ELECTROCHEMICAL STUDIES IN AQUEOUS AND ACETONE SOLUTIONS

with special reference to

salts of Hydrazine and

Dimethylketazine.

A thesis submitted to the

University of Cape Town for the

degree of Doctor of Philosophy

by

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PREFACE.

I would like to express my warmest thanks to Dr. A.H. Spong, Senior Lecturer in Physical Chemistry at the University of Cape Town, whose guidance and encouragement so willingly offered at all times has been of great assistance and a source of confidence to me.

The late Mr. Charles Gingold, who designed and built the oscillator and detector, gave valuable advice during the construction of the conductance bridge.

It has been a pleasure to be associated with Professor R.W. Guelke, Professor of Electrical Engineering in the University of Cape Town and Messrs. F.P. Anderson and C.C. Stavropoulis of the Oceanographic Division of the National Physical Research Laboratory in the development of the potentiometric method for measuring electrolyte conductance.

I very much appreciate the helpfulness of Mr. W.C. Lewis, who made the intricate glassware used in this research, and Mr. G. Reid, whose workshop was always at my disposal.

I am grateful to the directors of African Explosives and Chemical Industries Ltd. for an A.E. and C.I. Research Studentship

held during part of this investigation, and to the University of Cape Town for grants from the Fourcade Bequest and the Staff Research Fund for the purchase of equipment.

SUMMARY.

The preparation by the late Professor W. Pugh and his collaborators of compounds assumed to be salts of dimethylketazine raised the problem of the existence of a dimethylketazinium ion, as the base had previously been thought too weak to form salts. Acetone is the only solvent in which dimethylketazine is known to be stable, and it seemed that the occurrence of the ion might be demonstrated by comparison of conductance measurements on solutions of a supposed ketazinium salt in this solvent with similar measurements on aqueous solutions of the corresponding hydrazinium salt. Attempts by earlier workers to prepare simple salts of dimethylketazine were unsuccessful, only complex salts being crystallisable, and, as a first step, the conductances of aqueous solutions of hydrazinium chloroplatinate, perchlorate, and picrate were measured on a conventional Jones-type bridge at 25°C.

The chloroplatinate ion was found to be reduced by hydrazine, and this process was followed conductimetrically, the order of reaction being determined. Since the reduction was catalysed by platinised platinum, the measurements were repeated using a new A.C. potentiometric method for the determination of electrolyte conductance which employs polished electrodes. This method, which had been developed by the Oceanographic Division of the National Physical Research Laboratory and the Department of Electrical Engineering of the

University of Cape Town, was first tested on solutions of potassium chloride, the measurements being shown to be independent of frequency and in reasonable agreement with the results of earlier workers (cf. Chem. and Ind., 1953, 732). The rates of decomposition of the hydrazinium salts obtained by this method were lower than those measured on the Jones bridge, while their equivalent conductances were found to be somewhat higher. New values for the limiting equivalent conductance of the hydrazinium ion, and a value for the limiting conductance of the chloroplatinate ion have been determined. [$N_2H_5^+$: potentiometer 60.0, Jones bridge 59.6; $\frac{1}{2}$ $PtCl_6^{2-}$: potentiometer 59.5, Jones bridge 59.4].

The solubility of dimethylketazinium chloroplatinate in anhydrous acetone was too low to allow the preparation of solutions of suitable concentration for conductance work. Since simple salts could not be crystallised, an attempt was made to prove the existence of the ketazinium ion by conductimetric titrations of dimethylketazine with hydrogen chloride and calculation of its limiting equivalent conductance from the neutralisation points. It was intended to compare this value with a value for the hydrazinium ion in acetone calculated from its limiting conductance in aqueous solution. No limiting conductance could be obtained by this procedure, but the titration curves showed that products ionic in character result from the interaction of the ketazine with hydrogen chloride, and the form of the curves is consistent with the view that dimethylketazine is a weak

monoacid base in acetone. This conclusion was confirmed by potentiometric titrations in the cell

$$\mathrm{Pt, chloranil} \left| \begin{matrix} \text{Dimethylketazine} \\ + \ x\ \mathrm{HCl} \end{matrix} \right\| \mathrm{LiCl} \left| \mathrm{Hg_2Cl_2, Hg,} \right.$$

from which it was possible to calculate that dimethylketazine has an ionisation constant in acetone of about 10^{-11}.

A knowledge of the behaviour of hydrogen chloride in acetone was necessary for the interpretation of the results of the titrations, and, since the results of previous workers were either not reproducible or not published in detail, the conductances of a series of such solutions were measured. Hydrogen chloride molecules were shown to be associated in this solvent, and over the concentration range 2.75×10^{-4} to 9.3×10^{-4} mole $l.^{-1}$ it was estimated that the associated groups contain about ten monomeric molecules. The electrodes used in the potentiometric titrations were also studied, the following cells being investigated:

$$\mathrm{Pt, H_2 \left| HCl \right\| LiCl \left| Hg_2Cl_2, Hg}$$

$$\mathrm{Pt, choranil \left| HCl \right\| LiCl \left| Hg_2Cl_2, Hg}$$

$$\mathrm{Hg, Hg_2Cl_2 \left| LiCl \right\| HCl \left| AgCl, Ag.}$$

The standard emf.'s of these cells were calculated by the procedure adopted by Everett and Rasmussen (1954) and the standard emf. of the cell $\mathrm{Pt, H_2 \left| HCl \right| AgCl, Ag}$ calculated to be -0.56 volts, in reasonable agreement with Everett and Rasmussen's value (-0.53 volts).

C O N T E N T S.

LIST OF ILLUSTRATIONS.

INTRODUCTION.

This investigation was undertaken in an attempt to demonstrate the existence of the dimethylketazinium ion in acetone solution by electrochemical methods. Since the only supposed dimethylketazinium salts which had been crystallised were salts of complex halogeno-acids, it seemed desirable to examine the electrochemical behaviour of the hydrazinium salt of at least one of these complex anions in aqueous solution.

As there was much conflicting evidence relating to the electrochemistry of solutions in acetone, conductance and potentiometric experiments were carried out on solutions of hydrogen chloride and other electrolytes in this solvent to facilitate interpretation of the results for dimethylketazine.

This thesis therefore opens with an outline of the history of complex salts of hydrazine and other azines, and an account of previous electrochemical studies in acetone solution.

Part II deals with measurements on aqueous solutions of hydrazinium chloroplatinate, perchlorate and picrate, and contains a description of a new A.C. potentiometric method for the determination of electrolyte conductance.

In Part III are the results of measurements of the conductance of solutions of hydrogen chloride in acetone, while Part IV is concerned with potentiometric studies on solutions of tetrahydroquinoline, tetrahydroisoquinoline and dimethylketazine in aqueous and anhydrous acetone. It includes potentiometric titrations of dimethylketazine with hydrogen chloride, and details of the electrochemical cells used.

Conductance studies on solutions of dimethylketazine in anhydrous acetone are described in Part V, and the final part collates evidence for the existence of the dimethylketazinium ion.

PART I.

HISTORICAL SURVEY OF THE PROBLEM.

1. Salts of Hydrazine and the Azines.

Both during and since the war much attention has been directed to the chemistry of hydrazine and to solutions in hydrazine, but its aqueous solutions and salts have attracted very little attention since 1930 when Gilbert[1] studied the equilibrium between the hydrazinium ion, ammonia and hydrazine.

However, since 1950, the hydrazine-water system has been studied by several authors, and surface tensions, parachors, and freezing and boiling points of aqueous solutions have been reported[2]. Higginson[3] and Cahn and Powell[4] have examined the oxidation of hydrazine in water by an isotope technique, and Vivarelli at the dropping mercury electrode[5]. Extensive hydrogen bonding has been shown to occur both between the hydrazine molecules and with the water[6], and the pioneer work of Gilbert has shown that there is also limited reaction with water resulting in the formation of hydrazinium ($N_2H_5^+$) and hydroxyl ions[1]. He determined the ionisation constant of the base, but a later potentiometric study by Schwarzenbach provided values of K_b for both the first and second ionisations[7]. These values are compared in Table I.

TABLE I.

The Ionisation Constant of Hydrazine.

	First Ionisation	Second Ionisation
Gilbert[1]	$1.4 - 1.7 \times 10^{-6}$	-
Schwarzenbach[7]	8.5×10^{-7}	8.9×10^{-16}

1.1 The Work of the Cape Town School.

In 1952 the late Professor W. Pugh prepared the chlorostannate of hydrazine[8] and followed this with hydrazinium salts of complex halogeno-acids of tin, antimony, bismuth[10,14], aluminium[12], gallium, indium and platinum[18]. In an early attempt to prepare hydrazinium chlorostannate by precipitation with acetone, Pugh and Stephen[9] obtained a compound which on analysis gave figures consistent with the chlorostannate of dimethylketazine (N:N'-diisopropylidenehydrazine), while heating under reflux for several hours produced bis-1-isopropylidene-3:5:5-trimethyl-pyrazolinium chlorostannate[8,15,16]. As it was previously thought that the strength of dimethylketazine was too low for salt formation, and the postulation of a 1-isopropylidene-3:5:5-trimethyl-pyrazolinium ion proposed great difficulties, attempts to prepare complex and simple salts of a series of aldazines, ketazines and pyrazolines were immediately undertaken. Thus bromostannates and bromostannites of dimethylketazine and pentan-3-one hydrazone[11],

halogeno-antimonites and bismuthites of dimethylketazine, butanone hydrazone, pentan-3-one hydrazone and heptan-4-one hydrazone[13] were prepared, and soon followed by ten halogeno-antimonites and bismuthites of benzaldazine, salicylaldazine and anisaldazine[17]. Pugh and his school also prepared eleven halogeno-stannates and -platinates and ten halides and sulphates of these bases, and found that (1) aromatic aldazines and ketazines yield halides and salts of complex acids, (2) aliphatic ketazines gave salts less readily, no simple salts being obtained, (3) aliphatic aldazines yielded no crystalline salts, and (4) "mixed" azines, containing one molecule each of aromatic aldehyde and acetone per molecule of hydrazine, gave salts most readily. Complex salts of dimethylketazine were obtained, but no simple salts, while higher ketones yielded complex salts of the corresponding hydrazones[17]. Efforts to prepare halogeno-aluminates of dimethylketazine and 1-isopropylidene-3:5:5-trimethylpyrazoline were unsuccessful, the hydrochloride resulting in the latter case and an oil in the former[12].

It has been convenient to refer to all these compounds as complex salts, but although Schaffer has verified the presence of the chlorostannate ion in hydrazinium chlorostannate by X-ray crystallography[19], and Flora[54] has shown 1-isopropylidene-3:5:5-trimethylpyrazolinium chlorostannate to be a complex salt, it is by no means certain that all the others are true salts of complex halogeno-acids. Indeed the only other salt investigated

crystallographically has been trihydrazinium hexachloroaluminate hexahydrate in which Tessche showed that the aluminium ion is surrounded by six water molecules[20]; this is confirmed by the molar conductance measurements of Morrison[21], who found that the chloro- and bromoaluminates were completely broken down in aqueous solution. Hydrazine complex ions have been studied potentiometrically by Schwarzenbach and Zobrist[22], and polarographically by Rebertus, Laitinen and Bailar who have shown that the zinc ion adds successively four molecules of hydrazine to form $[Zn(N_2H_4)_4]^{2+}$[23].

Marks[18] found that several hydrazinium hexafluorogallate preparations appeared to have extra HF present. He unsuccessfully tried to distinguish between $N_2H_5^+$ and $N_2H_6^{++}$ ions by Raman spectroscopy, and then resorted to conductimetric and high frequency titrations of hydrazinium dihydrofluoride, gallium trifluoride, and the hydrazinium hexafluorogallates with lanthanum acetate. He also carried out molar conductance measurements on gallium trifluoride and the hexafluorogallates, and high frequency titrations on one of the complex indates in an attempt to determine the state of the additional HF molecules.

As all ketazines and aldazines are readily hydrolysed by small traces of moisture, Sohn[24] used dioxan as a solvent in which to measure spectroscopically the ionisation constant of benzaldazine

as a base. Using Hammett and Deyrup's equations[25], she was able to calculate an approximate value for K_b, and thus for the first time indicated the existance of an aldazinium ion in solution.

1.2 Electrochemical Studies on Solutions of Hydrazine Salts.

While much electrochemical work has been done on solutions in hydrazine, none of this is relevant to the present problem. Only Bredig[26], Gilbert[27], and Seward[28] had made conductance measurements on salts of hydrazine in water, and no work on solutions of salts of complex acids could be traced. Seward measured the conductance and viscosity of highly concentrated aqueous solutions of hydrazinium chloride and nitrate as a contribution to the theory of concentrated solutions, and was not able to determine a value for the limiting conductance of hydrazinium ion. Gilbert, however, worked with hydrazinium picrate, perchlorate and trinitro-m-cresylate and obtained values for λ^0_+, but much of his work is open to criticism. This work was done before the accurate Jones and Josephs and Shedlovsky bridges came into general use; moreover no correction for the hydrolysis of the hydrazinium ion was made, polished electrodes were used in a two-electrode cell to minimise decomposition of the hydrazine, and his ion conductances were based on values for the picrate and perchlorate ions which have since been modified. It therefore seemed desirable that Gilbert's work should be repeated with better apparatus and grey platinum electrodes to facilitate the interpretation of the results for hydrazinium

chloroplatinate.

As a result of this work, it appears that Gilbert's apparatus was not sufficiently sensitive to detect a slow reduction of the picrate and perchlorate ions by the hydrazine. While it is well known that platinum black catalyses the oxidation of hydrazine in solution[2], grey platinum does not appear to be so effective a catalyst, but repetition of the measurements by a new potentiometric method using bright platinum electrodes showed that the reduction process still occurred under these conditions, although more slowly.

2. Electrochemical Studies in Acetone.

2.1 Conductance Studies on Solutions of Salts in Anhydrous Acetone.

As dimethylketazine and its supposed salts are rapidly hydrolysed by small traces of moisture, potentiometric and conductance measurements must be carried out in a non-aqueous solvent. Gilbert[29] had studied the equilibrium between hydrazine and dimethylketazine and found that in the presence of excess anhydrous acetone conversion to the azine was virtually complete; accordingly acetone was selected as the solvent for this work.

A survey of the literature revealed that the electrochemistry of acetone solutions was not only a largely untouched field, but what little information existed was contradictory; for example, widely differing results for the equivalent conductance of potassium iodide were published in seven papers which appeared between 1926

and 1954.

Walden, Ulich and Busch measured the conductances of solutions of lithium picrate, sodium and potassium iodides and several tetraethylammonium and related organic salts in acetone[30]. They found that the Kohlrausch-Debye and Hückel square root law was valid in many cases, but that all the slopes were greater than those calculated by the Onsager equation.

Ross Kane's[31] results for tetraethylammonium salts agreed fairly well with those of Walden, but his limiting equivalent conductances for the alkali metal salts were all about 3% higher. While the alkali picrates, thiocyanates and iodides were found to be weak electrolytes in acetone, all the perchlorates appeared to be strong, an observation which is at variance with the results of more recent work[32]. Ross Kane used Walden's rule to calculate the limiting conductances of several ions; these values were generally slightly higher than those determined subsequently by Reynolds and Kraus[33].

The conductances of calcium and magnesium perchlorate were compared with Walden's values for barium perchlorate by van Rysselberghe and Fristrom[34], who found that the conductance-viscosity products were not as constant as previously claimed. Transport number calculations from their data produced impossibly large values, and they stated that the conditions appear to be different from those

postulated in the foundations of the Onsager theory, equilibria between simple ions, "neutral molecules" and complex ions affecting the limiting slope.

Fuoss and Kraus[35] had derived equations which accounted for the behaviour of ions in solutions of low dielectric constant, and these were used by Aecascina and Schiavo[32] in the interpretation of their results for the conductances of the alkali perchlorates. They found that these salts behave as weak electrolytes and do not obey the Onsager equation. Calculated cation mobilities were found to be out of line with the corresponding series of picrates[33], and this was attributed to specific solvation of the perchlorate ion.

Some of Walden's work was repeated by Reynolds and Kraus[33], who also measured the conductances of several substituted ammonium salts. Their results were the first on acetone solutions to be analysed by the Fuoss procedure, and values for the limiting equivalent conductances and dissociation constants were calculated. Ion conductances were determined by Fowler's method[36], assuming that the conductances of the tetrabutylammonium and triphenylborofluoride ions were equal. Anion conductances were found to be greater than the corresponding cation conductances, an observation in accord with an earlier suggestion made by Ross Kane[31] that specific interaction occurred between solvent and cation. The conductance of the fluoride ion, however, was abnormally low. The effects of ionic size on the solvation of alkali metal ions and steric effects on the dissociation

constants of salts of both the organic acids and bases were also discussed, and the purity of the acetone used by earlier workers criticised.

In view of the discrepancies in the measurements on potassium iodide, Dippy and Hughes[37] redetermined its equivalent conductance, and dielectric constant. They used Bjerrum's[38] and Stokes' equations to estimate the radii of the ions, and extended the Fuoss treatment to all the earlier work for comparison.

Limiting equivalent conductances of the ammonium, tetramethyl-, tetrapropyl- and tetraamylammonium ions and also the chloride ion were determined by McDowell and Kraus[39] by Fowler's method[36]. Their results were also handled by the Fuoss procedure, and they made comparisons of dissociation constants and ion conductances in water, pyridine, ethylene dichloride and nitrobenzene as well as acetone. They regarded the viscosity change as being insufficient to account alone for the change in mobility and state that structural and constitutional properties of the solvent must also be considered.

An opinion has been expressed[40] that the Shedlovsky extrapolation function[41], while providing the same value for the limiting equivalent conductance as that of Fuoss[35], is more suitable for the calculation of the dissociation constant of a weak electrolyte in a non-aqueous solvent when it is above 10^{-3}. When K is less than 10^{-3}, both functions give the same results, but although most salts in acetone appear to have dissociation constants between 10^{-3} and 10^{-1}, only

one calculation involving the use of the Shedlovsky function appears to have been made on a solution in this solvent[45].

2.2 Conductance Studies on Solutions of Acids in Anhydrous Acetone.

The conductances of solutions of picric and perchloric acids in acetone were measured by Ross Kane[31], who reported that the former was a weak acid and the latter a strong acid, while hydrogen chloride did not give reproducible results. He also noted that the perchloric acid solutions became brown on standing and the hydrogen ion concentration decreased, but solutions containing small amounts of water appeared to be more stable. In view of the uncertainty as to the state of perchlorates in acetone solution[32,34], new measurements on perchloric acid seem to be desirable.

Ross Kane calculated the limiting conductance of the hydrogen ion in acetone to be 88*. This low value was thought to be due to non-formation of the solvated ion $Me_2C=OH^+$, so that a Grotthus-type proton transfer mechanism could not occur. However, it is not easy to imagine the existence of an unsolvated proton in acetone solution, and Braude's[42] calculation from spectroscopic data of the equilibrium constants for proton transfer reactions from solvated protons in several solvents have indicated that the $Me_2C=OH^+$ ion exists. Grotthus conduction would not be as easy with an ion of this type as it is in aqueous solution, and this alone may be an adequate explanation of the low value of the ion conductance.

* All limiting equivalent conductances are expressed in ohm^{-1} $cm.^2$.

The conductances of solutions of hydrogen chloride in acetone have also been measured by Mackor[47]. He states that his results indicate a dimerisation of the solute, and Sparnaay[47] has confirmed that it does not behave as a simple acid, other equilibria being involved. Although neither were able to obtain very reproducible results, both found that hydrogen chloride was a weak acid in acetone solution having K_a 10^{-6} to 10^{-8}.

In view of the uncertainty as to the state of hydrogen chloride in acetone, Everett and Rasmussen[48] measured the solubility of silver chloride in HCl solutions. Mackor[58] had shown the complexity constant for the reaction

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

to be about 5, so that if hydrogen chloride was completely dissociated in acetone, silver chloride would be very soluble in HCl solutions. It is, in fact, very sparingly soluble and they calculated the dissociation constant to be of the order 10^{-8}.

Using the Hammett acidity function, Braude found dissociation of hydrogen chloride in acetone to be virtually complete. This is at variance with all the conductance work, including that described in this thesis, but Braude's calculations were based on Sackur's[86] inaccurate limiting slope as Ross Kane's results had never been published in detail.

French and Roe[43] have measured the conductances of solutions of

picric acid in acetone at 15°, 25° and 40°C, and developed a new conductance equation based on the assumption that triple ions of only one type are formed. They believe this to be $(Pi - H - Pi)^-$, and the results are analysed on the basis of triple ion, ion pair, and modified triple ion formation, it being shown that this assumption best explains the variation of conductance. Triple ion formation was first suggested by Fuoss and Kraus[44], but while agreeing that these conglomerates are likely to have a finite existance, Griffiths and Lawrence[45] consider that as the dissociation constant for ion pair formation of silver nitrate in acetone is of the same order as that obtained by the Shedlovsky extrapolation method, the triple ions are largely dissociated into simpler entities.

2.3 Potentiometric Studies on Solutions of Acids in Anhydrous Acetone.

As few non-aqueous cells without liquid-junction had been investigated, and in view of the conflicting evidence regarding the state of hydrogen chloride in acetone, Everett and Rasmussen studied the cell $H_2(Pt)|HCl|AgAgCl$ in this solvent[48]. Their results showed HCl to be a very weak acid in acetone, and, using an approximate dissociation constant, they calculated the standard potential of the silver-silver chloride electrode. Measurements of the solubility of silver chloride made possible a determination of the standard potential of the silver electrode in acetone. Molal activity coefficients were also calculated.

A 0.01 N/0.1 N HCl concentration cell has been used by Erdey-Gruz to determine transference numbers in acetone and acetone-water mixtures[49]. Although his values for the cation transference number of 0.22 and the anion transference number of 0.79 lead to a low value for the limiting equivalent conductance of HCl, it does not affect the order of magnitude of the approximate dissociation constant. Birkenstock[50] published transference numbers for lithium chloride and bromide and sodium iodide, but his results are not relevant to this work as he gave no concentration dependence.

Ulich and Spiegel[51] made a study of metal-metal halide electrodes in acetone and reported that most of these systems gave irreproducible potentials. They considered this to be due to the formation of complex ions of the type $M_m X_n^{(n-m)-}$, this view being supported by the observed increase in the solubility of mercury and silver halides in acetone on the addition of lithium halides. However, Everett and Rasmussen[48] found that the silver-silver chloride electrode behaved satisfactorily, and Arthur and Lyons[52] have used calomel electrodes for the polarography of acid halides in this solvent after thorough tests for reproducibility. These electrodes were used in this work and found to be satisfactory.

