PHYSICO-CHEMICAL STUDIES OF SOLUTIONS OF SOME ACIDS IN ACETONE

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by

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PREFACE

I would like to express my most sincere thanks to Dr. A.H. Spong, Senior Lecturer in Physical Chemistry at the University of Cape Town and Dr. M.C.B. Hotz, formerly of the Departement of Chemistry at the University of Cape Town and now at the Extraction Metallurgy Division, Department of Mines and Technical Surveys, Ottawa, Canada, under whose supervision and guidance this work was undertaken.

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SUMMARY

The work of Hotz showed the lack of knowledge of the behaviour of electrolytes in acetone solutions as well as the uncertainty as to the possibility of preparing anhydrous acetone and the stability of this solvent, if it could be prepared.

An extensive study was therefore undertaken in which the efficiency of various desiccants was studied in producing acetone as anhydrous as could be obtained.

A very efficient still was designed and the average water content of the acetone produced was of the order of 0.006 per cent which is much lower than reported by any previous investigator. Moisture determinations were done using a modified Karl Fischer reagent.

Stability studies of "anhydrous" acetone extending over a period of about fifteen months showed no remarkable increase in the moisture content and it was concluded that "anhydrous" acetone, if treated with care, is exceptionally stable to self-condensation.

Hydrogen chloride was shown to be an extremely weak acid in acetone solutions with an apparent dissociation constant of about 10^{-7}, whereas perchloric acid proved to be a relatively strong acid in acetone solutions with a

dissociation constant of about 10^{-4}. Extremely high values were obtained for the limiting equivalent conductances. In view of the fact that the limiting equivalent conductances of most electrolytes are up to 20% higher in acetone solutions than in water, these high values are acceptable.

Although solutions of hydrogen chloride in acetone are relatively stable at low temperatures (-80°C), at ordinary temperatures hydrogen chloride catalyses the self-condensation of acetone to mesityl oxide. An extensive study was made of this reaction and a mechanism proposed for the self-condensation of acetone to mesityl oxide.

The work of Everett and Rasmussen on the cell $Pt,H_2/HCl/AgCl,Ag$ in acetone was repeated and an improved equation was used for calculating the standard electromotive force of this cell. Remarkable agreement was obtained between the present results (-0.488 volt) and the recalculated value (-0.491 volt) from the results of Everett and Rasmussen.

Transport measurements, although in agreement with the work of Erdey-Gruz, proved to be extremely difficult under present conditions, due to excessively high cell resistances.

Diffusion measurements were done on solutions of hydrogen chloride in acetone, using hydrogen chloride labelled with chlorine-36 and employing the capillary tube method developed by Anderson and Saddington.

The shape of the diffusion coefficient-concentration curve showed a resemblance to the corresponding plot for sodium chloride in aqueous solution, but the much more pronounced minimum possibly indicates strong association or changes in the degree of association. Extrapolation of the plot gave a diffusion coefficient at infinite dilution of about $5 \times 10^{-5} cm^2 sec^{-1}$, which is in agreement with the value of $4.63 \times 10^{-5} cm^2 \ sec^{-1}$ calculated by the Nernst relation.

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INTRODUCTION

Our present day knowledge of the behaviour of solutions of electrolytes in non-aqueous organic solvents is rather meagre and even the latest monographs on electrochemistry hardly mention work in non-aqueous media.

Since 1926 a number of papers have been published covering different aspects of the electrochemistry of solutions of electrolytes in acetone. As there was much conflicting evidence relating to the electrochemistry of solutions in this solvent, the present investigations were undertaken in an attempt to improve on existing knowledge.

This thesis opens with a review of all previous work done in "anhydrous" acetone and proceeds to state the aims of and reasons for the present work.

Sections II and III deal with the preparation and stability of "anhydrous" acetone and conductance measurements on solutions of hydrogen chloride and perchloric acid in this solvent, respectively. The investigation of the stability of solutions of hydrogen chloride in acetone is described in section IV.

In sections V and VI are the results of electromotive force and diffusion coefficient measurements respectively on solutions of hydrogen chloride in acetone.

The thesis concludes with section VII in which ideas are presented for further research.

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SECTION I

SURVEY OF PREVIOUS WORK

1.1 INTRODUCTION

Since 1926 about nine papers have been published on electrochemical studies in acetone solutions, yet very little is known about the state of electrolyte solutions in this solvent and results reported in some of these papers are contradictory. For example, Sackur[1], in 1902, determining the conductance of solutions of hydrogen chloride in acetone, found it to behave as a strong acid. His results were accepted by Braude[2], who, using Sackur's extrapolated value of 12 $ohm^{-1}cm^{2}$ for the limiting equivalent conductance, reported hydrogen chloride to be largely dissociated in acetone solutions. His results were based on spectrophotometric measurements. Ross Kane, quoted by Hartley and Hughes[3], Mackor and Spaarnaay quoted by Everett and Rasmussen[4], and also Hotz[5] in 1958, came to the conclusion that hydrogen chloride is a weak acid in acetone solutions with an apparent dissociation constant of 10^{-7} to 10^{-8}.

Conductimetric studies of solutions of potassium iodide in acetone, although not contradictory, revealed widely differing results.

A possible explanation for these contradictory and differing results is the variation in quality of the acetone used in these studies or in the possibility of contamination of solutions by atmospheric moisture.

It was therefore thought appropriate to examine and compare all methods for the preparation of "anhydrous" acetone which have been described and to make a comparative survey of all previous electrochemical studies in anhydrous acetone solutions.

1.2 METHODS FOR THE PREPARATION OF "ANHYDROUS" ACETONE

All methods were essentially similar and involved desiccation of either commercially pure acetone, or acetone purified through the bisulphite addition compound, over suitable drying agents followed by refluxing and fractionation or distillation over the same or different drying agents or without drying agents.

Calcium chloride, potassium carbonate, sodium sulphate, copper sulphate, magnesium sulphate and phosphorus pentoxide have been used as desiccants, acetone being refluxed over these drying agents followed by fractional distillation. As criterion of purity the specific conductance of the purified acetone was used and widely differing results were reported.

Everett and Rasmussen[6] purified their acetone through the bisulphite addition compound, followed by distillation, kept the liquid over potassium permanganate for several days and finally fractionated the liquid. Their product had a specific conductance of $3.5 \times 10^{-9} ohm^{-1} cm^{-1}$. Dippy, Jenkins and Page[7], using analar acetone as starting material, as they considered this superior to the bisulphite purified liquid, examined the efficiency of various dehydrating agents e.g. phosphorus pentoxide, anhydrous sodium carbonate, sodium sulphate and magnesium sulphate. All these desiccants were, however, inefficient, phosphorus pentoxide reacting strongly with acetone.

Their final method was to fractionate acetone, which has been kept for two weeks over ground fused calcium chloride to which a little potassium carbonate has been added, through a long column packed with glass beads. They obtained a liquid which had specific conductances varying between 6×10^{-8} and $13 \times 10^{-8} ohm^{-1} cm^{-1}$. This method was also adopted by French and Roe[8] who obtained a product with specific conductance $9.99 \times 10^{-8} ohm^{-1} cm^{-1}$.

Walden, Ulich and Busch[9] used acetone purified through the bisulphite compound, dried the liquid over potassium carbonate followed by fractionation. The resulting acetone had a specific conductance of $6 \times 10^{-8} ohm^{-1} cm^{-1}$.

Daly and Smith[10] refluxed acetone over anhydrous copper sulphate, fractionally distilled it from a fresh sample of the salt and obtained a specific conductance of $6 \times 10^{-8} ohm^{-1} cm^{-1}$ for their solvent.

Lannung[11] dried Merck "pro-analysi" acetone for one day over potassium carbonate followed by a vacuum distillation of the liquid from fresh potassium carbonate in an all glass apparatus, producing acetone with a specific conductance of about $10^{-10} ohm^{-1} cm^{-1}$. He claimed that potassium carbonate drying followed by normal distillation leaves 0.15% water which can only be removed by efficient fractionation. Reynolds and Kraus[12] agitated acetone over calcium chloride for several days followed by a double distillation from activated alumina and obtained a solvent with a specific conductance of $1\text{-}2 \times 10^{-9} ohm^{-1} cm^{-1}$.

Dippy and Hughes[13] prepared a "Grade I" acetone by shaking analar acetone over calcium chloride for four days followed by refluxing for two to three hours.

The liquid was then allowed to stand over alumina for seven to ten days after which the acetone was filtered on to fresh alumina and the procedure repeated. Finally the acetone was fractionated and the product collected in a "dry-space" under an atmosphere of dry air. Manipulation inside the "dry-space" was performed through surgical gloves let into one side. Acetone so prepared had specific conductances varying between 2.08 x 10^{-8} and 2.36 x 10^{-8} $ohm^{-1}cm^{-1}$ and their lowest recorded specific conductance was 8 x 10^{-9} $ohm^{-1}cm^{-1}$.

Hotz[5] slightly modified the procedure of Dippy and Hughes[13] by reducing the periods of standing to twelve and twenty four hours respectively between the first and second reflux and the fractionation. Acetone was decanted from the first reflux flask on to freshly baked out alumina, twelve hours after refluxing; refluxed for three hours in the dark, allowed to stand for twenty four hours, then blown over, using dry nitrogen, on to baked out alumina in the distilling flask. The liquid was fractionated through a 1.1 metre column packed with glass rings and the product collected in a specially designed container inside a "dry-box" which was kept under a slight positive pressure of nitrogen.

No mention was made in his thesis of the spesific conductance of his acetone, but as a check on the quality of his solvent, he compared the conductance of solutions of potassium iodide in acetone with that obtained by Reynolds and Kraus[12] and Dippy and Hughes[13]. His results were intermediate between those of these investigators.

Dorofeeva and Kudra[14] measured conductances of solutions of hydrogen chloride in acetone, but did not report either their method of preparation of "anhydrous" acetone or the specific conductance of their solvent.

In the present investigation the procedure of Dippy and Hughes[13] was adopted and slightly modified by having two refluxes for three hours over activated alumina with periods of three to four days between the refluxes and fractionation. An improved acetone still was used and acetone dried over calcium chloride only came into contact with the atmosphere on being introduced into the apparatus. All further operations were carried out under an atmosphere of dry nitrogen, which is in itself a great improvement on all previous procedures, except perhaps for the vacuum distillation method of Lannung[11].

1.3 THE DETERMINATION OF THE MOISTURE CONTENT OF "ANHYDROUS' ACETONE

Very few of the previous investigators determined the actual moisture content of their purified acetone. Everett[15] was of opinion that acetone under conditions of low water content would self-condense with the production of water, so that truly anhydrous acetone could not exist. Eck[16] claimed that absolute purification is impossible and small traces of water always persist.

Mysels[17] made use of the conductances of saturated solutions of the alkali metal chlorides and caesium-and potassium fluorides in acetone to determine the moisture content of acetone. His results indicated that in truly anhydrous acetone the conductances of saturated solutions of the alkali halides would be close to zero.

A modified Karl Fischer reagent[18] for use with ketones as described by Mitchell and Smith[19] was used by Dippy and Hughes[13] in a potentiometric titration to determine the moisture content of their acetone. This titration was also performed by Hotz[5] who used a specially designed "moisture proof" apparatus. "Grade I" acetone as prepared by Dippy and Hughes had a water content of 0.18 per cent and Hotz's acetone had a water content varying between 0.08 and 0.13 per cent.

In the present investigations the modified Karl Fischer reagent was used and acetone having a water content less than 0.01 per cent was obtained.

1.4 CONDUCTIMETRIC STUDIES IN ANHYDROUS ACETONE

Since 1926 seven papers have been published on the conductance of solutions of potassium iodide in acetone.

Dippy and Hughes[13] redetermined the conductance of solutions of potassium iodide in their "Grade I" acetone, applied the Fuoss treatment[20] to their results and all previous results for comparisson. Widely differing values were obtained for the limiting equivalent conductance, the highest value of 196.6 $ohm^{-1}cm^{2}$, being that of Dippy and Hughes themselves, the nearest to this being 192.8 $ohm^{-1}cm^{2}$ from the results of Reynolds and Kraus[12]. Their study suggests that the variable factor in the solvent grades is the water content.

The effect of water on solutions of potassium iodide in acetone has previously been shown by Hughes and Hartley[21] to be preferential solvation of the potassium ion, increasing its effective radius and thus reducing the value of Λ_∞. As a further test Dippy and Hughes added weighed quantities of water to their "Grade I" acetone and redetermined the conductances of solutions of potassium iodide in these acetone-water mixtures.

The following table gives their results of the effect of added water on conductances.

TABLE 1.4.1

EFFECT OF ADDED WATER TO ACETONE ON THE CONDUCTANCES OF SOLUTIONS OF POTASSIUM IODIDE

Per cent water	Λ_{KI} at $c = 10^{-4}$ mole $litre^{-1}$
0.18 ("Grade I")	188.0
0.22	187.5
0.87	184.0
1.65	178.0

Conductance measurements were carried out by Walden, Ulich and Busch[9] on solutions of lithium picrate, sodium- and potassium iodide and several tetraethylammonium and related organic salts in acetone. The Debye-Hückel-Onsager square root law was valid in many cases, but limiting slopes were greater than those calculated by the Onsager equation.

Conductances of solutions of perchloric acid and some of its salts in acetone were determined by Ross Kane[3] who found these to behave as strong electrolytes in acetone solutions. Accascina and Schiavo's[22] conductance measurements on solutions of the alkali perchlorates in acetone, however, showed these salts to behave as weak electrolytes which do not obey the Onsager equation.

Ross Kane's[3] results for solutions of tetramethylammonium salts agreed fairly well with those of Walden, but his limiting equivalent conductances for the alkali metal salts were about 3 per cent higher.

Reynolds and Kraus[12] repeated some of Walden's work and extended their measurements to several substituted ammonium salts. Fuoss analyses[20] were applied to their conductance results and ion conductances calculated on Fowler's assumption that the conductances of the tetrabutylammonium and triphenylborofluoride ions were equal[23].

Anion conductances were found to be greater than corresponding cation conductances which is in accord with Ross Kane's suggestion that specific interaction occurred between solvent and cation. This observation has also been made by Pullen and Pollock[24] in their infra red studies of solutions of silver- and lithium picrate in acetone. These workers concluded that the cation is solvated by two acetone molecules.

The conductance of the fluoride ion as determined by Reynolds and Kraus[12] was found to be abnormally low and they discussed this in the light of ionic size and solvation of the alkali metal ions and steric effects on the dissociation constants of salts of organic acids and bases.

McDowell and Kraus[25] determined the conductances of solutions of ammonium salts and substituted ammonium salts in acetone and calculated the limiting equivalent conductances of the ammonium-, tetramethylammonium, tetrapropylammonium, tetraamylammonium ions and the chloride ion. Dissociation constants were determined by the Fuoss method.

They regarded viscosity changes as being insufficient to account alone for the change in mobility and were of opinion that structural and constitutional properties of the solvent must also be considered.

Conductances of solutions of picric acid, perchloric acid and hydrogen chloride in acetone were determined by Ross Kane[3]. He found hydrogen chloride and picric acid to behave as weak electrolytes, whilst perchloric acid was a strong acid in acetone solutions. He observed the perchloric acid solutions to be unstable and turn brown on standing with a decrease in hydrogen ion concentration. Added water stabilised these solutions.

Extrapolation of the plots of Λ against $\sqrt{c}$ produced limiting equivalent conductances of 199 $\text{ohm}^{-1}\text{cm}^{2}$ and 207 $\text{ohm}^{-1}\text{cm}^{2}$ for the hydrogen chloride and perchloric acid solutions respectively and gave a calculated limiting equivalent conductance of 88 $\text{ohm}^{-1}\text{cm}^{2}$ for the hydrogen ion. This low value for the proton conductance indicated the impossibility of a Grotthus-type proton transfer mechanism. Braude[2], however, in his spectrophotometric determinations of acidity functions has shown the existence of the Me_2COH^+ ion so that a form of Grotthus conduction could possibly occur.

Mackor[4] and Spaarnaay[4], measuring the conductance of solutions of hydrogen chloride in acetone, found this acid to be an extremely weak electrolyte in acetone solutions with an apparent dissociation constant between 10^{-7} and 10^{-8}. On the other hand, Braude[2] concluded that hydrogen chloride is almost completely dissociated in acetone solutions, but he based his calculations on a limiting equivalent conductance of 12 $ohm^{-1}cm^{2}$ as obtained by Sackur.

Everett and Rasmussen[6] determined the solubility of silver chloride in solutions of hydrogen chloride in acetone and on the basis of a complexity constant of 5 for the reaction

$$AgCl + Cl^{-} \rightleftharpoons AgCl_2^{-}$$

as determined by Mackor[26], found the apparent dissociation constant of the acid to be about 10^{-8}.

Measurements of the conductance of solutions of hydrogen chloride in acetone were also made by Hotz[5] and by Dorofeeva and Kudra[14]. These workers came to the same conclusions as Everett and Rasmussen. Hotz, extrapolating a plot of Λ against $\sqrt{c}$ obtained a limiting equivalent conductance of 210 $ohm^{-1}cm^{2}$ and an apparent dissociation constant of about 10^{-7} for hydrogen chloride in acetone solutions.

A new conductance equation was developed by French and Roe[8] to fit their results of the conductance of solutions of picric acid in acetone. They postulated triple ion formation, which was first suggested by Fuoss and Kraus[27], the ion being $(Pi-H-Pi)^-$, and explained the variation of conductance with concentration on this hypothesis.

Griffiths and Lawrence[28] measured the conductance of solutions of silver nitrate in acetone and concluded that triple ions would be largely dissociated to simpler species.

1.5 E.M.F. AND TRANSPORT STUDIES

Ulich and Spiegel[29] made a study of metal-metal halide electrodes in acetone solutions. Their results were irreproducible and they considered this to be due to the formation of ions of the type $M_mX_n^{(n-m)-}$.

However, Everett and Rasmussen[6] found the silver-silver chloride electrode to behave satisfactorily in acetone solutions and Arthur and Lyons[30] have used calomel electrodes successfully for their polarographic studies of solutions of acid halides in acetone.

Everett and Rasmussen[6] studied the cell $Pt,H_2/HCl/AgCl,Ag$ in acetone solutions. Their results indicate that the acid is a weak electrolyte in acetone solutions and using an approximate dissociation constant they were able to calculate the standard electromotive force of the cell.

Erdey-Gruz[31] determined transport numbers in acetone and acetone-water mixtures, making use of the cell $Pt,H_2/0.01M\ HCl//0.1M\ HCl/H_2,Pt$. Values of 0.22 and 0.79 were obtained for the cation and anion transport numbers respectively. Birkenstock[32] determined transport numbers in solutions of lithium chloride and bromide and sodium iodide in acetone by the Hittorf method.

1.6 AIMS AND OBJECTIVES OF THE PRESENT WORK

In view of the uncertainty as to the state of electrolytes in acetone solutions, investigations described in this thesis were undertaken with the following aims:

(i) The view has been expressed that anhydrous acetone could not be prepared as small amounts of water would always persist. An improved still was therefore designed and the efficiency of various desiccants investigated for the preparation of "anhydrous" acetone, such that the quality of the product would be as nearly the same from batch to batch as possible.

(ii) Everett[15] was of opinion that anhydrous acetone was unstable and would self-condense with the formation of water. Batches of acetone, having the lowest water content that could be obtained under present conditions, were therefore prepared and stored in sealed tubes for periods up to fifteen months. Conductance and moisture determination were carried out on these samples at various intervals.

(iii) Ross Kane[3] was not able to reproduce his conductance measurements on solutions of hydrogen chloride in acetone to a sufficient degree of precision and furthermore, although most investigators confirmed that hydrogen chloride behaves as a weak electrolyte in acetone solutions with an apparent dissociation constant of 10^{-8}, some contradictory results have been reported.

In an attempt to clarify the position conductance measurements on solutions of hydrogen chloride in acetone were repeated and extended to the highest obtainable dilution in order to obtain a more accurate extrapolation to infinite dilution. Special precautions were therefore taken in the preparation of anhydrous hydrogen chloride gas and its acetone solutions.

Solutions of perchloric acid in acetone had been studied by Ross Kane[3] who found that this acid behaves as a strong electrolyte in acetone solutions. Similar conclusions were arrived at by Coetzee and McGuire[33] in a publication, which appeared whilst this thesis was in preparation, on conductance studies of solutions of perchloric acid in acetone.

Neither Ross Kane or Coetzee and McGuire used a method for the preparation of their solutions which would give a pure solution of perchloric acid in acetone.

Fresh investigations of the problem were therefore desirable.

(iv) It has been observed by Ross Kane[3] and other workers[34] that solutions of perchloric acid and hydrogen chloride in acetone turned brown on ageing. Hotz[5] could not detect any change in conductance at low hydrogen chloride concentrations over periods up to twelve hours. Apart from this no other investigation into this problem of the stability of solutions of acids in acetone has been reported.

Since a knowledge of the rate of this reaction could throw light on the validity of conductance and other electrochemical studies of solutions of acids in acetone, it was desirable to make a detailed study of this reaction.

(v) In calculating the standard electromotive force of the cell Pt,H_2/HCl/AgCl,Ag in acetone Everett and Rasmussen[6], and also Hotz[5] used the approximate value of 10^{-8} for the dissociation constant, since conductivity data were not sufficiently reliable to calculate degrees of dissociation and mean ionic activity coefficients.

The present investigations therefore aimed at repeating Everett and Rasmussen's electrochemical studies. Combining these results with improved conductance data, use can be made of the equation[35]

$$E + 2k\log\alpha m - 2k'A\sqrt{\alpha m} = E^{o} - 2k'Cm$$

to obtain a more accurate value for the standard e.m.f. of the cell.

All limiting equivalent ionic conductances reported, were calculated on Fowler's assumption that the tetrabutylammonium and triphenylborofluoride ions have equal limiting equivalent conductances[23].

Accurately known cation and anion transport numbers were therefore highly desirable. The cells

$$\mathrm{Pt,H_2/}\underset{m_1}{\mathrm{HCl}}\mathrm{/AgCl,Ag,AgCl/}\underset{m_2}{\mathrm{HCl}}\mathrm{/H_2,Pt}$$

and

$$\mathrm{Ag,AgCl/}\underset{m_1}{\mathrm{HCl}}\,\vdots\,\underset{m_2}{\mathrm{HCl}}\mathrm{/AgCl,Ag}$$

in acetone solution were therefore investigated.

(vi) Mackor[26] was of opinion that hydrogen chloride dimerised in acetone solutions and Hotz[5] expressed the view that aggregates containing up to twelve hydrogen chloride molecules could exist in equilibrium with lower aggregates and postulated the equilibrium

$$xHCl \rightleftharpoons (HCl)_x \rightleftharpoons H^+ + (H_{x-1}Cl_x)^- \rightleftharpoons \quad ......$$

where $x = 1, 2, 3, ... 12.$

It was considered that a knowledge of the variation with concentration of the diffusion coefficient of hydrogen chloride in acetone solutions, might contribute to the solution of the problem. Diffusion coefficients of solutions of hydrogen chloride in acetone were therefore measured.

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SECTION II

THE PREPARATION AND STABILITY OF ANHYDROUS ACETONE

2.1 METHODS

The method developed by Dippy and Hughes[13] (p6) for the preparation of anhydrous acetone, was used and slightly modified. Analar acetone containing 1 per cent water was used as starting material. The liquid was shaken for four days over baked out calcium chloride, allowed to stand, then filtered on to activated alumina (Spence Type A) in the first reflux flask, A, (fig. 1). The entire apparatus was then gassed out with dry nitrogen after which refluxing was commenced and continued for three to four hours. All stopcocks immediately to the left and right of A were then turned so that this flask was isolated from the rest of the still.

The liquid in A was allowed to stand in the dark for four days. The liquid was then blown over with dry nitrogen to flask B, containing fresh alumina, and the procedure repeated. This was followed by blowing over the acetone to the first fractionation flask, C, and fractionating the liquid slowly through a 1.1 metre column packed with 1/8" Dixon gauze rings.

Acetone was first refluxed for about one hour in the column after which it was allowed to pass over into the second fractionation flask, D.

The final fractionation column was similar to the first, except that the top third of its length was packed with 1/16" gauze rings. Both still heads were so designed that most of the liquid returned to flasks C andD.

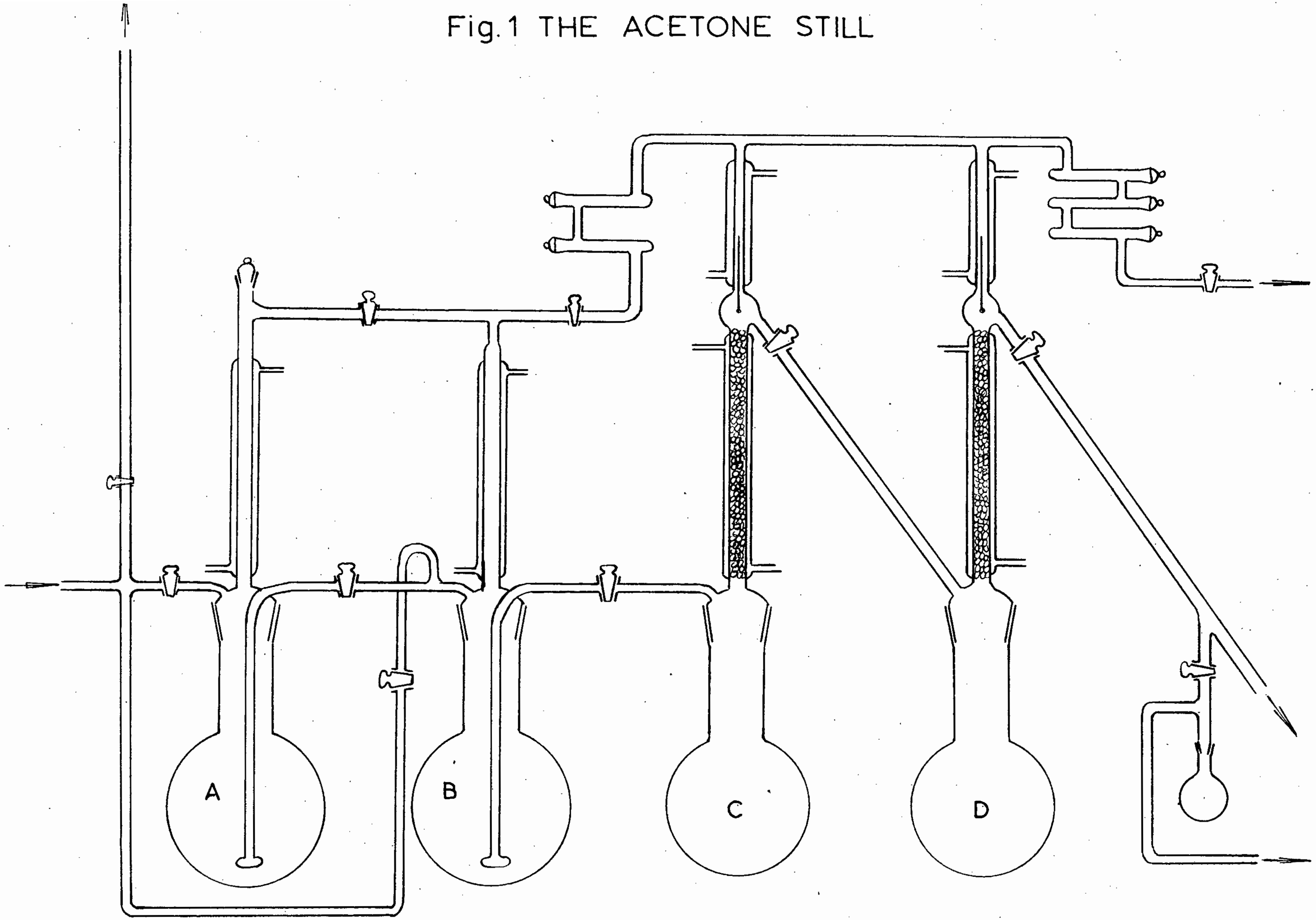
Fractionated acetone from D passed into a dry-box which was previously gassed out with dry nitrogen and kept at a slight positive pressure of the gas. All manipulations were carried out through neoprene gloves let into one side of the dry-box.

Anhydrous acetone so prepared was collected in a specially designed receiver (fig. 2) and kept in the dry-box. Most of the operations in preparing acetone were initially carried out in the dark, following Dippy and Hughes[13], to reduce the possibility of the photolysis of acetone.

However, it was found that carrying out the same procedure in dimmed light, did not seem to have any ill effect on the quality of the product and all further preparations were carried out under these conditions.

Dippy, Jenkins and Page[7] examined the efficiency of several drying agents and found phosphorus pentoxide, anhydrous potassium carbonate, sodium sulphate and magnesium sulphate inefficient.

Fig. 1 THE ACETONE STILL



In the studies described in this thesis, three desiccants were examined. In all three cases, the initial drying was over calcium chloride. The alumina in flasks A and B was consecutively replaced by calcium sulphate and barium oxide.

