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KARPAGAM ACADEMY OF HIGHER EDUCATION

(Deemed University Established Under Section 3 of UGC Act 1956)
COIMBATORE-21
DEPARTMENT OF CHEMISTRY
B.Sc Chemistry

16CHU411 ELECTROCHEMISTRY PRACTICAL 4H 2C

Instruction Hours/week:L:0 T:0 P:4 Marks: Internal: 40 External: 60 Total:100

Scope

This lab course deals with conductometric and chemical kinetics experiments

Programme Outcome

It enable the students to apply their knowledge in laboratory experiments like

1. Measurment of conductance
2. To determine cell constant, molar conductivity,degree of dissociation

Programme learning Outcome:

1. Students attained knowledge to determine cell constant.
2. Students know to perform Conductometric titrations
3. Students got the knowledge in chemical kinetics experiment.

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Methodology

Measurements with conductivity meters, reaction rate measurements

Conductometry:

I. Determination of cell constant

II. Determination of conductivity, molar conductivity, degree of dissociation and dissociation constant of a weak acid.

III. Perform the following conductometric titrations: i. Strong acid vs. strong base ii. Weak acid vs. strong base iii. Mixture of strong acid and weak acid vs. strong base iv. Strong acid vs. weak base

Chemical Kinetics:

IV. Study the kinetics of the following reactions.

1. Iodide-persulphate reaction (i) Initial rate method; (ii)Integrated rate method
2. Acid hydrolysis of methyl acetate with hydrochloric acid.
3. Saponification of ethyl acetate.
4. Comparison of the strengths of HCl and H_2SO_4 by studying kinetics of hydrolysis of methyl acetate.

Suggested Readings
Text Books:

1. Khosla, B. D., Garg, V. C. & Gulati, A. (2011). *Senior Practical Physical Chemistry*. New Delhi: R. Chand & Co.

2. V.Venkateswaran, R.Veeraswamy and A.R.Kulandaivelu “Basic principles of practical chemistry’’ Sultan Chand and Sons, 23, Daryaganj.New Delhi-110002

ELECTROCHEMISTRY LAB MANUAL

COMMON TO UG AND PG STUDENTS

CONTENTS

CONDUCTOMETRIC EXPERIMENTS

Experiment No 1

Determination of cell constant by conductometry

Aim

To determine the cell constant(s) of the given conductivity cell(s)

Principle:

The specific conductivity of a solution is given by

$$k=\frac{l}{a}\times\frac{1}{R}$$

k=cell constant x conductivity

Where l/a is called the cell constant of the conductivity cell. It is the ratio of the distance between the electrodes and the area of the electrodes. R is the resistance offered by the solution in ohms. Using a solution of known specific conductance, the cell constant is found out from the resistance measured in the conductivity bridge.

Materials Required

(i)Potassium chloride(analar)

(ii)Conductivity cell(s)

(iii)Conductivity bridge

(iv)Conductivity water

(v)Beaker(corning or borosil)100 ml

(vi)Connecting wires.

Procedure

Exactly N/10 Potassium chloride solution is prepared by accurately weighing out of 1.864 g of KCl of AR quality in an analytical balance and transfer it into a 250 ml standard flask. The solution is made upto the mark using freshly prepared conductivity water and thoroughly shaken to get a homogeneous solution. KCl solution thus prepared is taken in a 100 ml beaker such that the electrodes are completely immersed in the solution. The terminals of the cell are connected to a conductivity bridge based on wheatstone bridge principle.The resistance is so adjusted as to get a large band in the bridge. In the case of headphone arrangement, the known resistance is altered until a minimum sound is hear, when the jockey is kept at the mid-point of the sliding wire. As the resistance and specific conductance of N/10 KCl are known, the cell constant of the conductivity cell is calculated.

Result:

The cell constant of the given conductivity cell(s)

(i)----------------------------cm^{-1}

(ii)---------------------------cm^{-1}

Observations and calculations

The resistance of N/10 KCl solution measured= ohms

The specific conductance of N/10 KCl solution= ohm^{-1} cm^{-1}

The specific conductivity(k)= cell constant x conductivity

$$k=\frac{l}{a}x\frac{1}{R}$$

cell constant=Resistancexspecific conductivity of N/10 KCl

Cell constant=

= cm^{-1}

Experiment No 2

Determination of Dissociation constant of a weak acid

Aim

To determine the equivalent conductance of a weak electrolyte at various concentrations, its dissociation constant and to verify ostwald's law.

