CHAPTER III

EXPERIMENTAL TECHNIGUE FOR DETERMINING REDOX POTENTIAL AND RELATED STUDIES

This chapter consists of few sections such as the sources and the preparations of the reagents and the electrodes used in this work. The following sections of the chapter cover the experimental techniques employed in the determination of redox potential by the e.m.f. measurement and employed in the study of other properties of the solution and also those of the solvent.

3.1 Reagents

The following reagents were of A.R. grade, and were used without further purification. The solutions of acetic acid, hydrochloric acid*, sodium hydroxide, sodium thiosulphate, potassium bromate, potassium iodide and chloroplatinic acid were made to the desired concentration using distilled water as a diluent and were standardised by the conventional methods.

When a specially pure water was needed such as in the determination of the transport properties of

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*Hydrochloric acid solution used in the cell Pt, $H_2/HCl/Hg_2Cl_2$ / Hg was constant boiling point hydrochloric acid (8) electrolytes, deionized water was used. This was prepared by deionization of double distilled water by passage through "Elgastat" unit resulting in water of specific conductance of 1.45 microohm^{-1}cm.$^{-1}$.

3.1.1 Thallic acetate. Thallic acetate was prepared by dissolving pure thallous sulphate (obtained from Messer. BDH) in dilute sulphuric acid. After heating to about 60°c the thallous salt was oxidised with ammonium persulphate. The solution was then made alkali by the addition of concentrated ammonium hydroxide. The dark brown precipitate of thallic hydroxide was washed with distilled water by decantation until the supernatant liquid gave no test of sulphate when barium acetate was added. The precipitate was filtered and air dried. Thallic acetate was obtained by the addition of hot excess glacial acetic acid into this precipitate. It is essential that the precipitate occured have to be kept under the surface of glacial acetic acid. The product prepared by this method is silvery white crystal and was identified by I.R. spectroscopy.

3.1.2 Calomel. This was chemically precipitated calomel and prepared according to the method given by Hills and Ives (9). Five grams of mercurous nitrate were moistened with 1 ml. of concentrated nitric acid and dissolved in 100 ml. of distilled water. This solution was then added dropwise to about 500 ml. of 0.1 N hydrochloric acid contained in a covered beaker and mechanically stirred by means of a glass paddle. The addition was completed within 10 minutes and the suspension was stirred for a further hour. The precipitate was then allowed to settle, after which the supernatant solution was decanted and replaced by a further 50 ml. of 0.1 N hydrochloric acid. It was then stirred for a further 24 hours, during which period the hydrochloric acid solution was replaced twice again. The precipitated calomel was finally filtered on to a sintered glass crucible, rinsed quickly with four portions of cold distilled water, and transfered to a vacuum desiccator. The so called "precipitated calomel" is a white powder and turns to grey powder when it is ground together with mercury.

3.1.3 Mercurous acetate . This salt was obtained from the reaction between solutions of mercurous nitrate and dilute acetic acid, the precipitate was washed thoroughly with distilled water and air dried. It is a light grey plate precipitate. The identification was then made by I.R. spectroscopy.

3.2 The Electrodes

3.2.1 The hydrogen electrodes. These were prepared according to the method of Hills and Ives (10). Briefly, a clean, thin platinum plate was platinised thinly from a mixture of 2% of platinic chloride and 0.02% lead acetate in 2 N hydrochloric acid solution for about 20 minutes at a current density of 10 ma. $cm.^{-2}$. When it was used, the stream of cylinder hydrogen gas was passed through a deoxo catalytic purifier (Engelhard Industries Ltd.) before bubling continuously through the hydrogen electrode compartment.

3.2.2 The calomel electrodes. The calomel half cell was prepared according to the method of Hills and Ives (11). A small amount of dry precipitated calomel was ground together with a little mercury, until a grey skin was formed over the mercury. This grey skin was spreaded evenly over the whole surface of a pool of mercury in the cell vessel, and a constant boiling point hydrochloric acid solution with a desired concentration and which saturated with calomel was poured carefully on top.

3.2.3 The mercury-mercurous acetate electrodes. This half cell consisted of a pool of enough mercury to cover a platinum contact in the cell vessel. The mercury pool serface was covered with a thin, unbroken film taken from an adherent skin of mercurous acetate covered a ball of mercury resulted from the grinding of mercury and mercurous acetate together. The cell was then filled with acetic acid saturated with mercurous acetate.

3.3 Electromotive Force Measurements

The e.m.f. of a cell is equal to the sum of the potentials of the two electrodes. The potential of an electrode is determined by combining with a reference electrode which has an arbitrarily assigned potential and measuring the total voltage between the two electrodes. All electrode potentials are assigned numerical values on the assumption that potential of the standard hydrogen electrode (primary reference electrode) is zero. The standard hydrogen electrode is rather difficult to prepare and so it is usually replaced by the secondary reference electrodes. In this work, calomel electrode and mercury-mercurous acetate electrode were used and their potentials with respect to the hydrogen electrode were measured.

All the investigated cells were placed in an air thermostat at 25 ± 0.5°C and their potentials were measured by Vernier Potentiometer type 5590 B in conjunction with galvanometer type MR 4 No. 185276, both manufactured by H. Tinsley & Co. Ltd., London.

