BGS SCIENCE ACADEMY & RESEARCH CENTER
Agalagurki, Chikkaballapura

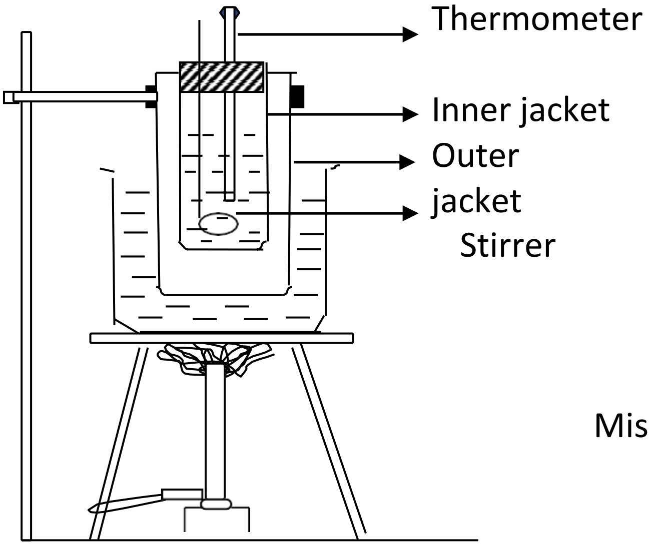
V Semester B.Sc.,
Paper VI
Physical Chemistry Laboratory Manual

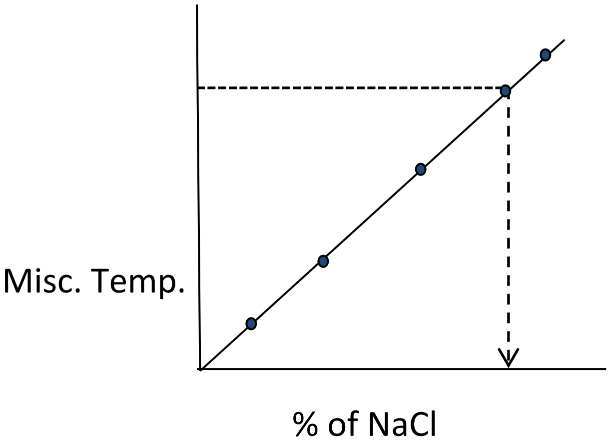
CONTENTS

OBSERVATIONS

Tabulations :

Sl. No.	Vol. of Phenol(ml)	Vol.of1% NaCl(ml)	Vol. of Water(ml)	% of NaCl	Miscibility temperature(°C)		
					T_1	T_2	$(T_1+T_2)/2$
1	5	0	5	0			
2	5	1	4	0.2			
3	5	2	3	0.4			
4	5	3	2	0.6			
5	5	4	1	0.8			
6	5	5	0	1.0			
7	5	5ml of the given solution	----				





EXPERIMENT NO.1

AIM: DETERMINATION OF PERCENTAGE COMPOSITION OF SODIUM CHLORIDE BY PHENOL-WATER MISCIBILITY TEMPERATURE METHOD

Principle : On mixing two partially miscible liquids a milky turbidity appears, this milky emulsion gets disappeared above a certain temperature and a clear solution is obtained, this temperature is called miscibility temperature. This temperature is affected in presence of small quantities of a salt as impurity.This effect is utilized to estimate the amount of such salts present as impurity in water.

PROCEDURE : 1 g of sodium chloride salt is weighed and dissolved in 100 ml of water in a standard flask to get 1% solution of the salt. 5 ml of phenol and 5 ml of waterare separately pipetted out and transferred into the inner tube of the Critical solution temperature set(CST), two liquid layers separates out. The apparatus is set as shown in the diagram using a cork, stirrer and a 1/10^o thermometer. The set is kept in the hot water bath, the solution is stirred slowly and continuously till a clear homogeneous liquid layer is obtained, the corresponding temperature(heating) is recorded(T_1). The inner tube is taken out from the outer jacket and stirred till a turbid solution isobtained,the corresponding temperature(cooling) is recorded(T_2). The average temperature of these two temperatures gives the miscibility temperature of the mixture.

Different compositions of sodium chloride are prepared from 1% stock solution(0.2 to 1%) in five different tubes. To each 5 ml of phenol is added, the miscibility temperature of each composition of the mixture is determined as explained above. The given unknown solution is taken in a tube, 5 ml of phenol is added and its miscibility temperature is determined. A standard graph is drawn by plotting miscibility temperature versus percentage of sodium chloride solution. From the calibrated graph the given percentage composition of sodium chloride solution can be estimated.

Result: The percentage composition of the given sodium chloride solution is ………..% ………g/ml

OBSERVATIONS

Tabulations :

1.Preparation of 0.1 N KCl and determination of cell constant

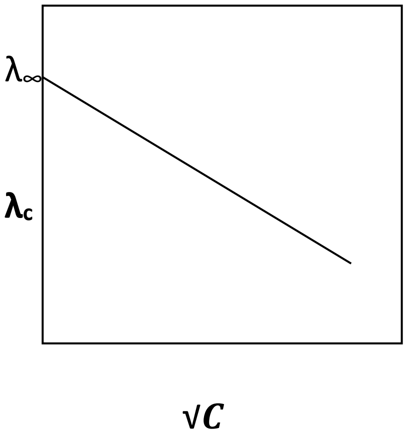
0.7456 g of KCl is weighed and dissolved in 100 ml of distilled or conductivity water
Conductance of 100 eq/m^3KCl (0.1 N) solution = ...S
Hence cell constant of the given conductance cell = 1.285 / conductance
= 1.285/........ m^{-1}.

2. Determination of equivalent conductivity of 100 eq/m^{-3}NaCl and verification of Debye-Huckel Onsager equation

Sl.No.	Conc. of the electrolyte(eq./m^3) c	√c	Conductance (mhos/S)	k = cell const x conduct. $S.m^{-1}$.	λ_c= k/c $S.m^2.eq^{-1}$
1.	100(0.1N)	10 (0.3162)			
2.	50(0.05N)	7.071 (0.2236)			
3.	25(0.025N)	5 (0.1581)			
4.	12.5(0.0125)	3.536 (0.1118)			

Debye-Huckel Onsager equation is $\lambda_c = \lambda_\infty - (A + B\lambda_\infty)\sqrt{c}$

A graphical plot of λ_c Vs √c is plotted, extrapolation of the straight line backwards gives the value of λ_∞.



The value of λ_∞ for NaCl is......................... $S.m^2.eq^{-1}$

A straight line graph with decreasing slope verifies Debye Huckel Onsager equation.

EXPERIMENT NO. 2

AIM: DETERMINATION OF EQUIVALENT CONDUCTIVITY OF 0.1NSODIUM CHLORIDE AND VERIFICATION OF DEBYE- HUCKELONSAGER EQUATION

PRINCIPLE: Conductivity is defined as the reciprocal of resistance of the solution. Debye-Huckel –Onsager obtained an expression relating equivalent conductivity at a given concentration to the concentration by the equation: $\lambda_c = \lambda_\infty - (A + B\ \lambda_\infty)\sqrt{c}$.Where$\lambda_c$ and λ_∞ are the equivalent conductivities of the electrolyte at concentration c and at infinite dilutions respectively, A and B are DHO constants. Cell constant of the given conductivitycell is determined by using the prepared 0.1N KCl solution. The conductance of 0.1N NaCl and for other concentrations the conductances are determined. A graph of λ_c Vs $\sqrt{c}$ gives a straight line with decreasing slope verifies DHO equation.