Principle

The equivalent conductance is the product of observed specific conductance and the volume in ml containing one gram equivalent of the electrolytes. The equivalent conductance of strong electrolytes do not vary much with concentration. In the case of weak electrolytes, equivalent conductance increases and specific conductance decreases with dilution. The equivalent conductance of the weak electrolyte at different concentrations is determined by measuring the resistance of these solutions. A plot of $\wedge_c$ vs $\sqrt{C}$ will result in a parabola.

The degree of dissociation of the electrolyte at different concentrations can be obtained from the equation.

$A=\frac{\wedge c}{\wedge 0}$ where $\wedge_0$ is the equivalent conductance of the weak electrolyte at infinite dilution.

The dissociation constant of a weak electrolyte is given by ostwald's dilution law,

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

By knowing the values of C, α,k_a is determined.

Materials required

(i)Analar KCl

(ii)N/10 acetic acid

(iii)Conductivity bridge

(iv)Conductivity cell

(v)Conductivity water

(vi)Burette, pipette, glass rod

(vii)Standard flasks(100 ml) 4 or 5 Nos

Procedure

Exactly N/10 KCl solution is prepared and its resistance is measured. From this value, the cell constant of the given conductivity cell is calculated.

A 0.1 N solution of a weak electrolyte, say acetic acid is prepared using conductivity water and its exact strength is determined by titrating it against standard sodium hydroxide solution using phenolphthalein indicator. From this stock solution, exactly 0.0025 N, 0.005 N, 0.01 N, 0.02 N, etc, solutions are prepared using conductivity water. Each solution is then taken in a beaker and the conductivity cell whose cell constant is determined previously is dipped into it. The resistance of the solution is measured by using conductivity bridge.

From the measured resistance and cell constant, the specific conductance and hence equivalent conductance of each solution is calculated. Using the equivalent conductance at infinite dilution of acetic acid, the degree of dissociation is calculated at different concentrations. The dissociation constant of the weak acid is calculated using Ostwald's dilution law.

Result:

The dissociation constant of the weak electrolyte k_a=----------------------

Observations and calculations

S.No	Concentration	Resistance ohms	k= $\frac{l}{R}$ xcell constant	$\wedge_0=\frac{1000XK}{c}$	A=$\frac{\wedge c}{\wedge 0}$	$K_a=\frac{C\alpha 2}{1-\alpha}$

$\sqrt{C}$	Λ_C

Experiment No 3

Conductometric titrations

Aim:

To determine the strength and amount of strong or weak acid by Conductometric titration.

Principle:

The principle of conductometric titration is based on the fact that during the titration, one of the ions is replaced by the other and invariably these two ions differ in the ionic conductivity with the result that conductivity of the solution varies during the course of titration. The equivalence point may be located graphically by plotting the change in conductance as a function of the volume of titrant added. In order to reduce the influence of errors in the conductometric titration to a minimum, the angle between the two branches of the titration curve should be as small as possible. If the angle is very obtuse, a small error in the conductance data can cause a large deviation.

The smaller the conductivity of the ion which replaces the reacting ion, the more accurate will be the result. Thus it is preferable to titrate a silver salt with lithium chloride rather than with HCl. Generally, cations should be titrated with lithium salts and anions with acetates as these ions have low conductivity

The larger the conductivity of the anion of the reagent which reacts with the cation to be determined, or vice versa, the more acute is the angle of titration curve.The titration of a slightly ionized salt does not give good results, since the conductivity increases continuously from the commencement. Hence, the salt present in the cell should be virtually completely dissociated; for a similar reason; the added reagent should also be as strong electrolyte.