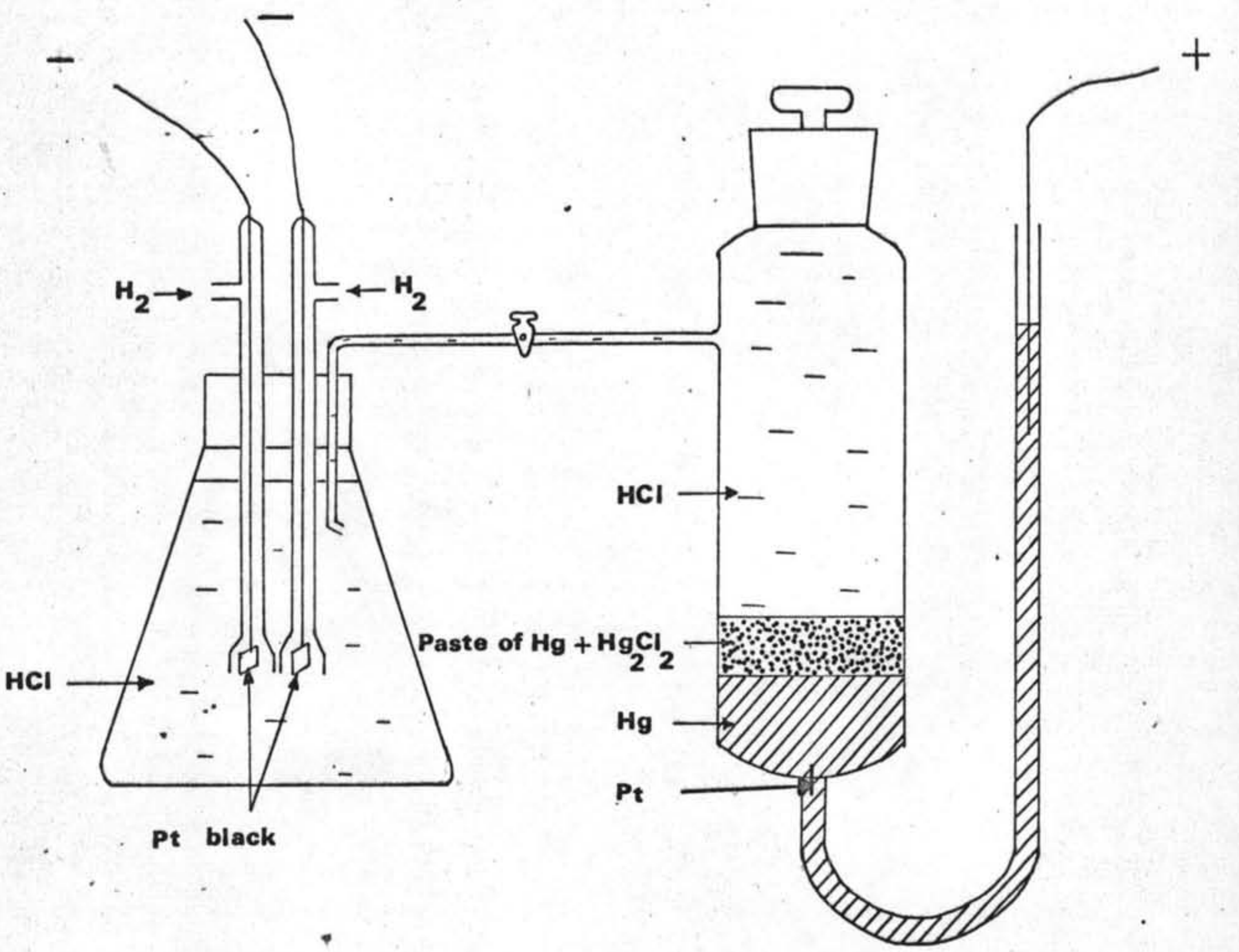

Fig. 3.1 The cell assembly :

$Pt, H_2 | HCl\ (c) | Hg_2Cl_2 | Hg$

3.3.1 The standard e.m.f. of the reference electrodes

A. The calomel electrodes

Pt, H_2/HCl (c) /Hg_2Cl_2/Hg I

The cell assembly is shown in Fig. 3.1 . Two platinum foil electrodes were dipped into the deoxygenated aqueous hydrochloric acid solution of various concentrations. The bias potentials measured at the equilibrium e.m.f. showed a potential difference of 0.1 mv. or less. Measurements have been made over the concentration range of 0.005-0.08 M of hydrochloric acid.

The standard electrode potential of the calomel electrode was calculated using Nernst equation. Experimental data are presented in Table 3.1 . which followed by the calculation of the standard potential of calomel electrode.

Table 3.1

Observed electromotive forces at 25° C as a function of hydrochloric acid concentrations

HCl (molarity)	E_{cell} (obsd.) (volt)
0.004897	0.543864
0.010151	0.508794
0.029920	0.455875
0.049968	0.431180
0.079910	0.408243

Calculation

Table 3.2

List of constants and their values

used in this calculation

Symbol	Value
T (Absolute temperature)	298°K (25°C)
F (Faraday)	96487 coulombs/equivalent
m (Molal concentration)	vary
R (Molar gas constant)	8.31436 joules/mole/degree
ρ_0 (Density of water)	0.997071 g./ml. (25°C)
A (Debye-Huckel constant for water)	0.5091 (25°C)
β (Debye-Hückel constant for water)	0.3286 (25°C)
f (Activity coefficient in molality scale)	vary

The cell reaction of cell I is written as

$$\tfrac{1}{2} H_{2(g)} + \tfrac{1}{2} Hg_2Cl_{2(s)} \longrightarrow Hg_{(1)} + Cl^- + H^+$$

The e.m.f. of the above reaction is given by

$$E = E^\circ - \frac{RT}{F} \ln m_{H^+} m_{Cl^-} f_{H^+} f_{Cl^-}$$

$$= E^\circ - \frac{RT}{F} \ln m^2_{HCl} \, f^2_{HCl} \qquad \ldots\ldots\ldots(1)$$

