MSCCH-605L

M.Sc III SEMESTER
LABORATORY COURSE III

DEPARTMENT OF CHEMISTRY

SCHOOL OF SCIENCES

UTTARAKHAND OPEN UNIVERSITY HALDWANI

NIANITAL, UTTARAKHAND

MSCCH-605L

LOBOTARY COURSE III

SCHOOL OF SCIENCES
DEPARTMENT OF CHEMISTRY
UTTARAKHAND OPEN UNIVERSITY

Phone No. 05946-261122, 261123
Toll free No. 18001804025
Fax No. 05946-264232, E. mail info@uou.ac.in
htpp://uou.ac.in

EXPERT COMMITTEE

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Department of Chemistry
Indira Gandhi National Open University
Maidan Garhi, New Delhi

Prof. A. K. Pant
Department of Chemistry
G. B. Pant Agriculture, University
Pantnagar

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Department of Chemistry
DSB Campus, kumaun University
Nainital

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Delhi

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Haldwani, Nainital

Dr. Charu C. Pant
Assistant Professor (AC)
Department of Chemistry
School of science,
Uttarakhand Open University
Haldwani, Nainital

PROGRAMME COORDINATOR

Dr. Shalini Singh
Assistant Professor
Department of Chemistry
School of science,
Uttarakhand Open University
Haldwani, Nainital

UNIT WRITERS	NO. OF UNITS
1. Mr. Bittu Singh Assistant Professor Department of Chemistry Govt. P.G. College Thatud	**01**
2. Dr. Manjul Gondwal Assistant Professor Department of Chemistry, LSM PG College pithoragarh	**02**
Dr. Nandan Singh Karki Assistant Professor Department of Chemistry, LSM PG College pithoragarh	**03**
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COURSE EDITOR

Dr. Deep Prakash
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Department of Chemistry
Uttarakhand Open University
Haldwani, Nainital

Dr. Charu C. Pant
Assistant Professor (AC)
Department of Chemistry
Uttarakhand Open University
Haldwani, Nainital

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BLOCK II INORGANIC CHEMISTRY

UNIT FIRST- THERMODYNAMIC

Contents:-

UNIT FIRST- THERMODYNAMIC

1.1 INTRODUCTION

The branch of science dealing with the relations between energy, heat, and work accompanying changes in the nature and behavior of various substances around us is called thermodynamics. The principles of thermodynamics have been enunciated in the form of a few laws of thermodynamics called zeroth law, first law, second law and third law. These laws find applications in physics, chemistry, engineering, medicine, biotechnology, biochemistry, geology and space sciences. The branch of chemistry dealing with the investigation of energetics and feasibility of chemical reactions and physical changes is called chemical thermodynamics. Its principles are simple, and its predictions are powerful and extensive.The predictive power of chemical thermodynamics is based on the characteristics of thermodynamic properties namely internal energy (U), enthalpy (H), entropy (S) and free energy functions (A and G) and their variations with variables like temperature, pressure, volume and Composition. The changes in these properties depend only on the initial and final states of the system, and are independent of the path followed for the system Therefore; these thermodynamic properties are called state functions.

1.2 OBJECTIVES

- In present unit students will be able to:-
- Determine order of reactions by using different parameters.
- Study of hydrolysis of methyl acetate in presence of hydrochloric acid at room temperature.
- Determine the order of the reaction of hydrolysis of ethyl acetate in presence of an acid. (Spoonification of ethyl acetate).
- Comparison of strength of hydrochloric acid, sulphuric acid used in equal concentrations for hydrolysis of methyl acetate
- To determine the activation parameters for the acid catalyzed hydrolysis of ester.

- Determination of free energy change of a reaction.
- Determination of the Equilibrium Constant for a Chemical Reaction.
- Determination of concentration of $FeSCN^{2+}$ by spectrophotometry

1.3 DETERMINATION OF ORDER OF A REACTION

1.3.1 Graphical method

This method is used when there is only one reactant. It involves the following steps:

1) The concentrations of the reactants are measured by some suitable method.

2) A graph is plotted between concentration and time.

3) The instantaneous rates of the reaction at different times are calculated by finding out the slopes of the tangents corresponding to different times.

4) The rate of reaction is plotted versus concentration, [A] or $(\text{concentration})^2$, $[A]^2$ and so on.

(a) If rate of reaction remains constant in rate versus concentration graph, it means that the rate is independent of the concentration of the reactant, i.e.

$$\text{Rate} = k\,[A]^0 = k$$

Therefore, the reaction is of zero order.

(b) If a straight line is obtained in rate versus concentration graph, it means that the rate is directly proportional to concentration of the reactant i.e.

$$\text{Rate} = k\,[A]$$

Therefore, the reaction is of first order.

(c) If a straight line is obtained in rate versus $(\text{concentration})^2$ graph, it means that

$$\text{Rate} = k\,[A]^2$$

Therefore, the order of the reaction is two.

(d) Similarly, if we get straight line in rate versus $(\text{concentration})^3$ graph, then

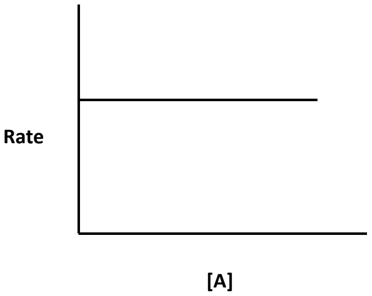
$$\text{Rate} = k\,[A]^3$$

Therefore, the order of reaction is 3

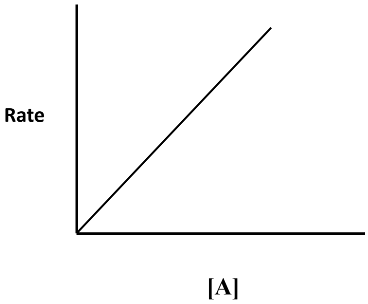
If we get straight line by plotting graph of rate versus (concentration)^n, where n =1, 2, 3…. so on, then

$$\text{Rate} = k\,[A]^n$$

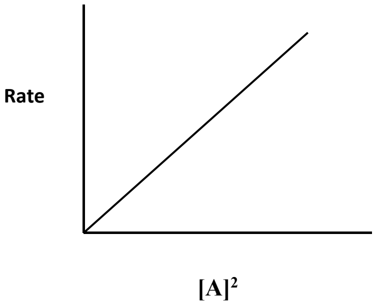
Therefore, the order of reaction is n.



Zero order



First Order



Second Order

Example: Decomposition of nitrogen pentoxide.

$$2N_20_5(g) \longrightarrow 4NO_2(g) + O_2(g)$$

This reaction involves the gaseous reactants and products. Therefore, the reaction can be easily studied by measuring the increase in pressure of the gaseous mixture at different intervals of time. From the measured values of total pressure, the partial pressure of N_2O_5 at different times can be calculated.

From this, the concentration of N_2O_5 in moles per liter can be calculated. The molar concentrations of N_2O_5 obtained are plotted against time. The rates at different times are obtained by measuring the slopes of the tangents corresponding to these times.

Rate = k $[N_2O_5]^n$

$[N_2O_5]$ (mol L^{-1})	Rate (mol L^{-1} min)
1.13×10^{-2}	3.4×10^{-4}
0.84×10^{-2}	2.5×10^{-4}
0.62×10^{-2}	1.1×10^{-4}
0.46×10^{-2}	1.3×10^{-4}
0.35×10^{-2}	1.0×10^{-4}
0.26×10^{-2}	0.8×10^{-4}
1.13×10^{-2}	3.4×10^{-4}

The plot of rate versus [N_2O_5] is a straight line.

1.3.2 Use of integrated rate equation

The kinetic data is fitted to different integrated rate equation. Wherever the data fit with the equation for the correct order of the reaction, it will give constant value of rate constant for all data points (concentrations at different times).

1.3.3 Ostwald Isolation Method

The order of the reaction is equal to the sum of the orders of reaction for individual reactants. This method is based on the principle that if the concentration of one reactant is taken in excess, the concentration of those reactants taken in excess will remain almost constant and hence variation in rate will correspond to the concentration of that reactant whose concentration is small. This process is repeated one by one and order with respect to each reactant is determined.

The overall order will be the sum of all these orders.

$$aA + bB + c\,C \longrightarrow \text{Products}$$

Suppose we isolate A by taking B and C in large excess and get order of reaction with respect to A. Similarly, we isolate B by taking A and C in B and and C.

Overall order of reaction

$$n = p + q + r$$

However experimentally it is found that out of moles of A, only ‘p’ moles are converted into product and out of b moles on only ‘q’ moles are converted into product then according to rate law expression

$$\text{Rate} = \mathbf{k[A]^p[B]^q}$$

∴ Order of the reaction = p + q

1.3.4 Kinetics of First Order Reaction:

A reaction is said to be first order if its rate depends upon one concentration variable

$$\mathbf{A \longrightarrow Product}$$

$$\text{Rate of reaction} = -\frac{dx}{dt} \propto (a - x)$$

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

Where a moles /liter is the initial concentration of A and (a-x) moles/liter is the concentration after time t. The integral expression for k of first order reaction is

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

The value of k can be calculate by graphical method i.e. Take log on both side of equation (ii) then

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

By plotting a graph between time't' along ordinate and log (a-x) along abscissa for various interval of time 't' then a straight line is obtained

$$slope = \frac{2.303}{k}$$

Units of k for first order reaction = time^{-1}

1.3.5 Pseudo Unimolecular Reaction:

Some reactions are first order i.e. the rate dependent on the concentration of only reaction even if there is more than one reaction which appears to be a higher order but actually follow first order kinetics energy called pseudo first order reaction.

E.g. Hydrolysis of ethyl acetate

$$CH_3COOC_2H_5 + H_2O \xrightarrow{H+} CH_3COOH + C_2H_5OH$$

Ethyl acetate Acetic acid Ethyl alcohol

The molecularity of above reaction is 2 so it is bimolecular reaction. The concentration of water is very large and it partially constant. Only the concentration of ethyl acetate charges during hydrolysis. Therefore the rate of the reaction depends only on the concentration of ethyl acetate and hence it is a first order reaction.

$$Rate \propto [CH_3COOOC_2H_5]$$

1.2.7 Gibbs Free Energy

Gibbs Free Energy, ΔG, can be used to determine if a reaction is spontaneous or not. A negative value of ΔG indicates that a given reaction is spontaneous at the measured conditions and will proceed in the forward direction. ΔG can be calculated using the Gibbs-Helmholtz equation: $\Delta G = \Delta H - T\Delta S$. In this experiment, ΔH (enthalpy) will be calculated from the temperature change of the reaction. ΔS (entropy) will be calculated using standard entropy values from the textbook.

Heat of solution: qsoln = mass x specific heat x ΔT, where

Mass = mass of solution, Specific heat = 4.184 J/g ^{o}C

$\Delta T = T_{final} - T_{initial}$

T_{final} is the maximum or minimum temperature reached $T_{initial,}$ is the initial temperature of water before adding salt,

Law of Conservation of Energy: qrxn + qsoln = 0 so that qrxn = - qsoln

Density of water: 1.00 g/mL; Use to find mass of measured volume

Enthalpy of reaction: $\Delta H_{rxn} = q_{rxn}$/moles of salt

1.4 STUDY OF HYDROLYSIS OF METHYL ACETATE IN PRESENCE OF HYDROCHLORIC ACID AT ROOM TEMPERATURE.

1.4.1 Object : Study of hydrolysis of methyl acetate in presence of hudrochloric acid at room temperature

1.4.2 Requirements: Five 50 mL and two 100 mL conical flasks with corks, beakers, one burette, pipettes of 25 mL, 10 mL, 5mL, and 2 mL: a thermostat or water bath, 0.5 N hydrochloric acid 0.05 N sodium hydroxide, methyl acetate, a stop watch enough ice cold distilled water and phenolphthalein indicator solution.

1.4.3 Theory: The hydrolysis of methyl acetate in presence of an acid may be represented as:

$$CH_3COOCH_3 + H_2O \overset{H+}{\rightarrow} CH_3COOH + CH_3OH$$

The concentration of water is high and practically remains constant, concentration of h$^+$ ions (which catalyses the reaction also remains constant. Thus rate of reaction appears to be determined by one concentration term only i.e. methyl acetate. Therefore rate equation can be written as:

$$\frac{dy}{dx} = K[CH_3COOCH_3]$$

and following formula for first order reaction may be used

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

$$t = \frac{2.303}{K} \log \frac{a}{a-x} \qquad (1)$$

The progress of reaction may be studied by titrating know volume of reaction mixture with a stander NaOH at suitable interval of time from the start of reaction and increased and acidity of solution will give amount of acetic acid formed hence amount of methyl acetate hydrolysed.

1.4.4 Procedure:

Take 50 mL of 0.5 NaOH in a clean 100 mL pure methyl acetate in a test tube, loosely cork both of them in a thermostat maintained at room temperature. Take 200 mL ice cold water free from CO_2 and put 25 mL of ice cold H_2O in five conical flasks, before titrations of a liquid of reaction mixture during the course of reaction. When both the ester and acid attain a constant temperature, pipette out 2mL methyl acetate from test tube into conical flask containing 50 mL 0.5 N NaOH solutions and star stop watch when half of the pipette has been discharged. Shake the mixture and out 2mL of the reaction mixture and transfer it to one of the flask containing 25 mL of ice cold water. Now titrate it quickly against 0.5 N NaOH using phenolphthalein as indicator and find out the volume of alkali required for the titration , Bulk of expected alkali Volume should be added quickly in each succeeding titration and then titration be completed carefully with Shaking to first appearance of pink color, which does not vanish in 10 second. Similarly 2 mL of reaction mixture is taken out at successive intervals of 10, 20, 30, 40 and 50 minutes and are in turn transferred to flask containing 25 mL if ice cold water and titrated against standard alkali. The volume of alkali required for each titration is noted. The volume of corresponding to titrated after t minutes from the start of reaction may be denoted by V_t

The volume of NaOH required when hydrolysis is complete can be calculate by talking 10 mL of reaction mixture in a clean dry small conical flask and loosely cork it. Put the corked flask in a water bath maintained at 50^0C for an hour so that hydrolysis is completed. Cool it to room temperature. Take out 2 mL of this mixture and titrate it as before against 0.05 N alkalis. This titrate value $V_{\propto}$ Corresponds to the total acid concentration after hydrolysis is complete.

1.4.5 Data Recording:

Temperature of bath ___ °C

Time in minutes	**Titre value(mL)**	**(a-x)mL**	**Log(a-x)**	$k = \frac{2.303}{t} log \frac{(V_\infty - V_d)}{V_\infty - V_t}$
0	$V_0 =$	$V_\infty - V_0$	—	
10	$V_{10} =$	$V_\infty - V_{10}$	—	
20	$V_{20} =$	$V_\infty - V_{20}$	—	
30	$V_{30} =$	$V_\infty - V_{30}$	—	

40	$V_{40} =$	$V_\infty - V_{40}$	—	
50	$V_{50} =$	$V_\infty - V_{50}$	—	
∞	$V_\infty =$		—	

1.4.6 Calculations:

V_o = Amount of HCL present in 2mL of the reaction mixture st zero time

V_∞ = amount of acid present in 2mL of the reaction mixture when hydrolysis is complete

Since we have a ratio of volumes in the integrated rate equation, the proportionality factor will cancel out and the $V_t - V_\infty$value can be used in place of the factor $a-x$ in the formula.

Let $V_t - V_\infty$ be equal to a (in the formula)

V_t = Amount of acid in 2 mL of reaction mixture after time t.

∴ $V_t - V_0$ =Amount of acetic acid formed upto time t.

Or V_t-V_0 = Amount of ester hydrolyzed upto time t.

∴ V_t- V_0 = x is above formula.

So $(a - x) = (V_\infty - V_0) - (V_t - V_0)$ or $(V_\infty - V_t)$

Substituting the titrate values in the formula for first order reaction, we get

$$K = \frac{2.303}{t} log\left(\frac{V_\infty - V_0}{V_\infty - V_t}\right) \qquad (2)$$

(i) Calculate values of K using the above formula for different values of t.

(ii) Plot graph of versus log ($V_\infty - V_t$) and t Vs log $\left(\frac{V_\infty - V_0}{V_\infty - V_t}\right)$

1.4.7 Results:

(i)The values of K calculated for different degrees of completion of the reaction should be reasonably constant. They should not differ in order.

(ii)The two graphs should be straight lines. Value of K can be obtained from the slope of either graph- Two graphs different their intercepts at t-axis (x-axis).

1.5 DETERMINE THE ORDER OF THE REACTION OF HYDROLYSIS OF ETHYL ACETATE IN PRESENCE OF AN ACID. (SPOONIFICATION OF ETHYL ACETATE).

1.5.1 Objective: Determine the order of the reaction of hydrolysis of ethyl acetate in presence of acid

1.5.2 Theory: The hydrolysis of ethyl acetate in the presence of an acid is an example of pseudo first order reaction because we water is present in large excess and its concentration remains constant.

$$CH_3COOC_2H_5 + H_2O \xrightarrow{H+} CH_3COOH + C_2H_5OH$$

The progress of this reaction can be studied by titrating known volume of reaction mixture against standard solution of NaOH

Since the reaction is catalyzed by an acid so volume of NaOH used is equivalent to the sum of HCI used as a catalyst and acetic acid formed in the reaction- The amount of acid used as a catalyst remains constant throughout for the same volume of reaction mixture is drawn at regular intervals.

At the start of i.e. at t=0 acetic acid is not formed, therefore volume of NaOH used (V_0) $\propto$ the amount of mineral present as a catalyst.

At anytime t,

$\therefore$ The volume of NaOH used (V_t) $\propto$ Amount of HCI+Amount of acetic acid formed

$\therefore$ The amount of acetic acid formed at any time t $\propto$ (V_t - V_0)

Or

The amount of acetic acid formed at any time $\propto$ Amount of ethyl acetate that has reacted (x)

$$\therefore \quad x \propto (V_t - V_0) \qquad (3)$$

At the end of reaction, let V_∞ be the amount NaOH used to neutralize the reaction mixture when the reaction is over. Then V_∞ $\propto$ Amount of HCI Present + Maximum amount of acetic acid formed at infinite time

From (1) and (2),

Maximum amount of acetic acid formed at infinite time $\propto (V_\infty - V_0)$

The maximum amount of acetic acid formed at infinite time $\propto$ initial concentration of ethyl acetate i.e. 'a' moles/litre

$$\therefore \quad a \propto (V_\infty - V_0) \qquad (4)$$

On comparing (3) and (4)

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

$$\text{Or} \quad (a-x) \propto V_\infty - V_t \qquad (5)$$

Substituting 'a' from (7) and $(a - x)$ from (8) in the first integrated rate equation

$$k = \frac{2.303}{t} log \frac{a}{a-x} \qquad (6)$$

We get

$$k = \frac{2.303}{t} log \frac{(V_\infty - V_0)}{(V_\infty - V_1)} \qquad (7)$$

Equation (7) is the general first order rate equation for hydrolysis of ethyl acetate.

1.5.3 Requirements:

five 50ml conical flasks, two 100 ml conical flasks with corks, beakers, burette , pipettes of 25ml,10ml,5ml indicator solution .