2.4 Electrochemical Measurements in Acetone-Water Mixtures.

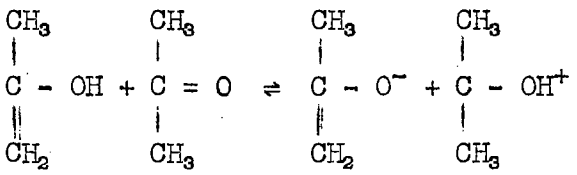
Feakins and French[53] have recently published a general discussion of the cell $H_2(Pt) \mid HCl \mid AgClAg$ in which standard potentials in aqueous and anhydrous acetone and several other organic

by refluxing over calcium chloride, potassium carbonate, sodium sulphate and copper sulphate, followed in each case by fractional distillation; and a wide range of specific conductance has been reported. Reynolds and Kraus[33] used activated alumina as a dessicant and, obtaining a specific conductance of 10^{-9} after fractionation, claimed that the discrepancies in the results of earlier workers could be ascribed to the degree of purity of the solvent. Substantially the same conclusions were reached by Dippy and Hughes[37], who also used the alumina method, but Everett and Rasmussen[48] preferred repeated distillation, since the use of strong dehydrating agents leads to condensation reactions. As it seemed likely that careful fractionation would remove such condensation products as well as water, a modified alumina method was used in this work.

Mysels[59] used the conductances of saturated sodium chloride and other salts to determine the moisture content of acetone, and expressed the view that it was not possible to obtain a water content of less than 0.05%, extrapolation of his results indicating that in truly anhydrous acetone the conductances of saturated solutions of alkali metal halides are close to zero. Everett[60] has expressed the view that acetone condenses under conditions of low water concentration and that consequently "anhydrous acetone" does not exist. As the ions are preferentially solvated by water molecules, the presence of small amounts of moisture would greatly affect electrochemical measurements.

(b) The Mechanism of Conduction in Pure Acetone.

It seems possible that the conductance of acetone may be due to ionisation of the enol form which exists to the extent of 2.5×10^{-4} percent[46] according to the reaction



but Eck[61], in a discussion of the theory of semi-conducting liquids, has claimed that acetone is a semi-conductor and therefore no fixed resistivity can be stated for it.

His experiments indicate that large ions similar to those occurring in gases appear to exist in acetone, and are responsible for its conductance. These ions have mobilities of less than a micron per second under a potential gradient of 1 volt/cm., and although the ions move more slowly than those of electrolytes in solution, acetone would be expected to show some of the properties of both electrolytes and ionised gases, depending on the experimental conditions.

On Eck's hypothesis there would be no reaction at the electrodes in pure acetone as the ions are groups of molecules and not produced by dissociation, but absolute purification, whether by successive fractional distillation or by prolonged passage of electricity is impossible, and small traces of moisture always persist. If there

are only a few oxonium and hydroxyl ions present they will become attached to the larger ions or provide charges for assemblages which are initially neutral, and will consequently not be easy to remove. Large amounts of moisture or other ionic impurities present in concentrations too great for all the ions to become attached to the groups of acetone molecules will be responsible for the conductance, so that in solutions of electrolytes the semi-conducting properties of acetone will be masked.

PART II.

THE ELECTROLYTIC CONDUCTANCE OF HYDRAZINIUM SALTS IN AQUEOUS SOLUTION.

1. An Outline of the Methods and Results.

It appeared that evidence of the existence of the ketazinium ion in acetone solution might be obtained by comparison of the conductances of a supposed ketazinium salt in this solvent with those of the corresponding hydrazinium salt in water. The only stable ketazinium salts are salts of complex halogeno-acids, and although the chlorostannate appeared to be the most satisfactory for this purpose, preliminary potentiometric measurements showed the chlorostannate ion to be extensively hydrolysed in aqueous solution. As the chloroplatinate ion, a complex of similar shape and size, was known to be stable in water, it was decided to measure the resistances of aqueous solutions of its hydrazinium salt.

The resistances of these solutions at constant temperature were found to vary with time, first decreasing and then increasing after passing through a minimum. When the cell was removed from the thermostat, its walls were seen to be coated with finely divided platinum, and analysis indicated that the chloroplatinate ion had been reduced by hydrazine. The reduction process was then followed by measuring the resistances of the solutions at fixed time intervals and the results extrapolated to zero time for calculation of the equivalent conductance. This procedure was carried out at frequencies

of 80 c./sec. and 1000 c./sec. at 20.7°C, 25°C and 31.7°C, and apparent activation energies determined.

The conductances of aqueous solutions of hydrazine perchlorate and hydrazine picrate were measured at 25°C to check Gilbert's[37] results for the limiting conductance of the hydrazinium ion, and in both cases a very slow reduction of the anion was observed. Gilbert's apparatus was not sufficiently sensitive to detect this; he had also worked with polished platinum electrodes which, although catalytically less efficient than the grey platinum electrodes used in the present work, may have led to polarisation errors. A new A.C. potentiometric method for the determination of electrolytic conductance was developed in collaboration with the Department of Electrical Engineering of the University of Cape Town and the Oceanographic Division of the National Physical Research Laboratory[62]. This circuit enabled bright platinum electrodes to be used with great precision, errors due to polarisation being avoided. The apparatus was tested on solutions of potassium chloride, after which the conductances of solutions of the hydrazinium salts were redetermined, the results indicating that the reduction reactions still proceeded, albeit at a much reduced rate.

The results of the conductivity measurements were used in conjunction with measurements of the change in pH during reduction to indicate a possible mechanism for the reduction of the chloroplatinate

2. The Instruments.

2.1 The Oscillator.

An 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 sinusoidal wave form. A push-pull power amplifier is incorporated and fixed frequencies of 80, 240, 480 and 1000 c./sec. were originally provided, but the range was later extended to include frequencies of 800, 2400, 4800 and 9200 c./sec. These frequencies were measured by comparison with a calibrated oscillator.

A circuit diagram is given in fig. 1.

2.2 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.

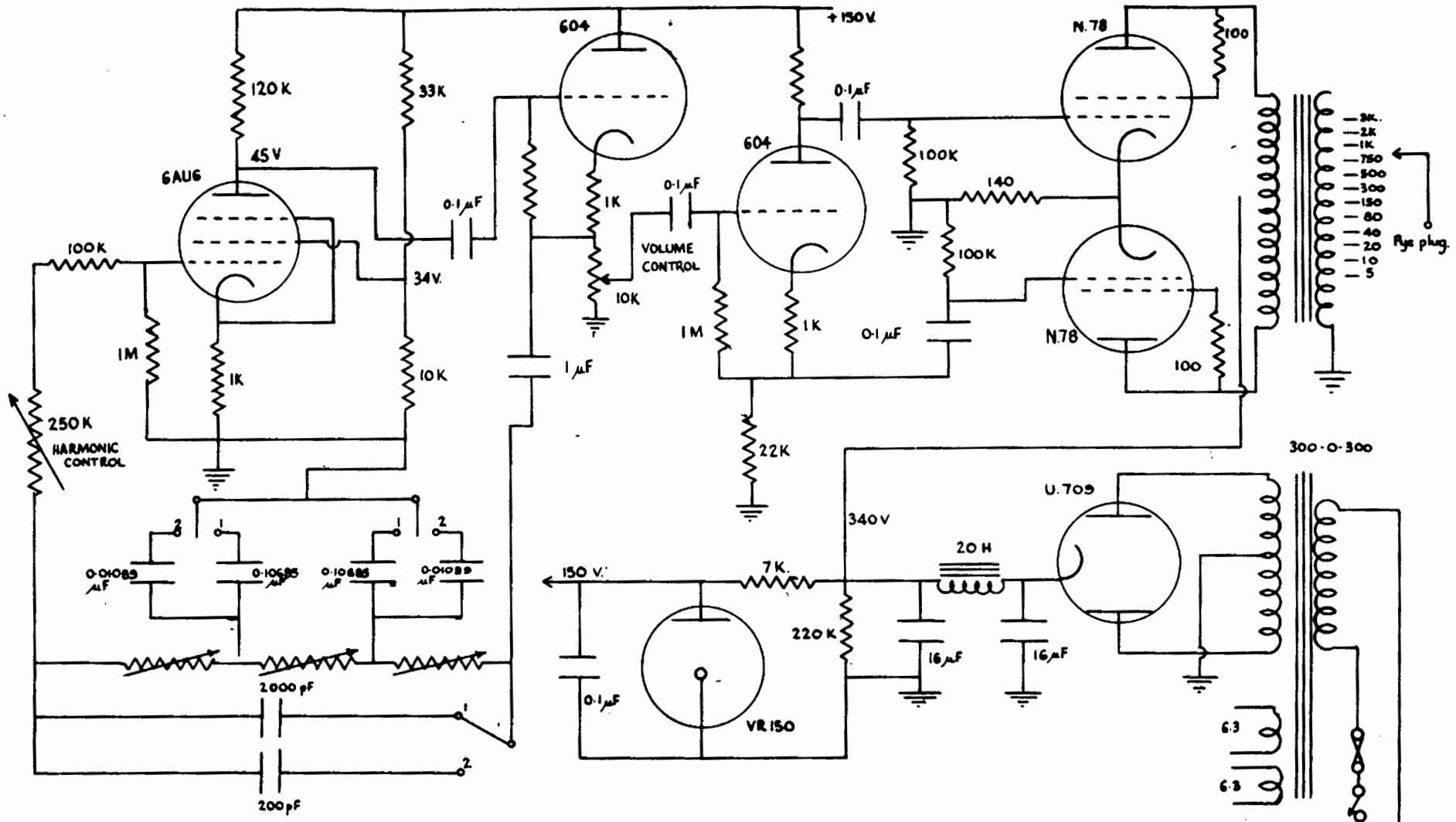


FIG 1. OSCILLATOR CIRCUIT DIAGRAM.

A circuit diagram of this instrument, which was also designed and constructed by Mr. Gingold, is given in fig. 2.

2.3 Measuring Systems.

Conventional two-electrode A.C. systems for the measurement of electrolyte conductance are all in some degree liable to errors due to polarisation or the state of the electrode surfaces. While this work required the use of unplatinised electrodes and the avoidance of errors arising from changes in their contact resistance, workers on the conductivity of sea water required an accuracy of 1 part in 6000 which could not be obtained conveniently in the usual conductance cells.

While such difficulties do not arise with D.C. systems, it is not always possible to find suitable reversible electrodes to use with these circuits[64], although Elias and Schiff[65] have recently published a D.C. circuit for which they claim that such electrodes are not necessary. Ives and Swaroopa[66] have described a modified direct current method which permits the use of a variety of reversible electrodes without the restriction of small size and accurate location within the cell.

For these investigations a four-electrode A.C. circuit based on that originally published by Wenner[67] for measuring resistivity in geophysical prospecting work was developed. This instrument is described in § II, 2.3.2 (page 29).

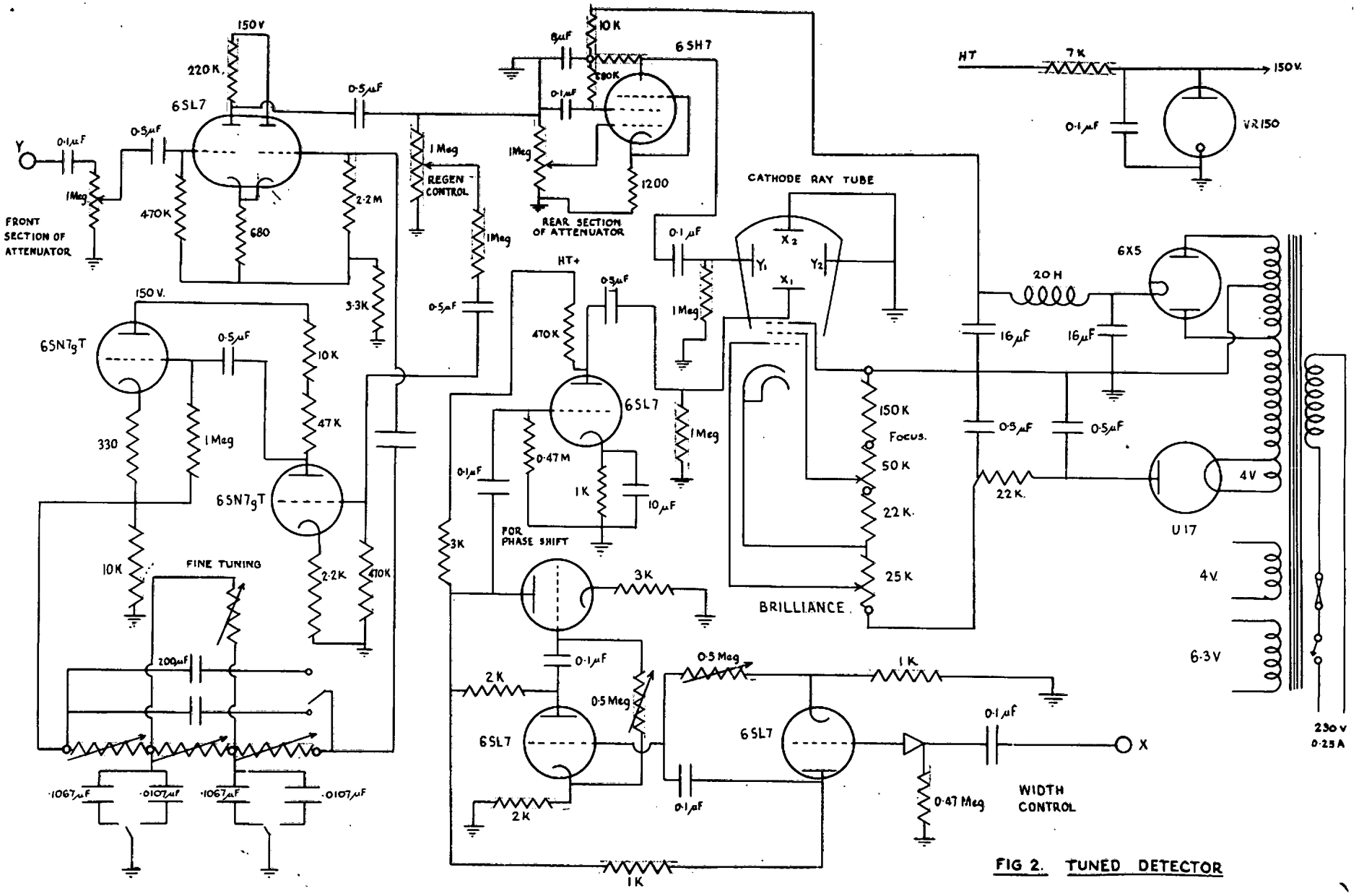


FIG 2. TUNED DETECTOR

2.3.1 The Jones-type Bridge.

The circuit used was very similar to that described by Bender, Biermann and Winger[63], but a few modifications were incorporated. A circuit diagram is given in fig. 3.

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 10000 : 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 800 pF 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 - 2200 pF, 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 120 pF mica condenser, C_3, was arranged in parallel

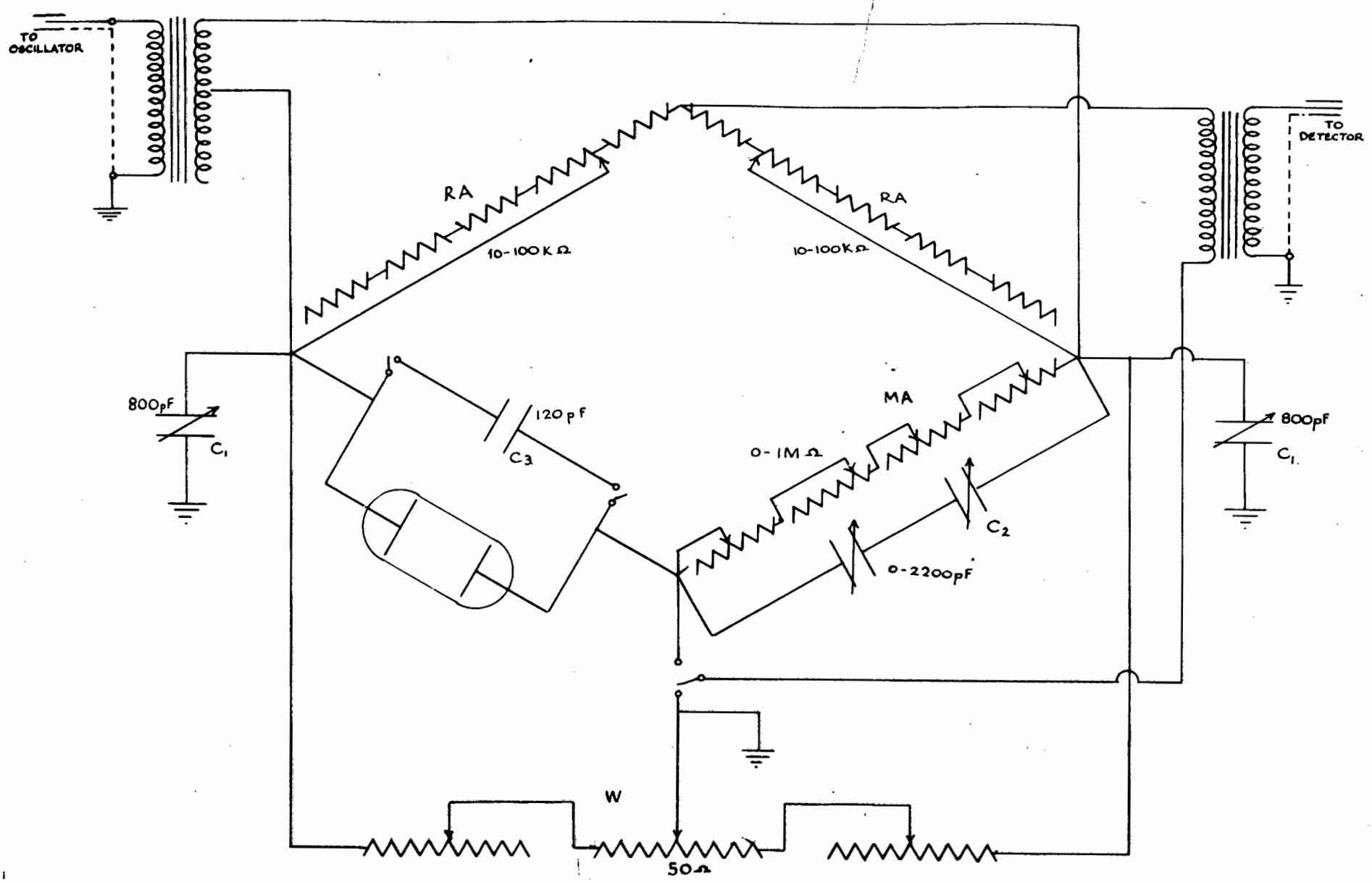


FIG 3. CIRCUIT DIAGRAM OF JONES BRIDGE

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. This was used as an additional control together with the output gain of the oscillator. An additional output, which by-passed the output transformer through a double-pole double-throw switch, was incorporated to permit the use of earphones or other detectors if required.

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.

2.3.2 The A.C. Potentiometric Method.

The circuit diagram shown in fig. 4 illustrates the principles involved. Current is supplied to the solution by the electrodes C_1 and C_2, and the potential difference between the probe electrodes P_1 and P_2 is measured, the conductance of the solution being given by the ratio of the current to the potential difference. This ratio is measured directly using an A.C. potentiometer, R, in

conjunction with a transformer, TC, which is placed in the current circuit, its output being applied to the "battery" terminals of the potentiometer and used as a reference with which the e.m.f. from electrodes P_1 and P_2 is compared. Fluctuations in the primary current caused by oscillator design and the possibility of variation of the contact resistance at the current electrodes are thus reflected in the secondary, and the ratio of the transformer remains constant even when the current through the cell varies. The measurement is also independent of the contact resistances of the electrodes P_1 and P_2 as they carry no current at balance. The variable condenser, L, is used to balance phase changes due to reactance in the transformer and cell.

Small circulating currents, which arise from interwinding and other stray capacitances, pass through the electrodes P_1 and P_2 producing contact resistances and false null balances. The effects of these currents are balanced out by the more elaborate circuit of fig. 5. A double current transformer, CT, and double potentiometer, M, the centre point of which is earthed, are employed to make the whole system symmetrical with respect to both resistance and capacitance; the circulating currents are thus either balanced out or by-passed through screens.

2.3.2(a) The Current Transformer.