Here the pressure of hydrogen gas is taken as one atmosphere.

f_{HCl}, the activity coefficient of hydrochloric acid can be evaluated from Debye-Hückel expression

$$\log f_{HCl} = -A' m^{1/2} + Bm \qquad .....(2)$$

Hence equation (1) can be re-written when f_{HCl} is substituted by equation (2) and the appropriate numerical values of the constants inserted.

$$E = E^{\circ} - 0.118319 \log m_{HCl} - 0.118319 (-A' m^{1/2} + Bm)$$

$$E = E^{\circ} - 0.118319 \log m_{HCl} + 0.118319A' m^{1/2} - 0.118319 Bm$$

$$E + 0.118319 \log m - 0.118319A' m^{1/2} = E^{\circ}_{m} - 0.118319 Bm \qquad .....(3)$$

but $A' = A \rho_0^{1/2}$

$= 0.5091 (0.997071)^{1/2}$

$= 0.50839$

Equation (3) is reduced to

$$E + 0.118319 \log m - 0.118319 \times 0.50839 m^{1/2} = E^{\circ}_{m} - 0.118319 Bm$$

$$E + 0.118319 \log m - 0.06014 m^{1/2} = E^{\circ}_{m} - 0.118319 Bm$$

If molarity is chosen as a concentration scale, (c)

$$E + 0.118319 \log c - 0.060144 c^{1/2} = E^{\circ}_{c} - 0.118319 Bc$$

If one plot a left hand member of the above equation against c, one should get a straight line with E° as an intercept. The calculated values of log c, $c^{1/2}$ and $0.118319 \log c - 0.060144 c^{1/2}$ are shown in Table 3.3 .

The direct extrapolation of the linear plot of $E + 0.118319 \log c - 0.060144 c^{1/2}$ versus c to zero ionic strength in Fig. 3.2 given the value of $E^{\bullet}_{c}$ as the intercept. As can be seen the value of $E^{\bullet}_{c}$ in this case is 0.2677 volt .

Table 3.3

c	log c	$c^{1/2}$	0.118319 log c-0.060144 $c^{1/2}$
0.004897	-2.31006	0.06998	-0.27653
0.010151	-1.99366	0.10074	-0.24192
0.029920	-1.52301	0.17318	-0.19057
0.049968	-1.30128	0.22356	-0.16735
0.079910	-1.09739	0.28269	-0.14689

B. The mercury-mercurous acetate electrodes

Pt, H_2/HOAc (c) / $Hg_2(OAc)_2$/Hg II

The cell assembly is similar to what shown in Fig. 3.1 , but the calomel electrode was replaced by a mercury-mercurous acetate electrode and the cell solution was changed to acetic acid solutions. The e.m.f. was measured over a concentration range of 0.05 - 4 M of acetic acid. The acetic acid solutions

