KARPAGAM ACADEMY OF HIGHER EDUCATION

(*Deemed to be University*)

(*Established Under Section 3 of UGC Act, 1956*)

Pollachi Main Road, Eachanari Post, Coimbatore –641 021.

Syllabus

M.Sc. Chemistry **2018-2019**

Semester-III

18CHP312 PHYSICAL CHEMISTRY PRACTICAL- II 4H 2C

(CHEMICAL KINETICS AND POTENTIOMETRIC TITRATIONS)

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

External Semester Exam: 6 Hours

Course Objectives

On successful completion of the course the students should have

1. Learnt about the principles of electrochemistry and determination EMF
2. Learnt about Chemical Kinetics and Potentiometric titrations.
3. Learnt the Principles of Adsorption experiments.

Course Outcomes

The student understood

1. To apply the principles of electrochemistry and determination electrochemical properties.
2. To carryout experiments in Chemical Kinetics and Potentiometric titrations.
3. The Principles of Adsorption experiments.

Contents

Electromotive force determination of standard potentials of Cu, Zn and Ag.

Determination of pH and pKa values using hydrogen and quinhydrone electrodes and glass electrode pH meter- potentiometric acid-base titrations.

Determination of formal redox potential of a redox system and redox titrations.

Determination of solubility product of a sparingly soluble salt concentration cell and chemical cell.

Determination of activity co-efficients from emf data.

Precipitation titration of a mixture of halides.

Chemical kinetics:

i. Evaluation of Arrhenius parameters using acid hydrolysis of an ester.

ii. Base catalyzed hydrolysis of an ester conductometrically.

iii. Rate of reaction between persulphate and iodide ions study of salt over the persulphate- iodide reaction.

Evaluation of catalytic constants for weak acids and verification of Bronsted catalysis law.

Adsorption Experiments:
Adsorption of oxalic acid and acetic acid on activated charcoal-Fruendlich isotherm.

SUGGESTED READINGS:

1. Lepse, P. A., & Lyle B. P., (1986). *Lab Manual for Lingren's Essentials of Chemistry*. New Delhi: Prentice Hall.
2. Pandey, O. P, Bajpai, D. N., &Giri, S. (2001). *Practical Chemistry* (VIII Edition). New Delhi: S. Chand Publications.
3. Santi Rajan Palit and Sadhan Kumar, (1971). *Practical Physical Chemistry* (I Edition). Calcutta: Joy Publishers.
4. Siddhiqui, Z. N. (2002). *Practical Industrial Chemistry* (I Edition). New Delhi: Anmol Publications Pvt. Ltd.
5. Thomas, A.O, (2003). *Practical Chemistry*. Cannanore: Scientific Book Center.
6. Venkateswaran, V., Veeraswamy, R., &Kulandaivelu, A. R. (2004). *Basic Principles of Practical Chemistry* (II Edition). New Delhi: S. Chand Publications

KARPAGAM ACADEMY OF HIGHER EDUCATION
(Deemed to be University)
(Established under section of UGC Act, 1956)

DEPARTMNENT OF CHEMISTRY

Name of the Staff	:	**B. PRABHA**
Subject	:	**Physical Chemistry Practical-II**
Subject Code	:	**18CHP312**
Class	:	**II M.Sc-Chemistry**
Year and Semester	:	**II / III**

S.No	NAME OF THE EXPERIMENT
1	***POTENTIOMETRIC TITRATIONS*** Titration of Strong acid Vs Strong Base
2	Titration of Weak acid Vs Strong Base
3	Titration of mixture of acids Vs Strong Base
4	Acid Hydrolysis of an Ester
5	Determination of pK_a of orthophosphoric acid using P^H meter.
6	**KINETIC EXPERIMENTS** Bronsted catalysis law
7	**ADSORPTION EXPERIMENT** Adsorption of oxalic acid on charcoal
8	Adsorption of acetic acid on charcoal
9	Reaction Kinetics of KI & $K_2S_2O_8$

Lab Manual on

Potentiometric Titrations and Chemical Kinetics

DEPARTMNENT OF CHEMISTRY

Enable | Enlighten | Enrich

KARPAGAM

ACADEMY OF HIGHER EDUCATION

(Deemed to be University)

(Established Under Section 3 of UGC Act, 1956)

Name of the Staff	:	**B. PRABHA**
Subject	:	**Physical Chemistry Practical-II**
Subject Code	:	**18CHP312**
Class	:	**II M.Sc-Chemistry**
Year and Semester	:	**II / III**

CONTENTS

POTENTIOMETRIC TITRATIONS

Experiment No 1

ESTIMATION OF HYDROCHLORIC ACID BYPOTENTIOMETRICALLY

Aim

To estimatethe strength and amount of hydrochloric acid present in the given solution (≈ N) using sodium hydroxide by potentiometrically.

