in the physical laboratory are designed to give you a knowledge regarding properties of matter. Successful performance of any experiment demands sound theoretical background regarding the subject matter of your experiment. Hence, if you want to have accurate results you must have sound theoretical knowledge.

While in the laboratory, you must be fully conscious about what is to be done and how it is to be done. It is better to have a systematic planning about the performance of the experiment before starting. Such pre-planning often saves much of your valuable time and unnecessary hazards during working. So it is better to read the detailed procedure and estimate first the number of flasks, beakers, reagent bottles, pipettes, burettes etc. necessary for your experiment and also the amount of chemicals, solutions etc. necessary for the experiment. This estimation is essential in order to avoid shortage of chemical and solution during the course of the experiment. After this estimation is over, a programming of the experiment should be made in such a way that it may be completed within minimum 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. **DON'T DERIVE THE FORMULA;**
- (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.

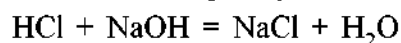
(C) Graph

During drawing a graph don't 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 of 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.

1.4 Determination of heat of neutralisation of a strong acid (HCl) by strong base (NaOH)

Theory :

The heat of reaction is defined as the amount of heat evolved when gram-equivalent quantities of reactants react completely.



When two reactants are mixed, a rise in temperature accompanies the neutralisation process. From the measurement of rise in temperature, the heat evolved can be calculated. The heat capacities of the product and the calorimeter are need to be considered.

Apparatus :

- (i) Calorimeter with stirrer
- (ii) 500 ml conical flask

- (iii) 250 ml conical flask
- (iv) Burette
- (v) Pipette
- (vi) Measuring cylinder
- (vii) thermometer

Reagents :

- (i) 500 ml N/4 HCl solution
- (ii) 500 ml N/4 NaOH solution
- (iii) 250 ml N/4 oxalic acid solution
- (iv) Phenolphthalein indicator

Preparation of Reagents :

- (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

Initial weight (g)	Final weight (g)	Amount of oxalic acid taken (g)	Strength of the solution (N/4)
W_1	W_2	$W_1 - W_2 = W$	$S_1 = W/3.9375$

Procedure :

1. Standardization of NaOH solution :

Table – 1

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

2. Standardization of HCl with standard NaOH solution :**Table – 2**

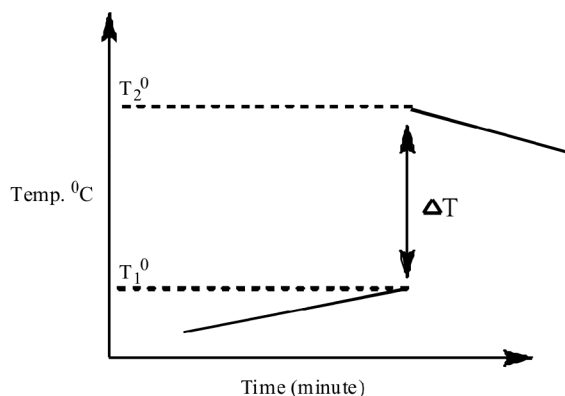
No. of obs. (ml)	Volm. of HCl Initial	Burette reading		Volm. of NaOH (ml)	Mean volm. of NaOH
		Final	(ml)		
1.	25	0	V ₂
2.	25	
3.	25	

- Determine the strength of NaOH Solution.
- Dilute the HCl or NaOH solution to make the equal strength.
- Take 250 ml of the alkali solution in the previously weighed calorimeter.
- Take 250 ml of the acid solution in a conical flask.
- Place two thermometers in both the acid and alkali solution with occasional stirring till temperature become equal.
- Pour the acid solution as rapidly as possible into the alkali solution kept in calorimeter and note the time.
- Mix the two solutions intimately with stirrer.
- 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.
- At first the temperature rises rapidly, then more slowly, and then begins to fall.

Experimental Results :**Table – 3 :**

Time (min)									
Temperature (°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 $T_2 \text{ } ^\circ\text{C} - T_1 \text{ } ^\circ\text{C} = \Delta T \text{ } ^\circ\text{C}$.

Graph :**Calculations :**

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

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 \times sp. heat, which is being equal to that of the water contained in it.

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

Determination the water equivalent of thermometer (immersed portion) :

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 = $2.5 \times 0.19 = 0.47$ and water equivalent of 1 cc of mercury = $13.6 \times 0.034 = 0.46$]

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]

1.5 Determination of heat of solution of oxalic acid from solubility measurement

Theory :

The solubility is expressed as grams of solute needed per 100 g of solvent in order to make a saturated solution at a specific temperature. The heat of solution so calculated is approximately the average heat of solution over the temperature range studied, and corresponds to the heat of solution at the saturation concentration.

Thus, by obtaining the solubility at different temperatures, and by applying the van't Hoff equation, it is possible to determine the heat of solution (ΔH). When applied to solubility, the van't Hoff equation can be expressed as :

$$\log S = - \Delta H / 2.303 RT \dots\dots\dots(1)$$

where "S" is the solubility at different temperatures (T), ΔH is the average heat of solution over the temperature range used, and $R = 1.987 \text{ cal. mol}^{-1} \text{ degree}^{-1}$ and ΔH (cal. mole^{-1}) is the heat of solution.

In this experiment, the heat of solution of **oxalic acid** in water will be measured at **4 different temperatures (40°, 35°, 30° and 25° C)**.

Apparatus Required :

- (i) Thermometer
- (ii) Water bath
- (iii) Hot plate or Sand bath
- (iv) Petri dish
- (v) Watch glass
- (vi) Beaker
- (vii) Pipette (2 or 5 ml)

Chemical Required :

- (i) Oxalic acid

Procedure :

1. Take about 30 ml of distilled water in a 100 ml beaker
2. Dissolve oxalic acid to make the solution saturated at higher temperature (40°C).
3. Stir the solution for about 3 minutes.
4. Now this solution is brought to different temperatures on the hot water bath (or ice cubes when required to lower temperature).
5. Weigh 4 dry and clean petri dishes / watch glasses accurately.
6. Pipette out tipped with cotton or glass wool plug 2 ml (or 5 ml) of the clear saturated solution in 4 different dishes at different temperature.

7. Note the temperature during collection of the saturated solution.
8. Weight the dishes with solution, collected at different temperature .
9. Evaporate the solutions to dryness on a sand bath or hot plate and dry in an oven at about 100°C , cool the dishes and weigh again accurately.

Experimental Result :

Temp. °C	Wt. of empty dish W_1 (g)	Wt. of dish + 2 (or 5) ml solution W_2 (g)	Wt. of dish + solute W_3 (g)	Wt. of solute $(W_3 - W_1)$ (g)	Wt. of solvent $(W_2 - W_3)$ (g)	Solubility $= \frac{(w_3 - w_1)}{(w_2 - w_2)} \times 100g/100$
40						
35						
30						
25						

Calculation :

$$\log S = - \Delta H / 2.303 RT \quad \therefore \Delta H = - 2.303 RT \times \log S \text{ Cal mole}^{-1}$$

$$\therefore \text{Mean } \Delta H = (H_{25} + H_{30} + H_{35} + H_{40}) / 4 \text{ Cal. mole}^{-1}$$

Alternative Method :

Chemicals Required :

- (i) Oxalic acid
- (ii) NaOH

Procedure :

1. Prepare 100 ml of ~ 0.2 (N) oxalic acid solution.
2. Prepare 250 ml of ~ 0.2 (N) NaOH solution.
3. Standardisation of NaOH solution against standard oxalic acid solution :
Pipette out 10 ml of standard oxalic acid in a conical flask and add 1-2 drops of phenolphthalein indicator. Titrate the solution with NaOH solution from burette till pink colour appears.
4. Take about 30 ml of distilled water in a 100 ml of beaker
5. Dissolve oxalic acid to make the solution saturated.
6. Stir the solution for about 3 minutes.
7. Now this solution is brought to different temperatures on the hot water bath (or ice cubes when required to lower temperature).
8. The saturated solution is maintained at **4 different temperatures**, in turn. At **each temperature, 2ml** of the saturated solution is pipetted out using a filter

tip attached to the pipette (a rubber tubing stuffed with glass wool / cotton), so as to prevent solid particles from entering into the pipette.

9. This solution is titrated against 0.2N NaOH solution, using phenolphthalein as indicator.

Experimental Results :

Table – 1 : Preparation of 100 ml 0.2 (N) oxalic acid solution

Initial weight (g)	Final weight (g)	Oxalic acid taken (g)	Amount of oxalic acid required (g)	Strength of oxalic acid solution
W_1	W_2	$W_1 - W_2$	0.126	$W_1 - W_2 / 0.126 = f \text{ (N)}$

Table – 2 : Standardisation of NaOH solution against standard oxalic acid solution

No. of obs	Volm. of oxalic acid (ml)	Burette reading		Volm. of NaOH (ml)	Mean volm. of NaOH (ml)	Strength of NaOH soln.
		Initial	Final			
1	10	0		
2	10	y(N)
3	10		

Table – 3

Temp. °C	Volm. of oxalic acid (ml)	Burette reading		Volm. of NaOH (ml)	Strength of NaOH soln. (N)	Strength of Oxalic acid soln. (N)	Solubility of oxalic acid (s) (g/100)	ΔH (cal. Mole ⁻¹)
		Initial	Final					
25	2	0	y	
30	2	y	
35	2	y	
40	2	y	

Calculation :

1. Strength of NaOH solution :

Volume of oxalic acid = 10 ml ; Strength of oxalic acid solution = f (N)

Volume of NaOH solution = V ml ; Strength of NaOH solution = ?

We know, $V_1 \times S_1 = V_2 \times S_2$ \therefore Strength of NaOH solution = $10 \times f / V$ (N) = y (N)

2. Solubility of oxalic acid :

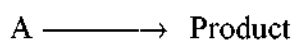
S = Strength of oxalic acid (N) x 63 / 10 (g/100)

 \therefore Mean $\Delta H = (H_{25} + H_{30} + H_{35} + H_{40}) / 4 \text{ cal.mole}^{-1}$

1.6 Study of kinetics of acid-catalysed hydrolysis of methyl acetate

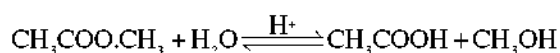
Theory :

A first order reaction can be defined as a chemical reaction in which the rate/speed of the reaction is directly proportional to the concentration of reactant at any moment/instant. First order reaction can be represented as



$$\therefore \text{Rate} \propto [A] = k [A]$$

The hydrolysis of methyl acetate, catalysed by acid, is a pseudo-unimolecular 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

$$\text{Rate} = k' [\text{ester}] [\text{H}_2\text{O}] = k [\text{ester}]$$

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

Expressed mathematically,

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

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

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

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

where k is the proportionality constant called *first-order rate constant* or *specific reaction rate*.

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

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

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

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, $\ln a = \text{constant}$.

Substituting the value of constant, we have

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

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

$$\text{or, } \frac{2.303}{t} \log_{10} \frac{a}{(a-x)} = k$$

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 (weak acid) and the strong acid used as catalyst (HCl, a constant quantity).

Let V_0 , V_t and V_∞ 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,

$$a \propto (V_\infty - V_0) \text{ and } (a-x) \propto (V_\infty - V_t)$$

Amount of ester consumed = amount of weak acid formed $(V_t - V_0)$

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

$$\therefore k = \frac{2.303}{t} \log_{10} \frac{(V_\infty - V_0)}{(V_\infty - V_t)}$$

So, a graph may be obtained by plotting $\log_{10} \frac{(V_{\infty} - V_o)}{(V_{\infty} - V_t)}$ 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 line will be obtained with slope equal to $-\frac{k}{2.303}$.

Apparatus required:

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

Chemicals Required :

- (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.

Preparation of Solution:

- (i) 250 ml 0.1 (N) NaOH solution: Dissolve about 1 gm of NaOH in 250 ml of distilled water.
- (ii) 100 ml 0.5 (N) HCl solution : Take 4.2 ml of concentrated HCl (12 N) and diluting with distilled water to 100 ml.

Procedure:

1. 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.
2. 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.
3. 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 .

4. 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 .
5. 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 .
6. Heat the rest of the solution at about 60-70°C in a water bath for about 30 minutes fitting an air condenser to mouth of the conical flask. Cool mixture, till it attain to room temperature. Pipette out 5 ml of the solution in 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_∞ .

Experimental Results:

1. Table – 1 : Room temperature

Temperature before experiment °C	Temperature after experiment °C	Mean temperature °C

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

Table – 2 :

No. of obs	Time in Mins. (t)	Vol. Of NaOH consumed (V_t) ml	($V_\infty - V_0$) ml	($V_\infty - V_t$) ml	Log ($V_\infty - V_t$)	$\frac{(V_\infty - V_0)}{(V_\infty - V_t)}$	k from graph
1	0	V_0					
2	5						
3	10						
4	15						
5	20						
6	25						
7	infinity	V_∞					

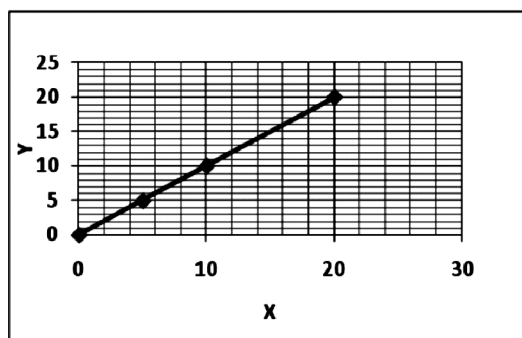
3. Graph :

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 = ---

$\therefore k = \text{slope} \times 2.303 = \text{-----} / \text{min at } \text{..... } ^{\circ}\text{C}$

[Expected value of $k = 3.37 \times 10^{-3} \text{ min}^{-1}$ at 25°C]

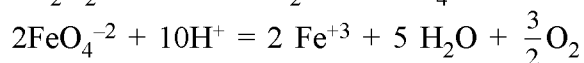
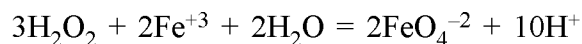


1.7 Study of kinetics of decomposition of H_2O_2

Theory :

Hydrogen peroxide decomposes spontaneously to H_2O and O_2 as $\text{H}_2\text{O}_2 = \text{H}_2\text{O} + \frac{1}{2} \text{O}_2$. 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 .