Standard Mu-metal stampings were used for the core of the transformer, CT, and no. 40 S.W.G. enamel-covered

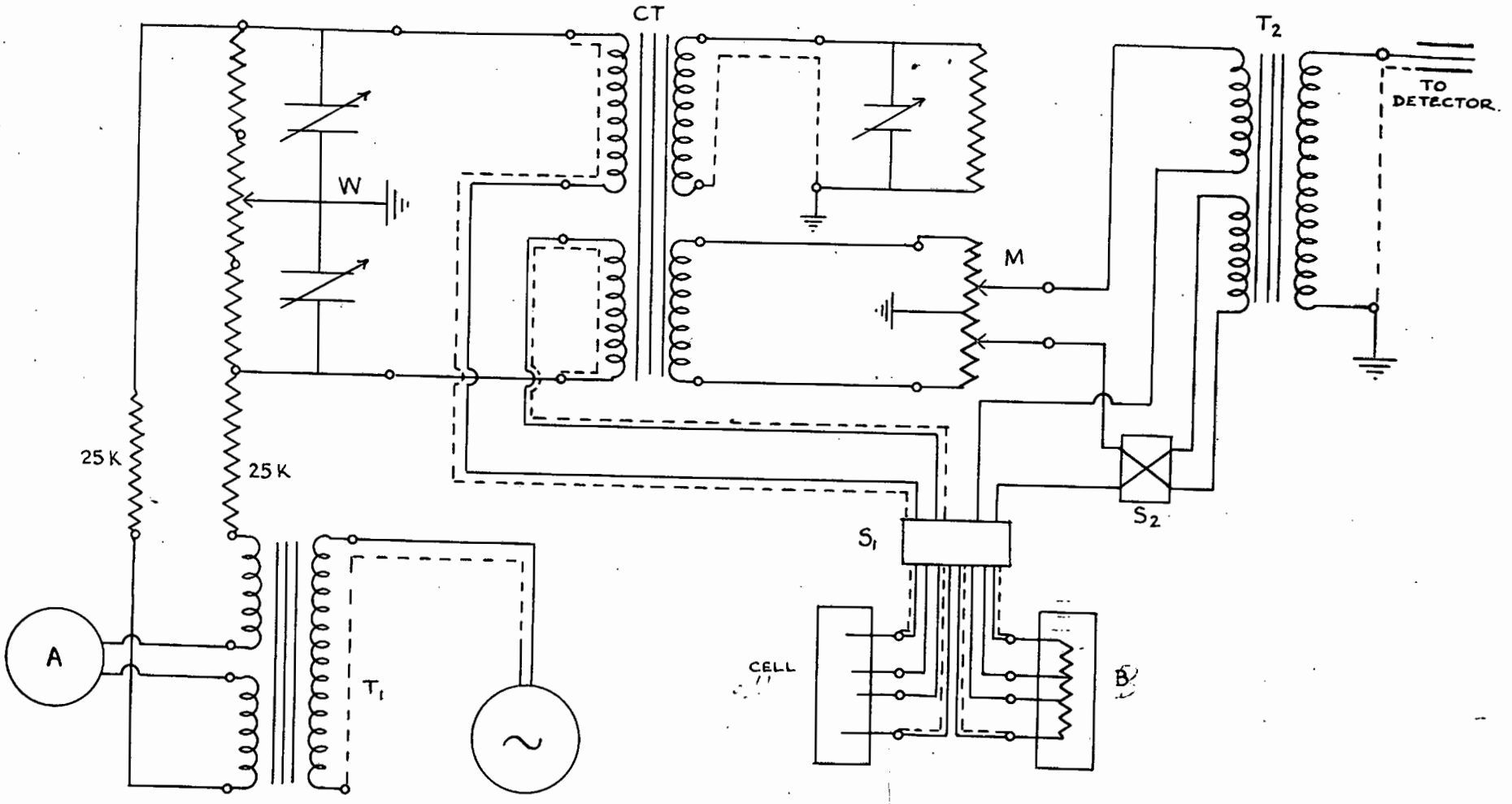


FIG 5. POTENTIOMETER CIRCUIT.

copper wire for the windings. The number of turns were as follows:

Primary: 320 turns (total)
Secondary: 300 turns (total)
Tertiary: 600 turns.

A resistance of 50,000 ohms was placed in the primary circuit to force this transformer to act as a current transformer. The current is then determined by the fixed resistor and not affected by fluctuations in the cell resistance or the input impedance of the current transformer. The high input impedance of the primary circuit required a matching transformer so arranged that the oscillator output impedance would be about 400 ohms. The centre point of the circuit is earthed (W, fig. 5), and two coupled variable condensers are provided to balance the earth capacity from each side of the circuit. This centre point is accurately found by placing a resistor with an earthed sliding contact across the circuit. The milliammeter, A, is placed in the centre of the secondary of the matching transformer to keep earth capacities as nearly balanced as possible.

For the same reason, the cell is placed between the two halves of the primary of the double current transformer CT; the earth potential point is thus in the centre of the cell. A tertiary winding with a variable condenser and resistance was fitted to enable different currents to pass through the potentiometer circuit without altering the primary, the ratio of the transformer being

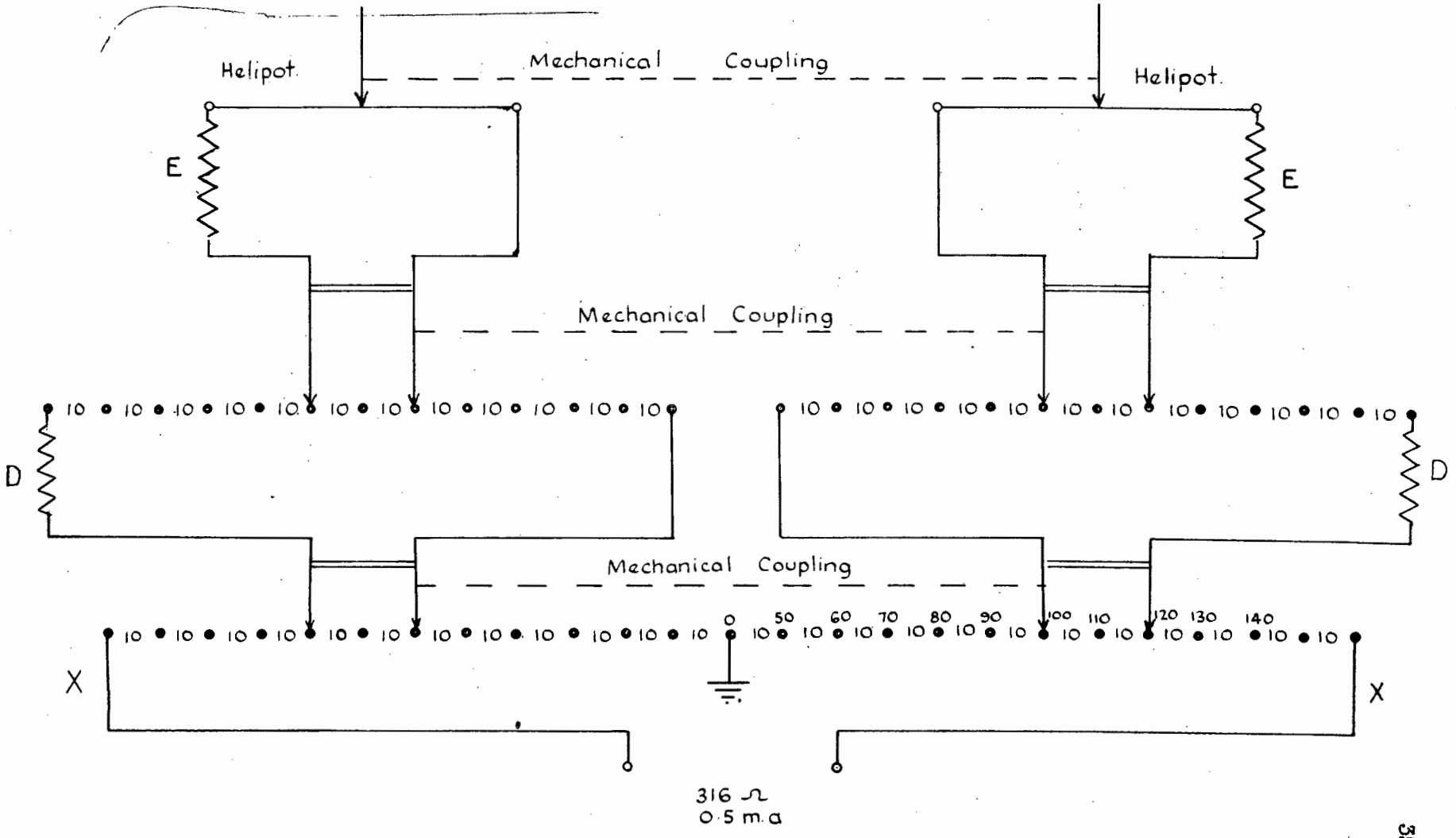
changed by variation of the load. In addition to the normal earthed screening between windings, each half of the primary is completely enclosed in a copper screen which is connected to the side of the circuit furthest from the cell. This prevents leakage currents which pass from one half of the winding to the other from having any transformer action. The current leads from the transformer to the cell were thus doubly screened, the inner screen being connected to the primary winding screen, and the outer to earth. All the other leads, both internal and external, were enclosed in earthed screens.

2.3.2(b) The Potentiometer.

The secondary winding of the current transformer is connected to a balanced potentiometer, M, which is shown in greater detail in fig. 6. Muirhead 10 ohm A70 resistors were matched and mounted on Muirhead type B710A/4 rotary stud switches, the best matched units being fitted in the first stage. The final stage is a double ganged 100 ohm - 10 turn model A Helipot of linearity $\pm$ 0.1% fitted with a duodial.

As it was not convenient to detect less than one microvolt electronically, and an accuracy of one part in ten thousand was desired, it was necessary that one division off balance on the helipot (i.e. 0.1 ohm) should correspond to this potential. For the current through the various sections of the potentiometer to have the correct value, fixed resistances of 62 and 80 ohms were

FIG 6. DETAILED CIRCUIT OF BALANCED POTENTIOMETER.



inserted at D and E in fig. 6. Two matched pairs of fixed resistances were arranged to be switched into the first stage of the instrument at positions X to extend the range of the potentiometer. Two of these resistors were 234 ohms, the other pair being 177.7 ohms, and the switch was wired so that (a) all the extra resistances could be shorted out, (b) one matched pair or (c) both matched pairs were in the circuit. The resistance values were selected to allow overlap of the ranges to such an extent that only one internal standard was necessary, but a separate calibration had to be made for each range. The internal standard was a 160.840 ohm woven resistor which was switched in by operation of the change-over switch, S_1 (fig. 5).

False null balances may be caused by unbalanced earth capacitances in the detector coupling transformer T_2; the reversing switch S_2 allows the two halves of the primary of this transformer to be connected additively or in opposition, and the potentiometer setting is adjusted until no current flows in the secondary of T_2, whichever the position of the switch.

2.3.2(c) Operation of the Potentiometer.

The oscillator gain control and the fine current control, I, are adjusted until the meter reads 0.8 milliamps, as the current through the instrument must remain fairly constant.

The built in standard resistance (B, fig. 5) is used to set the potentiometer in the following manner:

(i) Key A (fig. 7) is pressed down to "standardise", switching the resistor into the circuit in place of the cell.

(ii) With key A on "standardise", key S_2 is switched to "earth balance", reversing one half of the primary winding of the detector coupling transformer T_2 (fig. 5).

(iii) The resistance and capacity adjustments C and D are then adjusted for null balance, setting the earth position in the midpoint of the standard resistor.

(iv) The reversing key S_2 is then released and

(v) The potentiometer is set to its standard reading.

(vi) The instrument is adjusted for null balance using the capacity control E and the ratio control F, which sets the tertiary of the current transformer CT (fig. 5) to its required value. The position of the ratio control must not be altered during the course of a measurement.

To measure the resistance of the cell, the key A is released to the "cell" position and the procedure from (i) - (iv) above repeated, after which the potentiometer and capacity control E are adjusted for null balance. The switch H serves to extend the range of the potentiometer by adding additional resistances to its ends.

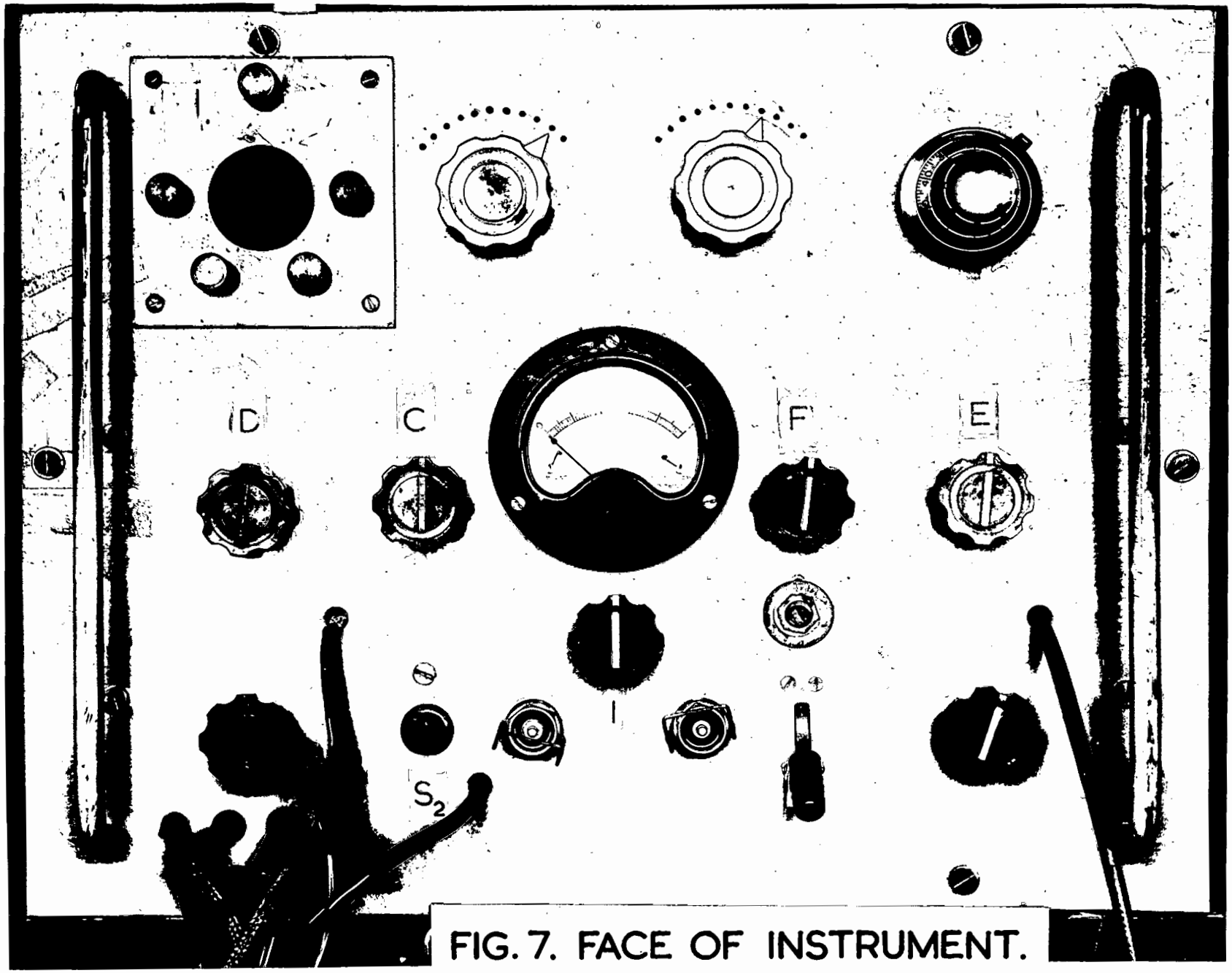


FIG. 7. FACE OF INSTRUMENT.

2.4 Conductance Cells.

2.4.1 The Daly and Smith Cell.[57]

The Daly and Smith cell shown in fig. 8a was used with the Jones-type bridge. It was designed to reduce Parker effect[68] as much as possible, and therefore has only one filling tube. Platinum electrodes 1 cm. in diameter were backed with glass and sealed into the walls approximately 2.5 cm. apart, electrical connections being made through mercury cups. The cell was built into a jacket through which oil from a thermostatically controlled reservoir was circulated. The oil in the outer jacket was maintained at a constant level by means of an overflow tube. The cell was closed with a B7 ground-glass stopper into which a thermistor could be sealed to measure the temperature of the solution.

2.4.2 Cells for use with the Potentiometer.*

A series of glass cells with platinum electrodes was made, the dimensions selected depending on the conductance of the solutions used (fig. 8b). The electrodes $C_1 C_2$ consisted of plates varying from 2 cm. to 4 cm. in diameter and between 0.8 and 1.5 cm. apart, while the probe electrodes were platinum wires sealed between the current electrodes and about 0.5 cm. apart. Electrical contact was made through mercury cups.

The current through the cells was kept as low as possible to

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* These cells will, for convenience, be referred to as "potentiometric cells".

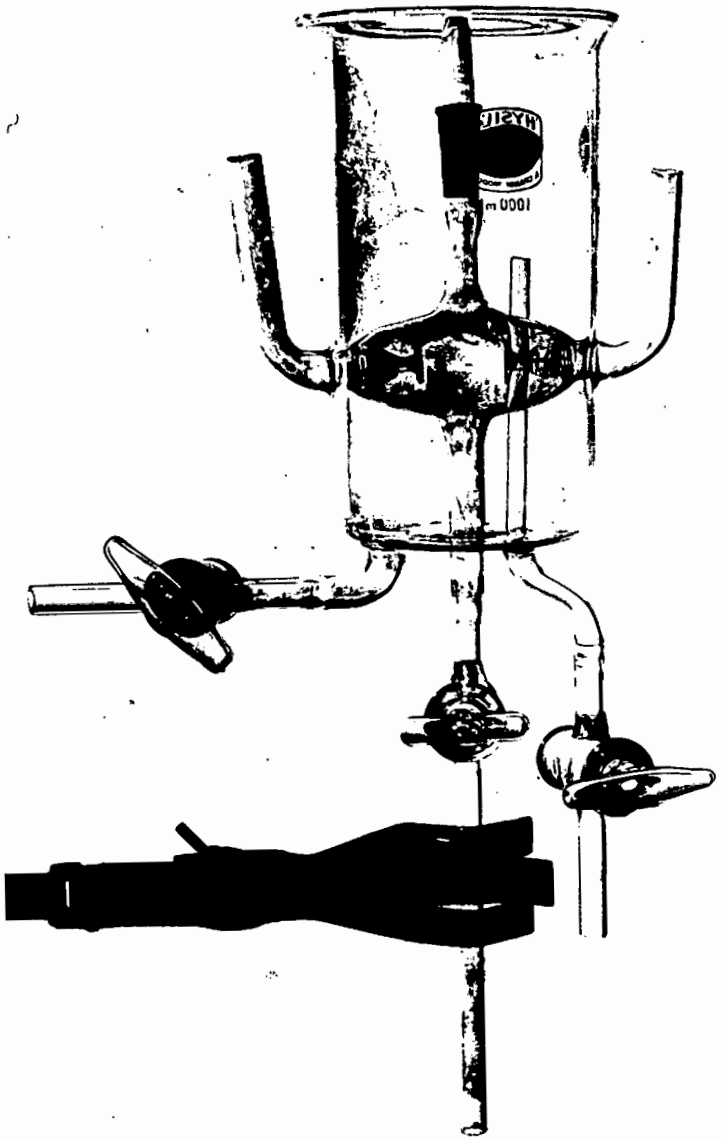


FIG. 8a. DALY & SMITH CELL.

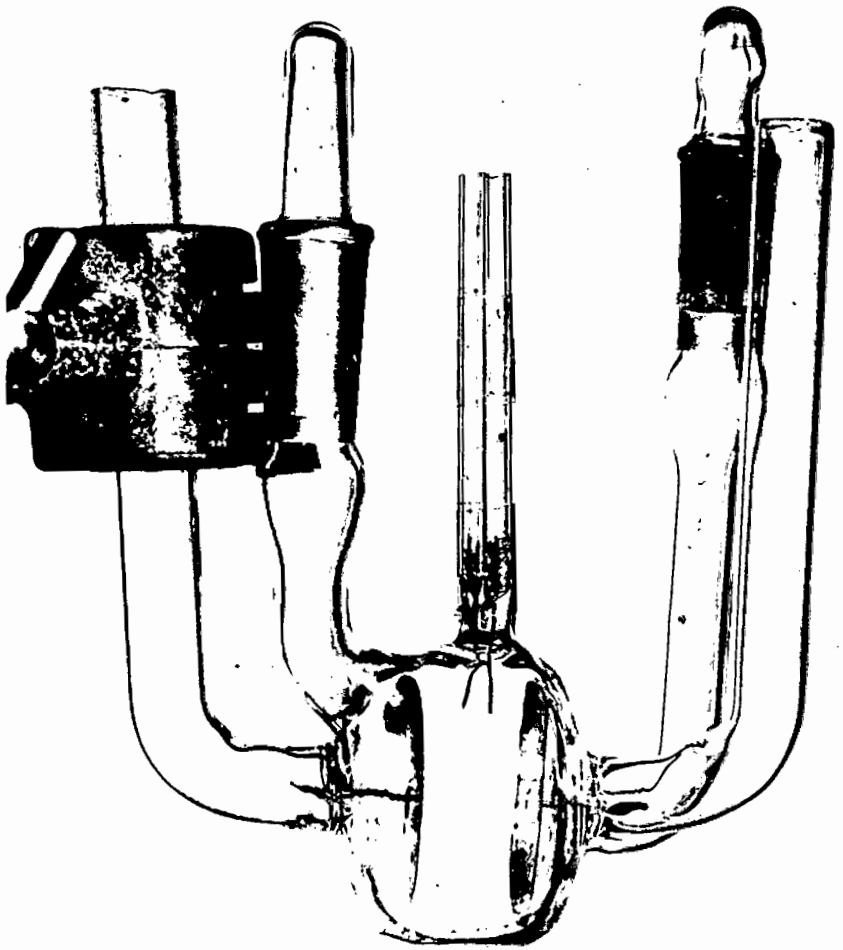


FIG. 8b. POTENTIOMETRIC CELL.

minimise heating effects, and contact or thermal emf's were avoided by using alternating current.

All solutions used were prepared and handled in a "dry box" maintained under a slight positive pressure of nitrogen at constant humidity for aqueous solutions, and as free from moisture as possible for acetone. Carbon dioxide was excluded in both cases, and the cells could be filled and sealed through B7 ground glass joints.

2.5 The Thermostats.

Control of temperature to within ± 0.01°C was achieved by using an independent circulating oil system, enclosed in an air thermostat. The function of the latter was to avoid excessive fluctuation of the temperature around the oil system and to ensure a fairly constant rate of heat loss from it.

The air thermostat was a felt-lagged hardboard box with a perspex front. It was built on a metal frame 30" x 18" x 12", and the air inside maintained at a temperature 1.5° ± 0.5°C below that of the oil thermostat by a Sunvic bimetallic strip thermoregulator connected to a Sunvic type 102 relay switch. The heating element was a 25 watt electric lamp, and air was circulated by a fan driven off the shaft of the oil pump. When measurements were made at 21.7°C, the temperature of the room was maintained at 15 - 17°C with a Frigidaire air conditioner kindly loaned by Modern Appliances Ltd.

A 12.5 watt heating element and a toluene-mercury thermoregulator of spiral pattern, operating through a Sunvic type 104 relay switch, were fitted in an oil reservoir near the roof of the air thermostat, and Shell Diala B transformer oil allowed to flow under gravity through a lead pipe fitted about half-way up the tank. The oil flowed through a two-way tap, either through the outer jacket of the Daly and Smith cell or through a perspex tank 5" in diameter, which contained a special perspex frame to hold the potentiometric cells. Constant levels were maintained in the upper oil reservoir, the perspex tank, and the Daly and Smith cell, oil overflowing into a lower reservoir from which it was pumped back to the upper tank. The perspex tank contained a stirrer driven off the pump shaft, temperatures in the tank being read on a calibrated thermometer.