Principle

When a strong acid is titrated with a strong base the change of potential at the equivalence point is large and even with accuracy. Thus by measuring potential change when a strong base is added to a strong acid, the strength of the acid can be determined. The concentration H^+ ion at any time is then equal to the concentration of strong acid present at that time. The quinhydroxine electrode is a redox electrode in which the following reversible reaction takes place.

$$C_6H_4O_2 + 2H^+ + 2e^- \leftrightarrows C_6H_4(OH)_2$$

$$Q + 2H + 2e^- \leftrightarrows H_2Q$$

The potential is given by,

$$EQ = E^\circ Q + \frac{RT}{2F} \ln \frac{aH_2Q}{(aH^+)^2 aQ}$$

Where 'a' term represents the activity of the respective species and E° is the standard electrode potential. By saturating solution with quinhydrone which is 1:1 molecular addition compound of quinine and hydroquinone the potential of such electrode is then,

$$EQ = E^\circ Q + \frac{RT}{2F} \ln \left(\frac{1}{aH^+}\right)^2$$

$$EQ = E^\circ Q - \frac{RT}{F} \ln H^+$$

$$= E^\circ Q + \frac{2.303}{F} RT - p^H$$

The electrode therefore used to measure the p^H in the same way as hydrogen electrode.

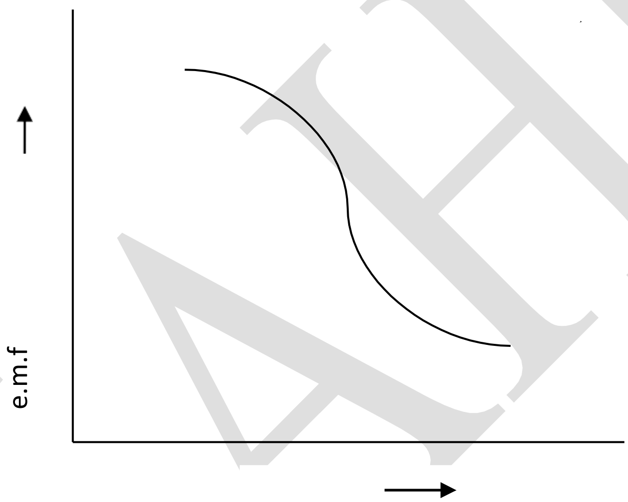
Materials Required

(i) Digital potentiometer
(ii) Calomel electrode
(iii) Platinum electrode
(iv) Quinhydrone
(v) N/10 NaOH

Procedure

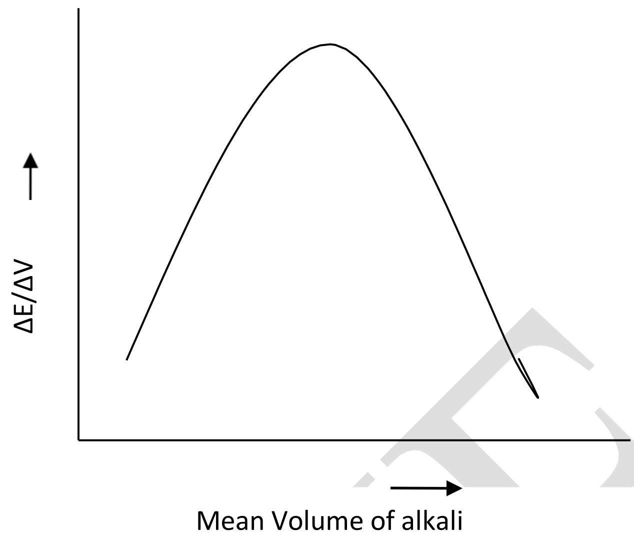
The given solution of HCl is making up to 100 ml in a standard flask. 20 ml of the solution is pipette out into a beaker. Add 0.5 g of quinhydrone and stirred vigorously to obtain a saturate solution. A platinum electrode is complete with a calomel electrode through a Kcl salt bridge. The two electrodes are connecting through a potentiometer. Add Sodium hydroxide in 1ml portions and after stirring the solution, measure the e.m.f. Rough titration is carried out to locate the end point. In fair titration near the end point NaOH was added in a 0.2ml portions. Continue the addition; take 3-4 readings after the equivalence point. Record the volume of alkali added and e.m.f.of the solution. The graph was drawn by taking $\Delta E/\Delta V$ in Y-axis and mean volume of NaOH in X axis, corresponding to the maximum value of $\Delta E/\Delta V$ give the end point, which corresponding to the volume of NaOH used to neutralized the HCl . The strength of hydrochloric acid was calculated from the liter values.

Rough Titration



Volume

Fair titration



Observations and calculations

Volume of NaOH (ml)	Emf in Volts	ΔE in Volts	ΔV in cc	ΔE/ΔV in Volt/cc	Mean volume of NaOH (ml)