PROCEDURE: 1. Determination of cell constant of the given conductivity cell

The given conductivity cell is cleaned using conductivity water. Exactly 0.1N KCl is prepared by weighing 0.7456 g of the solid and dissolving in 100 ml conductivity water. It is transferred into the conductivity cell till the two electrodes just dips in the solution, connected to the conductivity meter its conductance is determined. The cell constant is calculated by the equation = 1.288 / conductance.

2. Determination of equivalent conductance and verification of DHO equation

The above conductivity cell is cleaned with conductivity water and it is rinsed with the given 0.1N sodium chloride solution, then it is poured into the conductivity cell. It is connected to the conductivity meter, the conductance is measured. Its specific and equivalent conductances are calculated. The above given solution of 0.1N concentration is diluted properly to prepare other different concentrations(0.05,0.025 and 0.0125), the conductance of each solution is separately determined using the conductivity bridge. From that equivalent conductances are calculated. A graph of λ_c Vs $\sqrt{c}$ is plotted. The extrapolated value of λ_c backwards along Y axis gives the value of λ_∞ for NaCl.

Result : The equivalent conductance of 0.1N NaCl is ....S.m^2/eq.and λ_∞ For NaCl from the graph is ,

Conclusion:A straight line graph with decreasing slope verifies Debye- Huckel Onsager equation.

OBSERVATIONS

REACTION: $Na^+ OH^- + H^+ Cl^- \rightarrow Na^+ Cl^- + H_2O$

TABULATIONS: I. STANDARDIZATION OF SODIUM HYDROXIDE

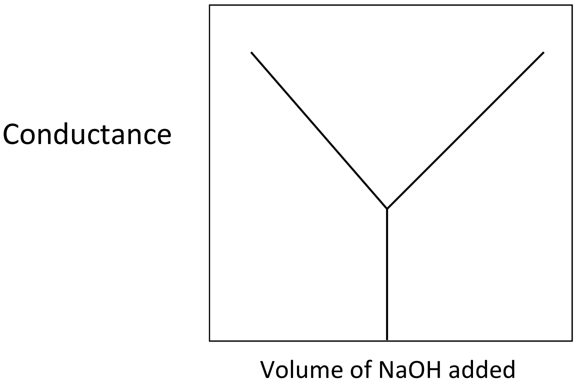
a) Preparation of 0.1N potassium hydrogen phthalate solution

i) Mass of PHP =… …………… g($W_1 – W_2$)
ii) Normality of PHP = ………… 10/204
= ______N

b) Standardization of sodium hydroxide

Burette: Potassium hydrogen phthalate solution
Conical flask: 10 cm^3 of Sodium hydroxide
Indicator: Phenolphthalein
End point: Pale pink to Colourless

Trial No.	1	2	3
Final Burette Reading(cm^3)			
Initial Burette Reading(cm^3)			
Volume of PHP (cm^3)			



Normality of Sodium hydroxide (N_1) = $\frac{\text{Vol.of PHP}(V_2) \times \text{Normality of PHP}(N_2)}{\text{Volume of NaOH}(V_1)}$

= ………x 0.1/10 = …………… N

II.ESTIMATION OF HYDROCHLORIC ACID USING THE STANDARDISED SODIUM HYDROXIDE SOLUTIONCONDUCTOMETRICALLY

Sl.No.	Vol. of NaOH added (Cm^3)	Conductance(S)	N_{HCl} = Graph value x N_1/25N

Amount of HCl present in 100 cm^3 of its solution =Normality x 36.5/10 g = --------------- g
=……………g

EXPERIMENT NO. 3

AIM : **TO ESTIMATE THE AMOUNT OF HYDROCHLORIC ACID PRESENT IN 100 cm^3 OF THE GIVEN SOLUTION USING APPROXIMATELY DECI-NORMAL SOLUTION OF SODIUM HYDROXIDE BY CONDUCTOMETRIC TITRATION**

PRINCIPLE: The reaction between sodium hydroxide and hydrochloric acid is an ionic reaction: $Na^+OH^- + H^+Cl^- \rightarrow Na^+Cl^- + H_2O$, Neutralization of the reaction followed by the change in the ionic mobilities near the end point and there is a sharp change in the concentration and conductivity. By noting the change in the ionic mobilities it is possible to estimate the strength by means of conductivity changes. The conductivity of HCl is more in the beginning, as titration proceeds by the addition sodium hydroxide, the conductivity decreases due to the formation of NaCl whose conductivity is less compared to HCl . After the neutralization, the conductivity increases due to the formation of highly mobile OH^- ions.

PROCEDURE : The estimation involves two steps

PART- I: STANDARDIZATION OF SODIUM HYDROXIDE USING THE Prepared 0.1N SOLUTION OF POTASSIUM HYDROGEN PHTHALATE

Standard decinormal potassium hydrogen phthalate is prepared by dissolving exactly 2.042 g of PHP crystals in distilled water and made up to 100 cm^3 in a standard flask. 10cm^3 of the given sodium hydroxide solution is pipetted out into a clean conical flask. 2drops of phenolphthalein indicator is added into it. The resulting pink solution is titrated against the standard potassium hydrogen phthalate solution taken in the burette till the pink color just disappears.The experiment is repeated for concordant values.

PART-II:ESTIMATION OF HYDROCHLORIC ACID USING THE STANDARDI DIZEDSOLUTIONOF SODIUM HYDROXIDE BYCONDUCTOMETRIC TITRATION

The given hydrochloric acid is made up to the mark using conductivity water, shaken well. 25 cm^3 of the made up hydrochloric acid is pipetted out into a cleaned conductivity cell till the two electrodes dips in it. The cell is connected into the conductivity meter. The standardized Sodium hydroxide solution from the above step is filled in a cleaned and rinsed burette. 0.5 cm^3 of sodium hydroxide is added to the conductivity cell containing HCl at a time, gently stirred, the conductance is measured from the meter. The titration is continued and the readings are recorded till the inflection point that is conductance decreases & increases. A graph is drawn by plotting conductance Vs volume of sodium hydroxide added. From the graph, the strength of the acid or base can be estimated.

Result:
1. Normality of sodium hydroxide solution............ N
2. Normality of the estimated hydrochloric acid............N
3. Amount of hydrochloric acid present in 100 cm^3 =..............g

OBSERVATIONS

Tabulations:

1.Preparation of 0.1 N KCl and determination of cell constant

0.7456 g of KCl is weighed and dissolved in 100 ml of distilled or conductivity water
Conductance of 100 eq/m^{3}KCl (0.1 N) solution = ...S
Hence cell constant of the given conductance cell = 1.288 / conductance

= 1.288/........ m^{-1}.

2. Determination of dissociation constant of the weak acid(acetic acid/mono chloro- acetic acid

Given λ_∞ of acetic acid = 390 x 10^{-4} S.m^2./eq.
λ_∞ of mono chloro acetic acid = 389 x 10^{-4} S.m^2./eq.