Materials Required:

(i)Strong acid(HCl)

(ii)Weak acid(CH_3COOH)

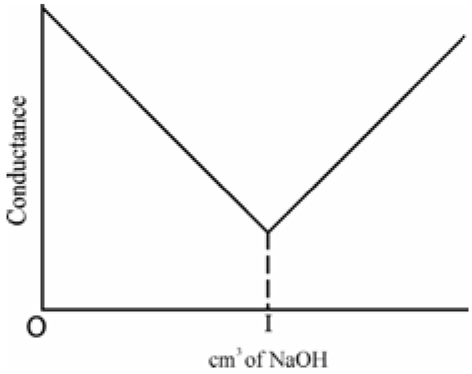
(iii)Strong base(NaOH)

(iv)Weak base(NH_4OH)

Procedure

1. **Strong Acid with a Strong Base**, e.g. HCl with NaOH: Before NaOH is added, the conductance is high due to the presence of highly mobile hydrogen ions. When the base is added, the conductance falls due to the replacement of hydrogen ions by the added cation as H+ ions react with OH − ions to form undissociated water. This decrease in the conductance continues till the equivalence point. At the equivalence point, the solution contains only NaCl. After the equivalence point, the conductance increases due to the large conductivity of OH ions

Conductometric titration of a strong acid (HCl) vs. a strong base (NaOH)



S.No	Volume of NaOH	Conductance

Volume of NaOH solution (V_1) = ……ml
Strength of NaOH solution (N_1) = 0.1 N
Volume of strong acid (HCl)(V_2) = 20 ml

Strength of strong acid (HCl)(N_2) $= \frac{V_1 N_1}{V_2}$

$= \ldots\ldots$ N

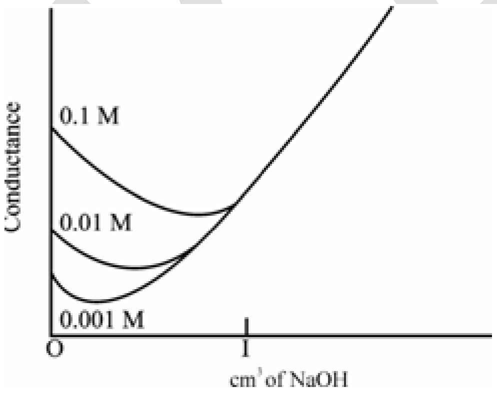
Amount of strong acid present in the whole of the given solution: $\frac{Normality \times Eq.wt}{20}$ **= ……… g**

Result

(i) The strength of the given acid was found to be = ……… N
(ii) The amount of acid present in the whole of the given solution=…g

2. **Weak Acid with a Strong Base**, e.g. acetic acid with NaOH: Initially the conductance is low due to the feeble ionization of acetic acid. On the addition of base, there is decrease in conductance not only due to the replacement of H^+ by Na^+ but also suppresses the dissociation of acetic acid due to common ion acetate. But very soon, the conductance increases on adding NaOH as NaOH neutralizes the un-dissociated CH_3COOH to CH_3COONa which is the strong electrolyte. This increase in conductance continues raise up to the equivalence point. The graph near the equivalence point is curved due the hydrolysis of salt CH_3COONa. Beyond the equivalence point, conductance increases more rapidly with the addition of NaOH due to the highly conducting OH^- ions

Conductometric titration of a weak acid (acetic acid) vs. a strong base (NaOH)



S.No	Volume of NaOH	Conductance

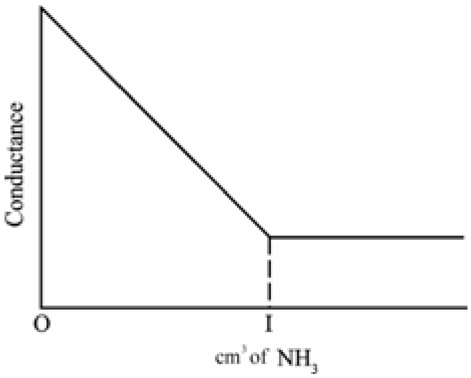
Volume of NaOH solution (V_1) = ……ml
Strength of NaOH solution (N_1) = 0.1 N
Volume of weak acid (CH_3COOH)(V_2) = 20 ml
Strength of weak acid (CH_3COOH)(N_2) = $\frac{V_1N_1}{V_2}$
= …… N

Amount of weak acid present in the whole of the given solution: $\frac{Normality \times Eq.wt}{20}$ = **………. g**

Result

(i) The strength of the given acid was found to be = ……… N
(ii) The amount of acid present in the whole of the given solution=…g

3. **Strong Acid with a Weak Base**, e.g. sulphuric acid with dilute ammonia: Initially the conductance is high and then it decreases due to the replacement of H $^+$. But after the endpoint has been reached the graph becomes almost horizontal, since the excess aqueous ammonia is not appreciably ionised in the presence of ammonium sulphate
   Conductometric titration of a strong acid (H_2SO_4) vs. a weak base (NH_4OH)