All three desiccants were found very efficient and the acetone so prepared contained approximately 0.005 per cent water.

The lowest specific conductance was obtained for the acetone prepared by the "alumina method", but the yield of product was higher for acetone prepared by the "calcium sulphate method" as in both cases where the basic desiccants were used, an appreciable fraction of the acetone was lost due to condensation of the starting material to mesityl oxide.

2.2 RESULTS

Several batches of "anhydrous" acetone were prepared using the three desiccants. The percentage water varied between 0.002 and 0.006 per cent and specific conductance were in the range 10^{-7} to 10^{-8} $ohm^{-1}cm^{-1}$.

Very few of the previous investigators made a careful study of the moisture content of their acetone, most workers comparing the conductance of solutions of potassium iodide in acetone as a check on the quality of their solvent.

TABLE 2.2.1

THE VARIATION OF WATER CONTENT AND SPECIFIC CONDUCTANCE OF ACETONE AS PREPARED BY DIFFERENT WORKERS USING VARIOUS DESICCANTS

Investigator	Desiccant	Percentage water	Specific Conductance ohm^{-1}cm^{-1}
This thesis	Alumina	0.003	2.8×10^{-8}
	$CaSO_4$ BaO	0.002_8 0.002_3	1.5×10^{-7} 8.0×10^{-8}
Hotz[5]	Alumina	0.08-0.13	-
Dippy and Hughes[13]	Alumina	0.18	$2.09-2.36 \times 10^{-8}$
Reynolds and Kraus[12]	K_2CO_3	-	$1-2 \times 10^{-9}$
Lannung[36]	K_2CO_3	0.2-0.3	approx. 10^{-10}

TABLE 2.2.2

THE EQUIVALENT CONDUCTANCE OF SOLUTIONS OF POTASSIUM IODIDE IN ACETONE

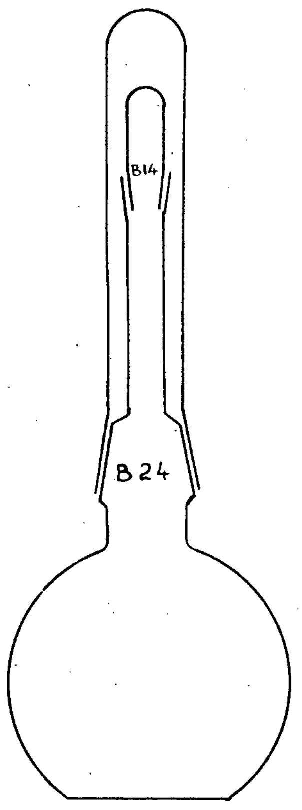
Conc. x 10^4 mole litre^{-1}	Equivalent Conductance			
	This work	Hotz	Dippy and Hughes	Reynolds and Kraus
6.250	171.8	170.7	171.5	168.2
9.000	166.4	164.7	166.0	163.1
12.25	161.0	159.0	160.7	158.0

2.3 THE STABILITY OF ANHYDROUS ACETONE

2.3.1 Introduction

In view of Everett's[15] opinion as to the instability of anhydrous acetone, batches of acetone were prepared, using the three desiccants alumina, calcium sulphate

Fig. 2 ACETONE RECEIVER



and barium oxide and having the lowest water content that could be obtained.

A number of samples of each batch were sealed in carefully cleaned and baked out glass tubes. At intervals over fifteen months, moisture determinations and specific conductance measurements were carried out on these samples.

2.3.2 The determination of the water content of "anhydrous" acetone

(a) The Karl Fischer reagent and apparatus

The reagent has been described by Mitchell and Smith[19] and modified by Ehmke[18] and consisted of a mixture of 270 ml pyridine, 668 ml benzene, 84.7 gm iodine and 64 gm sulphur dioxide per litre of reagent.

Standardisation of the reagent was achieved by titrating a known weight of "anhydrous" acetone, then taking further samples of the same batch, adding known weights of water to each sample and titrating each "wetted" sample. These readings enabled the calculation of the number of milligrams of water equivalent to one millilitre of reagent.

A special weight pipette, previously cleaned and baked out and kept inside the dry-box, was filled with acetone in an atmosphere of dry nitrogen. It was then removed from the dry-box, reweighed and fitted to the titration vessel of the "moisture proof" apparatus designed for the Karl Fischer titration. The apparatus was gassed out with dry nitrogen after which the sample was allowed to run into the titration vessel and titrated with the reagent. The end point was determined electrometrically using a titrimeter built by the Instruments Division at African Explosives.

As a result of the very low water content of the acetone, the original stock reagent had to be diluted with anhydrous benzene and restandardised.

(b) Results of Karl Fischer Titrations and specific conductance Measurements

TABLE 2.3.1

ACETONE PREPARED BY THE "ALUMINA METHOD"

BATCH I

Time days after preparation	Water Content %
0	0.0058
2	0.0059
15	0.0067
123	0.0100
456	0.009

TABLE 2.3.2

"ALUMINA METHOD"

BATCH II

Time days after preparation	Water Content %	Spec. Cond. $ohm^{-1} cm^{-1}$
0	0.003	2.8×10^{-8}
31	0.003	-
137	0.003	1.6×10^{-7}
426	0.003	-

TABLE 2.3.3

ACETONE PREPARED BY THE "CALCIUM SULPHATE METHOD"

Time days after preparation	Water Content %	Spec. Cond. $ohm^{-1} cm^{-1}$
0	0.0028	1.5×10^{-7}
122	0.0035	-
395	0.0034	-

TABLE 2.3.4

ACETONE PREPARED BY THE "BARIUM OXIDE METHOD"

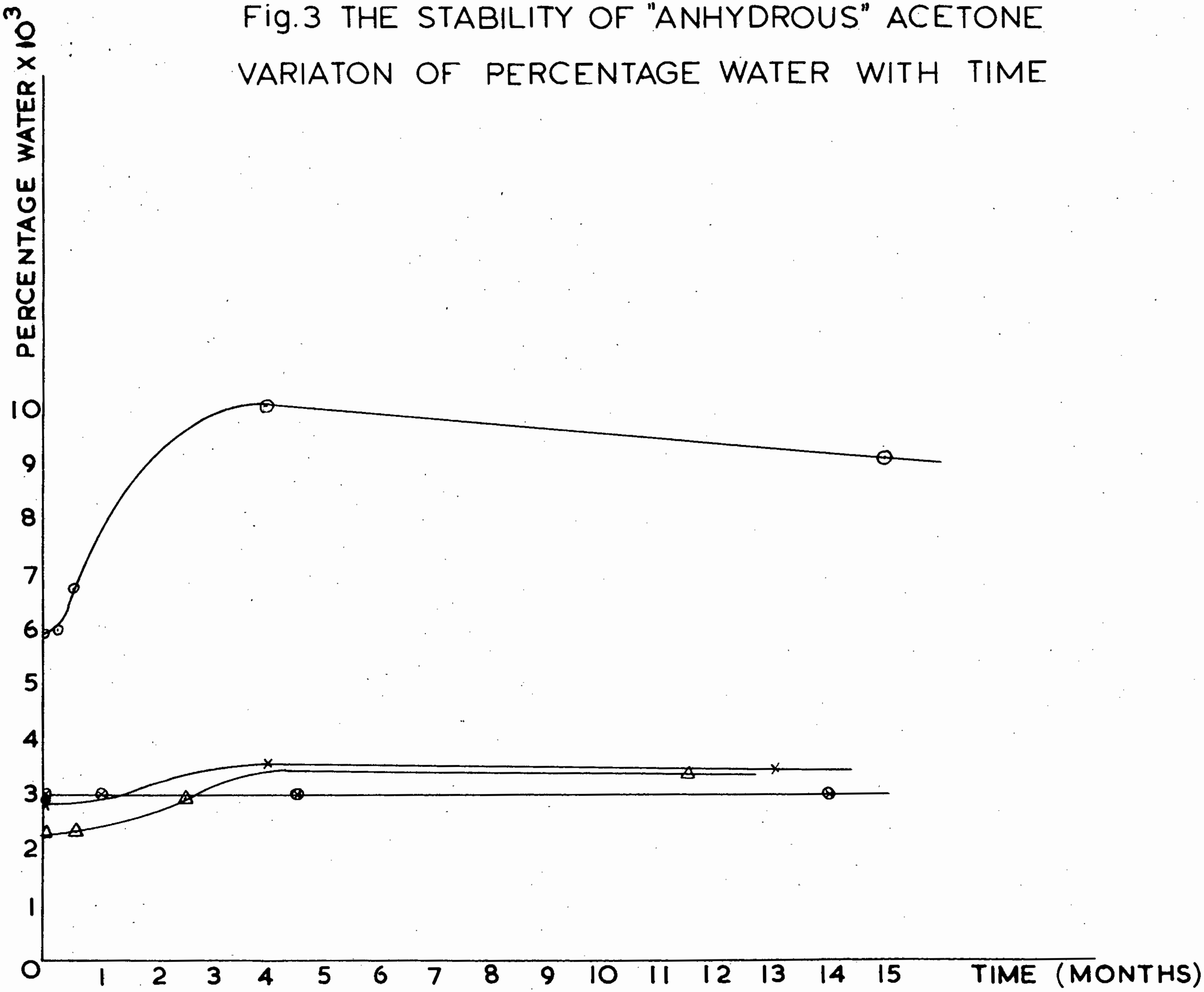
Time days after preparation	Water Content %	Spec. Cond. $ohm^{-1} cm^{-1}$
0	0.002_3	-
15	0.002_3	8×10^{-8}
76	0.0029	
357	0.003_3	

2.4 DISCUSSION

Although Everett and Rasmussen[6] criticised the use of strong dehydrating agents as these catalyse the self-condensation of acetone, most workers used strong desiccants and noted, especially in the cases where basic desiccants were used, the formation of a brownish condensation product. This condensation product is readily removed by fractionation, but its formation implies a loss of acetone. In the present work the wastage amounted to approximately 30-40% of the starting material when using alumina or barium oxide as dehydrating agents. Calcium sulphate does not appear to catalyse this condensation. Acetone prepared by this method had a water content of 0.002 - 0.006%, but the specific conductance was higher than that of the acetone prepared by the alumina method.

Fig.3 THE STABILITY OF "ANHYDROUS" ACETONE

VARIATON OF PERCENTAGE WATER WITH TIME

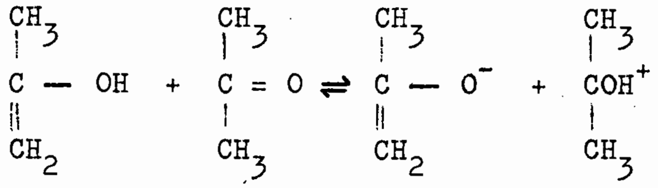


The only objection to the use of basic desiccants therefore, is the loss of starting material as other preparative methods have not been studied sufficiently for a complete comparisson to be made.

Some of the views expressed by earlier investigators have been proved fallacious. Mysels[17] considered it impossible to dehydrate acetone to below 0.05% water, but in the present work acetone containing as little as 0.002% water (by Karl Fischer titration) has been prepared. It is possible that with three to four very efficient fractionation colums and the greatest care in handling the "anhydrous" acetone inside a very well designed dry-box, acetone having still lower water content could be prepared.

The further opinion as to the instability of acetone under conditions of extremely low water content has also been controverted since stability studies of acetone containing between 0.002 and 0.006% water gave no indication whatsoever of this phenomenon.

Hotz[5] considered the mechanism of conduction in anhydrous acetone to be due to the ionisation of the enol form, which exists to the extent of 2.5×10^{-4} per cent as determined by Schwarzenbach[37], according to the reaction:



$$CH_2{=}C(CH_3){-}OH + (CH_3)_2C{=}O \rightleftharpoons CH_2{=}C(CH_3){-}O^- + (CH_3)_2COH^+$$

In the presence of small traces of water the conductance may proceed according to the reaction:

$(CH_3)_2\ C = O + H_2O \rightleftharpoons (CH_3)_2\ COH^+ + OH^-$ ... Eqn. 2.1

The work of Dippy and Hughes[13] indicated the water content to be the variable factor in the solvent grades. However, a tenfold change in the moisture content of acetone between 0.002 and 0.02 per cent has very little influence on the specific conductance and no correlation could be found between specific conductance and water content. This suggests that other impurities, for example ions desorbed from the glass apparatus, may play an important role.

---oo0oo---

SECTION III

CONDUCTIMETRIC STUDIES OF SOLUTIONS OF HYDROGEN CHLORIDE AND PERCHLORIC ACID IN ACETONE

3.1 BRIEF OUTLINE OF RESULTS

Braude[2] in his studies of acidity functions, claimed hydrogen chloride to be largely or completely dissociated in acetone solutions. However, he based his calculations on the results of Sackur[1] who obtained a limiting equivalent conductance of 12 ohm^{-1}cm^{2} for solutions of hydrogen chloride in acetone.

Ross Kane[3], and all subsequent workers in this field concluded that hydrogen chloride behaves as an extremely weak acid in acetone solutions with an apparent dissociation constant of 10^{-8}. Contrarily to Braude's view, hydrogen chloride seems to be highly associated in acetone solutions, Hotz[5] being of opinion that as many as twelve hydrogen chloride molecules could associate.

The plot of Λ against $\sqrt{c}$ for solutions of hydrogen chloride in acetone is extremely steep at high dilutions, making extrapolation inexact. The value of 223 ohm^{-1}cm^{2} obtained for the limiting equivalent conductance by this method has no meaning except as a comparisson with Ross Kane's value of 199 ohm^{-1}cm^{2} and Hotz's value of 210 ohm^{-1}cm^{2}.

A Fuoss plot[20] of the conductance results of solutions of hydrogen chloride in acetone, instead of producing the expected straight line, showed marked variations in the slope of the curve as in the case of Hotz's. No comparisson could be made with Ross Kane's work as his results have never been published in detail.

Hotz could not extrapolate his Fuoss plot to zero concentration, but in the present work measurements have been extended to slightly lower concentrations and extrapolation of this plot produced a limiting equivalent conductance of 444 $ohm^{-1}cm^{2}$.

Perchloric acid was claimed to be the only strong acid in acetone solutions. Its conductance has been measured by Ross Kane as quoted by Hughes and Hartley . His solutions of the acid in acetone were prepared by passing excess hydrogen chloride gas into a solution of silver perchlorate in acetone, precipitating silver chloride and using the decanted liquid as stock solution. A plot of Λ against $\sqrt{c}$ proved to be linear and extrapolated to 207 $ohm^{-1}cm^{2}$ for the limiting equivalent conductance.

Coetzee and McGuire[33] prepared solutions of perchloric acid in acetic acid, diluted this with acetone and measured the conductance of these solutions. They reported a value of 205 $ohm^{-1}cm^{2}$ for the limiting equivalent conductance of solutions of perchloric acid in acetone.

In the present investigations solutions of pure anhydrous perchloric acid in pure anhydrous acetone were studied (p 39). A plot of Λ against $\sqrt{c}$ was found to be linear and extrapolated to a value of about 509 $ohm^{-1}cm^{2}$ for the limiting equivalent conductance. A plausible explanation for this very high value is given on page 53.

3.2 APPARATUS

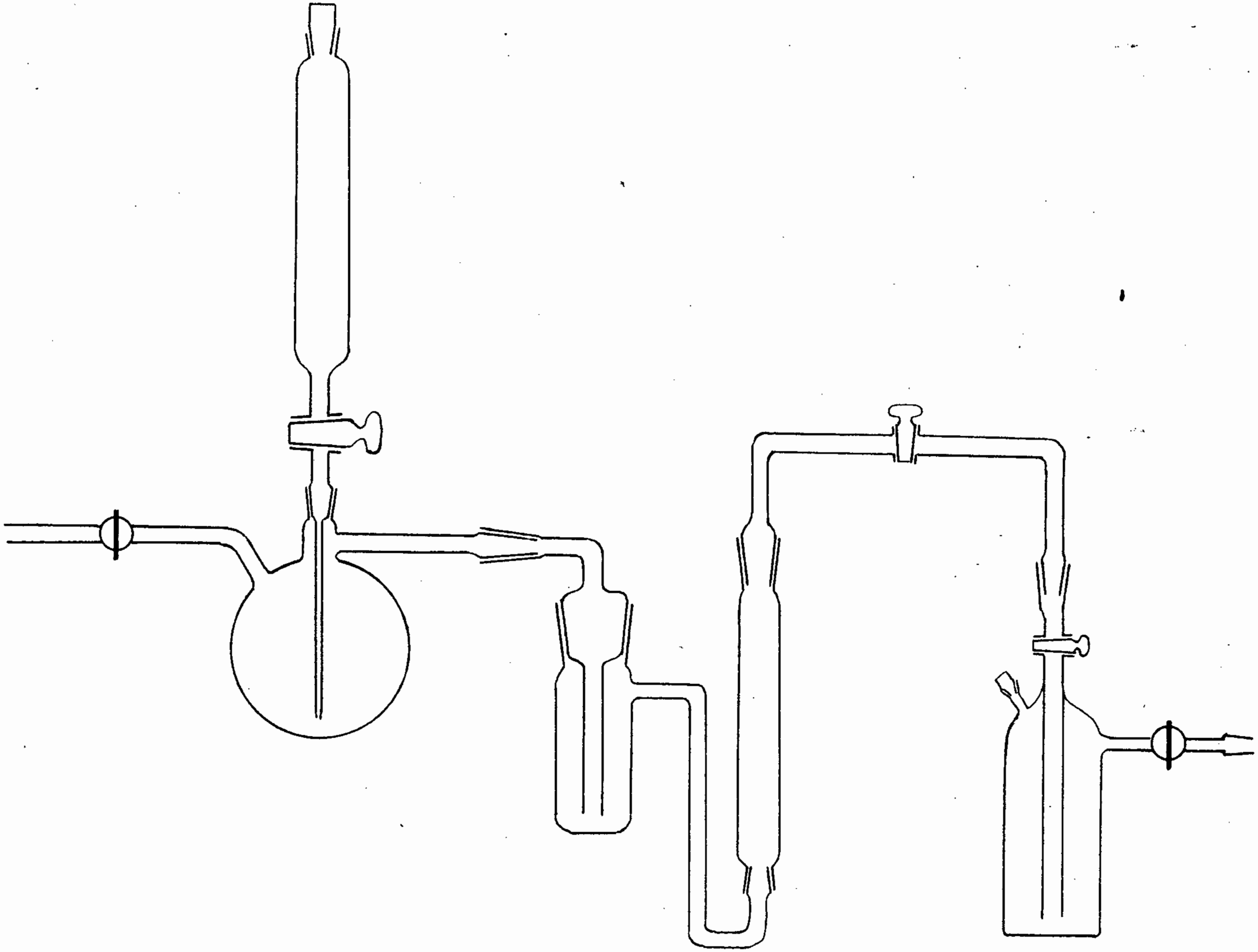
All apparatus used in the present conductimetric studies had been described by Hotz[5] and short descriptions are given in appendix 1.

3.3 THE PREPARATION AND ANALYSIS OF SOLUTIONS OF HYDROGEN CHLORIDE IN ACETONE

3.3.1 The hydrogen chloride gas generator

Pure anhydrous hydrogen chloride gas was prepared by running analar concentrated hydrochloric acid through a capillary tube into analar concentrated sulphuric acid producing a steady stream of the gas. The gas was bubbled through analar concentrated sulphuric acid, then passed through a column packed with anhydrous magnesium perchlorate containing some indicating silica gel and into a saturator (fig. 4) filled with anhydrous acetone in the dry-box. The open end of the saturator was connected to a drying train consisting of a number of glass tubes packed with magnesium perchlorate and indicating silica gel. Hydrogen chloride gas was allowed to pass through

Fig. 4 HYDROGEN CHLORIDE GAS GENERATOR



the acetone in the saturator for 10-15 minutes. All stopcocks were then closed and the saturated acetone solution returned to the dry-box.

Before use, the saturator was thoroughly rinsed with soap solution, then with distilled water followed by analar acetone after which it was baked out at 120°C.

A sample of the saturated solution was analysed by titration to give a rough estimate of the hydrogen chloride concentration. Three or four stock solutions were then prepared from this saturated solution and from each of these stock solutions a maximum of two dilutions, by accurately pipetting samples into a volumetric flask and making up to volume, or by weighing a portion of the stock solution in a weighed volumetric flask, filling up with acetone and reweighing. The stock solutions were accurately analysed gravimetrically.

It has been observed by Ross Kane[3] and Hotz[5] that acid solutions of acetone turned brown on standing. Hotz found no appreciable change in the conductance of the acid solutions over a period of twelve hours. Consequently all conductance measurements were done on the day of preparation. This procedure was followed in the present work and the conductance of solutions older than eight hours had never been measured.

3.3.2 Conductance measurements on solutions of hydrogen chloride in acetone

Conductance measurements were carried out at 25°C using the Jones-type bridge described in appendix I and equivalent conductances calculated.

TABLE 3.3.1

THE CONDUCTANCE OF SOLUTIONS OF HYDROGEN CHLORIDE SOLUTIONS IN ACETONE

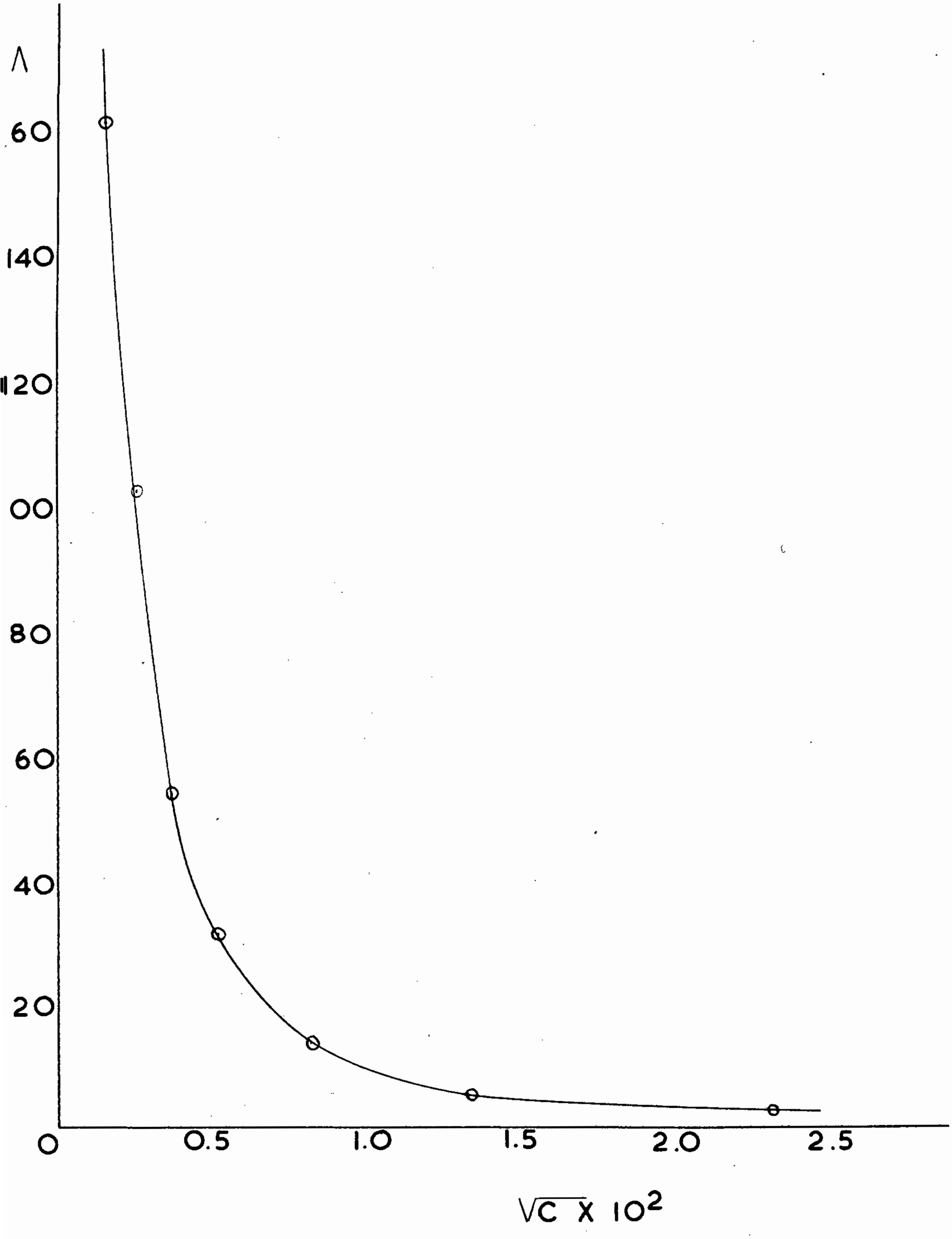
Concentration μ mole litre^{-1}	α	$f_{\pm}^{2}$	Λ ohm^{-1} cm^{2}	$10^{7}K_{a}$
2.280	0.3534	0.9968	160.75	4.389
6.77	0.2250	0.9956	102.40	4.407
13.54	0.1190	0.9954	54.18	3.433
27.14	0.0681	0.9951	31.01	1.344
67.70	0.0293	0.9949	13.36	5.958
135.4	0.0233	0.9936	10.62	7.478
181.0	0.0110	0.9949	5.02	2.204
541.6	0.0060	0.9935	2.73	1.948
$K_{av} = 5.13 \times 10^{-7}$				

3.4 THE PREPARATION OF ANHYDROUS PERCHLORIC ACID AND ITS SOLUTIONS IN ACETONE

The method for the preparation of anhydrous perchloric acid employed was developed by G.F. Smith[38] and is essentially a vacuum distillation of 72-84% perchloric acid over anhydrous magnesium perchlorate.

Fig. 5 HYDROGEN CHLORIDE IN ACETONE

EQUIVALENT CONDUCTANCE



3.4.1 Apparatus

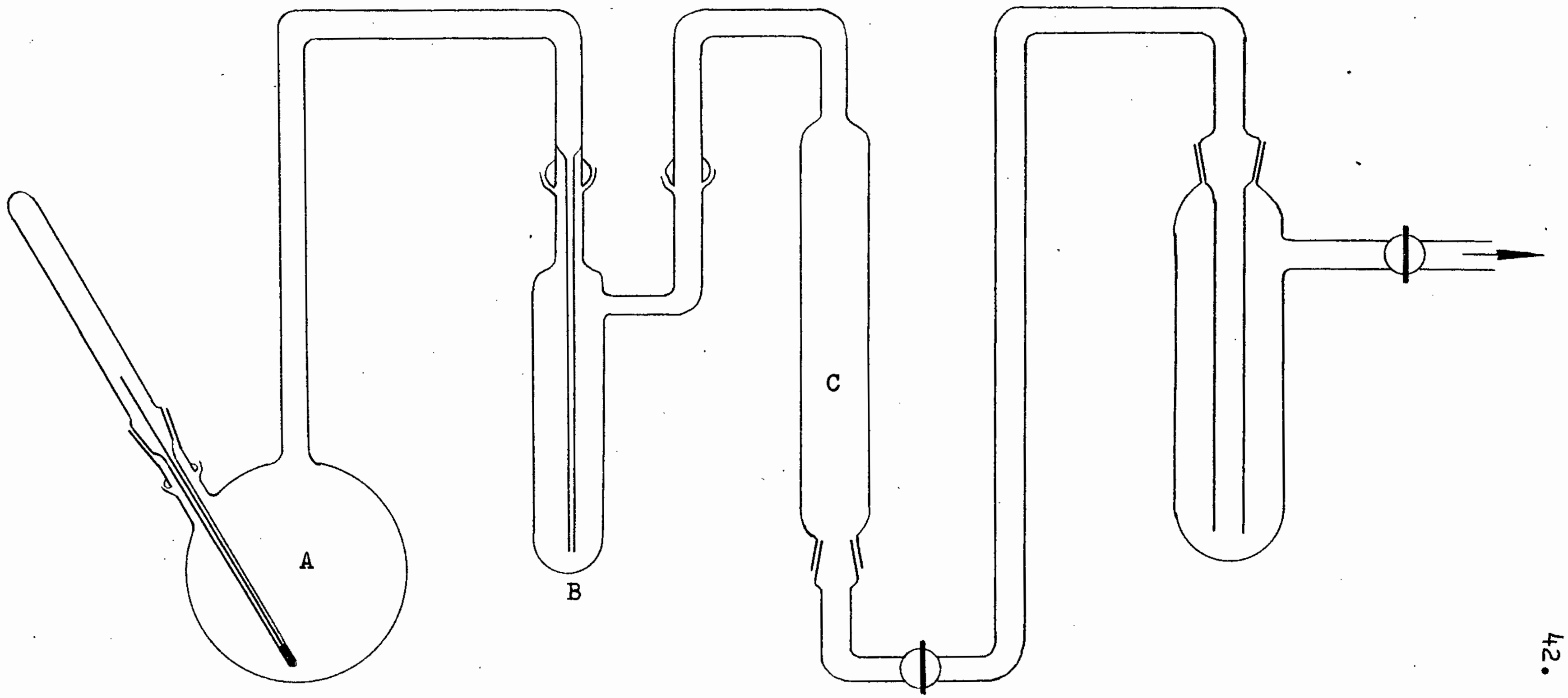
The still as described by Smith for the preparation of macro quantities up to 100 gms or more of acid was not suitable as such since small quantities less than 1 gram of acid were required at a time. Consequently the still was scaled down considerably.