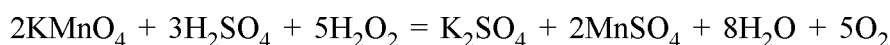
Decomposition of H_2O_2 catalysed by Fe^{+3} is believed to occur by the following paths. Here H_2O_2 decomposes by catalytic action of Fe^{+3} through the formation of Ferrate ion.



Adding, we have $3\text{H}_2\text{O}_2 = 3\text{H}_2\text{O} + \frac{3}{2}\text{O}_2$

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.



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,

$$k = \frac{2.303}{t} \log \frac{v_0}{v_t}$$

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

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

Apparatus :

- (i) Burette
- (ii) Pipette
- (iii) Conical flask
- (iv) Glass trough
- (v) Stop watch
- (vi) Volumetric flask
- (vii) Thermometer

Reagents :

- (i) 1 vol. H_2O_2
- (ii) 1% FeCl_3 solution
- (iii) 1(N) H_2SO_4
- (iv) N/50 KMnO_4 solution

Preparation of Reagents :

- (i) **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.
- (ii) **1% FeCl_3 solution** : Dissolve 1 gm. of FeCl_3 (using rough balance) in 100 ml of distilled water.

- (iii) **250 ml 1(N) H₂SO₄** : 7 ml concentrated H₂SO₄ (36 N) to be diluted with distilled water to 250 ml.
- (iv) **500 ml N/50 KMnO₄ solution** : Dissolve about 0.32 gm KMnO₄ in 500 ml of distilled water.

Procedure :

- (i) Take five or six 100 ml conical flask and transfer 25 ml (N) H₂SO₄ by pipette. Add some crush ice to make the solution ice cold.
- (ii) Take 100 ml of 1 vol. H₂O₂ in 250 ml conical flask and add 20 ml of 1% FeCl₃ solution by a pipette. When pipette was half-emptied time was noted. This is zero time.
- (iii) Pipette out 5 ml of the reaction mixture at an interval of 2 to 3 mins. and pour into 25 ml ice cold (N) H₂SO₄ solution and then titrate with KMnO₄ 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.
- (iv) To find the value of V₀, take 5 ml of 1 vol. H₂O₂ in a conical flask containing 25 ml (N) H₂SO₄ and titrate with KMnO₄ solution. However, in the reaction mixture 100 ml H₂O₂ solution was mixed with 20 ml FeCl₃ solution, so it was diluted by $(120 \div 100) = 1.2$ times. If in this titration V is the burette reading then $V_0 = \frac{V}{1.2}$.

Experimental Results :

1. **Table – 1: Room temperature**

Temperature before experiment °C	Temperature after experiment °C	Mean temperature °C

2. **Determination of V₀ :**

5 ml of original H₂O₂ solution \equiv ---- ml KMnO₄ (say V)

$$\therefore V_0 = \frac{V}{1.2} = \text{---- ml}$$

3.

Table – 2 :

No. of obs.	Time (mins)	Volume of N/50 KMnO ₄			log $\frac{V_o}{V_t}$
		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.					

4. Graph :

Now, plot a graph $\log \frac{V_o}{V_t}$ against time 't'; gives a straight line passing through the origin.

Its slope is = ---

∴ k = slope × 2.303 = ---- / min at °C

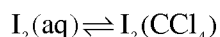
[Expected value of k = × 10⁻² min⁻¹ at 25°C]

1.8 Determination of Partition Coefficient for the distribution of I₂ between Water and CCl₄

Theory :

When a solute is shaken with two immiscible solvents, the solute will distribute itself in two solvents in such a way that the ratio of the concentration of the solute in the two liquids is constant at a constant temperature, provided the substance dissolves in both the solvents in the same form and no chemical reaction takes place, and also there is neither association or dissociation of the solute in the solvents. The constancy of the ratio is called the distribution co-efficient or partition co-efficient, followed from Nernst Distribution Law.

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



At equilibrium, the ratio of concentrations of the solute in two solvents is constant at a given temperature and independent of the actual amount of solute. Let, C_1 and C_2 be the concentration of solute in carbon tetrachloride and water respectively, then according to Nernst Distribution Law,

$$K = C_1/C_2 = \text{constant}$$

Where, K is known as distribution co-efficient or partition co-efficient.

The constancy of K follows from thermodynamic principles that when the two phases of the same solute are in equilibrium at a given temperature and pressure, the chemical potential of the dissolved solute becomes the same in both phases.

Let us assume that a solute is distributed between two immiscible solvents I and II. We also assume that μ_I and μ_{II} be the chemical potentials of the solute in solvents I and II, where its activities are a_I and a_{II} respectively. Therefore,

$$\mu_I = z_I + RT \ln a_I$$

$$\mu_{II} = z_{II} + RT \ln a_{II}$$

Where z_I and z_{II} are constant, R is gas constant and T is temperature.

We know that at equilibrium, $\mu_I = \mu_{II}$

$$\therefore z_I + RT \ln a_I = z_{II} + RT \ln a_{II}$$

$$\text{or, } RT \ln a_I/a_{II} = z_{II} - z_I = \text{constant}$$

$$\text{or, At constant temperature } a_I/a_{II} = \text{constant}$$

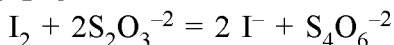
Replacing the activity terms by concentration terms, we have

Concentration of solute in solvent I

$$\text{-----} = \text{Constant} = K$$

Concentration of solute in solvent II

In this experiment I_2 in each layer is estimated by titrating against the standard $\text{Na}_2\text{S}_2\text{O}_3$ solution using starch as indicator.



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

$$C_2 = V_2 \times S_1/V_1$$

$$[C_2 = \text{Strength of } \text{I}_2 \text{ in aqueous layer}]$$

Similarly, if V_3 ml of CCl_4 layer of iodine requires V_4 ml of $\text{S}_2(\text{N})$ thiosulphate solution, then

$$C_1 = V_4 \times S_2/V_3 \quad [C_1 = \text{Strength of } \text{I}_2 \text{ in } \text{CCl}_4 \text{ layer}]$$

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 Required :

- (i) Saturated solution of I_2 in CCl_4
- (ii) Pure CCl_4
- (iii) N/10 $\text{K}_2\text{Cr}_2\text{O}_7$
- (iv) N/10 $\text{Na}_2\text{S}_2\text{O}_3$
- (v) 10% KI solution
- (vi) 1% freshly prepared starch solution

Procedure :

1. 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	15	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.

2. Prepare N/10 $\text{Na}_2\text{S}_2\text{O}_3$ by dissolving about 12.5 g $\text{Na}_2\text{S}_2\text{O}_3$ in 500 ml. distilled water.
3. Standardize N/10 $\text{Na}_2\text{S}_2\text{O}_3$ solution against standard N/10 $\text{K}_2\text{Cr}_2\text{O}_7$ solution : Pipette out 25 ml of $\text{K}_2\text{Cr}_2\text{O}_7$ solution in 500 ml conical flask and add 10 ml

of 5 ml conc. HCl and 2 g KI. Cover the mouth of the flask with watch glass, shake well and keep in a dark place for about 5 minutes. Add 175 ml of distilled water and titrated with thiosulphate solution from the burette until the colour turns to straw yellow. Add 2 ml of 1% starch solution and continue the titration until the blue colour turns to green. Note the burette reading and repeat experiment thrice.

4. Prepare 250 ml N/100 $\text{Na}_2\text{S}_2\text{O}_3$ solution by exact dilution. Pipette out 25 ml S N/10 $\text{Na}_2\text{S}_2\text{O}_3$ solution in a 250 ml volumetric flask followed by dilution up to the mark with distilled water.
5. 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 $\text{Na}_2\text{S}_2\text{O}_3$ solution.
6. Repeat the experiment 2-3 times for each separate bottles.
7. 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/10 $\text{Na}_2\text{S}_2\text{O}_3$ solution.
8. Repeat the experiment 2-3 times for each separate bottles.
9. Note the temperature just before and after the experiment.

Experimental Result :

Table -1 : Recording of room temperature

Temperature before experiment °C	Temperature after experiment °C	Mean temperature °C

Table – 2 : Preparation of 250 ml S (N/10) $\text{K}_2\text{Cr}_2\text{O}_7$ solution :

Initial weight (g)	Final weight (g)	Weight taken (g)	Weight required (g)	Volume to be made (ml)	Strength of $\text{K}_2\text{Cr}_2\text{O}_7$ solution
W_1	W_2	$W = W_1 - W_2$	1.2257	250	$W/1.2257$ (N/10) = S (N)

Table – 3 : Standardisation of $\text{Na}_2\text{S}_2\text{O}_3$ solution against standard $\text{K}_2\text{Cr}_2\text{O}_7$ solution :

No. of obs.	Volm. of $\text{K}_2\text{Cr}_2\text{O}_7$ (ml)	Burette reading		Volm. of $\text{Na}_2\text{S}_2\text{O}_3$ soln. (ml)	Mean volm. of $\text{Na}_2\text{S}_2\text{O}_3$ soln. (ml)
		Initial	Final		
1.	25	0	V ₁
2.	25	
3.	25	

Table – 4 : Titration of solvent layers

Bottle	Volm. of CCl_4 layer (ml)	Carbon tetrachloride layer				Aqueous layer				
		Burette reading		Volm. of N/10 $\text{S}_2\text{O}_3^{2-}$ (ml)	Mean volume (ml)	Volm. of aqueous layer (ml)	Burette reading		Volm. of N/100 $\text{S}_2\text{O}_3^{2-}$	Mean volume (ml)
		Initial	Final				Initial	Final		
1	5	0	50	0		
	5		50
	5		50
2	5	0	50	0		
	5		50
	5		50
3	5	0	50	0		
	5		50
	5		50

Calculation :

1. Determination of strength of $\text{Na}_2\text{S}_2\text{O}_3$ solution :

Volume of $\text{K}_2\text{Cr}_2\text{O}_7$ solution = 25 ml

Strength of $\text{K}_2\text{Cr}_2\text{O}_7$ solution = S (N)

Volume of $\text{Na}_2\text{S}_2\text{O}_3$ solution = V₁ ml

Strength of $\text{Na}_2\text{S}_2\text{O}_3$ solution = S₁ = ?

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

2. Determination of Partition co-efficient ;

Bottle - 1 :

CCl₄ layer : Volume of CCl₄ layer = 5 ml
 Strength of CCl₄ layer = C₁ = ?
 Volume Na₂S₂O₃ solution = V₁
 Strength of Na₂S₂O₃ solution = S₁
 $\therefore C_1 = V_1 \times S_1 / 5 (N)$

Aqueous layer : Volume of aqueous layer = 50 ml
 Strength of aqueous layer = C₂ = ?
 Volume Na₂S₂O₃ solution = V₂
 Strength of Na₂S₂O₃ solution = S₂
 $\therefore C_2 = V_2 \times S_2 / 50 (N)$
 $\therefore K_1 = C_1/C_2$

Similarly calculate the concentration of I₂ in aqueous and CCl₄ layers for two other bottles separately.

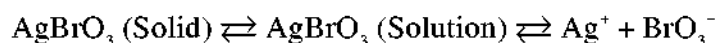
$$\therefore \text{Partition co-efficient} = K = (K_1 + K_2 + K_3)/3$$

1.9 Determination of solubility of sparingly soluble salt in water in electrolyte with common ions and in neutral electrolyte (using common indicator)

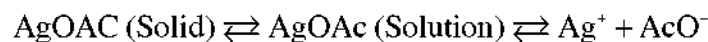
Theory :

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 :



Or,



Thermodynamically it can be shown that the products of activities of Ag⁺ and BrO₃⁻ (or AcO⁻) ions is a constant at a given temperature.

$$a_{\text{Ag}^+} \cdot a_{\text{BrO}_3^-} = S_a \text{ where, } S_a = \text{Activity solubility of Silver bromate}$$

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

We have,

$$S_a = a_{\text{Ag}^+} \cdot a_{\text{BrO}_3^-} = C_{\text{Ag}^+} \cdot C_{\text{BrO}_3^-} \cdot f_{\text{Ag}^+} \cdot f_{\text{BrO}_3^-} = C_{\text{Ag}^+} \cdot C_{\text{BrO}_3^-} \cdot (f_{\pm})^2$$

In very dilute solution,

$$f_{\text{Ag}^+} = f_{\text{BrO}_3^-} = 1$$

$$\begin{aligned} \therefore S_a &= C_{\text{Ag}^+} \cdot C_{\text{BrO}_3^-} = K_{\text{sp}} \text{ (concentration solubility product)} \\ &= S \times S = S^2 \quad (S = \text{molar solubility of ions}) \end{aligned}$$

$$\therefore S = S_a$$

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, $K_{\text{sp}} = C_{\text{Ag}^+} \cdot C_{\text{BrO}_3^-}$, does not remain constant when either C_{Ag^+} or $C_{\text{BrO}_3^-}$ 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 $C_{\text{BrO}_3^-}$ 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 influenced 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 in ionic strength (*i*) reduce the activity coefficient (f_{\pm}) 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.