S.No	Volume of H_2SO_4	Conductance

Volume of H_2SO_4 solution (V_1) = ……ml
Strength of H_2SO_4 solution (N_1) = 0.1 N
Volume of weak base (NH_4OH)(V_2) = 20 ml
Strength of weak base (NH_4OH)(N_2) $= \frac{V_1 N_1}{V_2}$
= …… N

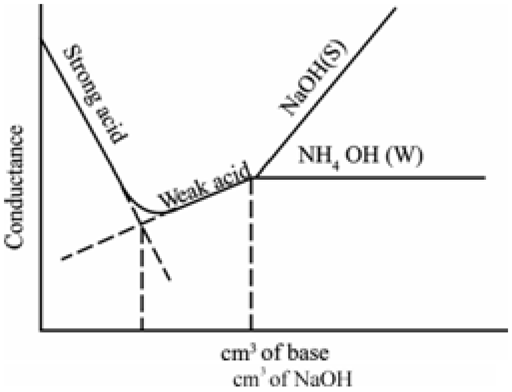
Amount of strong acid present in the whole of the given solution: $\frac{Normality \times Eq.wt}{20}$ = **……… g**

Result

(i) The strength of the given acid was found to be = ……… N
(ii) The amount of acid present in the whole of the given solution=…g

4. **Mixture of a Strong Acid and a Weak Acid vs. a Strong Base or a Weak Base**: In this curve there are two break points. The first break point corresponds to the neutralization of strong

acid. When the strong acid has been completely neutralized only then the weak acid starts neutralizing. The second break point corresponds to the neutralization of weak acid and after that the conductance increases due to the excess of OH − ions in case of a strong base as the titrant.



Conductometric titration of a mixture of a strong acid (HCl) and a weak acid (CH_3COOH) vs. a strong base (NaOH) or a weak base (NH_4OH)

S.No	Volume of NaOH	Conductance

Volume of NaOH solution (V_1) = ……ml
Strength of NaOH solution (N_1) = 0.1 N
Volume of strong acid (HCl)(V_2) = 20 ml
Strength of strong acid (HCl)(N_2) $= \frac{V_1 N_1}{V_2}$
= …… N

Amount of strong acid present in the whole of the given solution: $\frac{Normality \times Eq.wt}{10}$ = **………** g

Volume of NaOH solution (V_1) = ……ml
Strength of NaOH solution ($N_{1)}$ = 0.1 N
Volume of weak acid (CH_3COOH)(V_2) = 20 ml
Strength of weak acid (CH_3COOH)(N_2) = $\frac{V_1N_1}{V_2}$
= …… N

Amount of weak acid present in the whole of the given solution: $\frac{Normality \times Eq.wt}{10}$ = **……….**

Result

(i) The strength of the given acid(HCl) was found to be = ……… N
(ii) The amount of acid(HCl) present in the whole of the given solution=…g
(iii) The strength of the given acid (CH_3COOH)was found to be = ……… N
(iv) The amount of acid (CH_3COOH)present in the whole of the given solution=…g

KINETIC EXPERIMENTS

Experiment No 4

Reaction kinetics of Potassium Iodide and Potassium Persulphate

Aim

To determine the rate of the reaction between KI and potassium persulphate (Reaction kinetics of potassium iodide and potassium persulphate)

Principle

The reaction between potassium super sulphate and KI is represented as

$$K_2S_2O_8 + 2KI \rightarrow 2K_2SO_4 + I_2$$

The rate of the reaction was determined by the change in concentration of both the reactant. Hence it is a reaction of II order. The progress of reaction can be followed by titrating the I_2 liberated Vs Std thio sulphate solution from time to time. The titratte values are proportional to the concentration of I_2 formed and hence the amount of reactant which have disappeared due to the reaction. In other words the titre values are proportional to the value of 'x' at different time intervals. The rate constants of the reaction is given by

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

Provided the concentration of both KI and $K_2S_2O_8$ at the same initially being equal to 'a' gm moles/litre.

Materials required

(i) Conical flask with cork,
(ii) beaker,
(iii) burette,
(iv) pipette,
(v) thermostat and water bath,
(vi) Potassium iodide,
(vii) Potassium persulphate and stop watch.