1.5.4 Procedure:

(i) Take 50ml of 0.5NHCl in a clean 100ml conical flask and 10ml pure ethyl acetate in a test tube loosely cork both of them and place them in a thermostat for half an hour to acquire the temperature of bath maintain a stock of about 200 ml of ice cold water.

(ii) Arrange five conical flasks of 50ml capacity and put 25ml of ice cold water in each flask. Now add 2ml of ethyl acetate with the help of a pipette has been added. Shake the mixture and at once take out 5ml of HCL sol. immediately stop watch when half of the pipette has been added. Shake the mixture and at once take out 5ml of the reaction mixture and transfer to it one of flask containing 25ml of ice cold water.

This freezes i.e. Arrests the hydrolysis reaction. Now titrate it quickly against 0.05 N NaOH using phenolphthalein as an indicator and find out the volume of NaOH required for the titration. The volume V_0 of NaOH very nearly corresponds to the conc. of HCL in the reaction mixture before hydrolysis starts.

Similarly 5 ml of reaction mixture are taken out at successive intervals of 10,20,30,40 and 50 minutes and in turn transferred volume of flasks containing 25 ml of ice cold water and titrated against 0.05 N NaOH using phenolphthalein as an indicator . The volume of alkali required for each titration is noted which corresponds to the titration after *t*' minutes from the start of the reaction denoted by V_t.

(iii) To find the infinite time reading V_∞ i.e. when the hydrolysis is complete. Pipette out 10ml of the reaction mixture in a separate conical flask and loosely cork it. Put this flask in a water bath maintained at 50-60^0 C for half an hour so the hydrolysis is complete. Now cool it to the room temperature. Pipette out 5ml of this reaction mixture and titrate it as before against 0.05 N NaOH. This gives the value of V_∞

1.5.5 Observations:

temperature of both = ...°C

Volume of reaction mixture taken for each titration=5ML

S. No	Time in minutes(i) NaOH used ($v_1$ml)	Volume of 0.05N	$(V_\infty - V_t) = a - x$ (mL)	$(V_\infty - V_t) = a$ (mL)	$k = \frac{2.303}{t} log \frac{(V_\infty - V_0)}{V_\infty - V_t}$
1.	0	V_0			
2.	10	V_{10}			
3.	20	V_{20}			
4.	30	V_{30}			
5.	40	V_{40}			
6.	50	V_{50}			

1.5.6 General Calculations:

(i) **To find the value k**: the value of k can be calculated using equation at different intervals of time. it is found that the values are nearly constant.

(ii) **To find the order of reaction :** the value of k can also be found from the $slope = \frac{2.303}{k}$ by plotting time 't'(abscissa) against log V_∞-V_t (ordinate). A straight line is

Obtained which indicates that hydrolysis of ethyl acetate is first order reaction.

1.5.7 Result :

(i) the rate constant for the hydrolysis of ethyl acetate $(k) = \ ...min^{-1}$

(ii) order of the reaction is first order.

Instruction to lab staff provide :-

(i) 0.5 N hydrochloric acid (ii) 0.5 N sodium Hydroxide Solution

1.6 COMPARISON OF STRENGTH OF HYDROCHLORIC ACID, SULPHURIC ACID USED IN EQUAL CONCENTRATIONS FOR HYDROLYSIS OF METHYL ACETATE.

1.6.1 Object: Composition of strength of hydrochloric acid, sulphuric acid used in equal concentratios for hydrolysis of methyl acetate.

1.6.2 Apparatus: Five 50ml and two 100ml , conical flask with corks, beakers , one burrette, pipettes of 25ml,10ml , 5ml and 2ml ; thermostate or water 0.5 N HCl ,0.5 N NaOH , ice-cold water , phenolphthalein indicator solution .

1.6.3 Theory: the rate of hydrolysis of the specific reaction rate observed for the reaction will be proportional to the concentration of an acid used as catalyst , hence the specific reaction rate observed for the reaction will be proportional to the available concentration of H^+ ions. if equal volume of the two acids HCl and H_2SO_4 of same normality are used for catalysing , the hydrolysis of an ester K_1 and K_2 are the velocity constants in the two cases then the reaction of strenght (s) is given by

$$\frac{S_{HCl}}{S_{H2SO_4}} = \frac{K_1}{K_2}$$

$$K_1 = \frac{2.303}{t} log \frac{a_1}{a_1 - x}$$

$$K_2 = \frac{2.303}{t} log \frac{a_2}{a_2 - x}$$

1.6.4 Procedure: Take 50ml of 0.5N HCl in a clean 100ml conical flasks and about 10ml of methyl acetate in a clean conical flask. Cork them loosely and put them in a thermostat maintained at room temperature so that they can attain room temperature. Prepare 200 mL of ice-cold water free from CO_2 and take 25ml of ice-cold water in 5 conical flasks. when both ester and acid atttain same temperature ,take 2ml of methyl acetate and mix it in 50 ml of 0.5 N HCl . Start the stop watch when half the pipette has been discharged. Shake it quickly against 0.05N NaOH using Phenolphthalein as indicator and find out the amount of alkali. Appearance of pink colour which does not vanish up to 10 seconds shows end point similarly repeat the experiment by taking 2ml of reaction may be denoted by $V_{t.}$

Take out 10ml of reaction mixture in a clean dry conical flask and loosely cork it. Put this corked flask in a water bath maintained at 50^0C for an hour so that hydrolysis is complete. Now cool it to the room temperature, take out 2ml of this mixture and titrate before against 0.05N N alkali. This titrate value corresponds to the acid concentration after hydrolysis is complete. Similarly, precede the Experiment in a similar manner using 0.5 NH_2SO_4.

1.6.5 Data recording:

(i) Using 0.5N HCL

Time (sec.)	**Titrate value (ml)**	**(*a* - *x* ml)**	**Log (*a* - *x*)**	$k = \frac{2.303}{t} log \frac{a_1}{(a_1 - x)}$
0	$V_0 =$	$V_\infty - V_0$	—	
10	$V_{10} =$	$V_\infty - V_{10}$	—	
20	$V_{20} =$	$V_\infty - V_{20}$	—	
30	$V_{30} =$	$V_\infty - V_{30}$	—	
40	$V_{40} =$	$V_\infty - V_{40}$	—	
50	$V_{50} =$	$V_\infty - V_{50}$	—	
∞	$V_\infty =$			

V_0 $\propto$ amount of HCL at *t*= 0

$V_\propto$ $\propto$ Amount of 2mL H_2so_4 when hydrolysis is complete.

∴ $V_\infty - V_0 \propto$ Amount of acetic acid produces when hydrolysis is complete ($a_1$in formula).

Using 0.5N H_2SO_4 :

Time in sec.	**Rate value (mL)**	$(a_2 - x)mL$	**log** $(a_2 - x)$	$k = \frac{2.303}{t} log \frac{a_1}{a_1 - x}$
0	$V_0 =$	$V_\infty - V_0 \propto a_2$	—	
10	$V_{10} =$	$V_\infty - V_{10} =$	—	
20	$V_{20} =$	$V_\infty - V_{20} =$	—	
30	$V_{30} =$	$V_\infty - V_{30} =$	—	
40	$V_{40} =$	$V_\infty - V_{40} =$	—	
50	$V_{50} =$	$V_\infty - V_{50}=$	—	
∞	$V_\infty = 0$			

$\mathrm{V_0 \propto amount\ of\ HCl\ at\ t = 0}$

$\mathrm{V_\infty \propto amount\ of\ 2mL\ H_2SO_4\ when\ hydrolysis\ is\ complete.}$

$\mathrm{V_\infty - V_0 \propto amount\ of\ acetic\ acid\ produced\ when\ hydrolysis\ is\ complete\ (a_2\ in\ formula)}$

1.6.6 General Calculations:

Using formula $K_1 = \frac{2.303}{t}\log\frac{(V_\infty - V_0)}{(V_\infty - V_t)}$, K_1 and K_2 can be calculated.

Let $V_t - V_0$ be equal to a_1 (in case of HCl)

$V_t \propto$ x, the amount of acetic acid formed upto time t .

Or $V_t - V_0 \propto x, \textit{the amount of easter hydrolysed up to time t.}$

$\therefore$ $V_t - V_0 \propto \textit{factor x in}$ about formula.

So $(a - x) \propto (V_\infty - V_0) - (V_t - V_0) or (V_\infty - V_t)$

Substituting value in above formula

$$K_1 = \frac{2.303}{t}\log \left(\frac{V_\infty - V_0}{V_\infty - V_t}\right)$$

$$K_2 = \frac{2.303}{t}\log \left(\frac{V_\infty - V_0}{V_\infty - V_1}\right)$$

Ratio of strength of two acids is

$$\frac{S_{HCL}}{SH_2SO_4} = \frac{K_1}{K_2} =$$

1.7 TO DETERMINE THE ACTIVATION PARAMETERS FOR THE ACID CATALYZED HYDROLYSIS OF ESTER.

1.7.1 Objective : To determine the activation parameters for the acid catalyzed hydrolysis of ester

1.7.2 Principle : Velocity constants for the hydrolysis of ester by HCl at different temperatures are determined and the energy of activation is calculated using the equation.

1.7.3 Procedure : Buretted out 100 ml of 0.25N HCl into a clean conical flask. Ethyl acetate (ester) is also taken in another conical flask. Both the flasks are kept in a thermostat at temperature T 1, when both the flasks have attained the same temperature, 10ml of the ester is pipetted out into the acid. A stop watch is started at the instant when half of the ester is added. The contents are shaken and after 10 minutes, 5ml of the reaction mixture is run into ice cold water to arrest the reaction. The excess acid is titrated against 0.2N NaOH using phenolphthalein as indicator. The above process is repeated at intervals of 10 minutes for an hour. The remaining solution is heated in a water bath maintaining the temperature 60 - 70°C for 30 minutes. It is then cooled to room temperature, after which 5ml of the reaction mixture is run into ice cold water and titrated against 0.2N NaOH using phenolphthalein as indicator. The same experiment is repeated with the same acid but at two higher temperatures such as 37°C and 45°C. The velocity constants are calculated for the three experiments and then the energy of activation is calculated from Arrhenius slope.

1.7.4 Result:

1. The energy of activation Ea = --------------------- kJ mol $^{-1}$
2. Enthalpy of activation = ------------------------------kJ mol $^{-1}$
3. Free energy of activation = -----------------------------kJ mol $^{-1}$
4. Entropy of activation = ---------------------------------JK $^{-1}$ mol $^{-1}$

Table – 1

Ester hydrolysis with 0.25N HCl at 31°C

Time in minutes	Burette Readings (ml)		Volume of NaOH (ml)	$(V_\infty - V_t) = a - x$ (mL)	log $(V_\infty - V_t) = a$ (mL)
	Initial	Final			

Table – 2

Ester hydrolysis with 0.25N HCl at 37°C

Time in minutes	Burette Readings (ml)		Volume of NaOH (ml)	$(V_\infty - V_t) = a - x$ (mL)	log $(V_\infty - V_t) = a$ (mL)
	Initial	Final			

Table – 3

Ester hydrolysis with 0.25N HCl at 45°C

Time in minutes	Burette Readings (ml)		olume of NaOH (ml)	$(V_\infty - V_t) = a - x$ (mL)	log $(V_\infty - V_t) = a$ (mL)
	Initial	Final			

Table – 4

Determination of activation parameter

T(K)	1/T x 10^{-3}	kx10^{-3}	log (kx10^{-3})	3+log k

1.8 *DETERMINATION OF FREE ENERGY CHANGE OF A REACTION.*

1.8.1 Objective : Determination of free energy change of a reaction

1.8.2 Procedure:

1. Place the nested Styrofoam cups into a 400-mL beaker. Use a 100-mL graduated cylinder to measure about 25 mL of demonized water and add to the blue plastic cup inside the tyrofoam cups. Record the **exact volume** of water used.

2. Tare out (zero) the mass of the weighing cup. Remove the weighing cup from the balance and use a spatula to add the appropriate mass of ammonium chloride.

3. Place a thermometer in the DI water. This will be your initial temperature.

4. Add the salt to the water in the calorimeter and replace the lid. **Stir the solution vigorously** by swirling the beaker and contents, carefully holding the lid and thermometer in place, for two minutes. Record the temperature of the mixture every 10 seconds.

5. The highest (or lowest) temperature reached will be the final temperature.

6. Be sure to record your observations of the appearance of the salt solution in the calorimeter at the end of two minutes.

7. Repeat all steps for a second trial of ammonium chloride. Repeat all steps for two trials of calcium chloride.

1.8.3 Calculations:-

- Calculate the mass of ammonium chloride required to prepare 25 mL of a 2.0 M solution. Show your work**.**
- Calculate the mass of calcium chloride required to prepare 25 mL of a 2.0 M solution. Show your work**.**
- Write the balanced equation for the dissolution of ammonium chloride in water.
- Write the balanced equation for the dissolution of calcium chloride in water.
- Calculate the heat of solution (qsoln) if the mass of solution is 45.6 g, specific heat is 3.98 J/g ^{o}C, and ΔT is -34.5^{o}C.
- What is the heat of reaction (qrxn) for the above question?

Table 1: Mass, volume, and temperatures

	Ammonium Chloride			**Calcium Chloride**	
Calculated mass from pre- lab, g			Calculated mass from pre- lab, g		
Mass of salt, g			Mass of salt, g		
Volume of water, mL			Volume of water, mL		
Initial temp. of H_2O,Ti (°C)			nitial temp. of H_2O,Ti (°C)		
Time	**Temp. ^{o}C, Trial 1**	**Temp., ^{o}C, Trial 2**	**Time**	**Temp, ^{o}C, Trial 1**	**Temp., ^{o}C, Trial 2**
0:00			0:00		
0:10			0:10		
0:20			0:20		
0:30			0:30		
0:40			0:40		
0:50			0:50		
1:00			1:00		
1:10			1:10		
1:20			1:20		
1:30			1:30		
1:40			1:40		
1:50			1:50		
2:00			2:00		

Table 2: Observations of each salt after reaction and dissolution reaction in water:

- Observation after reaction - ammonium chloride: =
- Observation after reaction – calcium chloride: =

1.9 DETERMINATION OF THE EQUILIBRIUM CONSTANT FOR A CHEMICAL REACTION

1.9.1 Objective : Determination of the equilibrium constant for a chemical reaction.

1.9.2 Procedure: In this experiment we will study the equilibrium properties of the reaction between iron (III) ion, Fe^{3+}, and thiocyanate ion, SCN^-:

$$\mathbf{Fe^{3+}\,(aq) + SCN^-\,(aq) \leftrightarrow FeSCN^{2+}\,(aq)} \qquad (1)$$

Colorless Colorless Deep red

When solutions containing Fe^{3+} ion and SCN^- ion are mixed, Reaction 1 occurs to some extent, forming the iron (III) thiocyanate complex ion, $FeSCN^{2+}$, which has a deep red color. As a result of the reaction, the equilibrium amounts of Fe^{3+} and SCN^- will be less than they would have been if no reaction occurred; for every mole of $FeSCN^{2+}$ that is formed, one mole of Fe^{3+} and one mole of SCN^- will react. According to the Law of Chemical Equilibrium, the equilibrium constant expression K_c for Reaction 1 is formulated as follows:

$$Kc = \frac{[FeSCN^{2+}]}{[Fe^{3+}][SCN^-]} \qquad (2)$$

The value of K_c in Equation 2 is constant at a given temperature. This means that mixtures containing Fe^{3+} and SCN^- will react until Equation 2 is satisfied, so that the same value of the K_c will be obtained no matter what initial amounts of Fe^{3+} and SCN^- were used.

The objectives of this experiment are: (1) to find K_c for Reaction 2 for several mixtures of Fe^{3+} and SCN^- made up in varying proportions; and (2) to show that K_c indeed has the same value in each of the mixtures. The reaction is a particularly good one to study because K_c is of a convenient magnitude and the color of the $FeSCN^{2+}$ ion makes for an easy analysis of the equilibrium mixture.

The mixtures will be prepared by mixing solutions containing known concentrations of iron (III) nitrate, $Fe(NO_3)_3$, as a source of Fe^{3+} ions and potassium thiocyanate, KSCN, as a source of SCN^- ions. The color of the $FeSCN^{2+}$ ions formed will allow us to determine its equilibrium concentration using a spectrophotometer (discussed later). Knowing the initial concentrations of reactants in a mixture and the equilibrium concentration of $FeSCN^{2+}$, we can calculate the equilibrium concentrations of the rest of the pertinent species and then determine K_c.

Since the calculations required in this experiment may not be apparent, we will go through a step-by- step procedure by which they can be made. As a specific example, let us assume that we prepared a mixture by mixing 10.0 mL of 2.00×10^{-3} M $Fe(NO_3)_3$ ith 10.0 mL of 2.00×10^{-3} M KSCN. As a result of Reaction 1, some red $FeSCN^{2+}$ ion is formed. By the method of analysis described later, its concentration at equilibrium is found to be 1.50×10^{-4} M. Our problem is to find K_c for the reaction from this information. To do this we follow the five steps below:

1. Calculate the initial number of moles of each reactant in the mixture.
2. Determine the number of moles of product that were formed at equilibrium. Since the product was formed at the expense of reactants, we can calculate the amount of each reactant that was used up.
3. Calculate the number of moles of each reactant remaining in the equilibrium mixture.
4. Determine the concentration of each reactant.
5. Calculate K_c for each reaction using Equation 2.