Sl. No	Conc. of the Acid(eq/m^3)	Conductance (S)	$\Lambda_c = \frac{C.C \times cond.}{Concn.}$	$\alpha = \lambda_c/\lambda_\infty$	$K_a = \frac{\alpha^2 C}{10^3(1-\alpha)}$	Mean K_a
1	100 eq/m^3 (0.1N)					
2	50 eq/m^3 (0.05N)					
3	25 eq/m^3 (0.025N)					
4	12.5eq/m^3 (0.0125N)					
5	10 eq/m^3 (0.01N)					

(K_a of acetic acid = 1.75 x 10^{-5} and for monochloric acid K_a = 1.38 x 10^{-3})

EXPERIMENT NO. 4

AIM:DETERMINATION OF DISSOCIATION CONSTANT OF A WEAKACID (MONOCHLOROACETIC ACID OR ACETIC ACID) BY CONDUCTIVITY METHOD

PRINCIPLE: The dissociation constant of a weak acid is determined by using Ostwald's dilution law equation: $K_a = \frac{\alpha^2 C}{(1-\alpha)}$

where C is molar concentration of the acid,α is the of dissociation of the acid = $\lambda_c / \lambda_\infty$, λ_c is the equivalent conductance of the acid at the given concentration and λ_∞ is the equivalent conductance of the acid at infinite diln.λ_c can be calculated from cell constant of the conductivity cell and conductance of the acid for the prepared concentration. $\lambda_\infty$of the acid is calculated from Kohlrausch law.

PROCEDURE: 1. Determination of cell constant of the given conductivity cell The given conductivity cell is cleaned using conductivity water. Exactly 0.1N KCl is prepared by weighing 0.7456 g of the solid and dissolving in 100 ml conductivity water. It is transferred into the conductivity cell till the two electrodes just dips in the solution, connected to the conductivity bridge and its conductance is determined. The cell constant is calculated by the equation = 1.288 / conductance.

2. Determination of degree of dissociation and dissociation constant of the weak acid

The given solution of the weak acid having the concentration of 100 eq/m^3 is transferred into the cleaned and rinsed conductivity cell used in the above step and connected into the conductivity meter, its conductance is measured. By proper dilution of this stock solution 50, 25, and 10 eq./m^3 or 0.05,0.025 and 0.01N are prepared, the conductivity of each solution is separately determined using the same conductivity meter. From which the equivalent conductance and dissociation constant is calculated.

Result: The mean value of dissociation constant of the given weak acid is…………

OBSERVATIONS -

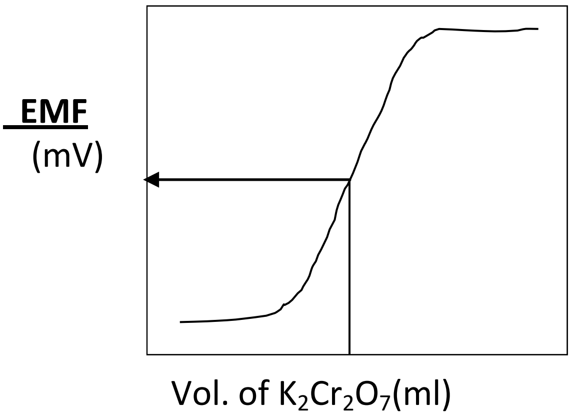
1. Preparation of 0.1N Ferrous ammonium sulphate solution:

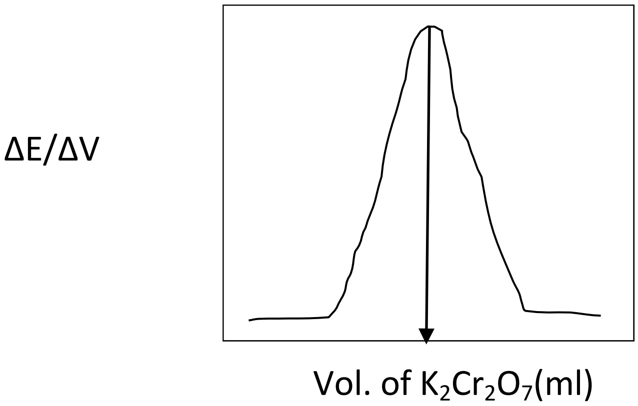
i)Mass of FAS+Empty weighing bottle =…............g.
ii) Mass of empty weighing bottle……g.
iii) Mass of FAS transferred ....g.
1. Normality = mass ....x 10/392 = …N

2. Estimation of potassium dichromate potentiometrically

Rough Titration			**Neat Titration**			
Sl.No.	**Volumeof $K_2Cr_2O_7$(ml)**	**E(mV)**	**Sl.No.**	**Volumeof $K_2Cr_2O_7$(ml)**	**E(mV)**	**ΔE/ΔV**
1						
2						
3						
4						
5						
6						
7						
8						
9						
10						
11						
12						
13						
14						
15						
16						

The Corresponding graphs are plotted as follows





Normality of $K_2Cr_2O_7$ = 10 x 0.1/ ------- (graph value)N.
Mass of Potassium di-chromate crystals present in 100 cm^3 of its solution = ...49/10
=… ....g.

EXPERIMENT NO. 5.

AIM: TO ESTIMATE THE AMOUNT OF POTASSIUM DI-CHROMATE PRESENT IN100 Cm^3 OF THE GIVEN SOLUTION USING THE PREPARED 0.1N FERROUSAMMONIUM SULPHATE SOLUTION BY POTENTIOMETRIC TITRATION

PRINCIPLE: A bright platinum electrode or a pretreated carbon electrode dipped in a solution of a red-ox system like Fe^{2+} / Fe^{3+} sets up a potential depending on the concentration ratio of the red-ox system. The ferric ion concentration in the beginning is less, if this solution is titrated with an oxidizing agent, the ratio changes rapidly. Hence there is a sharp inflection in the emf-volume curve near the end-point.

The red-ox reaction between ferrous ion and potassium di-chromate in acid medium is $Cr_2O_7^{2-} + 14 H^+ + 6Fe^{2+} \rightarrow 2 Cr^{3+} + 7H_2O + 6Fe^{3+}$

The potential developed is given by Nernst equation:

$E = E^o + 0.0591/1 \log [Fe^{2+}] / [Fe^{3+}]$. This equation implies that emf changes with the change in concentration change of the titrant involved in the reaction.

PROCEDURE: 3.92 of ferrous ammonium sulphate crystals are transferred into a clean beaker, a thin paste with little amount of con. sulphuric acid is made, then dissolved in little amount of water and then transferred into 100ml standard flask, then made up to the mark with distilled water and shaken well. The given potassium dichromate solution is made up to the mark with distilled water and shaken well. 10 cm^3 of the prepared 0.1N ferrous ammonium sulphate solution is pipetted out into a 100 ml beaker,10 cm^{3}of dil.sulphuric acid is added.A bright platinum electrode is dipped in it. A cell constructed using a saturated calomel electrode, it is then connected to a potentiometer.The constructed cell is

$Pt / [Fe^{2+}] / [Fe^{3+}](0.1M) || (satd)KCl; Hg_2Cl_2,Hg / Pt$

The made up potassium dichromate solution is filled in a burette and added to ferrous ammonium sulphate solution taken in the beaker 1ml at a time. The emf/potential is recorded from the potentiometer. The addition is continued up to the neutralization point and a few readings even after also. The experiment is repeated near the end point at finer ranges of addition of potassium dichromate solution by performing a neat titration. The results are tabulated and graphs are plotted as EMF Vs volume of dichromate added from rough titration and differential plot from the neat titration data. The strength and amount of dichromate present in the given solution is calculated.