Procedure

50 ml of exactly 0.1 M $K_2S_2O_8$ and 50 ml of exactly 0.1 M KI were burette out separately into a clean and dry 250 ml conical flask loosely corked and placed in a thermostat at a room temperature. After the solutions in the conical flask added attain the temperature of the bath of I_2 solution was quickly poured into per sulphate solution and simultaneously a stop watch was started. The mixture was shaken well and immediately 5 ml of the reaction mixture was withdrawn and run into ice cold water to arrest further reaction. The time in the stop watch was

noted, when the pipette was half empty and quickly titrated against N/100 $NaHSO_3$ solution using starch as indicator. The first complete disappearance of blue colour was marked at the end point. A blue colour may be appear if the reaction is not completely suppressed and it should be disregarded.

All regular intervals of 5 minutes, 5 ml of the reaction mixture was withdrawn and titrated against the same sodium thio sulphate. The titrations were carried out at regular intervals for a duration of 1 hour. Pipetted out 2.5 ml of $K_2S_2O_8$ and 2.5 ml water were added into a clean conical flask and then 5 ml of 10 % KI was added and titrated against sodium thio sulphate.

The titrate values were proportional to the initial concentration of $K_2S_2O_8$ and KI. The rate constant of the reaction was determined using the equation

$$K = \frac{1}{t}\,\frac{x}{a(a-x)}$$

The constancy of the value of K proved that the reaction under consideration is of II order. A graph was plotted by taking $\frac{1}{a-x}$ against a straight line was obtained. The slope of the straight line was equal to K, rate constant.

Observations and calculations

Volume of 0.1 N $K_2S_2O_8$ taken = ------ ml
Volume of KI reaction = ----- ml
Volume reaction mixture pipetted out = ----- ml
Initial concentration = -----ml

Time in sec	Volume of N/100 thio x in ml	1/a-x	$K = \frac{1}{t}\frac{x}{a(a-x)}$ Mol^{-1}lit sec^{-1}

Mean =

From graph

$\frac{dy}{dx}$ = ------ mol^{-1}lit sec^{-1}

Time in sec	Volume of N/10 thio in cc (x)	1/a-x	$K = \frac{1}{t}\frac{x}{a(a-x)}$ Mol^{-1}lit sec^{-1}

Mean =

From graph

dy/dx = ----- mol^{-1}lit sec^{-1}

Calculations

$\frac{K_A}{K_B}$ = --------

$\frac{K_A}{K_B} = \frac{C_A}{C_B}$ = ------N

Result

(1) The rate constant of the reaction between KI and $K_2S_2O_8$ (K_A) was found to be

- a) Calculated value = --------mol^{-1}lit sec^{-1}
- b) Graphical value = -------- mol^{-1}lit sec^{-1}

(2) The rate constant of the reaction between KI and $K_2S_2O_8$ (K_B) was found to be

- a) Calculated value = ------- mol^{-1}lit sec^{-1}
- b) Graphical value = -------- mol^{-1}lit sec^{-1}

(3) Concentration of the unknown solution = -------- N

Experiment No 5

Hydrolysis of Ester catalyzed by acid evaluation of Arrhenius parameter.

Aim

To determine the velocity constant for the hydrolysis of the given ester catalyzed by acid at room temperature using kinetic method and is determined as Arrhenius parameters.

Principle

The hydrolysis of ethyl acetate by dilute acid is an example of I order reaction.

$$CH_3COOC_2H_5 + H_2O \overset{H^+}{\leftrightarrow} CH_3COOH + C_2H_5OH$$

In this reaction one of the reactants namely water is present in large excess hence its concentration is taken as constant.

Materials required

(i) Conical flask with cork,
(ii) beaker,
(iii) burette,
(iv) pipette,
(v) thermostat and water bath,
(vi) 0.5 N HCl, 0.1 N NaOH, ethyl acetate and
(vii) Stop watch.

Procedure

100 ml of hydrochloric acid and 20 ml of ester were separately placed in a stoppered conical flask in constant temperature bath at room temperature. After both the solution had attained equilibrium which required about 20 minutes and 10 ml of ester was pipetted out into the acid. When half of the ester was added stop watch was started. The flask was shaken well and immediately 5 ml of solution was pipetted out into ice cold water contained in another conical flask to arrest further reaction. The chilled solution was titrated against 0.1 N NaOH using phenolphthalein indicator and the titre value V_0 is noted. Similarly 5ml of the reaction mixture was withdrawn at regular intervals of time and titrated against the same NaOH after freezing the mixture. The titre value gives the value of V_t at an interval of time ‘t’.