The apparatus consisted of a 150 ml distillation flask, A, (fig. 6) with a thermometer fitted to the bulb by means of a spherical ground joint. The delivery tube led into a collecting vessel, B, the latter being connected through a side arm to an absorption tower, C, packed with soda lime and sodium hydroxide pellets to prevent any acid vapour passing through to the vacuum pump. The absorption tower was connected to a vacuum train through a trap cooled in liquid nitrogen. The collecting vessel was kept in dry ice. The whole apparatus was built on a stand which was fixed to the bench top and walls and screened by perspex screens.

3.4.2 Method

The reagents used were anhydrous magnesium perchlorate and 72% perchloric acid. Approximately 5 grams magnesium perchlorate were added to the distillation vessel. Chilled perchloric acid (1 gram) was added slowly with stirring to ensure complete mixing. During the addition of the acid, the base of the distillation flask was chilled

Fig. 6 ANHYDROUS PERCHLORIC ACID STILL



in a bath of dry ice. The distillation vessel was then connected to the receiving vessel which was cooled in a flask containing dry ice. The mixture of acid and salt was then allowed to attain room temperature whilst evacuating the apparatus to a pressure $\leqslant$ 0.5 mm.

The temperature of the mixture was steadily increased from room temperature to approximately 60°C employing an isomantle heater and an energy input regulator. The total distillation time was about three hours.

In order to prove that the acid collected was anhydrous, the method of Smith was followed. Pure oxonium perchlorate, a white solid with a melting point of 49.9°C may be prepared by adding 64.286 gms of 72 per cent perchloric acid to 54.170 gms of anhydrous perchloric acid. Following this procedure addition of 0.59 gms of 72 per cent perchloric acid to 0.5 gms of the collected acid produced a white solid with a melting point of 50°C, proving the acid prepared to be anhydrous.

3.4.3 Solutions of Perchloric acid in acetone

Accurately weighed samples of perchloric acid were transferred to weighed volumetric flasks, made up to volume with anhydrous acetone and reweighed. From each of these stock solutions a maximum of two dilutions were made. As in the case of the solutions of hydrogen chloride in acetone, the solutions of perchloric acid also turned brown, but much more rapidly than in the former case. This showed perchloric acid to be a much more efficient catalyst in the observed reaction.

3.4.4 Conductance measurements on solutions of perchloric acid in acetone

Measurements were carried out under the same conditions as for the hydrogen chloride solutions (p 39). Equivalent conductances were calculated and a linear plot was obtained for Λ against $\sqrt{c}$ which extrapolated to 509 ohm^{-1}cm^{2} for the limiting equivalent conductance. The ratio of the experimental slope to the Onsager slope was found to be 4.75.

TABLE 3.4.1

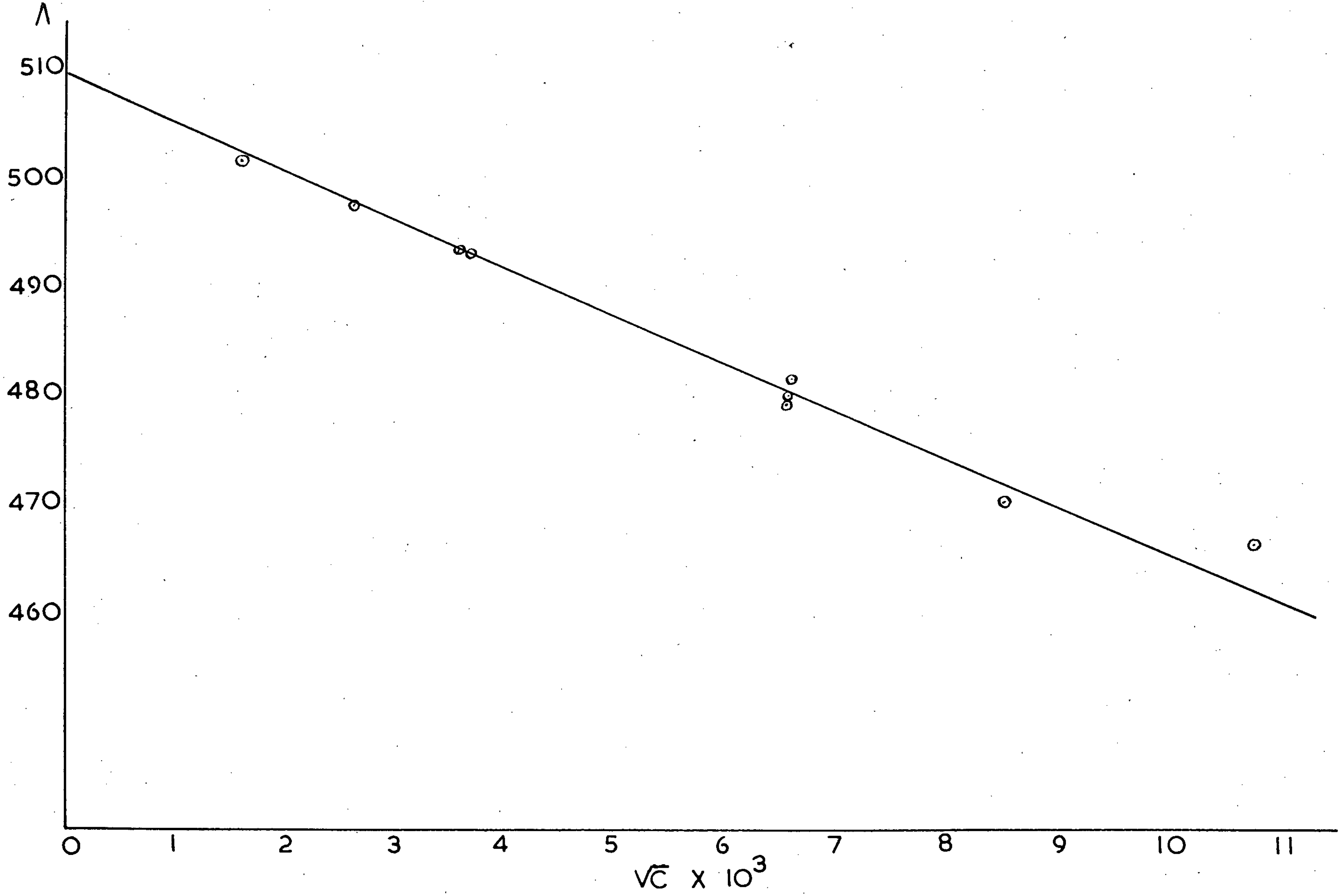
THE CONDUCTANCE OF SOLUTIONS OF PERCHLORIC ACID IN ACETONE

Concentration μ mole litre^{-1}	Λ ohm^{-1}cm^{2}	α	$f_{\pm}^{2}$	$10^{4}K$
2.545	501.3	0.9581	0.9945	0.5546
6.922	497.2	0.8692	0.9908	0.9802
7.168	499.8	0.8774	0.9906	0.9842
12.800	493.0	0.8261	0.9877	1.442
14.00	492.9	0.8206	0.9872	1.517
21.26	485.3	0.7700	0.9845	1.315
27.21	491.7	0.7709	0.9826	1.689
42.84	478.5	0.6932	0.9786	1.736
43.37	479.8	0.6956	0.9786	1.778
43.69	481,39	0.6994	0.9786	1.827
72.42	469.84	0.6152	0.9731	2,056
115.62	463.7	0.5405	0.9674	2.283

$10^{4}K_{av} = 1.738$

Fig. 7 PERCHLORIC ACID IN ACETONE

EQUIVALENT CONDUCTANCE



Experimental slope = 4.102×10^3

Onsager slope = 863.1

Ratio = 4.75

3.5 THEORY OF ELECTROLYTIC CONDUCTANCE AND DISCUSSION OF RESULTS

The Onsager[39] limiting law for electrolytic conductance, taking into account electrophoretic and relaxation effects, takes the form

$$\Lambda = \Lambda_\infty - \left[\frac{2.810 \times 10^6 |z_1 z_2| q \Lambda_\infty}{(\varepsilon T)^{3/2}(1 + \sqrt{q})} + \frac{41.25\,(|z_1| + |z_2|)}{\eta (\varepsilon T)^{\frac{1}{2}}}\right]\sqrt{I}$$

. . . . Eqn. 3.5.1

i.e. of the form

$$\Lambda = \Lambda_\infty - A\sqrt{c}$$

. . . . Eqn. 3.5.2

which was found by Kolrausch[40] to describe the variation of conductance with concentration in dilute solutions. The effect of finite ionic size on conductivity was discussed by Pitts and Falkenhagen[41], leading to an extended limiting law in which the ion size was introduced:

$$\Lambda = \Lambda_\infty - \left[\frac{8.204 \times 10^5 \Lambda_\infty}{(\varepsilon T)^{3/2}} + \frac{82.5}{\eta (\varepsilon T)^{\frac{1}{2}}}\right]\left[\frac{\sqrt{c}}{1 + 50.29\mathring{a}(\varepsilon T)^{\frac{1}{2}}\sqrt{c}}\right]$$

. . . . Eqn. 3.5.3

which may be rewritten as

$$\Lambda = \Lambda_\infty - \left[B_1 \Lambda_\infty + B_2\right]\left(\frac{\sqrt{c}}{1 + B\mathring{a}\sqrt{c}}\right)$$

. . . . Egn. 3.5.4

This may be rewritten as

$$\Lambda_\infty = \Lambda + \frac{(B_1\Lambda + B_2)\sqrt{c}}{1 + (B\mathring{a} - B_1)\sqrt{c}}$$

. . . . Eqn. 3.5.5

For a weak uni-univalent electrolyte the Onsager - Fuoss equation[20] takes the form

$$\alpha_c = \Lambda/\Lambda_\infty\left\{1 - (B_1\Lambda_\infty + B_2)\sqrt{\alpha_c c}/\Lambda_\infty\right\}$$

. . . . Eqn. 3.5.6

Replacing the factor in braces by

$$F(z) = 1 - z\left\{1 - z\left\{1 - z\{\ldots\}^{-\frac{1}{2}}\right\}^{-\frac{1}{2}}\right\}^{-\frac{1}{2}}$$

$$= \frac{4}{3}\cos^2\tfrac{1}{3}\cos^{-1}\left[(-3\sqrt{3z})/2\right]$$

. . . . Eqn. 3.5.7

where $z = (B_1\Lambda_\infty + B_2)\sqrt{\Lambda c}/\Lambda_\infty^{3/2}$

giving $\alpha_c = \Lambda/\Lambda_\infty F(z)$

Now $K_a = \alpha_c^2 c f_\pm^2/(1 - \alpha_c)$

To obtain Λ_∞, a rough estimate is made from the plot of Λ against $\sqrt{c}$. z is then calculated, and F(z) found from tables of F(z) as a function of z[42]. This enables the calculation of α_c and hence $f_\pm$ by means of the Debye-Hückel limiting equation.

Combination of the expressions for α_c and K_a leads to

$$F(z)/\Lambda = 1/\Lambda_\infty + c\Lambda f_\pm^2/F(z)K_a\Lambda_\infty^2$$

. . . Eqn. 3.5.8

A plot of $F(z)/\Lambda$ against $c\Lambda f_\pm^2/F(z)$ extrapolates to $1/\Lambda_\infty$. The procedure is repeated with the newly found Λ_∞ until a constant Λ_∞ is obtained. From the slope of the final plot K_a may be calculated. If K_a is extremely small, the plot is rather insensitive.

The Onsager-Fuoss equation may also be rewritten after Shedlovsky[43] as

$$1/\Lambda_\infty = \alpha_c/\Lambda - \alpha_c\left[B_1\Lambda_\infty + B_2\right]\sqrt{\alpha_c c}/\Lambda\Lambda_\infty \quad \ldots\ldots \text{ Eqn. } 3.5.9$$

putting $\alpha_c = S(z)\Lambda/\Lambda_\infty$

where $S(z) = \left\{\tfrac{1}{2} z + (1 + \tfrac{1}{4} z)^{\frac{1}{2}}\right\}^2$

$= 1 + z + \tfrac{1}{2} z^2 + \ldots\ldots$

and $z = (B_1\Lambda_\infty + B_2)\sqrt{\Lambda c}/\Lambda_\infty^{3/2}$

The equation may therefore be rewritten as

$$1/\Lambda S(z) = 1/\Lambda_\infty + c\Lambda S(z)f_\pm^{2}/K_a\Lambda_\infty^2 \quad \ldots\ldots \text{ Eqn. } 3.510$$

A plot of $1/\Lambda S(z)$ against $c\Lambda S(z)f_\pm^2$ has a slope of $1/K_a\Lambda_\infty^2$ and intercept $1/\Lambda_\infty$. Values for S(z) as a function of z have been tabulated[42].

In the range $10^{-3} \leqslant K \leqslant 1$ Shedlovsky's function is recommended. When $K < 10^{-3}$ both the Shedlovsky and Fuoss methods are equal and when $K \sim 10^{-6}$ the plots do not establish Λ_∞ or K_a with much precision and the only satisfactory method to deal with this is by applying the Kolrausch rule[40]:

$$\Lambda_\infty(HA) = \Lambda_\infty(HCl) - \Lambda_\infty(NaCl) + \Lambda_\infty(NaA)$$

but the success of this depends on the hydrogen chloride, sodium chloride and salt of the weak acid being at least largely dissociated in the solvent used.

It has been claimed by Ives and Ives[44] and by Sames[45] that if $K_a \nless 2 \times 10^{-5}$, Λ_∞ may be obtained directly from the conductance of the weak acid. K_a may be obtained

Fig. 8 HYDROGEN CHLORIDE IN ACETONE

FUOSS PLOT

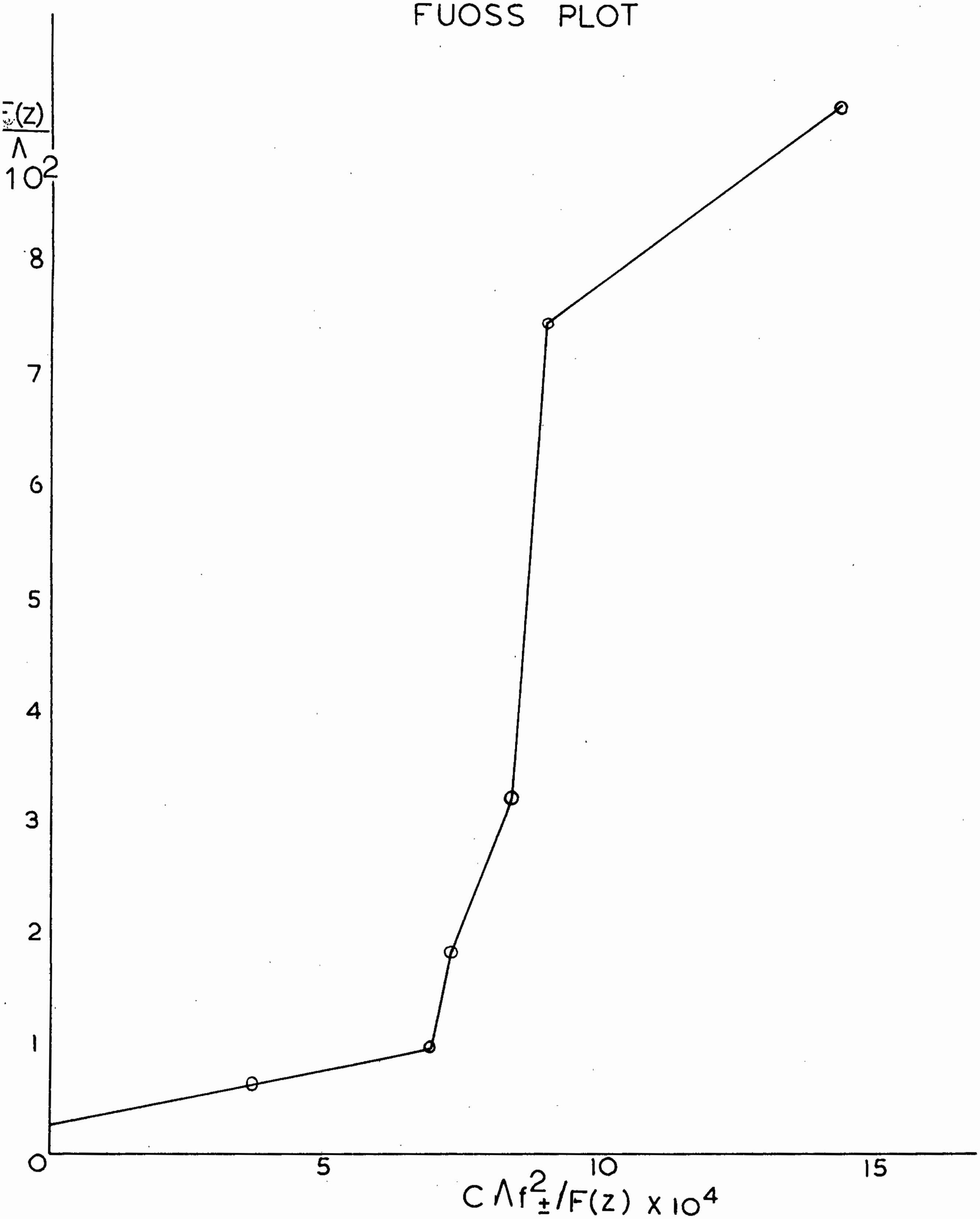
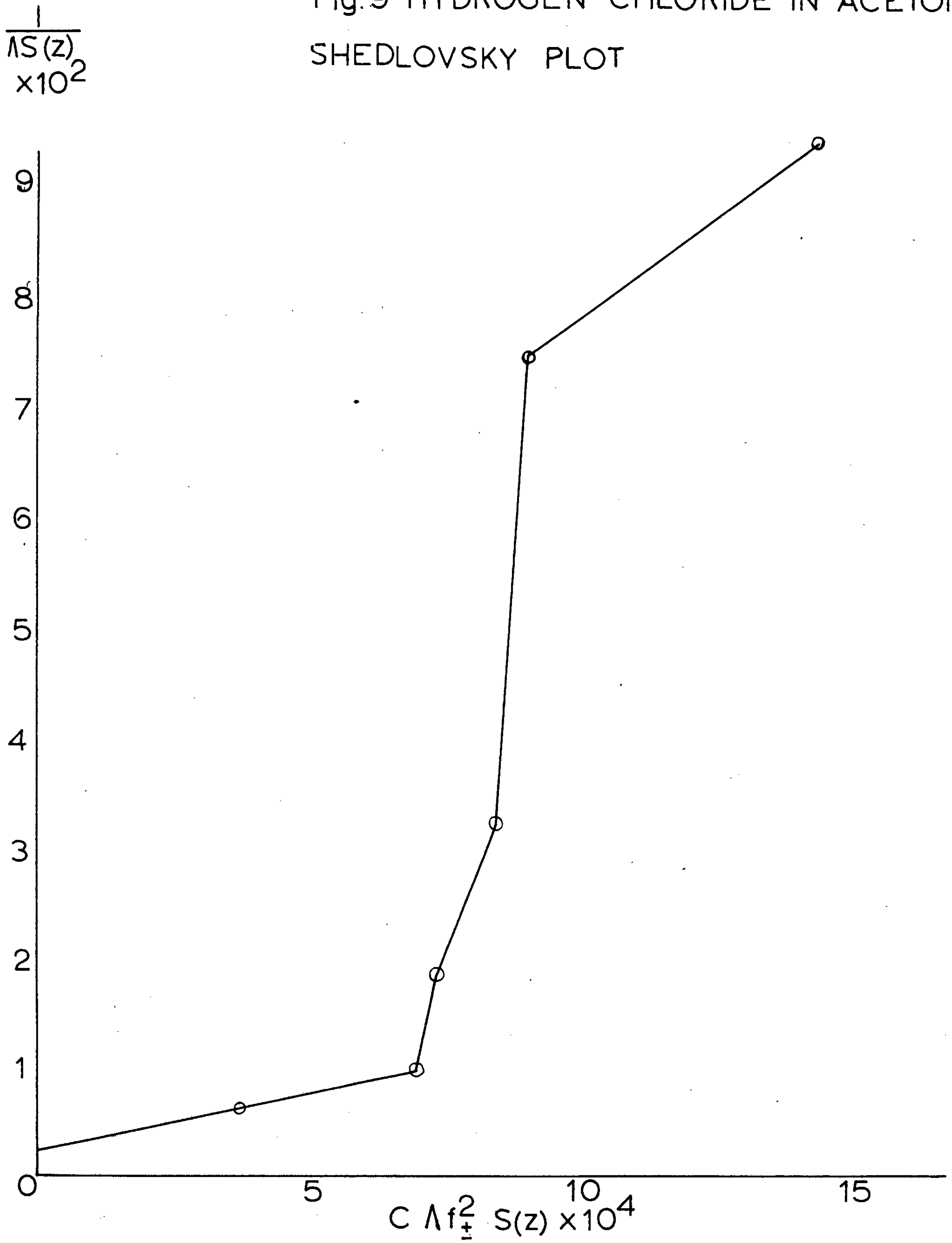


Fig.9 HYDROGEN CHLORIDE IN ACETONE SHEDLOVSKY PLOT



simultaneously.

The procedure is to add Λ_∞ to both sides of the equation

$$\Lambda - \Lambda_x = -\Lambda^2 f_\pm^{\,2} c/\Lambda_x K \quad ..... \quad \text{Eqn. 3.5.11}$$

where Λ_x is the sum of the conductances of the cation and anion in a completely dissociated electrolyte solution,

$$\text{i.e.} \quad \Lambda c/\Lambda_x = \alpha_c c$$

$$\therefore \quad \Lambda_x = \Lambda/\alpha_c$$

Then

$$\Lambda + (B_1\Lambda_\infty + B_2)\sqrt{\alpha_c c} = \Lambda_\infty - \Lambda^2 f_\pm^{\,2} c/\Lambda_x K \quad ... \text{Eqn. 3.5.12}$$

This may be rewritten as

$$y = \Lambda_\infty - m'x \quad ... \text{Eqn. 3.5.13}$$

A plot of y against x has a slope of $m' = 1/K$ and an intercept Λ_∞

A reasonable value of Λ_∞ is taken for the first plot, α_c and $f_\pm$ calculated. Then y and x are calculated for each measurement and a new value of Λ_∞ obtained by the method of least squares

$$\Lambda_\infty = \left\{\Sigma(x)\,\Sigma(xy) - \Sigma(x^2)\Sigma(y)\right\} / \left\{[\Sigma(x)]^2 - n\Sigma(x^2)\right\}$$

$$... \text{Eqn. 3.5.14}$$

where n is equal to the number of experimental points.

The process is repeated until Λ_∞ is constant. The upper concentration limit is 0.003N to 0.005N. K_a is also calculated by the method of least squares

$$-1/K_a = \left\{\sum(x)\sum(y) - n\sum(xy)\right\} / \left\{\left[\sum(x)\right]^2 - n\sum(x^2)\right\}$$

... Eqn. 3.5.15

Kilpatrick[46] found these equations to be suitable for K_a values as low as 10^{-6}.

Application of the Fuoss-Shedlovsky analyses produced a plot with varying slope from the conductance results of the solutions of hydrogen chloride and a straight line with a single change in slope at extremely high dilutions, from the results of the solutions of perchloric acid.

These plots extrapolated to 444 $ohm^{-1}cm^2$ and 509 $ohm^{-1}cm^2$ for the limiting equivalent conductances for hydrogen chloride and perchloric acid in acetone solutions respectively.

The Ives[44] calculations applied to the conductance results of hydrogen chloride solutions produced a limiting equivalent conductance of 187 $ohm^{-1}cm^2$ and a value of about 1 for the dissociation constant.

These calculations are given in appendix 2.

3.6 MECHANISM OF PROTON CONDUCTANCE IN ANHYDROUS ACETONE AND EFFECT OF ADDED WATER ON CONDUCTANCE

Hotz[5] considered the conductance of solutions of hydrogen chloride in acetone to be due to the partial dissociation into solvated protons and negatively charged anionic complexes, of the associated hydrogen chloride molecules, according to the reaction

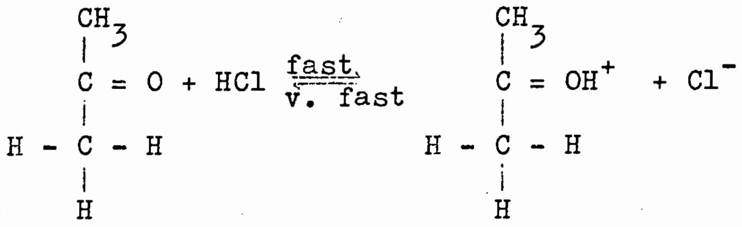
$$(HCl)_x + Me_2CO \rightleftharpoons Me_2COH^+ + (H_{x-1}Cl_x)^- \qquad \text{... Egn. 3.6.1}$$

In view of the precence of ions of the type Me_2COH^+, a Grotthus-type conductance is possible. At high acid concentrations the degree of dissociation is extremely small so that very few Me_2COH^+ ions exist, and the mobility of the anion $(H_{x-1}Cl_x)^-$ is small for high values of x. A very low conductance is therefore expected as is observed experimentally.

At very low acid concentrations more ions of the type Me_2COH^+ will be present, the anionic complex will be smaller and a large increase in the conductance is expected.

If the very high conductances as obtained for solutions of perchloric acid in acetone are true, a proton jump mechanism must occur comparable to that in aqueous solutions. The following two mechanisms are proposed, the one involving keto-enol tautomerism, the second involving only the ion Me_2COH^+.

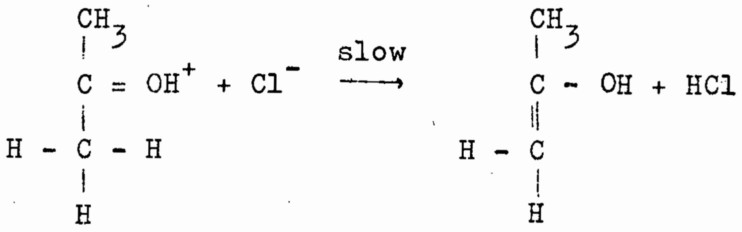
The acid catalysed enolisation of acetone has been proposed to proceed through the following mechanism[47]:



$$\mathrm{CH_3{-}C({=}O){-}CH_3} + HCl \underset{\text{v. fast}}{\overset{\text{fast}}{\rightleftharpoons}} \mathrm{CH_3{-}C({=}OH^+){-}CH_3} + Cl^-$$

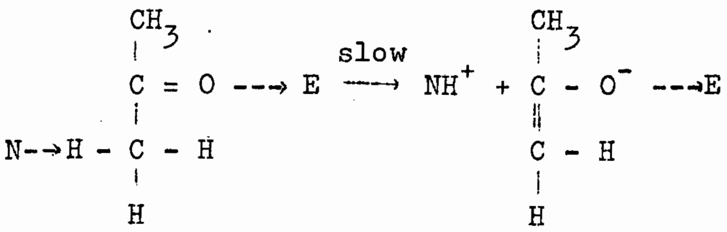
... Eqn 3.6.2

and



... Eqn. 3.6.3

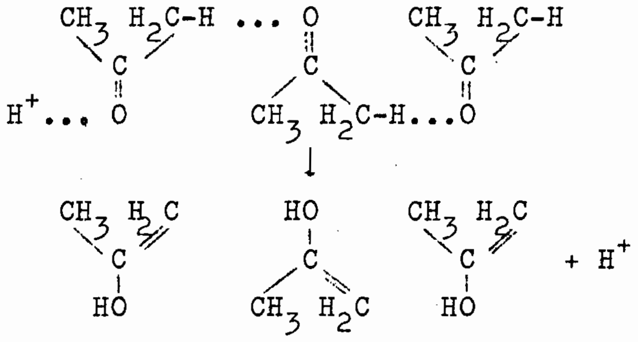
A push-pull mechanism for the enolisation of acetone has also been postulated[48]:



... Eqn. 3.6.4

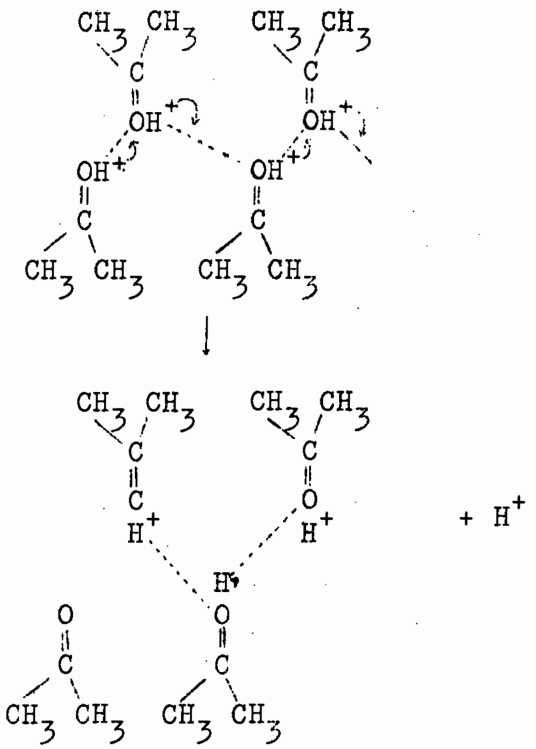
where N and E are nucleophilic and electrophilic groups or molecules respectively.