Result: 1. Normality of potassium dichromate solution = ...N

2. Mass of potassium dichromate crystals present in 100 cm^3 of the given solution =............. g.

OBSERVATIONS

REACTION: $CH_3COOCH_3 + H_2O \xrightarrow{H^+} CH_3COOH + CH_3OH$

TABULATIONS:

1. Determination of rate constant at temperature $T_1=25+273=298K$

Time (mins)	Burette readings		Titer value (cm^3)	$k = \frac{2.303}{t} \log \frac{V_\infty - V_o}{V_\infty - V_t}$ /min	Mean k_1 (min^{-1})
	Final	Initial			
0					
10					
20					
30					
40					
∞					

2. Determination of rate constant at temperature $T_2=35+273=308K$

Time (mins)	Burette readings		Titer value (cm^3)	$k = \frac{2.303}{t} \log \frac{V_\infty - V_o}{V_\infty - V_t}$ /min	Mean k_2 (min^{-1})
	Final	Initial			
0					
10					
20					
30					
40					
∞					

$\log(k_2/k_1) = E_a/2.303R(T_2-T_1)/T_1T_2,$

$E_a = 2.303RT_1T_2 \log(k_2/k_1)/(T_2-T_1)$

$E_a = 175740 \log(k_2/k_1) = 175740 \log[\qquad\qquad\qquad]$

=.................................kJ

EXPERIMENT NO. 6

AIM:DETERMINATION OF VELOCITY CONSTANT FOR THE ACID CATALYSE DHYDROLYSIS OF METHYL ACETATE AND DETERMINATION OF ENERGY OF ACTIVATION

PRINCIPLE: Methyl acetate undergoes hydrolysis with water in presence of a dilute mineral acid as catalyst to give acetic acid and methanol. The reaction is a bi-molecular first order reaction(Pseudo-I order reaction) since water is present in large excess, the rate depends only on the concentration of the ester. The progress of the reaction is followed by titrating a known volume of the reaction mixture at regular intervals of time and titrating against a standard solution of sodium hydroxide using phenolphthalein as indicator. As each molecule of the ester is hydrolysed, one molecule of the product acetic acid is formed. The increase in the acid concentration is a measure of the amount of ester is hydrolysed. Velocity constant is calculated using the equation: $k = 2.303/t \log [V_\infty - V_o / V_\infty - V_t]$
Where V_0 , V_t and V_∞ are the titre values at the times of zero, t and infinity. k is determined at two different temperatures and energy of activation is determined from Arrhenius equation: $\log(k_2/k_1)= E_a/2.303R(T_2-T_1)/T_1T_2$.

PROCEDURE: A 25°C thermostat is set up and in that 100 cm^3 of 0.35N hydrochloric acid and 15 cm^3 of methyl acetate taken in a conical flask and a stoppered bottle respectively and fixed in the thermostat prepared and allowed to attain the temperature. After 10 minutes, 5 cm3 of the ester is pipetted out and transferred into the conical flask containing acid solution. The contents are shaken gently, immediately 5 cm3 of the reaction mixture is pipette out and transferred into a conical flask containing ice cold water(to arrest the reaction). A stop watch is started, 2 drops of phenolphthalein indicator is added and titrated against standard 0.1N sodium hydroxide solution till a permanent pale pink color is obtained, the titer value is recorded(V_o). The experiment is repeated in the same manner as explained above at the end of 10, 20, 30 and 40 minutes, the corresponding titre values are recorded(V_t). Finally, the reaction mixture in the flask is taken out and heated in a water bath at about 80°C for half an hour to complete the reaction, cooled to the room temperature. 5 cm3 of the reaction mixture is pipetted out and titrated Vs the same sodium hydr-oxide solution till the end point, the titre value is recorded(V_∞). The results are tabulated and the mean velocity constant is calculated (k_1)

The experiment is repeated in the same manner as explained above at temperature of 35°C and the corresponding rate constant is determined (k_2)

Result: The velocity constant of acid catalysed hydrolysis of methyl acetate
at temp.25°C is …………………/min. & at 35°C is............................/min.
Hence E_a is...................J.

OBSERVATIONS

REACTION: $CH_3\,COO\,C_2H_5 + Na\,OH \longrightarrow CH_3COONa + C_2H_5OH$

TABULATIONS;

1. Initial concentration of the reactants: $V_o = (b\text{-}z)\ cm^3 = a\ mol/dm^3$
2. Volume of 0.01M sodium hydroxide required for neutralizing 20 ml of 0.01M HCl = b ml =………..
3. Volume of 0.01M NaOH required for titrating a mixture of 20 ml of 0.01M NaOH and 20 ml of 0.01M HCl = z ml =………………..
4. Volume of 0.01M NaOH required for titrating 20 ml of the reaction mixture and 20 ml of 0.01M HCl in a conical flask = y ml =………………
5. Concentration of the unreacted reactant: $(a\text{-}x) = V_t = (b\text{-}y)$ =………..
6. Concentration of the reactant at time t minutes = $x = (V_0 - V_t)$ =…………
7. Rate constant is calculated using the equation: $k = 1/\,V_o t\ [V_o - V_t]/\,V_t\ [mol/dm^3/s]^{-1}$

k can also be determined graphically by plotting a graph of $(V_0 - V_t)$ Vs time, slope of which gives the value of k.

Time (mins)	Vol. of NaOH(cm^3)	$V_o = (b\text{-}z)$ cm^3	$V_t = (b\text{-}y)$ cm^3	$\frac{V_o - V_t}{V_t}$	$\frac{1}{V_o t V_t}\ [V_o - V_t]$	Mean k
0						
3						
10						
20						
25						
30						

EXPERIMENT NO. 7.

AIM: DETERMINATION OF VELOCITY CONSTANT FOR THE SAPONIFICATION OF ETHYL ACETATE

PRINCIPLE: Alkaline hydrolysis of an ester is called saponification reaction. When ethyl acetate is hydrolysed in presence of sodium hydroxide, sodium acetate and ethanol is obtained. Velocity of the above reaction is directly proportional to the concentration of both the ester and andNaOH, which follows II order kinetics. The rate constant is calculated using the equation(when a=b) $k = 1/at\ [x/(a-x)]$, where x = concentration of the reactant at time t , a = initial concentration of the reactant, (a-x) = concentration of the unreacted reactant. A titrimetric or graphical method may be used for the progress of the reaction in which remaining sodium hydroxide is titrated using standard hydrochloric acid.