The pump motor was enclosed in an earthed screen, and the frame and all metal parts of the thermostats were earthed.

2.6 Tests and Measurements on Potassium Chloride Solutions.

Tests over a range of frequencies from 480 c./sec. to 9.2 Kc./sec. showed that the results are independent of frequency within the limits of accuracy of the resistances used in the construction of the potentiometer (1 part in 30,000 up to 4.8 Kc./sec., but falling to 1 part in 6000 at 9.2 Kc./sec. on account of skin effects, etc.). The results are summarised in Table II.

TABLE II.

Frequency Dependence of Potentiometer.

c x 10^3 mole l^{-1}	Instrument settings				
	480 c./s.	1 Kc./s.	2.4 Kc./s.	4.8 Kc./s.	9.2 Kc./s.
9.895	7521.9	7522.0	7521.5		
6.502	15115.0	15113.0	15114.0		
2.397	39141.5	39140.0	39142.1	39142.2	39146.0
0.6465	99444.8	99445.3	99445.7	99446.3	
0.3106	8837.2 *	8837.7 *	8837.4 *		

* Range III, remainder on range I

c x 10^3 mole l^{-1}	Resistances-ohms				
	480 c./s.	1 Kc./s.	2.4 Kc./s.	4.8 Kc./s.	9.2 Kc./s.
9.895	12.310	12.311	12.310		
6.502	24.721	24.717	24.719		
2.397	63.989	63.987	63.990	63.990	63.996
0.6465	162.55	162.56	162.56	162.57	
0.3106	330.32	330.33	330.32		

Measurements were then made on a series of solutions of Merck AR potassium chloride which had been recrystallised three times from good distilled water and twice from conductivity water, two separate samples of the salt being prepared and used in this work. Conductivity water, prepared according to the mixed-bed ion exchange resin procedure described by Jacobs[69], was used and found to have a specific conductance of 0.076 x 10^{-6} mho $cm.^{-1}$. The

cell constants of two cells, labelled L and S, were determined using Jones and Bradshaw's[70] value for the specific conductance of 0.01 Demal potassium chloride, and found to be 0.014172 and 0.024591 respectively.

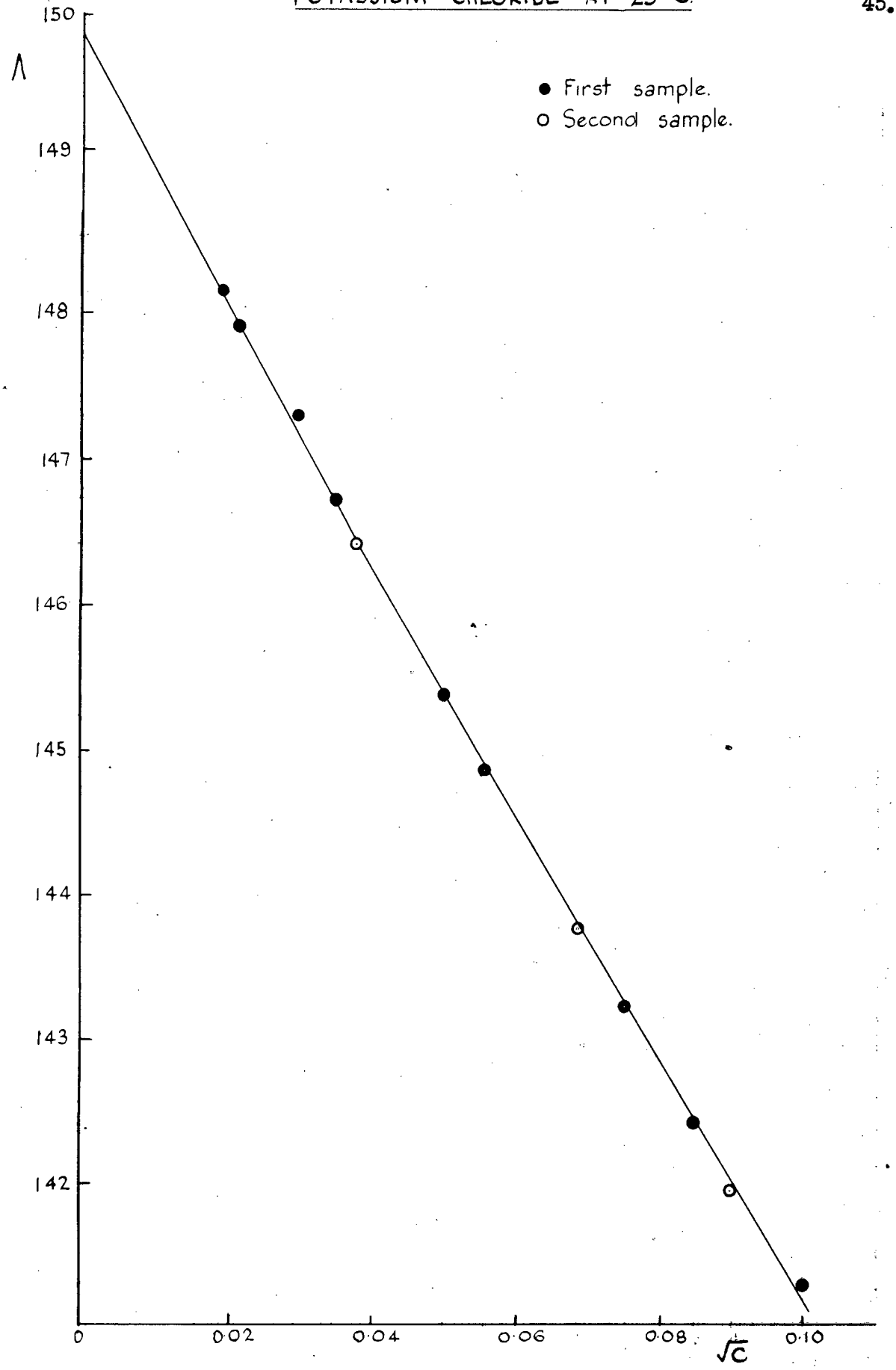
TABLE III.

Equivalent Conductance of Potassium Chloride in Water.

$c \times 10^3$ mole l^{-1}	$\kappa \times 10^5$ mho cm.$^{-1}$	$\Lambda_{measured}$	Equation of Gunning and Gordon	
			$\Lambda_{calc.}$	$\Lambda_{meas.} - \Lambda_{calc.}$
0.36375	5.3845	148.03	148.09	-.06
0.45865	6.7779	147.78	147.88	-.10
0.79893	11.774	147.26	147.25	+.01
1.1834	17.365	146.67	146.70	-.03
2.4493	35.731	145.31	145.37	-.06
3.0601	44.342	144.88	144.87	+.01
5.6221	80.468	143.13	143.23	-.10
7.1972	102.48	142.38	142.46	-.08
10.071	141.81	141.23	141.27	-.04
1.4353	21.011	146.34	146.39	-.05
4.6817	67.321	143.74	143.77	-.03
8.3584	118.60	141.89	141.95	-.06

The last three measurements were made on a freshly recrystallised sample of potassium chloride.

FIG. 9. THE EQUIVALENT CONDUCTANCE OF POTASSIUM CHLORIDE AT 25° C.



The resistances and equivalent conductances obtained are listed in table III, the latter being plotted against the square root of the concentration in fig. 9. The values of Λ all lie within 0.08% (standard error 0.049%) of those calculated from the equation of Gunning and Gordon[64]

$$\frac{\Lambda + 60.18\sqrt{c}}{1 - 0.2289\sqrt{c}} = 149.88 + 153.7c + 32.1c \log c$$

but are, with one exception, lower than the calculated. They may be represented (with a standard error of 0.028% - maximum deviation 0.056%) by the equation

$$\frac{\Lambda + 60.18\sqrt{c}}{1 - 0.2289\sqrt{c}} = 149.84 + 157.5c + 33.7c \log c.$$

However, until an absolute determination of the specific conductance of potassium chloride has been carried out by this method, and the range of the instrument extended to permit measurements on more dilute solutions, no great significance should be attached to this equation.

2.7 Tests on the Apparent Equivalent Circuit of the Potentiometric Cell.

In an attempt to deduce the equivalent circuit of the potentiometric cell, Mr. C.C. Stavropoulis set up the circuit shown in fig. 10, using wire-wound resistors of low inductance and good quality capacitances.

When capacitance was placed in parallel with the standard

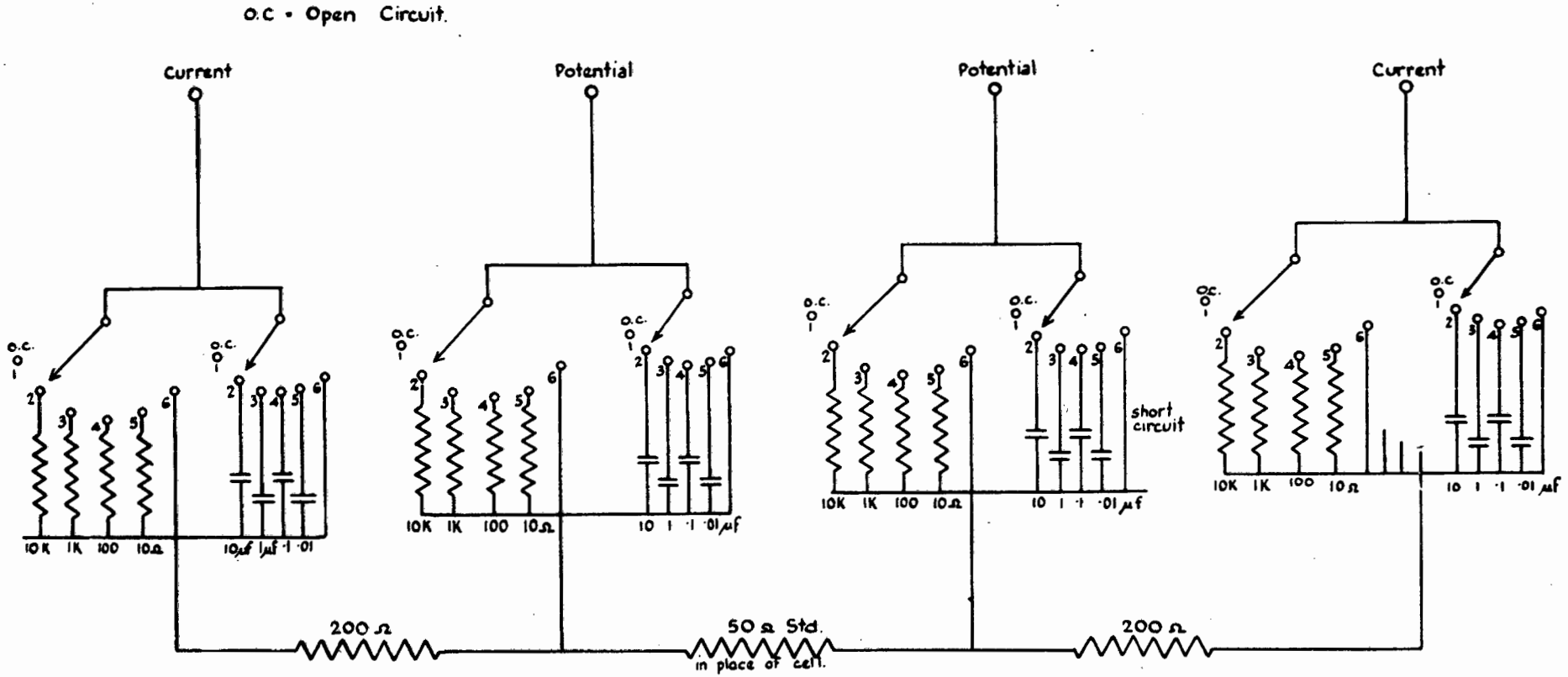


FIG 10. CIRCUIT USED TO INVESTIGATE EFFECT OF SERIES C & R ON READING OBTAINED ON STD 50Ω RESISTOR.

resistor, it was necessary to alter only the capacity balance of the potentiometer, the dial settings, which are a measure of the resistive component, remaining unchanged.

No effect on the measurement was produced by placing resistances of up to 100 ohms in series with the current leads, but a resistance of 1000 ohms required an adjustment of 1 part in 10,000 on the dial settings, and 10,000 ohms affected the measurement to the extent of 1 part in 1000. These results are not unexpected, as the introduction of a high resistance into the primary circuit of the current transformer reduces the current to such an extent that the transformer ratio is no longer constant. Changes produced by resistances in series with the potential leads are small, 10,000 ohms being required to produce a variation in the measurement of 1 part in 10,000. However, the sensitivity of the instrument is much reduced, since, as some current must flow before unbalance can be detected, the potential difference available for operating the instrument becomes smaller as the resistance increases.

Consideration of the equivalent impedances of capacitances placed in series with the current leads shows that the resulting changes are far greater than those which would be produced by resistances of the same value (Table IV). Since the effect of a series capacitance, the potential across which is out of phase with the resistance, on the ratio of the current transformer is unknown,

TABLE IV.

The Effect of Series Capacitance on Resistance Measurement.

Series capacitance and equivalent impedance	Effect of connection in current lead	Effect of connection in potential lead
10μF (16 Ω)	Change of 1 unit in 60,000	No change in 60,000
1μF (160 Ω)	Change of 1 unit in 4000	Change of 1 unit in 3000
0.1μF (1600 Ω)	Change of 1 unit in 500	Change of 1 unit in 600
0.01μF (16,000 Ω)	Change of 1 unit in 100 (sensitivity reduced)	Change of 1 unit in 100 (sensitivity reduced)

no reason for this can be suggested. However, the capacity between the electrodes and the solution must be very large, and any effect on the measurement is probably insignificant. The effects of connecting capacitances in series with the potential leads are almost the same as those of capacitances in series with the current leads (see Table IV).

The capacity between the electrodes and the solutions must, by its nature, be uncertain and unstable in value, but because stable measurements are obtained with the cell it appears that the capacity between the electrode and the liquid is at least 10μF, and possibly larger. This is corroborated by the fact that platinisation

of small electrodes improves their stability. Series resistances of up to 1000 ohms would be tolerated before the effects of unstable readings or loss of sensitivity are noticed. Furthermore, the independence of frequency over the range from 480 c./sec. to 9.2 Kc./sec. shown in § II, 2.3.6 (page 44) provides additional evidence that this instrument measures only the resistive component of the cell.

3. The Reduction of Hydrazinium Chloroplatinate.

3.1 Preparation of hydrazinium chloroplatinate.

Dihydrazinium chloroplatinate was prepared by treating an alcoholic solution of platinic chloride with a very concentrated aqueous solution of hydrazinium chloride, and precipitated by the addition of absolute ether[96]. The yellow precipitate was washed with ether, dried in vacuo and analysed, platinum being determined by combustion to the metal, and hydrazine by titration with potassium iodate[97].

(Found: N_2H_4 6.9%, Pt 22.3%; $(N_2H_5)_2PtCl_6$ requires N_2H_4: 7.1%, Pt 21.7%).

3.2 Results.

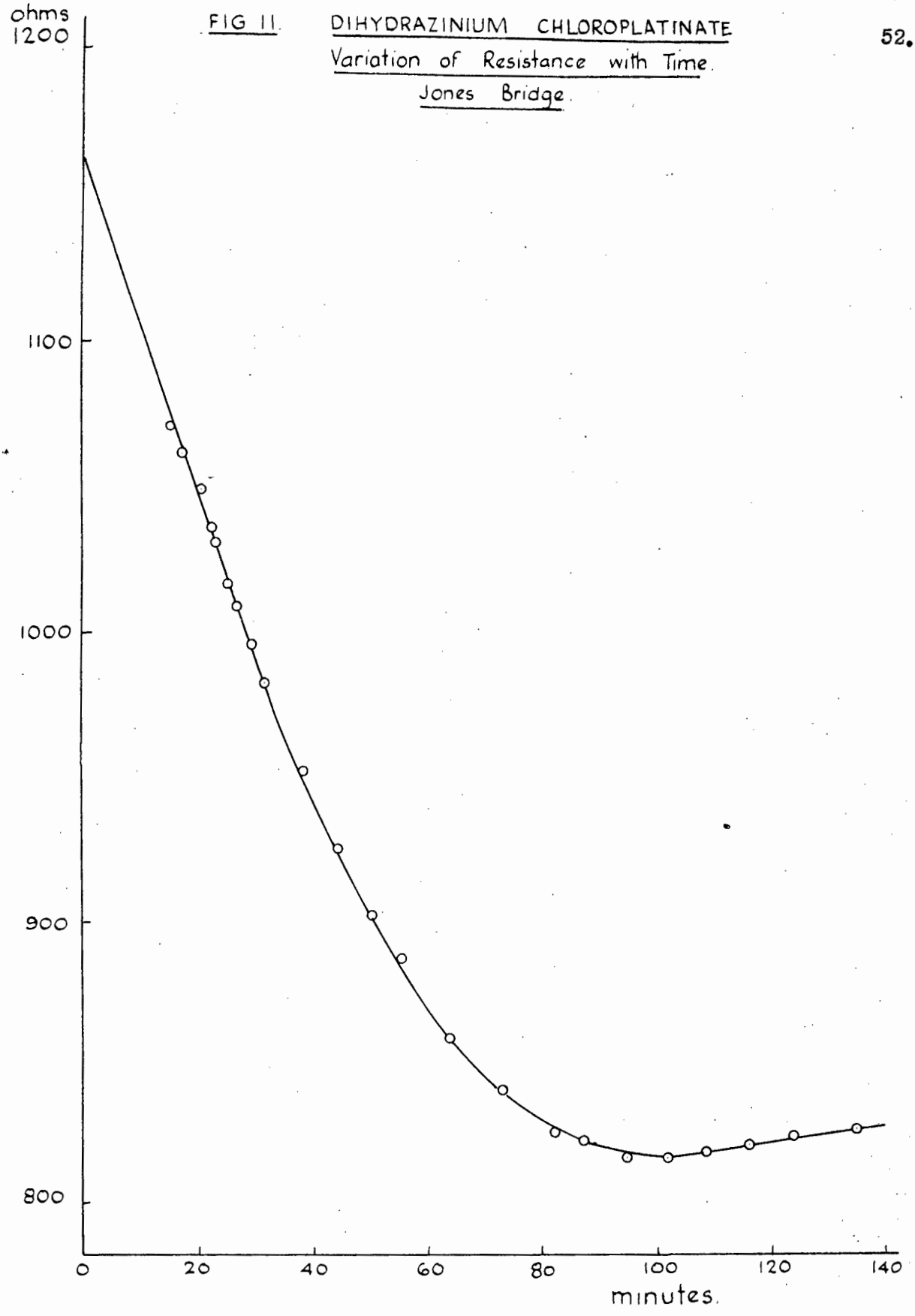
The resistances of solutions of dihydrazinium chloroplatinate were measured at frequencies of 1000 c./sec. and 80 c./sec. at 20.7°, 25° and 31.7°C on the Jones-type bridge and at 1000 c./sec. at 25°C with the potentiometer.

When measured on the Jones bridge, the resistances were found to vary with time, first decreasing linearly and then, after passing through a minimum, increasing. (Fig. 11, see also Appendix II.1, p. 171). During the course of the process, platinum was plated out on the electrodes and cell walls, colloidal platinum appeared in the solution, and bubbles of gas could be seen adhering to the electrodes and walls. Chloride analysis of the solution at the resistance

FIG II. DIHYDRAZINIUM CHLOROPLATINATE

Variation of Resistance with Time.

Jones Bridge.



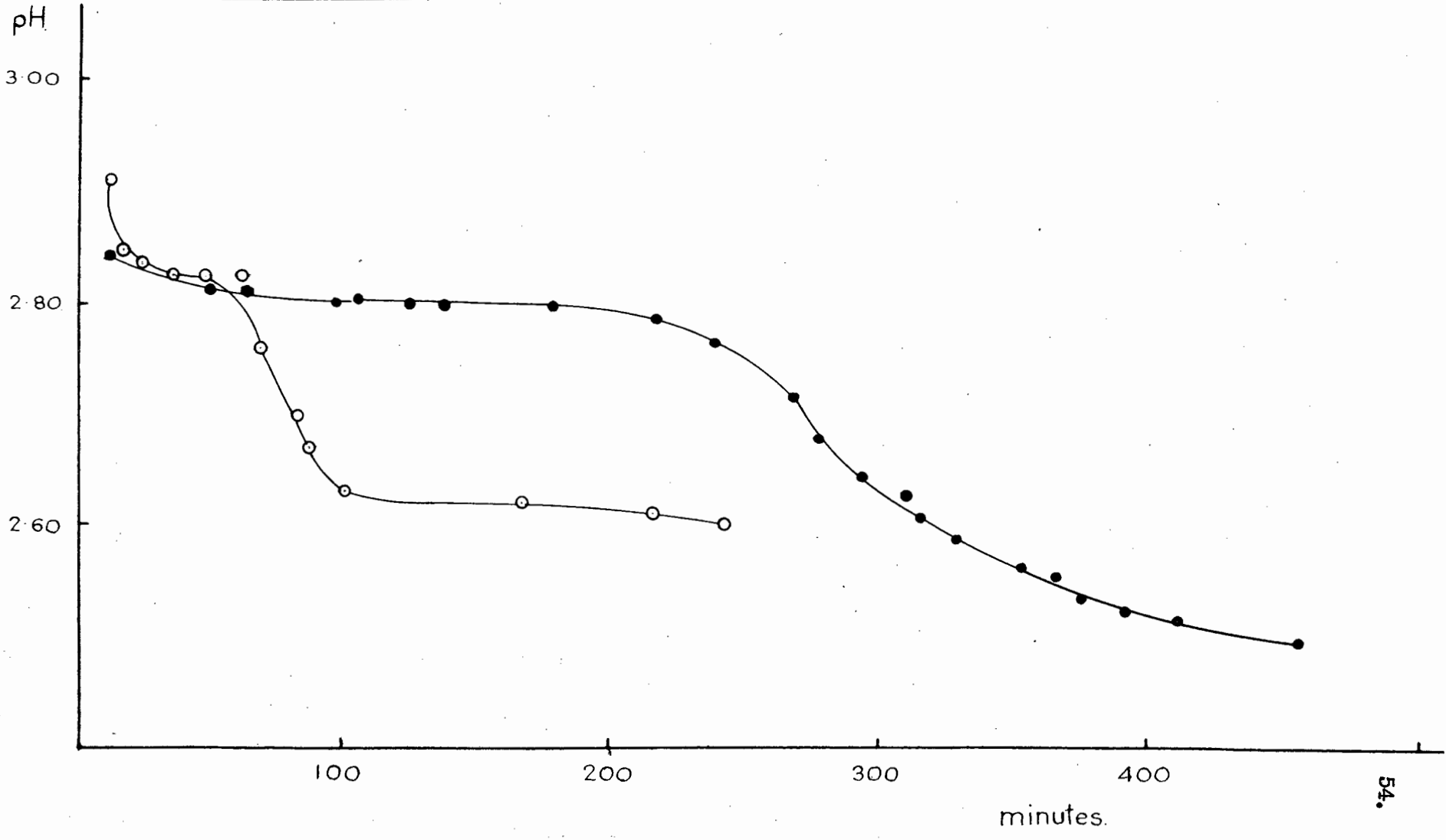
minimum by Volhard's method[98] showed that the chloroplatinate ion had been reduced completely to platinum and chloride, while titration with potassium iodate indicated that an appreciable amount of hydrazine remained unoxidised. The hydrazine titre, however, continued to decrease with time after this point was passed.