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**

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

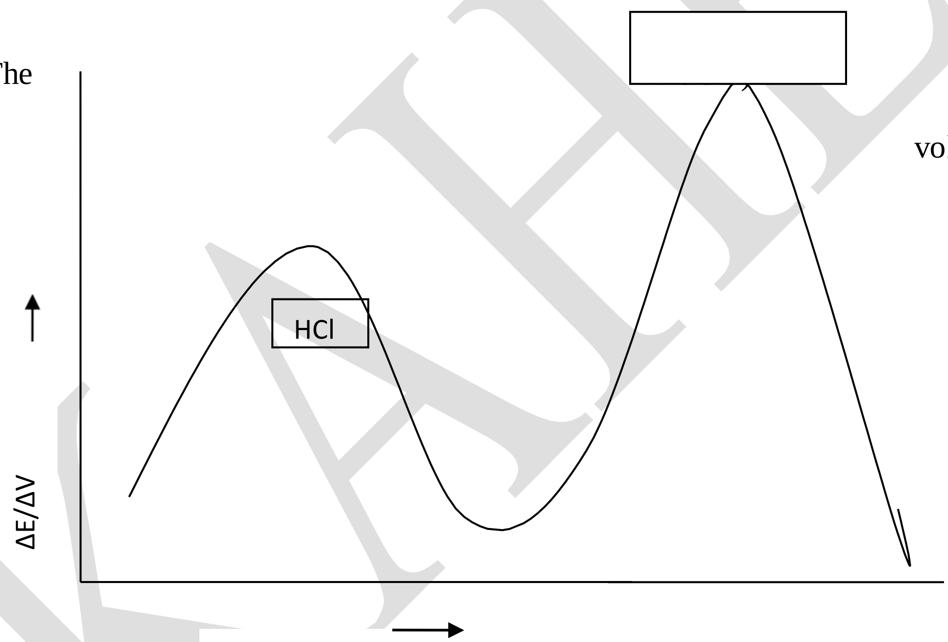
Note.

1. Filter paper is used for salt bridge, soaked with a relatively inert electrolyte, usually potassium chloride.
2. Equivalent weight of HCl = 36.5
   Equivalent weight of NaOH =40.0
3. Normality solution
   86 ml of HCl in 1 liter of water = 1N
   40g of NaOH in 1 liter of water = 1N
4. Some differential potentiometric titrations of
   a.Weak acid(acetic acid) (Vs) strong base(NaOH)

The nature of the plot ($\Delta E/\Delta V$ (Vs) mean volume of NaOH) is similar to that of strong acid Vs strong base

b.Mixture of strong acid and weak acid (Vs) strong base.

The nature of the plot ($\Delta E/\Delta V$ (Vs) mean volume o CH_3COOOH



Mean Volume of alkali

Experiment No. 2

TITRATION OF WEAK AGAINST STRONG BASE

Aim

To estimate the strength and amount of weak acid(Acetic Acid) present in the given solution (≈ 0.01 N) using sodium hydroxide by potentiometrically.

Principle

The titration of a weak acid with a strong base involves the direct transfer of protons from the weak acid to the hydoxide ion. The reaction of the weak acid, acetic acid, with a strong base, NaOH, can be seen below. In the reaction the acid and base react in a one to one ratio.

$C_2H_4O_{2(aq)}+OH^-_{(aq)}\rightarrow C_2H_3O^-_{2(aq)}+H_2O_{(l)}(1.1)(1.1)C2H4O2(aq)+OH(aq)-\rightarrow C2H3O2(aq)-+H2O(l)$

In this reaction a buret is used to administer one solution to another. The solution administered from the buret is called the titrant. The solution that the titrant is added to is called the analyte. In a titration of a Weak Acid with a Strong Base the titrant is a strong base and the analyte is a weak acid. In order to fully understand this type of titration the reaction, titration curve, and type of titration problems will be introduced.

Materials Required

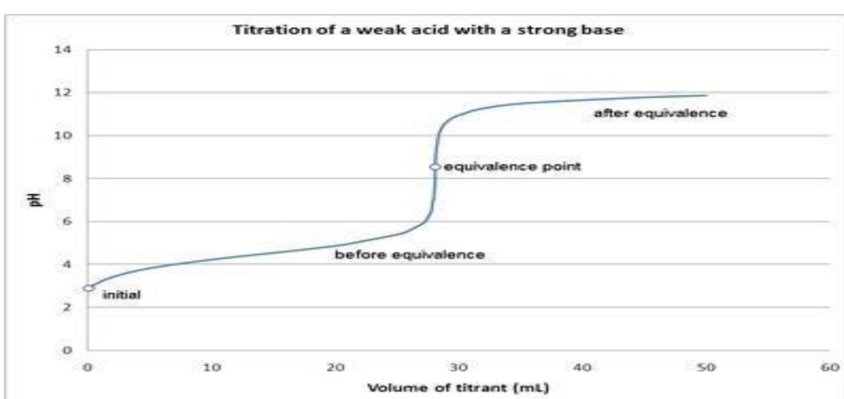
(i) Digital potentiometer
(ii) Calomel electrode
(iii) Platinum electrode
(iv) Quinhydrone
(v) N/10 NaOH

Procedure

The given solution is making up to 100 ml in a standard flask. 20 ml of the solution is pipette out into a beaker. Add 0.5 g of quinhydrone and stirred vigorously to obtain a saturate solution. A platinum electrode is complete with a calomel electrode through a KCl salt bridge. The two electrodes are connecting through a potentiometer. Add Sodium hydroxide in 1ml portions and after stirring the solution, measure the e.m.f. Rough titration is carried out to locate the end point. In fair titration near the end point NaOH was added in a 0.2ml portions. Continue the addition; take 3-4 readings after the equivalence point. Record the volume of alkali added and e.m.f.of the solution. The graph was drawn by taking $\Delta E/\Delta V$ in Y-axis and mean volume of NaOH in X axis, corresponding to the maximum value of $\Delta E/\Delta V$ give the end point, which corresponding to the volume of NaOH used to neutralized the HCl . The strength of hydrochloric acid was calculated from the liter values.