Step 1:Finding the Initial Number of Moles of Each Reactant. This requires relating the volumes and concentrations of the reagent solutions that were mixed to the numbers of moles of each reactant species in those solutions. By definition, the molarity of species A, M_A, is:

$$MA = \frac{\text{Moles of A}}{\text{Total volume of solution, Vsoln (in L)}} \quad 3a$$

Or

$$\text{Moles of A} = M_A \times V_{soln} \quad (3b)$$

Using Equation 3b, it is easy to find the initial number of moles of Fe^{3+} and SCN^-. For each solution the volume used was 10.0 mL, or 0.0100 L. The molarity of each of the solutions was 2.00×10^{-3} mol/L, so $M_{Fe3+} = 2.00 \times 10^{-3}$ mol/L and $M_{SCN-} = 2.00 \times 10^{-3}$ mol/L. Therefore, in the reagent solutions, we find that

Initial moles $Fe^{3+} = M_{Fe3+} \times V_{Fe3+} = 2.00 \times 10^{-3}$ mol/L x 0.0100 L = 2.00×10^{-5} mol

Initial moles $SCN^- = M_{SCN-} \times V_{SCN-} = 2.00 \times 10^{-3}$ mol/L x 0.0100 L = 2.00×10^{-5} mol

Step 2: Finding the Number of Moles of Product Formed. Here again we can use Equation 3b. Let's say that the molarity of $FeSCN^{2+}$ was found to be 1.50 x 10^{-4} mol/L at equilibrium using the spectrophotometer (described later). The total volume of solution or the mixture at equilibrium is the *sum* of the two volumes that were mixed, and is 20.0 mL, or 0.0200 L. So,

Moles $FeSCN^{2+}$ formed = $M_{FeSCN2+}$ x V_{soln} = 1.50 x 10^{-4} mol/L x 0.0200 L
= 3.00 x 10^{-6} mol

The number of moles of Fe^{3+} and SCN^- that reacted, or were *used up*, in producing the $FeSCN^{2+}$ must also be both equal to 3.00 x 10^{-6} moles since, by Equation 1; it takes *one mole* Fe^{3+} *and one mole* SCN^- to make each mole of $FeSCN^{2+}$. Thus:
Number of moles Fe^{3+} reacted = Number of moles $FeSCN^{2+}$ formed = 3.00 x 10^{-6} mol
Number of moles SCN^- reacted = Number of moles $FeSCN^{2+}$ formed = 3.00 x 10^{-6} mol

Step 3: Finding the Number of Moles of Each Reactant Present at Equilibrium. In Step 1 we determined that initially we had 2.00 x 10^{-5} moles Fe^{3+} and 2.00 x 10^{-5} moles SCN^- present. In Step2 we found that in the reaction 3.00 x 10^{-6} moles Fe^{3+} and 3.00 x 10^{-6} moles SCN^- reacted. The number of moles present at equilibrium must equal the initial moles minus the number of moles that reacted. Therefore, at *equilibrium,*

Number of moles at equilibrium = initial no. moles - no. moles reacted
Equil. Moles Fe^{3+} = 2.00 x 10^{-5} - 3.00 x 10^{-6} = 1.70 x 10^{-5} mol (4)
Equil. Moles SCN^- = 2.00 x 10^{-5} - 3.00 x 10^{-6} = 1.70 x 10^{-5} mol

Step 4 Finding the Concentrations of All Species at Equilibrium. Experimentally, say we obtained the concentration of $FeSCN^{2+}$ to be 1.50 x 10^{-4} M (as given in step 2). The number of moles of each of Fe^{3+} and SCN^- at equilibrium was obtained in Step 3. The volume of the mixture being studied was 20.0 mL, or 0.0200 L. So, at *equilibrium,* the concentrations of Fe^{3+} and SCN^- equal:

$[Fe^{3+}]_{eq}$ = $M_{Fe3+,\ eq}$ = (Equil. moles Fe^{3+}/V_{soln}) = (1.70 x 10^{-5} moles/0.0200L)
= 8.50 x 10^{-4} mol/L
$[SCN^-]_{eq}$ = $M_{SCN-,\ eq}$ = (Equil. moles SCN^-/V_{soln}) = (1.70 x 10^{-5} moles/0.0200L)
= 8.50 x 10^{-4} mol/L

Step 5: Finding the Value of K_c for the Reaction. Once the equilibrium concentrations of all the reactants and products are known, one needs merely to substitute into Equation 2 to determine $[FeSCN^{2}]$

$$Kc = \frac{[FeSCN^{2+}]}{[Fe^{3+}]\,[SCN^{-}]}$$

$$Kc = \frac{1.50 \times 10^{-4}}{(8.50 \times 10^{-4})(8.50 \times 10^{-4})}$$

$$= 204$$

In this experiment you will obtain data similar to that shown in this example. The calculations involved in processing your data are completely analogous to those we have made. (However, your results will differ from the ones we obtained, since the data in our example were obtained at a different temperature and so relate to a different value of K_c.)

In carrying out this analysis we made the assumption that the reaction which occurred was given by Equation 1. There is no inherent reason why the reaction might not have been:

$$Fe^{3+}\,(aq) + 2\,SCN^{-}\,(aq) \leftrightarrow Fe(SCN)_2^{+}\,(aq) \qquad (5)$$

Notice that in Reaction 5, 2 moles of SCN^- reacted with one mole of Fe^{3+}, so the reaction stoichiometry is *1:2*. If you are interested in matters of this sort, you might ask how we know whether we are actually observing Reaction 1 or Reaction 5. The line of reasoning is the following. If Reaction 1 is occurring, K_c for that reaction as we calculate it should remain constant with different reagent mixtures. If, however, Reaction 5 is going on, K_c as calculated for that reaction should remain constant. In part B of the Data and Calculations section, we will assume that Reaction 5 occurs and make the analysis of K_c

on that basis. The results of the two sets of calculations should make it clear that Reaction 1 is the one that we are studying.

Two analytical methods can be used to determine $[FeSCN^{2+}]$ in the equilibrium mixtures. The more precise method uses a spectrophotometer, which measures the amount of light absorbed by the red complex at 447 nm, the wavelength at which the complex most strongly absorbs. The absorbance, *A,* of the complex is proportional to its concentration, *M,* and can be measured directly on the spectrophotometer:

$$A = \mathrm{kM} \qquad (6)$$

Your instructor will show you how to operate the spectrophotometer, if available to your laboratory, and will provide you with a **calibration curve or equation** from which you can find [$FeSCN^{2+}$] once you have determined the absorbance of your solutions.

In preparing the mixtures in this experiment we will maintain the concentration of H^+ ion at 0.5 M. The hydrogen ion does not participate directly in the reaction, but its presence is necessary to avoid the formation of brown-colored species such as $FeOH^{2+}$, which would interfere with the analysis of [$FeSCN^{2+}$].

1.9.3 Procedure: In the hoods you'll find the solutions of 2.00×10^{-3} M KSCN and 2.00×10^{-3} M $Fe(NO_3)_3$ in 1 M HNO_3 . The volumes of reagents to be added to each test tube are summarized in Table 1. Note that the total volume in each test tube is 10.00 ml. Deliver the required amount of each chemical by means of a graduated or volumetric pipette, but do not mix the Fe^+ solution and SCN^- solution until you are ready to use the spectrophotometer. Do one trial at a time.

The moment $Fe(NO_3)_3$ solution is in contact with KSCN solution the reaction starts.

Table 1. Volumes of reagents needed

Volume of Reagents	**Test Tube No.**				
	1	**2**	**3**	**4**	**5**
Volume $Fe(NO_3)_3$ solution (mL)	5.00	5.00	5.00	5.00	5.00
Volume KSCN solution (mL)	1.00	2.00	3.00	4.00	5.00
Volume H_2O (mL)	4.00	3.00	2.00	1.00	0.00

Mix each solution thoroughly with the Vortexer or a glass stirring rod. Be sure to dry the stirring rod after mixing each solution.

1.9 DETERMINATION OF CONCENTRATION OF $FeSCN^{2+}$ BY SPECTROPHOTOMETRY

1.9.1 Objective : Determination of concentration of $FeSCN^{2+}$ by spectrophotometry

1.9.2 Theory: Place a portion of the mixture from test tube 1 in a spectrophotometer cuvette, as demonstrated by your instructor, and measure the absorbance of the solution at 447 nm. Determine the concentration of $FeSCN^{2+}$ from the calibration curve provided for each instrument or from the equation furnished to you. Record the value on the Data page. Repeat the measurement using the mixtures in each of the other 4 test tubes.

1.9.2 Calculation of K_c : Calculation is easily done by following Steps 1 through 5 in the procedure. Results are to be entered in the table either by hand or using Excel. If you are familiar with Excel, you may enter in the formulas directly and have the spreadsheet perform your calculations. Please keep all values to 3 significant figures.

Step 1. Find the initial number of moles of Fe^{3+} and SCN^- in the 5 mixtures. The initial number of moles is determined by the following: **initial moles = M x V (in L)** Enter these values into Columns 1 and 2 of the table.

Step 2. Determine the equilibrium concentration of $FeSCN^{2+}$ from the measured absorbance and the calibration curve. Since the light absorbed is proportional to the concentration (**A = k x M**): **$M_{FeSCN2+} = [FeSCN^{2+}]_{eq} = A/k$** where k is the slope of the line of the calibration curve. Enter this value into column 8 of the data table.

Next calculate the Equilibrium # of moles for $FeSCN^{2+}$ in a similar fashion as Step 1:

Equil. Moles $FeSCN^{2+} = [FeSCN^{2+}]_{eq} \times V_{soln}$ (in L)

Enter the value into column 5 of the data table. Please note that the equilibrium number of moles of $FeSCN^{2+}$ equals the number of moles of Fe^{3+} and the number of moles SCN^- that reacted.

Step 3. Determine the equilibrium moles of Fe^{3+} and SCN^- by subtracting the moles that reacted for Fe^{3+} or SCN^- (from step 2) from the initial moles present:

Equil. moles = Initial moles –Moles reacted. Enter these values into Columns 3 and 4 respectively.

Step 4. Determine the equilibrium concentrations of Fe^{3+} and SCN^-, $[Fe^{3+}]_{eq}$ and $[SCN^-]_{eq}$, by dividing the equil. Moles for each species by the total volume of the reaction mixture (total volume = 10.0 mL or 0.010 L): **[ ]$_{eq}$ = equil. Moles/V (in L)**. Enter these values into Columns 6 and 7.

Step 5 Calculate K_c for the reaction for each of the mixtures by substituting values for the equilibrium concentrations of Fe^{3+}, SCN^- and $FeSCN^{2+}$ into the equilibrium expression for the reaction. Enter these values into the last column and find the average value of Kc.

1.10 SUMMARY

The present unit comprises different methods to determine the order of reaction.

- Explain the relation between concentration and time graphically.
- How to change the rate of reaction by effect of concentration, temperature and pressure etc.
- Determination of the order of reaction by isolation method
- Determination of the order of reaction by half life period method
- Determination of the order of the reaction by Integration method.
- Determination of the entropy of activation of a reaction.
- Determination of free energy change of a reaction.
- Methods for determine of order of reaction and also discussed in details.
- Study of hydrolysis of methyl acetate in presence of hydrochloric acid at room temperature.
- Comparison of strength of hydrochloric acid, sulphuric acid used in equal concentrations for hydrolysis of methyl acetate.
- Determine of the Equilibrium Constant for a Chemical Reaction.

1.11 REFERENCES

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1.12 SUGGESTED READING

1. P. Atkins, 2010, the Laws of Thermodynamics: a Very Short Introduction, Oxford University Press, Oxford. This is a short book by an eminent chemist summarizing the foundations of thermodynamics for an interested general reader.
2. W. T. Grandy, 2008, Entropy and the Time Evolution of Macroscopic Systems, Oxford, Oxford. This monograph gives an enlightening description, fully informed by both historical and modern interpretations, of entropy and its evolution in the context of both continuum and statistical theories.
3. K. J. Laidler, 1987, Chemical Kinetics, Third Edition, Prentice-Hall, Upper Saddle River, NJ. This is a standard advanced undergraduate chemistry text on the dynamics of chemical reactions. It first appeared in 1965.
4. G. N. Lewis and M. Randall, 1961, Thermodynamics and the Free Energy of Chemical Substances, Second Edition, McGraw-Hill, New York. This book, first published in 1923, was for many years a standard reference text of physical chemistry.

UNIT SECOND - ELECTROCHEMISTRY

Content:

UNIT SECOND - ELECTROCHEMISTRY

2.1 INTRODUCTION

Electrochemistry is the study of the relationship between chemical and electrical reactions. The operation of all portable electronic devices that you own such as computer, mobile phone, etc. is made possible by electrochemical reactions. Pharmacists and engineers around the world are searching for ways to improve the technology by making products that will make batteries cheaper, less expensive, and more durable. Those electrochemical processes use oxidation and reduction reactions. Oxidation involves the loss of one or more electrons in a chemical form while a reduction in the advantage of one or more electrons by the chemical composition. When oxidation and reduction are paired together in a redox reaction, electrons can flow from a type of oxidized, reducing agent or reductant, to a reduced species, oxidizing agent or oxidant. That flow of electrons can be automatically generated by the reaction and converted into electricity, such as in a galvanic cell, or it can be placed in an external source to maintain an automatic reaction, such as an electrolytic cell

2.2 OBJECTIVES

After that unit you will be learn the :

- Learn about the relationship between the conductance, specific conductance, molar conductance, degree of dissociation and dissociation constant.
- Understand the difference between weak and strong electrolytes.
- Know the basic of Ostwald dilution law.
- Understand the solubility and solubility product.
- Understand the pH and hydrolysis.

2.3 SOME IMPORTANT TERMS

2.3.1 Electrical conductors

Substances, which allow an electric current to pass through them, are known as conductors or electrical conductors. Conductors can be divided into two types,

2.3.2 Metallic or Electronic conductors

Those conductors which conduct electricity without undergoing any chemical change are known as metallic or electronic conductors. As the name indicates, the conduction, in this case, is due to the flow of electrons. Metals (*e.g.,* copper, iron, aluminum, silver, etc.), non-metals like graphite, and certain minerals are common examples.

2.3.3 Electrolytic conductors or Electrolytes

Those conductors which undergo a chemical change when an electric current is passed through them are known as electrolytic conductors. In this case, the flow of electricity is due to the movement of ions. Solutions of acids, bases, and salts in water, fused salt, etc. are common examples. In electrolytic solutions, the passage of the electric current is due to the migration of positively and negatively charged particles, known as cations and anions respectively, in opposite directions. It is the valence, migration velocity, and the concentration of the ions which determine the strength of the current flowing through a solution of an electrolyte Electrolytic conductors too obey Ohm's law:

$$I = ER$$

where E volts is the potential difference between the ends of the conductor of resistance R ohms and I is the current strength (amp). Electrolytes are further divided into two types based on their strengths i.e. Strong electrolytes and Weak electrolytes.

2.3.3.1 Strong electrolytes

Those substances which are almost completely ionizing into ions in their aqueous solution are called strong electrolytes. *The degree of ionization for this type of electrolyte is one i.e.,* $\alpha \approx 1$. *For example,* HCl, H2SO4, NaCl, HNO3, KOH, NaOH, HNO_3, $AgNO_3$, etc. means all strong acids, bases, and all types of salts.

2.3.3.2 Weak electrolytes

Those substances which are ionized to a small extent in their aqueous solution are known as weak electrolytes. *The degree of ionization for these types of electrolytes is* α **<<<1.** *For example* H_2O. CH_3COOH, H_2O, CH_3COOH, NH_4OH, HCN, HCOOH Liq. SO_2 etc. Means all weak acids and bases.

2.3.4 Specific conductivity

The resistance, R of any conductor of the uniform cross-section at a given temperature varies directly as its length) and inversely as cross-sectional area (a); that is

$$R = \rho l/a$$

where ρ is a constant characteristic of the material of the conductor at a specified temperature and is known as specific resistance or resistivity of the conducting material. When both length and cross-sectional area of the conductor is unity, ρ equals R. The resistivity of the material may thus be defined as the resistance in ohm offered by a cube of unit length to the passage of electricity through opposite faces. The reciprocal of the resistivity is known as conductivity or specific conductance and is usually represented by κ (kappa).

$$\kappa = \frac{1}{f} = \frac{1}{R}(l/a)$$

From eq. (3) units of κ can be obtained as follows:

$$\kappa = \frac{1}{R}\left(\frac{l}{a}\right)\ \frac{\mathrm{ohm^{-1}\ x\ m}}{\mathrm{m^2}} = \mathrm{ohm^{-1}m^{-1}\ or\ S\ m^{-1}}$$

Thus, SI unit for κ is Siemens meter^{-1} (Sm^{-1}), But the conductivity is normally available in S cm^{-1}. To compare the conductance of electrolytes, it is necessary to take chemically comparable amounts of the electrolytes, such as equivalent weight and molecular weight.

2.3.5 Equivalent conductivity

It is the conducting power of all the ions produced by one g equivalent of an electrolyte at any particular concentration, i.e., the conductivity of solution containing 1 g equivalent of the electrolyte when placed between two large electrodes 1 cm apart. It is usually represented by λc. If κ is the conductivity of a solution containing 1 g equivalent of the electrolyte in V cm^3 of the solution, then it may be shown that,

$$\lambda_c = \kappa V\,[\mathrm{ohm^{-1}\ cm^{-1}}\ X\ \frac{cm^3}{g\ equiv.}]$$

$$= 1000\ \kappa/C\ \mathrm{ohm^{-1}}\ cm^2\mathrm{equiv.^{-1}}$$

where C is the concentration is g equivalents per dm^3.

2.3.6 Molar conductivity

Molar conductivity μc of an electrolyte at a particular dilution is the conductivity of the solution containing 1 g molecule of the substance when placed between two large electrodes one cm apart. It can easily be shown that

$$\mu_c = \kappa V = 1000\ k/m\ ohm^{-1}\mathrm{cm}^2\mathrm{mol}^{-1}$$

where V cm^3 is the volume of the solution containing 1 mole of the electrolyte and is the molarity of the solution.

2.3.7 Effect of dilution on conductivity

The specific conductivity decreases with increasing dilution due to the decrease of current-carrying ions per unit volume. On the other hand, the equivalent conductance increases with decreasing concentration and attains a limiting value at infinite dilution. This limiting value is called, equivalent conductance at 'zero concentration' or 'infinite dilution'. It is denoted by λo or λ∞. This increase of λc is attributed to the increased number of ions in the solution as a result of increased dissociation and to the increased migration velocity of the ions.

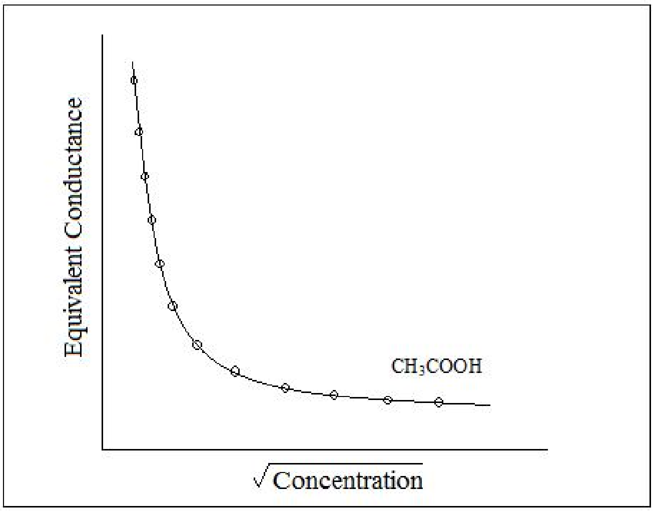
In the case of a solution of weak electrolytes, the former factor mainly operates, and λc at a particular dilution is the measure of the number of ions present in the solution At infinite dilution, i.e., zero concentration, the weak electrolyte will be completely dissociated and λo will attain a maximum value. Thus the ratio of equivalent conductivity at a finite dilution to that at infinite dilution gives the degree of ionization of a weak electrolyte at that dilution, i.e.,

$$\text{Degree of dissociation } \alpha = \lambda_c / \lambda_o$$

where λ_o is the equivalent conductivity at zero concentration infinite dilution). It can be calculated using Kohlrausch's law of independent ionic conductance:

$$\lambda_o = \lambda_o^+ + \lambda_o^-$$

where λ_o^+ and λ_o^- are the ionic conductance of the cation and the anion respectively at infinite dilution.