To obtain the titre value after the completion of the reaction remaining mixture was heated in a water bath with mouth of conical flask closed loosely for 1 hour at about 60 – 70 °C. It was then cooled and 5 ml of the solution was titrated against the same NaOH. The reading gave the value of V_∞. The velocity constant was calculated using the formula

$$k = \frac{2.303}{t}\log\left[\frac{V_\infty - V_0}{V_\infty - V_t}\right]$$

A graph was drawn by taking the value of log $V_\infty - V_t$ along the Y-axis and time‘t’ along the X-axis. The slope of the straight line obtained gave the value of k/2.303.

The value of k proved that the hydrolysis reaction was a I order reaction. Repeat the experiment at 5 different temperatures a graph was drawn by plotting log k values Vs V_t. The slope of the straight line obtained gave the value of Ea/2.303R. The value of Ea was calculated graphically from the slope of the straight line. The intercept of the straight line with Y-axis gave the value of A.

Observations and calculations

Volume of ethyl acetate added = 10 ml
Volume of HCl added = 100 ml
Volume of reaction mixture pipetted out = 5 ml
Temperature =23 °C

V_0 = --------- ml **V_∞ = ------ ml** **V_∞ - V_0 = ---------- ml**

Time in sec	**V_t (ml)**	**V_∞ - V_t (ml)**	**log (V_∞ - V_t) (ml)**	$k = \frac{2.303}{t}\log\left[\frac{V_\infty - V_0}{V_\infty - V_t}\right]$ **sec^{-1}**

Mean =

Volume of ethyl acetate added = 10 ml
Volume of HCl added = 100 ml
Volume of reaction mixture pipetted out = 5 ml
Temperature = 35 °C

V_0 = ---- ml V_∞ = ------ ml $V_\infty - V_0$ = ------- ml

Time in sec	V_t (ml)	$V_\infty - V_t$ (ml)	log ($V_\infty - V_t$) (ml)	$k = \frac{2.303}{t} \log \left[\frac{V_\infty - V_0}{V_\infty - V_t}\right]$ sec^{-1}

Mean =

Volume of ethyl acetate added = 10 ml
Volume of HCl added = 100 ml
Volume of reaction mixture pipetted out = 5 ml

Temperature = 45 °C

V_0 = -------- ml V_∞ = ------ ml $V_\infty - V_0$ = ------ ml

Time in sec	V_t (ml)	$V_\infty - V_t$ (ml)	log ($V_\infty - V_t$) (ml)	$k = \frac{2.303}{t} \log \left[\frac{V_\infty - V_0}{V_\infty - V_t}\right]$ sec^{-1}

Mean =

Graphical method

At 27 °C (room temperature)
Slope = dy/dx
$K = 2.303 \times slope$
K = ------sec^{-1}

Temperature in K	Rate constant	Log k	Log k/T	1/T m k^{-1}*10^{-3}

	k (sec^{-1})			

Mean =

From log k Vs 1/T

$$E_A = \text{Slope} \times 2.303 \times 8.314 = \text{KJmol}^{-1}$$

$$= \frac{\Delta H}{2.303R}$$

$$= Slope \times 2.303 \times R \times 10^3$$

=------- KJmol^{-1}.

$$Y_{intercept} = \log\left(\frac{K_B}{h}\right) + \frac{\Delta S^0}{2.303R}$$

$$\frac{-\Delta S}{2.303R} = \log\left(\frac{K_B}{h}\right) - Y_{Intercept}$$

$$\frac{-\Delta S}{2.303R} = 9.4288$$

ΔS = ------- J/mol^{-1}.

$$\text{Log}\,K = \frac{E_A}{2.303RT}$$

$$\log {K_2}/{K_1} = \frac{E_A}{2.303R}\left[\frac{1}{308} - \frac{1}{318}\right]$$

E_A = -------

Result

(1) Activation energy E_A
  a) Experimental value = ------ KJ mol^{-1}
  b) Graphical Value = ------ KJmol^{-1}
(2) Entropy change ΔS^* = ------- Jmol^{-1}
(3) Enthalpy change ΔH^* = ------KJ mol^{-1}
(4) Frequency factor = -------KJ mol^{-1}.