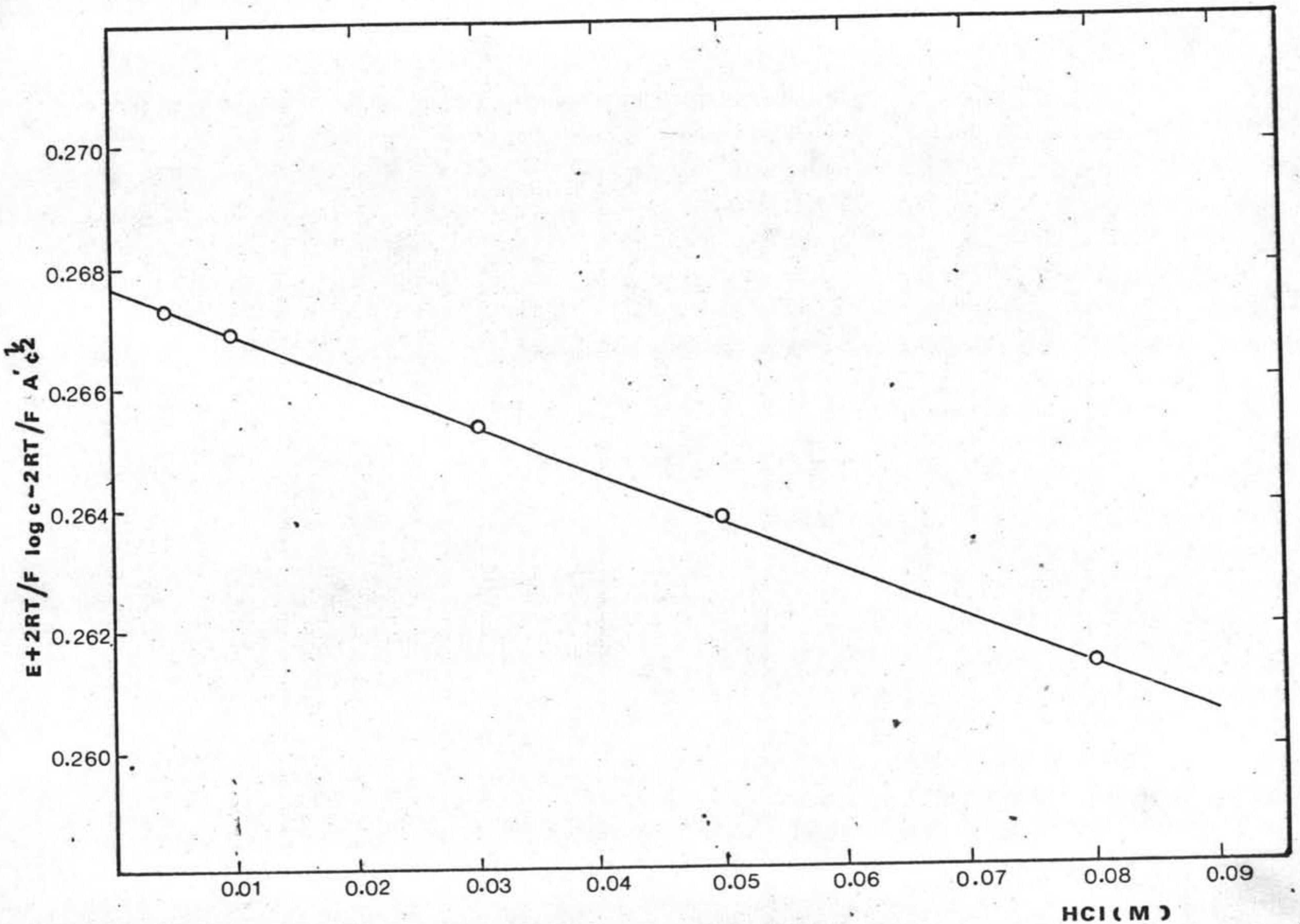

Fig . 3 . 2 The Plot of E parameters as a function of acid concentrations were standardised for their concentrations with sodium hydroxide which was pre-standardised with a standard solution of potassium hydrogen phthalate.

The observed potentials of cell II are shown in Table 3.4 which precede the method used in the calculation of the standard potential of the mercury-mercurous acetate electrode.

Table 3.4

Observed electromotive forces at 25°C as a function of acetic acid concentrations

HOAc (molarity)	E_{cell} (obsd.) (volt)
0.0496	0.868650
0.0794	0.856040
0.5352	0.805462
1.0556	0.790810
1.6604	0.780512
3.3451	0.772404

Calculation

In the following calculation, certain symbols are adopted and listed below.

The thermodynomic ionization constant of HOAc = K

Concentration express in molarity = c

Degree of ionization (α) = $(K/c)^{1/2}$

Ionic strength = I

The cell reaction of cell II is written as:

$$\tfrac{1}{2}\, H_{2(g)} + \tfrac{1}{2}\, Hg_2(OAc)_{2(s)} \longrightarrow Hg_{(1)} + OAc^- + H^+$$

Therefore from Nernst equation:

$$E = E^\circ - \frac{RT}{F} \ln \frac{a_{H^+} a_{OAc^-}}{P_{H_2}^{1/2}} \qquad \ldots\ldots\ldots(3)$$

where P_{H_2} is taken to be one atmosphere. We obtain

$$E = E^\circ - 0.0591 \log a_{H^+} a_{OAc^-}$$

If allowance is made for the incomplete dissociation of acetic acid over the range of concentrations under study, the following expression is obtained.

$$E = E^\circ - 0.0591 \log Kc(1-\alpha)\gamma^2_{HOAc}$$

$$E + 0.0591 \log Kc(1-\alpha) = E^\circ - 0.0591 \log \gamma^2_{HOAc} \quad \ldots(4)$$

The calculated values of the left hand member of equation (4) are given in Table 3.5 using the values of K and α at various c in table 4.7 . The plot of $E + 0.0591 \log Kc(1-\alpha)$ versus $I^{1/2}$ is a straight line and is illustrated in Fig. 3.3. At zero ionic strength the solution is an ideal solution hence γ approach unity. Consequently the value of $E+0.0593 \log Kc(1-\alpha)$ at zero ionic strength is equal to E° (see equation (4)). The value of E° obtained by this method is 0.5072 volt.

Table 3.5

The value of $E + 0.0591 \log Kc(1-\alpha)$ as a function of ionic strength

$I^{1/2}$	$E + 0.0591 \log Kc(1-\alpha)$
0.02883	0.503250
0.03243	0.502830
0.05080	0.500441
0.05964	0.500365
0.06490	0.498778
0.06973	0.498059