According to the Arrhenius theory, strong electrolytes dissociate completely at all dilution and thus increase of λ_o, with dilution is not due to the increased dissociation Fig. 7.1. Here increase in dilution results in the decrease of inter-ionic interaction, thereby, increasing the migration speed of the ions and hence the equivalent conductivity. The Onsagar's equation gives the variation of λ_o with concentration is dilute solutions upto (0.001 N)

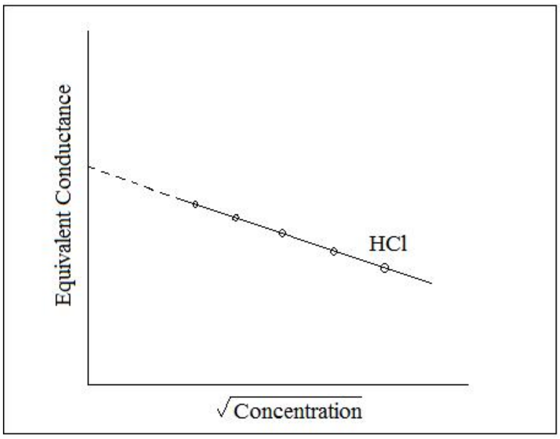
$$\lambda_c = \lambda_o - (a\lambda_o + b)\sqrt{c}$$

where c is the concentration in g equiv/dm^3 and a and b are the constants. For uni-uni valent electrolytes, the calculated values of Osagar equation constants at 25°C are:

$$A = 0.2273 \text{ and } b = 59.78$$

A plot of λ_c against $\sqrt{c}$ (abscissa) will give a straight line with a negative slope, $-(a\lambda_o + b)$ and intercept on the λ_c-axis equal to λ_o Fig. 7.2. Hence, λ_o can be obtained by extrapolating the graph to zero concentration. In case of weak electrolytes, the plots of λ_c vs $\sqrt{c}$, however, are not linear, so λ_o values for them can not be obtained by extrapolating the graph; λ_o is calculated from ionic conductance of the anion and the cation at infinite dilution using Kohlrausch's law of independent migration of ions.

$$\lambda_o = \lambda_o^+ + \lambda_o^-$$



2.3.8 Ostwald's dilution law

This law is based on the fact that only a portion of the electrolyte is dissociated into ions at ordinary dilution and completely at infinite dilution. According to ionic theory in aqueous solution of weak electrolytes, such as weak acids and bases, a state of equilibrium exists between the ionised and unionised molecules. It was noticed by Ostwald that the law of mass action could be satisfactory applied to them. Ostwald's dilution law describes the dissociation constant of the weak electrolyte with the degree of dissociation (α) and the concentration of the weak electrolyte.

Consider, one mole of a weak electrolyte AB is dissolved in water and the solution is made V dm^3 by volume. Let α is the degree of dissociation of the electrolyte at equilibrium. Weak electrolyte dissociates as

$$AB \rightleftharpoons A^+ + B^-$$

	AB	A^+	B^-
Initial conc.	c	0	0
Conc. at equilb.	c(1-α)	cα	cα

Then according to the law of mass action, the equilibrium constant K_{eq} will be given by

$$K_{eq} = \frac{[A^+][B^-]}{[AB]} = \frac{c\alpha \times c\alpha}{c(1-\alpha)} = \frac{\alpha^2 c}{1-\alpha}$$

This expression is called Ostwald's dilution law, K_{eq} is called the dissociation (or ionization) constant of the weak electrolyte.

2.4 DETERMINATION OF THE DISSOCIATION CONSTANT OF A WEAK ACID BY CONDUCTIVITY METHOD

2.4.1 Object: To determine dissociation constant of weak acid conductometrically.

2.4.2 Requirements: Saturated benzoic acid solution, approximately 0.1 N NaOH solution, conductivity water, 0.1N succinic acid solution, 0.1 N KCl solution, 25 ml pipette, 150 ml conical flask, 10 ml graduated pipette, 100 ml beakers, 100 ml standard measuring flask, standard conductometer and conductivity cell etc.

2.4.3 Theory: A standard solution is one for which the concentration is known accurately. Preparation of a standard solution is generally the first step in any quantitative experiment; hence it is important to know how to prepare a standard solution. These standard solutions are of two types: Primary standards and secondary standards. Primary standard solutions are prepared by using a substance having following specifications:

(1) A substance of sufficient purity.

(2) A substance with high molecular weight.

(3) It should not be hygroscopic.

2.4.4 Procedure:

Part I: Standardisation of sodium hydroxide and determination of molar concentration of Benzoic acid:

(1) Weigh accurately 0.59 g of succinic acid, dissolve it in minimum quantity of distilled water and dilute up to 100 ml in a standard measuring flask.

(2) Pipette out 10 ml of 0.1N succinic acid solution in a 150 cm^3 conical flask.

(3) Titrate it against (approximately) 0.IN NaOH solution from the burette using 1%phenolphthalein solution as an indicator.

(4) End point is colourless to pink colour.

(5) Filter the saturated benzoic acid solution and pipette out 25 cm^3 of it in a clean 150 cm^3 conical flask. Add 1-2 drops of 1% phenolphthalein indicator to it.

(6) Titrate it against standardised NaOH solution from the burette.

(7) End point is colourless to pink colour.

(8) Find the concentration of saturated benzoic acid.

Calculations:

$$N_{NaOH}\,X\,V_{NaOH} = N_{Succinic\,acid}\,X\,V_{succinic\,acid}$$

$$N_{NaOH} = \frac{N_{Succinic\,acid}\,X\,V_{succinic\,acid}}{V_{NaOH}}$$

Normality of NaOH =…………N.

Part II: Determination of molar concentration of weak acid:

Solution in Burette : N NaOH solution

Solution in conical flask: 25 cm^3 of saturated filtered solution of weak acid.

Indicator: 1% Phenolphthalein solution

End Point: Colourless to pink colour

Pilot reading between ______________ cm^3 and ___________cm^3.

Level	Burette Reading in cm^3			Constant reading in cm^3
	I	II	III	
Initial	0.0	0.0	0.0	______cm^3
Final				
Difference				

Part III: Preparation of appropriate dilutions of weak acid:

Saturated Benzoic acid = 0.02 N Benzoic acid

Normality of Benzoic acid X V_1 = 0.02 X 50

$$V_1 = (0.02 \text{ X } 50) / N_1$$

Where N_1 is the normality of Benzoic acid

Initial concentration of acid taken	Volume of weak acid taken in cm^3	Final volume with conductivity water in cm^3
0.02 M	50	
0.01M	50	
0.005 M	50	
0.0025 M	50	
0.00125 M	50	

Part IV: Standardise the conductometer and determine the cell constant

(1) Wash the conductivity cell and a 100 cm^3 beaker using conductivity water.

(2) Rinse both the cell and the beaker with a small quantity of 0.1N KCl solution.

(3) Take about 50-60 cm^3 of supplied 0.1N KCI solution in the rinsed beaker and dip the conductivity cell in it, so that platinum plates dip in the solution completely.

(4) Connect the cell to the conductometer and determine the conductance of KCl solution. Using this conductance, determine the cell constant of the cell.

Part V: Measurement of conductance of the prepared acetic acid dilutions:

(1) Wash three 100 cm^3 standard measuring flasks with conductivity water. Pipette out suggested volume of 0.1N acetic acid in the flasks as given in the Table 1.1 and dilute each flask with conductivity water up to the mark. Shake the solutions well.

(2) Wash the conductivity cell and a 100 cm^3 beaker with conductivity water carefully and then rinse it with 0.1N acetic acid solution.

(3) Take about 50-60 cm^3 of 0.1N acetic acid in the beaker and dip the cell in it. Determine the conductance of this solution.

Digital Conductivity meter

2.4.5 Observations and Calculation of dissociation constant:

(1) Equivalent conductance at infinite dilution (λ_∞) = 390.7 mhos $cm^2 eq^{-1}$ [S $cm^2 eq^{-1}$]

(2) Cell constant (from Part 1): __________________ cm^{-1}

Concentration g eq/dm^3	Conductance mhos [S]	Specific conductance K of solution mhos cm^{-1} [S cm^{-1}]	Equivalent Conductance mhos $cm^2 eq^{-1}$ [S $cm^2 eq^{-1}$]	Degree of dissociation	Dissociation constant
C	L x 10^{-3} mhos or [S]	K = cell constant x conductivity	$\lambda_c = \frac{1000 \text{ X } K}{C}$	$\alpha = \frac{\lambda_c}{\lambda_\infty}$	$K_\alpha = \frac{\alpha^2 C}{1-\alpha}$
0.1 0.05 0.025 0.0125					
K_a (mean) =_________					

2.4.6 Results:

Concentration of solution in gm equi lit^{-3} (C)	Value of Dissociation Constant (K_a)
0.1 0.05 0.025 0.0125	

2.4.7 Precautions:

1. The conductivity cell, when not in use, should be kept in distilled water to prevent drying of the platinum electrodes.
2. In case of fouling of the conductivity cell electrode plates, clean them by keeping in dilute $K_2Cr_2O_7$ containing H_2SO_4 solution (i.e. dilute chromic acid) for 24 hours and then washing with running water followed by with distilled water.

2.4 VALIDITY OF OSTWALD'S DILUTION LAW

2.4.5 **Object:** To verify Ostwald's dilution law for weak acid conductometrically.

2.4.6 **Requirements:** Conductometer and, conductivity water, 100 ml standard measuring flask, 100 ml beakers, 25 ml pipette, 10 ml graduated pipette, acetic acid, 0.1N KCI solution etc.

2.4.7 **Theory: (1)** Ostwald's dilution law states that at constant temperature, degree of dissociation of a weak electrolyte is inversely proportional to the square root of its concentration. The mathematical form of the law is represented as:

$$K_a = \frac{\alpha^2 C}{1-\alpha}$$

(2) In this experiment, the conductance of the acid solution is measured at different concentrations (C).

(3) Using the conductance of the solution, it is possible to calculate the specific conductance, equivalent conductance of the solution (1).

(4) It is possible to calculate the degree of dissociation α using the cquation,

$$\alpha = \frac{\lambda_c}{\lambda_\infty}$$

Λ_c = Equivalent conductance at infinite dilution and is obtained from Kohlrausch's law.

(5) The dissociation constant (K_a) can be obtained from Ostwald's law. The constant value of K, (within reasonable limits) verifies Ostwald's law.

2.4.8 Procedure:

(1) Standardization of sodium hydroxide and determination of molar concentration of Acetic acid.

(2) Determination of molar concentration of weak acid.

(3) Preparation of appropriate dilutions of weak acid.

(4) Standardize the conductometer and determine the cell constant .

(5) Measurement of conductance of the prepared acetic acid dilutions.

2.4.9 Observations and Calculation of dissociation constant:

(1) Equivalent conductance at infinite dilution (Λ_∞) = 390.7 mhos cm^2 eq^{-1} [S cm^2 eq^{-1}]

(2) Cell constant (from Part 1): __________________ cm^{-1}

Concentration g eq/dm^3	Conductance mhos [S]	Specific conductance K of solution mhos cm^{-1} [S cm^{-1}]	Equivalent Conductance mhos cm^2 eq^{-1} [S cm^2 eq^{-1}]	Degree of dissociation	Dissociation constant
C	L x 10^{-3} mhos or [S]	K = cell constant x conductivity	$\lambda_c = \frac{1000 \text{ X } K}{C}$	$\alpha = \frac{\lambda_c}{\lambda_\infty}$	$K_a = \frac{\alpha^2 C}{1-\alpha}$
0.1 0.05 0.025 0.0125					
K$_a$ (mean) =_________					

2.4.10 Results:

Concentration of solution in gm equi lit^{-3} (C)	Value of Dissociation Constant (K_a)
0.1 0.05 0.025 0.0125	

2.4.11 Precautions:

1. The conductivity cell, when not in use, should be kept in distilled water to prevent drying of the platinum electrodes.

2. In case of fouling of the conductivity cell electrode plates, clean them by keeping in dilute $K_2Cr_2O_7$ containing H_2SO_4 solution (i.e. dilute chromic acid) for 24 hours and then washing with running water followed by with distilled water.

3. All the solutions must be prepared in conductance water of specific conductivity less than 1x10-6 S cm-^{1}. If the conductivity exceeds 1 x 10-6 S cm^{-1}, it must be subtracted from that of the solution before calculating dc.

2.6 DETERMINATION THE EQUIVALENT CONDUCTIVITY OF A STRONG ELECTROLYTE CONDUCTROMETRICALLY.

2.6.1 Object: Determine the equivalent conductance of a strong electrolyte (e.g. KCl, NaCl, $AgNO_3$, HCI, KNO_3, etc.) conductrometrically.

2.6.2 Requirements: Standard conductometer, conductivity cell, potassium chloride,conductivity water, 25 cm pipette, 150 cm. conical flask, 10 cm graduated pipette, 100 cm beakers and 100 cm standard measuring flask etc.

2.6.3 Theory: According to Arrhenius theory strong electrolytes dissociate completely at all dilutions, and thus increase of λ_∞ with dilution is not due to the increased dissociation. Here increase in dilution results in the decrease of inter ionic interaction, thereby increasing the migration speed the ions and hence the equivalent conductivity. The Onsagar's equation gives the variation of λ_c with concentration in dilute solutions upto (0.001 N).

$$\lambda_c = \lambda_\infty - (a\lambda_\infty + b)\sqrt{C}$$

Where C is the concentration in g eq/dm^3 and a and b are the constants. For uni-univalent electrolytes, the calculated values of Onsagar equation constants at 25°C are:

$$A = 0.2273 \text{ and, } b = 59.78$$

From the plot of a graph between λ_c and $\sqrt{C}$, λ_∞ is obtained by extrapolating to $\sqrt{C} = 0$. The slope is compared with that obtained from Onsager’s equation.

2.6.4 Procedure:

(i) Standardize the conductometer and determine the cell constant of 0.1 N KCl solution.

(ii) Prepare 0.02, 0.01, 0.005, 0.0025 and 0.001 N KCl solutions in conductivity water.

(iii) Measurement of conductance of the prepared KCl dilutions.

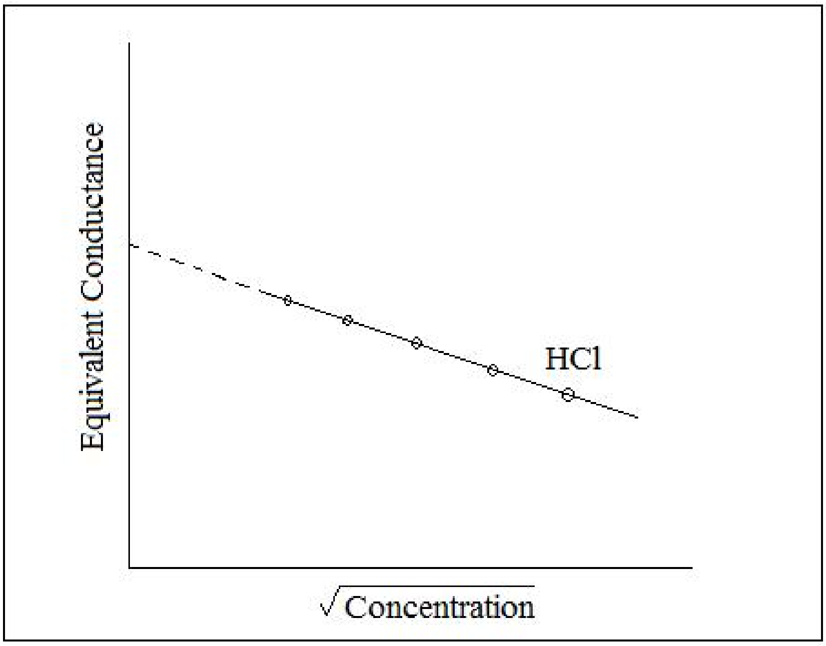
2.6.5 Observation:

Concentration g eq/dm^3	Conductance mhos [S]	Specific conductance K of solution mhos cm^{-1} [S cm^{-1}]	Equivalent Conductance mhos cm^2 eq^{-1} [S cm^2 eq^{-1}]	$\sqrt{C}$
0.02 0.01 0.005 0.0025 0.001				

2.6.6. Calculation of equivalent conductance:

(1) Cell constant (from Part 1): __________________ cm^{-1}

Plot a graph between λ_c (Y-axis) values and √C (X-axis). The graph will be a straigx2ht line. Extrapolate the linear portion of the graph to zero concentration. The value of λ_∞ is obtained by extrapolating to √C = 0. The slope is compared with that obtained from Onsager's equation.



2.6.7 Results:

The equivalent conductivity of strong electrolyte (KCl) = _________________ mhos cm^2 eq^{-1}

2.6.8 Precautions:

1. The conductivity cell, when not in use, should be kept in distilled water to prevent

drying of the platinum electrodes.

2. In case of fouling of the conductivity cell electrode plates, clean them by keeping in dilute $K_2Cr_2O_7$ containing H_2SO_4 solution (i.e. dilute chromic acid) for 24 hours and then washing with running water followed by with distilled water.
3. All the solutions must be prepared in conductance water of specific conductivity less than 1x10-6 S cm^{-1}. If the conductivity exceeds 1 x 10-6 S cm^{-1}, it must be subtracted from that of the solution before calculating dc.

2.7 DETERMINATION OF THE EQUIVALENT CONDUCTIVITY AT INFINITE DILUTION OF WEAK ELECTROLYTE CONDUCTROMETRICALLY.

2.7.1 Object: Determine the equivalent conductance of a weak electrolyte, say acetic acid, at infinite dilution following the Kohlrausch law.

2.7.2 Requirements: Standard conductometer, conductivity cell, hydrogen chloride, sodium chloride, sodium acetate, conductivity water, 25 cm pipette, 150 cm. conical flask, 10 cm graduated pipette, 100 cm beakers and 100 cm standard measuring flask etc.

2.7.3 Theory: λ_∞ for acetic acid can not be obtained by the method of extrapolation, for λ_c greatly increases at high dilutions. It can be evaluated using Kohlrausch law independent migration of ions, according to which the equivalent conductance at infinite dilution is the sum of the ionic conductances of the ions constituting the electrolyte. Thus

$$\lambda_\infty(CH_3COOH) = \lambda_\infty(CH_3COONa) + \lambda_\infty(HCl) - \lambda_\infty(NaCl) \qquad \text{........................(1}$$

$$= \lambda CH_3COO^- + \lambda Na^+ + \lambda H^+ + \lambda Cl^- - \lambda Na^+ - \lambda Cl^-$$

$$= \lambda CH_3COO^- + \lambda H^+$$

It is thus possible to evaluate λ_∞ for acetic acid by determining λ_∞ for sodium acetate, hydrochloric acid and sodium chloride. Since all these substances are strong electrolytes, λ_∞ c

2.7.4 Procedure:

(1) Standardise the conductometer and determine the cell constant of 0.1 N KCl solution.

(2) Preparation of 0.1 N stock solutions of CH_3COONa, HCI and NaCl, respectively.

(3) Prepare 0.2, 0.4, 0.8, 0.02 and 0.01 N solutions of each electrolyte in conductivity water from the stock solution, respectively.

(4) Measurement of conductance of the prepared dilutions.