The rates of change of conductance with time depended on the initial concentration of the solutions, increasing with increasing concentration. The concentrations of the solutions investigated ranged from 8×10^{-4} mole/l. to 2×10^{-4} mole/l. below which it was impossible to measure the resistance as the process was complete before temperature equilibrium could be attained.

Measurements of the pH of the solutions during the reaction were made using a Pye Universal pH and millivoltmeter fitted with a glass electrode. The results obtained are given in Appendix II, 2.

The initial pH of the solutions was low (ca 3). There was a slight initial drop with time, then the pH remained virtually constant for a short while, dropped fairly rapidly, and then decreased very slowly over a considerable period of time. When a heavily platinised platinum strip was placed in the vessel to act as a catalyst and duplicate the conditions in the conductance cell as closely as possible, the rate of fall of pH was more rapid than in its absence. Under these conditions there appeared to be an approximate correspondence in time between the position of the

FIG. 12. DIHYDRAZINIUM CHLOROPLATINATE.
Variation of pH with Time.



resistance minimum and the end of the rapid fall of pH for solutions of comparable concentration, but when the strip was absent the reaction took several hours to run to completion (see fig. 12).

The conductance measurements were then repeated using the four-electrode A.C. potentiometric method with bright platinum electrodes, detailed results being given in Appendix II, 3. The resistances were again found to decrease with time, but at a much lower rate than before, and they continued to fall even more slowly when reduction was complete (fig. 13). The higher rate observed with the Daly and Smith cell is believed to be due to catalysis of the reduction reaction by the platinised platinum electrodes.

Measurements at temperatures other than 25°C were not carried out as the air-conditioning unit, essential for work at lower temperatures, was not available.

3.3 Discussion.

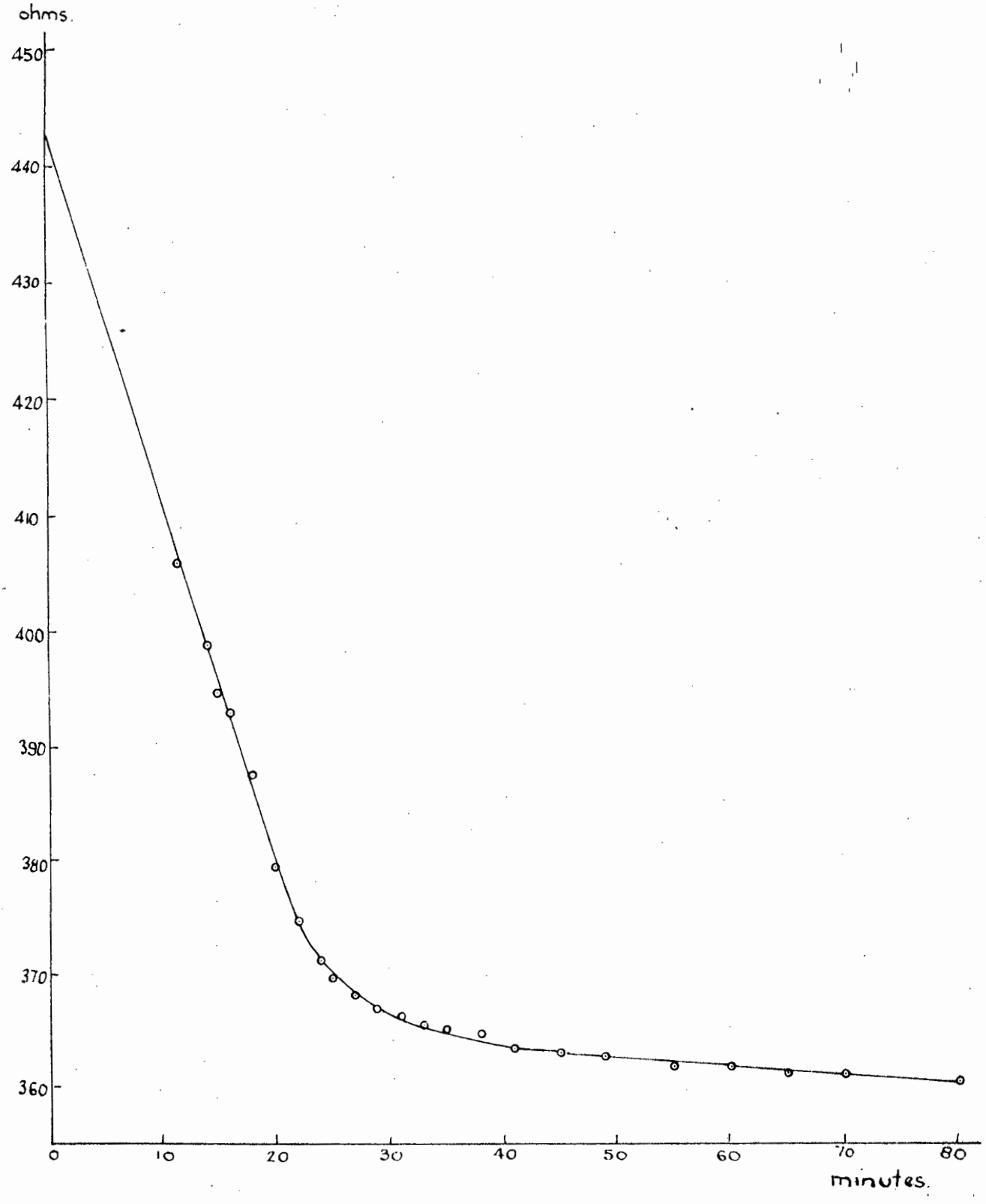
From the low initial pH of the solutions and the variation of the initial slopes of the resistance-time curves with concentration, it is concluded that on solution of the salt in water there is an almost immediate hydrolysis

$$N_2H_5^+ + H_2O \rightleftharpoons N_2H_4 + H_3O^+ \qquad \text{(II 3.1)}$$

which is followed by reduction of the chloroplatinate ion by the free hydrazine, possibly according to

FIG. 13. DIHYDRAZINIUM CHLOROPLATINATE.

Variation of Resistance with Time.
(measured on potentiometer).



$$N_2H_4 + PtCl_6^{2-} \rightarrow Pt + N_2 + 4H^+ + 6Cl^- \qquad (II\ 3.2a)$$

or $$2N_2H_4 + PtCl_6^{2-} \rightarrow Pt + N_2 + 2NH_3 + 2H^+ + 6Cl^- \qquad (II\ 3.2b)$$

This disturbs the equilibrium of reaction (II 3.1) as the hydrazine is oxidised, and results in the accumulation of oxonium ions in the solution, explaining the decrease in pH, and the Grotthus conduction which arises from the presence of these ions, together with the six chloride ions (limiting conductance 76.34) which replace each chloroplatinate ion (limiting conductance 119) is responsible for the increase in conductance.

Decomposition of hydrazine is also known to take place by the reaction

$$3N_2H_4 \rightarrow 4NH_3 + N_2 \qquad (II\ 3.3)$$

This reaction has been shown by Gutbier[71] to be catalysed by platinum black and colloidal platinum, both of which are present in this case. The ammonia produced by reactions (II 3.2b) and (II 3.3) should remove some oxonium ion from solution in accordance with

$$NH_3 + H_3O^+ \rightleftharpoons NH_4^+ + H_2O \qquad (II\ 3.4)$$

but it will be shown that the results are most satisfactorily interpreted by the assumption that, during the early stages at least, (II 3.2a) is the more important reaction, with (II 3.3) becoming significant only after the reduction is complete.

At this stage the reduction of hydrazine by (II 3.3) and consequent production of more oxonium ions by (II 3.1) should cause a further increase in the conductance of the solution and a fall in its pH. While the pH does indeed drop slightly, the resistance rises when the two-electrode Daly and Smith cell is used, but continues to fall steadily in the potentiometric cell. It is believed that this is due to the influence of electrode polarisation on the resistance in the former case, the potentiometer being unaffected by changes in the contact resistance of the current electrodes.

The relationships with concentration of the two rates of change of specific conductance $\frac{d\kappa}{dt}$ for the reduction period, and $\frac{d\kappa'}{dt}$ for the post-reduction period, were then investigated graphically.

The plot of log $\frac{d\kappa}{dt}$ against log (initial concentration) at 1000 c./sec. during the reduction of the chloroplatinate was found to be a straight line over the lower concentration range, and a virtually straight line of increased slope but with a slight curvature over the higher concentration range (fig. 14). The curve for 80 c./sec. lies below that for 1000 c./sec. and is almost parallel to it, but the curvature over the higher concentration range is slightly more marked.

FIG 14 DIHYRAZINIUM CHLOROPLATINATE.

Variation of Rate of Change of Specific Conductance with concentration at 25°C.

(logarithmic scale)

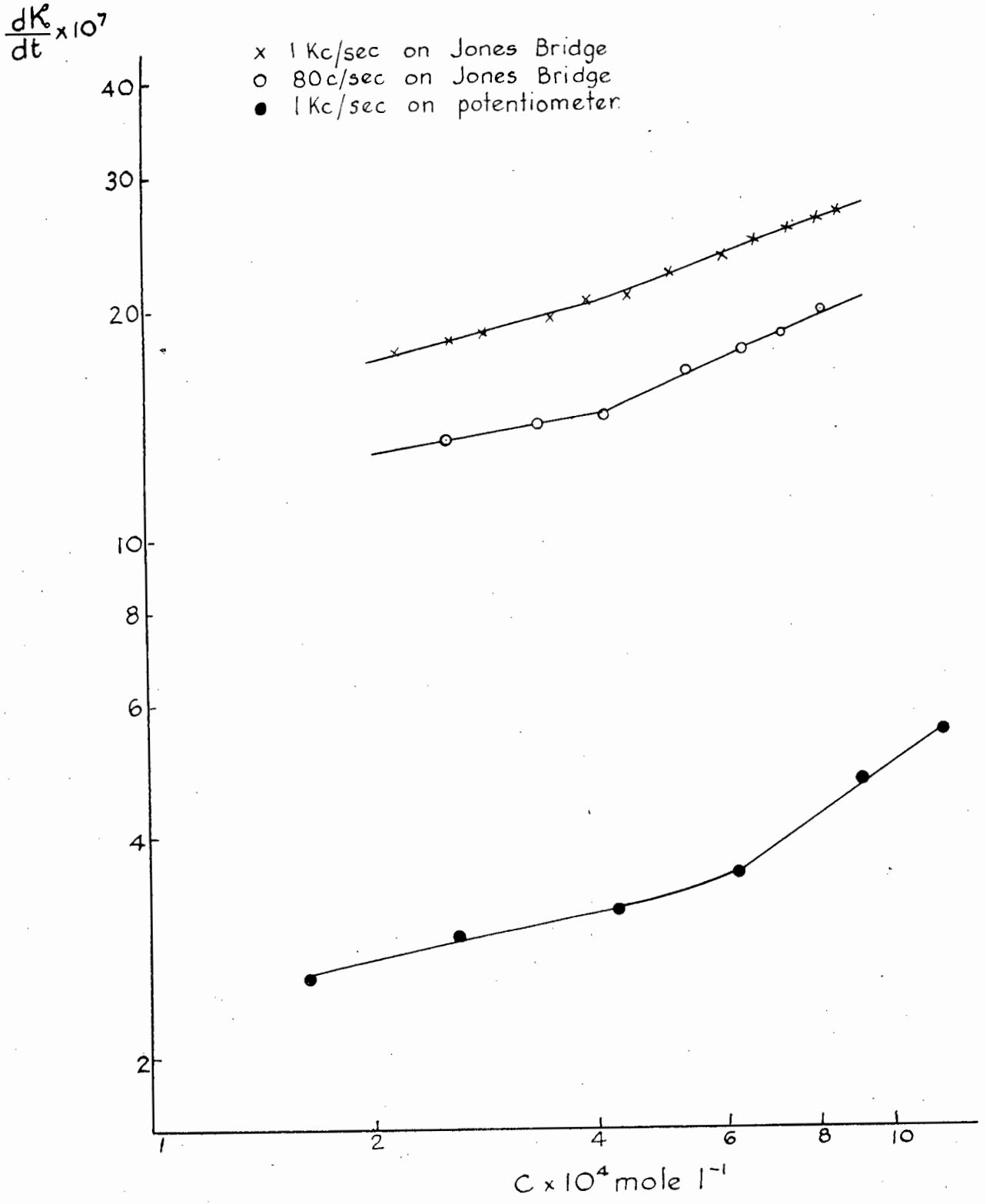


TABLE V.

Rates of change of specific conductance with time during and after chloroplatinate reduction measured on the Jones Bridge at 25°C.

(a) Frequency: 1000 c./sec.

$c \times 10^4$ mole l^{-1}	$\frac{dK}{dt} \times 10^6$ mho. cm.$^{-1}$ min.$^{-1}$	$\frac{dK'}{dt} \times 10^7$ mho cm.$^{-1}$ min.$^{-1}$
2.107	-	1.08
2.183	1.77	1.05
2.579	1.84	1.16
2.860	1.88	1.24
3.486	-	1.48
3.529	1.99	1.41
3.936	2.07	-
4.500	2.10	1.69
5.115	2.24	-
5.275	-	1.93
6.073	2.37	2.39
6.170	2.39	-
6.441	-	2.69
6.689	2.48	-
6.981	2.52	3.67
7.383	2.56	4.33
8.081	2.64	6.20
8.596	2.71	7.74

Results for the reactions at 20.69°C and 30.70°C are listed in Appendix II.4.

(b) Frequency: 80 c./sec.

$c \times 10^4$ mole l^{-1}	$\frac{dK}{dt} \times 10^6$ mho. cm.$^{-1}$ min.$^{-1}$	$\frac{dK'}{dt} \times 10^7$ mho cm.$^{-1}$ min.$^{-1}$
2.529	1.35	0.651
3.238	-	0.697
3.404	1.41	-
4.168	1.45	0.749
5.371	1.66	0.828
5.872	-	0.928
6.396	1.79	1.14
7.294	1.87	1.43
8.205	2.00	1.74

Since an appreciable amount of hydrazine remains unoxidised at the resistance minimum, it might be expected that reaction (II 3.2a) is predominant. The fact that the rate of change of conductance with time during reduction is a power function of concentration is to be expected if the reduction reaction is indeed of second order, as

$$\frac{d\kappa}{dt} = \frac{d^1/R}{dt} = \frac{d^1/R}{dR} \cdot \frac{dR}{dt} = -R^{-2}\frac{dR}{dt}, \quad \frac{dR}{dt} \text{ being the slope}$$

of the resistance-time curve.

The initial value of $\frac{d\kappa}{dt}$ is $-R_0^{-2}\frac{dR}{dt}$ where R_0 is the extrapolated value of the resistance at zero time. This initial value should be equal to kc^n where n is the order of reaction, and a plot of the logarithm of the initial value against log (initial concentration) should be a straight line of slope n.

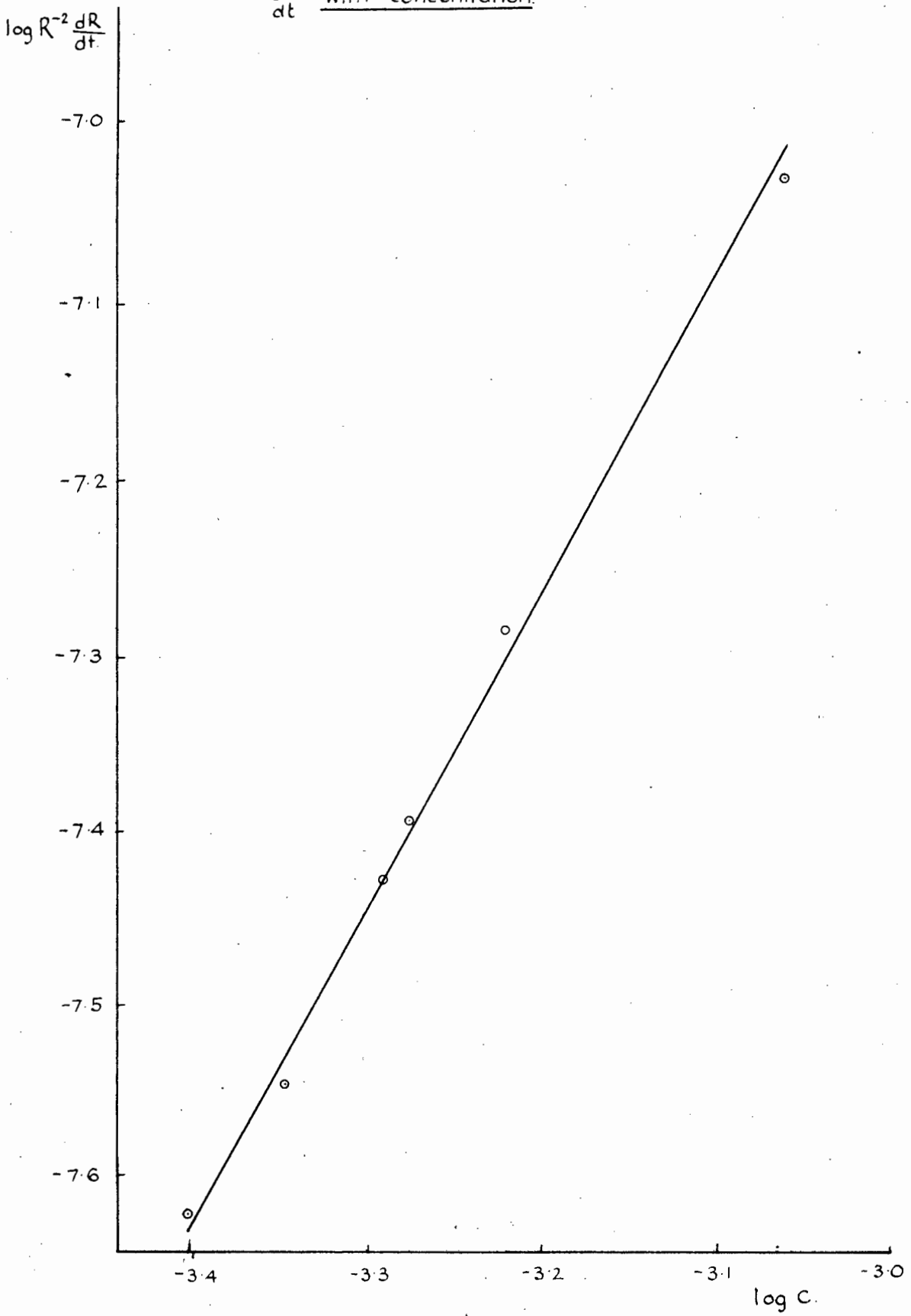
TABLE VI.

The initial values of $\frac{d\kappa}{dt}$ at 25°C.

c x 10^4 mole $l.^{-1}$	$\frac{dR}{dt}$ ohm $min.^{-1}$	$R_0^{-2}\frac{dR}{dt}$ x 10^8	log $R_0^{-2}\frac{dR}{dt}$	log C
3.936	3.25	2.370	-7.625	-3.405
4.500	3.27	2.843	-7.546	-3.347
5.115	3.59	3.764	-7.424	-3.291
5.275	3.63	4.024	-7.395	-3.278
6.170	3.96	5.209	-7.283	-3.210
8.596	4.06	9.383	-7.028	-3.066

FIG 15. DIHYDRAZINIUM CHLOROPLATINATE.

VARIATION OF INITIAL VALUE OF $\frac{dR}{dt}$ with concentration.



Values of $-R_o^{-2}\frac{dR}{dt}$ are listed in Table VI, and its logarithm plotted against log c in fig. 15, whence n is found to be 1.9.