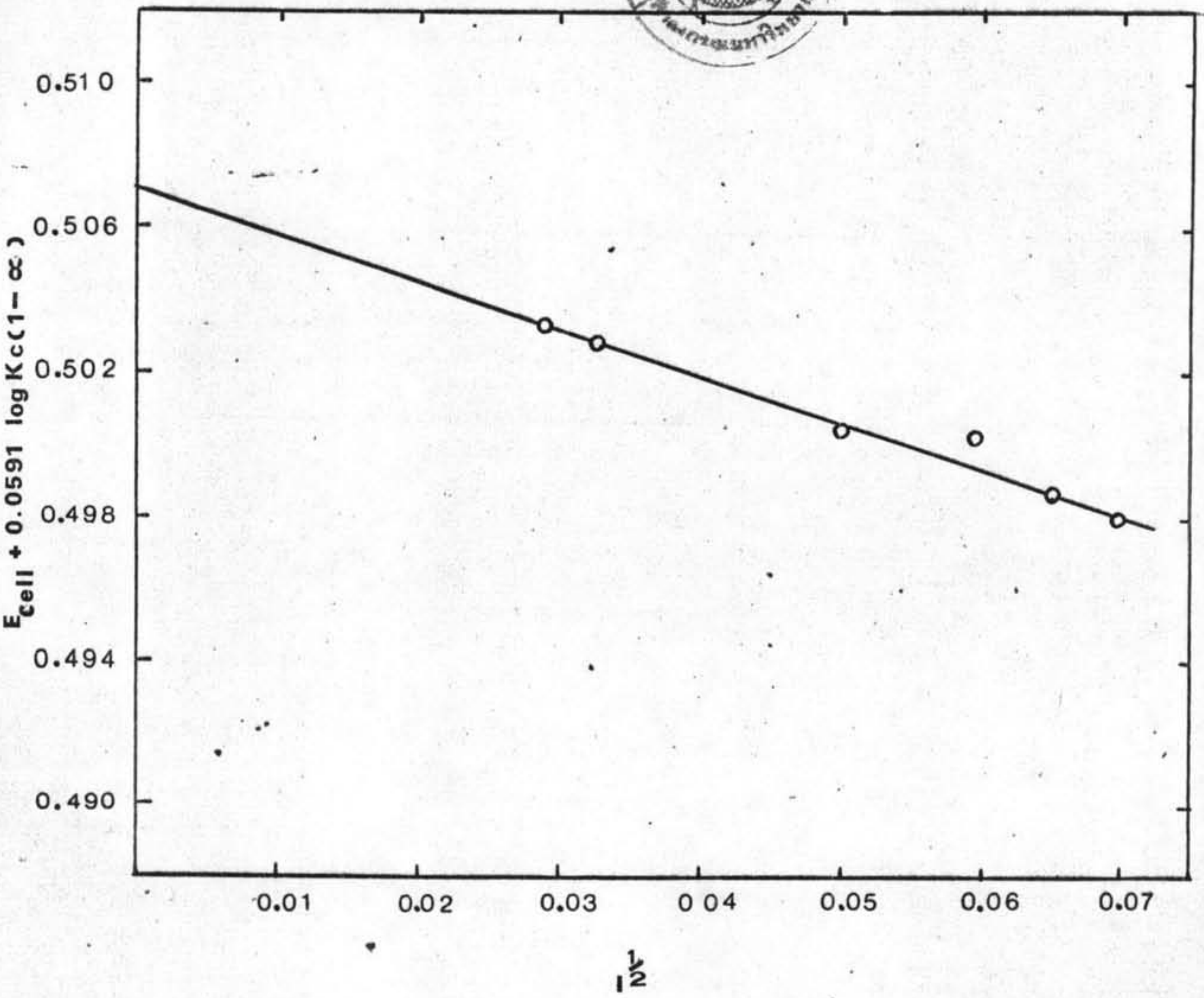

Fig. 3.3' The plot of E parameters as a function of ionic strength

3.3.2 The redox potential of Tl(III)/Tl(I) in glacial acetic acid

The potential of Tl(III)/Tl(I) in glacial acetic acid have been measured in this work using various cell types e.g., concentration cell with liquid junction, concentration cell without liquid junction and that with salt bridge to minimize a junction potential. In the first 2 types mercury-mercurous acetate electrode was used as a reference electrode whereas the third cell employed calomel electrode for a secondary reference electrode and minimize a junction potential by using a salt bridge. The preparation of the cell solution is described below.

As has been mentioned earlier that thallic acetate is unstable to the atmosphere hence must be kept under the surface of glacial acetic acid, the solution of thallic acetate therefore had to be determined for its concentration indirectly for weighing of the dried sample can not be done out of the dry box. The procedure chosen for this work is as follows.

The desired amount of thallous acetate was weighed out accurately and mixed with the approximately known weight of thallic acetate in acetic acid solution whose concentration range covering 1 M up to the concentrated one. Thallic ion concentration was determined by titration with sodium thiosulphate iodometrically at the beginning of the measurement and also afterwards. The mixed solution of thallium acetate and free acid was found unchanged in composition during the course of experimentation (about three months) if it is kept in the dark. The acetic acid concentrations were analysed by titration with standard sodium hydroxide.

A. Cell without liquid junctions

$$\mathrm{Hg}\left|\mathrm{Hg_2(OAc)_2},\ \mathrm{HOAc(c)},\ \begin{matrix}\mathrm{TlOAc}\\ \mathrm{Tl(OAc)_3}\end{matrix}\right|\mathrm{Pt}\ldots\mathrm{(AI)}$$

In this case the cell solution was identical both for the reference electrode i.e., mercury-mercurous acetate electrode and for Tl(III)/Tl(I) electrode. The solution was prepared by dissolving a known concentration of thallous acetate and thallic acetate in varying concentration of acetic acid starting from 1 M to 13 M. Care was taken to keep the concentration ratio of Tl(I) to Tl(III) to be approximately constant throughout. Two platinum foils were used as an inert electrode and dipped into the cell solution in one compartment to form a Tl(III)/Tl(I) electrode. The half cells were connected in a similar manner as shown in Fig. 3.1 . By this arrangement the liquid junction potential was eliminated.

Attempts have been made to measure the cell potential in the presence of glacial acetic acid but failed to obtain any readings. The redox potential of Tl(III)/Tl(I) in glacial acetic acid was then read off from the graph at 100% glacial acetic acid (17.41 M) by the method of direct extrapolation (see Fig. 5.1).

Calculation

The cell reaction of cell (AI) is written as:

$$2\mathrm{Hg}_{(l)} + 2\ \mathrm{OAc}^- + \mathrm{Tl}^{3+} \longrightarrow \mathrm{Hg_2(OAc)}_{2(s)} + \mathrm{Tl}^+$$

$$\text{Therefore}\quad E = E^{\circ} - \frac{RT}{2F} \ln \frac{a_{\mathrm{Tl}^+}}{a_{\mathrm{Tl}^{3+}}\, a^2_{\mathrm{OAc}^-}}$$

$$E = E^{\circ} - 0.0295 \log \frac{c_{\mathrm{Tl}^+}\,\gamma_{\mathrm{Tl}^+}}{c_{\mathrm{Tl}^{3+}}\,\gamma_{\mathrm{Tl}^{3+}}\,Kc(1-\alpha)\,\gamma^2_{\mathrm{OAc}^-}}$$

The value of E° at various acetic acid concentrations computed from the above equation are shown in Table 4.3 .