Apparatus Required :

- (i) 250 ml volumetric flask
- (ii) Burette
- (iii) Pipette
- (iv) 250 ml conical flask
- (v) Bottles with stopper

Chemicals Required :

- (a) Silver bromate (or Silver acetate)
- (b) Silver nitrate
- (c) KNO_3
- (d) NH_4CNS or KCNS
- (e) Ferric alum
- (f) C. HNO_3

Procedure :

- (i) Prepare 250 ml of AgNO_3 solution of the order 0.01(N) (or slightly higher) and 100 ml of KNO_3 solution of the order 0.01(N) (or slightly higher).
- (ii) Prepare 250 ml of exactly 0.01 (N) of AgNO_3 solution and 100 ml of exactly 0.01 (N) KNO_3 solution, by taking the required amounts of solutions already prepared under (i) and then by proper quantitative dilution.
- (iii) Prepare 250 ml of 0.05 (N) NH_4CNS or KCNS solution.
- (iv) 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.
- (v) 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.
- (vi) The bottles are then stoppered well and shaken in a mechanical shaker for about 30 minutes.

- vii) 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.
- viii) Repeat the procedure (vii) above for Bottle No. II & III.
- ix) Calculate the concentration of silver each bottle. Hence, the molar solubilities and “Concentration Solubility Products” of silver bromate (or Silver acetate) are found out.

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.

Experimental Result :

Table -1 : Recording of room temperature

Temperature before experiment °C	Temperature after experiment °C	Mean temperature °C

Table – 2 : Preparation of 250 ml of standard 0.01 (N) AgNO_3 solution

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	$W/0.4247$ $= S_1(N/100)$

Table – 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 (g)	Strength of KNO_3 Solution (N/100)
W_3	W_4	$W=W_3-W_4$	0.2528	100	$W/0.2528$

Table – 4 : Standardisation of NH₄CNS (or KCNS) solution with 0.01(N) AgNO₃ solution

Pipette out 25 ml of silver nitrate solution in a 250ml 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.

No. of obs.	Volm. of AgNO ₃ (ml)	Burette reading		Volm. of NH ₄ CNS soln. (ml)	Mean volm. of NH ₄ CNS soln. (ml)
		Initial	Final		
1	25	0
2	25	V ₂
3	25

Calculation :

Strength of NH₄CNS solution = S₂

Volume of NH₄CNS solution = V₂

Strength of AgNO₃ solution = S₁(N/100)

Volume of AgNO₃ solution = V₁ = 25 ml

∴ S₂ = (25 . S₁ / V₂) N / 100

Table – 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 : 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)	Mean volume (ml)	Molar concentration of Ag^+
		Initial	Final			
I	10	0	X_1	$X_1 \times S_2 / 10 = y_1 (\text{M})$
	10		
II	10	X_2	$X_2 \times S_2 / 10 = y_2 (\text{M})$
	10		
III	10	X_3	$X_3 \times S_2 / 10 = y_3 (\text{M})$
	10		

Table – 7 : Molar Solubility and Concentration Solubility Product of Silver Bromate (or Silver Acetate)

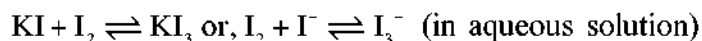
Bottle No.	Molar concentration of Ag^+	Molar concentration of BrO_3^- (or AcO^-)	Molar Solubility of AgBrO_3 (or AgOAc)	Solubility Product of AgBrO_3 (or AgOAc) (K_{sp})
I	$y_1 (\text{M})$	$y_1 (\text{M})$	$y_1 (\text{M})$	y_1^2
II	$y_2 (\text{M})$	$y_2 - 0.01 (\text{M})$	$y_2 - 0.01 (\text{M})$	$y_2 (y_2 - 0.01)$
III	$y_3 (\text{M})$	$y_3 (\text{M})$	$y_3 (\text{M})$	y_3^2

Expected Solubility product of $\text{AgBrO}_3 = 5.5 \times 10^{-5}$; $\text{AgOAc} = 1.94 \times 10^{-3}$ at 25°C

1.10 Determination of K_{eq} for $\text{KI} + \text{I}_2 = \text{KI}_3$, using partition coefficient between water and CCl_4

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



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

$$K = \frac{a_{\text{KI}_3}}{a_{\text{KI}} \times a_{\text{I}_2}}$$

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,

$$K = \frac{C_{\text{KI}_3}}{C_{\text{KI}} \times C_{\text{I}_2}}$$

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 and the ratio is known as partition or distribution coefficient. Applying this law to iodine for water and immiscible organic solvent (CCl_4), we have—

$$K_d = \frac{a_{\text{I}_2}(\text{org})}{a_{\text{I}_2}(\text{water})} = \frac{C_{\text{I}_2}(\text{org})}{C_{\text{I}_2}(\text{water})}$$

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

$$K = \frac{[\text{KI}_3]_{\text{aq}}}{[\text{KI}]_{\text{aq}}[\text{I}_2]_{\text{aq}}}$$

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_o = total iodine concentration in organic (CCl_4) layer at equilibrium.

- (ii) Concentration of free I_2 in aqueous layer = $[\text{I}_2]_{\text{aq}} = \frac{[\text{I}_2]_{\text{org}}}{K_d} = C_o/K_d$ [from definition of K_d]

- (iii) $[\text{KI}_3]_{\text{aq}} = (\text{total iodine conc. in aq. Layer}) - (\text{conc. of free iodine in aq. Layer})$
 $= (C_w - C_0/K_d)$
- (iv) $[\text{KI}]_{\text{aq}} = (\text{Initial conc. of KI}) - (\text{amount consumed to form equivalent amount of KI}_3)$
 $= C - (C_w - C_0/K_d)$

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

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.

Apparatus Required :

- (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 Required :

- (i) Saturated I_2 solution in CCl_4
- (ii) Pure CCl_4
- (iii) A.R KI
- (iv) A.R. $\text{K}_2\text{Cr}_2\text{O}_7$
- (v) (N/20) $\text{Na}_2\text{S}_2\text{O}_3$ solution [~ 12.5g in 1000 ml]
- (vi) 10% KI solution
- (vii) 1% freshly prepared starch solution.

Procedure :

1. Prepare 250 ml of standard S(N/20) $\text{K}_2\text{Cr}_2\text{O}_7$ solution by accurate weighing.
2. Prepare 500 ml of standard S (N/20) KI solution by accurate weighing.

3. Prepare 500 ml of S (N/20) $\text{Na}_2\text{S}_2\text{O}_3$ solution.
4. Standardize S(N/20) $\text{Na}_2\text{S}_2\text{O}_3$ solution with standard S(N/20) $\text{K}_2\text{Cr}_2\text{O}_7$ solution.

Pipette out 25 ml of standard S(N/20) $\text{K}_2\text{Cr}_2\text{O}_7$ 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 S (N/20) $\text{Na}_2\text{S}_2\text{O}_3$ 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.

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

Table – 1 : Mixture preparation

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

6. Shake the bottles for about 45 minutes and then allow to stand for 15 minutes for complete separation of layers.
7. 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) $\text{Na}_2\text{S}_2\text{O}_3$ solution as usual following iodometric method. Then calculate C_0 .
8. 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) $\text{Na}_2\text{S}_2\text{O}_3$ solution as usual following iodometric method. Then calculate C_w .
9. Determine partition coefficient (Kd) of iodine between CCl_4 and water.

Experimental Results :**Table – 2 : Recording of Room Temperature**

Temperature before the experiment $^{\circ}\text{C}$	Temperature after the experiment $^{\circ}\text{C}$	Mean temperature $^{\circ}\text{C}$

Table – 3 : Preparation of 250 ml (N/20) $\text{K}_2\text{Cr}_2\text{O}_7$ solution

Initial weight (g)	Final weight (g)	Weight taken (g)	Weight required (g)	Volume to be made (ml)	Strength of $\text{K}_2\text{Cr}_2\text{O}_7$ solution
W_1	W_2	$W = W_1 - W_2$	0.6128	250	$(W/0.6128)$ N/20

Table – 4 : 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

Table – 5 : Standardisation of S (N/20) $\text{Na}_2\text{S}_2\text{O}_3$ solution against standard $\text{K}_2\text{Cr}_2\text{O}_7$ solution

No. of obs.	Volm. of $\text{K}_2\text{Cr}_2\text{O}_7$ (ml)	Burette reading		Volm. of $\text{Na}_2\text{S}_2\text{O}_3$ soln. (ml)	Mean volm. of $\text{Na}_2\text{S}_2\text{O}_3$ soln. (ml)	Strength of $\text{Na}_2\text{S}_2\text{O}_3$ solution (N)
		Initial	Final			
1.	25	0	
2.	25	0	
3.	25	

Table – 6 : Titration of solvent layers

Bottle Nos.	No. of obs.	Vol. of aliquot (ml)	Burette reading		Vol. of Na ₂ S ₂ O ₃ (ml)	Mean Vol. of Na ₂ S ₂ O ₃ (ml)	Value of C ₀	Vol. of aliquot (ml)	Burette reading		Vol. of Na ₂ S ₂ O ₃ (ml)	Mean Vol. of Na ₂ S ₂ O ₃ (ml)	Value of C _w	Partition co-efficient K _d = C ₀ /C _w	Conc. of free I ₂ in aq. layer (C ₀ /K _d) in M	Conc. of [KI ₃]aq = C _w - C ₀ /K _d (M)	Conc. of [KI] in M	Equilibrium constant (K _{eq})
			Initial	Final					Initial	Final								
1	1	25	0			10	0							
	2	5			10							
	3	5			10							
2	1	5	0			10	0							
	2	5	0			10	0							
	3	5			10							
3	1	5	0			10	0							
	2	5			10							
	3	5			10							

Calculations :

$$(1) \text{ Partition coefficient} = K_d = C_{(\text{org})} / C_{(\text{aq})} = C_0 / C_w = K_1$$

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

$$(2) K_{\text{eqm}} = \frac{C_w - \frac{C_0}{K_d}}{\left\{ C - \left(C_w - \frac{C_0}{K_d} \right) \right\} \frac{C_0}{K_d}}$$

$$K_{\text{eqm}} = (K_{\text{eqm}} + K_{\text{eqm}} + K_{\text{eqm}}) / 3 = K_{\text{eqm}} \text{ at } \dots \text{ } ^\circ\text{C}$$

1.11 Determination of K_{eq} for acetic acid, using partition coefficient between water and 1-Butanol

When a system consists of parts which have different physical properties and are separated by boundary surface, the system is said to be a heterogeneous one. The Nernst distribution law states that at constant temperature when different quantities of a solute are allowed to distribute between two immiscible solvents in contact with each other, then at equilibrium the ratio of the concentration of the solute in two layers are constant at a particular temperature.

When a solute is shaken in two immiscible liquids, then the solute is found to be distributed between the liquids in a definite manner, if the solute is soluble in each of the solvent. According to the distribution law the distribution coefficient at a

particular temperature is given by $K = \frac{S_1}{S_2}$ Where S_1 and S_2 represent the concentration of the solute in solvent-1 and solvent- 2 respectively.

Consider a liquid- liquid system, say water and 1-Butanol (two immiscible solvents), to which a little quantity of acetic acid is added. Acetic acid will dissolve partly in water and partly in 1-Butanol. The two solutions of acetic acid will separate into two layers at equilibrium. The concentration of acetic acid in two layers is different but their ratio is fixed at a constant temperature.

The partition coefficient = $K_d = C_{org} / C_{aq}$

Apparatus Required :

- (i) Two dry 250 ml glass- stoppered bottles
- (ii) Volumetric flask (250 ml)
- (iii) Burette
- (iv) Pipette
- (v) Conical flask (250 ml)
- (vi) Mechanical shaker

Chemicals Required :

- (i) Pure 1- Butanol
- (ii) Glacial acetic acid
- (iii) (N/2) NaOH solution
- (iv) Oxalic acid
- (v) Phenolphthalein indicator

Procedure :

1. Prepare 100 ml standard (N/2) oxalic acid solution
2. Prepare 250 ml ~ (N/2) NaOH solution [5 g in 250 ml of distilled water]
3. Prepare 250 ml ~ 2 (N) acetic acid solution [31.25 ml glacial acetic acid in 250 ml of solution]
4. Standardization of (N/2) NaOH solution with standard oxalic acid solution. Pipette out 10 ml of standard oxalic acid solution in 250 ml conical flask and add about 10 ml of distilled water and then titrate with (N/2) NaOH solution using phenolphthalein as indicator till pink colour appears.
5. Standardization of ~2(N) AcOH solution with standard NaOH solution. Pipette out 5 ml of ~2(N) acetic acid solution in 250 ml conical flask and add about 20 ml of distilled water and then titrate with (N/2) NaOH solution using phenolphthalein as indicator till pink colour appears.
Now prepare exactly 2(N) AcOH solution, by taking required volume of the solution already prepared by quantitative dilution.
6. Prepare the following mixtures in dry, clean, leak proof glass stoppered 250 ml bottles

Table – 1 :

Bottle No. – I	Bottle No. - II
50 ml of 1- Butanol	75 ml of 1 - Butanol
50 ml of distilled water	-----
50 ml 2 (N) AcOH solution	75 ml of 2(N) AcOH solution

Shake the bottles for about 30 minutes in a mechanical shaker and then allow to stand for another 20 minutes for complete separation of layers.

7. Pipette out 5 ml aqueous layer into a conical flask. Add 20 ml water and 2-3 drops of phenolphthalein indicator. Shake the mixture and titrate against standard NaOH solution till pink colour appears.
8. Pipette out 5 ml organic layer (1-Butanol) into a conical flask. Add 20 ml water and 2-3 drops of phenolphthalein indicator. Shake the mixture and titrate against standard NaOH solution till pink colour appears.
9. Determine partition coefficient (K_d) of acetic acid between 1- Butanol and water.