The Titration Curve

The titration curve is a graph of the volume of titrant, or in our case the volume of strong base, plotted against the pH. There are several characteristics that are seen in all titration curves of a weak acid with a strong base. These characteristics are stated below.



1. The initial pH (before the addition of any strong base) is higher or less acidic than the titration of a strong acid
2. There is a sharp increase in pH at the beginning of the titration. This is because the anion of the weak acid becomes a common ion that reduces the ionization of the acid.

3. After the sharp increase at the beginning of the titration the curve only changes gradually. This is because the solution is acting as a buffer. This will continue until the base overcomes the buffers capacity.
4. In the middle of this gradually curve the half-neutralization occurs. At this point the concentration of weak acid is equal to the concentration of its conjugate base. Therefore the $pH=pK_a$. This point is called the half-neutralization because half of the acid has been neutralized.
5. At the equivalence point the pH is greater then 7 because all of the acid (HA) has been converted to its conjugate base (A-) by the addition of NaOH and now the equilibrium moves backwards towards HA and produces hydroxide, that is:

   A−+H2O⇌AH+OH−(1.2)(1.2)A−+H2O⇌AH+OH−
6. The steep portion of the curve prior to the equivalence point is short. It usually only occurs until a pH of around 10.

The image of a titration curve of a weak acid with a strong base is seen below. All of the characteristics described above can be seen within it.

Observations and calculations

Volume of NaOH (ml)	Emf in Volts	ΔE in Volts	ΔV in cc	ΔE/ΔV in Volt/cc	Mean volume of NaOH (ml)

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

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

= …… N

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

Experiment No. 3

DETERMINIMATION OF pH

Aim

To determine the pHof the given solution potentiometrically.

Principle

The pH of a solution is defined as the negative logarithm to the base 10 of hydrogen ion concentration.

$$pH = -\log_{10}[H^+]$$

In the potentiometric method, pH value is measured by balancing the potential difference that is to be measured against a known opposite voltage. The quinhydrone electrode when combined with a saturated calomel electrode gives a cell in which quinhydrone is +ve up to pH 8 at 25^0 C. The cell used is

Hg, Hg_2Cl_2 KCl Quinhydrone Pt
(Saturated) saturated with HCl

The pH of the given solution was then calculated by making use of the following equation

$$E_{(Pt,Q,H_2Q,H^+)} = K^{\circ}_{(Pt,Q,H_2Q,H^+)} - \frac{2.303\,RTp^H}{F}$$

Materials Required

(i) Digital potentiometer
(ii) calomel electrode
(iii) platinum electrode
(iv) quinhydrone

Procedure

25 to 30 ml of the test solution is placed in a beaker and 0.2 g of quinhydrone is added to the given solution and stirred well. A platinum electrode was dipped in solution and was connected to the calomel electrode through KCl salt bridge. The cell was introduced into the potentiometric circuit and e.m.f was measured. The quinhydrone electrode is connected to the +ve of the potentiometer and the calomel electrode to the –ve and e.m.f is measured.

Observations and calculations

Solution	e_{obs}	pH
Acid solution		
Buffer solution		

$$E_{(Pt,Q,H_2Q,H^+)} = K^{\circ}_{(Pt,Q,H_2Q,H^+)} - \frac{2.303\,RTp^H}{F}$$

Where, E (Pt,Q,H2O,H^+) = E calomel + E observed
E observed is the e.m.f. of the cell.
E calomel at 25^0 C = 0.2415 volts (at other temperature between 15^0C and 40^0C, the following

relationship may be applied; E calomel= 0.2415 – 0.00076(T- 25^0C)

E^0 (Pt,Q,H_2O,H^+) is e.m.f. of quinhydrone electrode

E^0 (Pt,Q,H_2O,H^+) = 0.6996 volts

T= temperature at Kelvin(^{0}C + 273 = K)

R = 8.314

F= 96,500

E (Pt,Q,H_2O,H^+) = **E^0** ($Pt,Q,H2O,H^+$) – ([2.303x 8.314 x T] / 96,500) pH

0.2415 + E obs = 0.6996 - ([2.303x 8.314 x T] / 96,500) pH

Result

The pH of the given solution was found to be

a) Strong acid =
b) Buffer solution =

Note.

1. pH is also given by, pH = 0.4575-e_{obs}/ 0.0591 at 25^0C
2. pH at any other temperature is given by pH = $e^0{}_Q - e_{sat\ cal} - e_{obs}$/ 0.0001984 T
   T is the absolute temperature, $e^0{}_Q$ is the e.m.f. of quinhydrone electrode and $e_{sat\ cal}$ is the e.m.f. of the saturated calomel electrode at temperature T.
3. Acetic acid (0.2 M) – Mix 11.55 ml of acetic acid in 1000 ml distilled water.
   Sodium acetate (0.2 M) ; Dissolve 16.4 g of sodium acetate in 1000 ml distilled water.
   Mix 4.8 ml of 0.2M acetic acid with 54.2 ml of 0.2 M sodium acetate, adjust the volume to 100 ml with distilled water to get buffer (pH = 5.6).
4. Quinhydrone electrode cannot be used in solution more basic than about pH 9, because hydroquinone, a weak acid, is neutralized by base, giving incorrect values of pH.