Measurement has also been made on the following cell,

$$\mathrm{Hg}\left|\ \mathrm{Hg_2(OAc)_2,\ HOAc(c)}\ \right|\ \begin{matrix}\mathrm{HOAc(c),\ TlOAc}\\ \mathrm{Tl(OAc)_3}\end{matrix}\ \left|\ \mathrm{Pt}\ldots\mathrm{(AII)}\right.$$

slightly different cell e.m.f. and $E^{\circ}_{\mathrm{Tl(III)/Tl(I)}}$ were obtained when a similar treatment of data as the preceding cell was made. The comparison can be made by the study of Table 4.3 and 4.4, Fig. 5.1 and 5.2 .

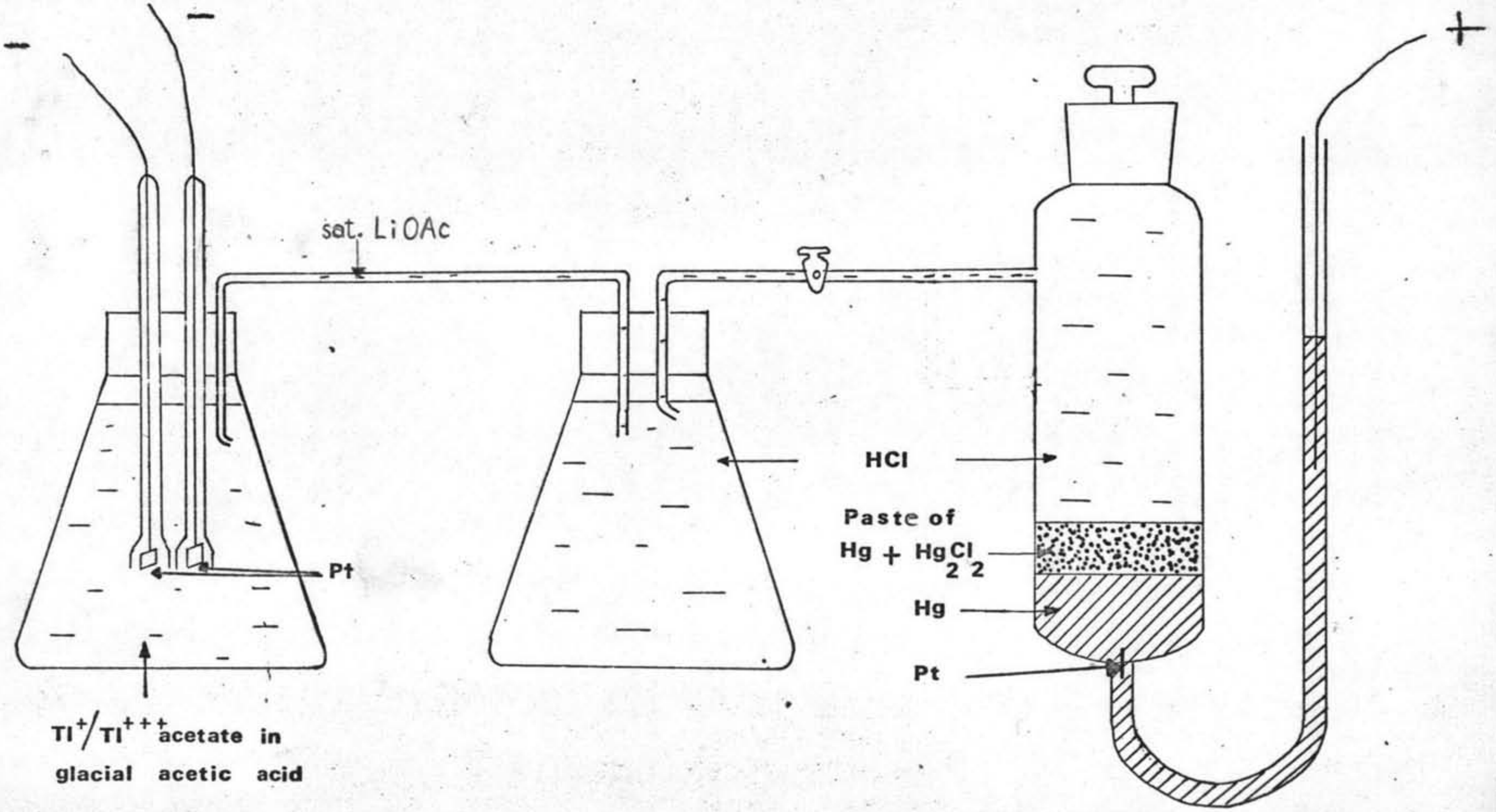

Fig. 3.4 The cell assembly :

$$Hg \left| Hg_2Cl_2, HCl(c) \right| \text{sat. LiOAc} \left| \begin{matrix} \text{pure HOAc, TlOAc} \\ Tl(OAc)_3 \end{matrix} \right| Pt$$

B. Cell with salt bridge

$$\mathrm{Hg}\,|\,\mathrm{Hg_2Cl_2},\ \mathrm{HCl}\,|\,\text{sat. LiOAc}\,|\ \text{pure HOAc},\ \begin{matrix}\mathrm{TlOAc}\\ \mathrm{Tl(OAc)_3}\end{matrix}\ \Big|\,\mathrm{Pt}\ldots(\mathrm{B})$$

When calomel was used as a reference electrode, it is necessary to use a salt bridge in order to minimize the liquid junction potential. The salt bridge was prepared by mixing lithium acetate and agar in a hot glacial acetic acid. The cell assembly is illustrated in Fig. 3.4.