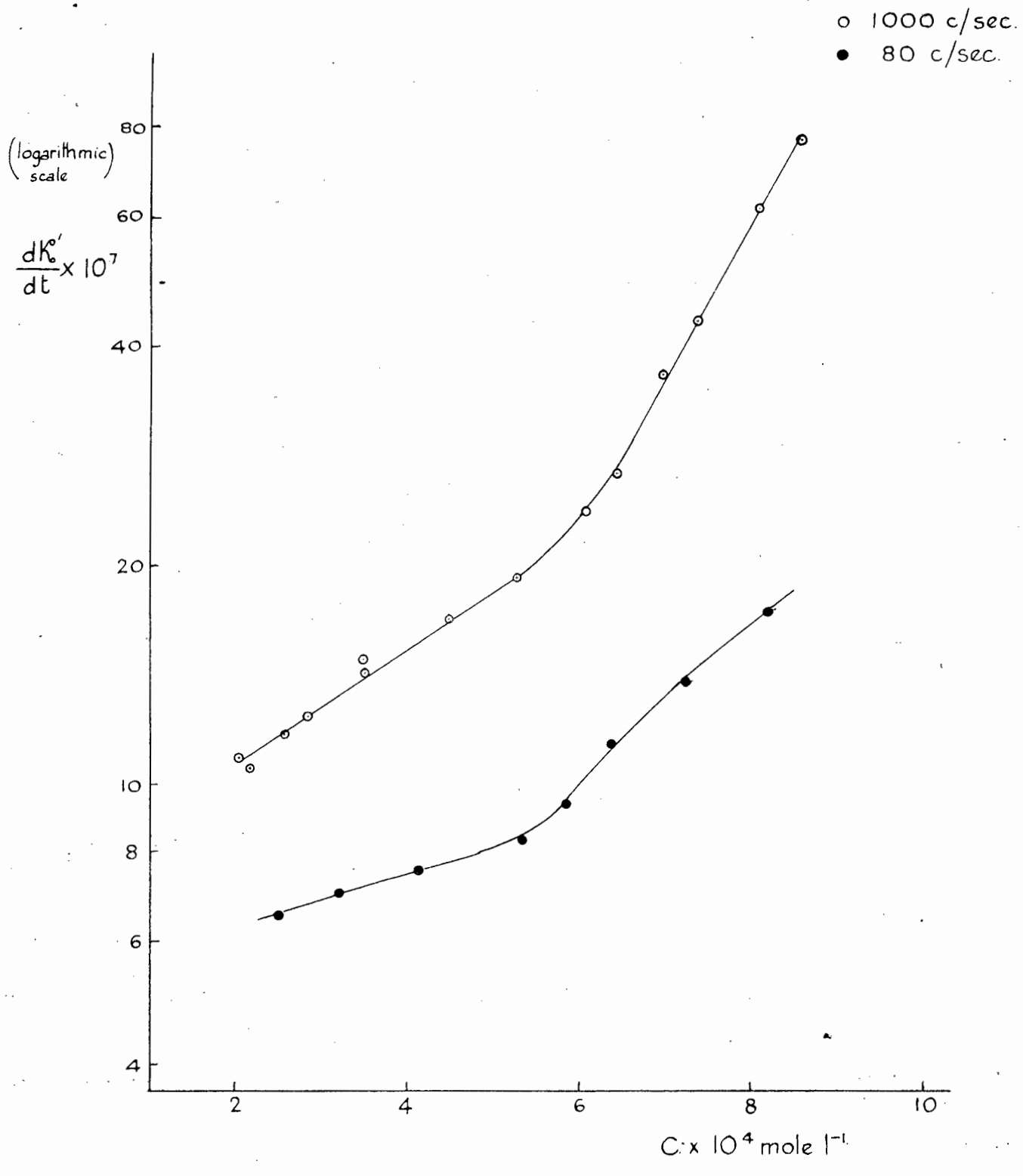
When $\log\left(-\frac{d\kappa'}{dt}\right)$ for the post-reduction period at 1000 c./sec. and 80 c./sec. was plotted against initial concentration, curves similar in appearance to those for the reduction period were obtained (fig. 16), but the curves lay further apart and the curvature over the higher concentration region at 80 c./sec. was much more marked. The slope over the higher concentration range was approximately twice that over the lower for both frequencies. When the reactions were carried out at 31.70°C and 20.69°C curves of the same shape were obtained.

As it would appear that $\frac{d\Lambda}{dt}$ and $\frac{d \log \kappa}{dt}$ are more closely related to the actual rate of reaction than $\frac{d\kappa}{dt}$, these quantities were also plotted as functions of the initial concentration, but the same general trends were observed and no more detailed information could be obtained from them. (These functions are listed in Appendix II.5).

On the basis of these results it is believed that when all the chloroplatinate ion has been reduced and renewal of the electrode surfaces by deposited platinum is no longer possible, electrode polarisation becomes more important and is responsible for the increase in resistance after the minimum. This is borne out by the fact that the 80 c./sec. curves in both the reduction and post-

FIG 16. DIHYDRAZINIUM CHLOROPLATINATE.

Variation of Rate of Change of Specific Conductance with Concentration after Reduction at 25°C.



reduction cases lie below those for 1000 c./sec., in accord with expectation as decreased frequency increases polarisation and a smaller area of the surface is catalytically active. The exponential form of the plots of $\log\left(-\frac{dK'}{dt}\right)$ against concentration is in conformity with all the expressions for excess polarisation resistance and capacitance at A.C. electrodes which have been derived in recent years. It was not possible, however, to compare the observed results with the equations of Jaffé[72], Remick[74], and Grahame[76] as no equipment for the measurement of polarisation resistance and capacitance was available.

Jaffé has derived equations for the conductance of solutions in which it was found necessary to define two types of ion - those of the first and second kinds - one of which carried the "permanent" current, and the other which could not cross the boundary at the electrode. It has been reported by Remick and McCormick[75], as well as by Jaffé and Chang[73], that as the concentration of a solution increases, the thickness of the electrode double layer increases. The change of slope of $\log \frac{dK'}{dt}$ when plotted against concentration is believed to be due to ion association, and it is therefore postulated that to cross the polarisation layer and be discharged at the electrode, the ion requires a certain activation energy. At higher concentrations the layer is thicker, and much of the kinetic energy of the ions is dissipated by the formation of ion pairs, and also by more frequent collisions which result only in transitory association.

sufficient energy to cross the double layer and be discharged at the

(ii) those which do not. When it is remembered that in the case of dihydrazinium chloroplatinate there is a platinum catalysed reaction which gives rise to adsorbable products, the continued increase of resistance may also be partially due to the poisoning of active sites on the electrode surface, which would no doubt tend to increase the polarisation layer still further. Decreased frequency also tends to increase the thickness of the electrode double layer, and almost

certainly has an effect on the energy of the ions as well, so it is not surprising to find the curve for 80 c./sec. lying below that for 1000 c./sec. The increased curvature of the plot of $\frac{dK'}{dt}$ at 80 c./sec. over the higher concentration range (fig. 16) may be due to increased ion association permitted by the lower frequency of oscillation.

To obtain experimental confirmation of the views expressed above, the reduction and decomposition reactions were followed at 20.69°C and 31.70°C, and apparent activation energies calculated from the rates. Some of the plots of $\log \frac{dK}{dt}$ against $\frac{1}{T}$ for the chloroplatinate reduction are shown in fig. 17, and for the decomposition period in fig. 18. The apparent activation energies obtained are given in Table VII. In the latter case it is easy to see that the apparent activation energies are indeed higher at lower frequencies and higher concentrations, but for the chloroplatinate reduction the

TABLE VII.

(a) The apparent activation energies for the reduction of the chloroplatinate ion.

$c \times 10^4$ mole l^{-1}	E_A at 1 Kc./s.	E_A at 80 c./s.
3.0	9.7	9.2
5.5	9.7	9.6
7.5	9.6	9.7

FIG 17. RATE OF CHANGE OF CONDUCTANCE DURING CHLOROPLATINATE REDUCTION AGAINST $\frac{1}{T}$.

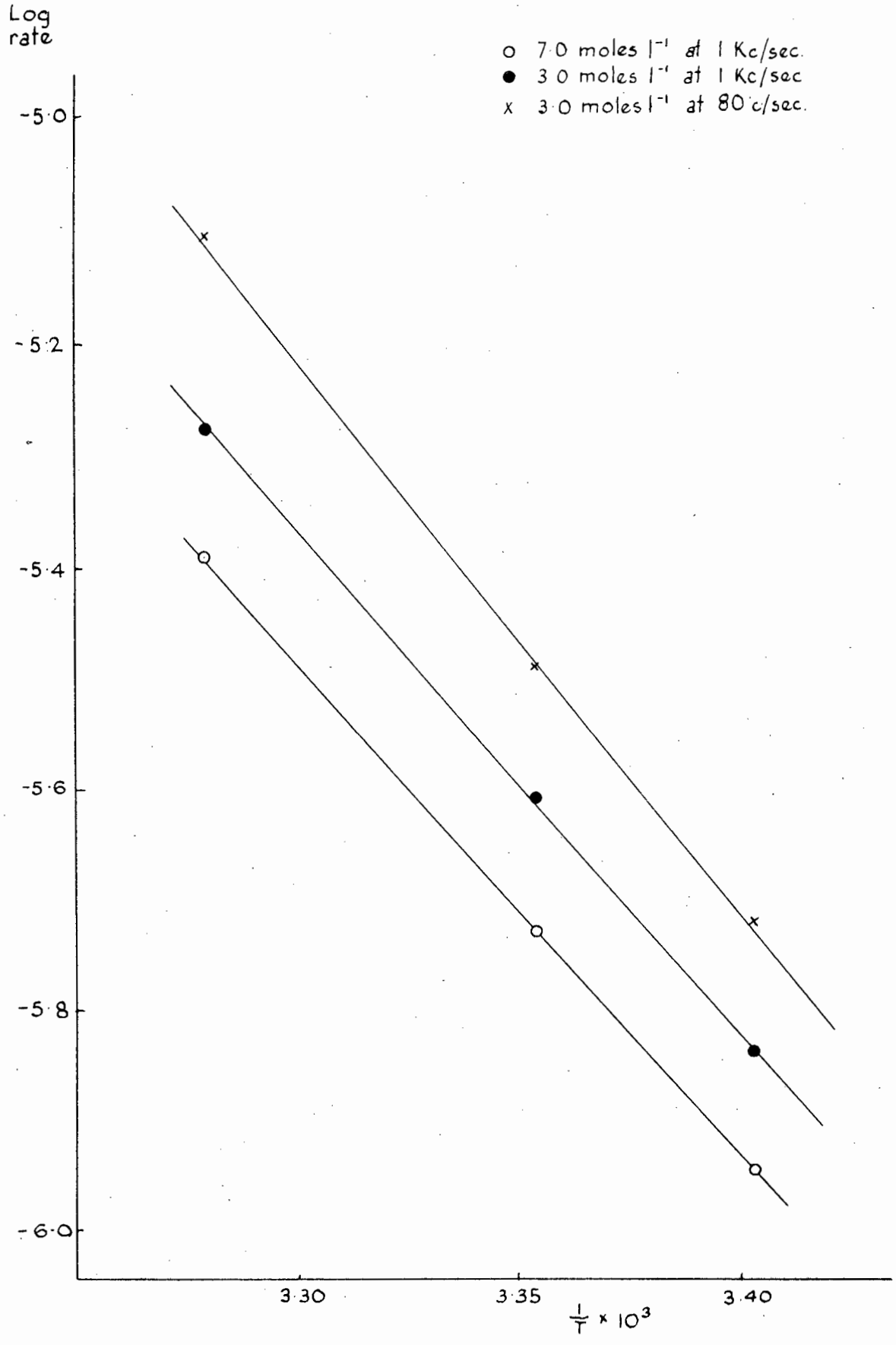
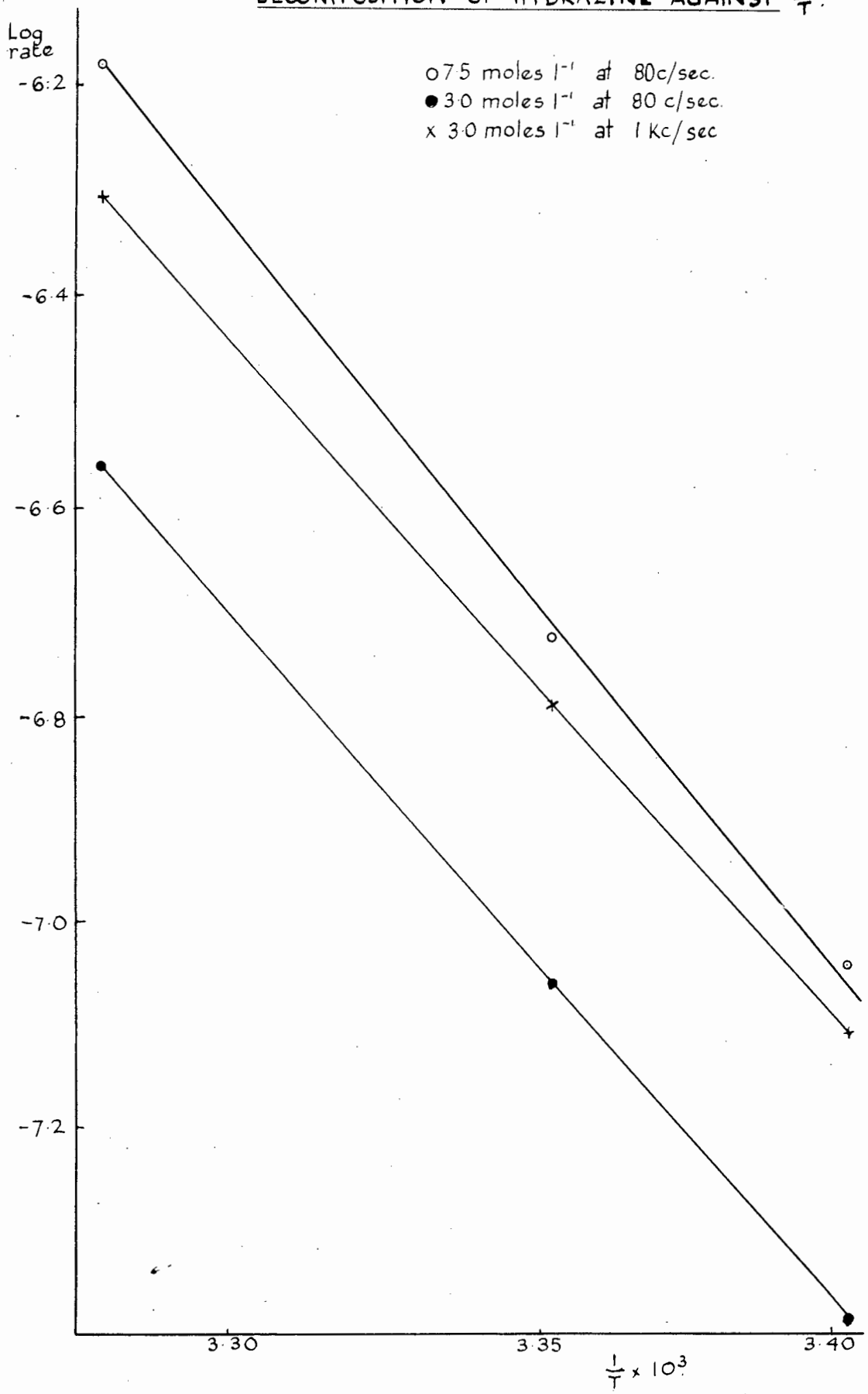


FIG. 18. RATE OF CHANGE OF CONDUCTANCE DURING DECOMPOSITION OF HYDRAZINE AGAINST $\frac{1}{T}$.



(b) The apparent activation energies for the decomposition of hydrazine.

C x 10^4 mole l^{-1}	E_A at 1 Kc./s.	E_A at 80 c./s.
3.0	12.8	13.1
5.0	13.0	13.4
7.5	13.7	14.7

values are closer together and no distinct trend is discernible. This is probably due to the constant resurfacing of the electrodes with fresh platinum, producing new active sites. It also seems likely that ions which can be chemisorbed can cross the electrode double layer because of their relatively high energy of adsorption[77].

TABLE VIII.

Rates of change of specific conductance with time during chloroplatinate reduction measured on the potentiometer at 25°C at a frequency of 1000 c./sec.

c x 10^4 mole l^{-1}	$\frac{d\kappa}{dt}$ x 10^7 mho cm.$^{-1}$ min.$^{-1}$
1.619	2.55
2.603	2.90
4.297	3.15
6.282	3.52
9.167	4.89
11.88	5.47

When measurements are made with the potentiometer, changes in the contact resistances of the cell do not affect the current-voltage ratio, and the shapes of the resistance-time curves are consequently similar to those of the pH-time graphs, no minimum being observed (fig. 13). As the rates of change of conductance with time are lower, this curve lies below the corresponding curve for the two-electrode system (fig. 14).

The foregoing appears to justify extrapolation of the reduction slopes of the resistance-time curves to zero time, and calculation of the limiting equivalent conductance from the values thus obtained. The values of the equivalent conductance at various concentrations are listed in Table IX. The plot of the equivalent conductance against the square root of the concentration obtained by the potentiometric method at 1000 c./sec. lies slightly above that found by the conventional two-electrode method, but both curves extrapolate almost to the same point (see fig. 20). The limiting equivalent conductances were found to be 119.6 and 119.0 respectively.

FIG 20 DIHYDRAZINIUM CHLOROPLATINATE

Equivalent Conductance.

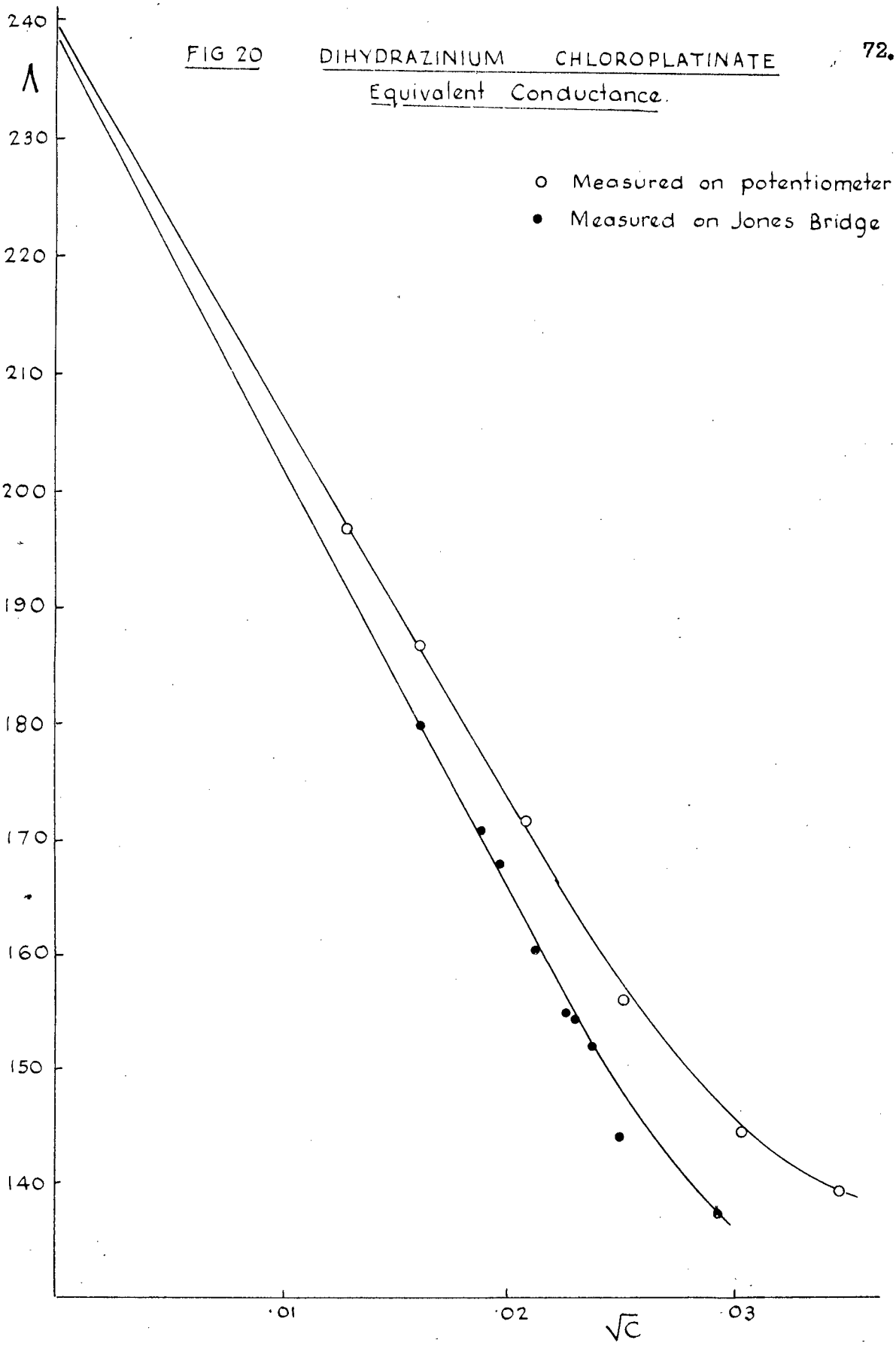


TABLE IX

The equivalent conductance of dihydrazinium chloroplatinate.

(a) Measured on Jones Bridge.

c x 10^4 mole l^{-1}	Specific conductance at zero time x 10^6 mho $cm.^{-1}$	Equivalent conductance mho $cm.^2$
2.579	5.998	179.9
3.529	7.787	170.7
3.936	8.539	167.8
4.500	9.323	160.3
5.115	10.24	154.9
5.275	10.53	154.4
5.675	11.15	152.0
6.170	11.47	143.8
8.596	15.20	136.8
24.26	32.92	105.0
39.08	48.30	95.61

(b) Measured on Potentiometer.

c x 10^4 mole l^{-1}	Specific conductance at zero time x 10^6 mho $cm.^{-1}$	Equivalent conductance mho $cm.^2$
1.619	3.182	196.5
2.603	4.857	186.6
4.297	7.383	171.8
6.282	9.794	155.9
9.167	13.22	144.2
11.88	16.54	139.1

4. The reduction of hydrazinium perchlorate and hydrazinium picrate.

Gilbert measured the conductances of solutions of hydrazinium picrate, perchlorate and trinitro-m-cresylate, and calculated values for the limiting conductance of the hydrazinium ion[27]. These were based on the picrate ion mobility of Thomas and Marum[78] (30.1) [which has been superseded in the literature by Daggett, Bair and Kraus' value (30.39)[79]], and on Gilbert's own measurements on potassium perchlorate, which differ from a more recently determined value by about 2%[80]. For these reasons, and because Gilbert's apparatus was not as sensitive as the Jones-type bridge which later came into general use, it was decided to repeat this work, using grey platinum electrodes with the two-electrode circuit, and finally bright platinum electrodes with the potentiometric circuit.

Hydrazine picrate and perchlorate were prepared by adding concentrated solutions of the pure acids slowly to 85% aqueous hydrazine solution in an ice bath. The crystals were filtered off, recrystallised once from ethyl alcohol, and in the case of the perchlorate, twice from conductivity water. Because of losses and handling dangers, the picrate was recrystallised once only from conductivity water. The salts were then dried in vacuo for several days and their compostion checked by hydrazine analysis. (Hydrazinium perchlorate, found N_2H_4: 24.2%, requires N_2H_4: 24.2%; hydrazinium picrate, found N_2H_4: 12.5%, requires N_2H_4: 12.3%).

Solutions varying in concentration from 4 x 10^{-4} molar to 5 x 10^{-3} molar were prepared in the "dry box", using previously warmed conductivity water to speed the attainment of temperature equilibrium in the thermostat, and their conductances measured by both techniques. For both salts the resistances were found to decrease with time, albeit very slowly, and equivalent conductances were calculated by the extrapolation procedure. These are given together with the rates of change of conductance of the perchlorate in Tables X and XI, and the Onsager limiting slopes for both salts are compared with those of Gilbert in Table XII.

TABLE X.