Experiment No. 4

DETERMININATION OF DISSOCIATION CONSTANT OF A WEAK ACID (PK_A VALUE)

Aim

To find out the dissociation constant of a weak acid by titrating against sodium hydroxide potentiometrically by using quinhydrone electrode (pk_a value).

.Principle

Consider the reversible reduction of quinone (Q) and hydroquinone (H_2Q) in acid solution.

$C_6H_4(OH)_2 \leftrightarrows C_6H_4O_2 + 2H^+ + 2e^-$

This is a reversible redox system and the oxidation potential of an inert electrode such as platinum immersed in the system is given by

$$E = E^\circ - \frac{RT}{2F}\log\frac{aQ}{aH_2Q} - \frac{RT}{F}\log a_{H^+}$$

The oxidation reduction where aQ, aH_2Q, aH^+ are the activities of quinone hydroquinone and hydrogen ion respectively. E° in the standard electrode potential relating to normal hydrogen electrode. If the solution contain equimolar amount of quinone and hydroquinone the ratio aQ

$$= E^\circ - \frac{RT}{F} \log aH^+ \qquad \overline{aH_2Q} \text{ is taken as unity}$$

The value of E° has been determined by direct reference to normal hydrogen electrode and it has the value of 0.6996 V at 25° C. Suppose quinhydrone is combined with a standard calomel electrode for carrying out the titration. A cell of the following type is set.

$Hg/HgCl_{2(s)}$, KCl_{std} // Hg^+ unknown QH_2/Pt in this cell calomel undergo reduction. The observed of the cell will be

$$E_{obs} = E_R - E_F$$

Where both E_L corresponds to standard reduction potential of the electrode.

$$E_{obs} = E^0 + \frac{RT}{F} \ln aH^+ - E_{calomel}$$

Materials Required

(i) Digital potentiometer,
(ii) calomel electrode,
(iii) platinum electrode,
(iv) quinhydrone,
(v) N/10 NaOH,
(vi) N/10 CH_3COOH

Procedure

20 ml of the test solution is placed in a beaker and 0.2 g of quinhydrone is added to the given solution and stirred well. A platinum electrode was dipped in solution and was connected to the calomel electrode through KCl salt bridge. The cell was introduced into the potentiometric circuit. The quinhydrone electrode is connected to the +ve of the potentiometer and the calomel electrode to the – ve ______ and e.m.f is measured. NaOH is added in 1 ml portions and after stirring the solution well, the e.m.f was noted. Rough titration was carried out to locate the point. pH of the solution was calculated for ¼, ½, 3/4 neutralization and e.m.f was found. From the graph using Flender's equation P_{Ka} is calculated,

$$PK_a = P^H - \log \frac{[Salt]}{[Acid]}$$

Observations and calculations

Volume of NaOH(ml)	E_{obs}

Volume of NaOH required for ¾ neutralization = $^{3}/_{4} \times 20$

= 15

E.m.f for ¾ neutralization = ... Volts

$$E_{obs} = E^0 - \frac{RT}{nf} \ln \frac{aH_2Q}{aQa_{H^+}} - E_{calomel}$$

$$0.15 = 0.6996 - \frac{8.314 \times 301 \times 2.303}{96500} \log \frac{1}{H^+} - E_{calomel}$$

Where,
E observed is the e.m.f. of the cell.
E calamel at 25^0 C = 0.2415 volts
E^0 is e.m.f. of quinhydrone electrode
E^0 = 0.6996 volts
T= temperature at Kelvin(^{0}C + 273 = K)
R = 8.314
nf= 96,500
0.15 = 0.6996 –0.0597 p^H – 0.2422

$$p^H = \frac{0.6996 - 0.15 - 0.2422}{0.0597}$$

= 5.1490

$$P^H = PK_a + \log\frac{[salt]}{[Acid]}$$

$$PK_a = -\log K_a$$

$$= 5.1490 - \log \frac{3/4}{1/4}$$

= 5.1490 0.4771

= 4.6719

×

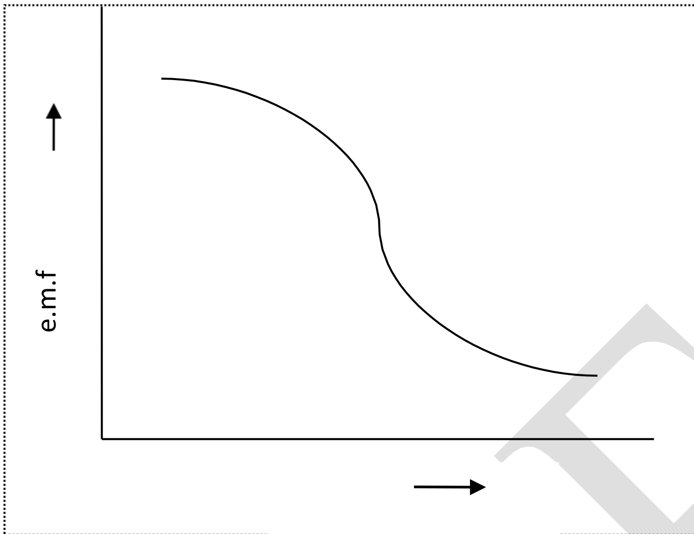
$$\log K_a = -PK_a$$

= – 4.6719

K_a = Antilog of (–4.6719)

= 2.1286 10^{-5}.