Experimental Results :**Table – 2 : Recording of Room Temperature**

Temperature before the experiment °C	Temperature after the experiment °C	Mean temperature °C

Table – 3 : Preparation of 100 ml (N/20) Oxalic acid solution

Initial weight (g)	Final weight (g)	Weight taken (g)	Weight required (g)	Volume to be made (ml)	Strength of K_1 solution
W_1	W_2	$W = W_1 - W_2$	0.3152	100	$W/0.3152$ (N/20)

Table – 4 : Standardisation of ~ (N/20) NaOH solution against standard oxalic acid solution

No. of obs.	Volm. of Oxalic acid (ml)	Burette reading		Volm. of NaOH soln. (ml)	Mean volm. of NaOH soln. (ml)	Strength of NaOH solution (N)
		Initial	Final			
1.	10	0		
2.	10		
3.	10		

Table – 5 : Standardisation of ~ 2(N) AcOH solution against standard NaOH solution

No. of obs.	Volm. of AcOH (ml)	Burette reading		Volm. of NaOH soln. (ml)	Mean volm. of NaOH soln. (ml)	Strength of NaOH solution (N)
		Initial	Final			
1.	5	0		
2.	5		
3.	5		

Table – 6 : Initial Concentration of acetic acid in mixtures (C)

Bottle No.	Concentration of AcOH (N)
I	0.6666
II	1.0

Table – 7 : Titration of solvent layers

Bottle Nos.	No. of obs.	Vol. of aliquot (ml)	Burette reading		Vol. of Na ₂ OH (ml)	Mean Vol. of NaOH (ml)	Value of C ₀	Vol. of aliquot (ml)	Burette reading		Vol. of NaOH (ml)	Mean Vol. of Na ₂ S ₂ O ₃ (ml)	Value of C _w	Partition co-efficient $K_d = C_o/C_w$
			Initial	Final					Initial	Final				
I	1	5	0			5	0			
	2	5			5			
	3	5			5			
II	1	5	0			5	0			
	2	5			5			
	3	5			5			

Calculations :**Bottle – I :**

Acetic acid in organic layer,

$$V_1 S_1 = V_2 S_2 \quad [\text{Where, } V_1 = \text{Volume of the acetic acid solution,}$$

$S_1 = \text{Strength of the acetic acid, } V_2 = \text{Volume of NaOH solution, } S_2 = \text{Strength of NaOH solution}]$

$$\therefore S_1 = \frac{V_2 S_2}{V_1} \quad (i)$$

Acetic acid in aqueous Layer,

$V_3S_3 = V_4S_4$ [Where, V_3 = Volume of the acetic acid solution,
 S_3 = Strength of the acetic acid, V_4 = Volume of NaOH solution,
 S_4 = Strength of NaOH solution]

$$\therefore S_3 = \frac{V_4S_4}{V_3} \text{ (ii)}$$

From equation (i) & (ii),

The partition co-efficient of acetic acid in bottle I is

$$K_d^I = \frac{S_1}{S_3} = \frac{C_o}{C_w}$$

(Where C_o and C_w are the concentration of acetic acid in organic and aqueous layers respectively)

Bottle – II :

Acetic acid in organic layer,

$V_1S_1 = V_2S_2$ [where, V_1 = Volume of the acetic acid solution, S_1 = Strength of the acetic acid, S_2 = Strength of the NaOH Solution,
 V_2 = Volume of the NaOH solution]

$$\therefore S_1 = \frac{V_2S_2}{V_1} \text{ ---(iii)}$$

Acetic acid in aqueous layer,

$V_3S_3 = V_4S_4$ [where, V_3 = Volume of the acetic acid solution,
 S_3 = Strength of the acetic acid,

$$\therefore S_3 = \frac{V_4S_4}{V_3} \text{ ---(iv) } V_4 = \text{Volume of the NaOH solution,}$$

S_4 = Strength of the NaOH Solution]

From equation (iii) & (iv),

The partition co-efficient of acetic acid in bottle II is

$$K_d^{II} = \frac{S_1}{S_3} = \frac{C_o}{C_w}$$

(where C_o and C_w are the concentration of acetic acid in organic and aqueous layers respectively)

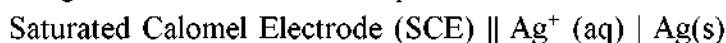
Hence the mean partition co-efficient of acetic acid in between n-butanol and water is

$$K_d = \frac{K_d^I + K_d^{II}}{2} \text{ at } \dots\dots\dots^\circ\text{C}$$

1.12 Determination of K_{sp} for AgCl potentiometric titration of AgNO_3 solution against standard KCl solution

Principle :

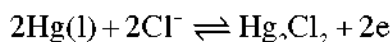
When a solution of AgNO_3 is taken in a beaker and clean Ag wire is inserted in it to act as an electrode the $\text{Ag}^+/\text{Ag}(\text{s})$ half-cell is produced, which is reversible with respect to Ag^+ ions. If this electrode is coupled with a reference electrode, such as saturated calomel electrode (SCE), $(\text{Pt}) \text{Hg}(\text{l}) | \text{Hg}_2\text{Cl}_2(\text{s}) | \text{KCl}(\text{sat}, \text{aq})$, the following electrochemical cell is produced :



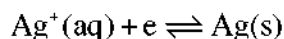
Where, \parallel represents salt bridge (agar-agar, KNO_3 or NH_4NO_3), which eliminates the liquid junction potential.

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

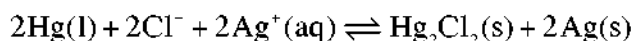
At left hand electrode,



At right electrode,



The cell reaction is,



The *emf* of the cell at 25°C is given by,

$$E_{\text{cell}} = E_{\text{Ag}^+/\text{Ag}}^0 + 0.059 \log \frac{a_{\text{Ag}^+(\text{aq})}}{a_{\text{Ag}(\text{s})}} - E_{\text{SCE}} \dots\dots\dots \text{(i)}$$

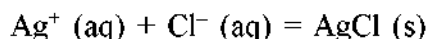
Where ‘a’ is represented as the activity of the species, E^0 is the standard electrode potential (means when all species being at the standard state of unit activity).

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°C becomes,

$$E_{\text{cell}} = E_{\text{Ag}^+/\text{Ag}}^0 + 0.059 \log [\text{Ag}^+] - E_{\text{SCE}} \dots \dots \text{(ii)}$$

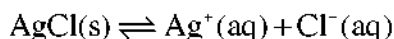
The *emf* of the cell varies with the change of $[\text{Ag}^+]$, as E_{SCE} remains unchanged at a given temperature and $E_{\text{Ag}^+/\text{Ag}}^0$ is constant.

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.



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 from the dissociation of sparingly soluble salt AgCl.



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

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

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

$$K_s = a_{\text{Ag}^+} \times a_{\text{Cl}^-} = [\text{Ag}^+][\text{Cl}^-] = [\text{Ag}^+]^2 \quad \because [\text{Ag}^+] = [\text{Cl}^-]$$

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

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

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

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

If the room temperature is $T^\circ \text{K}$ 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 $[\text{Ag}^+]$ due to the common ion effect of Cl^- ions. Hence E_{cell} will gradually decrease with increase of $[\text{Cl}^-]$.

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.

Apparatus :

- (i) Potentiometer
- (ii) Silver electrode
- (iii) Saturated calomel electrode
- (iv) Beaker
- (v) Pipette
- (vi) Burette
- (vii) $\sim 2(\text{M}) \text{KNO}_3$ (or NH_4NO_3) – Agar-Agar salt bridge

Chemicals required :

- (i) Standard $\sim (\text{M}/10)$ KCl solution
- (ii) Standard $\sim (\text{M}/100)$ AgNO_3 solution

Procedure :

- (1) Prepare a salt bridge using $\sim 2(\text{M}) \text{KNO}_3$ (or NH_4NO_3) solution and Agar-Agar.
- (2) Prepare 100 ml of standard $\sim (\text{M}/100)$ AgNO_3
- (3) Prepare 100 ml of standard $\sim (\text{M}/10)$ KCl solution
- (4) Take 10 ml S $(\text{M}/100)$ AgNO_3 solution in a 100 ml beaker and add sufficient amount of distilled water so that the Ag- electrode can be properly dipped.
- (5) Connect this half – cell with the SCE through the prepared salt bridge.
- (6) Connect the experimental cell with the potentiometer.
- (7) Standardise the potentiometer against the standard cell (most cases it is inbuilt). Then measure the *emf* of the experimental cell.
- (8) 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.
- (9) Plot the observed *emf* vs. n (number of drops of KCl added).
- (10) Determine the end point from the graph
- (11) Calculate the solubility product from the known value of $E_{\text{Ag}^+/\text{Ag}}^0$ and E_{SCE}

Table – 1 : Recording of Room Temperature

Temperature before the experiment °C	Temperature after the experiment °C	Mean temperature °C

Table – 2 : Preparation of 100 ml of (M/100) AgNO₃ 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

Table – 3 : Preparation of 100 ml of (M/10) KCl solution

Initial wt. (g)	Final wt. (g)	Wt. of KCl taken (g)	Weight required (g)	Concentration of KCl soln.
W ₁	W ₂	W ₁ – W ₂ = W	0.7455	W/0.7455 = f ₁

Table – 4 : Potentiometric Titration of AgNO₃ 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			

Calculation :

Calculate K_s using the relation :

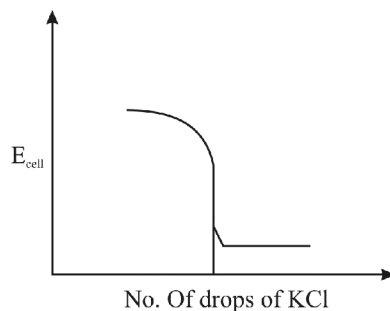
$$E_{\text{cell}}(\text{eqv.}) = E_{\text{Ag}^+/\text{Ag}}^0 + (0.059/2) \log K_s - E_{\text{SCE}}$$

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

Literature values of $E_{\text{Ag}^+/\text{Ag}}^0 = + 0.779 \text{ V}$ and E_{SCE} at room temperature (t°C) is, $E_{\text{SCE}}(\text{saturated}) = 0.2415 - 7.6 \times 10^{-4} (t - 25)$ in Volt.

Graph :

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

**1.13 Summary**

In this unit we learned about heat of neutralisation of acid-basic reaction and heat of solution of basic acids. We also performed experiments to determine order and rate constants of chemical reactions. The distribution of a solute in two immisible solvents are estimated and with the help of the partition co-efficient the equilibrium constant of a reaction has been estimated. Performing these experiments gives us a basic idea about estimation of different physical parameters of physical and chemical process.

1.14. Questions and Answers**Experiment- 1.6****1. Distinguish between order and molecularity.**

Ans :

ORDER	MOLECULARITY
1. Kinetic order is a purely experimental property connected with the Rate equation. It is not necessarily connected with the chemical equation of the reaction. 2. In a reaction, $A + B + \dots = \dots$, if the observed Rate = $[A]^x \times [B]^y \dots$,	1. Molecularity is a theoretical property. In the classic definition, it is connected with the overall chemical equation, and in the modern definition with the mechanism. 2. Molecularity (classical) is defined as the sum of the

ORDER	MOLECULARITY
The order of reaction = x + y + --- 3. Order may change with physical condition, such as pressure, solvent etc	stoichiometric co-efficient in the simplest chemical equation, whereas Molecularity (modern) is defined as the number of molecules taking part in the rate determining step of its mechanism. 3. Molecularity (classical) is an invariant number for a given chemical reaction.

EXAMPLE

Reaction	Observed Rate Law	Order	Molecularity
$pA + qB = \text{product}$	$\text{Rate} \propto [A]^x \times [B]^y$	$x + y$	$p + q$
$2N_2O_5 = 4NO_2 + O_2$	$\text{Rate} \propto [N_2O_5]$	1	2
$2NO + O_2 = 2NO_2$	$\text{Rate} \propto [NO]^2 \times [O_2]$	3	3
$S_2O_8^{2-} + 2I^- = 2SO_4^{2-} + I_2$	$\text{Rate} \propto [S_2O_8^{2-}] \times [I^-]$	2	3

2. What is pseudo-first order reaction?

Ans : In some hydrolysis reactions, water (solvent) takes part but its order does not appear in the Rate law because its concentration change is negligibly small. Such solvolytic first order reactions are called pseudo-unimolecular or pseudo-first order. Another example is hydrolysis (inversion) of cane sugar to glucose and fructose.

3. How rate constant varies with temperature?

Ans : Arrhenius equation : $k = Ae^{-\frac{E_a}{RT}}$ or, $\log k = \log A - \frac{E_a}{2.303 RT}$;
 where E_a = energy of activation and A = frequency factor.

4. The graph you draw, points corresponding to high 't' values being to show deviation, why ?

Ans. Reversibility of the reaction becomes important at later stage and so simple first order equation is not valid then.

5. Why NaOH is not necessary to standardize in this experiment?

Ans : In first order rate equation k is dimensionless ; as $\frac{a}{a-x}$ is concentration

ratio. If same NaOH is used concentration ratio = volume ratio; hence standardisation is not required.

6. What is the dimension of rate constant?

Ans : (Concentration)^{1 - n} Time⁻¹ ; n = order

7. Why Baryta gives more accurate result compare to NaOH for this experiment?

Ans : When NaOH is used as a titrate there is a possibility of saponification reaction (second order) between ester and NaOH. This side reaction (usually slow) may bring some error. In case of Baryta such error does not happen.

8. For a reaction, rate is found to be (a) independent of time (b) falling exponentially with time (c) zero at beginning, then increases and reaches to maximum and then falls. Predict their natures.

Ans : (a) Zero order (b) Non- zero order (c) Order less chain reaction.