2.7.5 Observation:

Electrolyte	Concentr-ation g eq/dm^3	Conductance mhos [S]	Specific conductance K of solution mhos cm^{-1} [S cm^{-1}]	Equivalent Conductance mhos cm^2 eq^{-1} [S cm^2 eq^{-1}]	√C
HCl	0.2 0.4 0.8 0.02 0.01				
NaCl	0.2 0.4 0.8 0.02 0.01				
CH_3COONa	0.2 0.4 0.8 0.02 0.01				

2.7.6 Calculation of equivalent conductance:

(1) Cell constant (from Part 1): __________________ cm^{-1}

(2) The equivalent conductivity at infinite dilutions of:

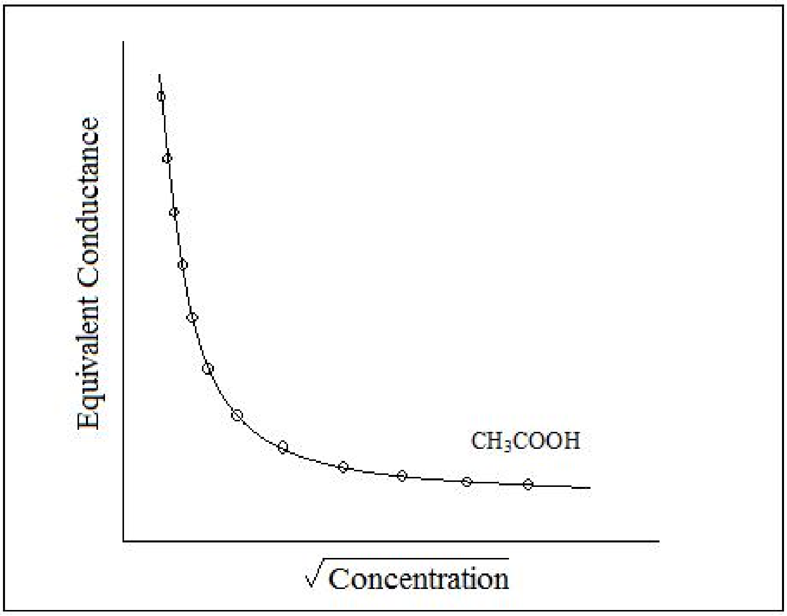
HCl = _____________ mhos cm^2 eq^{-1}

NaCl = _____________ mhos cm^2 eq^{-1}

CH_3COONa = _____________ mhos cm^2 eq^{-1}

Plot a graph between λ_c (Y-axis) values and √C (X-axis). The graph is not linear in case of weak electrolyte. Extrapolate the linear portion of the graph to zero concentration. The value of λ_∞ is obtained by extrapolating to √C = 0. The value of the intercept on the ordinate gives the value of λ_∞ for HCl. Similarly, find he values of λ_∞ for NaCl and CH_3COONa. Then calculate λ_∞ for acetic acid using the given equation below:

$$\lambda_\infty(CH_3COOH) = \lambda_\infty(CH_3COONa) + \lambda_\infty(HCl) - \lambda_\infty(NaCl)$$



2.7.7 Results:

The equivalent conductivity at infinite dilutions of CH_3COOH = _____________ mhos cm^2 eq^{-1}

2.7.8 Precautions:

- The conductivity cell, when not in use, should be kept in distilled water to prevent drying of the platinum electrodes.
- n case of fouling of the conductivity cell electrode plates, clean them by keeping in dilute $K_2Cr_2O_7$ containing H_2SO_4 solution (i.e. dilute chromic acid) for 24 hours and then washing with running water followed by with distilled water.
- All the solutions must be prepared in conductance water of specific conductivity less than 1x10-6 S cm^{-1}. If the conductivity exceeds 1 x 10-6 S cm^{-1}, it must be subtracted from that of the solution before calculating dc.

2.8 DETERMINATION OF THE DEGREE OF DISSOCIATION/ ASSOCIATION CONDUCTOMETRICALLY.

2.8.1 Object: Determination of the degree of dissociation/ association conductometrically.

2,8.2 Requirements: Conductometer and, conductivity water, 100 cm standard measuring flask, 100 cm beakers, 25 cm pipette, 10 cm graduated pipette, 0. 1N acetic acid, 0.1N KCI solution etc.

2.8.3 Theory: Degree of dissociation is defined as the fraction of total molecules which dissociate into simpler molecules or ions. Degree of association is defined as the fraction of the total number of molecules which associate or combine together resulting in the formation of a bigger molecules. The degree of dissociation of a weak electrolyte is determined by the application of expression:

$$\alpha = \frac{\lambda_c}{\lambda_\infty}$$

λ_∞=Equivalent conductance at infinite dilution and is obtained from Kohlrausch's law.

2.8.4 Procedure:

(1) Standardize the conductivity meter.

(2) Determine the cell constant of the given conductivity cell using 0.1 N KCl solution.

(3) Prepare 0.1, 0.05, 0.025 and 0.0125 N solutions of the above weak acid by appropriate dilutions.

(4) Measurement of conductance of the prepared acetic acid solutions.

2.8.5 Observations and Calculations:

(1) Equivalent conductance at infinite dilution (λ_∞) = 390.7 mhos $cm^2 eq^{-1}$ [S $cm^2 eq^{-1}$]

(2) Cell constant: __________________ cm^{-1}

Concentration	Conductance	Specific	Equivalent	Degree of

g eq/dm^3	mhos [S]	conductance K of solution mhos cm^{-1} [S cm^{-1}]	Conductance mhos cm^2 eq^{-1} [S cm^2 eq^{-1}]	dissociation
C	L x 10^{-3} mhos or [S]	K = cell constant x conductivity	$\lambda_c = \frac{1000 \times K}{C}$	$\alpha = \frac{\lambda_c}{\lambda_\infty}$
0.1 0.05 0.025 0.0125				

(3) Degree of dissociation________________

$$\alpha = \frac{\lambda_c}{\lambda_\infty}$$

2.8.6 Results:

Degree of dissociation________________

2.8.7 Precautions:

1. The conductivity cell, when not in use, should be kept in distilled water to prevent drying of the platinum electrodes.

2. In case of fouling of the conductivity cell electrode plates, clean them by keeping in dilute $K_2Cr_2O_7$ containing H_2SO_4 solution (i.e. dilute chromic acid) for 24 hours and then washing with running water followed by with distilled water.

3. All the solutions must be prepared in conductance water of specific conductivity less than 1x10-6 S cm^{-1}. If the conductivity exceeds 1 x 10-6 S cm^{-1}, it must be subtracted from that of the solution before calculating dc.

2.9 DETERMINATION OF PH BY ELECTRICAL CONDUCTIVITY METHOD

2.9.1 Object: Determination of pH by electrical conductivity method.

2.9.2 Requirements: Conductometer and, conductivity water, 100 cm standard measuring flask, 100 cm beakers, 25 cm pipette, 10 cm graduated pipette, 0. 1N acetic acid, 0.1N KCI solution etc.

2.9.3 Theory: pH is a measure of the acidity or alkalinity of a water solution. The acidity or alkalinity of a water solution is determined by the relative number of hydrogen ions (H+) or hydroxyl ions (OH) present. Acidic solutions have a higher relative number of hydrogen ions, while alkaline (also called basic) solutions have a higher relative number of hydroxyl ions. Acids are substances which either dissociate (split apart) to release hydrogen ions or react with water to form hydrogen ions. Bases are substances that dissociate to release hydroxyl ions or react with water to form hydroxyl ions. pH is the negative logarithm of the hydrogen ion concentration.

$$pH = - \log10 [H^+] \qquad ....(1)$$

In water solutions, the product of the molar concentrations of hydrogen and hydroxyl ions is equal to dissociation constant (K_a). Knowing the value of the constant and the concentration of hydrogen ions makes it possible to calculate the concentration of hydroxyl ions, and vice versa. The relationship between the dissociation constant K_a and pH.

$$CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COOH$$

$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$$

$$CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COOH$$

Initial	0.1	0	0
Change	-x	+x	+x
Equillibrium	0.1-x	x	x

$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$$

$$K_a = \frac{x.x}{0.1-x} = \frac{x^2}{0.1-x} = \frac{x^2}{0.1}$$

$$x^2 = K_a.0.1$$

$$x = \sqrt{K_a.0.1}$$

Put the value of x in the equation no. 1

$$\text{pH} = -\log 10\,[H^+]$$

$$\text{pH} = -\log 10\,[x]$$

2.9.4 Procedure:

(1) Standardize the conductivity meter.

(2) Determine the cell constant of the given conductivity cell using 0.1 N KCl solution.

(3) Prepare 0.1 N acetic acid solution by appropriate dilution.

(4) Measurement of conductance of the prepared acetic acid solution.

2.9.5.Observations and Calculations:

(1) Equivalent conductance at infinite dilution (λ_∞) = 390.7 mhos cm^2 eq^{-1} [S cm^2 eq^{-1}]

(2) Cell constant: __________________ cm^{-1}

Concentration g eq/dm^3	Conductance mhos [S]	Specific conductance K of solution mhos cm^{-1} [S cm^{-1}]	Equivalent Conductance mhos cm^2 eq^{-1} [S cm^2 eq^{-1}]	Degree of dissociation	Dissociation constant
C	L x 10^{-3} mhos or [S]	K = cell constant x conductivity	$\lambda_c = \frac{1000\,X\,K}{C}$	$\alpha = \frac{\lambda_c}{\lambda_\infty}$	$K_a = \frac{\alpha^2 C}{1-\alpha}$
0.1 N					

(3) pH of 0.1 N acetic acid__________________

$$x = \sqrt{K_a.0.1}$$

Put the value of x in the below equation

$$pH = -\log 10\,[H^+]$$

$$pH = -\log 10\,[x]$$

2.9.6. Results: pH of 0.1 N acetic acid_________________

2.9.7 Precautions:

1. The conductivity cell, when not in use, should be kept in distilled water to prevent drying of the platinum electrodes.

2. In case of fouling of the conductivity cell electrode plates, clean them by keeping in dilute $K_2Cr_2O_7$ containing H_2SO_4 solution (i.e. dilute chromic acid) for 24 hours and then washing with running water followed by with distilled water.

3. All the solutions must be prepared in conductance water of specific conductivity less than 1x10-6 S cm^{-1}. If the conductivity exceeds 1 x 10-6 S cm^{-1}, it must be subtracted from that of the solution before calculating dc.

2.10 DETERMINATION OF SOLUBILITY AND SOLUBILITY PRODUCT OF SPARINGLY SOLUBLE SALTS (E.G., $PbSO_4$, $BaSO_4$) CONDUCTOMETRICALLY.

2.10.1 Object: To determine the solubility and solubility product of $BaSO_4$, /$PbSO_4$, at room temperature conductometrically.

2.10.2 Requirements: Saturated solution of $BaSO_4$, Conductometer and, conductivity water, 100 cm standard measuring flask, 100 cm beakers, 25 cm pipette, 10 cm graduated pipette, 0.1N KCI solution etc.

2.10.3 Theory: The salts like $BaSO_4$, $PbSO_4$, etc. are called sparingly soluble salts because their solubilities are extremely low at room temperature. These salts are sparingly soluble in water and solubility of these salts cannot be determined by other weighing methods. Using Kohlrausch's law and by conductance measurement, solubility of this type of salt can be determined easily. A very little quantity of these salts dissolve in water and a saturated solution can be obtained. Though it is a saturated solution yet it contains very little quantity of salt. It is supposed to be completely ionized and considered as equal to infinite dilution.

2.10.4 Procedure:

(1) Standardize the conductivity meter.

(2) Determine the cell constant of the given conductivity cell using 0.1 N KCl solution.

(3) Measure of conductance of the conductivity water.

(4) Preparations of salt solution:

Make a saturated solution of Barium sulphate by dissolving 1 g of $BaSO_4$ in 100 ml of conductivity water in a 250 ml beaker. Shake the solution well for about 5 minutes and turbid solution formed. After that filter the barium sulphate solution with the help of Whatman filter paper. The filtrate is used as salt solution.

(5) Measure the conductance of the barium sulphate solution.

2.10.5 Observation:

(1) Cell constant = X = ___________________cm^{-1}

(2) Determination of solubility product:

- The conductance of conductivity water = L_w =_______________ S.
- The specific conductance of conductivity water = = k_w =_______ S cm^{-1} = L_w x X
- The equivalent conductance at infinite dilution for $BaSO_4$ = Λ° = 143.5 S cm^2 eq^{-1}

Saturated solutions	Conductance Ls (S)	Specific conductance of solution $k_a = L_s$ x X (S cm^{-1})	Specific conductance of salts $k_{salt} = k_a - k_w$	Solubility ‘S’ $S_e = \frac{1000 X k_{salt}}{\Lambda^\circ}$	Solubility product K_{sp}
$BaSO_4$					

2.10.6 Calculations:

(1) Solubility of $BaSO_4$, in g equivalent per dm^3.

$$S_e = \frac{1000 X k_{salt}}{\Lambda^\circ}$$

S_e=________________g equivalent/dm^3

(2) Solubility in g/dm^3

$S_g = S_e$ x equivalent weight of $BaSO_4$,

=S_e X 116.72

=__________g/dm^3

(3) The solubility product of $BaSO_4$,

The solubility product of $BaSO_4$ = K_{sp} =

The equilibrium of salt $BaSO_4$, is can be represented as.

$BaSO_4 = Ba^{2+} + SO_4^{2-}$

$$K = \frac{[Ba^{2+}]x[SO_4^{2-}]}{[BaSO_4]}$$

$K [BaSO_4] = [Ba^{2+}] x [SO_4^{2-}]$

$Ksp = [Ba^{2+}] x [SO_4^{2-}]$

As the solution contain equal number of both the ions and concentration of ions equal to the solubility of salt,

The solubility product of $BaSO_4$, = Ksp = S^2

2.10.7 Results:

(1) Solubility of $BaSO_4$, in $g/dm^3 = S_g =$__________g/dm^3

(2) Solubility product of $BaSO_4$ = Ksp =____________

2.10.8 Precautions:

1. The conductivity cell, when not in use, should be kept in distilled water to prevent drying of the platinum electrodes.

2. In case of fouling of the conductivity cell electrode plates, clean them by keeping in dilute $K_2Cr_2O_7$ containing H_2SO_4 solution (i.e. dilute chromic acid) for 24 hours and then washing with running water followed by with distilled water.

3. All the solutions must be prepared in conductance water of specific conductivity less than $1x10^{-6}$ S cm^{-1}. If the conductivity exceeds 1×10^{-6} S cm^{-1}, it must be subtracted from that of the solution before calculating dc.

2.11 HYDROLYSIS OF THE SALTS BY ELECTRICAL CONDUCTIVITY METHOD

2.11.1 Object: To determine the Hydrolysis of ammonium chloride by electrical conductivity method

2.11.2 Requirements: Conductometer, conductivity cell, thermostat. Chemicals: Conductivity water, 0.01 N KCI, N/32 ammonium chloride in water, N/32 ammonium chloride in ammonia etc.

2.11.3 Theory: Hydrolysis of a salt may be regarded as the interaction of the ions of the salt with the corresponding ions of water to produce either acidity or alkalinity. When salt of a weak acid or a weak base or both is dissolved in water, it gets hydrolysed to produce either acidity or alkalinity. The conductivity of the solution is due to the formation of ions of the unhydrolysed salt and ions of acid or base, when the salt is hydrolysed.

The degree of hydrolysis (h) is defined as, the fraction of the total salt hydrolysed on the attainment of equilibrium'.

Consider a salt of weak base and strong acid, say ammonium chloride. If h be the degree of hydrolysis, then for every mole of the salt, the number of moles of every species at equilibrium will be as shown below:

$$NH_4Cl + H_2O \rightleftharpoons NH_4OH + HCl$$

(Initially)	1	0	0
(At equilibrium)	1-h	h	h

Ammonium hydroxide, being a weak base, may be taken as completely un-ionised and contribute little or nothing towards the total conductivity of the solution. The equivalent conductivity (λ) of this solution as determined experimentally will be the sum of the conductivity of (1-h) gram equivalent of unhydrolysed ammonium chloride and h gram equivalent of hydrochloric acid.

Therefore,

$$h = (1 - h)\lambda_C + h\lambda_\infty \text{ (HCI)}$$

where, λ_c is the equivalent conductivity of the unhydrolysed salt and λ_∞ (HCI) is the equivalent conductivity of hydrochloric acid at infinite dilution. HCl is a strong electrolyte and is assumed to be completely ionised at all dilutions. From equation (1), we get,

$$h = \frac{\lambda - \lambda_C}{\lambda_\infty \text{ (HCI)} - \lambda_C} \qquad \text{………..(2)}$$

The value of n is obtained by adding excess of non-conducting ammonium to such a large extent that the equivalent conductivity of the mixture can be taken hydroxide to the salt solution. This supresses the hydrolysis of ammonium chloride to a such a large extent that the equivalent conductivity of the mixture can be taken as λ_c, the conductivity of the unhydrolysed salt. The value of hydrolysis constant K_h, is given by,

$$K_h = \frac{h^2}{(1 - h)V} \qquad \text{………..(3)}$$

2.11.4 Procedure:

Part I: Determination of cell constant.

1. Standardize the instrument as per the instructions given by the manufacturer.
2. Wash and clean the electrode with conductivity water and dip it in the conductivity cell containing 0.01 N KCl solution it. And see that the electrodes are completely covered by the solution.
3. Find out the conductivity of the solution and calculate the cell constant.

Part II: Determination of equivalent conductivity of Aniline Hydrochloride.

1. Prepare N/64 and N/128 ammonium chloride solutions using water as a solvent from stock solution of N/32 ammonium chloride in water. Similarly prepare N/64 and N/128 ammonium chloride solutions using N/32 ammonia as a solvent from stock solution of N/32 ammonium chloride in N/32 ammonia.
2. Measure the conductivities of N/32, N/64 and N/128 ammonium chloride solutions in water. Similarly measure the conductivities of N/32, N/64 and N/128 ammonium chloride solutions in N/32 ammonia.

3. Record the observations as given the observation table and find out equivalent conductivity, degree of hydrolysis and hydrolysis constant of these systems using above relations.

2.11.5 Observations:

SI.No.	Solution of ammonium chloride	Conductivity in mhos	Specific conductivity mhos/cm	Equivalent conductivity mhos cm^2	Degree of hydrolysis (h)	Hydrolysis constant (K_h)
1	N/32 solution in water					
2	N/32 solution in N/32 ammonia					

SI.No.	Solution of ammonium chloride	Conductivity in mhos	Specific conductivity mhos/cm	Equivalent conductivity mhos cm^2	Degree of hydrolysis (h)	Hydrolysis constant (K_h)
1	N/64 solution in water					
2	N/64 solution in N/32 ammonia					

SI.No.	Solution of ammonium chloride	Conductivity in mhos	Specific conductivity mhos/cm	Equivalent conductivity mhos cm^2	Degree of hydrolysis (h)	Hydrolysis constant (K_h)
1	N/128 solution in water					
2	N/128 solution in N/32 ammonia					

The values of for HCl are seen to be as follows :

For N/32, λ_∞ = 393 ohm^{-1}

For N/64, λ_∞ = 399 ohm^{-1}

For N/128, λ_∞ = 401 ohm^{-1}

2.11.6 Calculations:

The degree of hydrolysis of ammonium chloride can be calculated, from equation (2). Thus, the values of degree of hydrolysis can be calculated at each dilution, viz., N/32, N/64, N/128. The hydrolysis constant K, can now be calculated at each dilution according to equation (3). V is the volume in litres containing one gram mole of the salt, e.g., for N/32, N/64, N/128 solutions, the values of V will be 32, 64 and 128, respectively. It is seen that the values of K, come out to be practically constant.

2.11.7 Result:

(i) Degree of hydrolysis of ammonium chloride at different dilutions,

viz., N/32, N/64, N/128 is... percent.

(ii) Hydrolysis constant of ammonium chloride =…….

2.11.8 Precautions:

1. The conductivity cell, when not in use, should be kept in distilled water to prevent drying of the platinum electrodes.

2. In case of fouling of the conductivity cell electrode plates, clean them by keeping in dilute $K_2Cr_2O_7$ containing H_2SO_4 solution (i.e. dilute chromic acid) for 24 hours and then washing with running water followed by with distilled water.