On the basis of the push-pull mechanism, the proton jump mechanism proposed is as follows:



... Eqn. 3.6.5

The mechanism involving the ion Me_2COH^+ only is given as:



... Eqn. 3.6.6

The mechanism as depicted by Eqn. 3.6.5 does not agree with experimental results since the rate of enolisation appears to be too slow. The second mechanism given by Eqn. 3.6.6, based on Eqn. 3.6.2 could produce fast proton jumps, provided the transfer of charge from one acetone molecule to another as depicted, is faster than the transfer of the proton on the carbonyl group to a chloride ion or a complex anion.

A trace of water added to a solution of hydrogen chloride or perchloric acid in acetone causes a marked drop in the electrical conductivity[3]. This is due to partial suppression of proton jumps resulting from capture of protons from the Me_2COH^+ ion according to the reaction

$$Me_2COH^+ + H_2O \longrightarrow Me_2CO + H_3{}^+O \qquad \text{... Eqn. 3.6.7}$$

A small trace of water produces a large effect, and the magnitude of the effect suggests that the equilibrium of equation 3.6.7 lies far over to the right, indicating that the water molecule dissolved in acetone provides a vacant level for an additional proton that lies lower than the level occupied by the proton in the $>COH^+$ group of the Me_2COH^+ ion. A proton captured in this lower level of the water melecule cannot jump back to an acetone molecule until it receives the necessary energy[49]. In the meantime the $H_3{}^+O$ ion can only contribute to the conductance by drifting slowly in the field. Only when the proton has returned to an acetone molecule can rapid proton jumps be resumed.

3.7 COMPARISSON OF LIMITING EQUIVALENT CONDUCTANCES OF ELECTROLYTES IN ANHYDROUS ACETONE AND AQUEOUS SOLUTIONS

A comparrisson of limiting equivalent conductances of various electrolytes in "anhydrous" acetone and in aqueous solutions, shows the very striking feature that the conductances are up to 20% and even higher in acetone solutions than in water. This is most probably due to the non-solvation of the anion and the much lower viscosity of the solvent.

On the assumption of Fowler[23] the chloride ion conductance at infinite dilution is 111 $ohm^{-1}cm^2$. Calculation of cation conductances using this value, shows cations to have limiting equivalent conductances very nearly the same as in water. Furthermore, in view of the possibility of a proton jump mechanism in acetone, solutions of acidsin acetone may be expected to have limiting equivalent conductances similar to or even higher than those found in water.

The very high limiting conductances obtained for solutions of hydrogen chloride and perchloric acid in acetone in the present investigations, can therefore be understood to some extent. If the proton conductance at infinite dilution was exactly the same in acetone solutions as in water, Λ_∞ for the solutions of perchloric acid in acetone should be at least 470 $ohm^{-1} cm^2$. That the experimental value exceeds this, may be due in part to viscosity effects. There is also the possibility of enhanced enolisation in the acid solutions, catalysed by the platinum black of the electrodes in the conductivity cell.

TABLE 3.7.1

LIMITING EQUIVALENT CONDUCTANCES OF SOME ELECTROLYTES IN ACETONE AND IN AQUEOUS SOLUTIONS AT 25°C

Electrolyte	Acetone Solutions		Aqueous Solutions[52]
	Λ_∞	Reference	Λ_∞
$AgClO_4$	181.5	50	129.3
$LiClO_4$	187.3	51	106.1
$NaClO_4$	191.2	"	117.5

Electrolyte	Acetone Solutions		Aqueous Solutions[52]
	Λ_∞	Reference	Λ_∞
$KClO_4$	188.7	51	140.9
KI	196.6	"	150.3
LiPi	158.1	"	69.1
NaPi	163.7	"	80.5
KPi	165.9	"	103.9
NH_4Pi	180.2	"	103.9
$(nC_4H_9)_4NClO_4$	182.4	"	86.9
$(nC_4H_9)_4NPi$	152.4	"	49.9
$(nC_4H_9)_4NI$	179.4	"	96.3
$(nC_4H_9)_4NCl$	172.3	"	95.3
HCl	444.4		426.2
$HClO_4$	509.0		417.2

---oo0oo---

SECTION IV

KINETICS OF THE ACID CATALYSED SELF-CONDENSATION OF ACETONE

4.1 THE STABILITY OF SOLUTIONS OF HYDROGEN CHLORIDE IN ACETONE

The stability of pure anhydrous acetone has been discussed in section II and in relation to the conductance measurements in section III it was necessary to consider the stability of solutions of electrolytes in acetone.

The earliest relevant observations have been made by Bayer[53] in 1886. A saturated solution of hydrogen chloride in acetone was allowed to stand in a closed vessel for fourteen days. The solution turned dark brown and on adding water after this period an aqueous and an oily layer were obtained. Analysis of the oily layer showed the presence of mesityl oxide and phorone.

Similar colour changes have been observed by numerous later workers for example Ross Kane[3]. None of these investigated the phenomenon thoroughly.

It therefore appeared desirable to investigate whether this condensation, in which water is produced, proceeds sufficiently rapidly as to have a significant effect on the conductance and other electrochemical measurements.

4.1.1 Preliminary experiments

The following methods were considered for the investigation of the condensation:

(a) Karl Fischer titrations

(b) Conductance measurements

(c) Ultra violet absorption studies

(d) Infra red absorption studies

(a) Karl Fischer titrations

Small quantities of water may be determined in non-aqueous media by means of the Karl Fischer titration[19]. Since water is produced in the condensation reaction, the Karl Fischer method was thought suitable for following the rate of the reaction by determining the rate of formation of water. However, it has been stated that in acid media the reagent is unreliable; hence this method was rejected.

(b) Conductance measurements

The conductance of solutions of hydrogen chloride in acetone would change with time with the formation of water, but would not be a true measure of the water produced since any other product or intermediate in the condensation reaction might contribute to the total conductance.

(c) Ultra violet absorption studies

Pure acetone has absorption bands at 2790 Å and 1880 Å[54] and inbetween these two bands the absorption falls to practically zero. It has been observed that in the presence of water, the band at 2790 Å is shifted towards the shorter wavelengths and a solution of acetone in water absorbs at 2650 Å [55]. If relatively large quantities of water are produced in the condensation reaction, the rate of formation may be determined by measuring the shift it produces in the absorption band at 2790 Å.

Mesityl oxide has an extremely strong absorption band at 2310 Å with a molar extinction coefficient of 1.2×10^4 (56). The formation of this product could therefore easily be followed by this method. The absorption of diacetone alcohol in the ultra violet region is very poorly defined with no sharp absorption bands.

(d) Infra red absorption studies

Water may be detected by the OH absorption band, but any alcohol(s)that may be produced during the course of the reaction, will also absorb at more or less the same frequency and no true measure of the water produced will be obtained.

A camparisson of the infra red absorption spectra of acetone and mesityl oxide and various synthetic mixtures of these, showed some absorption bands of the two components to be very well resolved, providing a further method for investigating the reaction.

4.2 THE CONDENSATION OF ACETONE TO MESITYL OXIDE

4.2.1 APPARATUS AND EXPERIMENTAL METHODS

Absorbance measurements on solutions of hydrogen chloride in acetone of various acid concentrations were carried out using 1 cm and 0.2 cm quartz cells. Preliminary experiments were made on a Beckman DU ultra violet-visible spectrophotometer and final measurements on a Zeiss 100 point instrument.

Solutions were either kept at constant temperature in a thermostat or in the cells in the thermostatically jacketed cell compartment of the spectrophotometer.

The undiluted reaction mixtures were used in the 0.2 cm cells during the initial stages of the reaction. During the later stages, dilution of the reaction mixtures was necessary and for this purpose spectroscopically pure cyclohexane was found to be suitable. Optical measurements on these dilute solutions were made using the 1 cm cells.

Dilutions of reaction mixtures in cyclohexane were prepared by dissolving a weighed quantity of the reaction mixture in a weighed quantity of cyclohexane.

4.2.2 ACID BASE CATALYSIS AND PROPOSED MECHANISM

The condensation of acetone to mesityl oxide catalysed by hydrogen chloride, although taking place through a number of intermediate steps may be formulated generally[57] as follows:

$$A + HCl \underset{k_2}{\overset{k_1}{\rightleftharpoons}} AH^+ + Cl^- \qquad \text{... Eqn. 4.2.1}$$

$$AH^+ + A \xrightarrow{k_3} \text{Products} \qquad \text{... Eqn. 4.2.2}$$

Application of the steady state method leads to:

$$[AH^+] = \frac{k_1[A][HCl]}{k_3[A] + k_2[Cl^-]} \qquad \text{... Eqn. 4.2.3}$$

and

$$\frac{d[\text{Product}]}{dt} = \frac{k_1k_3[A]^2[HCl]}{k_3[A] + k_2[Cl^-]} \qquad \text{... Eqn. 4.2.4}$$

Two limiting possibilities arise:

(a) $k_3[A] \gg k_2[Cl^-]$

whence $$\frac{d[P]}{dt} = \frac{k_1k_3[A]^2[HCl]}{k_3[A]}$$

$$= k_1[A][HCl] \qquad \text{... Eqn. 4.2.5}$$

(b) $k_3[A] \ll k_2[Cl^-]$

and $$\frac{d[P]}{dt} = \frac{k_1k_3[A]^2[HCl]}{k_2[Cl^-]}$$

$$= \frac{k_1k_3[A]^2[H^+]}{k_2K_a} \qquad \text{... Eqn. 4.2.6}$$

where K_a is the ionisation constant of HCl

Equation 4.2.5 corresponds to general acid catalysis and equation 4.2.6 to specific catalysis by H^+.

The reaction is therefore either first order or second order in acetone and the rate will vary from run to run with acid concentration.

The reaction was found to be extremely slow and following any particular reaction mixture for up to three weeks, no appreciable change could be observed in the acetone concentration.

At low acid concentrations rates were found to vary approximately linearly with acid concentration, becoming independent of concentration above 1.5M acid.

The rate of condensation being exceedingly slow, the change in the concentration of acetone could be neglected, especially as it was present in great excess, the reaction mixtures being dilute solutions of hydrogen chloride in pure acetone.

The acetone concentration could therefore be considered constant and as the catalyst is regenerated in the final stages of the reaction, its concentration will be constant. The rate may therefore be expressed as

$$\frac{d[P]}{dt} = k \qquad \ldots \text{ Eqn. 4.2.7}$$

Previous studies of this condensation have been carried out in aqueous[58] acetone and no record of a study in the anhydrous medium has been found. The depolymerisation of diacetone alcohol catalysed by sodium hydroxide has also been studied[59] and the acid catalysed dehydration of diacetone alcohol to mesityl oxide[60].

It is probable that in anhydrous media the self-condensation of acetone to mesityl oxide catalysed by an acid (or a base) would proceed through diacetone alcohol as an intermediate.

Infra red spectra of reaction mixtures were compared with those of the pure substances acetone, diacetone alcohol and mesityl oxide and synthetic mixtures of these three components. A relatively strong absorption band of diacetone alcohol was resolved at 920 cm^{-1} in these synthetic mixtures. In the reaction mixtures, a weak band could be detected at 920 cm^{-1}, indicating the presence of diacetone alcohol. This band was too weak for quantitative measurements to be made.

The following two mechanisms have therefore been proposed:

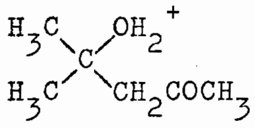
First alternative:

$$A + HCl \underset{k_2}{\overset{k_1}{\rightleftharpoons}} AH^+ + Cl^- \qquad \ldots \quad \text{Eqn. } 4.2.8$$

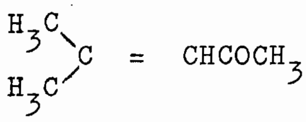
$$AH^+ + A \underset{k_4}{\overset{k_3}{\rightleftharpoons}} DH^+ \qquad \ldots \quad \text{Eqn. } 4.2.9$$

$$DH^+ + A \xrightarrow{k_5} M + H_2O + AH^+ \qquad \ldots \quad \text{Eqn. } 4.2.10$$

where A represents acetone, AH^+ the ion Me_2COH^+, DH^+ the ion



and M, mesityl oxide,



The final stage as depicted by equation 4.2.10 is considered irreversible for all practical purposes, since a synthetic mixture of acetone and mesityl oxide with a minute quantity of diacetone alcohol in aqueous hydrogen chloride solution, separated into two layers and no detectable decrease in the oily (mesityl oxide) layer could be observed over a period of one month. This final stage must therefore be irreversible or the reverse reaction must be exceedingly slow compared to the forward reaction. Furthermore, mesityl oxide itself will condense slowly with acetone to produce phorone. This has been demonstrated by allowing a saturated solution of hydrogen chloride in anhydrous acetone, to stand for one to two days, after which phorone could be detected by infra red spectroscopy.

Consider equations 4.2.8 to 4.2.10.

Assume $\frac{d[AH^+]}{dt} = \frac{d[DH^+]}{dt} = 0$ ... Eqn. 4.2.11

$$\frac{d[AH^+]}{dt} = k_1[A][HCl] - k_2[AH^+][Cl^-] - k_3[AH^+][A] + k_4[DH^+] + k_5[DH^+][A]$$

... Eqn. 4.2.12

$$\frac{d[DH^+]}{dt} = k_3[AH^+][A] - k_4[DH^+] - k_5[DH^+][A]$$

... Eqn. 4.2.13

adding equations 4.2.12 and 4.2.13

$$k_1[A][HCl] - k_2[AH^+][Cl^-] = 0$$

... Eqn. 4.2.14

$$\therefore [AH^+] = \frac{k_1[A][HCl]}{k_2[Cl^-]}$$

... Eqn. 4.2.15

and $$[DH^+] = \frac{k_3[AH^+][A]}{k_4 + k_5[A]}$$

$$= \frac{k_1[A][HCl]}{k_2[Cl^-]} \cdot \frac{k_3[A]}{k_4 + k_5[A]} \qquad \text{... Eqn. 4.2.16}$$

Assume $k_4 \ll k_5[A]$

whence $$\frac{d[M]}{dt} = k_5[DH^+][A]$$

$$= \frac{k_1 k_3 [A]^2 [HCl]}{k_2[Cl^-]} \qquad \text{... Eqn. 4.2.17}$$

$\sim k$ for any one run.

Second alternative:

$$A + HCl \underset{k_2}{\overset{k_1}{\rightleftharpoons}} AH^+ + Cl^- \qquad \text{... Eqn. 4.2.18}$$

$$AH^+ + A \underset{k_4}{\overset{k_3}{\rightleftharpoons}} DH^+ \qquad \text{... Eqn. 4.2.19}$$

$$DH^+ \xrightarrow{k_5} M + H_3{}^+O \qquad \text{... Eqn. 4.2.20}$$

Assume $$\frac{d[AH^+]}{dt} = \frac{d[DH^+]}{dt} = 0$$

$$\frac{d[AH^+]}{dt} = k_1[A][HCl] - k_2[AH^+][Cl^-] - k_3[AH^+][A] + k_4[DH^+] \qquad \text{... Eqn. 4.2.21}$$

$$\frac{d[DH^+]}{dt} = k_3[AH^+][A] - k_4[DH^+] - k_5[DH^+] \qquad \text{... Eqn. 4.2.22}$$

Adding equations 4.2.21 and 4.2.22:

$$k_1[A][HCl] - k_2[AH^+][Cl^-] - k_5[DH^+] = 0 \qquad \text{... Eqn. 4.2.23}$$

From 4.2.22 $$[DH^+] = \frac{k_3[AH^+][A]}{k_4 + k_5}$$

Substitute in 4.2.23

$$k_1[A][HCl] = k_2[AH^+][Cl^-] + \frac{k_3[AH^+][A]}{k_4/k_5 + 1} \qquad \text{... Eqn. 4.2.24}$$

Assume $k_4/k_5 \ll 1$

$$\therefore\ [AH^+] = \frac{k_1[A][HCl]}{k_2[Cl^-] + k_3[A]} \qquad \ldots \quad \text{Eqn. } 4.2.25$$

Assume $k_2[Cl^-] \gg k_3[A]$

Then $$[AH^+] = \frac{k_1[A][HCl]}{k_2[Cl^-]} \qquad \ldots \quad \text{Eqn } 4.2.26$$

Now $$\frac{d[M]}{dt} = k_5[DH^+]$$

$$= k_1[A][HCl] - k_2[AH^+][Cl^-] \qquad \ldots \quad \text{Eqn. } 4.2.27$$

$$= 2k_1[A][HCl] \qquad \ldots \quad \text{Eqn. } 4.2.28$$

$= k$ for any one run.

The final rate equations in both alternatives yield on integration

$$[P] - [P_o] = kt \qquad \ldots \quad \text{Eqn. } 4.2.29$$

Experimental plots of product concentration or absorbance, A, against time were found to be linear, with slopes depending only on the acid concentration. Extrapolating these plots to zero time, the intercepts, A_o, were found to coinside with the absorbances of fresh solutions of hydrogen chloride in acetone of the same acid concentrations.

Plots of absorbance against time for various acid concentrations for the three temperatures viz. 20°C, 30°C and 40°C are given in fig. 10 to fig. 12.

The zero order velocity constants k_z have been calculated from the slopes of these lines and catalytic coefficients k_{H^+} from them by dividing by the acid concentration.

TABLE 4.2.1

RATE CONSTANTS FOR VARIOUS CONCENTRATIONS OF HYDROGEN CHLORIDE IN ACETONE

(a) At 20°C

10^2 [HCl] mole litre^{-1}	$10^2 k_z$ mole litre^{-1} hr.$^{-1}$	$10 k_z$ / [HCl] hr.$^{-1}$	k_{H^+} min.$^{-1}$
2.148	1.375	6.400	1.062×10^{-2}
3.129	1.990	6.361	
3.542	2.260	6.382	
11.74	7.520	6.404	
29.67	18.85	6.353	

(b) At 30°C

10^2 [HCl] mole litre^{-1}	$10^2 k_z$ mole litre^{-1} hr.$^{-1}$	k_z / [HCl] hr.$^{-1}$	k_{H^+} min.$^{-1}$
1.092	1.40	1.280	2.007×10^{-2}
1.725	2.06	1.187	
4.280	5.08	1.210	
17.48	20.68	1.183	

(c) At 40°C.

10^2 [HCl] mole litre^{-1}	$10^2 k_z$ mole litre^{-1} hr.$^{-1}$	k_z / [HCl] hr.$^{-1}$	k_{H^+} min.$^{-1}$
1.285	2.70	2.200	3.603×10^{-2}
5.572	1.16	2.082	
8.710	1.90	2.177	
38.21	82.4	2.153	
105.9	223	2.201	

Using catalytic coefficients a plot of log k against 1/T produce a straight line (fig. 13) and from the slope the activation energy E_A is found to be 11.21K cal. mole^{-1} for the overall condensation of acetone to mesityl oxide. Calculation of the frequency factor gave an average value of $10^{6.386}$.

4.3 THE DEHYDRATION OF DIACETONE ALCOHOL TO MESITYL OXIDE

In order to obtain support for the assumption made in postulating the mechanism for the overall condensation reaction, the dehydration of diacetone alcohol to mesityl oxide was investigated.

When dry hydrogen chloride gas was passed into pure anhydrous diacetone alcohol the dehydration was so rapid that it was impossible to follow the reaction spectrophotometrically.

Dilute solutions of diacetone alcohol in spectroscopically pure cyclohexane were therefore used in this investigation, cyclohexane being chosen as a solvent because of its previous use as a diluent (p. 62).

The solutions of diacetone alcohol were mixed with solutions of hydrogen chloride in cyclohexane of known acid concentration.

In any particular series, the initial diacetone alcohol concentration was kept constant and the acid concentration varied from run to run.