Experiment 1.7

1. Why standardization of KMnO_4 is not necessary in this experiment?

Ans : In first order rate equation k is dimensionless ; as $\frac{a}{(a-x)}$ is concentration ratio. If same KMnO_4 is used concentration ratio = volume ratio; hence standardisation is not required.

See experiment -1.6 for other relevant questions.

Experiment 1.9

Q-1: Distinguish between 'activity product' and 'concentration solubility product'.

Ans : See theory.

Q-2: What accurate method are known to you for solubility product measurements ?

Ans : When solubility of salt is really very small then analytical methods failed to give good result. The instrumental e.g., conductivity method, potentiometric method etc. are more suitable to get accurate result.

Q-3 : How does solubility of sparingly soluble salt change in presence of (i) common ion (ii) un-common or inert ion ?

Ans : (i) Decreases (ii) Increases [see theory]

Q-4: What is the most important application of solubility product principle ?

Ans : Inorganic qualitative analysis of cations by wet methods is based on solubility product principle.

Q-5: Can it be possible to measure heat of solution from solubility product value?

Ans : Solubility product changes with temperature. If K_{s_1} and K_{s_2} are solubility products at T_1 and T_2 temperature respectively, then from Vant Hoff's equation, we have $\ln K_{s_1}/K_{s_2} = \Delta H/R (T_2 - T_1/T_1T_2)$. Where ΔH is heat of solution.

Experiment 1.10

1. How many types of equilibrium constant are known to you ? Which equilibrium conc. is used here?

Ans : There are three types, K_p , K_c & K_x . Here K_c has been used.

2. What are the dimensions of equilibrium constant ?

Ans : $K_p = (\text{atm.})^{\Delta n}$; $K_c = (\text{M/L})^{\Delta n}$ and K_x is dimension less. [Δn = difference in number of moles products and reactants].

3. For this reaction equilibrium constant decreases with rise in temperature – what does it mean?

Ans : This reaction is exothermic.

Unit 2 □ Study of physical parameter

Structure

- 2.1 Objective**
- 2.2 Introduction**
- 2.3 Determination of unknown Concentration of liquid (glycerol, sugar) with respect to water by viscosity measurement**
- 2.4 Determination of pH of unknown buffer solution, by color matching method.**
- 2.5 Conductometric titration of an acid against strong base**
- 2.6 Study of saponification reaction conductometrically**
- 2.7 Potentiometric titration of Mohr's salt solution against standard $K_2Cr_2O_7$ solution**
- 2.8 To study the Kinetics of the Persulphate-Iodide reaction by Colorimetric Method**
- 2.9 Study of the phase diagram of a binary system (phenol-water)**
- 2.10 pH-metric titration of weak acid (mono-and di-basic) against strong base**
- 2.11 Summary**
- 2.12 Questions and Answers**

2.1 Objectives

After studying this unit and performing all the experiments, the learner will be able to—

- Gain basic knowledge about the working principle of different instruments used in physical chemistry laboratory.
- Process different samples using Ostwald's viscometer, stalagmometer, conductometer, potentiometer, pH meter etc.
- Comprehend titration using conductometric procedures and study chemical reaction conductometrically.
- Explain the fundamental concepts of a binary phase diagram.
- Explain basic operational principle of a pH meter, glass-electrode etc. and pH-titration.
- Understand Lambert-Beer law and its use.

2.2 Introduction

Physical chemistry experiments involve several measurement apparatus and instruments. In this unit, we will learn some of their use. The very basic apparatus used in a chemical laboratory for measurement of viscosity and surface tension of liquid samples are Ostwald's visometer and stalagmometer. In both cases, the physical parameter is measured with respect to water or a standard liquid. Conductometry is a versatile technique used in several important research. Here, we will learn about conductometric titration which does not require an indicator and thus more accurate. Similarly potentiometric titrations can be performed if an oxidation-reduction reaction is happening during neutralisation. pH-metric titrations are useful for weak acid-or weak base estimation. These are all alternative techniques and are more versatile than pipette-burette methods. We will also learn about colourimetric method and phase diagram.

2.3 Determination of unknown concentration of liquid (glycerol, sugar) with respect to water by viscosity measurement

Theory :

When a liquid flows, each portion of the liquid experiences a resistance to flow relative to another neighbouring 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 symbol η (called as 'eta') whose unit is thus dyne-second/sq.cm which is generally known as poise after the name of Poiseuille.

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

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

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. If exactly the same volume of a liquid of viscosity ρ_2 is introduced into the same tube, the driving force is equal to ρ_2hg where ' ρ_2 ' is the density of the second liquid.

Now from Poiseuille's equation $\eta = \frac{\pi Pr^4 t}{8Vl}$ 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-

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

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

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

Apparatus and Chemicals Required :

- (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
- (vi) Supplied 'standard' solution (let 20% glycerine);
- (vii) Supplied solution of unknown strength for same thing (let glycerine)

Procedure :

1. The specific gravity bottle is thoroughly washed and dried and then weighed accurately.
2. It is next filled with water and weighed again.
3. It is dried and filled with the supplied standard solution (let 20% glycerine) and weighed again.
4. 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.

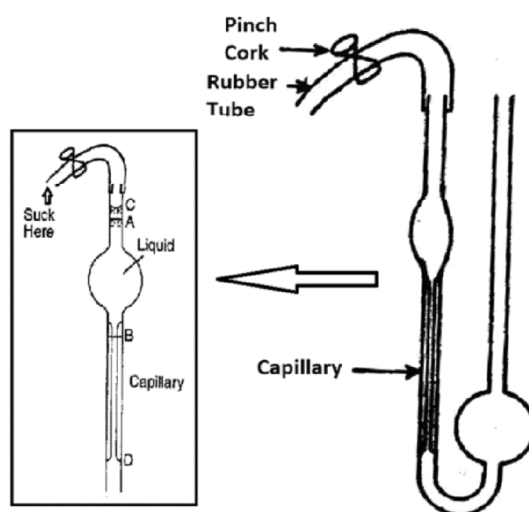


Fig. 2.3.1 : Ostwald's Viscometer

- The Ostwald's, Viscometer (see Fig. 2.31) 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, the volume 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.

10. 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% solⁿ) and here also the time of fall is noted as above. This observation is repeated twice.
11. 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.
12. 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.

Experimental Results :

Table 1: Recording of room temperatures

Temperature before experiment °C	Temperature after experiment °C	Mean temperature °C

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

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

Table 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 $\frac{w_3 - w_1}{w_2 - w_1} \times \rho_{H_2O} \text{ gm / cc}$
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.

Table 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 by taken 3rd Standard (5%)	Time taken by unknown solution	Mean Time taken by unknown solution
1										
2										
3										
4										

Table 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					

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.

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 $\pm 0.1^\circ$.

Critical Comments on the Experiment on Viscosity

As viscosity is a measure of the resistance offered to the flow of a liquid, there is a term fluidity which is defined as the measure of the tendency of flow of a liquid. Fluidity (ϕ) is thus reciprocal viscosity and thus $\phi = \frac{1}{\eta}$ and it is additive in nature.

In the Ostwald's viscometer as the flow of the liquid is simply due to hydrostatic pressure difference between the two limbs partial or full opening of the pinch cock has no effect on the time of flow. However, volume of the liquid introduced in each time must be the same, otherwise difference in height of the liquid level in the two limbs will be different in different cases.

Viscosities of non-associated liquids decrease with rise in temperature and it has a linear relationship with reciprocal of temperature. In case of associated liquids however, viscosity increases with the increase in temperature.

2.4 Determination of pH of unknown buffer solution, by colour matching method.

Theory :

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

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

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,

$$\text{pH} = -\log_{10} C_{H^+} \dots\dots\dots(2)$$

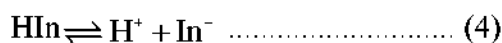
Buffer solution is a solution whose pH doesn't change on addition of a little quantity of acid or alkali. The resistance offered by the solution to change the pH of the solution is known as buffer action. Generally buffer solution is a mixture of a weak acid and its salt or a weak base and its salt. 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 case may be. pH of a buffer solution consisting of a weak acid and its salt with a strong base is expressed by the Henderson equation:

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

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,



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

$$K_{in} = \frac{[\text{H}^+][\text{In}^-]}{[\text{HIn}]} \quad \text{.....(5)}$$

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,

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

$$pH = pK_{in} + \log_{10} \frac{[\text{In}^-]_{\text{colour}}}{[\text{HIn}]_{\text{colour}}} \quad \text{.....(7)}$$

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 (HIn) when $[\text{HIn}] \geq 10 [\text{In}^-]$ and it will show the colour of its basic form $[\text{In}^-]$ when $[\text{In}^-] \geq 10[\text{HIn}]$. That is, the colour change interval of the indicator will be :

$$[\text{HIn}] \geq 10[\text{In}^-] \quad pH = pK_{in} - 1 \quad \text{..... colour of HIn}$$

$$[\text{In}^-] \geq 10[\text{HIn}] \quad pH = pK_{in} + 1 \quad \text{..... colour of In}$$

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, ($[\text{acid}] / [\text{salt}]$). 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 : $(\text{pK}_{\text{in}} - 1) < \text{pH} < (\text{pK}_{\text{in}} + 1)$ and pK_{a} of the weak acid falls within $\text{pH} \pm 1$ of the unknown solution.

Apparatus and chemicals required

- (i) Hard glass test-tubes
- (ii) Burette
- (iii) Beaker
- (iv) ~ (N/10) oxalic acid solution
- (v) ~ 0.5 (N) NaOH solution
- (vi) 0.4 (N) acetic acid solution
- (vii) phenolphthalein indicator
- (viii) Supplied Unknown buffer solution of unknown pH

Procedure :

(For acetic acid-acetate buffer, pK_{a} of acetic acid = 4.74 at 25°C)

- (i) 100 ml standard ~ (N/10) oxalic acid solution is prepared by exact weighing followed by dilution.
- (ii) 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.
- (iii) 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.
- (iv) 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.
- (v) Find the strength of the acetic acid solution and prepare 100 ml exact 0.4 (N) acetic acid solution by dilution using a burette.

- (vi) 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.
- (vii) 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-1**) and mix uniformly. pH of each set is determined from Henderson equation.

Table-1: Preparation of different standard buffer solution

Test-tube No.	Volume of 0.4(N)CH ₃ COOH (ml)	Vol. of 0.4(N) NaOH(ml)	Vol. of H ₂ O (ml)	Total Volume (ml)	pH (experimental)
1	5.0	0.5	4.5	10.0	3.72
2	5.0	1.0	4.0	10.0	4.05
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

- (viii) 2-3 drops of bromocresol green indicator (pK_{in} close to pK_a of the acid) is added to each test tube (1 to 9) and mixed well.
- (ix) 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.

Experimental results :**Table-2: Preparation of 100 ml Standard ~ (N/10) oxalic acid solution**

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

Table-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)	Mean Volume of NaOH solution required(ml)	Strength of NaOH solution
		Initial	Final			

Table-4 : Standardisation of ~0.5 (N) acetic acid solution 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			

Conclusion :

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 solution is

2.5 Conductometric titration of an acid against strong base

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).

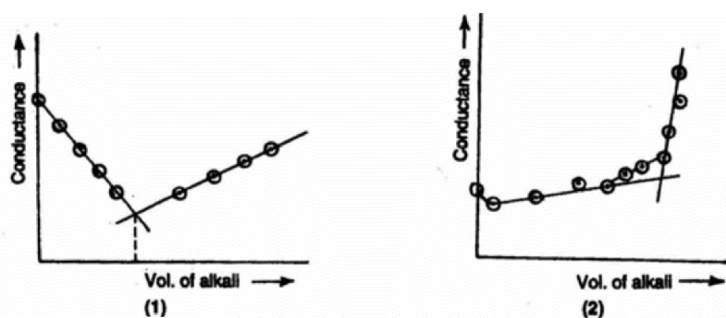


Fig. (1) & (2) : Conductometric titration curve for strong acid strong base and weak acid strong base

[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.]

Apparatus and Chemicals

- (i) Conductivity bridge
- (ii) Conductivity cell
- (iii) Microburette or ordinary burette
- (iv) Pipette
- (v) Volumetric flask
- (vi) Hydrochloric acid and Acetic acid of (N/10) order
- (vii) Sodium hydroxide solution of (N) order and (N/10) Oxalic acid.

Procedure

1. 250 ml oxalic acid solution of strength N/10 is prepared by exact weighing. [1.575 gm oxalic acid dissolved in 250 ml. water gives a N/10 solution].
2. 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].
3. Exact strength of NaOH is determined by titrating with standard N/10 oxalic acid as usual procedure.
4. The conductivity cell is thoroughly washed with deionised water and is kept in a 100 ml beaker. 25 ml of the supplied HCl 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.
5. 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.]
6. From the burette 3 to 4 drops of NaOH is added to the HCl solution in the conductivity cell. The solution is stirred thoroughly and its conductance is measured. Again another 3 to 4 drops of 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).
7. 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.

8. 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.

Experimental Results :

Table 1: Recording of room temperatures

Temperature before experiment °C	Temperature after experiment °C	Mean Temperature °C

Table-2: Preparation of 100 ml Standard ~ (N/10) oxalic acid solution

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

Table-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)	Mean Volume of NaOH solution required (ml)	Strength of NaOH solution
		Initial	Final			

Table-4: Standardisation of ~ (N/10) acetic acid solution 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			

Table-5: Measurement of conductance

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

Conclusion :

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]

$$S = \frac{V \times f}{25} (N)$$

Strength of HCl =(N)

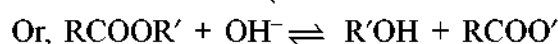
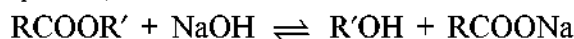
Critical Comments

Conductometric titrations are of various types. For titration of a mixture of strong and weak acid (e.g. HCl + CH₃COOH) by an alkali two break points are obtained. Volume corresponding to first break point is volume consumed by HCl and volume in between first and second break point is volume required for CH₃COOH. For a weak dibasic acid where $K_{a1} \gg K_{a2}$ similar curve with two break points are observed. Titration between CH₃COONa Vs HCl; NH₄Cl Vs NaOH are also acid base titrations. Precipitation titrations can also be done. These are much accurate. For details consult any standard text book on electrochemistry.