3. All the solutions must be prepared in conductance water of specific conductivity less than 1x10-6 S cm^{-1}. If the conductivity exceeds 1 x 10^{-6} S cm^{-1}, it must be subtracted from that of the solution before calculating dc.

2.12 HYDROLYSIS OF THE SALTS BY EMF

2.12.1 Object: To determine the hydrolysis constant of aniline hydrochloride by e.m.f. method.

2.12.2 Requirements: Silver wire, saturated calomel electrode, potentiometer and its accessories, beaker, burette, stirrer etc.

2.12.3 Theory: Aniline hydrochloride is a salt of a weak base and a strong acid. It hydrolyses as follows:

$$C_6H_5NH_2.HCl \rightleftharpoons C_6H_5NH_2 + HCl$$

1	0	0	(Initially)
(1-h)c	ch	ch	(At equilibrium)

The hydrolysis constant K_h, is given by the expression,

$$K_h = \frac{[C_6H_5NH_2][HCl]}{[C_6H_5NH_2.HCl]}$$

$$K_h = \frac{(ch).(ch)}{(1-h)c} = \frac{c^2h^2}{(1-h)c} \quad ....(1)$$

where, h is the degree of hydrolysis and c is the total concentration of the salt in mole per litre. The concentration of the free acid ch, may be taken as equal to c_{H^+}, because hydrochloric acid is completely ionised. Therefore, from equation (1), we have,

$$K_h = \frac{c^2_{H+}}{c - ch} = \frac{c^2_{H+}}{c} \quad ......(2)$$

Thus, from equation (2) it is clear that by measuring the hydrogen ion concentration of the salt in the solution, we can easily calculate the hydrolysis constant. For this purpose, we construct the following cell:

$$Pt, H_2 \text{ (1 atm)}. H^+ \parallel KCl \text{ (satd)}; Hg_2C1_2 \text{ (8)} \mid Hg$$

The observed e.m.f. is given by,

$$E_{obs} = 0.0591 \text{ pH} + E_1$$

$$pH = \frac{E_{obs} - 0.2415}{0.0591} = -\log c_{H+}$$

2. 12.4 Procedure:

(i) Prepare solutions of aniline hydrochloride at different strengths, say M/10, M/50, M/100, M/200, M/250 etc.

(ii) Take 10 ml of M/10 aniline hydrochloride in a 400 ml beaker and add enough water so that the electrode is at such a level as to prevent air diffusing back into the region of the electrode. The hydrogen gas is passed at a steady rate. Now add N/10 NaOH solution from a burette. Stir the solution after each addition and note the e.m.f. from the potentiometer. Initially 1 ml portion of alkali is added from the burette, but as the end point is approached, readings should be taken on adding 0.1 ml portion of the alkali. After the end point has passed, larger amount of alkali (1 ml) can again be added.

(iii) Now measure the e.m.f and pH of each solution.

2.12.5 Observations: Note the e.m.f. of all solutions.

Concentrations	e.m.f
M/10	
M/50	
M/100	
M/200	
M/250	

2.12.6 Calculations: Calculate the values of the hydrolysis constant K_h, vide equation (2). Take the mean of all the values of K_h.

2.12.7 Result: The hydrolysis constant of aniline hydrochloride is___________________________.

2.12.8 Precautions:

(1) Aniline hydrochloride should be freshly prepared. It can be prepared by adding concentrated HCl to freshly distilled aniline. Cool and stir the solution in ice. Filter the salt and dry it.

2.13 SUMMARY

The electrochemistry unit comprises a systematic analysis of dissociation constant, solubility, solubility product, pH, hydrolysis by conductrometrically. The overall unit may be summarized as follows:

- In this present unit students would learnt about the fundamental and principle of conductivity method.
- The determination of conductivities of aqueous solution of strong and weak electrolytes at different concentrations provides information regarding the extent of ionization of electrolytes in water.
- Students understand the effect of dilution on conductivity by determination of equivalent conductivity of a strong and weak electrolyte conductrometrically.
- Determination of solubility and solubility product of sparingly soluble salts (e.g., $PbSO_4$, $BaSO_4$) conductometrically.
- Determination of hydrolysis constant by EMF and conductivity method.
- Students also learnt how to maintain the laboratory record file in a proper sequential manner.

2.14 REFERENCES

1. J.N. Gurtu, A. Gurtu, Advanced Physical Chemistry Experiments by 2017, Pragarti Prakashan, Meerut.

2. J.N. Gurtu, R. Kapoor, Advanced Experimental Chemistry by 1984, S.Chand & Company Ltd, New Delhi.

2.15 TERMINAL QUESTIONS

1. Difference between strong and weak electrolytes?
2. Relation between molar conductivity and specific conductivity?
3. Define Ostwald dilution law?
4. Explain the effect of dilution on conductivity?
5. The equivalent conductivity of a solution containing 2.54g of $CuSO_4$ per litre is 91.0 $\Omega^{-1}cm^2eq^{-1}$. Calculate its conductivity?
6. The solubility of barium sulphate at 298 K is 1.05×10^{-5} mol dm^{-3}. Calculate the solubility product.
7. Calculate the degree of hydrolysis and ph of 0.1 M sodium acetate solution. Hydrolysis constant of sodium acetate is 5.6×10^{-10}.

UNIT THIRD: QUANTITATIVE ANALYSIS

CONTENTS:

UNIT THIRD : QUANTITATIVE ANALYSIS

3.1 INTRODUCTION

Analysis of mixture

There are two branches in the analytical chemistry for the separation of components present in the mixture, these two branches of analytical chemistry are given below.

Qualitative analysis: Qualitative analysis is the determination of chemical composition of a sample. This gives the information about the components presents within a sample without providing the information of their quantity within the mixture.

Quantitative analysis: Quantitative analysis is the method used to give information about the quantity of individuals present within the sample.

Quantitative analysis can be of various types, some of these are given below.

i) Gravimetric analysis

ii) Volumetric analysis

3.2 OBJECTIVE

In this unit you able to the learn :

- How the estimation of the inorganic ions present in the solution by Gravimetric analysis.
- How the estimation of the inorganic ions present in the solution by Volumetric analysis.
- Demasking agent in complexometric titration.
- Experiment complexometric estimate of Cu^{2+} and Co^{2+} ions present in a solution with the help of EDTA as a complexing agent by adopting masking method.
- Experiment Complexometric estimation of Ca^{2+} and Pb^{2+} ion present in a solution with the help of EDTA as a complexing agent by adopting masking method.
- Standardization of EDTA solution by using standard ZnO solution.
- Estimation of both Ca^{2+} and Pb^{2+} ions.

3.3 GRAVIMETRIC ANALYSIS

This is the method used for the separation of the constituents to be estimated in the form of insoluble compounds of known composition. The insoluble compound obtained is washed to remove the impurities, dried, and weighed. Now with the help of known composition and weight obtained, the quantity of constituents in the given sample is calculated.

3.3.1 Precautions

Some of the precautions which must be taken during the gravimetric analysis are given below.

1. Precipitation should be completed during the estimation.
2. Washing of precipitate should be done properly.
3. Weighting of the chemicals during estimation should be done accurately.
4. Chemicals should be in powder form.

3.3.2 Apparatus used in the gravimetric estimation

Some of the apparatus used in gravimetric estimation are given below

Beaker: This is used to prepare the solution. Pyrex beaker must be used because normal beaker can be broken during the strong heating or sudden cooling the solution prepared in beaker. The beaker should be covered by watch glass to protect the beaker's solution from dust and any other foreign impurity particles.

Glass rod: It is used to stirring the liquids and for transferring the precipitate from the beaker into the filter paper. Rubber tubing is provided at the one end of the glass rod called a policeman. The policeman is used to detaching the particles of precipitate from the wall of beaker.

Wash bottle: The wash bottle is a squeeze bottle with nozzle used rinse laboratory glassware.

Filter paper: It is used for filtration of precipitate and it should be ashless. According to the pore of filter paper, it can be of several types.

Crucible: It is used for heating the precipitate. Mostly silica crucible is used for heating purpose due to their high thermal resistivity.

Sintered glass crucible: It is also used for filtration purpose of precipitate which need no ignition. Sintered glass crucible can also be of different grade like G-2, G-3, G-4 sintered glass crucible.

Desiccator: It is used for allowing hot crucible to cool it in a dry atmosphere. The dehydrating agent used in the bottom part of desiccator may be either $CaCl_2$ or silica gel.

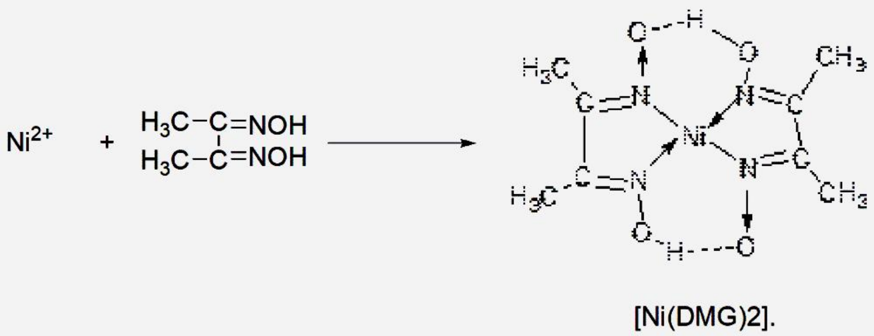
Volumetric flask: This is used to prepare the solutions.

3.4 ESTIMATE Ni AND Zn PRESENT IN A SOLUTION BY GRAVIMETRIC METHOD

3.4.1 Principle

For the estimation of Ni and Zn present in the solution at first Ni is estimated as nickel(II)dimethylglyoximate [Ni(DMG)$_2$] and then after that in filtrate, zinc is estimated as zinc(II) ammonium phosphate ($ZnNH_4PO_4$).

For this purpose at first by the addition of dimethylglyoxime solution (1%solution of HDMG in ethanol) in the mixed solution of Ni and Zn followed by immediate addition of ammonia solution to the hot fainty acidic solution, nickel is estimated as nickel(II) dimethylglyoximate[Ni(DMG)$_2$]. Nickel in this estimation is obtained as scarlet red coloured precipitate of nickel(II) dimethylglyoximate [Ni(DMG)$_2$], according to following equation.



[Ni(DMG)2].

After filtering precipitate of [Ni(DMG)$_2$], zinc is precipitated as zinc ammonium phosphate from filtrate by the addition of diammonium hydrogen phosphatesolution in filtrate according to following equation

$$ZnCl_2 + (NH_4)_2HPO_4 \longrightarrow ZnNH_4PO_4 + 2HCl + NH_3$$

3.4.2 Chemicals required

100 ml mixed solution of nickel ammonium sulphate and zinc oxide in 1:1 [50 ml nickel ammonium sulphate (11g/litre) and 50 ml zinc oxide (5g/litre)]

1% solution of HGMG in ethanol.

10% solution of diammonium hydrogen phosphate.

HCl and HNO_3.

Methyl red indicator.

3.4.3 Estimation of Nickel

In the given 100 ml solution of nickel ammonium sulphate and zinc oxide 4-5 ml of concentrated HCl is added and makes the volume up to 200 ml. Now heat the solution at 70^0

C and 1% solution of dimethyl glyoxime prepared in ethanol is added in excess followed by immediate addition of dilute ammonia solution dropwise with stirring until precipitate cannot be obtained. Add ammonia solution in excess till the smell of ammonia cannot obtain. Digest the precipitate in a water bath for about 30 minutes. Allow the precipitate to settle for 1 hour and test the supernatant liquid for complete precipitation. Finally filter the precipitate by using a previously weighed sintered glass crucible (generally a G-4 sintered glass crucible), washing the precipitate with hot water until the chloride ion impurity cannot be removed completely. Dry the sintered glass crucible in oven 100-120^{0}C, cool in a desiccator and weigh.

3.4.4 Calculation

Weight of sintered glass crucible = W_1 g

Weight of sintered glass crucible + precipitate = W_2 g

Weight of nickel dimethylglyoximate precipitate = (W_2-W_1)g

Since the molecular weight of nickel dimethylglyoximate = 289.9

The molecular weight of nickel ammonium sulphate ($NiSO_4.(NH_4)_2SO_4.6H_2O$) = 394.69

The atomic weight of Ni = 58.69

$$\text{Thus, weight of nickel} = \frac{58.69 \text{ X Weight of precipitate}}{289.9}$$

3.4.5 Gravimetric estimation of Zinc

Remove all nickel, transfer all filtrate obtained from above in 500ml beaker and evaporate the solution to 70-90 ml at 80 ^{o} C. Now add 60 ml aqua regia (Aqua regia is a mixture of nitric acid and hydrochloric acid, in ratio of 1:3 respectively) and evaporate until dryness, in fuming hood. Now add 100 ml of distilled water and 1-2ml concentrated hydrochloric acid.Add a few drops of methyl red and solution become red. Now add a dilute solution of ammonia dropwise, until the solution become yellow. Add 1 gram of ammonium acetate and 5 g of ammonium chloride heat the solution almost to boiling for 30 minute and add 50 ml of a freshly prepared 10% solution of diammonium hydrogen phosphate. Maintain the temperature below boiling point for furthers 30 minute, Now allow precipitate for crystallization by removing it from heating and stand for 1 hour.

3.2.6 Calculation

Weight of empty sintered glass crucible = W_1 g

Weight of sintered glass crucible + precipitate = W_2 g

Weight of zinc ammonium phosphate precipitate = $(W_2 – W_1)$ g

Since weight of zinc oxide (ZnO) = 81.38

Atomic weight of zinc = 65.38

Molecular weight of zinc ammonium phosphate = 178.38

$$\text{Accordingly, weight of Zn} = \frac{65.38 \text{ X Weight of Zinc ammonium phosphate}}{178.38}$$

$$\text{Weight of ZnO} = \frac{81.38 \text{ X } (W_2 - W_1)}{178.38}$$

3.5 VOLUMETRIC ANALYSIS

Volumetric analysis is also known as titration. It may be defined as the quantitative chemical analysis in which the amount of substance is determined by measuring its occupied volume. Volumetric analysis or titration is divided into following four category-

1 Complexometric titration

2 Acid base titration

3 Redox titration

4 Precipitation titration

3.5.1 Terms used in volumetric analysis

Some of the different terms used in volumetric analysis or titration are given below

Titrant: Titrant is the substance filled in burette during titration and slowly delivered into the analyte present in conical flask.

Titrate or Analyte: Analyte or titrate is a substance whose quantity or concentration is to be determined.

Indicator: Indicator is the substance that indicates the end point during the titration bycolour change.

End point: Point in titration where color change occur due to indicator is called as end point. This gives the indication of completion of titration.

Standardization: It is the process of determining the exact concentration of the solution.

Primary standard: Solution of the reagent of accurately known concentration is called as primary standard.

Secondary standard: That chemical substance which is standardized by titrating against the primary standard is known as secondary standard.

3.5.2 Masking agent in complexometric titration

Such type of process which used to convert any one component into inert form during the estimation of other component present in the sample without using any physical separation is known as masking and those substances used for this type of processes are called as masking agent. In other word such type of process which is used to mask the impurity present in the analyte solution is called as masking and chemical substance used for this purpose is known as masking agent.

Example: If we have to analyse Ca^{2+} ion present in solution containing Ca^{2+} and Mg^{2+} ions then for this purpose at first we have to mask the Mg^{2+} ion. If Mg^{2+} will not be masked in that case result will be altered or deviate from the actual value because under such condition both Ca^{2+} and Mg^{2+} will react with standard solution.

3.5.3 Methods used to mask the impurity present in the analyte

1. **By the precipitation method**:

In this method, five different types of precipitating agents are used to mask the impurity of metal ions which are given below-

S.N	Precipitating agent	Metals which can be masked
1	Sulphides	Pb, Cu
2	Sulphates	Pb, Ba
3	Oxalates	Ca, Pb
4	Fluorides	Ca, Mg, Pb
5	Thioglycerols	Cu

2. By the complexation method

Complexation method is a better method than the precipitation method to mask the impurity of metal ions due to the following two advantages

(a) In complexation method stable complexes of metal ion are formed.

(b) During precipitation method there can occur the chance of co-precipitation or post-precipitation of analyte with impurity.

S.N	Complexation agent	Metals which can be masked
1	Ascorbic acid	Fe

2	Potassium iodide	Hg
3	Potassium cyanide	Ag, Cu, Mg
4	Ammonium fluoride	Al, Fe
5	Triethanol amine	Al

3.6 DEMASKING AGENT IN COMPLEXOMETRIC TITRATION

Demasking agents are the reagents which regain the ability of masked ion to enter the reaction with indicator or EDTA.

Example: Suppose we have to determine the individual concentration of Ca^{2+}, Cd^{2+} and Cu^{2+} ions present in the solution. This can be done byfollowing steps of masking demasking process.

Step I: Ca^{2+}, Cd^{2+} and Cu^{2+}, ion solution is titrated with EDTA by which EDTA complexes of Ca^{2+}, Cd^{2+} and Cu^{2+} ions are obtained.

Step II: By using the masking agent KCN in the sample of Ca^{2+}, Cd^{2+} and Cu^{2+} ions there occur the masking of Cd^{2+} and Cu^{2+} ions while Ca^{2+} ion is not masked. Now on titration with EDTA only Ca^{2+} undergo complexation with EDTA.

Step III: By using demasking agent chloral hydride / formaldehyde in the solution containing masked Cd^{2+} and Cu^{2+} ions, there occur the demasking of Cd^{2+} ion while Cu^{2+} ion remain masked. Now on titration with EDTA both $Ca^{2+}$and Cd^{2+} ions undergo complexation while Cu^{2+} ion remain as such in solution.

Suppose combined concentration of Ca^{2+}, Cd^{2+} and Cu^{2+} ions from the titration of step I = X

Concentration of Ca^{2+} alone from the titration of step II = Y

And concentration of $Ca^{2+}$and Cd^{2+} ions from titration of step III = Z

Thus the final concentration of Ca^{2+} ion = Y

Concentration of Cd^{2+} ion = Z-Y

Concentration of Cu^{2+} ion = X-Z

3.7 COMPLEXOMETRIC ESTIMATE OF Cu^{2+} AND Co^{2+} IONS PRESENT IN A SOLUTION WITH THE HELP OF EDTA AS A COMPLEXING AGENT BY ADOPTING MASKING METHOD

3.7.1 Principle : According to the principle of complexometric estimation at first Co^{2+} and Cu^{2+} ions are estimated with murexide indicator. Then the Cu^{2+} ion is selectively masked by masking agent thiourea in acidic medium, as a result of which Cu^{2+} ion are reduced into Cu^{+} ion. Now on adding EDTA solution only Co^{2+} undergo complexation while Cu^{2+} ion cannot undergo complexation, by which amount of Co^{2+} ion in solution is determined. On subtracting the Co^{2+} ion value from total value we can determine the amount of Cu^{2+} ion in solution.