Fig.10 THE SELF-CONDENSATION OF ACETONE

VARIATION OF ABSORBANCE WITH TIME AT 20°C

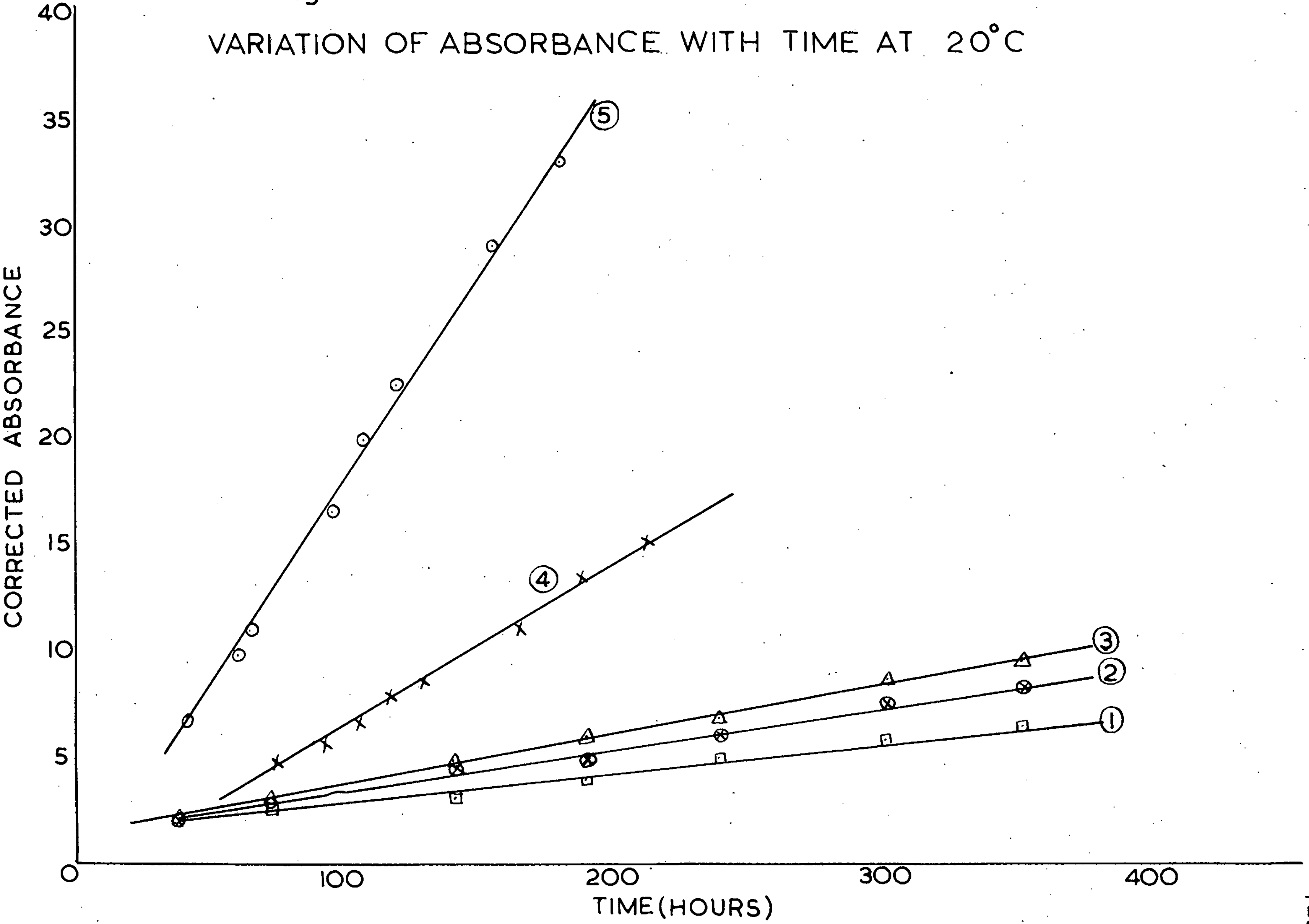


Fig. 11 THE SELF-CONDENSATION OF ACETONE

VARIATION OF ABSORBANCE WITH TIME AT 30°C

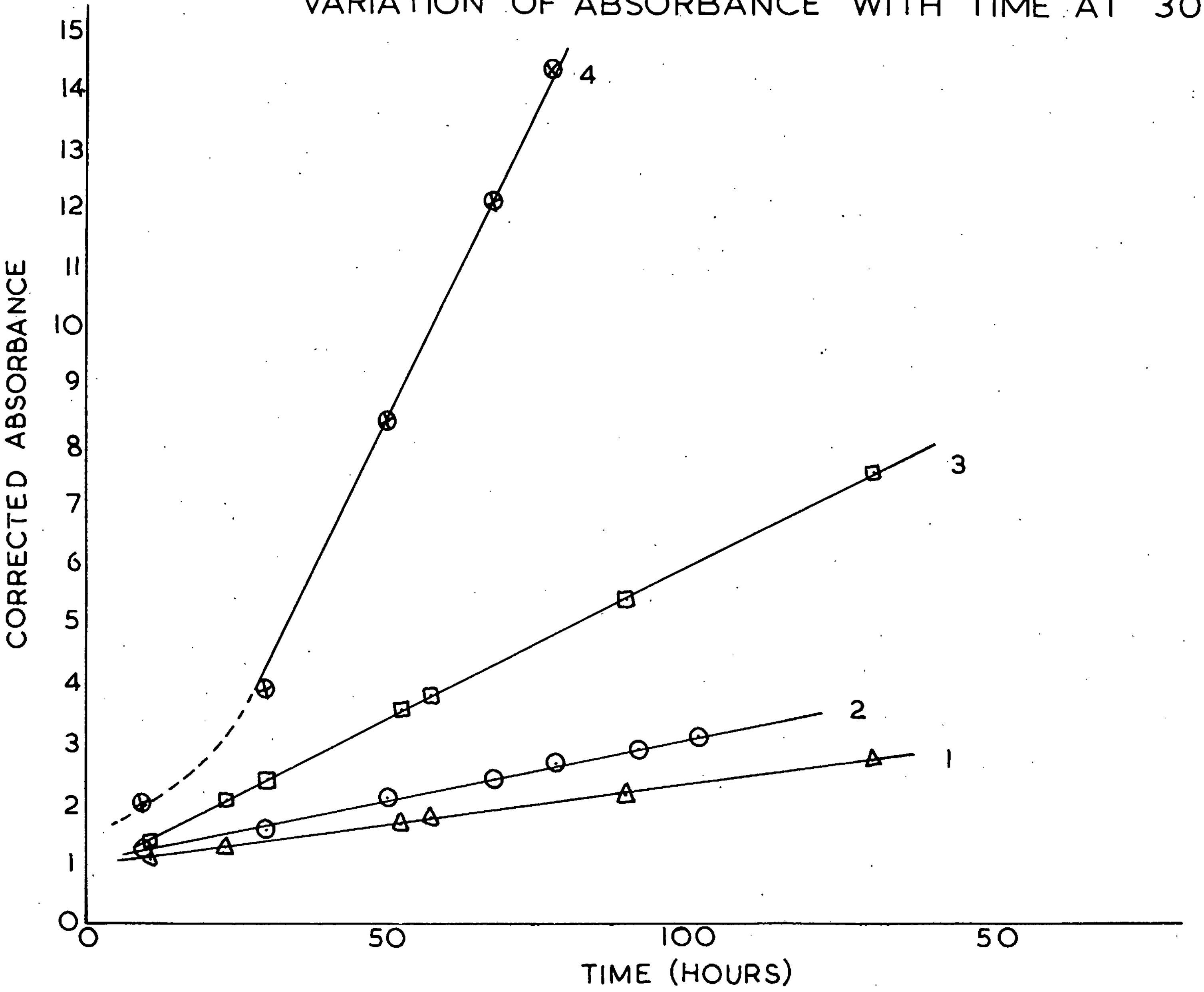


Fig.12 THE SELF-CONDENSATION OF ACETONE

VARIATION OF ABSORBANCE WITH TIME AT 40°C

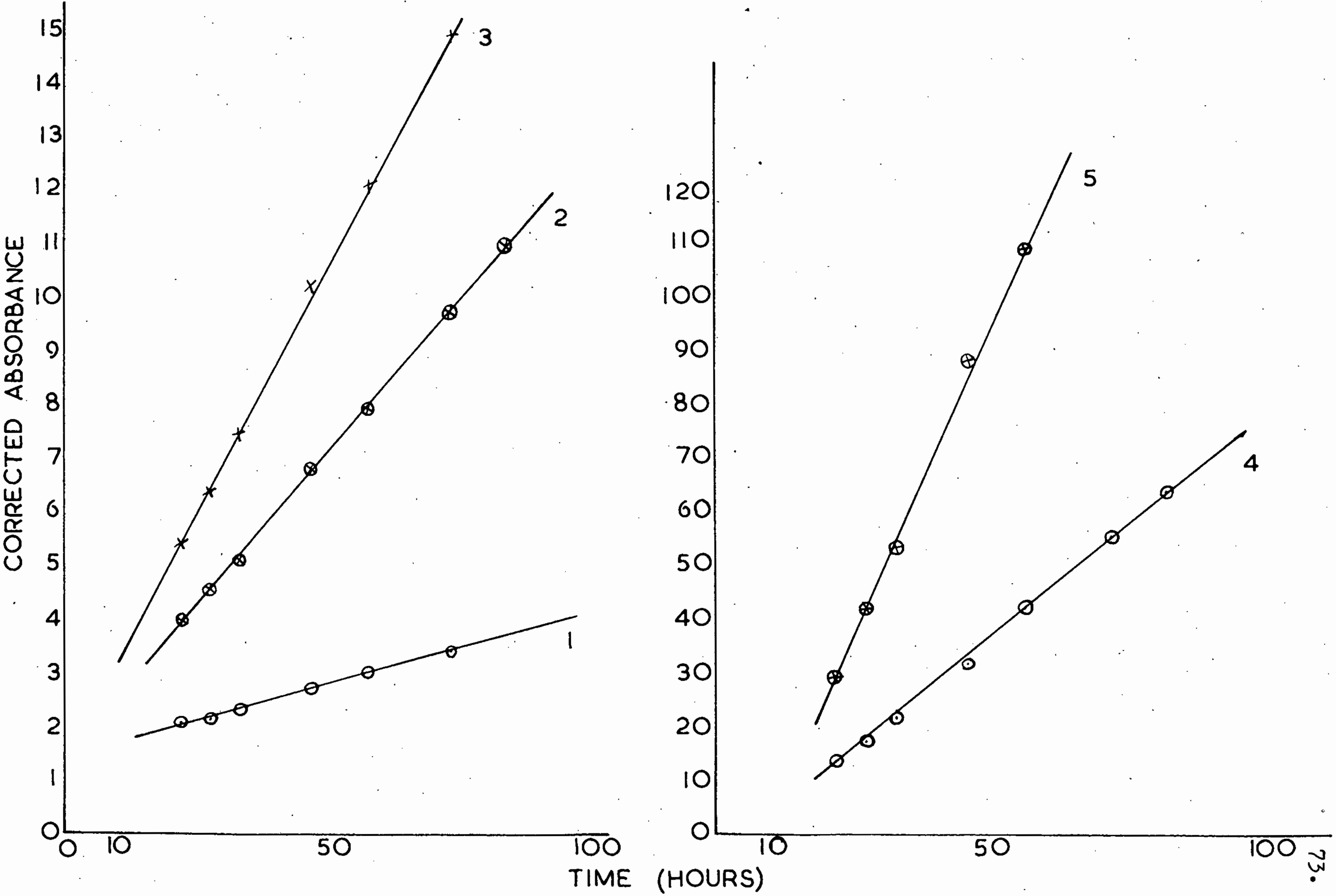
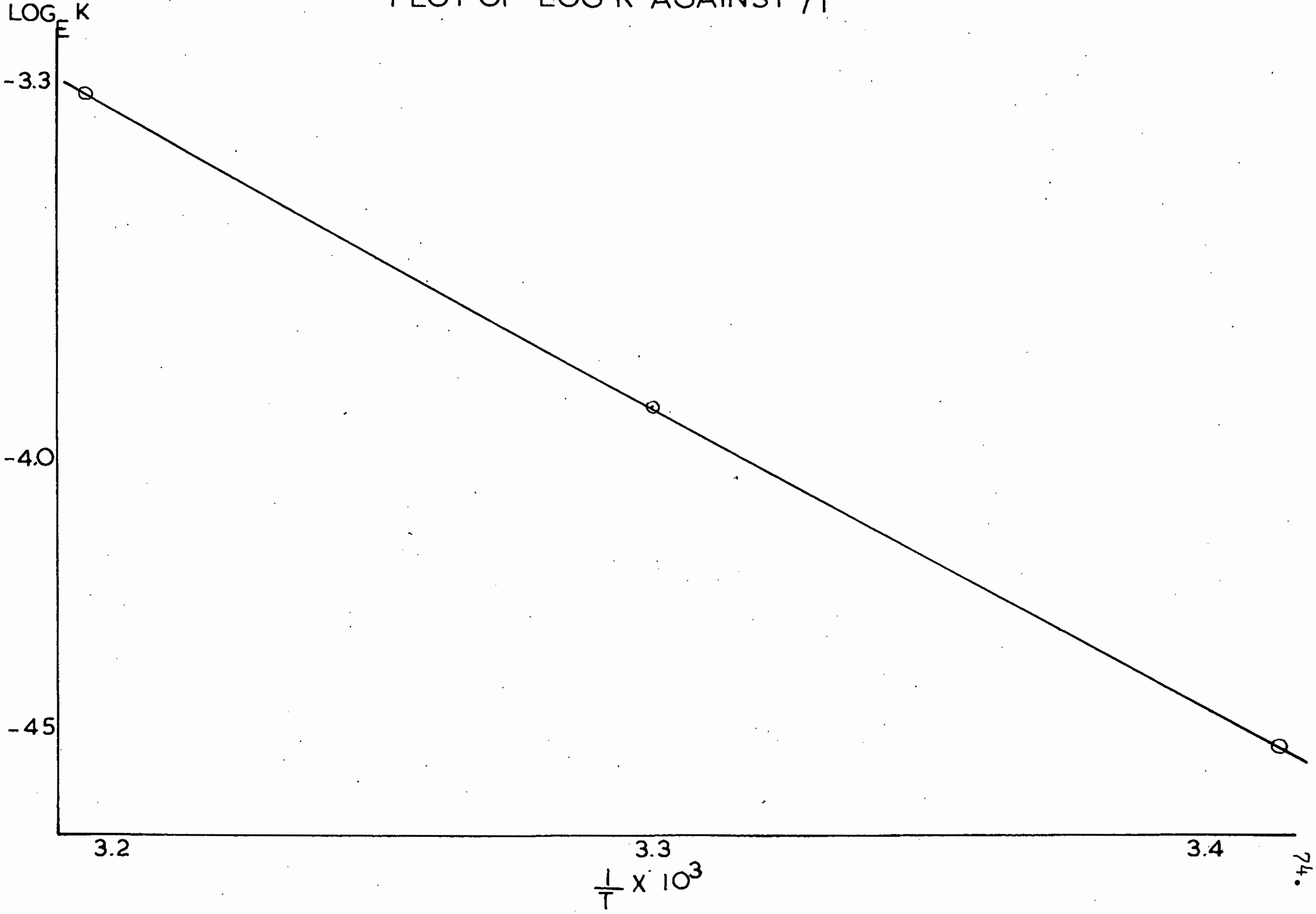


Fig. 13 THE CONDENSATION OF ACETONE TO MESITYLOXIDE

PLOT OF LOG K AGAINST $^1/_T$



These studies were carried out at various temperatures so as to enable the calculation of the activation energy and as in the previous studies product concentrations were measured at various time intervals by following the change in absorbance at 2310Å of the reaction mixture.

Plots of product concentration against time proved to be linear and slopes varied with acid concentration.

Because of the high molar extinction coefficient of mesityl oxide (1.2×10^4 at 2310Å) measurements could only be made during the initial stages of the reaction over a time period where the diacetone alcohol concentration remained virtually constant.

Plots of product concentration against time for various temperatures and differing acid concentrations are given in fig.14 to fig.16.

Runs were also made in order to determine the order of the reaction with respect to either reactant and final measurements were made at a diacetone alcohol concentration which would produce a first order reaction with respect to this reactant. Acid concentrations were varied over a region where the reaction is very nearly first order with respect to acid concentration.

Results were calculated similarly as in par. 4.2 and are summarised in table 4.3.1.

TABLE 4.3.1

RATE CONSTANTS FOR THE REACTION DIACETONE ALCOHOL TO MESITYL OXIDE

(a) At 19°C.

Diacetone alcohol concentration: 1.022×10^{-2} mole litre^{-1}.

10^3 [HCl] mole litre^{-1}	$10^3 k_z$ mole litre^{-1} min.$^{-1}$	$10^{-2} k_z$/[HCl][DAA] litre^2 mole^{-2} min.$^{-1}$	$10^{-2} k_{bim}$
2.248	5.70	2.479	2.480
5.187	13.14	2,481	

(b) At 31.5°C.

Diacetone alcohol concentration: 1.001×10^{2} mole litre^{-1}

10^3 [HCl] mole litre^{-1}	$10^3 k_z$ mole litre^{-1} min.$^{-1}$	$10^{-2} k_z$/[HCl][DAA] litre^2 mole^{-2} min.$^{-1}$	$10^{-2} k_{bim}$
1.294	4.7	3.628	3.632
2.575	11.8	3.636	
3.441	12.5	3.630	

(c) At 38°C.

Diacetone alcohol concentration: 1.001×10^{-2} mole litre^{-1}.

10^3 [HCl] mole litre^{-1}	$10^2 k_z$ mole litre^{-1} min.$^{-1}$	$10^{-2} k_z$/[HCl][DAA] litre^2 mole^{-2} min.$^{-1}$	$10^{-2} k_{bim}$
1.962	0.800	4.075	4.071
4.295	1.750	4.070	
7.053	2,873	4.068	

THE DEHYDRATION OF DIACETONE ALCOHOL

FIG. 14 VARIATION OF ABSORBANCE WITH TIME AT 19°C

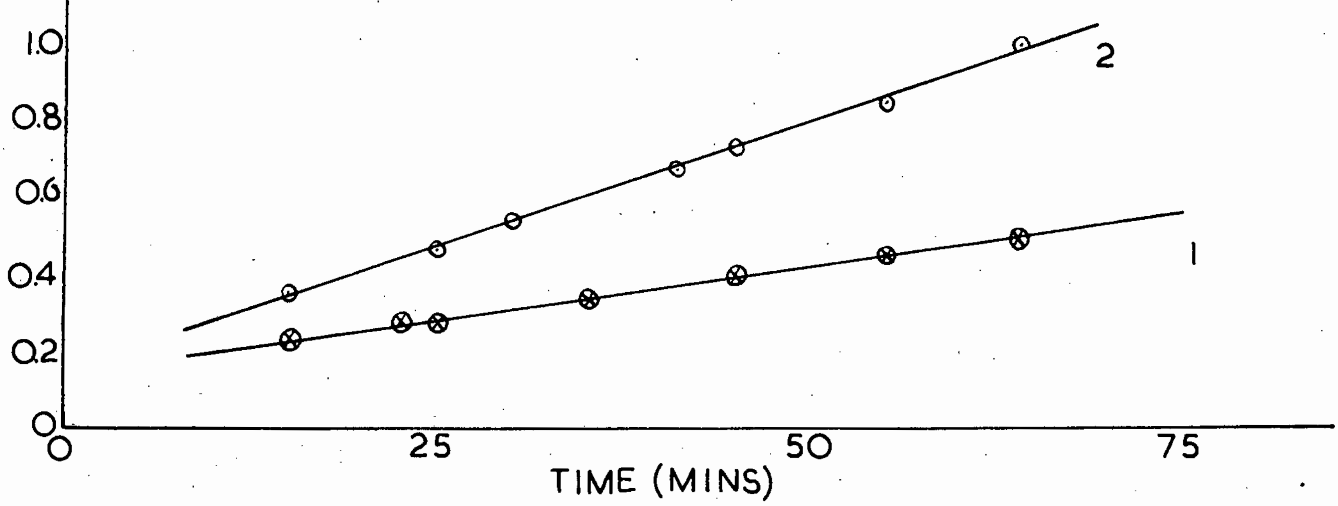


FIG. 15 VARIATION OF ABSORBANCE WITH TIME AT 32°C

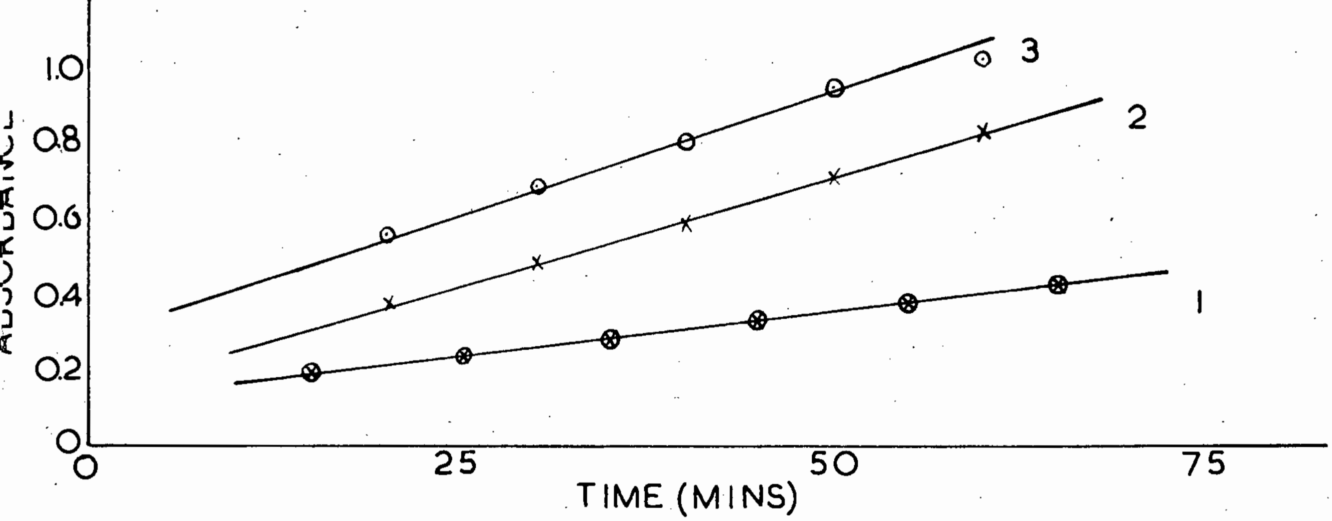


FIG. 16 VARIATION OF ABSORBANCE WITH TIME AT 38°C

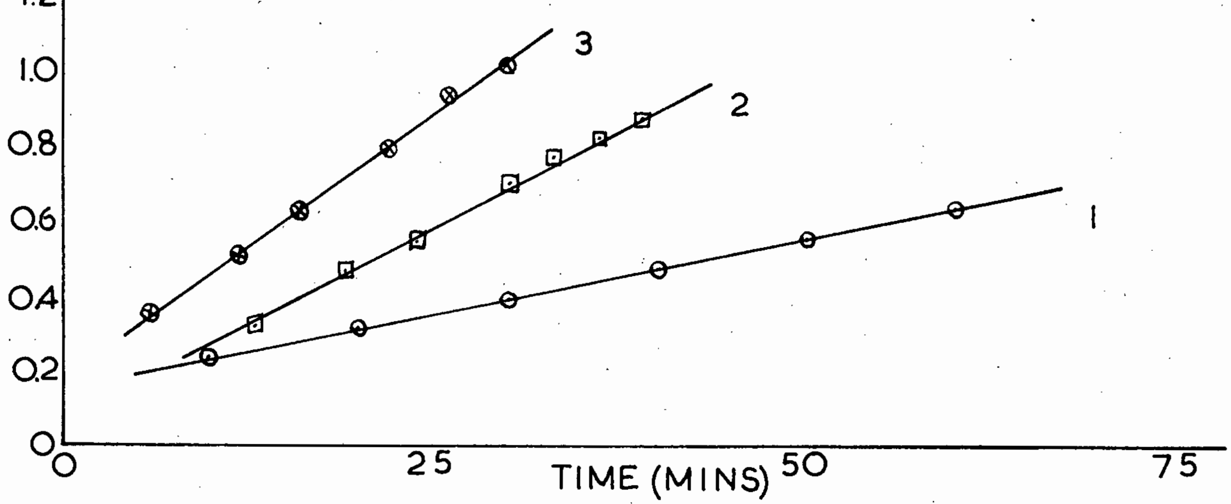
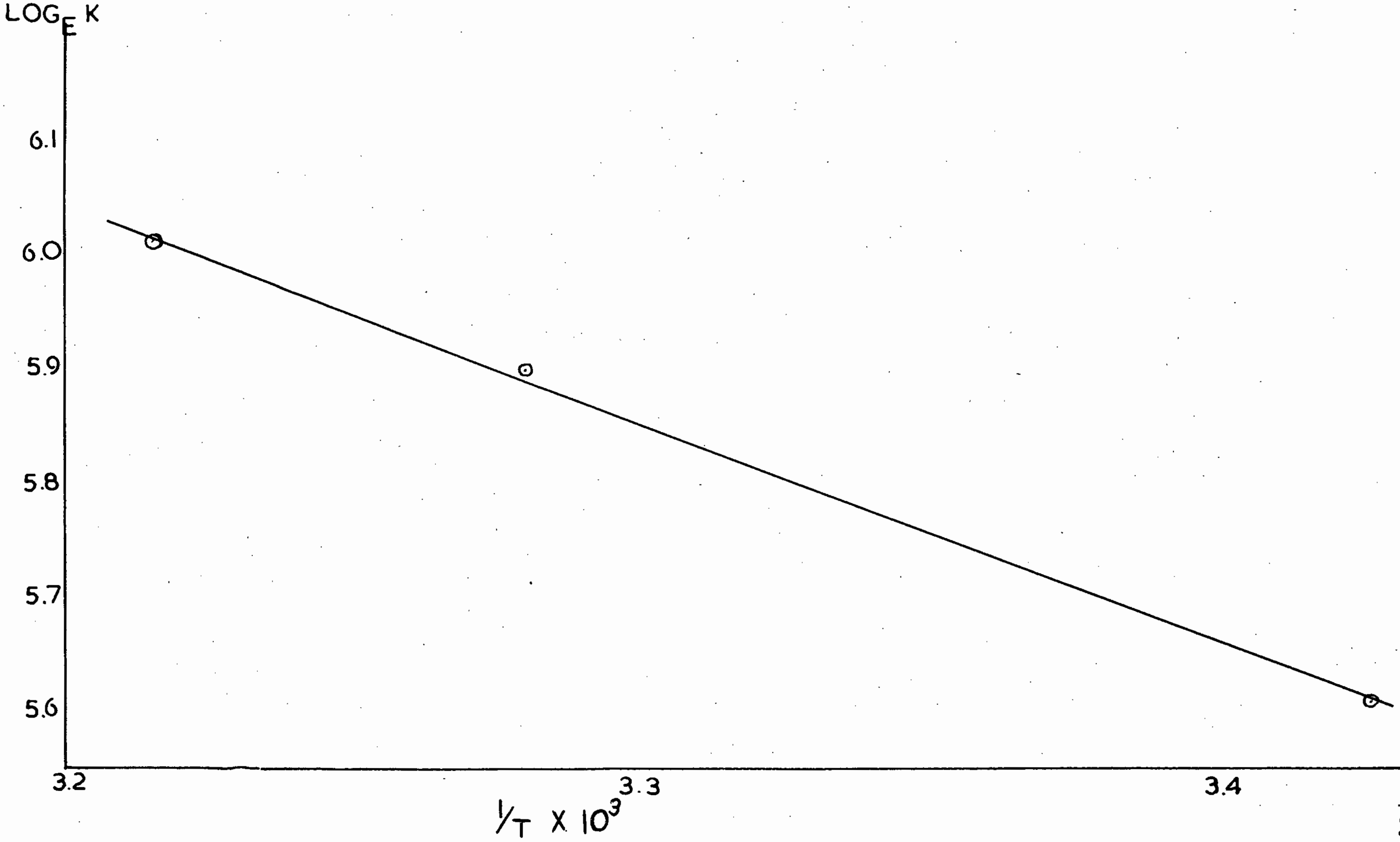


Fig.17 THE DEHYDRATIN OF DIACETONE ALCOHOL

PLOT OF LOG K AGAINST $1/T$



4.4 CALCULATION OF THERMODYNAMIC DATA

TABLE 4.4.1

THE CONDENSATION REACTION

Temp. ^{o}K	10^{2} k min.$^{-1}$	E_A Kcal mole^{-1}	A min.$^{-1}$	S e.u.
293.0	1.062	11.21	$10^{6.386}$	-31.25
303.0	2.007		$10^{6.389}$	-31.34
313.0	3.603		$10^{6.384}$	-31.43

TABLE 4.4.2

THE DEHYDRATION REACTION

Temp. ^{o}K	$10^{-2}k_{bim}$ litre^{2} mole^{-2} min.$^{-1}$	E_A Kcal mole^{-1}	A litre^{2} mole^{-2} min.$^{-1}$
292.0	2.480	3.69	$10^{5.16}$
304.5	3.632		$10^{5.31}$
311.0	4.071		$10^{5.30}$

4.5 DISCUSSION

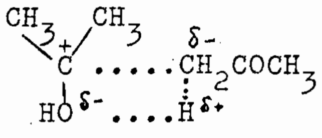
Complicated molecules are involved in the reactions studied, and in agreement with the transition state theory[61], the expected low values are obtained for the frequency factors as well as negative entropies of activation for the overall reaction. This is because of a conversion of rotational degrees of freedom into vibrations in the activated complex.

The large negative value of the entropy of activation for the overall reaction is in agreement with the slow rate of reaction. Although the dehydration reaction is known to be fast, an extremely low value was obtained for the frequency factor. However, combination of this low value with the small activation energy, may explain the fast rate of reaction.

Koelichen[62] studied the base catalysed acetone-diacetone alcohol reaction in aqueous medium and has measured the equilibrium constant. He obtained a standard entropy change $\Delta S^{o}=-32$ e.u. Comparing this value with the value of the entropy of activation, $\Delta S^{\ddagger}= -31.4$ e.u., as found in the present studies, it seems likely that the activated complex must be similar in structure to diacetone alcohol.

In each of the two possible mechanisms proposed for the acid catalysed self-condensation of acetone to mesityl oxide, the formation of diacetone alcohol (Egn. 4.2.9 page 65 and Eqn. 4.2.19 page 67) was assumed to be the rate determining step.

A possible activated complex can be formulated as:



This is a four centre complex, hence its entropy of formation $\Delta S^{\ddagger}$ will be negative and large in magnitude. Therefore, the frequency factor will be low for both the forward and reverse reactions, but A_3 will be less than A_4 because the carbon-carbon bond already exists in DH^+ whereas in forming DH^+ from acetone and the ion AH^+, the partial bond must be formed and the translational entropy of one molecule lost. However, $\Delta E_4^{\ddagger} > \Delta E_3^{\ddagger}$ (probably) because of bond breaking.

In the first alternative (p.65) k_4 is assumed very much less than k_5. Now k_5 is known empirically to be high and $\Delta E_5^{\ddagger}$ small. $\Delta S_5^{\ddagger}$ is also likely to be small.

In alternative two (p.67) k_4 is again assumed very much less than k_5 and $k_3[A]$ is assumed less than $k_2[Cl^-]$ so that $k_3 \ll k_2$.

The reverse reaction in equation 4.2.8 (p.65) and 4.2.18 (p.67) occurs between oppositely charged ions, one being very simple. This has been shown to be an extremely fast reaction in aqueous acetone and acetone solutions[48]. The entropy loss in such a reaction may be expected to be small and the activation energy ($\Delta E_2^{\ddagger}$) also small.

---ooOoo---

SECTION V

POTENTIOMETRIC MEASUREMENTS IN ANHYDROUS ACETONE

5.1 E.M.F. MEASUREMENTS ON SOLUTIONS OF HYDROGEN CHLORIDE IN ACETONE

Ulich and Spiegel[29] made a study of metal-metal halide electrodes in acetone and came to the conclusion that most of the systems gave irreproducible results. They considered this to be due to the formation of complex ions of the type $M_mX_n^{(n-m)-}$.

Everett and Rasmussen[6] found the silver-silver chloride electrode to behave satisfactorily and made an extensive study of the cell Pt,H_2/HCl/AgCl,Ag in acetone. Their results show hydrogen chloride to be a very weak acid in acetone solutions and using an approximate dissociation constant $K_a=10^{-8}$, they calculated the standard e.m.f. of the cell.

Erdey-Gruz[31] determined transference numbers in acetone and acetone-water mixtures using the cell

Pt,H_2/0.01M HCl// 0.1M HCl/H_2,Pt in acetone.

Although the work of Everett and Rasmussen was fairly extensive, they based their calculations on an uncertain dissociation constant for hydrogen chloride in acetone solutions.

An equation given by Glasstone[35] was employed, making use of activity coefficients and degrees of dissociation which were derived from conductivity work described in section III. The cell Pt,H_2/HCl/AgCl,Ag in acetone was reinvestigated and a new value for the standard e.m.f. of the cell determined.

The value of -0.488 volt for the standard e.m.f. of the cell found in the present investigation, agrees remarkably well with the value obtained when applying Everett and Rasmussen's results to Glasstone's equation.

Measurements were also made on concentration cells with and without transport in an attempt to evaluate transport numbers. This could only be done at relatively high concentrations of hydrogen chloride in acetone as the cell resistances were exceptionally high. Values of transport numbers of the positive ion over high concentration regions are in reasonable accord with those of Erdey-Gruz[31].

5.1.1 Preparation of the Electrodes

(a) The silver-silver chloride electrode

(i) Method:

Stout platinum wires were sealed in glass tubes which were to serve as electrode holders. The tips of the platinum wires were either fused or sandpapered to remove sharp edges formed on cutting[63]. Carmody's method[64] was then employed for cleaning the platinum wires in boiling concentrated nitric acid. After rinsing the electrodes with distilled water, silver was plated on the platinum and the surface chloridised electrolytically.

(ii) Silver plating solution

Potassium silvercyanide was prepared by adding excess silver cyanide to a hot filtered solution containing 20% potassium cyanide. The solution was stirred for about half an hour, undissolved silver cyanide filtered off and the solution allowed to cool. Potassium silvercyanide crystallised from the solution and was dried by centrifuging on sintered glass filters.

The silver plating solution[63] was made up by dissolving about 10 grams potassium silvercyanide in 1000 ml. water. Free cyanide was reduced by adding sufficient dilute silver nitrate solution to produce a feint cloud of silver cyanide which was allowed to settle. The clear solution was decanted.

(iii) Electrolysis

As an electrode vessel a beaker was used, covered with a perspex disc through which holes were drilled for insertion of the electrodes.

A platinum electrode was used as anode and contamination of the cathode solution was prevented by separating anode and cathode compartments by means of a sintered glass diaphragm.

Electrolysis was carried out for about two hours at 2mA and the electrodes were then carefully rinsed and left in distilled water.

The electrodes were then chloridised by electrolysis for half an hour at 2mA in a 0.1N hydrochloric acid solution. A platinum electrode was used as cathode.

The silver-silver chloride electrodes so obtained had a purplish colour and as was stated by Brown[63], who developed this method, these electrodes were not affected by light. There was, therefore no need for the preparation of the electrodes to be carried out in dimmed light.

Before use, these electrodes were allowed to stand interconnected, for two weeks in the electrode vessel in a dilute hydrochloric acid solution in order to come to equilibrium.

Basset and Corbet[65] claimed an average reproducibility for electrodes prepared in this manner as 0.02mV in a concentration range $2.0 - 2 \times 10^{-4}$N. In the present investigations no difference in potential could be detected in these electrodes when put in the same solution.

(b) The hydrogen electrode

Stout platinum wires sealed in glass tubes were treated and cleaned as described on page 83. They were then platinised over a period of ten minutes by reversing the current every 30 seconds.

The platinising solution[66] used was made up by dissolving 3 gm. of platinum chloride and about 0.03 gm. of lead acetate in 100 ml. distilled water.

5.2 APPARATUS

(i) Potentiometric cells

The following cells were investigated:

(a) $Pt,H_2/HCl/AgCl,Ag$

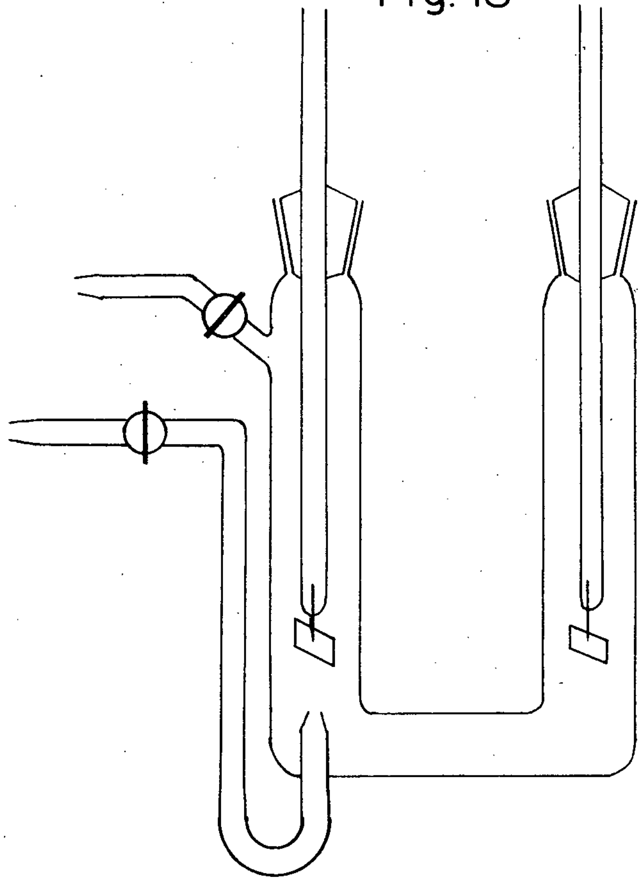
(b) $Ag,AgCl/\underset{m_1}{HCl}\vdots\underset{m_2}{HCl}/AgCl,Ag$

(c) $Pt,H_2/\underset{m_1}{HCl}/AgCl,Ag,AgCl/\underset{m_2}{HCl}/H_2,Pt$

Diagrams of these cells are given in fig. 18.