Graph



Volume

--

Result

Dissociation constant for weak acid for

(a) ¾ neutralization = 2.1286 × 10^{-5}.

(b) ½ neutralization = 1.5346 × 10^{-5}.

(c) ¼ neutralization = 1.6270 × 10^{-5}.

Note.

1 .pH is also given by

pH = 0.4575-eobs/ 0.0591 at 25^0C

2. pH at any other temperature is given by pH = $e^0{}_Q - e_{sat\ cal} - e_{obs}$/ 0.0001984 T

T is the absolute temperature, e^0Qis the e.m.f. of quinhydrone electrode and $e_{sat\ cal}$ is the e.m.f. of the saturated calomel electrode at temperature T.

3. NH_4OH – NH_4Cl buffer (pH = 10) is prepared by dissolving 64 g of NH_4Cl in distilled water, adding 570 ml of ammonia solution and diluting to 1 liter with distilled water.

4. N/10 acetic acid, 58 ml of acetic acid in 1 liter distilled water

Experiment No 5

ESTIMATION OF FERROUS AMMONIUM SULPHATE

Aim

To determine the weight of ferrous ammonium sulphate present in the whole of the given solution potentiometrically using standard potassium dichromate (redox - titration).

Principle

Potassium dichromate in acid medium will oxidize ferrous state to the ferric state and ferrous- ferric system is formed. A platinum electrode in a solution of ferrous salt takes up a potential dependent on the ratio Fe^{2+} / Fe^{3+}.. Fe^{3+} is infinitesimally small initially, but as the solution is titrated against $K_2Cr_2O_7$, the ratio of Fe^{2+} / Fe^{3+} changes rapidly. Therefore, at equivalent point, there will be a sudden change in the potential of the electrode. This electrode can be connected to standard calomel electrode (SCE) to form the cell.

S.C.E./KCl (sat) Fe^{2+},Fe^{3+} / Pt

Materials Required

(i) Digital potentiometer,
(ii) calomel electrode,
(iii) platinum electrode,
(iv) N/10 $K_2Cr_2O_7$,
(v) N/10 Ferrous ammonium sulphate,
(vi) dil H_2SO_4

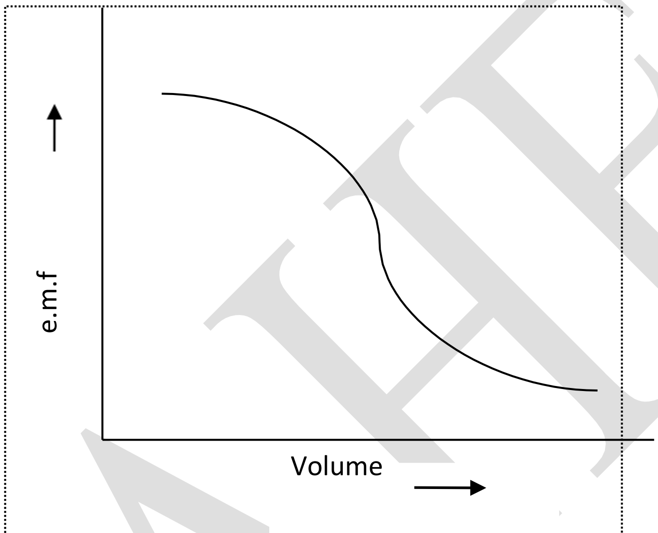
Procedure

The given FAS was made up to 100 ml in a standard flask and 10 ml of the solution was pipetted out into a beaker added 10 ml of 4N H_2SO_4. Dipped a platinum electrode and connected to a saturated calomel electrode by means of a KCl salt bridge. The $K_2Cr_2O_7$ solution was taken in a burette and added in 1ml portions and emf is noted for each addition. Near the end point $K_2Cr_2O_7$ solution was added in 0.2 ml portions and emf was found out. A graph was drawn by taking ΔE/ΔV on Y axis and the mean volume of potassium dichromate along X axis. The end point is the volume corresponding to the maximum value of ΔE/ΔV. From the strength of $K_2Cr_2O_7$, the strength of FAS was found out and also the weight of ferrous ammonium sulphate present in the whole of the given solution.

Observations and calculations

Volume of $K_2Cr_2O_7$ (ml)	Emf in Volts	ΔE in Volts	ΔV in cc	ΔE/ΔV in Volt/cc	Mean volume of $K_2Cr_2O_7$ (ml)

Graph



Determination of strength of FAS

Volume of $K_2Cr_2O_7$ solution (V_2) = …… ml

Strength of $K_2Cr_2O_7$ solution (N_2) = 0.1 N

Volume of FAS solution (V_1) = 20 ml

Strength of FAS solution (N_1) $= \frac{V_2N_2}{V_1} =$

= ------N

Amount of FAS Present in the whole of the given solution = $\frac{Normality \times Eq.\ wt}{10}$

$= \frac{N \times 392}{10}$

=……….g

Result

The amount of ferrous ammonium sulphate present in the whole of the given solution = ... g.

Note.