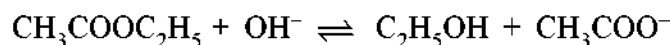
2.6 Study of saponification reaction conductometrically

Theory :

When an ester, RCOOR' , derived from a monocarboxylic acid, RCOOH , and a monohydric alcohol $\text{R}'\text{OH}$, 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,



Such alkaline hydrolysis of an ester is called saponification. Ethyl acetate ($\text{CH}_3\text{COOC}_2\text{H}_5$) on alkaline hydrolysis produces ethanol ($\text{C}_2\text{H}_5\text{OH}$) and acetate ion (CH_3COO^-):



$t = 0$	a	a	0	0
$t = t$	$a - x$	$a - x$	x	x
$t = \infty$	0	0	a	a

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

$$\frac{dx}{dt} = k[\text{CH}_3\text{COOC}_2\text{H}_5] \cdot [\text{OH}^-] = k \cdot (a - x)^2$$

The solution of the differential equation is $\int \frac{dx}{(a-x)^2} = \int k dt$ 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 $\text{mole}^{-1} \cdot \text{litre} \cdot \text{second}^{-1}$.

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

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

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

$$\text{a.k.t} = \frac{x}{(a-x)}$$

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 ($\lambda_0 = 198.5 \text{ ohm}^{-1} \text{ cm}^2 \cdot \text{mol}^{-1}$) are replaced by weakly conducting CH_3COO^- ions ($\lambda_0 = 40.9 \text{ ohm}^{-1} \text{ cm}^2 \cdot \text{mol}^{-1}$). 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, $t = \infty$) respectively then, total change of conductivity is proportional to total concentration of ethyl acetate. Then we may write

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

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

$$(a - x) \propto (C_t - C_\infty)$$

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

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

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

Since ' a ' is known. Here, a is calculated by diluting a known amount of the ester to a definite volume with water. C_∞ may be indirectly determined by measuring the conductance of a solution of sodium acetate, $\text{CH}_3\text{COO}^- \text{Na}^+$, of the same concentration, ' a ', i.e., exactly equal to the 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 ∞ (infinity) respectively.

Apparatus required :

1. Conductometer with dip type cell.
2. Exactly (N/50) NaOH solution,
3. Oxalic acid solution ~ (N/10) for standardising NaOH solution,
4. KCl solution exact (N/10) for standardising the conductometer,
5. 100 ml dry and clean beakers to be used as reaction vessel.
6. Volumetric Flask (100 ml & 250 ml)
7. Pipette
8. Burette etc.

Procedure :

1. 100 ml (N/10) (exact) KCl solution is prepared and standardize the conductometer following the instruction manual. [0.745 gm KCl dissolved in 100 cc. water produces (N/10) (exact) solution. To get exactly (N/10), initially ~0.8 gm KCl is dissolved in 100 cc. water. This will produce a solution whose concentration is > (N/10). Now calculated amount of water is added to make it exactly (N/10). Water used should be deionised water.]
2. 100 ml (N/25) oxalic acid solution is prepared by accurate weighing followed by dilution with distilled water.
3. **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.
4. **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 indicator. Prepare 100 ml of exact (N/50) acetic acid solution by accurate dilution of the standard ~(N/25) solution using the formula $V_1S_1 = V_2S_2$.
5. **Measurements of Conductance C_0 :** Prepare 100 ml exact (N/100) NaOH solution by accurate dilution of standard (N/50) NaOH with water in a volumetric flask. Now 50 ml (N/100) NaOH is taken in a 100 ml beaker. Conductivity cell is dipped and conductance is measured. This gives the value of C_0 .
6. **Measurements of Conductance C_α :** Prepare 50 ml exact (N/100) solution of sodium acetate, $\text{CH}_3\text{COO}^-\text{Na}^+$, 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_α .
7. **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 calculate damount 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]

8. **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.
9. 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.

Experimental Results :

Table 1: Recording of room temperatures

Temperature before experiment °C	Temperature after experiment °C	Mean temperature °C

Table-2 : Preparation of 100 ml Standard ~ (N/25) oxalic acid solution

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

**Table-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)	Mean Volume of NaOH solution required (ml)	Strength of NaOH solution
		Initial	Final			

**Table-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)	Mean Volume of NaOH solution required (ml)	Strength of NaOH 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 : $V_1S_1 = V_2S_2$]

Table-5: Measurements of Conductance C_0 & C_{∞}

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

Table-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	$C_0 - C_\infty$ (in mho)

Plotting values against time (t) which will give a straight line passing through the origin.

Conclusion :

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

Slope = $k \cdot a$. $\therefore k = \text{Slope}/a$ [a = initial concentration to be supplied solution *i.e.* 0.01 (N)]

Critical Comments

Such reactions are reversible. Effect of reversibility becomes significant after some time. So readings of first fifteen minutes are to be considered.

2.7 Potentiometric titration of Mohr's salt solution against standard $K_2Cr_2O_7$ solution

POTENTIOMETRIC TITRATIONS : A suitable electrochemical cell is constructed, which permits the measurement of concentration of a wide range of solutes. All electrochemical cells consist of two electrodes (i) a reference electrode, the voltage of which is independent of the nature and composition of the solutions into which it is placed and (ii) an indicator electrode, the voltage of which is dependent on the concentration or more correctly the thermodynamic activity of one of the component in solution. When the two electrodes are connected, an electrochemical cell is constructed. The e.m.f. of the cell can be determined by connection to a suitable potentiometer or millivoltmeter which can read to ± 0.2 mv. The e.m.f. of the cell is defined by

$$E_{\text{cell}} = E_+ - E_- + E_j$$

Where E_j is the liquid junction potential, which in practice is eliminated by the use of a salt bridge. Thus when the electrode or 'half cell' is coupled to another electrode through external electrical connection of the measuring apparatus, a spontaneous chemical reaction

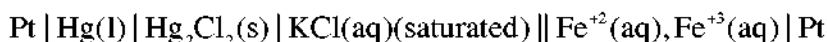
occurs with the passage of electrons through external circuit from anode (-) to cathode (+). Reduction or gain of electrons from the chemical system takes place at the cathode and oxidation at the anode.

The Nernst equation is the basis for the relationship between the voltage generated and the concentration at each electrode.

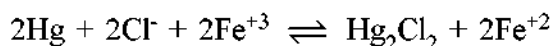
$$E = E^0_{\text{ox/red}} + \frac{RT}{nF} \ln \frac{[\text{ox}]}{[\text{Red}]}$$

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.



The cell reaction is :



$$E_{\text{cell}} = E_{\text{R}} - E_{\text{L}} = E_{\text{Fe}^{+3}/\text{Fe}^{+2}} - E_{\text{sat.cal}}$$

E_{cell} increases as $[\text{Fe}^{+3}]/[\text{Fe}^{+2}]$ varies during titration of Fe^{+2} with $\text{Cr}_2\text{O}_7^{-2}$ and at the half equivalence point the ratio $[\text{Fe}^{+3}]/[\text{Fe}^{+2}]$ becomes unity

At this point,

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

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

$E_{\text{sat.cal}}$ is obtainable from the literature. Thus, $E^0_{\text{Fe}^{+3}/\text{Fe}^{+2}}$ 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 $\text{Cr}_2\text{O}_7^{-2}$ 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.

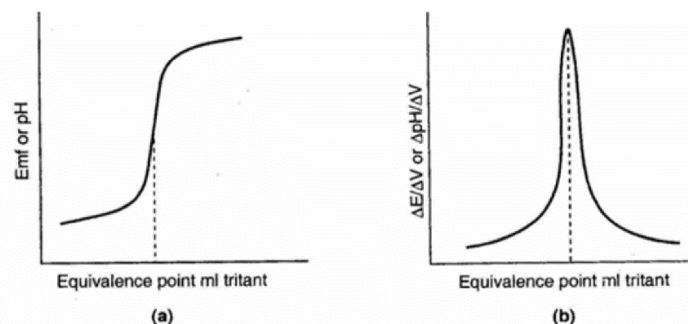


Fig. 2.7.1 Typical titration curve, b) Typical first derivative titration curve

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 titrant added.

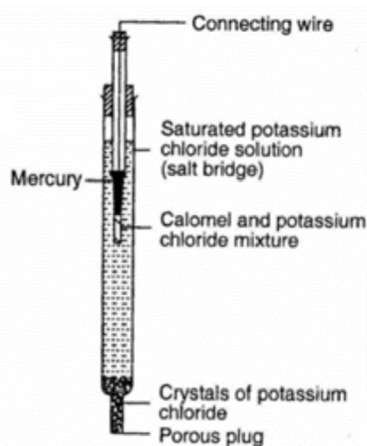


Fig. 2.7.2 : Saturated calomel electrode

Apparatus & Chemicals required:

1. A digital potentiometer with saturated calomel electrode (Fig. 2.7.2) fitted with salt bridge.
2. Standard cell
3. Platinum electrode
4. Volumetric flask, pipette, burette etc.
5. $K_2Cr_2O_7$ solution - (N/2)

6. Mohr's salts - (N/10) [Add 9.8 gm Mohr's salt in 250 ml distilled water and dissolve to make Fe^{+2} solution]
7. H_2SO_4 - 2(N)

Procedure :

1. 250 ml standard (N/2) $\text{K}_2\text{Cr}_2\text{O}_7$ solution is made. [6.125 gm $\text{K}_2\text{Cr}_2\text{O}_7$ when dissolved in 250 ml water produces a (N/2) solution.]
2. 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]
3. 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.
4. Potentiometer is now standardised against a standard cell (e.g. with a Weston cadmium cell)
5. Then e.m.f. of the experimental cell is measured. $\text{K}_2\text{Cr}_2\text{O}_7$ solution is now added from a burettedrop-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 $\text{K}_2\text{Cr}_2\text{O}_7$ added from burette (at the beginning calculate the number of drops in 1 ml of $\text{K}_2\text{Cr}_2\text{O}_7$ 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 $\text{K}_2\text{Cr}_2\text{O}_7$ (say 1 cc. at a time) but near end point readings should be taken frequently (say after 0.1 cc. has been added)].

6. Plot (a) E_{cell} versus number of drops (x) of $\text{K}_2\text{Cr}_2\text{O}_7$ solution, (b) plot $\frac{\Delta E}{\Delta V}$ or

$\frac{\Delta E}{\Delta x}$ (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 system with the aid of the relation (1) using the literature value of $E_{\text{sat.cal}}$.

Experimental Results :**Table 1: Recording of room temperatures**

Temperature before experiment °C	Temperature after experiment °C	Mean temperature °C

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

Initial weight (W ₁)	Final Weight (W ₂)	Weight of K ₂ Cr ₂ O ₇ taken (W= W ₂ -W ₁)	Strength of K ₂ Cr ₂ O ₇ solution prepared
			$\frac{W}{6.125} \left(\frac{N}{2} \right)$

Table-3: Potentiometric titration of Mohr's salt solution against K₂Cr₂O₇ solution

No. of observation	Volume of Mohr's salt taken	No. of drops of K ₂ Cr ₂ O ₇	Observed e.m.f.	$\Delta E/\Delta V$
1.	25 ml			
2.				
3.				

Graph : Plot e.m.f. Vs x (number of drops of K₂Cr₂O₇ solution) and find the value of E_{1/2} and the volume of K₂Cr₂O₇ solution added to reach the equivalence point.

Calculation :

1 ml of K₂Cr₂O₇ solution = x drops

Number of drops of K₂Cr₂O₇ added at equivalence point = n

$$\text{Strength of Mohr's salt solution} = \frac{V_{\text{K}_2\text{Cr}_2\text{O}_7} \times S_{\text{K}_2\text{Cr}_2\text{O}_7}}{V_{\text{Mohr}}}$$

So, concentration of Fe⁺² is Hence amount of Fe⁺² is gm/litre

The E_{1/2} value is calculated

The E_{1/2} value gives E⁰_{Fe⁺³/Fe⁺²} from the equation (1)

Critical Comments :

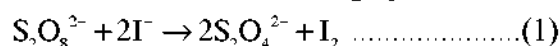
Other potentiometric titration, e.g., titration of KCl by $AgNO_3$ can be done in such manner. Here KCl will be test solution. Ag -wire will be electrode instead of Pt -wire and NH_4NO_3 salt-bridge should be used.

2.8 To study the kinetics of the persulphate-iodide reaction by colorimetric method

When light is incident upon a body it may undergo reflection, absorption and transmission. The wavelength (λ) of light which a particular substance absorbs depend(s) upon its chemical constitution and to a certain extent on the environment in which the substance is placed. Each substance has its own characteristic absorption spectrum which depends critically on the quantised energy levels available and their quantum mechanical description.