ELECTRODE VESSELS

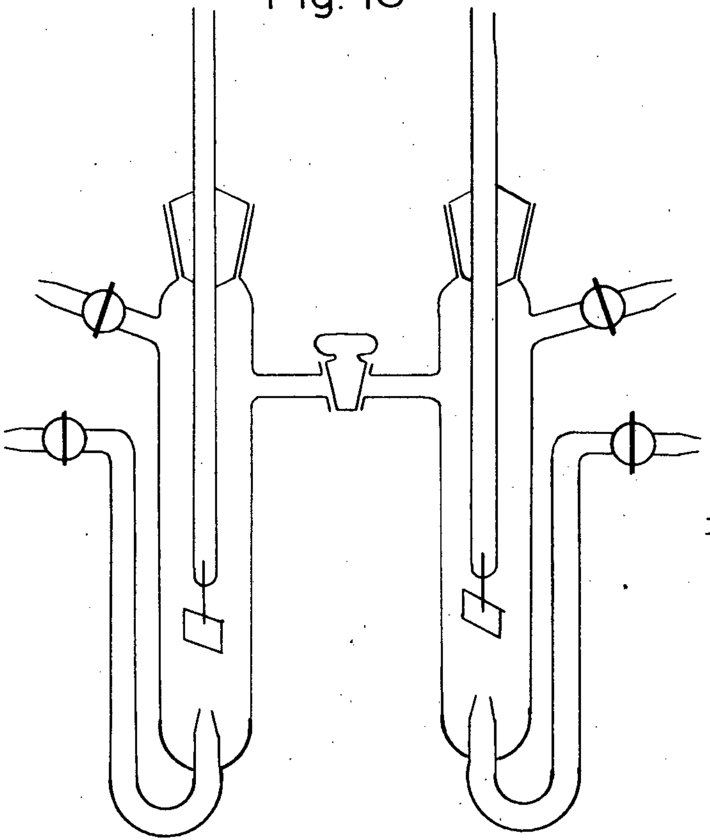
Fig. 18^a



THE CELL

Pt, H_2 / HCl / AgCl, Ag

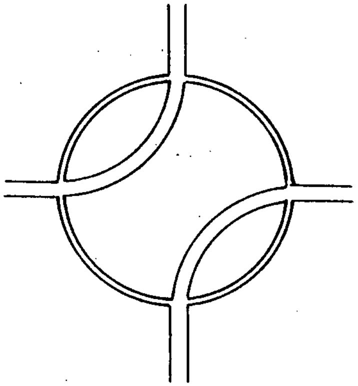
Fig. 18^b



THE CELL

Pt, H_2 / HCl M_1 ⋮ HCl / H_2, Pt M_2

Eig. 18^c



STOPCOCK IN 18^b
FOR LIQUID —
LIQUID BOUNDARY

(ii) The hydrogen train

Commercial hydrogen was purified by passing the gas through a tube packed with copper gauze inside a furnace, at a temperature of about 600°C, then through a drying tower containing anhydrous magnesium perchlorate followed by a trap cooled in liquid air. The gas was then bubbled through pure anhydrous acetone and finally through a solution of hydrogen chloride in acetone of the same hydrogen chloride concentration as that in the cell. The volume of the liquid in each saturator was about 4 to 5 times the volume used in the cell[6].

In all runs the bubble rate was regulated between 60 and 80 bubbles per minute. It was, however, noted that a bubble rate up to 100 per minute did not affect the e.m.f. measurements.

The hydrogen train is depicted in fig. 19.

(iii) The thermostat

A large glass tank water thermostat was used and the temperature was kept constant to within 0.01°C. Circulation and fast heating of the water were obtained by a Braun Thermomix II whose temperature was set at one degree below the required temperature. The bath was heated to 25° ± 0.01°C by a normal heating spiral in glass, the filament being covered by oil

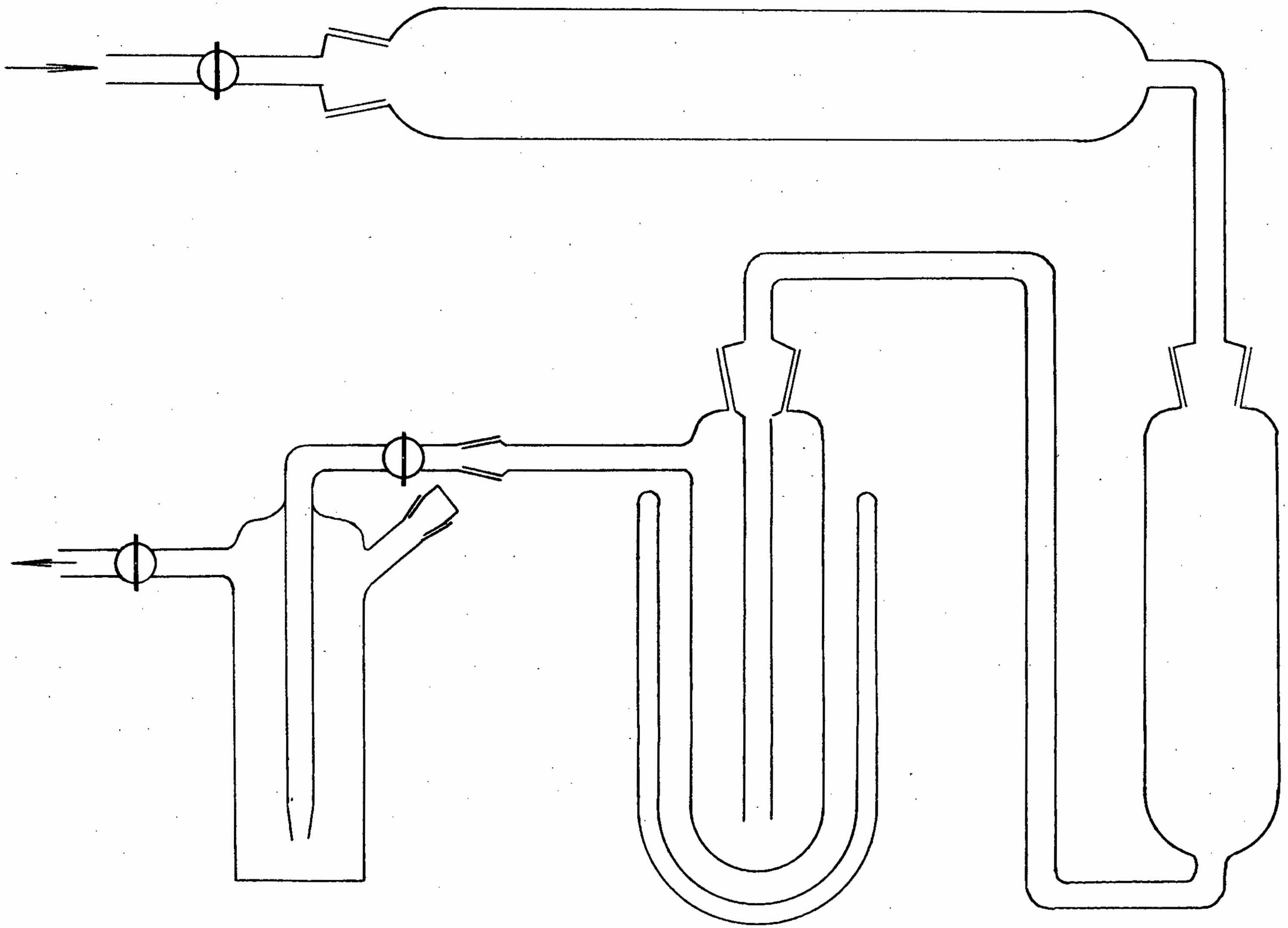


Fig.19 THE HYDROGEN GAS PURIFICATION TRAIN

and fine regulation was by a mercury-toluene regulator connected to a Sunvic hot wire vacuum switch.

5.3 RESULTS OF E.M.F. MEASUREMENTS

5.3.1 The cell Pt,H_2/HCl/AgCl,Ag

Everett and Rasmussen[6] found their cells to require 6 to 12 hours to reach equilibrium whereas in the present studies cells came to equilibrium within 3 to 4 hours.

The Nernst relation for the e.m.f. of the cell is given by

$$E = E^{o} - \frac{2RT}{F} \ln a \qquad \ldots \quad \text{Eqn. 5.3.1}$$

$$= E^{o} - \frac{2RT}{F} \ln \alpha m \gamma \qquad \ldots \quad \text{Eqn. 5.3.2}$$

This may be rewritten as

$$E + \frac{2RT}{F} \ln \alpha m = E^{o} - \frac{2RT}{F} \ln \gamma \qquad \ldots \quad \text{Eqn. 5.3.3}$$

Reverting to common logs

$$E + 2\frac{2.303RT}{F} \log \alpha m = E^{o} - 2\frac{2.303RT}{F} \log \gamma \qquad \ldots \quad \text{Eqn. 5.3.4}$$

Now γ is given by the Debye-Hückel-Brønsted equation as

$$\ln \gamma = -A\sqrt{\alpha m} + Cm \qquad \ldots \quad \text{Eqn. 5.3.5}$$

where A is a constant for a particular solvent depending on the dielectric constant and temperature.

$$\therefore \log \gamma = \frac{-A\sqrt{\alpha m} + Cm}{2.303}$$

Substitution of this value for $\log \gamma$ in eqn. 5.3.4 leads to

$$E + 2\frac{2.303RT}{F}\log\alpha m = E^{o} + 2\frac{2.303RT}{F}\;\frac{A\sqrt{\alpha m} - Cm}{2.303}$$

... Eqn. 5.3.6

or

$$E' = E + 2k\log\alpha m - 2k'A\sqrt{\alpha m} = E^{o} - 2k'Cm$$

... Eqn. 5.3.7

where

$$k = \frac{2.303RT}{F} \quad \text{and} \quad k' = \frac{RT}{F}$$

A plot of E' against m should be a straight line with slope $-2k'C$ and intercept E^{o}.

It has been observed that in aqueous solutions plots of E' against m for strong electrolytes produce straight lines which tend to curve slightly at very high dilutions, but the curvature is such that extrapolation to zero concentration could still be obtained relatively accurately[67]. The observed e.m.f. measurements for various hydrogen chloride concentrations are tabulated below with the calculated values for E'. A detailed table showing all calculations in arriving at E' is given in appendix 4.

TABLE 5.3.1

CALCULATED VALUES FOR E' AT VARIOUS HYDROGEN CHLORIDE CONCENTRATIONS

m molality x 10^3	E volt observed	E' volt calculated
5	0.1040	-0.4431
20	0.0470	-0.4900

m molality x 10^3	E volt observed	E' volt calculated
50	0.0098	-0.4895
75	-0.0060	-0.4848
100	-0.0178	-0.4787
171	-0.0274	-0.4553
210	-0.0286	-0.4390

TABLE 5.3.2

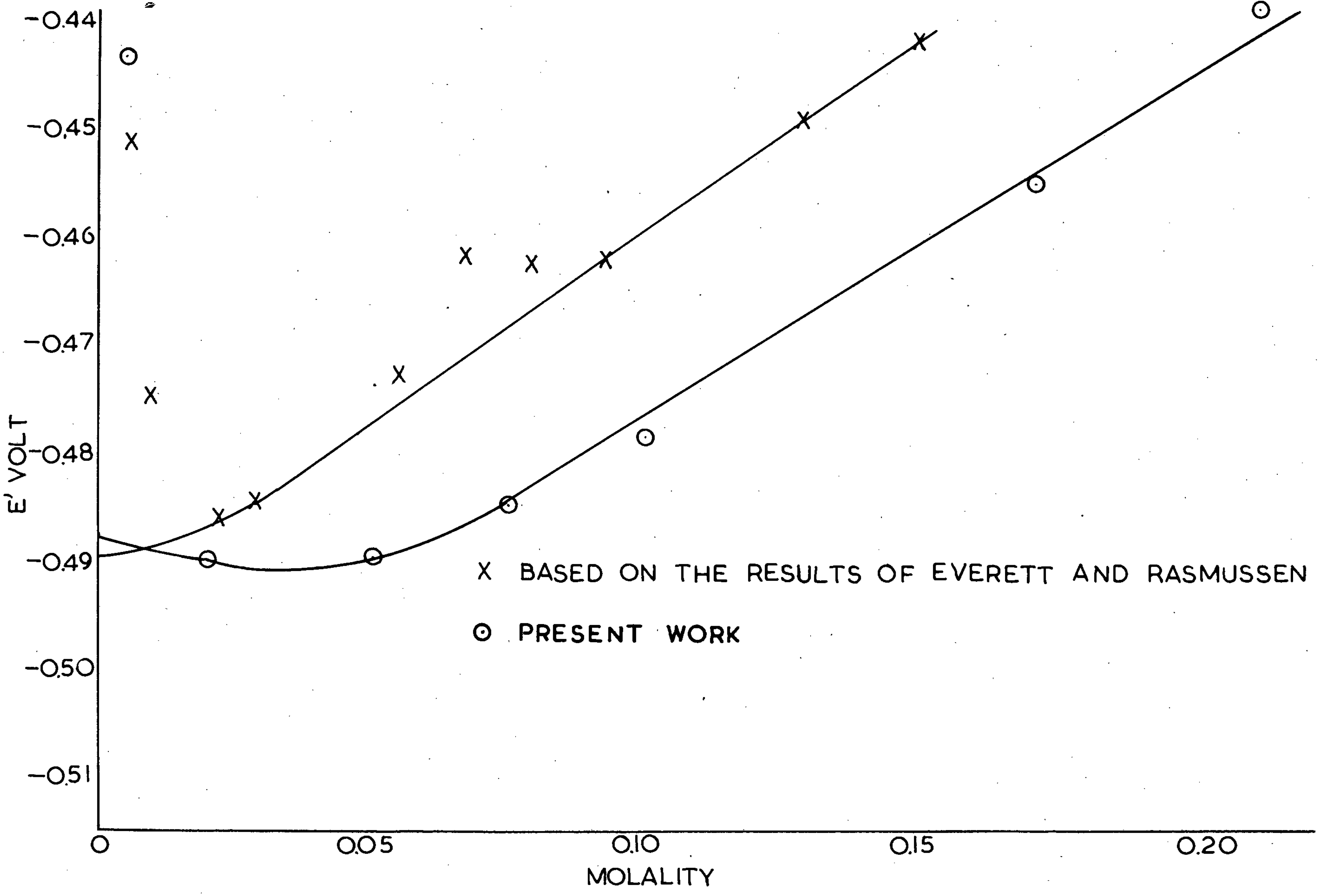
CALCULATED VALUES FOR E' FROM THE RESULTS OF EVERETT AND RASMUSSEN

m molarity x 10^3	E volt observed	E' volt calculated
5.6	0.0938	-0.4513
9.0	0.0811	-0.4749
21.9	0.0483	-0.4859
29.0	0.0392	-0.4845
55	0.0226	-0.4729
67	0.0226	-0.4620
79	0.0126	-0.4628
93	0.0092	-0.4623
128	-0.0004	-0.4496
149	-0.0046	-0.4422

Plots of E' against m extrapolate to -0.4882 volt (this work) and -0.4914 volt (Everett and Rasmussen). In their original work, making use of an approximate dissociation constant of 10^{-8} for hydrogen chloride in acetone, Everett and Rasmussen obtained a standard e.m.f.

Fig. 20 THE CELL Pt, H_2/ HCl IN ACETONE/ AgCl, Ag

PLOT OF E' AGAINST MOLALITY



for the cell of -0.52 volt. Linear extrapolation of the plot on the present measurements gives a value of -0.508 volt.

The values for the constant C in equation 5.3.7. were -6.229 for the present investigation and -6.929 from the recalculated results of Everett and Rasmussen.

The standard e.m.f. results agree remarkably, which is a further proof of the suitability and reproducibility of the silver-silver chloride electrode in acetone solutions.

Attempts were also made at determining transport numbers using the cells (b) and (c) (page 86), but proved difficult for accurate work as cell resistances were extremely high in the case of cell (b). The latter cell (c) could be calculated from measurements on the cell $Pt,H_2/HCl/AgCl,Ag$ in acetone. It was only possible to obtain three transport numbers over a relatively high concentration region and these are tabulated below.

The value of the transport number at infinite dilution was determined from conductance data using calculating ion conductances.

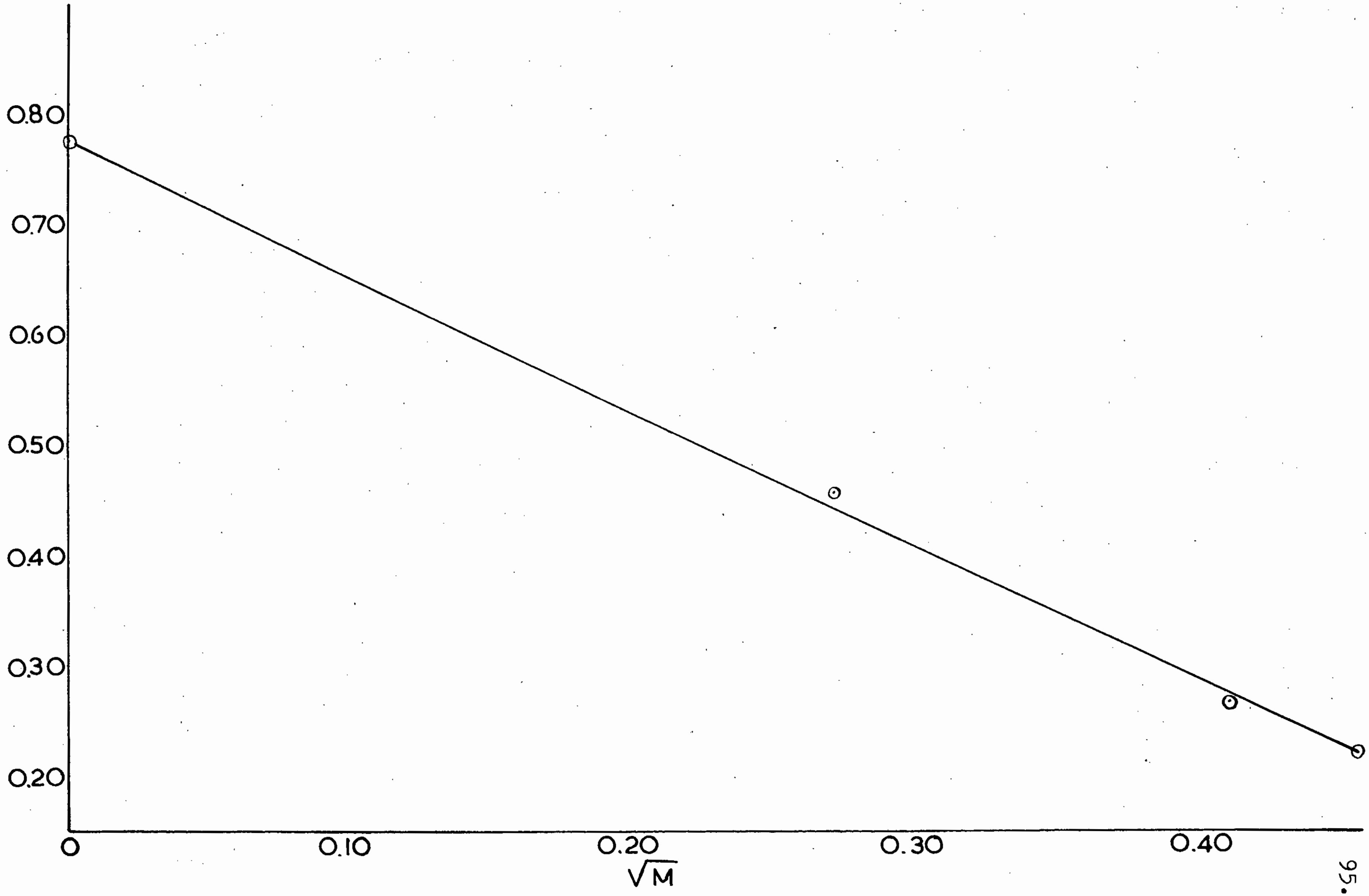
TABLE 5.3.3

OBSERVED TRANSPORT NUMBERS FOR THE POSITIVE ION FOR VARIOUS HYDROGEN CHLORIDE CONCENTRATIONS

m Molality	t_+
0	0.775 (calc.)
0.0751	0.455
0.1705	0.267
0.2098	0.220

Fig. 21 TRANSPORT STUDIES

VARIATION OF t_{H^+} WITH $\sqrt{M}$



5.4 DISCUSSION OF RESULTS

In view of the remarkable agreement between the values obtained for the standard electromotive force of the cell Pt,H_2/HCl/AgCl,Ag in acetone in this work and Everett and Rasmussen's work, it is clear that this electrode is very suitable for studies of solutions in anhydrous acetone. Furthermore, Arthur and Lyons[30] used this electrode and the calomel electrode successfully in non-acqueous media for their polarographic studies. Hotz[5] also employed the calomel and silver-silver chloride electrodes in acetone solutions and found them reproducible. Ulich and Spiegel's[29] conclusions are therefore proved to be fallacious.

The differences in measured e.m.f. values for more or less the same acid concentrations as shown in tables 5.3.1 and 5.3.2 may possibly be ascribed to differences in solvent quality and experimental conditions. For example, Everett and Rasmussen reported their cells to require 6 to 12 hours to reach equilibrium, after which the potential was constant to ± 0.5mV, whereas in the present studies equilibrium was attained in three to four hours. Such long equilibration times could introduce errors arrising from concentration changes and ingress of moisture. With this there is also the possibility of a slight degree of self-condensation.

Although extreme difficulty was encountered in the attempts to measure transport numbers, the results obtained compare fairly well with those of Erdey-Gruz[31] and exact transport numbers will not be obtained until more refined methods are employed.

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SECTION VI

DIFFUSION STUDIES OF SOLUTIONS OF HYDROGEN CHLORIDE IN ACETONE

6.1 THEORY OF ELECTROLYTIC DIFFUSION

Both diffusion and electrical conductance involve the motion of ions and a relation might exist[68] between these two phenomena.

The major differences are:-

(i) In conductance positive and negative ions move in opposite directions whereas in the diffusion process they move in the same direction.

(ii) At infinite dilution the various ions move independantly of one another in the case of conductance, but in diffusion they move at equal speeds otherwise separation of electrical charge will result.

In diffusion each diffusing entity may be regarded as moving under the influence of two forces:

(a) The gradient of the chemical potential for that ionic species.

(b) The electrical field produced by the motion of the oppositely charged ions; the resultant speeds of both species must, however, be the same.

For a single electrolyte producing ν_1 cations and ν_2 anions per molecule and of algebraic valencies z_1, and z_2 respectively, the chemical potential of the solute as a whole is given by[69]

$$\mu = \nu_1\mu_1 + \nu_2\mu_2 \qquad \ldots \text{ Eqn. } 6.1.1$$

where μ_1 and μ_2 refer to the separate ions, assuming complete dissociation.

The forces acting on single ions due to the gradient of the chemical potential are therefore:

$$-\frac{1}{N}\frac{\partial\mu_1}{\partial x} \quad \text{and} \quad -\frac{1}{N}\frac{\partial\mu_2}{\partial x}$$

where N is the Avogadro number.

The unequal mobilities of the ions produce an electrical field of intensity E which excerts additional forces on the ions given by z_1eE and z_2eE respectively. The total forces are therefore:

$$F_1 = -\frac{1}{N}\frac{\partial\mu_1}{\partial x} + z_1eE$$
$$F_2 = -\frac{1}{N}\frac{\partial\mu_2}{\partial x} + z_2eE$$

These forces acting on ions of absolute mobilities u_+ and u_- produce equal velocities v given by

$$v = u_+\left(-\frac{1}{N}\frac{\partial\mu_1}{\partial x} + z_1eE\right) = u_-\left(-\frac{1}{N}\frac{\partial\mu_2}{\partial x} + z_2eE\right) \qquad \ldots \text{ Eqn. } 6.1.2$$

If c' be the concentration of solute in mole cm^{-3} at the point considered, on eliminating eE in equation 6.1.2 and using the condition of electrical neutrality:

$$\nu_1z_1 + \nu_2z_2 = 0,$$

the flux, J, of the solute is given by

$$J = c'v = -\frac{u_{+}u_{-}}{\nu_1 u_{-} + \nu_2 u_{+}} \cdot \frac{c'}{N}\frac{\partial \mu}{\partial c'} \cdot \frac{\partial c'}{\partial x}$$

... Eqn. 6.1.3

The flux also defines the diffusion coefficient, D, in terms of the concentration gradient:

$$J = -D\frac{\partial c'}{\partial x}$$ ... Eqn. 6.1.4

Therefore, D is given by:

$$D = \frac{u_{+}u_{-}}{\nu_1 u_{-} + \nu_2 u_{+}} \cdot \frac{1}{N}\frac{\partial \mu}{\partial \ln c'}$$ ... Eqn. 6.1.5

Replacing c' by the ordinary molar concentration, c, since dlnc' = dlnc and from the definition of mean molar activity coefficient, the differential in equation 6.1.5 is:

$$\frac{\partial \mu}{\partial \ln c'} = RT(\nu_1 + \nu_2)\left(1 + \frac{d\ln \gamma_{\pm}}{d\ln c}\right)$$ ... Eqn. 6.1.6

Writing u in terms of the limiting equivalent conductances, $\Lambda^{\infty}_{\pm}$,

$$u_{\pm} = 6.469 \times 10^{6}\, \Lambda^{\infty}_{\pm} / |z|$$

Equation 6.1.5 then becomes:

$$D = \frac{6.469 \times 10^{6} RT\, (\nu_1 + \nu_2) . \Lambda^{\infty}_{+} \Lambda^{\infty}_{-}}{\nu_1 |z_1| (\Lambda^{\infty}_{+} + \Lambda^{\infty}_{-})} \cdot \left(1 + \frac{d\ln \gamma_{\pm}}{d\ln c}\right)$$

... Eqn. 6.1.7

or

$$D = \frac{(\nu_1 + \nu_2)\Lambda^{\infty}_{+}\Lambda^{\infty}_{-}}{\nu_1 |z_1| (\Lambda^{\infty}_{+} + \Lambda^{\infty}_{-})} \cdot \frac{RT}{F^2}\left(1 + \frac{d\ln \gamma_{\pm}}{d\ln c}\right)$$

... Eqn. 6.1.7a

and is known as the Nernst-Hartley relation.

The limiting value of D at infinite dilution where $\frac{d\ln\gamma_{\pm}}{d\ln c} \longrightarrow 0$, is

$$D^{o} = \frac{RT}{F^{2}} \cdot \frac{(\nu_1 + \nu_2)}{\nu_1 |z_1|} \cdot \frac{\Lambda^{\infty}_{+} \cdot \Lambda^{\infty}_{-}}{(\Lambda^{\infty}_{+} + \Lambda^{\infty}_{-})} \quad \ldots \text{ Eqn. 6.1.8}$$

an expression due to Nernst[68].

Now

$$\nu_1 |z_1| = \nu_2 |z_2| \text{ and } t^{\infty}_{+} = \Lambda^{\infty}_{+}/(\Lambda^{\infty}_{+} + \Lambda^{\infty}_{-}) = \Lambda^{\infty}_{+}/\Lambda_{\infty}$$

Therefore

$$D = \frac{RT}{F^{2}} \cdot \frac{|z_1| + |z_2|}{|z_1 z_2|} \cdot \Lambda_{\infty} \cdot t^{\infty}_{+} \, t^{\infty}_{-} \left(1 + \frac{d\ln\gamma_{\pm}}{d\ln c}\right) \quad \ldots \text{ Eqn. 6.1.9}$$

or

$$D = D^{o} \left(1 + \frac{d\ln\gamma_{\pm}}{d\ln c}\right) \quad \ldots \text{ Eqn. 6.1.10}$$

However, the effects present in conductance i.e. relaxation and electrophoretic effects have to be considered[70].