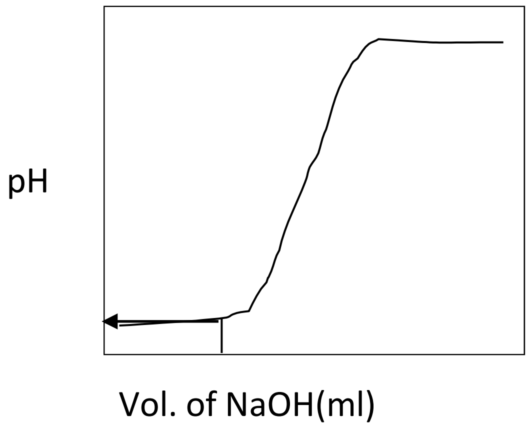
PROCEDURE : 2.43 cm^3 of ethyl acetate (or 2.3g) is dissolved in 250 ml of distilled water to get 0.01M concentration. 100 mg of sodium hydroxide is dissolved in 250 ml of distiller water to get 0.01M concentration. 100 cm^3 of 0.01M ethyl acetate and 100 cm^3 of 0.01 M NaOH are taken in two separate conical flasks and fixed in a thermostat. 20 cm^3 of 0.01M hydrochloric acid is taken in 6 to 7 conical flasks separately. When both the solutions attains the temperature of the thermostat, 100 cm^3 sodium hydroxide is added to the ester at once, the resulting mixture is thoroughly shaken and a stop watch is started at the time of mixing. 20 cm^3 samples of the reaction mixture is pipette out at intervals of 3,5,10,20,25 and 30 minutes and transferred into the conical flasks containing 20 ml of 0.01M HCl solutions(to arrest the reaction), the excess acid is titrated against the standard 0.01M NaOH solution taken in the burette using phenolphthalein as indicator. The titer values are recorded(y). Initial concentration of the reactant NaOH is determined by titrating 20 cm^3 of 0.01M HCl against 0.01M NaOH taken in the burette using phenolphthalein as indicator, the titer values are recorded(b). Then 20 cm^3 of 0.01M NaOH + 20 cm^3 of 0.01M HCl are mixed and titrated against 0.01M NaOH solution, the burette reading is recorded(z).

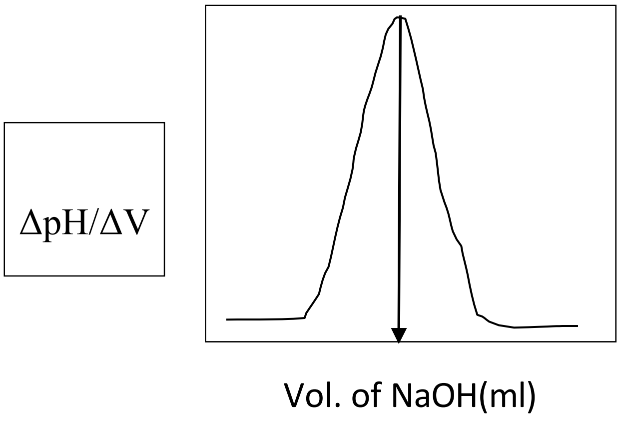
Result: The mean value of the velocity constant of saponification of ethyl acetate is .... $[mol/dm^3/s]^{-1}$.

OBSERVATIONS

1.Rough titration			2. Neat titration			
Sl.NO	Vol. of NaOH added (ml)	pH	Sl.No	Vol. of NaOH added(ml)	pH	ΔpH/ΔV
1	2					
2	4					
3	6					
4	8					
5	10					
6	12					
7	14					
8	16					
9	18					
10	20					
11	22					
12	24					
13	26					
14	28					
15	30					

The Corresponding graphs are plotted as follows





pK$_a$ of the given weak acid is…………….

EXPERIMENT NO. 8

AIM: DETERMINATION OF pK_a OF A WEAK ACID BY pH METRIC METHOD

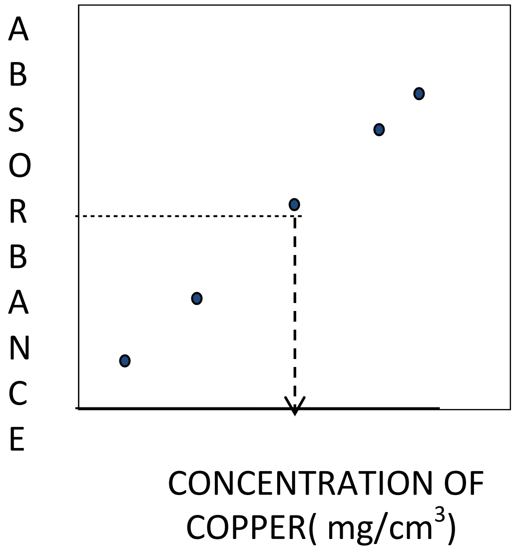
PRINCIPLE: During the titration of an acid with a base, the pH of the solution rises gradually at first, then more rapidly, until at the equivalence point, there is a very sharp increase in pH for a very small quantity of the added base. After the equivalence point, the pH increases slightly on the addition of excess base. The titration curve is obtained by plotting changes in pH at different amount of the base added. A cm3 ording to Henderson's equation: $pH = pK_a + \log [Salt]/[acid]$. Where K_a is the dissociation constant of the acid and $pK_a = -\log K_a$. At half-equivalence point, [Salt] = [Acid] and hence $pH = pK_a$. Hence pH at equivalence point gives the pK_a of the weak acid.

PROCEDURE: 15 cm^3 of the given weak acid(acetic acid) of concentration 0.01N is pipetted out into a beaker. A glass electrode-calomel electrode assembly is immersed in it and connected to a pH meter, pH of the acid is measured. A burette is filled with the given 0.01N sodium hydroxide solution. 1ml of the base is added at a time to the beaker,stirred gently, pH is measured. pH increases slowly, then rapidly and finally it becomes steady. The experiment is repeated near the equivalence point with the slow additions of the base. Plot the graphs of pH Vs volume of the base added and the differential plot of pH. Determine the equivalence point from the differential plot and determine the pH at the half neutralization point which gives the pK_a value of the acid.

Result : The pK_a value of the given weak acid(acetic acid) is……………

OBSERVATIONS

Volume of standard $CuSO_4$ solution(cm^3)	Volume of NH_3 added in cm^3	Concentration of Cu solution(mg/cm^3)	Absorbance(O.D)
5	5		
10	5		
15	5		
20	5		
25	5		
Test solution	5		



The Amount of copper present in 100 cm^3 of the givensolution is...............g
A= εct, Absorbance Vs concentration plot givesst. line passing through the origin verifies Beer-Lambert's law.

EXPERIMENT NO. 9.

AIM: ESTIMATION OF COPPER COLORIMETRICALLY AND VERIFICATION OFBEER-LAMBERT'S LAW

PRINCIPLE: When a monochromatic radiation of intensity I_o is incident on a transparent medium, a part of the intensity is absorbed(I_a), a part of it is reflected(I_r) and the remaining part is transmitted(I_t). $I_o = I_a + I_r + I_t$, For a glass-air interface I_r is negligible. Therefore, $I_o = I_a + I_t$, $I_t/I_o = T$ called the transmittance. $\log 1/T = \log I_o/I_t$, is called the absorbance or optical density A. The relation between absorbance A and concentration c(in mol/lit) and path length t (in cm) is given by Beer-Lambert's law: $A = \log I_o/I_t = \varepsilon ct$. Where ε is the molar extinction coefficient, t is the path length. ε is a constant for a given substance at a given path length. If t, the path length is kept constant, then $A \alpha c$. Hence a plot of absorbance against concentration gives a straight line. A series of standard solutions of copper is treated with ammonia to get blue cuprammoniumsulphate complex and is diluted to a definite volume. The absorbance of each of these solutions is measured at 620 nm since the complex shows maximum absorbance at this wavelength. The absorbance values are plotted against concentration to get a calibration curve. A known volume of the test solution is treated with strong ammonia and diluted to the same volume as above. The absorbance of this solution at 620 nm is measured and its concentration is determined from the calibration curve.