Theory:

Their overall reaction between Persulphate ($S_2O_8^{2-}$) and Iodide (I^-) is



If 'a' equivalent / litre of both the reactants, $S_2O_8^{2-}$ and I^- are mixed, and if 'n' be the overall order of the reaction, then the time 't' required for definite fraction of the reactants to react will be inversely proportional to a^{n-1} . i.e.,

$$t \propto \frac{1}{a^{n-1}} \dots\dots\dots(2)$$

Thus, if a_1 and a_2 equivalent/litre be the two starting concentrations of the two reactants and t_1 and t_2 be the times required for a definite fraction of the reactants to react, then, according to eqn (2),

$$\frac{t_1}{t_2} = \left(\frac{a_2}{a_1} \right)^{n-1} \dots\dots\dots(3)$$

On taking logarithm and rearranging, the eqn. (3) is transformed to eqn.(4) which gives the order of the reaction, 'n',

$$n = 1 + \frac{\log \frac{t_1}{t_2}}{\log \frac{a_2}{a_1}} \dots\dots\dots(4)$$

Experimentally the value of 'n' is found to be 2, i.e., the reaction (1) is a second order reaction, being first order with respect to $[S_2O_8^{2-}]$ and first order with respect to $[I^-]$ and the rate law may be expressed according to,

$$\text{Rate} = -\frac{d[S_2O_8^{2-}]}{dt} = k.[S_2O_8^{2-}][I^-] \dots\dots\dots(5)$$

Where, k = second order rate constant in $\text{eqv.}^{-1} \text{lit. s}^{-1}$

If x equivalent/litre of $S_2O_8^{2-}$ has reacted by the time 't', then, the rate law eqn. (5) takes the form:

$$\frac{dx}{dt} = k \cdot (a - x)^2 \dots\dots\dots(6)$$

Since at $t = 0$, $x = 0$ and at $t = t$, $x = x$, the eqn. (6) on integration takes the form (7)

$$\frac{x}{a(a - x)} = k \cdot t \dots\dots\dots(7)$$

Since one of the product, I_2 , is coloured ($\lambda_{\max} = 525 \text{ nm}$). If we measure the absorbances due to liberation of I_2 at different intervals of time, we can determine the k for reaction as follows-

The amount x should be proportional to the absorbance (A_t) measured at time 't', where x = the fraction decomposed at time 't' and the initial concentration 'a' is proportional to absorbance (A_{∞}) at infinite time

$$x \propto A_t \text{ and } a \propto A_{\infty}$$

According to Beer's Law the eqn. (7) is then transformed to :

$$k \cdot t = \frac{1}{a} \cdot \frac{A_t}{A_{\infty} A_t} \dots\dots\dots(8)$$

On rearrangement, eqn. (7) is then transformed to,

$$\frac{1}{A_t} = \frac{1}{A_{\infty}} + \frac{1}{a \cdot k \cdot A_{\infty}} \times \frac{1}{t} \dots\dots\dots(9)$$

Thus, a plot of $\left(\frac{1}{A_t}\right)$ against $\left(\frac{1}{t}\right)$ will give a straight line with intercept equal to $\left(\frac{1}{A_{\infty}}\right)$

and slope equal to $\left(\frac{1}{a \cdot k \cdot A_{\infty}}\right)$ from which the value of the rate constant, 'k', may be evaluated using the relation:

$$k = \frac{\text{intercept}}{a \times \text{slope}} \dots\dots\dots(10)$$

Apparatus and chemicals required :

- (i) Colorimeter
- (ii) Pipette,

- (iii) Volumetric flask, etc.
- (iv) Iodine flask
- (v) Standard $K_2Cr_2O_7$, KI, $K_2S_2O_8$ solution

Procedure :

1. 250 ml standard $\sim(N/10)$ $K_2Cr_2O_7$ solution is prepared.
2. 100 ml of standard KI solution is prepared by weighing accurately KI, the strength should be somewhat greater than (N/10). Now, prepare an exact (N/10) KI solution by exact dilution of this prepared standard ($> N/10$) KI solution.
3. 250 ml $\sim(N/10)$ $Na_2S_2O_3$ solution is prepared by accurate weighing and standardize the thiosulfate solution against the standard (N/10) $K_2Cr_2O_7$ following the usual procedure.
4. 100 ml of standard $K_2S_2O_8$ solution is prepared by weighing accurately $K_2S_2O_8$, the strength should be somewhat greater than (N/10) and standardise as follows- Take 10 ml of the prepared $K_2S_2O_8$ solution in a 500 ml conical flask, add 10 ml of 10% (w/v) KI solution and 2 ml of glacial acetic acid. Cover the conical flask with watch glass and keep the mixture in dark for 25 - 30 minutes. Add 80 ml distilled water and then titrate the liberated iodine with the standard $\sim(N/10)$ $Na_2S_2O_3$ solution using starch indicator. Calculate the strength of the $K_2S_2O_8$ solution. Prepare an exact (N/10) $K_2S_2O_8$ solution by accurate dilution this solution.
5. The experiment is carried out with two sets by mixing the $K_2S_2O_8$ and KI solutions as follows, one at a time, and note the time of half discharge of anyone of the reactants in each case.

Set Number	(N/10) KI solution	(N/10) $K_2S_2O_8$ solution	Water
Set I	10	10	0
Set II	10	10	20

6. Record the absorbance (A_t) of these two sets of solutions at 525 nm wavelength by taking the solution in colorimeter tube at an interval of 2 mins for both the sets. The colorimeter tube should be shaken occasionally for reaction to take place properly.
7. The readings are recorded in a tabular form and plot A_t against t for each of two sets. Select any A_t for Set I and find the corresponding time t_1 , from the graph. Similarly from the graph of Set II find the time t_2 for the value of A_t that is just half of the A_t chosen for Set I. Calculate the order (n) of the reaction using the relation (4).

8. Plot $1/A_1$ against $1/t$ for both the sets and find k from the slopes and intercepts of the resulting straight lines.

Experimental Results :

Table 1: Recording of room temperatures

Temperature before experiment °C	Temperature after experiment °C	Mean temperature °C

Table-2: Preparation of 250 ml standard (N/10) $K_2Cr_2O_7$ solution

Initial weight (W_1)	Final Weight (W_2)	Weight of $K_2Cr_2O_7$ taken ($W = W_2 - W_1$)	Strength of $K_2Cr_2O_7$ solution prepared

Table-3: Preparation of 100 ml standard (N/10) KI solution

Initial weight (W_1)	Final Weight (W_2)	Weight of KI taken ($W = W_2 - W_1$)	Strength of KI solution prepared

Table-4: Standardisation of $\sim(N/10)$ $Na_2S_2O_3$ solution

No. of obs	Volume of $K_2Cr_2O_7$ solution taken (ml)	Burette reading of $Na_2S_2O_3$ solution		Volume of $Na_2S_2O_3$ solution required (ml)	Mean Volume of $Na_2S_2O_3$ solution required (ml)	Strength of $Na_2S_2O_3$ solution
		Initial	Final			

Table-5: Standardisation of $\sim(N/10)$ $K_2S_2O_8$ solution

No. of obs	Volume of $K_2S_2O_8$ solution taken (ml)	Burette reading of $Na_2S_2O_3$ solution		Volume of $Na_2S_2O_3$ solution required (ml)	Mean Volume of $Na_2S_2O_3$ solution required (ml)	Strength of $K_2S_2O_8$ solution
		Initial	Final			

Table-6: Preparation of 50 ml of exact (N/10) solutions of KI and $K_2S_2O_8$

Preparation of 50 ml exact (N/10) KI solution		Preparation of 50 ml exact (N/10) $K_2S_2O_8$ solution	
Vol. of stock KI solution (V_1) ml	Vol. of water added ($50 - V_1$) ml	Vol. of stock $K_2S_2O_8$ solution (V_2) ml	Vol. of water added ($50 - V_2$) ml

Table-7: Measurement of absorbance (A_t)

Set-I		Set-II	
Time in minute	Absorbance (A_t)	Time in minute	Absorbance (A_t)

Graph:

- (a) Plot in the graph paper A_t against t for each of two sets accordingly and determine the order (n).

Table-7 : Determination of value of n from the graph

No of set	Corresponding Absorbance (A_t) chosen	Corresponding time, t
I	$A_1 =$	$t_1 =$
II	$A_2 =$	$t_2 =$

(b) Plot $1/A_t$ against $1/t$ for both the sets and find the slopes and intercepts of the resulting straight lines. Now calculate the value of k using the equation-(10)

2.9 Study of the phase diagram of a binary system (phenol-water)

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 in stoppered 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.

The two phases has an unique composition 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 $t_c = 65.9^\circ\text{C}$ is

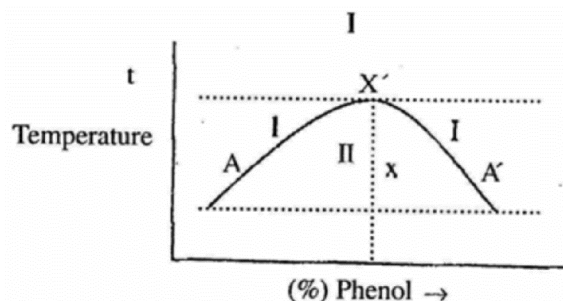


Fig.1: Solubility curve of phenol-water system

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 outside 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 (I) outside 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 will be trivariant. Since, pressure is fixed (i.e., 1 atm.), 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 atm.), 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 (1 atm.), 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_c i.e., $C = 1$, $P = 2$, hence, $F = C - P + 2 = 1 - 2 + 2 = 1$. The pressure being kept fixed (i.e., 1 atm.), 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 of the two liquids, and consequently *consolute temperature* rises. When the third substance dissolves in both the liquids *consolute temperature* is generally lowered.

Apparatus required :

- (i) Hard glass test tube.
- (ii) Stirrer
- (iii) Beaker
- (iv) Burette
- (v) Thermometer etc.
- (vi) Distilled water (or 0.5% NaCl solution)
- (vii) Phenol

Procedure :

1. Weigh out accurately 2-3 g of phenol (Caution, Corrosive) from a weighing bottle into 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.

Experimental Results :**Table 1: Recording of room temperatures**

Temperature before experiment °C	Temperature after experiment °C	Mean temperature °C

Table-2: Weighing of Phenol

Initial weight (W_1)	Final Weight (W_2)	Weight of Phenol taken $W = (W_2 - W_1)$ gm

Table-3 : Recording of miscibility temperature

No of obs.	Volume of water added in mL	Percent of phenol	Miscibility Temperature °C		Mean Temperature °C
			Turbidity disappearance	Turbidity reappearance	

Graph :

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

Conclusion :

Critical solute temperature =

Critical composition for the system =

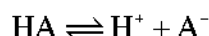
Note :

- (i) (M) KCl raises the CST of phenol-water system by - 8°C.
- (ii) Succinic acid lowers the CST of phenol-water system.
- (iii) CST of phenol-water system is raised by ~12.3°C if D₂O is used in place of ordinary water, H₂O.
- (iv) Phenol is hygroscopic and hence it should be kept in stoppered bottles.

- (v) Phenol is a poisonous substance and attacks skin producing painful burns. So it is necessary to become conscious about its handling.

2.10 pH-metric titration of weak acid (mono-and di-basic) against strong base

Theory : A weak monobasic acid HA dissociates as



Where, K_a = dissociation constant, a = activity.

In dilute solutions, a (activity) may be replaced by c (the molar concentration) since activity coefficient f tends to unity ($a = c \times f$).

The pH of the solution is defined as

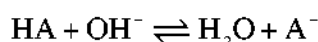
$$\text{pH} = -\log_{10} a_{\text{H}^+} \approx -\log_{10} C_{\text{H}^+}$$

If c be the concentration of HA and α is the degree of dissociation, then it may be shown that

$$[\text{H}^+] = c\alpha \approx \sqrt{K_a c}$$

$$\text{Thus, } \text{pH} = \frac{1}{2} \text{pk}_a - \frac{1}{2} \log c$$

Thus a strong alkali like NaOH is added to HA, neutralisation occurs:



And $[\text{H}^+]$ decreases with consequent increase of pH. When partial neutralisation has occurred, the solution contains HA and A^- and acts as buffer whose pH is given by Henderson's equation :

$$\text{pH} = \text{pk}_a + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

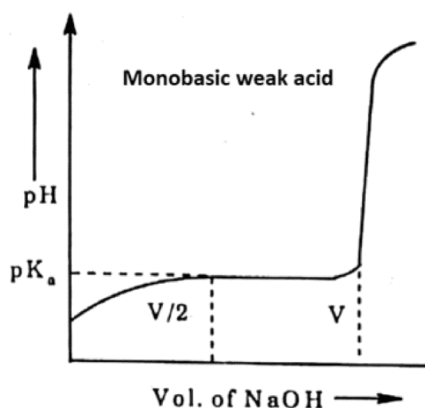
However, when all the weak acid has been neutralized, then solution contains the salt (Na^+A^-) which is extensively hydrolysed : $\text{A}^- + \text{H}_2\text{O} \rightleftharpoons \text{HA} + \text{OH}^-$ and the solution has a high pH (>7). Further addition of NaOH increases pH still further.

So, a titration of HA with NaOH when followed using a pH-meter will show a gradual increase of pH followed by a sharp increase at the equivalence point.

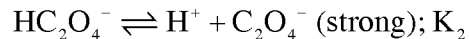
If the volume of alkali required for neutralisation be V then at $V/2$ i.e. at the half neutralisation point the solution is a buffer with $[\text{A}^-] = [\text{HA}]$ Following Henderson equation,

the resulting $\text{pH} = \text{pK}_a$. Thus the dissociation constant may be determined from the pH curve. Also the concentration of HA may be determined from a knowledge of V because

$$(V \times S)_{\text{NaOH}} = (10 \times 5)_{\text{HA}} [\text{aliquot} = 10\text{mL say}].$$



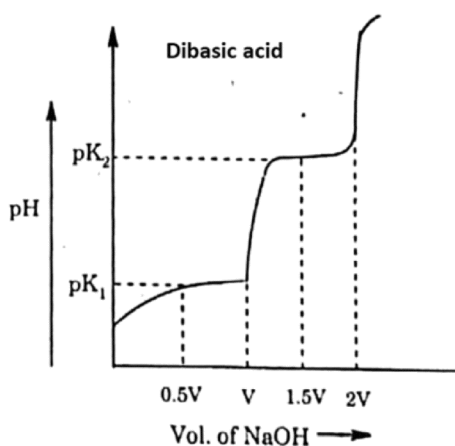
For a dibasic acid like $\text{H}_2\text{C}_2\text{O}_4$, the plot of pH versus number of drops of NaOH consists of two break points.