It can be shown in the case of a single diffusing electrolyte that the symmetry of the ionic distribution is not disturbed so that the relaxation effect is absent.

As a result of the electrophoretic effect, the velocity of an ion is increased by Δv and provided Δv_{+} and Δv_{-} is small compared to v, the electrophoretic effect in diffusion may be treated by increasing the mobilities of the ions by factors $(1 + \frac{\Delta v_{+}}{v})$ and $(1 + \frac{\Delta v_{-}}{v})$ respectively.

If we now replace the factor $\Lambda_+^{\infty}\Lambda_-^{\infty}/(\Lambda_+^{\infty} + \Lambda_-^{\infty})$ in the Nernst-Hartley relation (Eqn. 6.1.7a) by

$$\frac{\Lambda'_+\Lambda'_-}{\Lambda'_+ + \Lambda'_-} = \frac{\Lambda_+^{\infty}\Lambda_-^{\infty}\left(1 + \frac{\Delta v_+}{v}\right)\left(1 + \frac{\Delta v_-}{v}\right)}{\Lambda_+^{\infty}\left(1 + \frac{\Delta v_+}{v}\right) + \Lambda_-^{\infty}\left(1 + \frac{\Delta v_-}{v}\right)}$$

... Eqn. 6.1.11

Putting

$\Lambda_+^{\infty} = t_+^{\infty}\Lambda_{\infty}$ and $\Lambda_-^{\infty} = t_-^{\infty}\Lambda_{\infty}$ and expanding the series in $\frac{\Delta v_+}{v}$ and $\frac{\Delta v_-}{v}$ as far as the first powers, equation 6.1.11 becomes

$$\frac{\Lambda'_+\Lambda'_-}{\Lambda'_+ + \Lambda'_-} = t_+^{\infty}\, t_-^{\infty}\Lambda_{\infty} + t_+^{\infty}\, t_-^{\infty}\Lambda_{\infty}\left(t_+^{\infty}\frac{\Delta v_-}{v} + t_-^{\infty}\frac{\Delta v_+}{v}\right)$$

... Eqn. 6.1.11a.

and inserting values for $\frac{\Delta v_+}{v}$ and $\frac{\Delta v_-}{v}$ we obtain

$$D = (D^{o} + \Sigma\Delta_n)\left(1 + c\,\frac{d\ln\gamma_{\pm}}{dc}\right) \qquad \text{... Eqn. 6.1.12}$$

where D^{o} is the Nernst[68] limiting value given by equation 6.1.8 and the electrophoretic terms, Δ_n, are given by

$$\Delta_n = \frac{1.546 \times 10^{-7}RT}{F^2} \cdot A_n \frac{(z_1^n t_-^{\infty} + z_2^n t_+^{\infty})^2}{\mathring{a}^n\,|z_1 z_2|}$$

... Eqn. 6.1.13

The coefficients A_n are functions of the dielectric constant and viscosity of the solvent, the temperature and the dimensionless concentration-dependent quantity κa and are defined by

$$A_n = \frac{(-1)^n 10^{8n}}{n!\;6\pi\eta} \cdot \left(\frac{e^2}{\varepsilon kT}\right)^{n-1} \Phi_n(\kappa a)$$

$$\Phi_n(\kappa a) = (\kappa a)^2 \left(\frac{e^{\kappa a}}{1 + \kappa a}\right)^n S_n(\kappa a)$$

$$\frac{S_n(\kappa a)}{a^{n-2}} = \int_a^{\infty} \frac{e^{-n\kappa r}}{r^{n-1}}\, dr$$

For symmetrical type electrolytes, first and second order electrophoretic terms are sufficient:

$$\Delta_1 = \frac{-1.546 \times 10^{-7} RT}{F^2} (t_-^{\infty} - t_+^{\infty}) \left(\frac{\kappa}{1 + \kappa a}\right) \quad \ldots \quad \text{Eqn. } 6.1.14$$

$$\Delta_2 = \frac{1.546 \times 10^{-7} RT}{F^2} \cdot \frac{e^2}{\varepsilon kT} (\kappa a)^2 \left(\frac{e^{\kappa a}}{1 + \kappa a}\right)^2 \mathrm{Ei}(2\kappa a) \left(\frac{|z|}{\mathring{a}}\right)^2 10^{16}$$

$$\ldots \quad \text{Eqn. } 6.1.15$$

where

$$\mathrm{Ei}\ (x) = \int_x^{\infty} e^{-y} y^{-1} dy$$

y being a variable of integration.

The complete equation therefore becomes, for completely dissociated electrolytes[70]

$$D = (D^{\circ} + \Delta_1 + \Delta_2)\left(1 + c\, \frac{d\ln \gamma_{\pm}}{dc}\right) \quad \ldots \quad \text{Eqn. } 6.1.16$$

In associated electrolytes a large fraction of the transport of solute may occur as result of motion of ion pairs or larger aggregates.

Ion association reduces the activity of the solute as compared to the fully dissociated electrolyte leading to lowering of the free energy gradient with concentration; secondly, when two particles merge into one they offer less resistance to motion through the liquid, which has the effect of increasing the diffusion coefficient.

If the mobilities of ions are given by u_+ and u_-, and that of an ion-pair or molecule by u_{12}, and with a degree of dissociation α, we obtain for associated symmetrical electrolytes in dilute solution

$$D = 2kT\left(1 + c\,\frac{d\ln\gamma_{\pm}}{dc}\right)\left[\alpha\,\frac{u_{+}\,u_{-}}{u_{+} + u_{-}} + (1-\alpha)\,u_{12}\right]$$

... Eqn. 6.1.17

Equation 6.1.17 reduces to[71]

$$D = \left[\alpha(D^{o} + \Delta_1 + \Delta_2) + 2\,(1-\alpha)D^{o}_{12}\right]\left(1 + c\,\frac{d\ln\gamma_{\pm}}{dc}\right)$$

... Eqn. 6.1.18

where D^{o}_{12} represents the diffusion coefficient of an isolated ion-pair at infinite dilution and is defined as

$$D^{o}_{12} = kTu^{o}_{12}$$

6.2 METHODS FOR MEASURING DIFFUSION COEFFICIENTS

Numerous methods have been described for the measurement of diffusion coefficients of electrolytes e.g. diaphragm cell method, radioactive tracer techniques, conductance and optical methods.

The diaphragm cell method only gives relative results, conductance methods are unsuitable owing to the instability of solutions of hydrogen chloride in acetone, for in this method a single run takes up to seven days. Optical methods would not be adequate since dilute solutions were to be studied and refractive indices would not change sufficiently from solution to solution. A radioactive tracer method therefore appeared to be the only method applicable.

Three radioactive tracer methods have been reported:

(a) Jehle[72] allowed active material to diffuse vertically from one tube into another tube across an originally sharp boundary. He measured concentration changes with time at a known distance from the original boundary. A screened collimated counter was used and a diffusion coefficient calculated from the data obtained.

This method involves difficulties in operation due to the necessity of eliminating convection in the tube and vibration of the apparatus.

According to Wang and Kennedy[73], this method does not produce results accurate to better than 1%.

(b) A porous diaphragm cell method incorporating radioactive materials[74]. Here the cell has to be calibrated with material with known diffusion coefficient and is therefore only a relative method.

(c) A capillary tube method developed by Anderson and Saddington[75] and modified by Wang[76]. A tube of small diameter and sealed at one end, filled with a solution of active material is immersed in a large bulk of inactive solution of the same electrolyte concentration as the active solution to ensure that diffusion does not affect the originally established concentration gradient of active to inactive material.

The activity of the solution in the capillary tube is determined before and after diffusion has taken place and the diffusion coefficient calculated[77].

The equation

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} \qquad \ldots \text{ Eqn. } 6.2.1$$

may be solved as follows:

Put the concentration $c = F(x)f(t)$.

Then

$$\frac{\partial c}{\partial t} = F(x)\frac{d}{dt}f(t)$$

$$\frac{\partial^2 c}{\partial x^2} = f(t)\frac{d^2}{dx^2}F(x)$$

Equation 6.2.1 then becomes:

$$\frac{1}{D\,f(t)}\cdot\frac{d}{dt}f(t) = \frac{1}{F(x)}\frac{d^2}{dx^2}F(x) \qquad \ldots \text{ Eqn. } 6.2.2$$

Now both sides are respectively functions of t and x only and the equation can only be satisfied if each side is separately equal to the same constant $-k^2$

$$\text{i.e. } \frac{d}{dt}f(t) = -k^2Df(t) \qquad \ldots \text{ Eqn. } 6.2.3$$

$$\frac{d^2}{dx^2}F(x) = -k^2F(x) \qquad \ldots \text{ Eqn. } 6.2.4$$

A physically permissible solution is

$$c = be^{-k^2Dt}\cdot F(x)$$

where $F(x)$ is a solution of equation 6.2.4 and b and k are constants.

In the capillary tube method, boundary conditions for a tube closed at $x = 0$ and open at $x = a$ are:

at $t = 0$, $c = c_o$ for $0 < x < a$; $c = 0$ for $x > a$

at $t > 0$, $c = 0$ at $x = a$ and $\dfrac{\partial c}{\partial x} = 0$ at $x = 0$.

These conditions can be satisfied only if $k = \dfrac{2n + 1}{2a} . \pi$ where $n = 0, 1, 2 \ldots$. since $F(x)$ must be a sine or cosine function.

The solution is therefore:

$$c = \sum_{n=0}^{n=\infty} B_n e^{-\left[\pi^2(2n + 1)^2 Dt/4a^2\right]} . \cos \frac{\pi(2n + 1)x}{2a}$$

... Eqn. 6.2.5

The coefficients B_n are given by the Fourier analysis.

$$B_n = (-1)^n 4c_o/\pi(2n + 1)$$

... Eqn. 6.2.6

$$\therefore \frac{c}{c_o} = \sum_{n=0}^{n=\infty} (-1)^n \frac{4}{\pi(2n + 1)} . e^{-\pi^2(2n + 1)^2 Dt/4a^2} . \cos \frac{\pi(2n + 1)x}{2a}$$

... Eqn. 6.2.7

The average concentration in the tube at time t is:

$$c_{av} = \frac{1}{a}\int_0^a c\,dx$$

... Eqn. 6.2.8

whence

$$\frac{c_{av}}{c_o} = \sum_{n=0}^{n=\infty} \frac{8}{\pi^2(2n + 1)^2} . e^{-\pi^2(2n + 1)^2 Dt/4a^2}$$

... Eqn. 6.2.9

6.3 APPARATUS

Diffusion tubes and cells

The diffusion tubes were constructed following a method developed by Davies[78]. The tubes were about 2cm. long with an internal diameter of about 0.05 cm. They were fused at one end to give a flat inner base and with a B7 ground cone sealed on to the base end of each tube. The open ends were ground to cones of approximately 30 degrees to ensure a smooth flow of bulk solution over these ends when filling the diffusion cell. The tubes were calibrated using a traveling microscope for measuring their internal lengths and mercury for volume determinations.

The cell construction is depicted in figs. 22 and 23. Prior to each run the capillary tubes were mounted in the B7 ground sockets on the stem which also served as a stirrer. The coil served to ensure an even inflow of inactive solution. Since it was not possible to assemble the diffusion train in the open atmosphere a blow-over vessel, B, had to be incorporated as a storage vessel for inactive solution.

6.4 THE PREPARATION OF SOLUTIONS OF ACTIVE HYDROGEN CHLORIDE IN ACETONE

(a) Apparatus

The hydrogen chloride gas generator used for the

Fig.22 THE DIFFUSION CELL AND CAPILLARIES

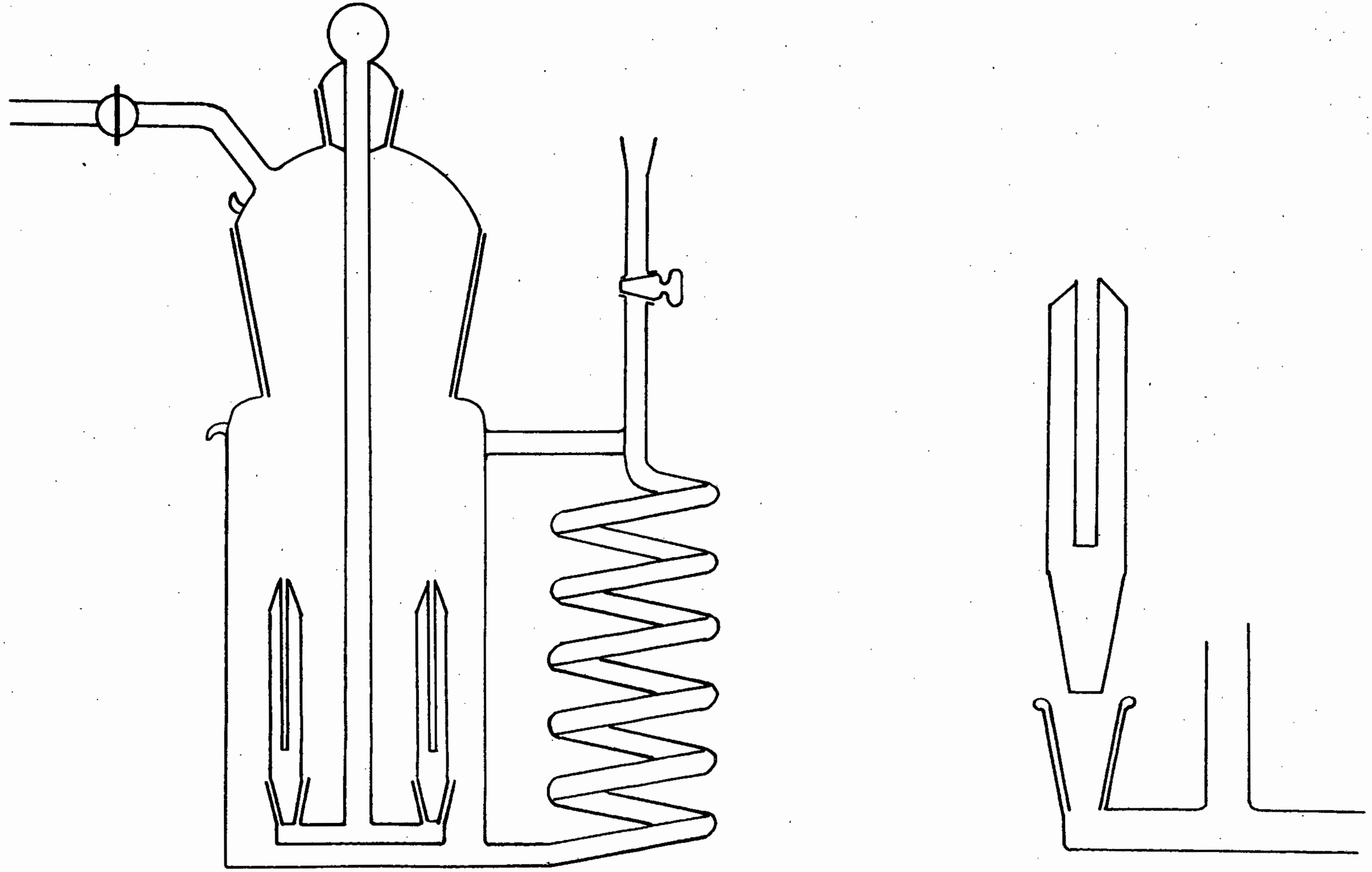
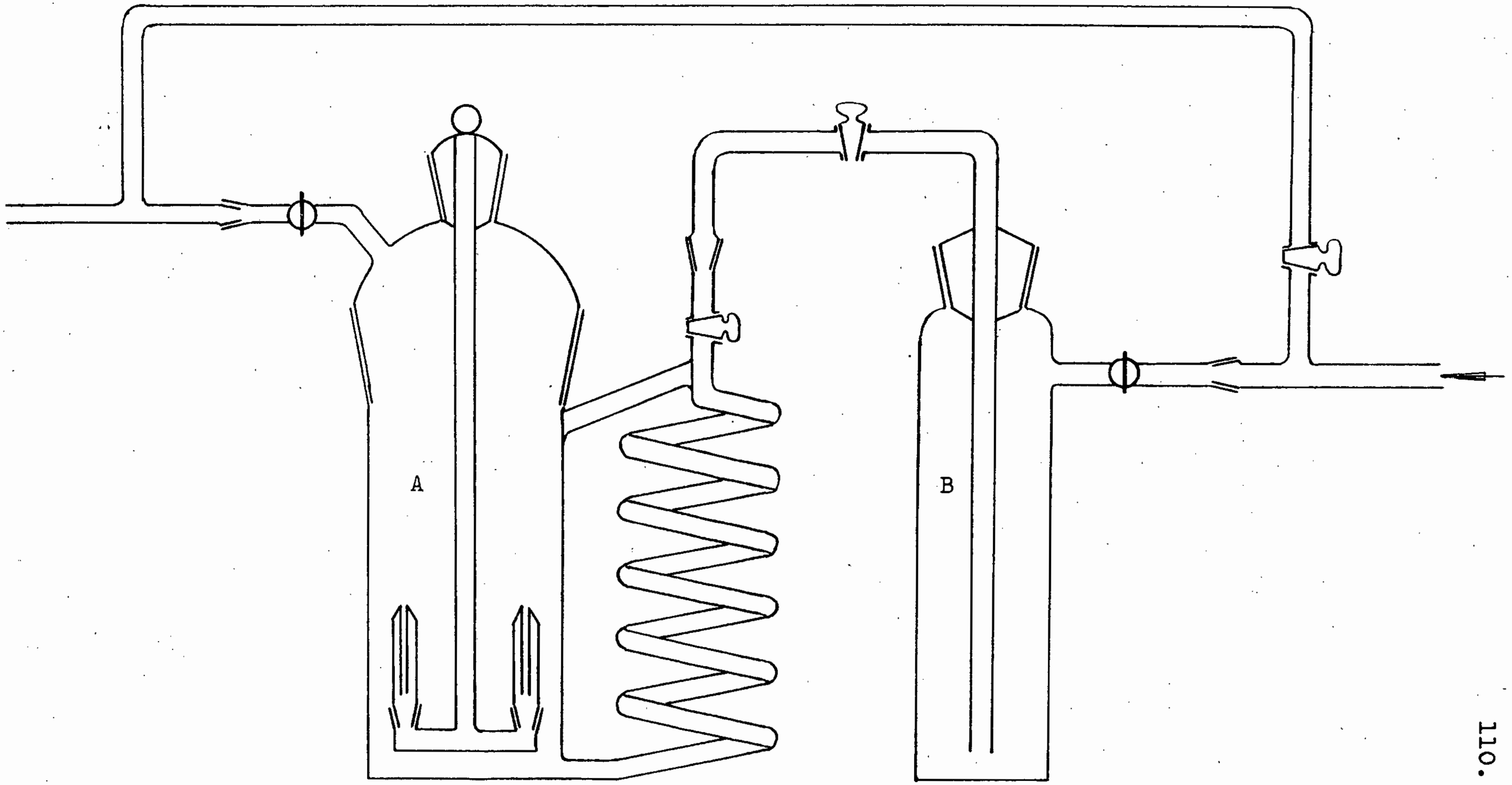


Fig. 23 THE DIFFUSION TRAIN



preparation of the active gas was exactly similar to the generator described in section III page 36 except that it was scaled down to about $\frac{1}{4}$ the original size since only small quantities of active hydrochloric acid solutions were available.

(b) Preparation and Analysis of Solutions

For the preparation of active hydrogen chloride gas, 2 ml. of 2N hydrochloric acid containing 50μc chlorine-36 were mixed with about 5 ml analar concentrated hydrochloric acid. This was allowed to pass through a capillary tube into analar concentrated sulphuric acid, generating the the active gas.

Active solutions of hydrogen chloride in acetone were prepared and analysed similarly to the inactive solutions (section III p. 36) used in the conductance and other studies.

(c) Storage of solutions of active hydrogen chloride in acetone

Since only small quantities of active hydrochloric acid were available for the preparation of the active solutions, series of solutions had to be prepared from a saturated stock solution and had to be stored. Now solutions of hydrogen chloride in acetone are unstable and attempts were made to slow down the reaction by cooling the solutions considerably.

Experiments were performed on inactive solutions by cooling them to -80°C. At various time intervals ranging over about 10 days ultra violet absorption spectra of these inactive solutions were taken and over this period no change in the molar extinction coefficient could be observed in the region of 2310Å where mesityl oxide, one of the products of the reaction, has a very intense absorption.

It could therefore be assumed that at a temperature of -80°C the self-condensation of acetone catalysed by hydrogen chloride virtually ceases. Hence all active solutions were sealed in pyrex glass tubes and kept at -80°C and all diffusion measurements on these solutions were done within 10 days of preparation.

6.5 EXPERIMENTAL PROCEDURE

(a) The filling of the tubes

The diffusion tubes were thoroughly cleaned with chromic acid, rinsed with distilled water, followed by washings with analar acetone and then dried.

The tubes were filled using a 1.0 ml. hypodermic syringe with a stainless steel needle bent in the shape of a shallow u[78]. In order to avoid the formation of bubbles inside the tubes, the needle was lowered to the bottom and the active liquid slowly injected with the slow lifting of the needle such that the liquid level was always above the tip of the needle. The diffusion tubes were filled in all cases with an excess of solution on top of the tubes.

(b) Starting the run

All solutions in acetone were handled inside the dry-box. Having filled the capillary tubes, they were placed in the cups on the cup holder which in turn was fitted in the diffusion cell containing sufficient inactive solution, of the same hydrogen chloride concentration as the active solution, to cover about two-thirds of the length of the capillary tubes. The blow-over vessel, B, (fig. 23) was filled with inactive solution. Having closed all stopcocks, the complete train was removed to a thermostat at $25^{\circ} \pm 0.01^{\circ}C$ and quickly assembled. When the complete apparatus and liquid reached temperature equilibrium, inactive solution was very carefully blown over with dry nitrogen, from B, through the coil into the complete cell and the exact time taken when inactive solution just covered the diffusion tubes. The final level of the inactive solution was about 1 to 2 cm. above the diffusion tubes.

Diffusion was allowed to proceed for about ten hours when the bulk solution was blown back to B and the exact time taken when the diffusion tubes just appeared above the level of the inactive solution.

(c) Emptying the capillary tubes

On completion of the run the hypodermic syringe was filled with distilled water. The capillaries were then removed from the diffusion cell and flushed out thoroughly with water into volumetric flasks which in turn were filled up to the mark with distilled water and the activity of these solutions determined.

The efficiency of washing out the capillary tubes was checked by collecting further washings and determining the activity of those washings.

(d) The determination of the initial activity c_o

In order to determine the initial activity, c_o, of the solutions in the capillary tubes, the exact procedure for a normal diffusion run was repeated up to the point just before blowing over the inactive solution from the storage vessel, B, to the diffusion cell, A. The capillaries were then emptied into volumetric flasks as above (c) and the activities, c_o, determined.

6.6 CALCULATION OF THE DIFFUSION COEFFICIENT

The equation[77]

$$\frac{c_{av}}{c_o} = \sum_{n=0}^{n=\infty} \frac{8}{\pi^2} \frac{1}{(2n+1)^2} . e^{-\pi^2(2n+1)^2 Dt/4a^2}$$

may be rewritten as

$$\frac{c_{av}}{c_o} = \gamma = \frac{8}{\pi^2} \left(\frac{e^{-\theta}}{1} + \frac{e^{-9\theta}}{9} + \frac{e^{-25\theta}}{25} + \frac{e^{-49\theta}}{49} + \ldots \right)$$

... Eqn. 6.6.1

where

$$\theta = \pi^2 Dt/4a^2$$

$$\therefore \gamma = \frac{8}{\pi^2} e^{-\theta} \left(1 + \frac{e^{-8\theta}}{9} + \frac{e^{-24\theta}}{25} + \ldots\right)$$

$$= \frac{8}{\pi^2} e^{-\theta} . F$$

... Eqn. 6.6.2

Taking logs:

$$\log \gamma = \log \frac{8}{\pi^2} - \pi^2 Dt/4a^2 \; . \; \log e + \log F$$

... Eqn. 6.6.3

and

$$D = \frac{4a^2}{\pi^2 t \log e} \left(\log \frac{8}{\pi^2} - \log \quad + \log F\right)$$

... Eqn. 6.6.4

For a given temperature D is constant and so is a for a given tube. The only variable in θ is therefore t. By choosing suitable values of θ a plot of F against θ was constructed.

The ratio $\frac{c_{av}}{c_o} = \gamma$ was then calculated for various values of F according to equation 6.6.2. A plot of F against γ was made and hence equation 6.6.4 was solved for D.

6.7 EXPERIMENTAL RESULTS

6.7.1 ULTRA VIOLET ABSORPTION MEASUREMENTS ON SOLUTIONS OF HYDROGEN CHLORIDE IN ACETONE AT -80°C

These measurements were done at 2310Å on a solution of 0.65M hydrogen chloride in acetone, which was a much higher acid concentration than the highest used in the diffusion runs. The total mesityl oxide concentration after 250 hours was about 5×10^{-8} moles per litre. The results of these measurements are summarised in table 6.7.1 and mesityl oxide concentrations calculated for the final measurement using a molar extinction coefficient of 1.2×10^{4} for mesityl oxide at 2310Å.

TABLE 6.7.1

HYDROGEN CHLORIDE CONCENTRATION 0.65M

Time	Absorbance corr. for equal wts. of soln. Sample		Mesityl Oxide concentration moles litre^{-1} Sample	
Hours	1	2	1	2
0	0.7011	0.7000		
20.10	0.6671	0.6761		
44.30	0.7039	0.7190		
68.20	0.7211	0.7204		

Time	Absorbance corr. for equal wts. of soln. Sample		Mesityl Oxide concentration moles $litre^{-1}$ Sample	
Hours	1	2	1	2
102.45	0.7273	0.7186		
150.20	0.7900	0.7359		
200.30	0.7457	0.7436		
250.60	0.7661	0.7521	5×10^{-8}	4.2×10^{-8}

6.7.2 The diffusion coefficients

All diffusion results are summarised in table 6.7.2.(p.118) The calibration values for the capillary tubes and calculated values for F and γ for various values of θ are given in appendix 5.

A plot of diffusion coefficient against the square root of the concentration is given in fig. 24.