3.7.2 Chemicals required: EDTA solution, Cu^{2+} and Co^{2+} ions mixed solution, Murexide, indicator, Thiourea, Lead nitrate solution

3.7.3 Procedure :

3.7.3.1 Step I Standardization of EDTA solution by standard lead nitrate solution:

At first 0.33 g of lead nitrate crystals place in 250 ml measuring flask and makes the volume 250 ml by the addition of distilled water. About 20 ml of this solution is pipetted out in a conical flask and diluted with 25 ml of distilled water. Now 50 ml of xylenol orange and KNO_3 mixture is added. In this solution hexamine is added until the color cannot become intense red. Finally, this intense red-coloured solution of the conical flask is titrated by using EDTA solution in burette. The end point is noted when colour is changed from intense red to yellow colour. The titration is repeated until concordant titre value cannot obtained.

Observation table:

S. No	Volume of lead nitrate (ml)	Burette reading (ml)		Volume of EDTA (ml)
		Initial	Final	
1	20	0		
2	20	0		
3	20	0		
4	20	0		

Calculation: Since weight of lead nitrate = 0.33 g

And the molecular weight of lead nitrate = 331.21

$$\text{So strength of lead nitrate solution} = \frac{1000 \text{ X } .33}{100 \text{ X} 331.21} = .01\text{N}$$

i.e. Normality of lead nitrate solution (N_1) = .01N

Volume of lead nitrate solution (V_1) = 20 ml

Volume of EDTA solution (V_2) = ……..

Normality of EDTA solution (N_2) = ………

Thus, according to normality equation $N_1V_1 = N_2V_2$

$$\text{Strength of EDTA solution } N_2 = \frac{N_1V_1}{V_2} = \frac{20\text{X}.01}{V_2}$$

3.7.3.2 Step II, Estimation of both Cu^{2+} and Co^{2+}

At first the given solution of Cu^{2+} and $Co^{2+}$is placed in 250 ml measuring flask and make up the volume 250 ml by diluting with the help of distilled water. 20 ml of this solution is pipetted out in the conical flask and diluted by same volume of distilled water. About 50 ml of muroxide and KNO_3 indicator mixture is added in the conical flask and titration is carried out against standard EDTA solution taken in till the colour of solution cannot become pink. To this content of conical flask about 4 ml of buffer solution (pH = 10) is added by which colour is changed to yellow. Now the titration is continued till the end point is reached. After the addition of few ml of EDTA solution colour changed from yellow to pink. If further addition of buffer solution colour change occur from pink to yellow, this indicate that the reaction is not completed and require more EDTA. Thus, the end point is the colour change from yellow to pink.

Observation:

S.No	**Volume of Cu^{2+} and Co^{2+} ions(ml)**	**Burette reading (ml)**		**Volume of EDTA (ml)**
		Initial	**Final**	
1.	20	0		
2.	20	0		
3.	20	0		
4.	20	0		

The titre value obtained from this titration gives the volume of EDTA corresponding to the amount of Cu^{2+} and Co^{2+} present in the given solution.

3.7.3.3 Step III, Estimation of Co^{2+} ion only (Masking method)

Another 50 ml of made up solution is pipetted into a clean conical flask and dilute it by about 25 ml distilled water. 5 ml of concentrated HCl is added to make the solution acidic in nature, as a result of which Cu^{2+} ions are reduced into Cu^{+} ions by boiling the solution with thiourea. The solution is cooled. Now 20 ml of EDTA solution is placed in this flask by which Co^{2+} ion alone undergo complexation with EDTA while Cu^{+} remain as such in solution. The uncomplexed EDTA is determined by adding 20 ml of lead nitrate solution. Now 50 ml of xylenol orange and KNO_3 indicator mixture and sufficient amount of hexamine is added until the solution become pink. The uncomplexed Pb^{2+} ions are titrated against standardized EDTA solution. The colour change from pink to yellow indicate the end point of this titration. From the titre value, the volume of EDTA required to complex the Co^{2+} ion can be calculated.

Observation Table

S.No	Volume of Co^{2+}ions (ml)	Burette reading (ml)		Volume of EDTA (ml)
		Initial	Final	
1.	20	0		
2.	20	0		
3.	20	0		
4.	20	0		

3.7.4 Calculation

Volume of EDTA usedin step III experiment = 20 ml added in titration + burette reading for titration of remaining Pb^{2+} ions (back titration) …………….**1**

In step third added 20 ml lead nitrate consume EDTA = In step I, 20 ml lead nitrate took EDTA = Step I burette reading………**2**

So the volume of EDTA used for Co^{2+} ions only**V_4**= Equation 1- equation 2…………..**3**

3.5.4.1 Estimation of Cobalt(II) ion

Volume of EDTA for Co^{2+} ionsV_3 =…………………………From equation **3**

Normality of EDTA N_2 =………………………………………From step **1**

Volume of Co^{2+} ions= 20 ml

$$\text{So, normality of } Co^{+2}(N_3) = \frac{V_4 \text{ X } N_2}{V_3}$$

The amount of Co^{+2} ions present in the given solution of known N_3= NEV/1000

$$= \frac{\text{Strength of the } Co^{2+} \text{ ion X Equivalent weight of } Co^{2+} \text{ ion X 250}}{1000}$$

3.7.4.2 Estimation of Copper (II)ion

From II steps

Volume of EDTAused for Cu^{2+} (V_5) = Burette reading rom step II - Volume of EDTA for Co^{2+} ions (V_3)

Normality of EDTA N_2 =……………………………………… From step I

Volume of Cu^{2+} taken in step III= 20 ml

$$\text{So, normality of} Cu^{2+}(N_6) = \frac{V_5 \text{ X } N_2}{20}$$

The amount of Cu^{+2} ions present in the given solution = NEV/1000

$$= \frac{\text{Strength of the } Cu^{2+} \text{ ion X Equivalent weight of } Cu^{2+} \text{ ion X 250}}{1000}$$

3.7.5 Results

The amount of Co^{+2} ions present in the given solution=…….gram

The amount of Cu^{+2} ions present in the given solution=…….gram

3.8 COMPLEXOMETRIC ESTIMATION OF Ca^{2+} AND Pb^{2+} ION PRESENT IN A SOLUTION WITH THE HELP OF EDTA AS A COMPLEXING AGENT BY ADOPTING MASKING METHOD

3.8.1 Principle : According to the principle of complexometric estimation at first Ca^{2+} and Pb^{2+} ions are estimated with eriochrome black-T indicator. Thenthe Pb^{2+} ion is selectively masked by the masking agent diethyl dithiocarbonate. Now on adding EDTA solution only Ca^{2+} undergo complexation while Pb^{2+} ion cannot undergo complexation with EDTA, by which the amount of Ca^{2+} ion in solution is determined. On subtracting the Ca^{2+} ion value from the total value we can determine the amount of Pb^{2+} ion in the solution.

3.8.2 Chemicals required: EDTA solution, Ca^{2+} and Pb^{2+} ions mixed solution, Eriochrome black-T indicator, Sodium diethyl dithiocarbonate

3.8.3 Procedure

3.8.3.1 Step I, Standardisation of EDTA solution by using standard ZnO solution

At first 0.1g of ZnO is weighed and dissolved in 2N HNO_3 solution, made up 100 ml in simple measuring flask. 20 ml of this solution is pipetted out in a conical flask and this solution is diluted 25 ml of distilled water. Now 2 ml of pH = 10 buffer solution and few drop of eriochrome black-T indicator are added. The end point is noted when colour change occur from wine red to blue colour. Titration is repeated for concordant value.

Observation table

S.No	Volume of ZnO(ml)	Burette reading (ml)		Volume of EDTA (ml)
		Initial	Final	
1.	20	0		
2.	20			
3.	20			
4.	20			

Calculation

Since weight of ZnO = 0.1 g

And molecular weight of ZnO= 81.4

So strength of ZnO solution = $\frac{1000 \text{ X } 0.1}{100 \text{ X } 81.4} = .012 \text{ N}$

i.e. Normality of ZnO solution (N_1) = .012N

Volume of ZnO solution (V_1) = 20 ml

Volume of EDTA solution (V_2) = ……..

Normality of EDTA solution (N_2) = ………

Thus according to normality equation $N_1V_1 = N_2V_2$

$$\text{Strength of EDTA solution } N_2 = \frac{N_1V_1}{V_2} = \frac{20\text{X}.012}{V_2}$$

3.8.3.2 Step II, Estimation of both Ca^{2+} and Pb^{2+} ions

For the estimation of both Ca^{2+} and Pb^{2+} ions present in solution at first given solution is made up in the 250 ml measuring flask. 20 ml of this solution is pipetted out in a conical flask and diluted to 50 ml by distilled water then 5 ml of eriochrome black-T indicator is added. Now this solution is titrated against the standardized EDTA solution taken in the burette. When colour change occur from wine red to blue that indicate the end point of titration which is noted. This gives the total value of both Ca^{2+} and Pb^{2+} ions in the solution.

Observation table

S.No	**Volume of Pb^{2+} and Ca^{2+} ions (ml)**	**Burette reading (ml)**		**Volume of EDTA (ml)**
		Initial	**Final**	
1	20	0		
2	20			
3	20			
4	20			

3.8.3.3 Step III, Estimation of Ca^{2+} ions only (Masking method)

20 ml of given made up solution is pipetted out into another conical flask and 50 mg of sodium diethyl dithiocarbonate is added in this solution to mask Pb^{2+}ions. Now 20 ml of standard EDTA solution and 20 ml of standard Zn^{2+} ion solution are added for back titration then 4 ml of pH = 10 buffer solution and few drop of eriochrome black-T indicator are added.

The excess of Zn^{2+} ion are titrated against the standardized EDTA solution until end point cannot be obtained. Colourchange from wine red to blue indicates the end point of titration. This is the titre value only for Ca^{2+}ions. The titration is repeated for concordant value.

Observation Table:

S.No	Volume of Ca^{2+} ions (ml)	Burette reading (ml)		The volume of EDTA (ml)
		Initial	Final	
1	20	0		
2	20			
3	20			
4	20			

3.8.4 Calculation

Volume of EDTA used in step III experiment = 20 ml added in titration + burette reading for titration of remaining Zn^{2+} ions (back titration) ……………**1**

In step third added 20 ml zinc ion consume EDTA = In step I, 20 ml ZnO took EDTA = Step I burette reading………**2**

So the volume of EDTA used for Ca^{2+} ions only $\mathbf{V_4}$= Equation 1- equation 2 ……... **3**

3.8.4.1 Estimation of Calcium (II) ion

Volume of EDTA for Ca^{2+} ions only (V_3) =…. From equation **3**

Normality of EDTA N_2 =…… From step **1**

Volume of Ca^{2+} ions= 20 ml

$$\text{So, normality of } Ca^{+2} (N_3) = \frac{V_4 \text{ X } N_2}{V_3}$$

The amount of Ca^{+2} ions present in the given solution of known N_3= NEV/1000

$$= \frac{\text{Strength of the } Ca^{2+} \text{ ion X Equivalent weight of } Ca^{2+} \text{ ion X } 250}{1000}$$

3.8.4.2 Estimation of Pb^{2+} ion

From II steps

The volume of EDTA used for Pb^{2+} (V_5) = Burette reading in step II - Volume of EDTA for Ca^{2+} ions (V_3)

Normality of EDTA (N_2)=………………………………………. From step I

Volume of Pb^{2++} taken in step III= 20 ml

$$\text{So, normality of } Pb^{2+}(N_6) = \frac{V_5 \text{ X } N_2}{20}$$

The amount of Pb^{2+}ions present in the given solution = NEV/1000

$$= \frac{\text{Strength of the } Pb^{2+} \text{ ion X Equivalent weight of } Cu^{2+} \text{ ion X 250}}{1000}$$

3.8.5 Results

The amount of Ca^{+2} ions present in the given solution=…….gram

The amount of Pb^{2+}ions present in the given solution=…….gram

3.9 SUMMARY

Summary of the present unit is the:-

- In this unit you know the how to the estimate the various ion by Gravimetric analysis and Volumetric analysis.
- Estimate Ni and Zn present in a solution by gravimetric method.
- Demasking agent in complexometric titration.
- Experiment complexometric estimate of Cu^{2+} and Co^{2+} ions present in a solution with the help of EDTA as a complexing agent by adopting masking method.
- Experiment Complexometric estimation of Ca^{2+} and Pb^{2+} ion present in a solution with the help of EDTA as a complexing agent by adopting masking method.

3.10 REFERENCES

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3.11 TERMINAL QUESTIONS

1. Why EDTA is used in complexometric titration?
2. Define the role of masking and demasking agents during the complexometric titration?
3. What is the difference between qualitative analysis and quantitative analysis?
4. What are the different types of complexometric analysis?
5. Which apparatus is used for the gravimetric analysis?
6. What are the factors affecting gravimetric analysis?
7. What are the different types of gravimetric analysis?
8. Define the following terms related to quantitative analysis?
    (a) Standardization process
    (b) External and internal indicator
    (c) Analyte
    (d) Precipitation

UNIT-FOURTH: CHROMATOGRAPHY SEPARATION OF CATIONS AND ANIONS BY PAPER

CONTENTS:

4.1 Introduction
4.2 Objective
4.3 Types of chromatography
4.4 Introduction to Paper chromatography
    4.4.1 Principle of chromatography
    4.4.2 Mechanism of separation
    4.4.3 Descending and ascending techniques
    4.4.4 Radial paper chromatography
4.5 Paper chromatography separation of Ag(I), Hg(II), and Pb(II) ions
4.6 Paper chromatography separation of Bi (III), Cu (II), Cd (II) Pb (II) ions
4.7 Paper chromatography separation and identification of Unknow mixture of As(III), Sb(III) and Sn(II)ions
4.8 Paper chromatography separation and identification of Unknow mixture of Fe(III), Al(III) and Cr(III)ions.
4.9 Paper chromatography separation and identification of Unknow mixture of halide ions.
4.10 Summary.
4.11 References.
4.12 Terminal Questions.

UNIT FOURTH: CHROMATORAPHY SEPARATION OF CATION AND ANIONS BY PAPER

4.1 INTRODUCTION

In most cases before the analysis and characterization of any analyte, its purification is essential. Several methods and techniques are used to purify the analytes from the mixtures such as distillation, crystallization, extraction, etc. But if the mixture is in fewer quantities and resembles to each other then the separation is very difficult by the above method. For example, the separation of amino acids, and sugars. There is a need for new techniques to separate the mixture. In 1906 Michael Tswett, a Russian botanist, first separate the chlorophyll and other pigments from warsaw. These techniques have been known as Chromatography.

The term chromatography is derived from the Greek words Chroma (color) and graphy (to write) because the compounds that are separated are colored. In his experiment, hetook a glass tube packed with chalk. He placed apetroleum ether solution containing plant pigments on top of this glass tube. When he eluded the sample through the column with additional petroleum ether, he observed that the pigments were separated into various colorzone. After this, they remove the packing and were able to extract the individual components. Tswett explains the component which has more affinity with the stationary phase comes last and the component which has less affinity comes first. However, the chromatographic methods are most recommended and widely used in the separation of analytes. Actually, chromatography based on the differential distribution of the sample components between two phases. One phase which remains fixed called the stationary phase and those flow through intesties over the surface of the stationary phase is called mobile phase.

OBJECTIVE 4.2

In this chapter you learn about the :

- Types of chromatography

- What is the Paper chromatography, Principle of chromatography, Mechanism of separation of the paper chromatography.
- Descending and ascending techniques, Radial paper chromatography.
- Paper chromatography separation of Ag(I), Hg(II), and Pb(II) ions.
- Paper chromatography separation of Bi (III), Cu (II), Cd (II) Pb (II) ions.
- Paper chromatography separation and identification of Unknow mixture of As(III), Sb(III) and Sn(II)ions.
- Paper chromatography separation and identification of Unknow mixture of Fe(III), Al(III) and Cr(III)ions.
- Paper chromatography separation and identification of Unknow mixture of halide ions.

4.3 TYPES OF CHROMATOGRAPHY

Based on the nature of the stationary phase and mobile phase chromatography can be divided into following types :

- Gas-liquid chromatography
- Gas solid chromatography
- Liquid-liquid chromatography
- Liquid solid chromatography

Based on the mechanism establishing the phase distribution chromatography can further be divided into following types

1. Adsorption chromatography
2. Partition chromatography

Table 1-

Mobile Phase	Stationary Phase	Mechanism	Examples
Liquid	Solid	Adsorption	Thin layer chromatography (TLC), Ion exchange chromatography
Gas			Gas solid chromatography
Liquid	Liquid	Partition chromatography	Paper chromatography
Gas			Gas Liquid chromatography

4.4 INTRODUCTION TO PAPER CHROMATOGRAPHY

This is the type of liquid- liquid or partition chromatography that was introduced by Martin and Synge in 1941. In 1944 Consden, Gordon and Martin introduced paper chromatography using a sheet of paper stationary phase and liquid in the mobile phase. The stationary phase is water because the polymeric cellulose structure contains several glucose units liked by the 1-4 glycosidic bond. One glucose unit has three hydroxyl groups, so it holds the water molecules and other polar solvents through the hydrogen bonds.

The different types of papers such as Whatmam. No 1,3,31, acetyl acid paper, kieselguhr paper, silicon treated paper and ion exchanges paper may be used for paper chromatography.

4.4.1 Principle of chromatography

Paper chromatography is based on the partition principle, which is given by A.J.P. Martin and R.L.M. Synge. The distribution of sample molecules (analyte) between the mobile and stationary phase (two immiscible phases) is governed by an equilibrium constant known as the distribution coefficient. Equilibrium is a dynamic process and a given molecule passed rapidly back and forth between the two phases so in equilibrium the concentration will not change in each phase.

$$K = \frac{Cs}{Cm}$$

Cs = Concentration of sample molecules in Stationary phase

Cm = Concentration of sample molecules in Mobile phase

K = Partition co-efficient

If K is high so the affinity of sample molecules are high to stationary phase means analyte concentration is higher in stationary phase than mobile phase.

4.4.2 Mechanism of separation

If the mixture contains two components than the component which have high K value will come last because it has more solubility or more affinity with stationary phase so its rate is low while the second component whose K value is low have more affinity or solubility with Mobile phase, have high rate so come first.