PROCEDURE: 0.3929 g of AR $CuSO_4.5H_2O$ crystals is dissolved in 100 ml of distilled water, which acts as the stock solution containing 1mg of copper in 1 cm^3. The stock solution prepared is filled in a cleaned and rinsed burette. 5,10,15,20 and 25 cm^3 of this solution are transferred into 50 cm^3 standard flasks. 5 cm^3 of ammonia solution is added to each of them and diluted up to the mark with ion exchange water, the flasks are stoppered and shaken well. The test solution is taken in another 50 ml standard flask, 5 cm^3 of ammonia is added , diluted to 50 ml using ion-exchange water and mixed well. A blank solution is prepared by diluting 5 cm^3 of ammonia solution. After 10 minutes the absorbance is measured for each solution against blank at 620 nm using a photoelectric colorimeter. A calibration curve is drawn by plotting absorbance against concentration of copper(in mg/ml). Using the calibration curve, the concentration of copper in the test solution and the amount present in 100 cm^3 of the given solution can be calculated.

Result:

1. The Amount of copper present in 100 cm^3 of the givensolution is..............g
2. $A = \varepsilon ct$, Absorbance Vs concentration plot gives st. line passing through the origin verifies Beer-Lambert's law.

OBSERVATIONS:

Equations: 1. $K_2S_2O_8 + 2KI \longrightarrow 2K_2SO_4 + I_2$

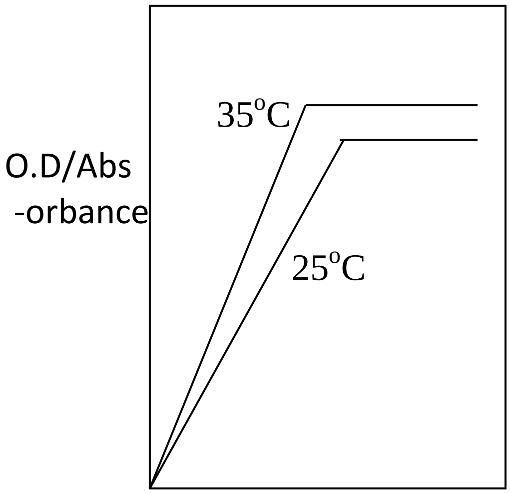
2. $2Na_2S_2O_3 + I_2 \longrightarrow 2NaI + Na_2S_4O_6$(sodium tetrathionate)

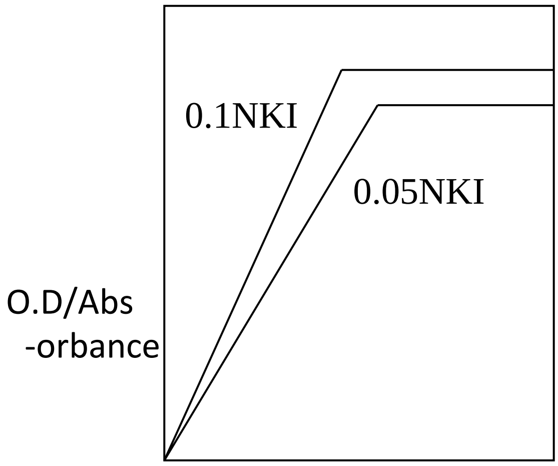
i) Effect of temperature: Absorbance is measured at 525nm

25°C(298K)		35°C(308K)	
100ml of 0.1N $K_2S_2O_8$ + 100ml of 0.1N KI		**100ml of 0.1N $K_2S_2O_8$ + 100ml of 0.1N KI**	
Time (mins)	Absorbance(O.D)	Time (mins)	Absorbance(O.D)
0			
2			
4			
6			
8			
10			
12			
14 and so on			

ii) Effect of concentration: Measured at lab.temperature

100ml of 0.1N $K_2S_2O_8$ + 100ml of 0.05N KI		**100ml of 0.1N $K_2S_2O_8$ + 100ml of 0.1N KI**	
Time (mins)	Absorbance(O.D)	Time (mins)	Absorbance(O.D)
0			
2			
4			
6			
8			
10			
12			
14 and so on			





Time(mins) Time(mins)

EXPERIMENT NO.10.

Kinetics of Potassium Persulphate and Potassium Iodide

AIM:To Study the effect of temperature and concentration on the rate of oxidation of potassium iodide by potassium persulphate using colorimeter

PRINCIPLE:

Potassium persulphate reacts with potassium iodide and liberates iodine
The reaction can be followed by titrating the liberated iodine against standard hypo
The reaction rate depends on concentration of KI and temperature.

Procedure:

i) **Effect of Temperature**:

About 100ml each of 0.1N $K_2S_2O_8$ and 0.1N KI are taken in two separate bottles and kept in a constant temperature bath (T_1 K) for about half an hour. They are mixed in one bottle and a stop clock is started. After every interval of two minutes the values of absorbance for the reaction mixture are recorded using colorimeter at 525nm. The above process is repeated at another temperature(T_2 K) without altering the concentrations of $K_2S_2O_8$ and KI. A graph of absorbance versus time is plotted for both the temperatures.

ii) **Effect of Concentration**:

About 100ml each of 0.1N $K_2S_2O_8$ and 0.1N KI are taken in two separate bottles and kept in a constant temperature bath for about half an hour.

They are mixed in one bottle and a stop clock is started. After every interval of two minutes the values of absorbance for the reaction mixture are recorded using a colorimeter at 525nm.

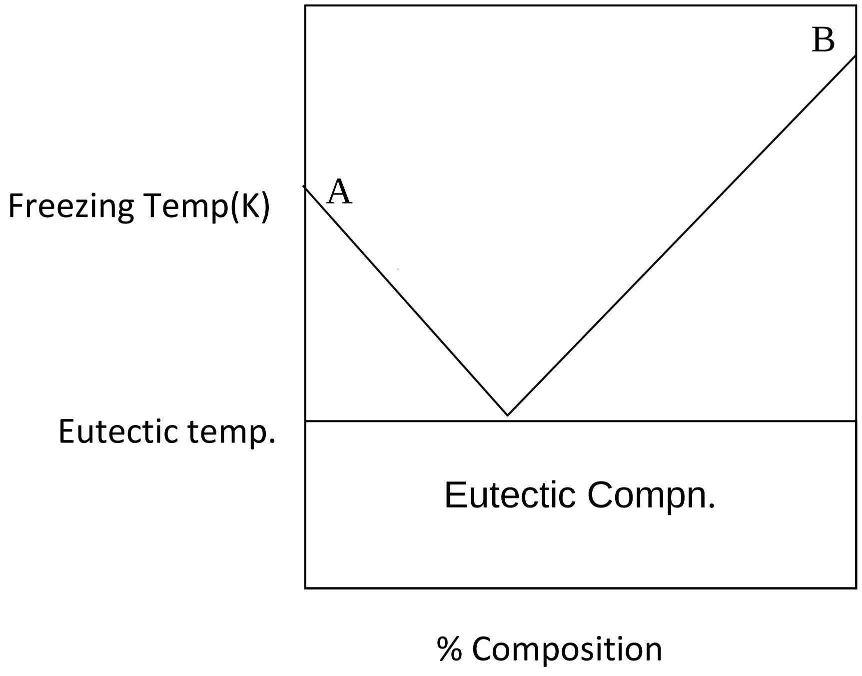
The above process is repeated using 0.2NKI and 0.1N $K_2S_2O_8$ without altering the temperature. A graph of absorbance versus time is plotted for both the concentrations.