Calculation

The cell reaction of cell (B) is written as:

$$2\mathrm{Hg}_{(l)} + 2\mathrm{Cl}^- + \mathrm{Tl}^{3+} \longrightarrow \mathrm{Hg_2Cl}_{2(s)} + \mathrm{Tl}^+$$

Therefore $E = E^\circ - \frac{RT}{2F} - \ln \frac{a_{\mathrm{Tl}^+}}{a_{\mathrm{Tl}^{3+}}\ a^2_{\mathrm{Cl}^-}}$

$$= E^\circ - 0.0295 \log \frac{c_{\mathrm{Tl}^+}\ \gamma_{\mathrm{Tl}^+}}{c_{\mathrm{Tl}^{3+}}\ \gamma_{\mathrm{Tl}^{3+}}\ c^2_{\mathrm{Cl}^-}\ \gamma^2_{\mathrm{Cl}^-}}$$

The values of E° are calculated and shown in Table 4.5.

3.4 Other Experimental Studies

3.4.1 The stability of thallic acetate

As can be seen from chapter I that the Tl(III) salts are more unstable than the Tl(I) salts. It was therefore thought necessary to perform a series of experiments to find the optimum conditions under which the thallic acetate will be most stable. The solution of thallic acetate in acetic acid once prepared was determined for the salt concentration by the conventional iodometric method such as that given in Vogel "A Text Book of Quantitative Inorganic Analysis". In this work the dead stop end point technique was used in the titration. The reactions which are liable to occur are as follows.

$$Tl^{3+} + 3I^- \longrightarrow TlI + I_2$$

$$I^- + I_2 \longrightarrow I_3^-$$

$$I_3^- + 2S_2O_3^= \longrightarrow 3I^- + S_4O_6^=$$

Therefore $Tl^{3+} \equiv 2S_2O_3^=$

The change in concentration was followed every day for a period of fortnight. A slightly different concentration of solutions of thallic acetate in varying strength of acetic acid ranging from 10% to 100% acid at 10% interval were studied by the above

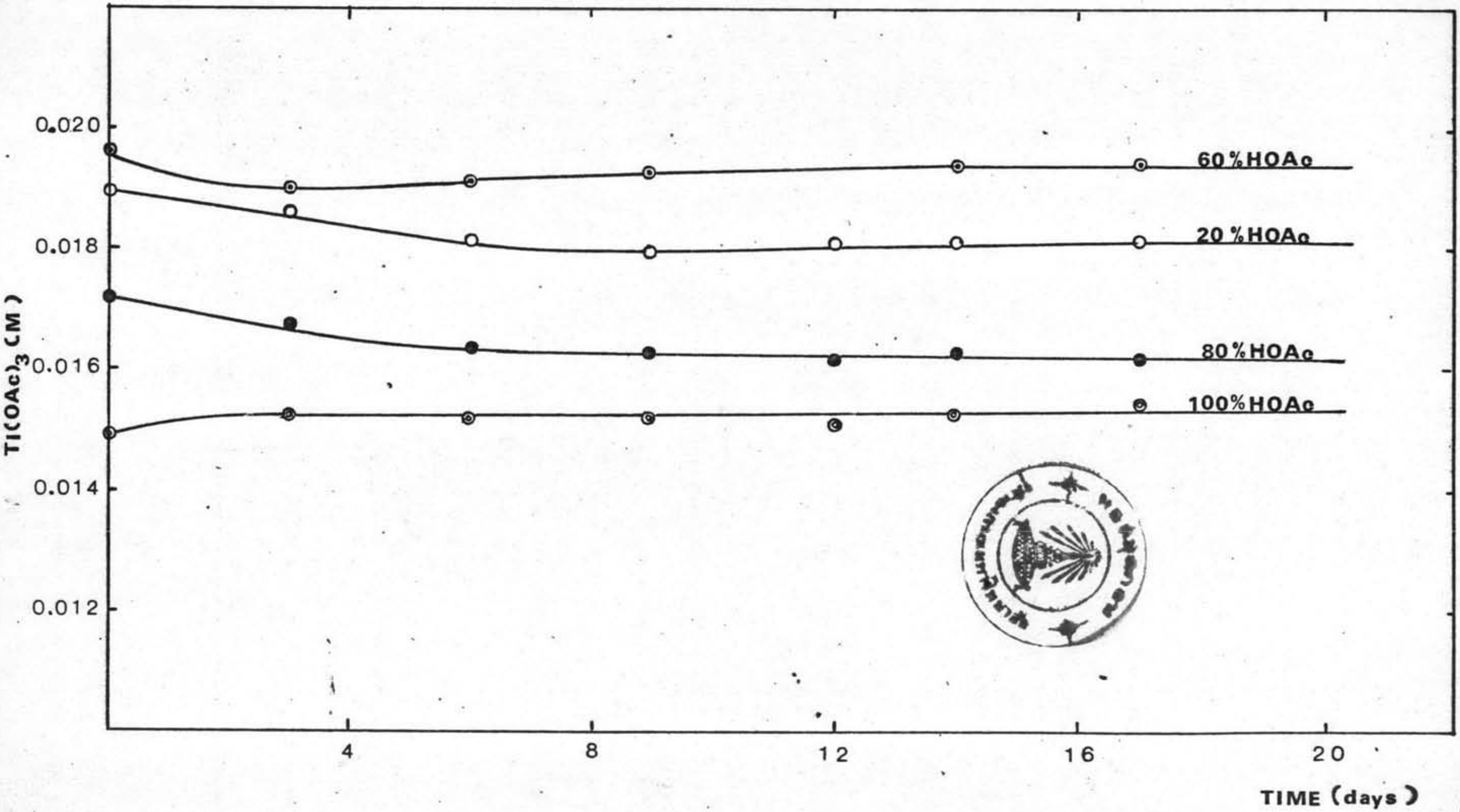

Fig. 3.5 Changes in composition of TI(OAc)$_3$ with time and strength of acetic acid

mentioned procedure. Results are tabulated in Table 4.6 and shown graphically in Fig. 3.5