Hydrazinium perchlorate in water: Equivalent conductance and rate of change of specific conductance with time at 25°C.

(a) Measured on the Jones Bridge.

c x 10^4 mole l^{-1}	Specific conductance at zero time x 10^5 mho $cm.^{-1}$	Equivalent conductance mho $cm.^2$	$\frac{d\kappa}{dt}$ x 10^7 mho $cm.^{-1}$ $min.^{-1}$	$\frac{d\Lambda}{dt}$ x 10^4 mho $cm.^2$ $min.^{-1}$
7.699	9.499	123.4	9.78	12.70
7.916	9.759	123.3	9.39	11.86
10.73	13.19	122.9	9.67	9.012
13.34	16.54	122.5	11.42	8.561
17.69	21.53	121.7	10.66	6.033
20.39	24.72	121.4	11.78	5.777
24.88	30.04	120.7	7.56	3.064
37.84	45.26	119.6	5.63	1.488

(b) Measurement on the Potentiometer.

$c \times 10^4$ mole l^{-1}	Specific conductance at zero time $\times 10^5$ mho $cm.^{-1}$	Equivalent conductance mho $cm.^2$	$\frac{d\kappa}{dt} \times 10^7$ mho $cm.^{-1}$ $min.^{-1}$	$\frac{d\Lambda}{dt} \times 10^4$ mho $cm.^2$ $min.^{-1}$
4.859	6.049	124.4	0.762	1.568
8.075	9.971	123.5	0.530	0.6564
15.53	18.99	122.3	0.393	0.2530
23.51	28.48	121.1	0.323	0.1374
30.18	36.35	120.5	0.213	0.07058
42.51	50.79	119.5	0.208	0.04893
53.65	63.56	118.5	0.136	0.02535

Note: $\frac{d \log \kappa}{dt}$ at these concentrations is listed in Appendix II.6.

The resistances of solutions of both hydrazinium picrate and hydrazinium perchlorate decreased continuously with time and no minimum was observed. One series of measurements on the perchlorate was continued for several days, analysis at the end of this period indicating the presence of chlorate ions.

The measurements were repeated with the potentiometer, and substantially the same results obtained, although once again the plot of the equivalent conductance against the square root of the concentration found by this method lay above those determined by the two-electrode system (figs. 21 and 22).

FIG 21. HYDRAZINIUM PERCHLORATE

Equivalent Conductance.

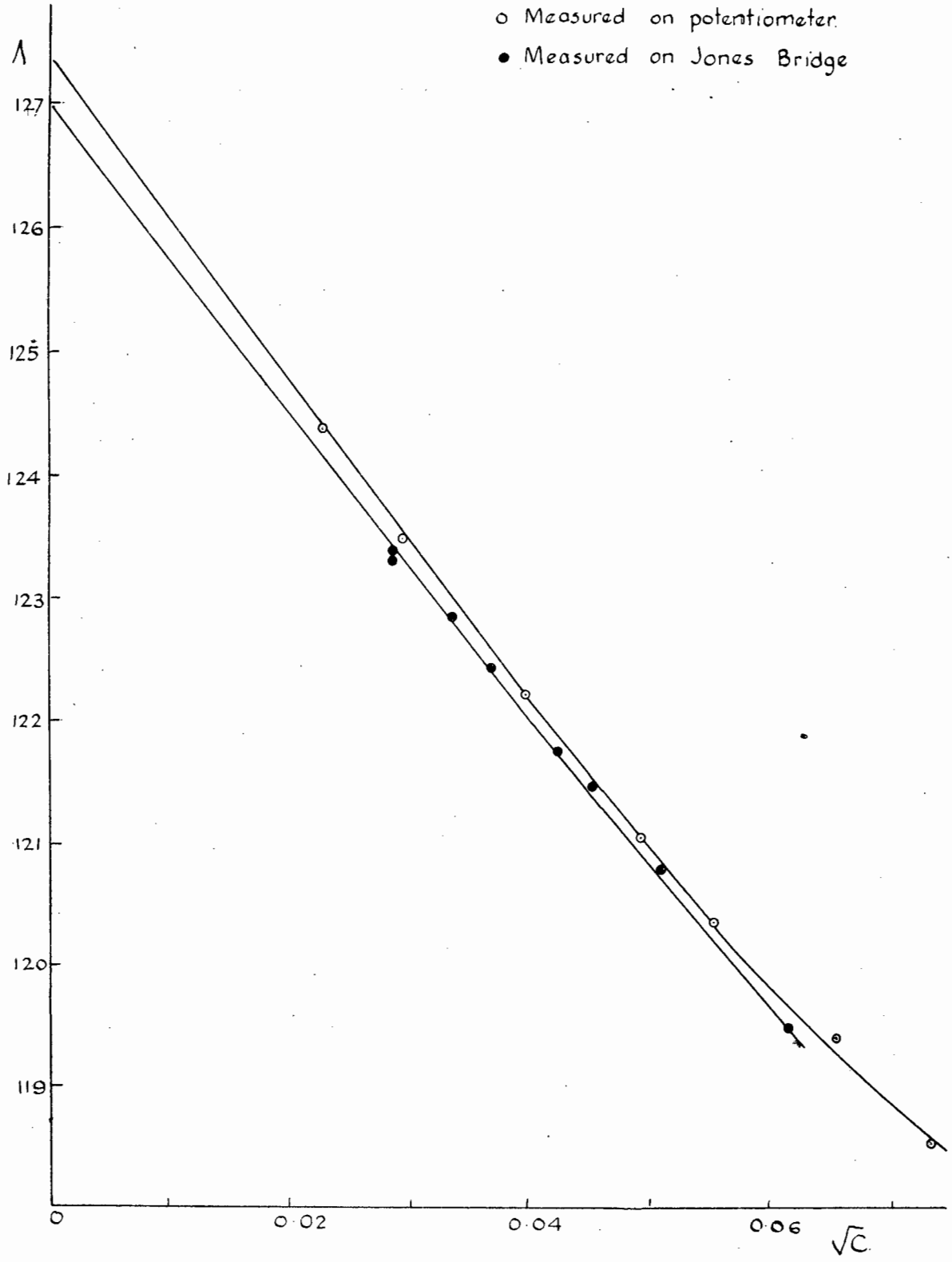


TABLE XI.

The equivalent conductance of hydrazinium picrate in water at 25°C.

(a) Measured on the Jones Bridge.

c x 10^4 mole l^{-1}	Specific conductance at zero time x 10^4 mho $cm.^{-1}$	Equivalent conductance mho $cm.^2$
4.116	0.3638	88.38
6.732	0.5902	87.67
10.11	0.8788	86.92
13.81	1.193	86.36
19.27	1.651	85.68
23.97	2.043	85.22

(b) Measured on the Potentiometer.

c x 10^4 mole l^{-1}	Specific conductance at zero time x 10^4 mho $cm.^{-1}$	Equivalent conductance mho $cm.^2$
4.181	0.3708	88.68
4.694	0.4156	88.53
9.236	0.8094	87.64
13.70	1.189	86.79
21.00	1.805	85.98
27.42	2.345	85.54

As the picrate did not appear to be as pure as the perchlorate, examination of the results for this salt was not pursued beyond comparison of the limiting slope with that of Gilbert (see Table XII). The effect of concentration on the rate of change of conductance of the perchlorate was then investigated. As in the case of the

FIG 22. HYDRAZINIUM PICRATE.

Equivalent Conductance.

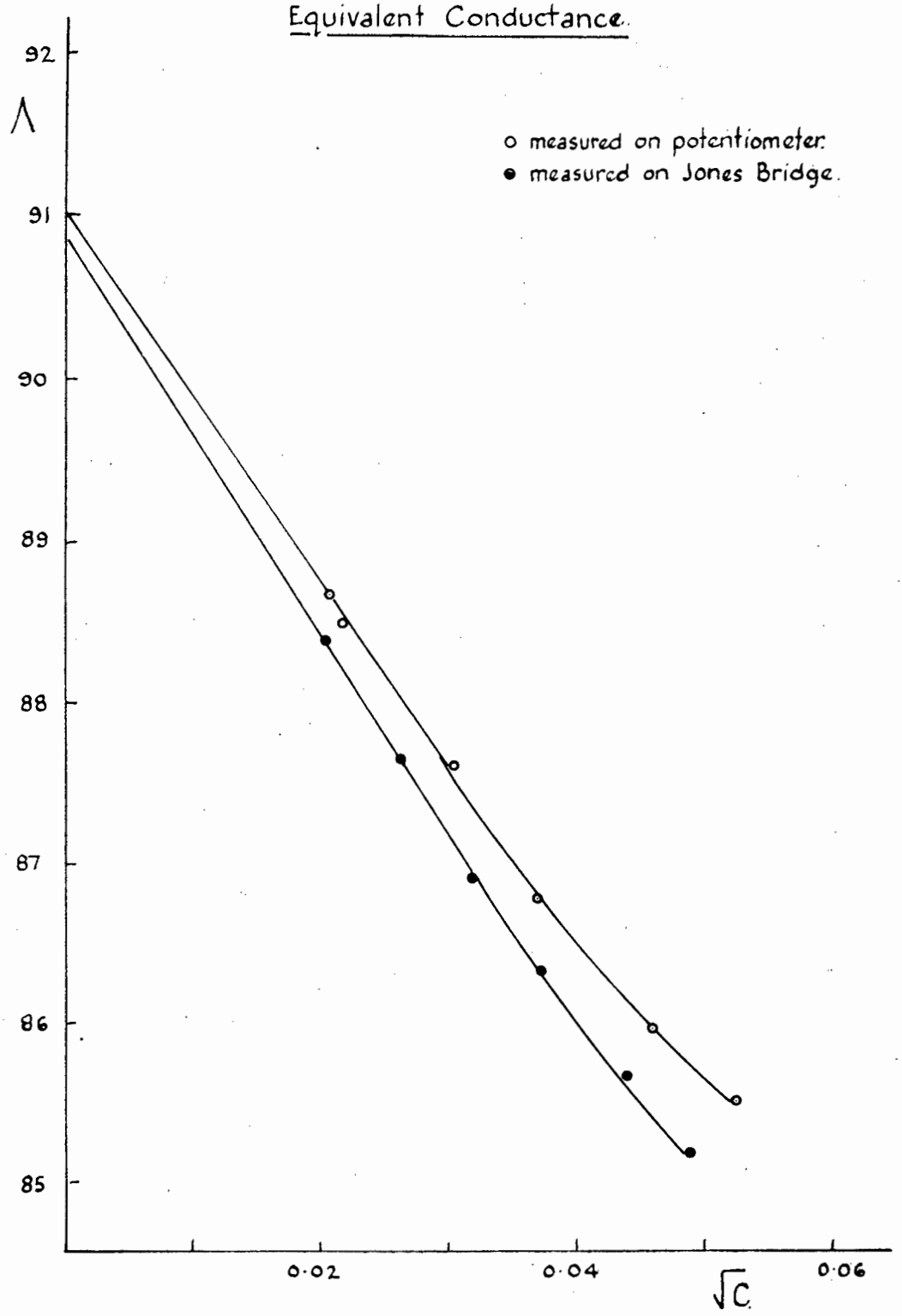


TABLE XII.

The Onsager limiting slopes for hydrazinium perchlorate and hydrazinium picrate.

	Hydrazinium Perchlorate	Hydrazinium Picrate
Gilbert	100	81
This work on Jones bridge	125	126
This work on potentiometer	131	112

chloroplatinate, all rates found by the potentiometric method were lower than rates measured by the two-electrode system and Jones bridge at the same concentration.

When $\log \frac{d\kappa}{dt}$ was plotted against log (initial concentration), the points at low concentration were so scattered that the shape of the curve in this region could not be determined with certainty (fig. 23), but the graphs of $\log \frac{d\Lambda}{dt}$ against log c obtained from measurements on both the Jones bridge and the potentiometer appeared to have the same general form, although the latter lay below the former (fig. 24).

5. The limiting conductances of the hydrazinium and chloroplatinate ions.

Extrapolation of the graphs of the equivalent conductance against the square root of the concentration provides values for the limiting equivalent conductance of hydrazinium

FIG. 23. HYDRAZINIUM PERCHLORATE.
Variation of Rate of Change of Specific Conductance with Concentration.
(logarithmic scale.)

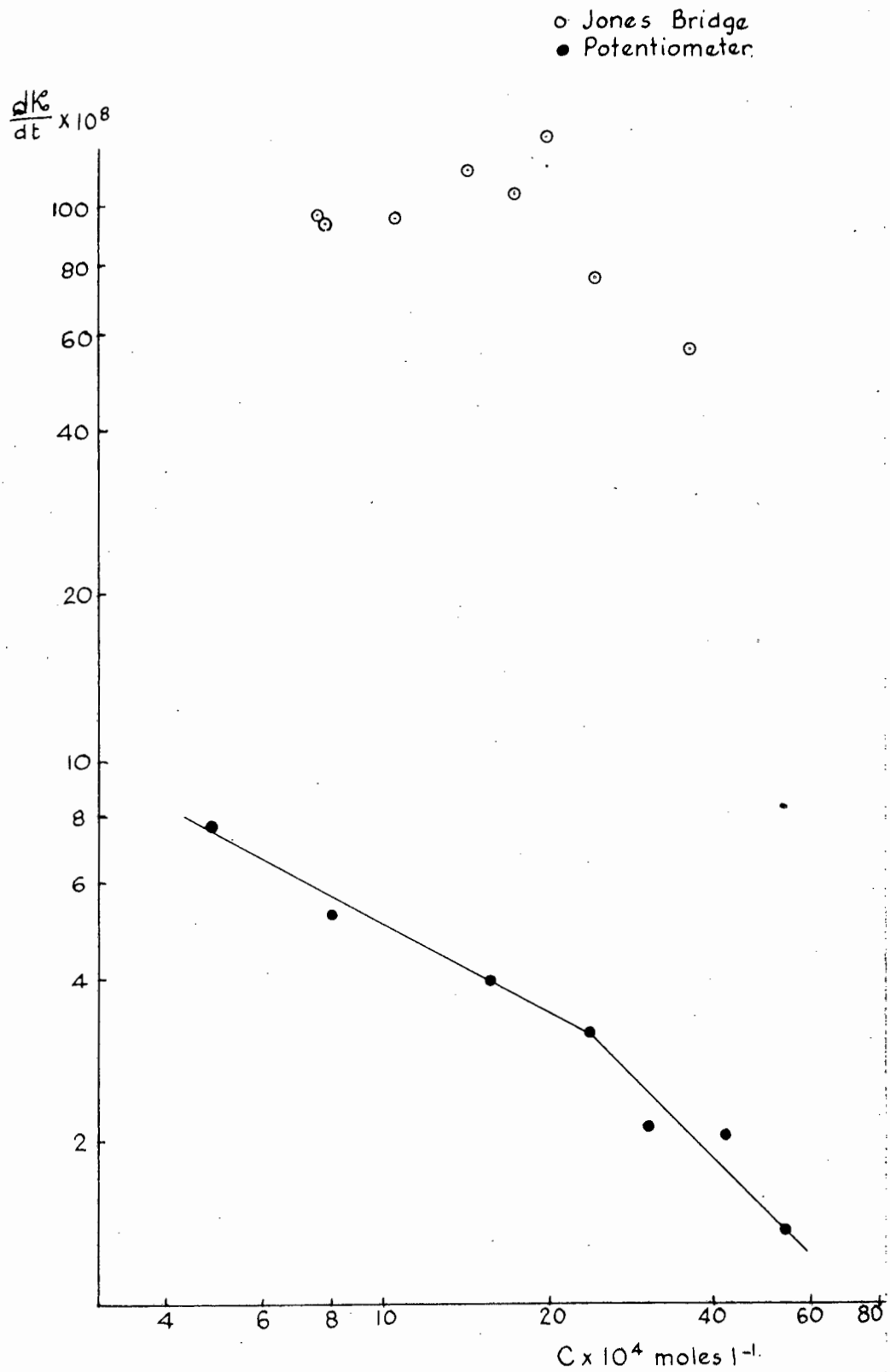
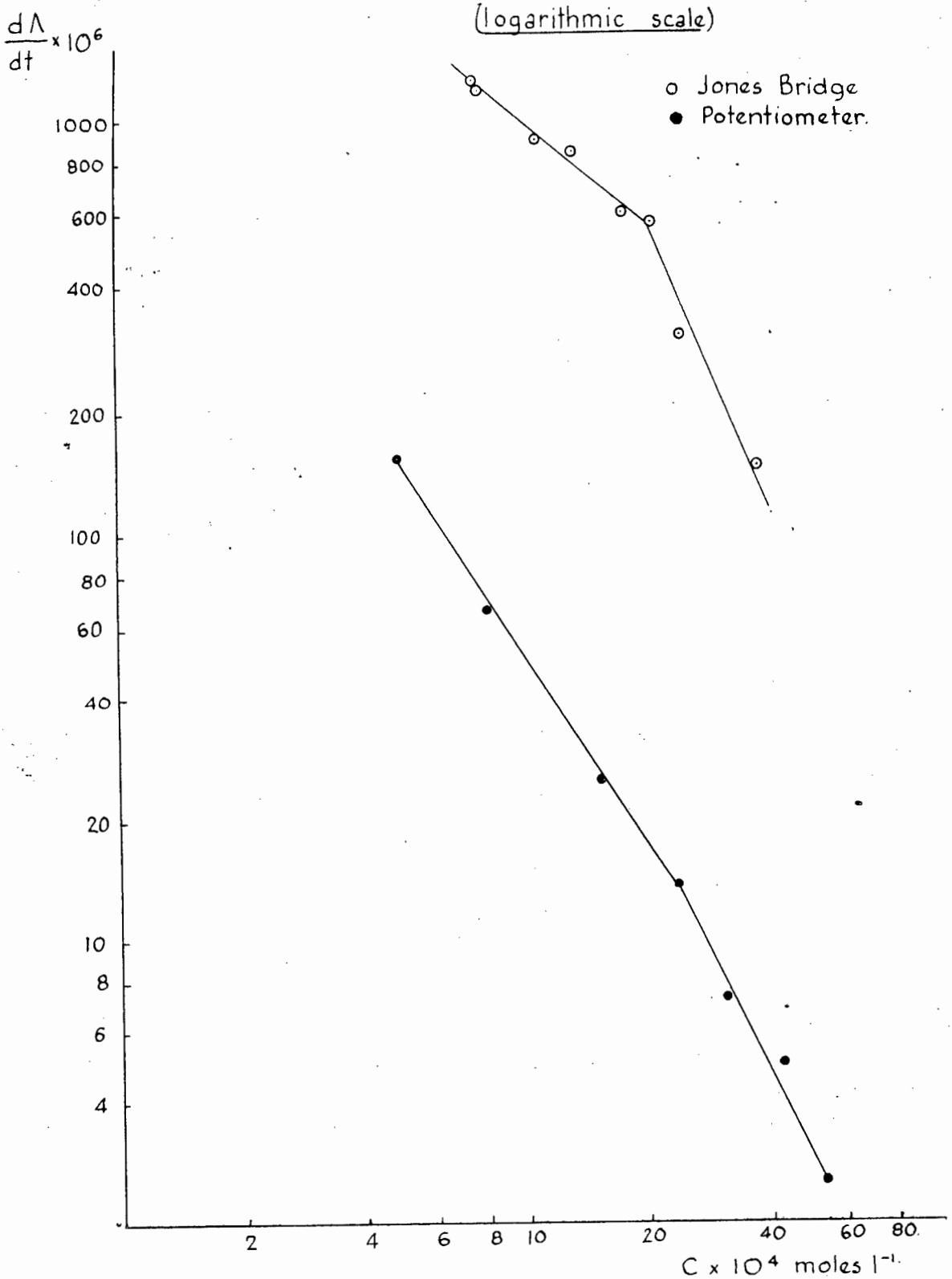


FIG 24. HYDRAZINIUM PERCHLORATE.

Variation of Rate of Change of Equivalent Conductance with Concentration at 25°C

(logarithmic scale)



perchlorate of 126.9 and 127.3 when measured on the Jones bridge and the potentiometer respectively. Gilbert found the limiting equivalent conductance to be 125.2, and, on subtraction of his own limiting conductance for the perchlorate ion (66.1), calculated the limiting equivalent conductance for the hydrazinium ion to be 59.1. His value for the perchlorate ion has been superseeded by that of Jones[80] (67.36), and use of this figure in conjunction with the results of the present work leads to a limiting equivalent conductance for the hydrazinium ion of 60.0 when measured on the potentiometer, while the value found by the two-electrode method is 59.6.

Gilbert obtained a limiting equivalent conductance for hydrazinium picrate of 88.5, and calculated the limiting conductance of the hydrazinium ion to be 58.4. This value was based on Thomas and Marum's[78] picrate ion conductance of 30.1.

Extrapolation to infinite dilution of equivalent conductances measured on the Jones bridge provided a limiting equivalent conductance of 90.9 for hydrazinium picrate, the value obtained from measurements made with the potentiometer being 91.0. Subtraction of Daggett, Bair and Kraus'[79] limiting conductance for the picrate ion (30.39) leads to hydrazinium ion conductances of 60.5 and 60.6 respectively. This value differs from that of Gilbert by 3.5%, but since there is some uncertainty as to the purity of the salt,

much reliance should not be placed on this figure. The date for these salts are summarised in the following table.

Limiting conductances of the hydrazinium ion.

	Gilbert		This work	
	Original	Revised	Jones Bridge	Potentiometer
Perchlorate	59.1	57.8	59.6	60.0
Picrate	58.4	58.1	60.5	60.6

Original values - those given by Gilbert.

Revised values - obtained from Gilbert's values for the salts with later values for the anions.

Using the appropriate limiting conductances for the hydrazinium ion, the limiting equivalent conductances for the chloroplatinate ion (viz.: $\frac{1}{2}\ PtCl_6^{2-}$) are found to be 59.5 (potentiometer) and 59.4 (Jones bridge). No literature values exist for comparison.

PART III.

CONDUCTANCE MEASUREMENTS ON SOLUTIONS OF HYDROGEN CHLORIDE IN ACETONE.

1. The Preparation and Handling of Anhydrous Acetone.

In recent years most workers have started with "Analar" or similar grade acetone, and the problem has become mainly one of desiccation. Everett and Rasmussen[48], however, purified their acetone through the bisulphite addition compound, kept it over potassium permanganate for several days and then fractionally distilled it to remove water. Their solvent had a specific conductance of 3.5×10^{-9} ohm^{-1} cm.$^{-1}$, and they criticised the use of strong dehydrating agents, stating that these led to condensation reactions.