Result: The rate of reaction increases with increase in concentration of KI and also with increase in temperature.

OBSERVATIONS:

A= Diphenyl amine,   B = Benzophenone

Sl. No.	Mass of A (g)	Mass of B (g)	% Compostion of A	% Compostion of B	Freezing temperature(K)
1	0.5	4.5	10	90	
2	1	4	20	80	
3	2	3	40	60	
4	3	2	60	40	
5	4	1	80	20	
6	4.5	0.5	90	10	



Phase Diagram

EXPERIMENT NO.11.

AIM:To Construct the Phase diagram of two component system-Diphenyl amine-benzophenone by cooling curve method and hence determination of eutectic temperature and eutectic composition

Principle: The number of degrees of freedom is related to the phase and component by the equation F = C- P + 2 (Gibb's phase rule). For a two component system like the one described below, the vapour phase is neglected and the modified form of the phase rule or the condensed phase rule, F = C-P + 1 is used. Phase relationships can be demonstrated with the help of a mixture of organic compounds. When one solid is added to the other the freezing point decreases, reaches a minimum value and increases again.The minimum value of freezing point observed for the mixture is called eutectic temperature and the composition corresponding to this temperature is called the eutectic composition.

Procedure: The following mixtures are prepared in 6 glass tubes by weighing the compounds A and B so that the weight of the mixture is 5g: (i) 0.5g of A + 4.5g of B, (ii) 1.0g of A + 4.0g of B, (iii) 2.0g of A + 3.0g of B, (iv) 3.0g of A + 2.0g of B, (v) 4.0g of A + 1.0g of B and (vi) 4.5g of A + 0.5g of B.

The tubes are closed with corks, fitted with a thermometer and stirrer, heated in a water bath till the components melts, taken out and allowed to cool with constant stirring till the mixture begins to solidify. This temperature is noted which gives the freezing point. (The temperature remains constant for a certain interval of time at the freezing point).

In a similar way, freezing points of remaining mixtures and that of the unknown mixture are determined. Freezing point against percentage composition of A is plotted. From the graph eutectic temperature, eutectic composition and percentage of A in the unknown mixture are determined.

Result: The eutectic temperature of the given mixture is .... ,
Eutectic composition is …………
The percentage of A in the given unknown mixture is ………….

OBSERVATIONS

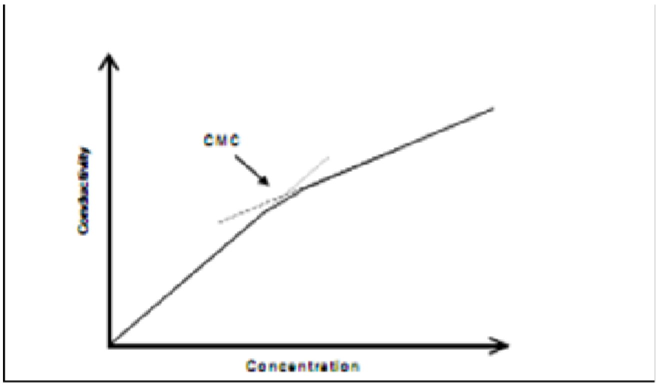
Tabulations :

1.Preparation of 0.1 N KCl and determination of cell constant

0.7456 g of KCl is weighed and dissolved in 100 ml of distilled or conductivity water
Conductance of 100 eq/m^{3}KCl (0.1 N) solution = ...S
Hence cell constant of the given conductance cell = 1.288 / conductance
= 1.288/........ m^{-1}.

2. Determination of equivalent conductivity of sodium lauryl sulphate

Sl.No.	Conc. of the electrolyte(eq./m^3) c	Conductance (mhos/S)	k = cell const.x conduct. (S/m)
1.	50(0.05M)		
2.	25(0.025M)		
3.	12.5(0.0125M)		
4.	6.25(0.00625M)		
5.	3.125(0.003125)		



The CMC of the surfactant sodium lauryl sulphate from the graph is ---------------.

EXPERIMENT NO.12. Critical Micellar Concentration

Aim:Determination of Critical Micellar Concentration (CMC) by conductivity method.

Principle: Surfactants or surface - active agents are organic molecules such as sodium lauryl sulphate or detergents which lower the surface tension of water. In water such molecules slowly o cm3 upy the surface completely and form a micelle with hydrophobic tail inside away from water and the hydrophilic head towards water. A minimum concentration of the surfactant is required to form the micelle. The minimum surfactant concentration at which micelle formation begins is known as critical micellar concentration. At the point of formation of micelle the conductance suffers a sudden change which so far changed regularly with concentration of the surface active agent. Thus by measuring the conductance CMC value can be estimated.

Procedure:Part A: Determination of cell constant:

A solution of 0.1N KCl is prepared by dissolving exactly 0.745g of KCl crystals in distilled water and made up to 100 cm^3 in a standard flask. The conductivity cell is dipped in the KCl solution taken in a beaker and the two leads from the cell are inserted in the respective slots provided at the back of the conductometer. The conductometer is switched on and the temperature knob is set for the room temperature. The knob corresponding to the conductivity range is placed in 20mS position. The pointer knob indicating 'check/cond/cell constant' is kept in the 'cell constant' position. Now the calibration knob at the back is slowly rotated to read the cell constant display as 1.000. The pointer knob is now moved to 'cond' position and the calibration knob in front is slowly rotated to read the display a 12.88 mS. The pointer knob is now moved to 'check' position and the cell constant displayed is recorded.

Part B:Measurement of conductance: A standard solution (0.05M) of sodium lauryl sulphate is prepared by dissolving 7.2095g in 500 cm^3 of the solution. Exactly 50 cm^3 of this solution is pipetted out in to a clean and dry beaker. The conductivity cell is rinsed in distilled water, wiped dry using a filter paper and dipped in the solution. The pointer knob is moved to 'cond' position and conductance displayed is noted selecting a suitable range. By diluting the above solution with distilled water the solutions of concentrations, namely 0.025 M, 0.0125M, 0.00625M, 0.003125M etc. are prepared and their conductivities are measured. The values of specific conductance for all the solutions are calculated. A graph of k Vs c is plotted at the corresponding point of sudden change in value of specific conductance is determined which gives the CMC of the surfactant.

Result: Critical micellar concentration for sodium lauryl sulphate is ………………

Observations and Calculations:

1. Turn on the computer and monitor. Once the computer has been booted, thesystem software will automatically display the Windows Program Managerserver.

2. Click on '**Start**', shown on bottom left corner of screen, and then clic on'**Programs**', followed by '**CS-1090**" and finally on "**CV**", which will open thecyclic voltammetry software (described in menu as cyclic stiarcase voltammetry).

3. An empty graphics screen will be seen, providing a plotting area similar to that ofan X-Y recorder. At the top of the screen, a menu bar will display the names ofthe various menus, eg., **File**, **Setup**, **Display**,**Date**, **Simulation** and **Help**.

4. Change the screen display by going to the **Setup** menu and then to **Screen**. Thiscommand allows the selection of the background, as well as the displayconvention, of the screen. Change the background from 'normal background' to'zeroline', and change the display convention from 'polarographi cm3 onvention' to'IUPAC convention'. Also under the **Setup** menu, choose **System.** Set **CellStatus**

After Run to Cell OFF, Dummy Cell at Initial Potential.