3.4.2 Determination of water content in glacial acetic acid by Karl Fischer titration

The Precision Auto-Aquatrator manufactured by Precision Scientific Company is used for a Karl Fischer titration. The Karl Fischer (K.F.) reagent, consisting of a mixture of pyridine-sulphur dioxide, iodine and methanol, reacts with the water in the sample to give an apparent resistance change due to the depolarization effect on the electrode.

The automatic aquatrator utilizes either the "direct" or "back" titrations. In direct titration, Karl Fischer reagent is added to a moisture bearing sample until a moisture free state is reached. In the back titration, excess Karl Fischer reagent is added to the sample to carry it beyond the end point, and then this solution is automatically titrated with standard water methanol solution (W.M.) to the end point. In either method, the equivalent water content of the Karl Fischer reagent must be known by standardisation with standard water methanol solution.

If back titration was used, the error would occur due to the sensitivity of Karl Fischer reagent to water and the long time in operation. So in this study, only direct titration was employed.

Standardisation and titration

Five ml. of a standard water methanol solution were pipetted into a beaker and automatically titrated with a Karl Fischer reagent. This apparatus uses the "dead stop" method for determining the end point of the titration. Shortly afterwards the 10 ml. portion of glacial acetic acid was titrated against the Karl Fischer reagent by the so called "direct titration" method. By comparing the amount of the Karl Fischer reagent needed to react with a known amount of water in a water methanol solution to that used for glacial acetic acid, the percentage of water content in glacial acetic acid was obtained.

Calculation for water content in glacial acetic acid

It was found by titration that 5 ml. of water methanol solution needed 9.3 ml. of Karl Fischer reagent in the standardisation of the Karl Fischer reagent. Hence 1 ml. of Karl Fischer reagent is equivalent to 0.5376 ml. of water methanol solution. This relationship can be written as:

$$\frac{5\text{ ml. W.M.}}{9.3\text{ ml. K.F.}} = \frac{0.5376\text{ ml. W.M.}}{1\text{ ml. K.F.}}$$

From manufacturer data, 1 ml. water methanol solution contains 1.01 mg. $H_2O \pm 0.01$ mg.

Therefore $$\frac{0.5376 \text{ ml. W.M.}}{1 \text{ ml. K.F.}} = \frac{0.5736 \text{ ml. W.M.}}{1 \text{ ml. K.F.}} \times \frac{1.01 \text{ mg. } H_2O}{1 \text{ ml. W.M.}}$$

$$= \frac{0.5794 \text{ mg. } H_2O}{1 \text{ ml. K.F.}} \quad .....(1)$$

Ten ml. of glacial acetic acid was reacted completely with 4.03 ml. of Karl Fischer reagent.

From equation (1), it was found that every 1 ml. of Karl Fischer reagent react with 0.5794 mg. H_2O. Therefore 4.03 ml. of Karl Fischer reagent should react with 0.5794 x 4.03 mg. H_2O.

It follows that 10 ml. of glacial acetic acid contain 0.5794 x 4.03 mg. H_2O which is corresponding to 0.0234% water content in glacial acetic acid.

3.5 Conductivity Measurements

The degree of dissociation of acetic acid solution can be computed from the conductivity data, from which the dissociation constant of acetic acid at various concentrations are derived. The formula used for such a calculation is presented in Appendix II . Similarly, solutions of thallous acetate and thallic acetate in glacial acetic acid were measured for their conductivities.

The Serfass conductance bridge manufactured by Messr. Arthur H. Thomas Company was used in the measurement of conductivities of acid and salts at 25 ± 0.5°c. The cell is a dipped cell type constructed of glass, with a pair of platinised platinum plate electrodes separated by a definite distance. The so called "cell constant" was determined by measuring the resistance of the standard solution of a 0.01 demal potassium chloride as specified by Jones and Bradshaw (12) and whose specific conductivity is accurately known to be 0.0014087 $\text{ohm}^{-1}\ \text{cm.}^{-1}$. The deionized water with 1.45 $\text{microohm}^{-1}\text{cm.}^{-1}$ specific conductance was used in the dilution. The cell constant of the dipped cell was obtained by inserting the value of L, specific conductance in $\text{ohm}^{-1}\text{cm.}^{-1}$ and R, resistance in ohm, into the expression:

$$\text{cell constant} = LR$$

The acetic acid solutions of different concentrations were prepared and standardised by a conventional method as mentioned in the previous chapter. The specific conductance at each concentration was measured. Results were then converted to the equivalent conductance using the well known relationship viz $\Lambda = 1000\ L/c$.

Since Λ_0 value is well established and known to be 390.71 $\text{ohm}^{-1}\text{cm.}^{2}$/equivalent. It was thought practical to use this value in the computation of α (see Appendix II) in conjunction with the Λ value obtained by this work. Table 4.7 shows the conductivity data and its related parameters.