6.8 DISCUSSION

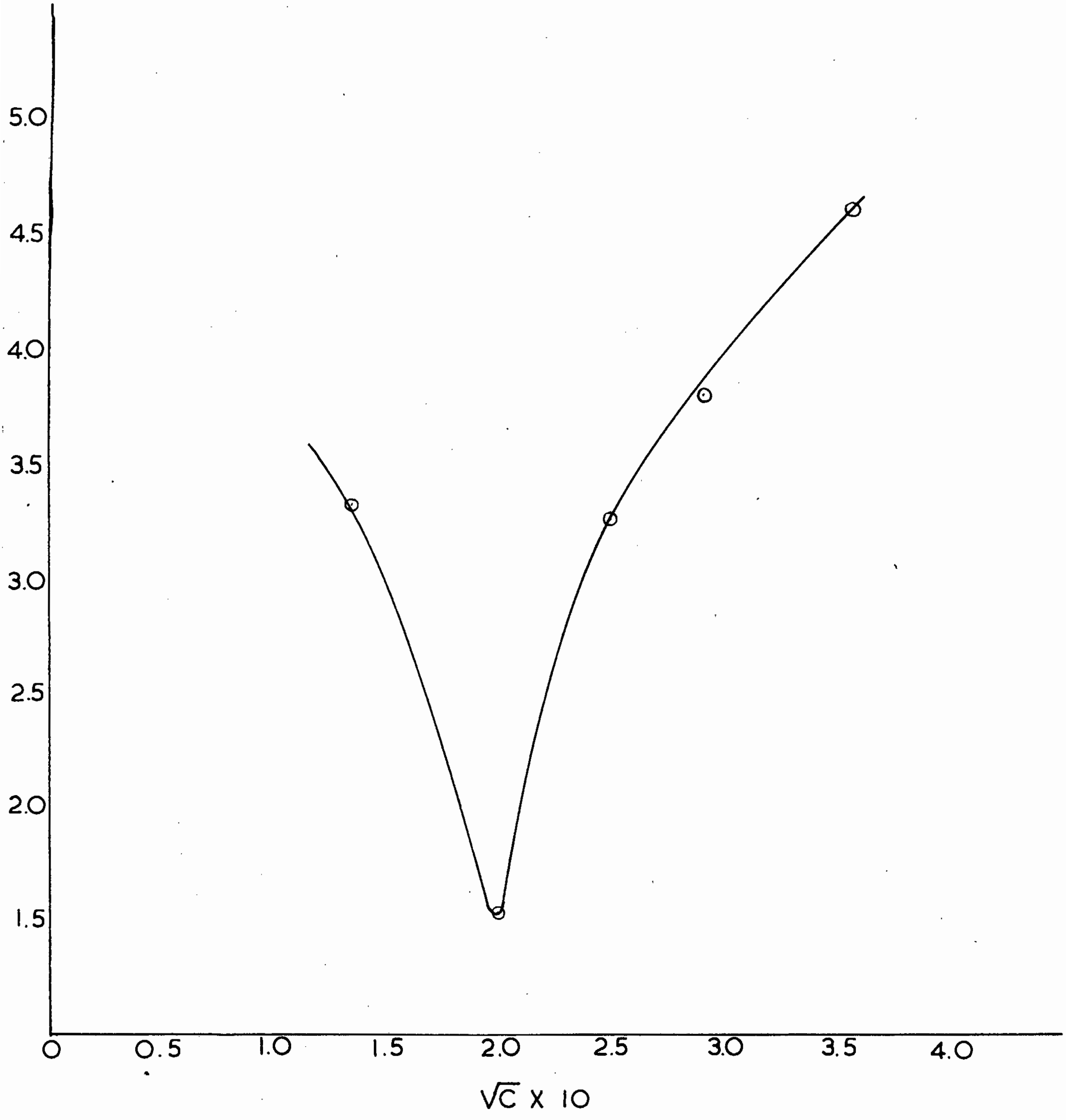
The curve of D against $\sqrt{c}$ is similar in form to the corresponding plot for sodium chloride in aqueous solutions[79], but the minimum is much more pronounced in the present case. Extrapolation to infinite dilution is unreliable since only two values of D could be obtained at low concentrations, but gives a D^{o} value of

TABLE 6.7.2

RESULTS OF DIFFUSION COEFFICIENT MEASUREMENTS

Hydrogen Chloride Conc. mole litre^{-1}		Time of Run Seconds	Initial Conc. c_o Corr. C.p.m.		Final Conc. c_{av} Corr. C.p.m.		Ratio $c_{av}/c_o = \gamma$		$10^5 D$ cm^2 sec^{-1}		$10^5 D$ cm^2 sec^{-1}
Active Solutions	Inactive Solutions		Tube I	Tube II	Tube I	Tube II	Tube I	Tube II	I	II	Average
0.0171	0.0178	36115	31.5	39.7	18.3	15.6	0.5809	0.3929	1.527	3.339	3.340
0.0410	0.0396	36105	83.4	97.1	45.0	55.4	0.5395	0.5706	-	1.649	1.649
0.0635	0.0620	36060	141.4	136.9	55.4	54.6	0.3918	0.3988	3.262	3.275	3.268
0.0833	0.0835	36150	277.7	258.9	95.9	92.2	0.3453	0.3561	3.818	3.789	3.803
0.1296	0.1255	36120	449.8	457.0	97.0	133.1	0.2160	0.2954	5.903	4.637	4.637

Fig. 24 HYDROGEN CHLORIDE IN ACETONE
VARIATON OF DIFFUSION COEFFICIENT WITH $\sqrt{C}$



about $5 \times 10^{-5} cm^2 sec^{-1}$. Calculation of D^o from the Nernst relation[68] (equation 6.1.8 page 101), using approximate limiting equivalent conductances of the ions, gives a value of $4.63 \times 10^{-5} cm^2 sec^{-1}$.

The very pronounced minimum in the plot of D against $\sqrt{c}$ possibly indicates a change in the degree of association of the hydrogen chloride molecules.

Attempts were made to calculate the theoretical curve using equation 6.1.18 for associated electrolytes. Arbitrary assumptions had to be made as to the ion size parameter $\overset{o}{a}$ and D^o_{12}, the diffusion coefficient at infinite dilution of an ion pair.

The diffusion coefficient at infinite dilution of an ion pair, D^o_{12} is given by the relation[71]:

$$D^o_{12} = kTu^o_{12}$$

and[80]

$$D = \frac{kT}{\varepsilon} \cdot \left(\frac{2u^o_+ u^o_-}{u^o_+ + u^o_-}\right)$$

Using values for u^o_+ and u^o_- the mobilities of the proton and the chloride ion in acetone solutions calculated from approximate transport numbers and assuming these to be the diffusing entities, an estimate was made of the value of u^o_{12}. Calculation of D^o_{12} gave a value of $3.1 \times 10^{-5} cm^2 sec^{-1}$.

Substituting the values $4.63 \times 10^{-5} cm^2 sec^{-1}$ for D^o and $3.1 \times 10^{-5} cm^2 sec^{-1}$ for D^o_{12} in equation 6.1.18 and using an ion size parameter $\overset{o}{a} = 6.5$, produced extremely high and nearly constant values for the calculated diffusion coefficient over the entire concentration range studied. This could be partially due to the fact that the term

$$\alpha(D^o + \Delta_1 + \Delta_2)$$

in equation 6.1.18, is extremely small as compared to D^o_{12}.

When diffusion coefficients for sodium chloride[79] in aqueous solutions were calculated using equation 6.1.16 (p.103), the theoretical curve fitted the experimental only over the very low concentration region. In the case of calcium chloride corrections had to be made for solvent transport, and although the shape of the calculated curve is similar to the experimental, the fit is highly unsatisfactory.

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SECTION VII

CONCLUSION AND PROPOSED FURTHER WORK

This work was undertaken in an attempt to improve our knowledge of the behaviour of acids in acetone solution and to this end the two acids, hydrogen chloride and perchloric acid, were studied. The first acid was chosen because of contradictory results of previous investigators; the latter because it has never before been studied in pure acetone solutions. Perchloric acid was also said to be the only strong acid in acetone solutions.

The stability studies of pure acetone and solutions of hydrogen chloride in acetone, proved their value in that they indicated that anhydrous acetone is very stable if sufficient care is taken in storing and that solutions of weak acids in acetone are sufficiently stable for short term studies on a particular solution.

No evidence could be found for the actual degree of association of hydrogen chloride in acetone solutions, but the change of slope in the Fuoss-Shedlovsky plots and the very pronounced minimum in the diffusion coefficient plot, possibly indicates that association takes place.

Remarkable agreement was obtained between the present e.m.f. results and that of Everett and Rasmussen which is strong evidence that metal-metal halide electrodes can be used satisfactorily in acetone solutions.

The following is a list of proposed further work.

(a) Redetermination of the conductance of solutions of hydrogen chloride by an improved potentiometric method in order to establish conductances at very low concentrations.

(b) Redetermination of the conductance of solutions of anhydrous perchloric acid in acetone by a potentiometric method using bright platinum electrodes, as it is possible that platinised electrodes might affect the conductance of a strong oxidising agent such as perchloric acid in acetone solutions. Re-establishment of the limiting equivalent conductance of perchloric acid together with measurements of conductances of solutions of sodium perchlorate and sodium chloride in acetone will enable the calculation of the limiting equivalent conductance of hydrogen chloride in acetone solutions.

(c) Measurement of transport numbers at very low concentrations in acetone solutions, by a moving boundary method to enable the calculation of ion conductances.

(d) Re-determination of the diffusion coefficient of solutions of hydrogen chloride in acetone.

(e) The self-diffusion coefficient of anhydrous acetone and of solutions of perchloric acid and a perchlorate in acetone.

(f) Re-investigation and extention of the kinetics of the acid catalysed self-condensation of acetone.

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APPENDIX I

APPARATUS

(a) The Oscillator

A R-C oscillator designed and built by the late Mr. Charles Gingold, B.Sc. (Elect. Eng.) was used. This instrument employs a bridged double "T" R-C network which provides positive feedback at the frequency desired. This network gives a large phase change at other frequencies, ensuring stable frequency of oscillation and the magnitude of the feedback is adjusted to obtain a good sinusiodal wave form. A push-pull power amplifier is incorporated and fixed frequencies of 240, 480, 1000 c/sec. were provided. These frequencies were measured by comparisson with a calibrated oscillator.

A circuit diagram is given on page 129.

(b) The Tuned Detector

An R-C network identical to that of the oscillator is employed here, but the positive feedback is adjusted to a point below oscillation to obtain adequate selectivity. Fine tuning to match the frequency of the oscillator is provided by an additional trimming condenser across the bridge. The amplifier drives the Y-plates of a cathode ray tube which serves as a balance indicator. The X-plates are driven from the oscillator through a phase shift amplifier to obtain the required pattern on the cathode ray tube screen.

This instrument was also designed and constructed by Mr. Gingold and a circuit diagram is given on page 130.

(c) The Jones-type Bridge

The circuit used was similar to that described by Bender, Bierman and Winger[81], but a few modifications were incorporated. A circuit diagram is given on page 131.

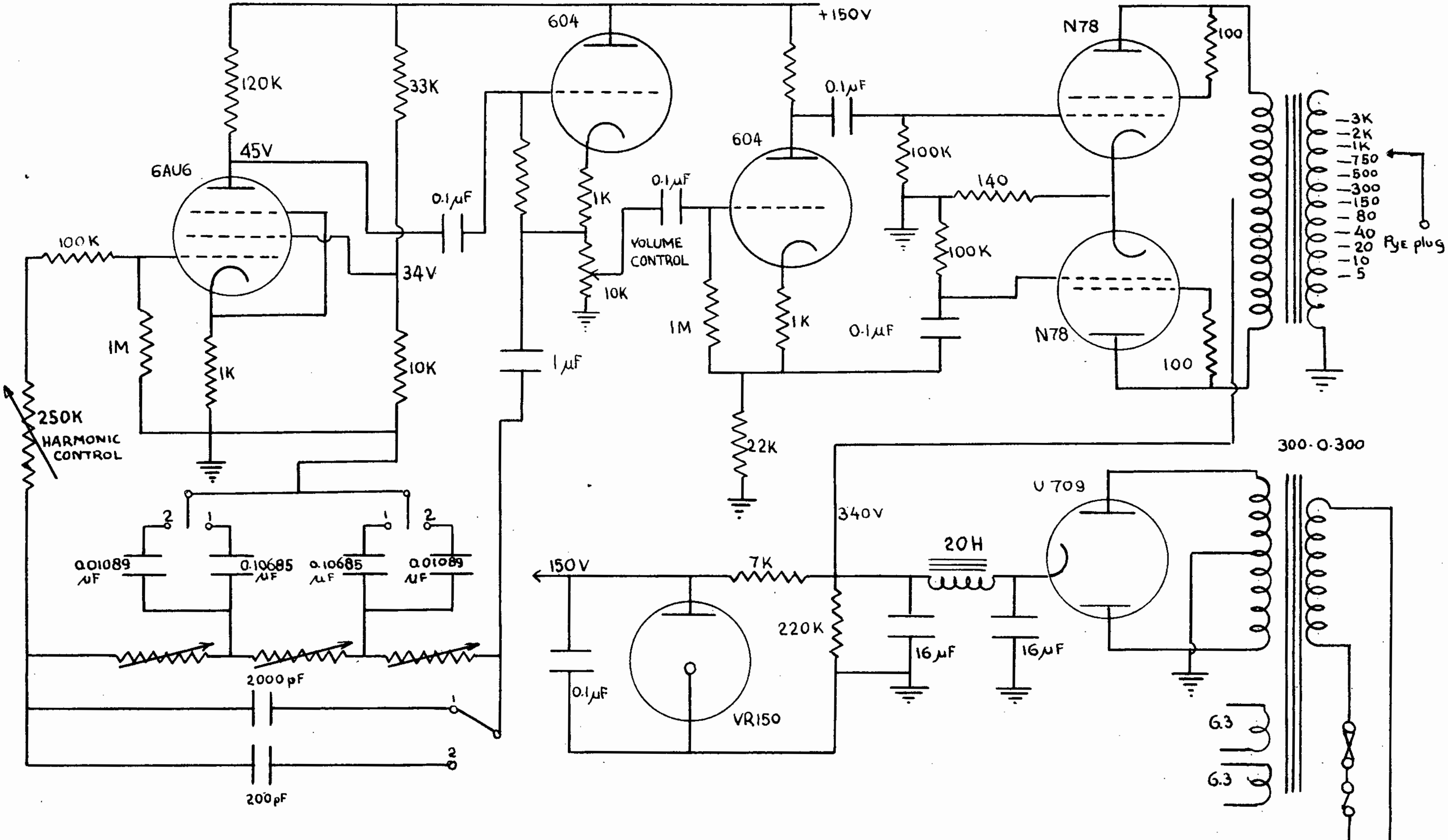
The measuring arm MA consisted of a series of Muirhead type A5 decade resistance units, covering a range from one ohm to one megohm and an A2A 1.2 ohm slide wire. Every setting of these units was calibrated using NPL-certified Muirhead D333 ceramic encased resistors, which were subsequently mounted on Muirhead type B704-B/4 switches and built in as the ratio arms. These ratio arms, RA, permitted a choice of ratios between 1000 : 1 and 1 : 10000 in tenfold steps and different combinations for greater sensitivity.

The Wagner earth, W, was made up of two banks of stable wire wound resistances joined by a 50 ohm 10 watt potentiometer; for satisfactory balancing of the earthing system it was found necessary to connect an 800pF variable air condenser, C_1, from each bank of resistances to earth.

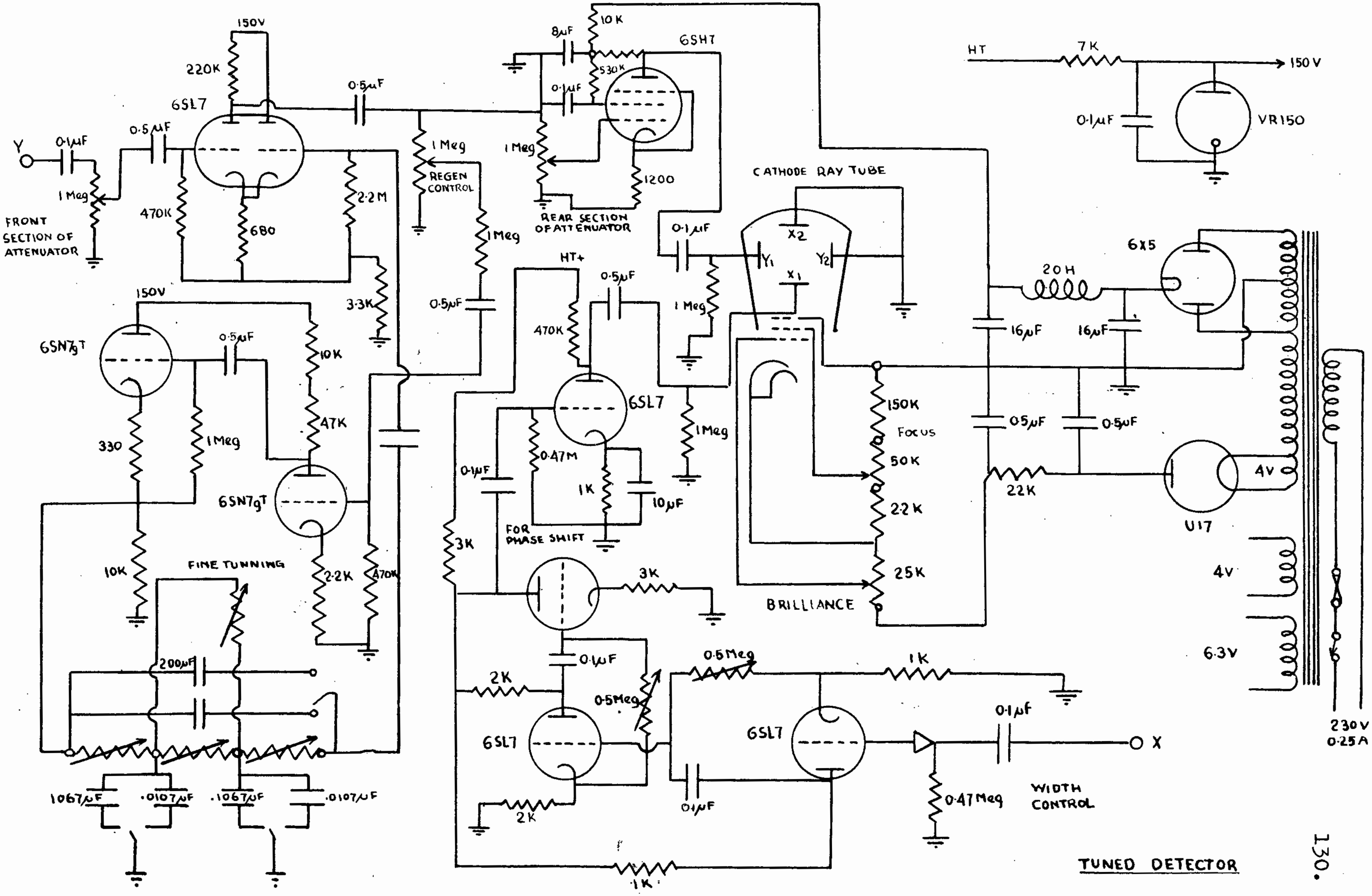
A bank of variable air and fixed mica condensers, C_2, having a range of 0-2200pF, was connected in parallel with the measuring arm to balance the capacity of the cell. When the bridge was used with solutions of very high resistance, it was found that the capacity of the measuring arm was greater than that of the cell; accordingly a 120pF mica condenser, C_3, was arranged in parallel with the cell and switched in when required.

Both the input from the oscillator and output to the detector were transformer coupled to the bridge, the input transformer having tappings which permitted a variation of input voltage.

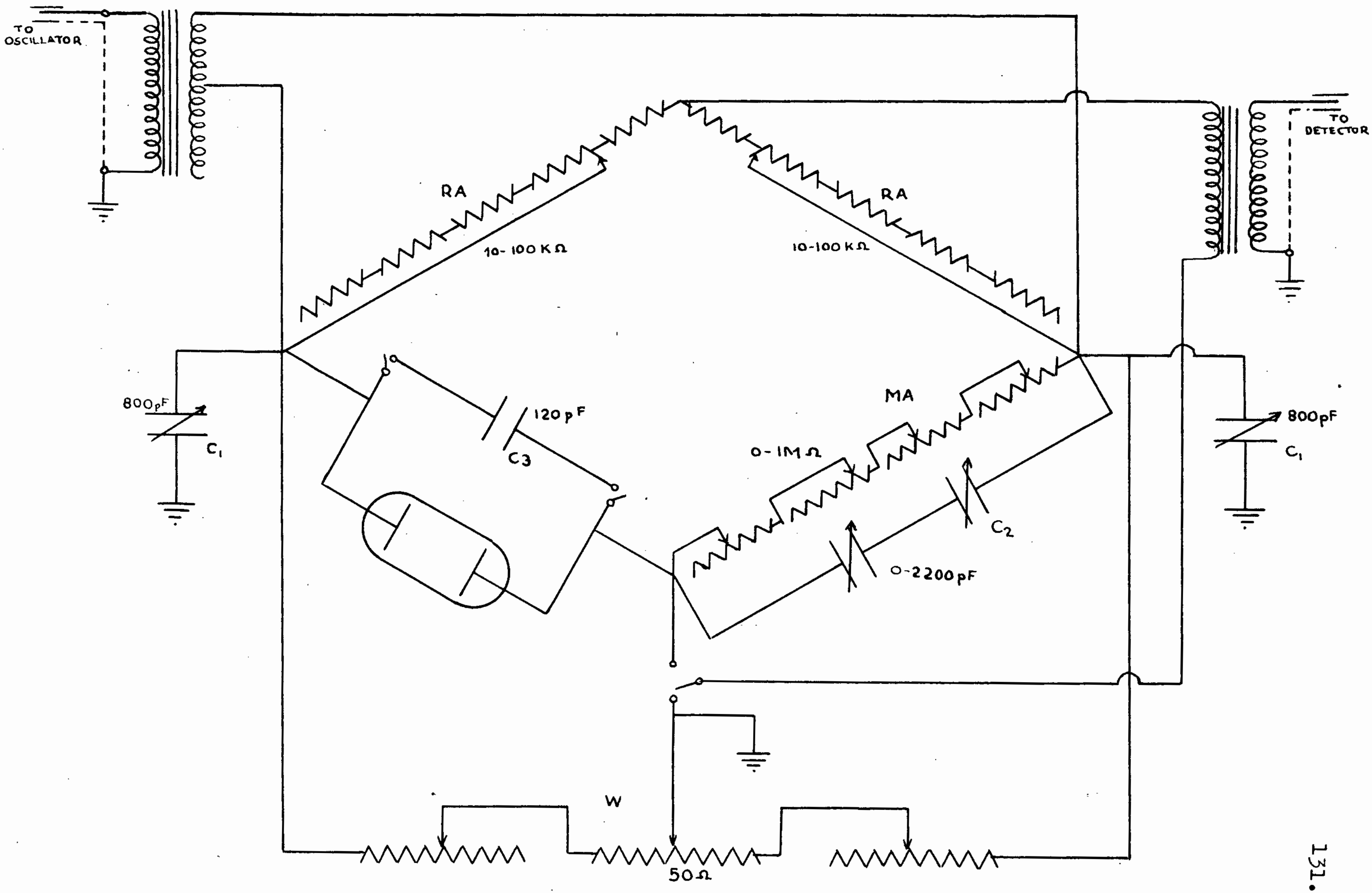
The measuring arm, ratio arms, Wagner earth system, balancing capacitances and transformers were each encased in an earthed screen, and the cell leads were carefully shielded and let out through the bridge casing directly into the air thermostat. Lengths of internal wires were kept as short as possible and shielded only where necessary to avoid large internal earth capacitances. The bridge was connected to the oscillator and detector through short leads of heavy coaxial cable.



OSCILLATOR CIRCUIT DIAGRAM



TUNED DETECTOR



CIRCUIT DIAGRAM OF JONES BRIDGE

APPENDIX 2

THE CONDUCTANCE OF SOLUTIONS OF HYDROGEN CHLORIDE IN ACETONE - FUOSS PLOT

Concentration μmole litre^{-1}	Λ ohm^{-1} cm^{2}	F(z)	$f_{\pm}^{2}$	$\frac{10^{2}F(z)}{\Lambda}$	$\frac{10^{3}c\Lambda f_{\pm}^{2}}{F(z)}$
2.280	160.75	0.99813	0.9968	0.621	0.366
6.770	102.40	0.99742	0.9956	0.974	0.692
13.54	54.18	0.99735	0.9954	1.841	0.732
27.14	31.01	0.99716	0.9951	3.216	0.840
67.7	13.36	0.99706	0.9949	7.463	0.902
135.4	10.62	0.99629	0.9936	9.381	1.435
181.0	5.02	0.99705	0.9949	19.86	0.906
541.6	2.72	0.99624	0.9935	36.89	1.470

THE CONDUCTANCE OF SOLUTIONS OF HYDROGEN CHLORIDE IN ACETONE - IVES PLOT

Concentration μ mole litre^{-1}	Λ_{x}	y	x	$10^{3}\Lambda^{2}f_{\pm}^{2}$
2.280	208.06	161.26	123.58	25.713
6.770	222.32	103.10	46.86	10.419
13.54	222.23	54.90	13.12	2.916
27.14	222.13	31.79	4.30	0.955
67.7	222.96	14.16	0.79	0.177
135.4	222.18	11.71	0.53	0.117
181.0	222.12	5.80	0.11	0.025
541.6	221.92	3.75	0.03	0.007

THE CONDUCTANCE OF SOLUTIONS OF PERCHLORIC ACID IN ACETONE - FUOSS PLOT

Concentration μ mole litre^{-1}	Λ ohm^{-1} cm^{2}	F(z)	$f_{\pm}^{2}$	$\frac{10^{3}F(z)}{\Lambda}$	$\frac{10^{2}c\Lambda f_{\pm}^{2}}{F(z)}$
2.545	501.3	0.97279	0.9945	1.941	0.1304
6.992	497.2	0.95491	0.9908	1.920	0.3608
7.168	499.8	0.95397	0.9906	1.908	0.3720
12.80	493.0	0.93840	0.9877	1.904	0.6639
14.00	492.9	0.93547	0.9872	1.898	0.7283
21.26	485.3	0.92044	0.9845	1.897	1.104
27.21	491.7	0.90890	0.9826	1.848	1.480
42.84	478.5	0.88568	0.9786	1.850	2.266
43.37	479.8	0.88483	0.9786	1.844	2.301
43.69	481.4	0.88419	0.9786	1.837	2.382
72.42	469.8	0.84963	0.9731	1.808	3.895
115.6	463.7	0.80699	0.9674	1.740	6.472

APENDIX 3

THE SELF-CONDENSATION OF ACETONE

Typical data for the variation of absorbance with time

At 20°C		At 30°C		At 40°C	
Time Hours	Corrected Absorbance	Time Hours	Corrected Absorbance	Time Hours	Corrected Absorbance
42	6.75	10	1.30	21.5	5.36
61	9.75	23	2.08	27	6.32
66	10.90	30	2.41	32.5	7.40
97	16.35	52	3.57	45.5	10.15
109	19.80	57	3.85	56.8	12.05
121	22.20	90	5.40	72.0	14.83
157	29.00	130	7.52		
182	33.00				
HCl conc : 2.967×10^{-1}		HCl conc : 4.280×10^{-2}		HCl conc : 8.710×10^{-2}	

THE DEHYDRATION OF DIACETONE ALCOHOL

Typical data for the variation of absorbance with time

At 19°C		At 32°C		At 38°C	
Time Mins.	Corrected Absorbance	Time Mins.	Corrected Absorbance	Time Mins.	Corrected Absorbance
15.0	0.35	20.0	0.21	10.0	0.23
25.0	0.46	30.0	0.26	20.0	0.31
30.0	0.53	40.0	0.30	30.0	0.39
41.0	0.67	50.0	0.35	40.0	0.47
45.0	0.73	60.0	0.40	50.0	0.55
55.0	0.85			60.0	0.63
64.0	1.00				
HCl conc : 5.187×10^{-3}		HCl conc : 1.294×10^{-3}		HCl conc : 1.962×10^{-3}	

APPENDIX 4

CALCULATION OF E' IN THE EQUATION

$$E' = E + 2k \log \alpha m - 2k'A\sqrt{\alpha m} = E^{o} - 2k'Cm$$

(a) Calculation of α, the degree of dissociation

Run No	Concentration molality x 10^3	Λ_m ohm^{-1} cm^2	$10\sqrt{\Lambda_m m}$	$10^3 z$	F(z)	$10^3\alpha$
1	5.00	2.40	1.095	8.3036	0.99167	4.840
2	20.00	0.73	1.208	9.1605	0.99080	1.474
3	50.00	0.60	1.732	13.1341	0.98678	1.216
4	75.00	0.61	2.139	16.2205	0.98365	1.240
5	100.00	0.65	2.550	19.3372	0.98408	1.326
6	170.00	0.74	3.536	26.8142	0.97282	1.521
7	210.00	0.84	4.200	31.8494	0.96762	1.736

(b) Calculation of E'

Run No	$2k \log \alpha m$	$2k'A\sqrt{\alpha m}$ x 10^3	E Measured	E'
1	-0.54617	0.9175	0.1040	-0.4431
2	-0.53603	1.0127	0.0470	-0.4900
3	-0.49880	1.4544	0.0098	-0.4895
4	-0.47699	1.7989	-0.0060	-0.4848
5	-0.45877	2.1488	-0.0178	-0.4787
6	-0.42499	2.9845	-0.0274	-0.4553
7	-0.40680	3.5627	-0.0286	-0.4390

$k = \dfrac{2.303RT}{F}$; $k' = \dfrac{RT}{F}$

$A = 3.6308$

APPENDIX 5

(a) Calibration of the Capillary Tubes

Tube	Internal Length cm.	Internal volume ml.
I	2.0450	0.0183
II	2.0050	0.0166

(b) Calculated values of F and γ

θ	F	γ
0	1.1715	0.9499
0.2	1.02275	0.6789
0.3	1.01011	0.6067
0.4	1.00453	0.5459
0.5	1.0020	0.4927
0.7	1.0004	0.4028
0.9	1.00008	0.3299
1.0	1.00004	0.2983
1.1	1.00002	0.2699
1.2	1.00000	0.2442
1.4	1.00000	0.1992

APPENDIX 6

DIFFUSION STUDIES OF SOLUTIONS OF HYDROGEN CHLORIDE IN ACETONE

CALCULATION OF THE THEORETICAL CURVE

Concentration molality x 10^2	$10^3\alpha$	$\gamma_\pm$	$\left(1 + c\frac{d\ln\gamma_\pm}{dc}\right)$	$10^7\Delta_1$	$10^7\Delta_2$	$10^5 D_{calc.}$ $cm^2 sec^{-1}$	$10^5 D_{obs.}$ $cm^2 sec^{-1}$
1.5	1.715	0.9585	0.9906	-0.685	0.920	5.475	3.45
2.0	1.474	0.9557	0.9875	-0.798	1.066	5.461	2.88
4.0	1.214	0.9434	0.9750	-0.988	1.516	5.391	1.66
6.0	1.197	0.9315	0.9625	-1.210	1.819	5.321	3.13
8.0	1.220	0.9206	0.9500	-1.417	2.076	5.252	3.70
10.0	1.285	0.9097	0.9375	-1.636	2.492	5.182	4.10
12.0	1.391	0.8976	0.9250	-1.876	2.986	5.113	4.46
13.0	1.475	0.8906	0.9188	-2.018	3.311	5.079	4.63

APPENDIX 7

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