Experiment No 6

Determination of the velocity of the saponification of Ethyl Acetate

Aim

To determine the velocity constant of the hydrolysis of ethyl acetate using sodium hydrate.

Principle

The reaction between ethyl acetate and alkali takes place as follows

$$CH_3COOC_2H_5 + NaOH \rightarrow CH_3COONa + C_2H_5OH$$

There not only concentration of ester but the concentration of alkali also changes during the course of the reaction. The velocity of the reaction depends on the concentration of both the reactants and hence the reaction is of second order. On this respect, the saponification reaction different from the hydrolysis of ester by acid. Because in the later case the concentration of hydrogen ions remain unchanged during the course of the reaction and so the reaction of first order. The rate constant of second order reaction is given by

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

Where a and b the initial concentration of alkali and ester respectively, after the time. The course of the reaction is followed by remaining a definite quantity of a reaction mixture from time to time and running into excess of acid. The unused acid is titrated against standard alkali using phenolphthalein as indicator.

Materials required

- (i) Conical flask with cork
- (ii) Beaker, burette
- (iii) Pipette
- (iv) Thermostat and water bath
- (v) 0.04 N HCl, 0.04 N NaOH, ethyl acetate and
- (vi) Stop watch.

Procedure

The solutions of 0.01 N ethyl acetate were prepared and 50 ml of each was transferred to a separate conical flask. The solutions were kept in a water bath at room temperature. When the solution had attained a temperature of the bath, the alkali was poured rapidly into ester and stop watch was started. Then all the alkali was poured into the ester and 10 ml of the reaction mixture was pipetted out into a conical flask, containing 20 ml of 0.04 HCl to arrest the reaction ice cold water was added. The excess of acid was titrated with 0.04 N NaOH with phenolphthalein indicator. The titrate value is V_0 ml. The titrations are repeated at regular intervals of 10 min up to one hour each time withdrawing 10 ml of the reaction mixture and running into 20 ml of same 0.04 N HCl. The remaining solution was taken in a loosely corked conical flask and heated for an hour at 60 °C. It is then cooled and 10 ml of the mixture was run into a 20 m of 0.04 N HCl and titrated against same NaOH. The titer value corresponds to infinite reading (V_∞). A blank titration was carried out between 20 ml of 0.04 N HCl and 0.04N NaOH. The titrated value corresponds to 'b'. The initial concentration of alkali and ester was taken as 'a' and 'b'. In after time't', x moles of alkali and ester has reacted then (a-x) and (b-x) would be concentration of alkali and ester after 't' seconds. Also 'a' is proportional to $V-V_t$, that is the volume of NaOH required for 20 ml of 0.04 N HCl. V_0 is the initial titrate value and V_t is tt he titrate value after 't' seconds. Hence rate constants of the reaction K is

$$k = \frac{2.303}{(a-b)t}\log\frac{(V_\infty - V_0)(V - V_t)}{(V_\infty - V_t)(V - V_0)}$$

The plot was made between time and

$$\log\frac{(V_\infty - V_0)(V - V_t)}{(V_\infty - V_t)(V - V_0)}$$

The slope of the curve gives the value of $\frac{K(V-V_\infty)}{2.303}$ from which the value of k can be calculated.

Observations and calculations

No	Time in sec	Volume of NaOH (ml)	$\log\frac{(V_\infty - V_0)(V - V_t)}{(V_\infty - V_t)(V - V_0)}$	$k = \frac{2.303}{(a-b)t}\log\frac{(V_\infty - V_0)(V - V_t)}{(V_\infty - V_t)(V - V_0)}$

Mean =

Concentration of alkali = 0.02 N
Concentration of ester = 0.01 N
V_0 = ------- ml V = ------- ml V_∞ = --------- ml
$V_\infty - V_0$ = -------ml $V - V_0$ = ------- ml
Slope = dy/dx

$$Slope = \frac{K(a-b)}{2.303}$$

$$K = \frac{slope \times 2.303}{a-b}$$

K = -------mol $l^{-1}sec^{-1}$.

Result

The rate constant for the hydrolysis of ethyl acetate using NaOH at room temperature
(1) Calculated value = 0.0214 mol l^{-1} s^{-1} = -------10^{-2} mol l^{-1} s^{-1}

(2) Graphical value = 0.0237 mol l^{-1} s^{-1} = --------10^{-2} mol l^{-1} s^{-1}