1. Potassium dichromate , 49.04 g / 1 liter distilled water = 1N
2. Ferrous ammonium sulphate, 392 g / 1 liter distilled water = 1N (About 5 ml of concentrated H_2SO_4 is added to it and the volume is made up to the mark. H_2SO_4 is added to avoid the hydrolysis of ferrous sulphate)
3. Sulphuric acid , 28 ml / 1 liter distilled water = 1N

KINETIC EXPERIMENTS

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}

Experiment No 7

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)	$V_\infty - V_t$ (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 = 35 °C

V_0 = ---- ml V_∞ = ------ ml V_∞ - 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 k (sec^{-1})	Log k	Log k/T	1/T m $k^{-1}*10^{-3}$

Mean =

From log k Vs 1/T

E_A = Slope × 2.303 × 8.314 = $KJmol^{-1}$

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

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

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

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

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

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

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

ΔS = ------ J/mol^{-1}.

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

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 8

REACTION KINETICS OF POTASSIUM IODIDE AND POTASSIUM PERSULPHATE

Aim

To determine the rateof 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 $K_2S_2O_8$ M 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 $K_2S_2O_8$ sodium thio sulphate. The titrations were carried out at regular $K = \frac{1}{t}\frac{x}{a(a-x)}$ 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 $\frac{1}{a-x}$ of 10 % KI was added and titrated against sodium thio sulphate.

The titrate values were proportional to the initial concentration of

The constancy of the value of K proved that the reaction under consideration is of II order. A graph was plotted by taking 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 9

DETERMINATION OF THE RATE OF THE REACTION BETWEEN $K_2S_2O_8$ AND KI BY KNO_3 - PRIMARY SALT EFFECT

Aim

To study the effect of ionic strength on the rate of the reaction between $K_2S_2O_8$ and KI by KNO_3 and also to determine the strength of the given salt solution **(peroxy disulphate and iodine reaction-primary salt effect)**

Principle

The reaction between KI and $K_2S_2O_8$ is represented by the following equation

$$S_2O_8^{2-} + I^- \rightarrow 2SO_4^{2-} + I_2$$

The rate of equation cannot be measured directly by finding the amount of iodide and liberated since the iodide forms triodide ions and for iodide. The rate of reaction is found from the time taken for a certain fraction of the reaction to occur.

$$\frac{\Delta S}{\Delta t} = K_2[S_2O_8]^{2-}[I^-]$$

Where ΔS is defined as the strength of $Na_2S_2O_3$. There is a reaction between the ions of like charges. The reaction between ions is influenced by ionic strength of the medium. Ionic strength of the medium is given by the relation

$$\mu = {}^1/_2 \sum_i C_i Z_i^2$$

The C_i is molarity of each type of ion and Z_i is the charge of the ion.

According to Bronsted-Jerrum equation for a dilute solution $\log K = \log K_0 + A_{ZaZb}\sqrt{\mu}$ where K is the rate constant μ μ_0

Materials required

(i) Peroxy disulphate,
(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

About 250 ml of 0.01 M $K_2S_2O_8$, 250 ml of 1 M KNO_3, 100 ml of KI, 50 ml of 1% starch was prepared. 25 ml of KNO_3, 10 ml of $Na_2S_2O_3$, 20ml of $K_2S_2O_8$ and 5 ml of starch and 30 ml of H_2O were pipetted out into a clean conical flask. This mixture along with KI was kept in a thermostat. Where the solution attained the temperature of the bath, 10 ml of KI was pipetted out into a clean conical flask containing the mixture. When the pipette was half emplied a stop watch was started and noted the time of appearance of blue colour.

In the same manner, the concentration of KNO_3 was varied and the time of appearance of blue colour and hence the rate constant was calculated. Ionic strength was calculated using the relation,

$$\mu = {}^1/_2 \sum_i C_i Z_i^2$$

Then log K was plotted against $\sqrt{\mu}$. The plot was found to be a straight line with the slope = $A_{Z^+Z^-}$

Observations and calculations

Volume of 0.1 N $K_2S_2O_8$ in cc	Volume of 0.00001N $Na_2S_2O_3$ in cc	Volume of starch in cc	Volume of 1N KNO_3 cc	Volume of H_2O in cc	Volume of 0.4 NKI in cc	Time in sec

Flask No	**1**	**2**	**3**	**4**	**5**	**6**
Strength of KNO_3						
μ KNO_3 in (M)						
μ $K_2S_2O_8$ + μ $Na_2S_2O_8$ + μ KI						
μ total						

1) Ionic strength of $Na_2S_2O_3$

$Na_2S_2O_3 \rightarrow 2Na^+ + (S_2O_3)^{2-}$

$$\mu Na_2S_2O_3 = {}^1/_2 \sum_i c_i Z_i^2$$

2) Ionic strength of KI

$KI \rightarrow K^+ + I^-$

$$\mu KI = {}^1/_2 \sum_i c_i Z_i^2$$

3) Ionic strength of $K_2S_2O_8$

$K_2S_2O_8 \rightarrow 2K^+ + (S_2O_8)^{2-}$

$$\mu K_2S_2O_8 = {}^1/_2 \sum_i c_i Z_i^2$$

4) Ionic strength of KNO_3

$KNO_3 \rightarrow K^+ + NO_3^-$

$$\mu KNO_3 = {}^1/_2 \sum_i c_i Z_i^2$$

5) Calculation of μ total

μ total = $\mu K_2S_2O_8 + \mu Na_2S_2O_3 + \mu KI + \mu KNO_3$

= -------M

$$\frac{\Delta S}{\Delta t} = K_2\, [S_2O_8]^{2-}\, [I^-]$$

$$\Delta S = \frac{Concentration\ of\ thio\ sulphate\ in\ moles/lit}{2} = \text{-----}\ mol/lit$$