The first neutralisation occurs at V and the second (last) occurs when 2V mL of NaOH is added. From Henderson equation,

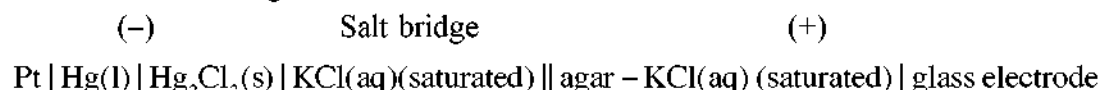
$\text{pK}_1 = \text{pH}$ of solution when 0.5V mL of NaOH is added.

$\text{pK}_2 = \text{pH}$ of solution when 1.5V mL of NaOH is added.



Measurement of pH using Glass-Calomel electrode pH Meter

The pH of an aqueous solution can be measured using glass-calomel electrode system in which the following electrochemical cell is formed:



The left-hand electrode is the saturated calomel electrode (SCE) and the right hand electrode is the glass electrode. This ion selective membrane electrode has a potential which is reversible with respect to H^+ ions. The electric potential difference between a glass surface and an aqueous solution varies regularly with pH of the aqueous solution.

The electrode is made of a thin walled bulb of low melting glass of high electrical conductivity. Inside the bulb a solution of constant pH (a buffer solution, or, (N) HCl solution) is placed together with a little quinhydrone and a platinum wire for electrical contact, The Potential (E_g) of the glass electrode at 25°C may be expressed as :

$$E_g = E_g^\circ + 0.059 \log_{10} a_{\text{H}^+} = E_g^\circ - 0.059\text{pH} \dots\dots\dots(1)$$

For actual pH measurement, the glass electrode is standardised in buffer solutions of known pH value Usually potassium hydrogen phthalate (pH 4), phosphate (pH 7) and borax (pH 9.2)

Buffer solutions are used for calibration of pH meter.

The e.m.f. (E_{cell}) the glass-calomel electrode cell, at 25°C , is given by:

$$E_{\text{cell}} = E_g - E_{\text{SCE}} = E_g^\circ - 0.059\text{pH} - E_{\text{SCE}} \dots\dots\dots(2)$$

$$\text{pH} = \frac{(E_g^\circ - E_{\text{SCE}} - E_{\text{cell}})}{0.059} \dots\dots\dots(3)$$

The pH value can be read off directly from the digital pH-meter calibrated with standard buffer solutions.

Instruments and Chemicals Required :

- (a) pH meter
- (b) (i) Dip type calomel and glass electrode (Fig.1) or (ii) Now-a-days single electrode are used (Fig.2)
- (c) Buffer solution of known pH, say pH = 4 and, 7
- (d) Standard (N/10) oxalic acid, (N/2) NaOH, (N/10) acetic acid solutions.
(N.B.: Prepare acetic acid solution for the study of monobasic acid and prepare succinic acid/ oxalic acid solution for the study of dibasic acid).

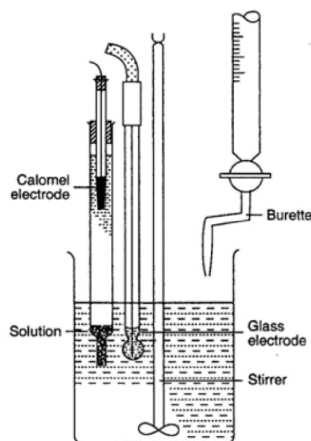


Fig.2.10.1: pH potentiometric titration apparatus

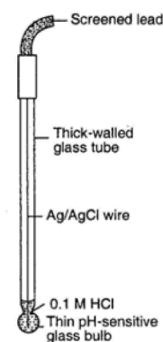


Fig.2.10.2 : Glass pH electrodes

Procedure :

- (i) Prepare 100 mL each of (N/2) NaOH solution and (N/10) acetic acid solutions by accurate weighing.
- (ii) Standardise (N/2) NaOH solution with standard (N/10) oxalic acid using phenolphthalein indicator as usual procedure and find the actual strength of the solution.
- (iii) pH meter is connected with glass electrode and the saturated calomel electrode and the two electrodes are dipped in distilled water for half an hour before starting the experiment.
- (iv) Prepare two buffer solutions of pH = 4 and pH = 7 by dissolving the two buffertablets in definite volume of distilled water.
- (v) Calibrate the pH-meter by alternately dipping the glass - calomel electrode assembly in pH = 4 and pH = 7 buffer solutions and adjusting the instrument accordingly at the experimental temperature.
- (vi) Now wash the electrode with distilled water. Pipette out 10 mL of (N/10) acetic acid solution in a 100 mL beaker and add 40 ml distilled water. Homogenize and dip the electrodes of the pH meter gently in to this solution, allow the system to attain the equilibrium at the experimental temperature and record the pH.
- (vii) Add 2 drops of standard (N/2) NaOH solution at each time from a burette (micro burette) stir gently to mix uniformly and record the pH. Repeat the process until the end-point is reached (indicated by sharp rise in the pH). Record the pH and the number of drops of the titrant in a tabular form. Take a few more readings beyond the end point in each time.

- (viii) Plot pH against number of drops of alkali added and determine the pH at the half neutralisation point from which pK_a can be calculated.
- (ix) Plot ΔpH versus n and find the strength of the acid from the equivalence point. Determine the number of drops per ml of the titrant solution and calculate the, titre value.
- (x) For dibasic acid, repeat the procedure with 10 mL of the acid.

Experimental Results :

Table 1: Recording of room temperatures

Temperature before experiment °C	Temperature after experiment °C	Mean temperature °C

Table-2: Preparation of standard $\sim(N/10)$ oxalic acid 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

Table-3: Standardisation of $\sim(N/2)$ NaOH solution

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

Table-4 : pH-metric titration for monobasic acid (acetic acid)

No. of reading	Volume of acid taken (ml)	Number of drops of alkali added	pH of the solution

Table-5 : pH-metric titration for dibasic acid (succinic acid or oxalic acid)

No. of reading	Volume of acid taken (ml)	Number of drops of alkali added	pH of the solution

Graph plotting :

- (i) Plot pH vs. number of drops of NaOH solution
- (ii) Calculation of pK_a value:
 1 mL of NaOH a" drops of NaOH solution.
 Number of drops of alkali added at the equivalence point $\equiv a \times a \equiv x/n$ mL of S(N)
 NaOH solution

$$\text{Hence the strength of acetic acid} \equiv \frac{(x \times S)}{(n \times 10)} (N)$$

Find out pH at the half neutralisation point from the graph which is equal to pK_a

- (iii) For dibasic acid, the pH of the solution tit $1/4^{\text{th}}$ and $3/4^{\text{th}}$ neutralisation stages represent pK_1 and pK_2

2.11 Summary

In this unit, we learned about several quantitative techniques used in a chemical laboratory. The basic properties of a liquid sample such as viscosity and surface tension can be easily measured w.r.t. a standard. We also learned about conductometric, potentiometric and pH-metric titrations. None of these techniques require an indicator and thus more flexible than simple titration methods. We also learned about construction of phase diagram and colourimeter method.

2.12 Questions and Answers

Experiment : 2.3

Q.1. What do you mean by viscosity?

Ans.: Some of the liquids flow more readily than others. This phenomenon can be said in other way. Liquid molecules impose resistance to the flow of one layer past the other. This property of liquid (fluids) which determines their flow is known as viscosity.

Q.2. What are the factors responsible for the property of viscosity?

Ans.: (i) Intermolecular attractive forces, (ii) The molecular weight, (iii) The structure and shape of molecule, (iv) Temperature, (v) Pressure.

Q.3. What is the unit of co-efficient of viscosity?

Ans.: It is 'poise' in c.g.s unit. One poise means a force of one dyne maintaining a velocity gradient of 1 cm/sec between the two parallel layers of liquid 1 cm apart and having an area of contact 1 cm².

Q.4. What is the effect of temperature on viscosity of liquids?

Ans.: The viscosity of a liquid generally decreases with increase of temperature.

Q.5. Do you determine the absolute or relative viscosity?

Ans. : It is the relative viscosity which is determined experimentally

Q.6. What is the Poiseuille equation?

Ans.: See theory

Q.7. Can Poiseuille equation be applied in case of a liquid flowing through a pipette or a burette?

Ans.: No.

Q.8. What is fluidity and how is it related with viscosity?

Ans : [See Critical comments]

Q.9. What is intrinsic viscosity? How molecular weights of high polymer can be determined?

Ans: [See Critical comments]

Q.10. How does viscosity of a fluid change with temperature?

Ans: [See Critical comments]

Q.11. What will happen if the capillary part of the viscometer is replaced by a tube of wider bore?

Ans : Poiseuille's equation is valid for stream-lined motion, here motion may be turbulent

Q.12. Why it is necessary to take exactly same volume of liquid in each case?

Ans : When volume is exactly same difference in heights of liquids levels in two limbs in same in each case. Hence driving pressure becomes same and when ratio is taken they cancel each other.

Experiment : 2.4**Q.1. Why a buffer solution has reserved acidity and alkalinity? Or explain the buffer action?**

Ans. : see buffer action in the text book

Q.2. When the buffer action is optimum?

Ans. : When the reserved acidity of solution becomes equal to reserved alkalinity, for that [salt] should be equal to [acid]. So, $\text{pH} = \text{pK}_a$.

Q.3. Give the pH range of the buffer action?

Ans. : The buffer acts well between the pH range : $\text{pH} = \text{pK}_a \pm 1$

Q.4. What do you mean by sensitiveness of an indicator?

Ans. : Each indicator has a definite pH at which the indicator gives its neutral colour. The pH range at which the colour change is shown is known as sensitiveness of indicator. The neutral colour is shown when $\text{pK}_a = \text{pH}$ and sensitiveness is given by $\text{pH} = \text{pK}_{\text{In}} \pm 1$, i.e. ratio $[\text{In}^-] : [\text{HIn}] = 1:10$ to $10:1$.

Q.5. What do you mean universal indicator ?

Ans. : Mixture of indicators acts better than the single indicator and can be used in almost all cases of acid alkali titrations. Universal indicator (B.D.H.) is a mixture of methyl orange, methyl red, bromothymol blue and phenolphthalein.

Experiment : 2.5**Q.1. Is cell constant determination necessary for conductometric titration?**

Ans : No.

Q.2. Why the electrodes of a cell are platinised?

Ans : To prevent overvoltage.

Q.3. Why we use A.C.?

Ans : To avoid electrolysis and polarisation.

Q.4. In conductometric titration between weak acid and strong base, readings near end point usually do not lie in the straight lines drawn in titration curve-why?

Ans : Salts of weak acid and strong bases are hydrolysable and effect of hydrolysis becomes important near end point, so experimental conductance values are a bit higher than theoretically expected values.

Experiment : 2.6**Q.1. What are conductometric titrations?**

Ans : The titrations in which conductivity measurements are used in determining the end point are known as conductometric titration. The titration may be of acid alkali type, the precipitation reaction, hydrolysis etc.

Q.2. How in conductometric titration the end point is determined? (b) What is ionic mobility?

Ans : In these titrations advantage is taken of the fact that the conductance of a solution at a constant temperature depends on the number of ions present in the solution and ionic mobility. For this purpose a titrant is added from a burette into a known volume of the solution to be titrated which is taken in a conductivity cell and the readings for the conductance are taken and plotted against the volume of titrant added. Two linear curves are obtained. The point at which they intersect is the end point.

Q.3. What is the main principle of conductometric titration?

Ans. : The main principle is based on Ohm's law-
 $V = IR$; where $V =$ Voltage; $I =$ Current; $R =$ Resistance.

Q.4. On what factor conductivity depends ?

Ans. : Conductivity depends on ionic concentration and tends to zero as the solution is diluted.

Q.5. What is molar conductivity ?

Ans. : The molar conductivity is the conductivity of a solution at a concentration of 1 mole m^{-3} .

Q.6. When does the conductivity of weak electrolyte reaches its maximum value?

Ans. : The conductivity reaches its maximum value (λ_{max}) at infinite dilution, because at this stage the complete elimination of ionic interaction takes place.

Q.7. How the kinetics of an ester hydrolysis reaction is studied conductometrically ?

Ans. : Here, as the fast moving OH^- ions are replaced by the slow moving RCOO^- and the conductance of the reaction mixture decreases with time.

Q.8. What are the advantages of a conductometric titration?

Ans.: (i) For coloured solutions, where no indicator suitably works, end point can be detected satisfactorily, (ii) The method is suitable for detecting the end point of titration of weak acid against weak base. (iii) More accurate results are obtained.

Q.9. What precautions are to be taken for conductometric titrations?

Ans. : (i) Temperature should remain constant throughout the experiment. (ii) The titrant should be about ten times stronger than the solution to be titrated.

Q.10. What are order and molecularity?**Q.11. What is half-life?****Q.12. What is the difference between half-life of first and second order reaction?****Experiment : 2.7**

- (a) What are the advantages of calomel electrode?
- (b) Why only KCl and NH_4NO_3 are used in salt-bridge?
- (c) What are standard and formal potentials?
- (d) Standard potentials for $\text{Fe}^{3+}/\text{Fe}^{2+}$ and $\text{Ce}^{4+}/\text{Ce}^{3+}$ systems are 0.77 and 1.61 V respectively. Which one will be the oxidant ?