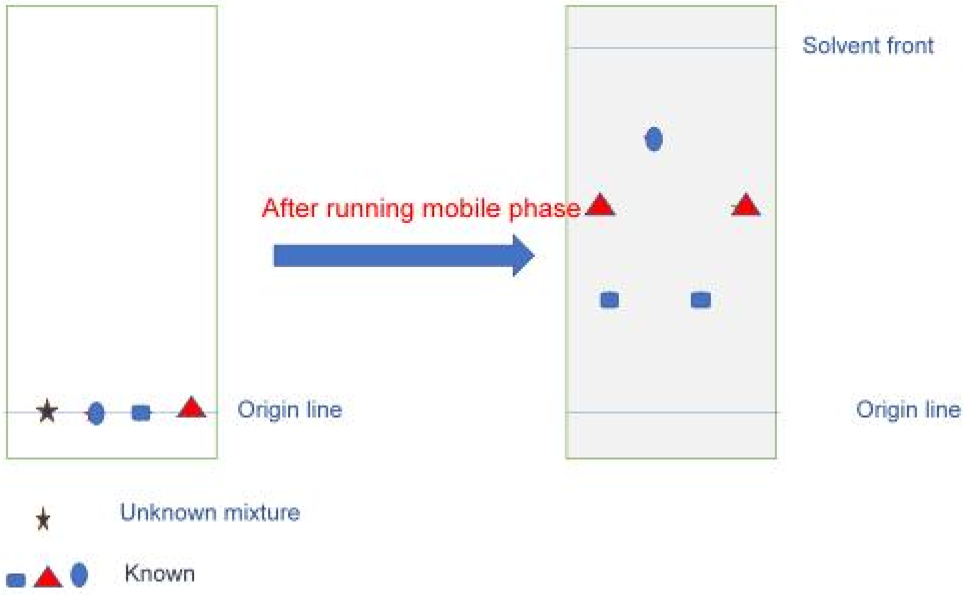

Fig. 4.1 Mechanism of separation

The rate at which components has moved is then determined by its retardation factor or retention factor.

$$R_f = \frac{\text{Distance travelled by the cation from the origin line}}{\text{Distance travelled by the solvent from the origin line}}$$

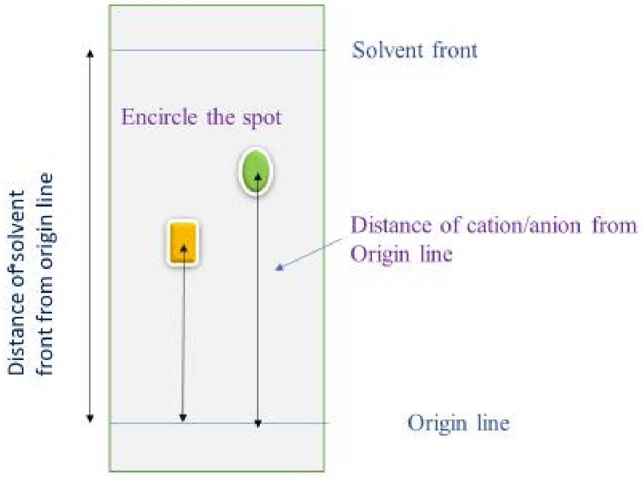

Fig. 4.2

R_f value of a substance depends upon the following factors :

1. Solvent combination.
2. Type and quality of the chromatographic paper.
3. Nature of mixture.

4. Temperature
5. Size of the container in which the operation is carried out.

4.4.3 Descending and ascending techniques

When the mobile phase travel up the paper it is known as ascending technique. In this chromatographic paper strip is hung from top of the chromatographic jar and its edge dips in the solvent which is kept in a tray. When the mobile phase travel down the paper is known as descending technique. Both techniques are used to separate inorganic cations. But if the Rf of various constituents are almost same than descending technique used preferentially.

4.4.4 Radial paper chromatography

Radial paper chromatography is also known as circular paper chromatography. In this technique chromatography circular filter paper is employed. Various anlyte are placed at it centre. After drying the spot, the paper is fixed horizontally on the Petri dish and passes the mobile phase rises through the wick or tonque. Cover the paper by means of a Petridis cover. When solvent front has moved through a sufficient distance, the components get separated in the form of concerted circular zones.

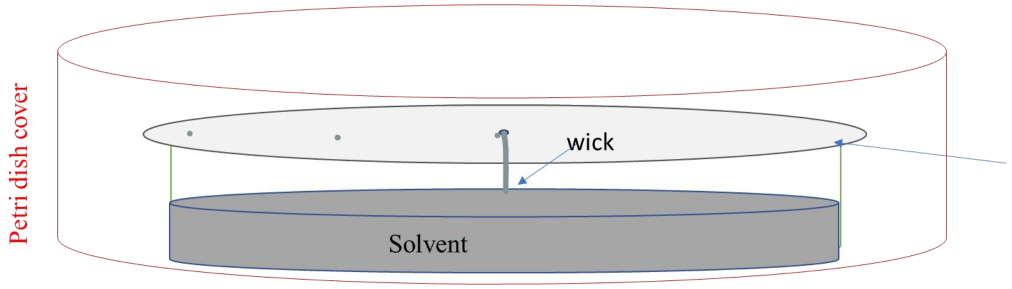

Fig. 4.3 Radial paper chromatography

4.5 PAPER CHROMATOGRAPHY SEPARATION OF Ag(I), Hg(II) AND Pb(II) IONS

4.5.1 Requirements

Apparatus	**Chemicals**
Chromatography paper	$AgNO_3$
Petridish	$HgNO_3$
Wick	$PbNO_3$
Test tube	Deionized water
Spotting capillary	

Measuring cylinder

4.5.2 Solution provided

4.5.2.1 Sample solution

1% aqueous solution of silver nitrate.

1% aqueous solution of Mercurous nitrate.

1% aqueous solution of Lead nitrate.

The solution is slightly acidified with dilute nitric acid.

Unknown sample solution. It can be any oneor two salt from given salt for experiment

4.5.2.2 Developing solvent

Any one of the two of the following detectors may be prepared

1. Prepare it by adding tertiary butanol, acetone, water, and Nitric acidin the ratio of 4:3:1.2:8.
2. Distilled or deionized water.

4.5.2.3 Visualizing agents

Following visualizing agents may be prepared

1. 0.25molar solution of $K_2CrO_4$and add 3-4 drops of ammonia.
2. 0.5% dithizone in chloroform solution.

4.5.3 Procedure

For this experiment, use the same apparatus arrangement as discussed in the radial chromatography section. Make off equally spaced points along this circular separated from each other then the sample will be applied in these points. Cut the chromatographic paper approximately 11 cm in diameter. From 1cm apart from the centre make a circle. Make off equally spaced marks (x) along this circle, then three known samples Ag^+,Pb^{2+}, Hg^{2+} and an unknown sample or mixture of metals will be applied in the seamarks using capillaries or toothpick. Always use different capillaries of each sample solution. After spotting the spots should be dry and repeat spotting again. Remember the position of the known and unknown sample by giving the name.

Make a hole in the centre of circular Whatman paper, from where the wick is attached with the mobile phase. As discussed in this chromatography, the paper keeps in the horizontal position over the petri dish containing the developer and the wick insert in any of two develop.And covers it with a big petri dish. When the solvent reaches a reasonable distance, keep out the Whatman paper and make a line for the solvent front then dry it by the blower. Now sports can be visualized by either of the following reagents

1. Dipped into 0.25 molar K_2CrO_4, gives yellow color with lead ion, Orange Red color with silver ion, and black color with Mercury ion.
2. Spay with dithizone gives orange spot by silver ion, pink spot by Mercurous ion, and rose pink spot by Lead ion.

4.5.4 Observations and Calculation

Encircle the colored zones and mark the center of each zone. Calculate the Rf values of individual cations with that of their Rf values in the mixture to identify the cations in the mixture and unknown sample solution.

Observation Table 2:

S.N	Cation	Distance travel by cation from origin line	Distance travel by solvent from origin line	R_f
1	Ag^+			
2	Hg_2^{2+}			
3	Pb^{2+}			
4	Unknown mixture			

4.5.5 Results

The given unknown mixtures have ………..metals ion.

4.6 PAPER CHROMATOGRAPHY SEPARATION OF Bi (III), Cu(II), Cd(II) Pb(II) IONS

4.6.1 Requirement

Apparatus	**Chemicals**
Chromatography paper	n-Butanol
Chromatography tank	3M HCl
Test tube	Bismuth chloride
Spotting capillaries	Lead chloride
Measuring cylinder	Cuprous chloride
Whatman No. 1. Filterpaper sheet	Cadmium chloride

4.6.2 Solution provided

4.6.2.1 Sample Solution

1% solution of $BiCl_3$

1% solution of $PbCl_2$

1% solution of $CuCl_2$

1% solution of $CdCl_2$

Dissolve 1 gram of salt in 100 ml of H_2O and add a few drops of dilute acid to suppress hydrolysis.

4.6.2.2 Unknown solution

It can prepare by addinga few drops of any two known sample solutions in a test tube.

4.6.2.3 Developing Solvent

Any one of the following developing solvents.

1. 1-butanol saturated with 3M HCl Take equal volumes of n butanol and 3 M hydrochloric acids in a separatory funnel, shake well and allow to stand to separate the layers. Remove the lower -aqueous layer and use the organic layer as the developer.
2. Ethanol + water + 1 M HCI (18: l:l).

4.6.2.4 Visualizing agents: Following visualizing agents may be prepared.

1. Colorless ammonium sulfide solution is prepared by passing H_2S gas water and adding a few drops of ammonia to it. Keep it in a covered container.
2. 0.5 % solution of dithizone in chloroformor carbon tetrachloride.

4.6.3 Procedure

Cut Whatman No. 1 filter strips of about 25 x 7 cm make a line horizontally 1 cm apart from one edge of the paper across the width of the paper strip using a pencil, and put the various“x” marks at least 1 cm away from each other and apply each solution of bismuth. Cadmium, copper, lead, and unknown solutions at these “x” marks by capillary tubes. Use a fresh capillary for each solution after drying the spots, the paper strip is allowed carefully into the jar having the developing solvent for ascending techniques. The spot should always be above the developer level. The jar is then covered properly. The developer will rise along the paper and wait till the developer reaches near the upper end of the paper then remove the paper strip and mark the solvent front with the help of a pencil. Leave the paper for some time to get it dried. After drying the sports, spay with visualizing agent colourless ammonium sulfide produces black sports except yellow with cadmium or it spays by 0.5 % solution of dithizone in chloroform produced different colors viz, bismuth (Purple) Cadmium (Purple), copper(Purple brown), lead (Rose pink).

Encircle the colored zones and mark the center of each zone. Calculate the Rf values of individual cations and compare those Rf values to the unknown mixture.

4.6.4 Observations and Calculation

Measure the distance travelled by the centre of the colored zone from the marked line and the distance traveled by the solvent front on the paper chromatogram. Calculate the R_f value of salt.

Observation Table 3:

S.N	Cation	Distance travel by cation from origin line	Distance travel by solvent from origin line	R_f
1	Pb^{2+}			
2	Cu^{2+}			
3	Cd^{2+}			
4	Bi^{2+}			
5	Unknown mixture			

4.6.5 Results

Metal ions present in the unknown sample are:

4.7 PAPER CHROMATOGRAPHY SEPARATION AND IDENTIFICATION OF UNKNOW MIXTURE OF As(III), Sb(III) and Sn(II)IONS.

4.7.1 Requirements

Apparatus	Chemicals
Chromatography paper	Arseniousoxide
Chromatographic tank	Stannous chloride
Test tube	Antimony(III)chloride
Spotting capillaries	Hydrochloric acid
Measuring cylinder	
Whatman No. 1. Filterpaper sheet	

4.7.2 Solution provided

4.7.2.1 Sample Solution

1% solution of Arsenious oxide

1% solution of Stannous chloride

1% solution of Antimonous chloride

Dissolve1gram of salt of antimony (III) chloride and stannous chloride in 100 ml of H_2O and add a few drops of dilute acid to suppress hydrolysis.

Dissolve 1 gram of As_2O_3 in 100 ml of water and add a few drops of dilHClto neutralize the solution.

4.7.2.2 Unknown solution

It can be prepared by dissolving any one or two salts in water.

4.7.2.3 Developing Solvent

Any one of the following developing solvents.

1. Collidine saturated with 0.4N HNO_3
2. Ethanol + Propanol + 5NHCl(9:9:1)
3. Take 7.5 ml of acetyl acetone and saturated with water in a separating funnel, shake well and allow to stand to separate the layers. Remove the lower -aqueous layer and add .05ml of conc. HCl and 2-5 ml of acetone in the organic layer, use the organic layer as the developer.

4.7.2.4 Visualizing agents

Following visualization agents may be prepared.

1. Colourless ammonium sulphide solution is prepared by passing H_2S gas water and adding a few drops of ammonia to it. Keep it in a covered container.
2. 0.5 % solution of dithizone in chloroform or carbon tetrachloride.

4.7.3 Procedure

Proceed according to the following step: -

Cut Whatman No. 1 filter strips of about 25x7 cm make a line horizontally 1 cm apart from one edge of the paper across the width of the paper strip using a pencil, and put the various “x” marks at least 2 cm away from each other and apply each solution of arsenic, stannous, tin salt and unknown solutions at these “x” marks by capillary tubes. Use a fresh capillary for each solution After drying the spots, the paper strip is allowed carefully into the jar having the developing solvent for ascending techniques. The spot should always be above the developer level. The jar is then covered properly. The developer will rise along the paper and wait till the developer reaches near the upper end of the paper then remove the paper strip and mark the solvent front with the help of a pencil. Leave the paper for some time to get it dried. After drying the sports, spay with visualizing agent colorless ammonium sulfide produces different colorsvizas (Yellow) Sb (Red) and Sn (Purple) and other visualizing agent dithizone gives yellow color for arsenic, red color for Sb and Sn for purple.

Encircle the colored zones and mark the centre of each zone. Calculate the Rf values of individual cations with that of their Rf values in the mixture to identify the cations in the mixture and unknown sample solution.

4.7.4 Observations and Calculation

Measure the distance travelled by the center of the colored zone from the marked line and the distance travelled by the solvent front on the paper chromatogram. Calculate the R_f value of salt

Observation table 4:

S.N	Cation	Distance travel by cation from origin line	Distance travel by solvent from origin line	R_f
1	As^{3+}			
2	Sn^{2+}			
3	Sb^{3+}			
4	Unknown mixture			

4.7.5 Result

Metal ions present in the unknown sample are:

4.8 PAPER CHROMATOGRAPHY SEPARATION AND IDENTIFICATION OF UNKNOWN MIXTURE OF Fe(III), Al(III), and Cr(III) *IONS.*

4.8.1 Requirements

Apparatus	**Chemicals**
Chromatography paper	Ferric chloride
Petridish	Aluminium chloride
Wick	Chromium chloride
Test tube	Hydrochloric acid
Spotting capillaries	
Measuring cylinder	

Whatman No. 1. Filterpaper sheet

4.8.2 Solution provided

4.8.2.1 Known solution

1% solution of Ferric chloride, Aluminium chloride, and Chromium chloride.

Dissolve 1gram of salt of Ferric chloride, Aluminium chloride and Chromium chloride in 100ml of H_2O and add a few drops of dilute acid to suppress hydrolysis.

4.8.2.2 Unknown solution

It can be prepared by adding anytwo salts solution in one test tube.

4.8.2.3 Developing Solvent

Any one of the following developing solvents.

1. Ethanol + Isopropyl alcohol + 5N HCl(9:9:2).
2. Glacial acetic acid and Dry methyl alcohol(3:1).

4.8.2.4 Visualizing agent

For visualizing the spots, prepare the following three solutions-

1. 1% solution of alizarin in ethyl alcohol.
2. 0.5% of benzidine in acetic acid.
3. 5% solution of sodium peroxide.

4.8.3 Procedure

In this experiment always apply two samples of unknown and one known chromium salt spot on one side of the paper. The procedure is the same as discussed above. After running the mobile phase and drying the spots, cuts the Whatman paper from where chromium salt and one unknown sample is present. Now spray first part of the filter paper which has Al and Fe ion with visualizing agent alcoholic 1% solution of alizarin, expose to ammonia vapour and warm the filter paper. The Aluminium ion spot change into red colour and Fe(III) ion into purple colour. Now spay sodium peroxide solution into the second part of Whatman filter paper followed by benzidine solution chromium ion gives blue spot.

Encircle the colored zones and mark the centre of each zone and calculate the Rf values of known and unknown samples and compare these values to know the unknown cations.

4.8.4 Observations and Calculation

Measure the distance travelled by the centre of the colored zone from the marked line and the distance travelled by the solvent front on the paper chromatogram. Calculate the R_f value of salt

Observation table 5:

S.N	Cation	Distance travel by cation from origin line	Distance travel by solvent from origin line	R_f
1	Al^{3+}			
2	Fe^{3+}			
3	Cr^{3+}			
4	Unknown mixture			

4.8. 5Result

Metal ions present in the unknown sample are:

4.9 PAPER CHROMATOGRAPHY SEPARATION AND IDENTIFICATION OF UNKNOW MIXTURE OF HALIDES ION

4.9.1 Requirements

Apparatus	Chemicals
Chromatography paper	Sodium fluoride
Chromatography tank	Sodium chloride
Measuring cylinder	Sodium bromide
Test tube	Sodium iodide
Spotting capillaries	
Whatman No. 1. Filterpaper sheet	

4.9.2 Solution provided

4.9.2.1 Known solution

1% solution of Sodium fluoride, Sodium chloride, Sodium bromide, and Sodium iodide.

Dissolving 1gram salt in 100ml of distilled water.

4.9.2.2 Unknown solution

It can be prepared by adding any two known solutions in one test tube.

4.9.2.3 Developing Solvent

Take Acetone and Water in4:1.

4.9.2.4 Visualizing agent

Make 0.05 M solution of silver nitrate and dilute aqueous of hydrogen sulfide.

4.9.3 Procedure

The procedure is same as discussed above. But takes slotted Whatman paper filter and every slot spot three known and one unknown mixture. Dry the paper with hot air blower. After running the mobile phase, solution of acetone and water, drying the sports, Now immerse the filter paper in .05 M $AgNO_3$ solution and then wash it with distilled water to remove the excess $AgNO_3$, spay it with an aqueous solution of H_2S, all halides ions gives a black colour spot of Silver sulphide.

4.9.4 Observations and Calculation

Encircle the black zones and mark the center of each zone. Calculate the Rf values of individual anions, with that of their Rf values to identify the anions in the mixture of unknown sample solution.

Measure the distance travelled by the center of the colored zone from the marked line and the distance travelled by the solvent front on the paper chromatogram. Calculate the R_f value of anions.

Observation table 6:

S.N	Anion	Distance travel by cation from origin line	Distance travel by solvent from origin line	R_f
1	F^-			
2	Cl^-			
3	Br^-			
4	I^-			
5	Unknown mixture			

4.9.5 Result

Anion ions present in the unknown sample are:

4.10 SUMMARY

In the present unit you learned the :

- What is the chromatography and how it is useful for the the separation of deferment type of organic and inorganic mixture. In this section cover the types of chromatography, definition paper chromatography, Principle of chromatography, Mechanism of separation of the paper chromatography and descending and ascending techniques, Radial paper chromatography.
- Paper chromatography separation of Ag(I), Hg(II), and Pb(II) ions, Bi (III), Cu (II), Cd (II) Pb (II) ions.

- Paper chromatography separation and identification of Unknow mixture of As(III), Sb(III) and Sn(II)ions, Paper chromatography separation and identification of Unknow mixture of Fe(III), Al(III) and Cr(III)ions.
- Paper chromatography separation and identification of Unknow mixture of halide ions.

4.11 REFERENCE

1. Gurdeep Raj "Advanced practical inorganic chemistry" Goel Publishing House.
2. Singh, J., Singh, R.K.P., Singh, J., Yadav, L.D.S., Siddiqui, I.R., Srivastava, J. (2012), Advanced Practical Chemistry, PragatiPrakashan Meerut
3. Elsa Lundanes, Leon Reubsaet, and TygeGreibrokk "Chromatography: Basic principle, sample preparation, and related method." 2013.

4.12 TERMINAL QUESTIONS

Q. 1. Which types of solvents are generally used in chromatography?

Q. 2. What is meant by the term R_f value?

Q. 3. What are the moving phase and stationary phases in paper chromatography?

Q. 4. What type of paper is used for paper chromatography?

Q. 5. What you know by the term loading in paper chromatographic technique?

Q. 6. What are the advantages of chromatographic technique over the other techniques?

Q. 7. On which factors does the R_f value of a compound depend?