$$K_2 = -----mol\ l^{-1} sec^{-1}$$

S.No	K_2 in $mol^{-1}\ l^{-1}\ sec^{-1}$	Log K_2	µ total	$\sqrt{\mu}$

From graph

Slope dy/dx = 2A A = ------

$\sqrt{\mu}$ = ------

µ total = ----------

log K_0 = $Y_{intercept}$

K_0 = ------- $mol\ l^{-1} sec^{-1}$

µ total = $\mu K_2S_2O_8 + \mu Na_2S_2O_3 + \mu KI + \mu KNO_3$

$$\mu\ KNO_3 = {}^1/_2 \sum C_i Z_i^{\,2}$$

Calculated value of k

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

Result

(1) The rate constant of the reaction is found to increase with increase in ionic strength of KNO_3.

(2) Calculated value of K **= ---------** $mol\ l^{-1} sec^{-1}$

Graphical value of K = -------- $mol\ l^{-1} sec^{-1}$

(3) Strength of the given solution of KNO_3 is found to be --------M.

(4) The value of A is found to be -------- --.

ADSORPTION EXPERIMENT

Experiment No 9

ADSORPTION OF OXALIC ACID ON CHARCOAL

Aim

To construct classical adsorption isotherm by studying adsorption of $(COOH)_2$ from its aqueous solution on activated charcoal and also to determined the initial concentration of $(COOH)_2$ supplied in bottle A and B (A**dsorption of oxalic acid on charcoal)**

Principle

Adsorption is the accumulation of the substance at an interference and with its varies concentration of the solution. When oxalic acid is brought in contact with activated animal charcoal it is absorbed according to Freundlich adsorption isotherm,

$$x/_{m} = KC^{1/_n}\, a$$

Where 'n' denotes number of moles of acid adsorbed
'm' is the weight of adsorbent in gms
'c' is the equilibrium concentration of the acid
'a' is the order of adsorption
'K' is the adsorption co-efficient
A graph is drawn between log x/m and log c gives a straight line. Its slope is equal to 'n' and intercept is log K.

Materials required

(i) Glass stoppered bottles,
(ii) cork, beaker,
(iii) Oxalic acid,
(iv) Charcoal,
(v) $KMnO_4$,
(vi) Orbital shaker.

Procedure

A solution of 0.5 N oxalic acid in 250 ml and 0.1 N $KMnO_4$ solutions were prepared. The $KMnO_4$ solution is standardized using standard oxalic acid. Seven glass stoppered bottles are cleaned with chromic acid washed, dried. Exactly 1 gm of activated charcoal are weighed and put into each of the bottles 50, 40, 30, 20 and oxalic acids are pipetted out into each of the five bottles and total volume is adjusted with water. The volume of $(COOH)_2$ of unknown concentration in bottles 6 and 7 was also adjusted to 50 ml. The bottles are stoppered well and then shaken well for about an hour till attained equilibrium. The contents of the bottles are filtered through a filter paper. The first 5 ml of the filtrate is rejected.

The concentration of the acid in different bottles is estimated by titration with standard $KMnO_4$. Titrations are repeated for concordant values from the titre value, equilibrium concentration of $(COOH)_2$ is calculated. A graph is plotted between log x/m and log c where x denotes weight of $(COOH)_2$ adsorbed on charcoal in equilibrium. From the slope and intercept of the straight line the value of n and K are calculated respectively.

Observations and calculations

Weight of oxalic acid in 100 ml = 0.63 g

Normality of oxalic in 100 ml $= \frac{Wt/lit}{Eq.Wt}$ =----- N

Standardisation of potassium permanganate Titration of standard oxalic acid Vs $KMnO_4$

Volume of oxalic acid (ml)	Burette reading (ml)		Volume of $KMnO_4$ (ml)
	Initial	Final	

Volume of oxalic acid (V_1) = 20 ml
Normality of oxalic acid (N_1) = -- N
Volume of $KMnO_4$ (V_2) = --- ml
Normality of $KMnO_4$ (N_2) = ---- N

Amount of charcoal gm	Volume of oxalic acid (ml)	Volume of water (ml)	Concen. Of oxalic acid before adsorption	Volume of filtrate (ml)	Volume of $KMnO_4$ (ml)	Concen. Of oxalic acid after adsorption	Amount of oxalic acid adsorbed × 10cc /20 × 63

x/m	Log x/m	Log Ce

Unknown log Ce = –0.4380

(i) From graph
Log (x/m) = -----
X = ------

(ii) To f in C_0

$$x = \frac{C_0 - C_e \times 63}{20}$$

$$C_0 = \frac{x \times 20}{63} + C_e$$ = ---------

(iii) n = ------

(iv) K = -------

Result

The classical adsorption isotherm is constructed.

The strength of oxalic acid in flask = ---- N

Order of adsorption (n) = -------

Adsorption co-efficient (K) = -------