5. Again in the **Setup** menu, choose Parameters. Set the values in the dialogue boxas follows (Do not press 'enter'key until all parameters are selected.) Initial potential (mV) +500, Forward potential(mV)-0

Reverse potential (mV) 0, Final potential (mV) +500, Scan rate (mV/s) 50, Current range (uA) eg., 10

Setting up BAS System (carried out by TA while demonstrating to the students)

1. Turn on the computer, the monitor and the potentiostat. Once the computer hasbeen booted, the system software will automatically display the WindowsProgram Manager server.

2. Click on the **Epsilon EC** icon shown on the desktop to open the cyclicvoltammetry software.

3. Select GRAPH-DISPLAYCHANGE DISPLAY TYPE, IUPAC, GRID. ZERP-LINE, APPLY.

4. Select EXPERIMENT, and then:SELECT NEW EXPERIMENT-CYCLIC VOLTAMMETRY INITIAL POTENTIAL (500 mV)

\# OF SEGMENTS (2)

SWITCHING POTENTIAL 1 (0 mV)

SCAN RATE (50mV per second)(switching potential 2 - not used)

QUIET TIME (12 seconds)

FINAL POTENTIAL (500 mV)

FULL SCALE (10 µA)

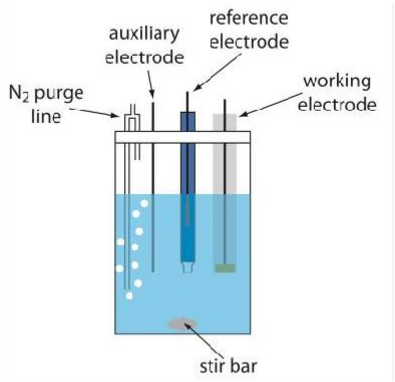
APPLY EXIT

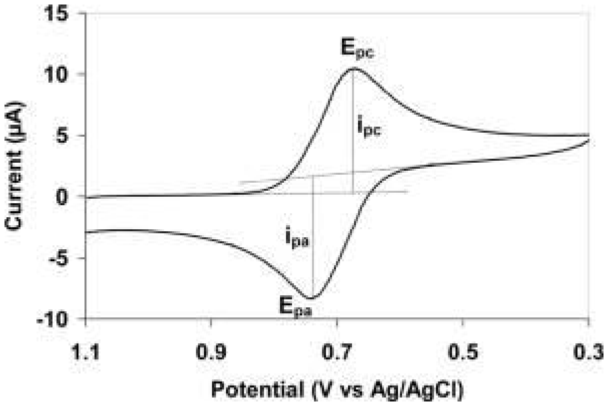
5. To run a CV select:EXPERIMENT, RUN (F5), After the run is complete, set the display, GRAPH-DISPLAY/ Manual Display- Set Y-upper and Y-lower to the same magnitude, with valueschosen to maximize the peak currents.Your extrapolated baseline.

(Note: Do not use peak currents provided by the instrument. You will have far more a cm3 urate results if you draw your own baseline and establish your own peak currents.)

The x-intercept of this plot is -1 x the number of moles of unknown in the solutions you analyzed. Determine the concentration of ferricyanide in the 50.00 mL of unknown, solution you prepared from the original. (Unknown concentration range should be 0.08 to 0.12 M.)

Trial No.	E-(Potential)mV	i(Current)mA	Peak potential anodic-E_{pa} (mV)	Peak potential cathodic-E_{pc}(mA)





Average value of formal red-ox potential = $E^o = (E_{pa} + E_{pc})/2$

EXPERIMENT: 13

CYCLIC VOLTAMMETRY ANALYSIS OF IRON

Aim: **DETERMINATION OF OXIDATION AND REDUCTION POTENTIAL OF $K_4Fe(CN)_6$/ $K_3Fe(CN)_6$ SYSTEM BY CYCLIC VOLTAMETRY**

Principle: Cyclic voltammetry (CV) is a very versatile electroanalytical technique, used forthe study and analysis of electroactive species like a redox reaction of iron is often represented as: Fe^{3+}(aq)+e^-→Fe^{2+}(aq),During a CV experiment, the current which flows between two electrodes (the working and counter electrodes) is plotted on the y- axis, and the potential of the electrode of interest vs a reference electrode potential, is plotted on the x-axis.The resulting plot is called a cyclic voltammogram (also referred to as a CV), the potential of the peaks,or the pote-ntial half-way between peaks can be related to the identity of the analyte through its Eo value.

Solutions and electrodes: 1. SupportingElectrolyte: 0.2 M KCl solution. 2. Standard $K_3Fe(CN)_6$ solution: A cm3 urately weigh out 1.6 g of $K_3Fe(CN)_6$(0.1M) and dilute to volume with 0.2 M KCl in a 50.00 mL.volumetric flask.2. Sample: Dilute to 50.00 mL with 0.2 M KCl Potassium ferricyanide stock solution. 3. Potassium- ferricyanide standard solutions: The above 0.1M pot.ferricyanide stock solution is used to prepare 25ml solutions of 0.02, 0.04, 0.06, 0.08M$K_3Fe(CN)_6$. Use the 0.2M KClto make all of the dilutions.4. Working electrode: Pt. wire. of area 1cm^2 as anode. 5. Counter/auxilliary electrode: High area Pt-guaze electrode as cathode. 6. Reference electrode: Ag/AgCl electrode or saturated Calomel electrode.

Procedure:Pipette out 10ml of 0.1M ferricyanide solution into the electrolytic cell.To ensure reproducible results, the platinum working electrode may need to be polished with alumina polishing powder on a moist polishing pad prior to the experiment. Use a figure-eight motion and polish for a few seconds. Sonicate the electrode in DI water for 30 seconds, and then rinse with DI water. Fill the reference electrode compartment with 0.2 M KCl supporting electrolyte solution. Tip the cell sideways with the Luggin capillary up and apply air pressure to force the electrolyte through the porous frit and displace any air from the Luggin capillary. Remove any excess supporting electrolyte solution from the working electrode compartment. Then pipette in 5.00 mL of supporting electrolyte. (The dilution factor in this experiment is small, so the exact volume in the cell is not especially critical.) Then,with an Eppendorf pipet, add 50 µL of your unknown solution to the cell. Use a Pasteur pipet to mix the solution. Insert a silver wire in the reference electrode compartment. Connect the reference and counter electrodes to the potentiostat, and insert the working electrode. The initial potential should be set to +0.5 Volts, and the switching potential to 0 V. Set the instrument to run a single scan at a scan rate of 50 mV per second, and set the current range to 10 µA. Turn the cell on and initiate the scan. When the scan is complete, turn the cell off and remove the working electrode.

Manually scale your voltammogram using manual zoom (Epsilon BAS system) or KBD zoom (Cypress Systems) and obtain a printout. You will use this background voltammogram to determine the backgroundcurrents underlying the peak currents found in subsequent voltammograms.

Repeat this procedure after having added 3 su cm3 essive standard additions of 50 µL each

of 0.10 M $K_3Fe(CN)_6$. For these voltammograms, you may need to use a larger current range (100 µA). For each voltammogram, extrapolate a baseline under the cathodic peak, and determine the peak current as indicated in diagram. The formal redox potential is calculated using the graph values $E^o = (E_{pa} + E_{pc})/2$; where E_{pa} andE_{pc} are the anodic and cathodic peak potentials.

Result:

The red-ox potential of potassium ferricyanide/ferrocyanide system is...........V.