Dippy, Jenkins and Page[81] found that "Analar" acetone was superior to bisulphite-purified acetone, and also examined the efficiency of several drying agents. Phosphorus pentoxide produced a brown colour and the mixture warmed up very rapidly, while anhydrous potassium carbonate, sodium sulphate and magnesium sulphate were not efficient. Their procedure was to keep the acetone for two weeks over finely ground fused calcium chloride to which a little potassium carbonate had been added, and then to fractionate it through a long column packed with glass beads. The specific conductances were found to be in the range $6 - 13 \times 10^{-8}$

ohm^{-1} $cm.^{-1}$. This method was also used by French and Roe[43] who obtained a specific conductance of 9.99×10^{-8} ohm^{-1} $cm.^{-1}$ at 25°C.

Walden, Ulich and Busch[30] obtained a solvent of specific conductance 6×10^{-8} ohm^{-1} $cm.^{-1}$ by first distilling Kahlbaum bisulphite-purified acetone and shaking it with potassium carbonate. It was then fractionated and stored in a special container. When anhydrous copper sulphate was used instead of potassium carbonate, the specific conductance of the product was 1.0×10^{-7} ohm^{-1} $cm.^{-1}$, but Daly and Smith refluxed acetone over copper sulphate and fractionally distilled it from the fresh anhydrous salt, obtaining a value of 6×10^{-8} ohm^{-1} $cm.^{-1}$.

A superior grade of acetone which had a specific conductance of about 10^{-10} ohm^{-1} $cm.^{-1}$ was prepared by Lannung[32]. Merck "pro analysi" acetone was shaken for one day with previously dried potassium carbonate, and then vacuum distilled from fresh potassium carbonate in an all glass apparatus. The fractionating column was 1.25 metres high and packed with small pieces of glass tubing. Lannung criticised the use of calcium chloride as a dessicant as it forms an addition compound with acetone, and stated that potassium carbonate drying followed by simple distillation leaves 0.15% water which can only be removed by efficient fractionation.

Reynolds and Kraus[33] prepared anhydrous acetone by shaking the liquid with calcium chloride for several days, after which it was

twice distilled from activated alumina. Their acetone had a specific conductance of 1 - 2 x 10^{-9} ohm^{-1} $cm.^{-1}$, and they deplored the use of non-aqueous solvents of such quality as to require solvent corrections.

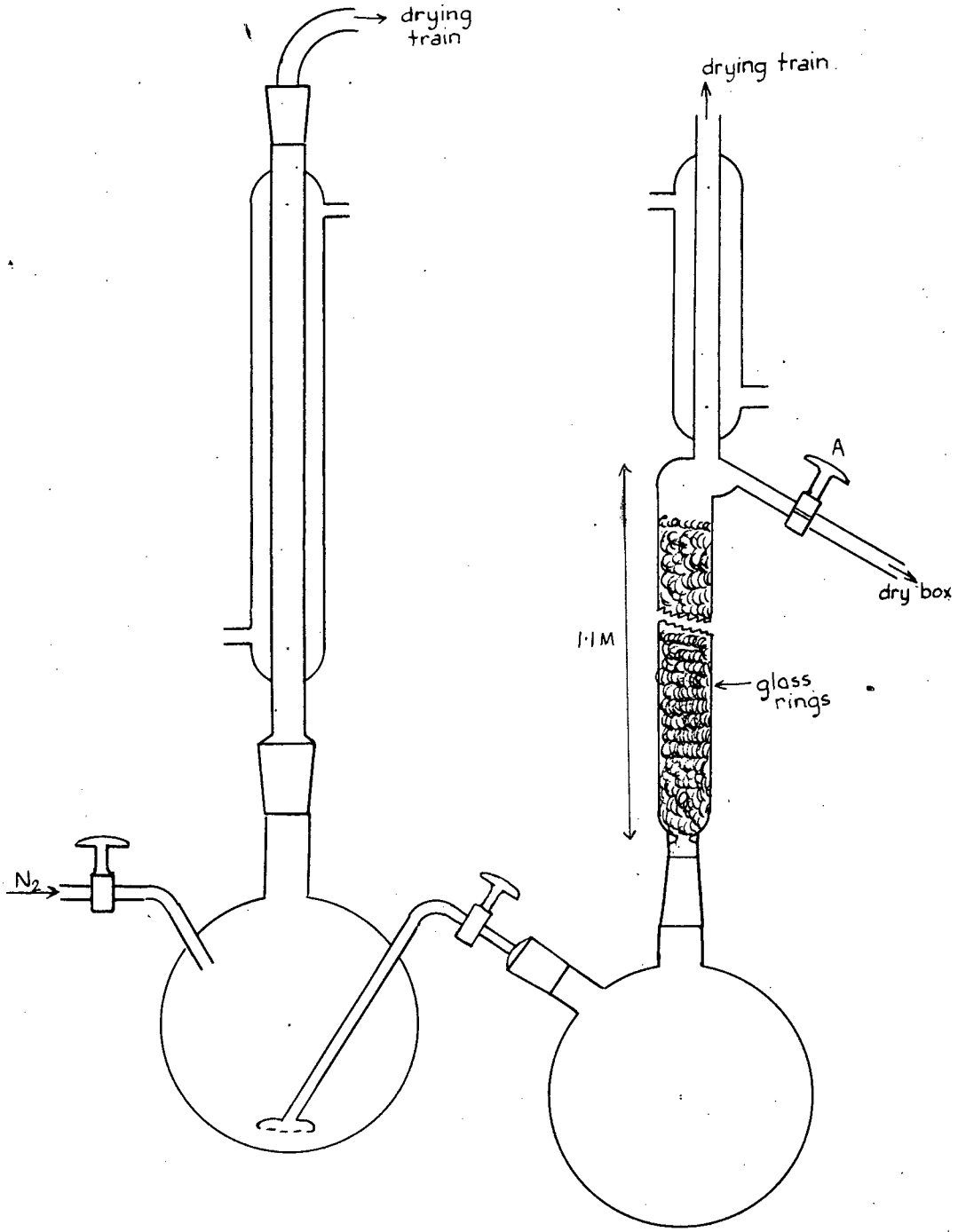
Dippy and Hughes[37] modified this procedure. "Analar" acetone was shaken with calcium chloride for four days, rapidly filtered, and refluxed from baked-out alumina for two to three hours. After being left in the dark for seven to ten days, it was rapidly filtered on to fresh alumina, refluxed again, filtered and finally fractionated. The specific conductance of this acetone was 8 x 10^{-9} ohm^{-1} $cm.^{-1}$. Dippy and Hughes obtained consistent results with batches of acetone which they considered to be of Grade I quality. The specific conductances of this acetone varied between 2.08 x 10^{-8} ohm^{-1} $cm.^{-1}$ and 2.36 x 10^{-8} ohm^{-1} $cm.^{-1}$, and they concluded that a moderate solvent correction was permissible, but that large divergences in solvent quality must be avoided.

The self condensation of acetone to mesityl oxide is catalysed by activated alumina, but the contaminants produced by the reaction should be removed by fractional distillation, and in spite of the wastage inherent in the alumina method, this appeared to be the most convenient and reliable way in which to prepare acetone of high quality.

"Analar" acetone was shaken with anhydrous "Analar" calcium chloride for three days and rapidly filtered on to Spence type A alumina pellets which had been activated by heating at 160°C. The acetone was then refluxed for about three hours in the dark, allowed to stand for twelve hours and decanted into the reflux flask of the apparatus shown in fig. 25. It was again refluxed from fresh alumina and allowed to stand, this time for twenty-four hours, after which the flask was connected to the dry nitrogen line, and the liquid blown over on to baked-out glass beads in the distilling flask, without coming into contact with the atmosphere. It was then refluxed for about half-an-hour in the 1.1 metre fractionating column which was packed with short pieces of glass tubing, after which the capillary tap A (fig. 25) was opened enough to permit a slow drip of acetone. The stillhead and reflux condenser were so designed that most of the liquid returned to the distilling flask, and all ground glass joints and stopcocks were lubricated with Eimer and Amend "Nonaq" grease. The suitability of this grease was tested by inverting a small "Quickfit" flask filled with acetone. The stopper of this flask was lubricated with "Nonaq", and no signs of leakage were apparent after six weeks.

The distilled acetone passed directly into a dry box which contained two dishes of magnesium perchlorate. Before any containers inside were opened, the box was gassed out for half an hour with nitrogen, which had been dried by passing through tubes containing

Fig. 25. ACETONE STILL.



silica gel and phosphorus pentoxide. Apparatus was handled through neoprene gloves. All solutions were prepared, and the conductance cells filled and sealed in the drybox, which was maintained at a slight positive pressure of nitrogen.

The acetone was collected in a specially designed receiver (fig. 25a) kept in the drybox, the distillation being carried out as far as possible in the dark. The detachable flasks and other small glassware were baked out in an oven at 140°C, and the condensers and calibrated flasks washed with distilled acetone and gassed out with dry nitrogen before use.

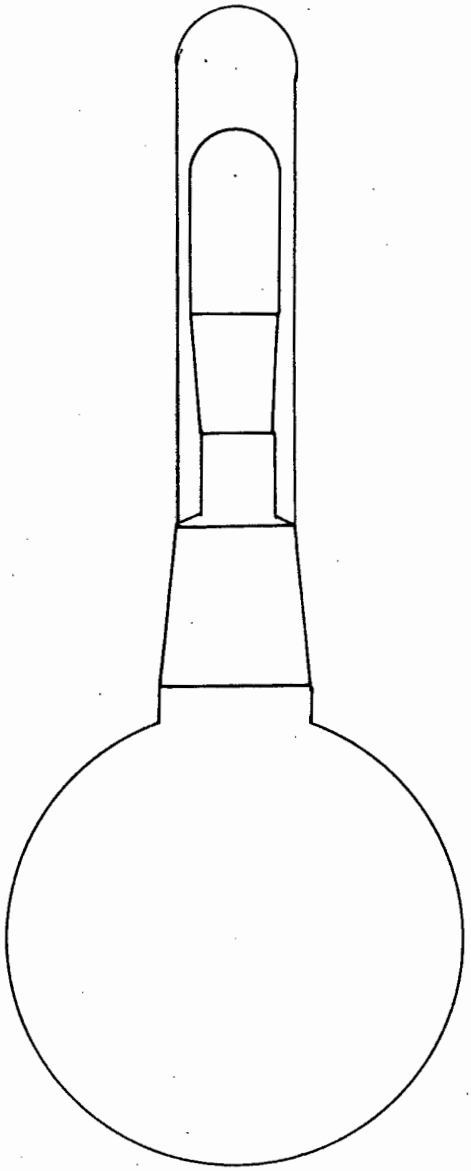
Measurements of the conductances of solutions of potassium iodide in acetone were made to check the quality of the solvent used. The conductances are given in Table XIII, and compared with the results of Reynolds and Kraus[33] and Dippy and Hughes[37] (for Grade I acetone) in fig. 26.

TABLE XIII.

The conductance of potassium iodide in acetone.

c x 10^4 mole l^{-1}	Specific conductance at x 10^4 mho cm.$^{-1}$	Equivalent conductance mho cm.^{2}
6.400	1.0835	169.3
12.82	2.0230	157.8
16.64	2.5498	153.2

Fig 25a. ACETONE RECEIVER.



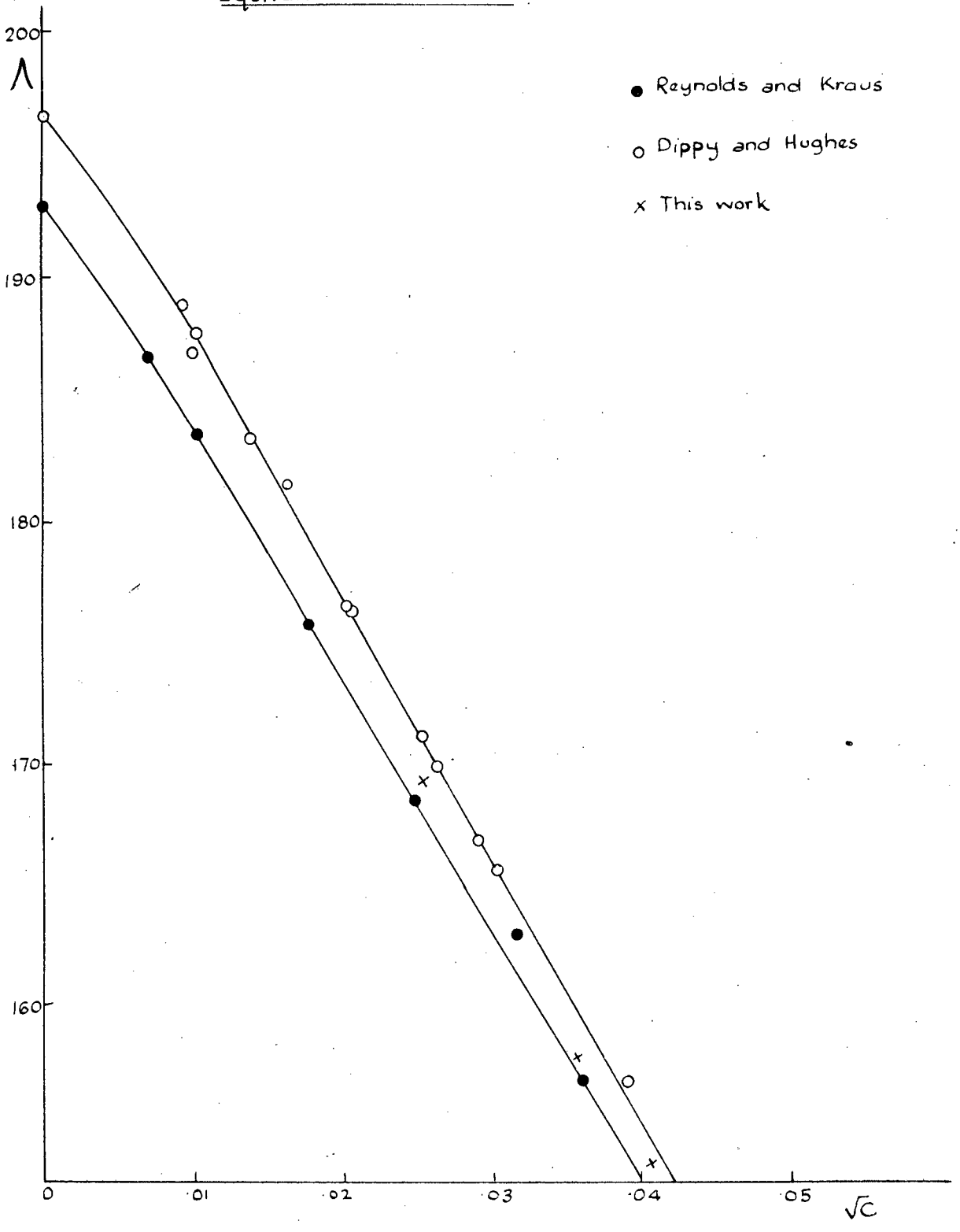
2. Determination of the Moisture Content of Acetone.

Mysels[59] used the conductances of saturated solutions of sodium, potassium, caesium and rubidium chlorides, and caesium and potassium fluorides, to determine the moisture content of acetone, and expressed the view that it is not possible to obtain a water content of less than 0.05%.

As suitable modified reagents extending the applicability of the Karl Fischer titration to the determination of moisture in ketones had been described[83], Dippy and Hughes[37] used the potentiometric Karl Fischer titration to determine the water content of their acetone, and it was decided to follow a similar procedure in the present work. Most so-called "moisture proof" burettes and "Karl Fischer Apparatus" commercially available are sealed with rubber gaskets and incorporate rubber tubing which may allow considerable ingress of moisture[84]. In view of the hygroscopic nature of acetone, an all glass and polythene apparatus was designed to enable satisfactory performance of these titrations. This apparatus is shown in fig. 27.

A special weight pipette (fig. 28a) was weighed, filled with acetone in the drybox, weighed again, and fitted on to the titration vessel. The apparatus was then gassed out with dry nitrogen, after which the sample was allowed to run into the titration vessel, mixed with excess pyridine from the second burette, and titrated with the reagent. The end point was determined electrometrically using the circuit shown in fig. 28b. The reagent used consisted

FIG 26 POTASSIUM IODIDE IN ACETONE
Equivalent Conductance.



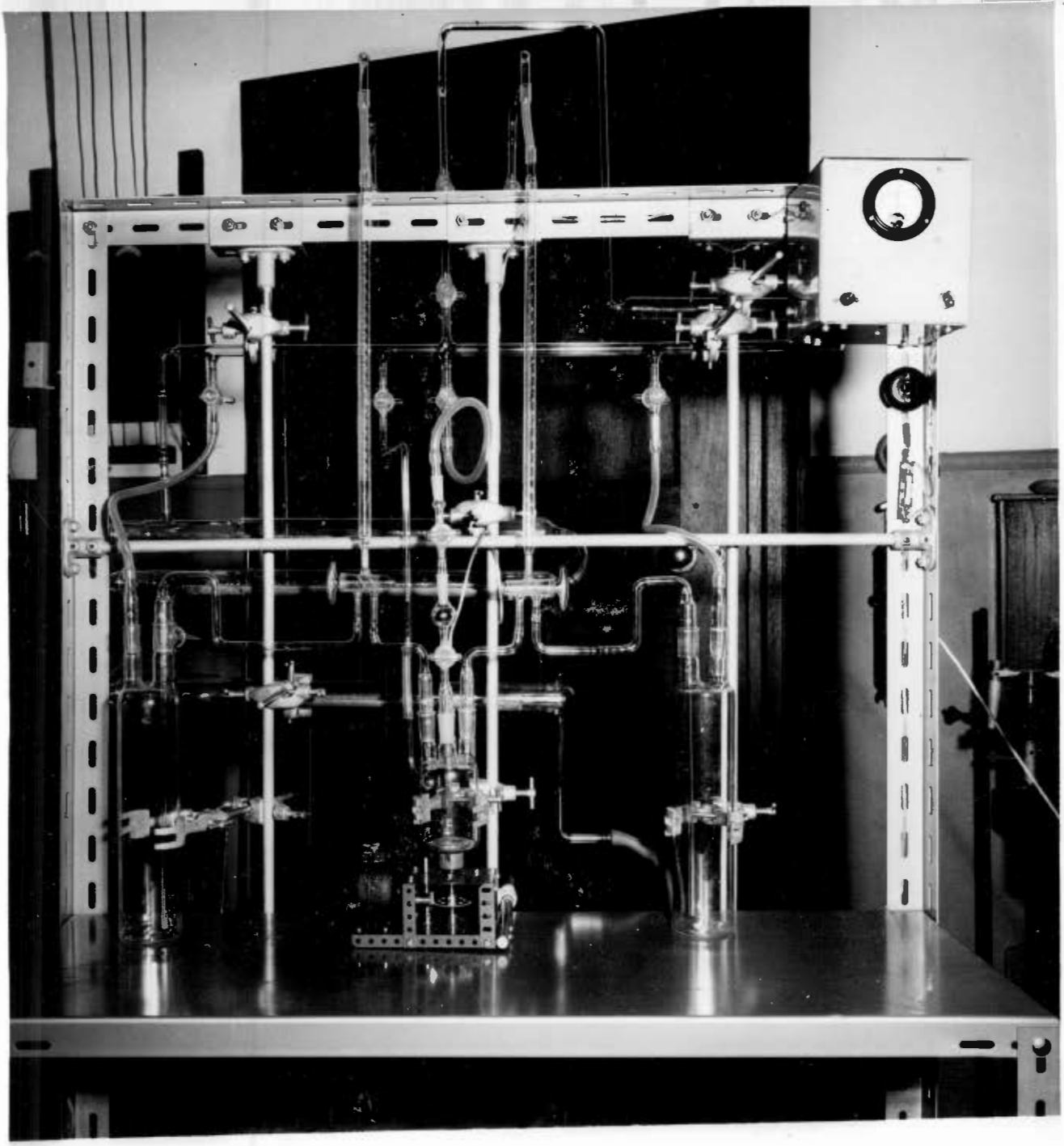


FIG. 27. KARL FISCHER APPARATUS.

FIG. 28a WEIGHT PIPETTE.

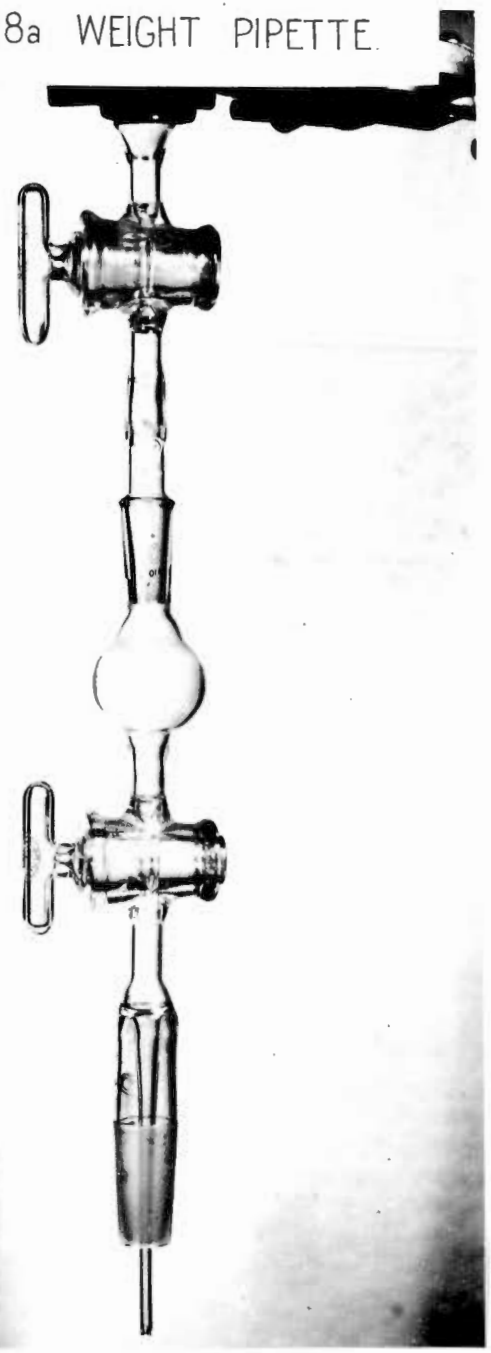
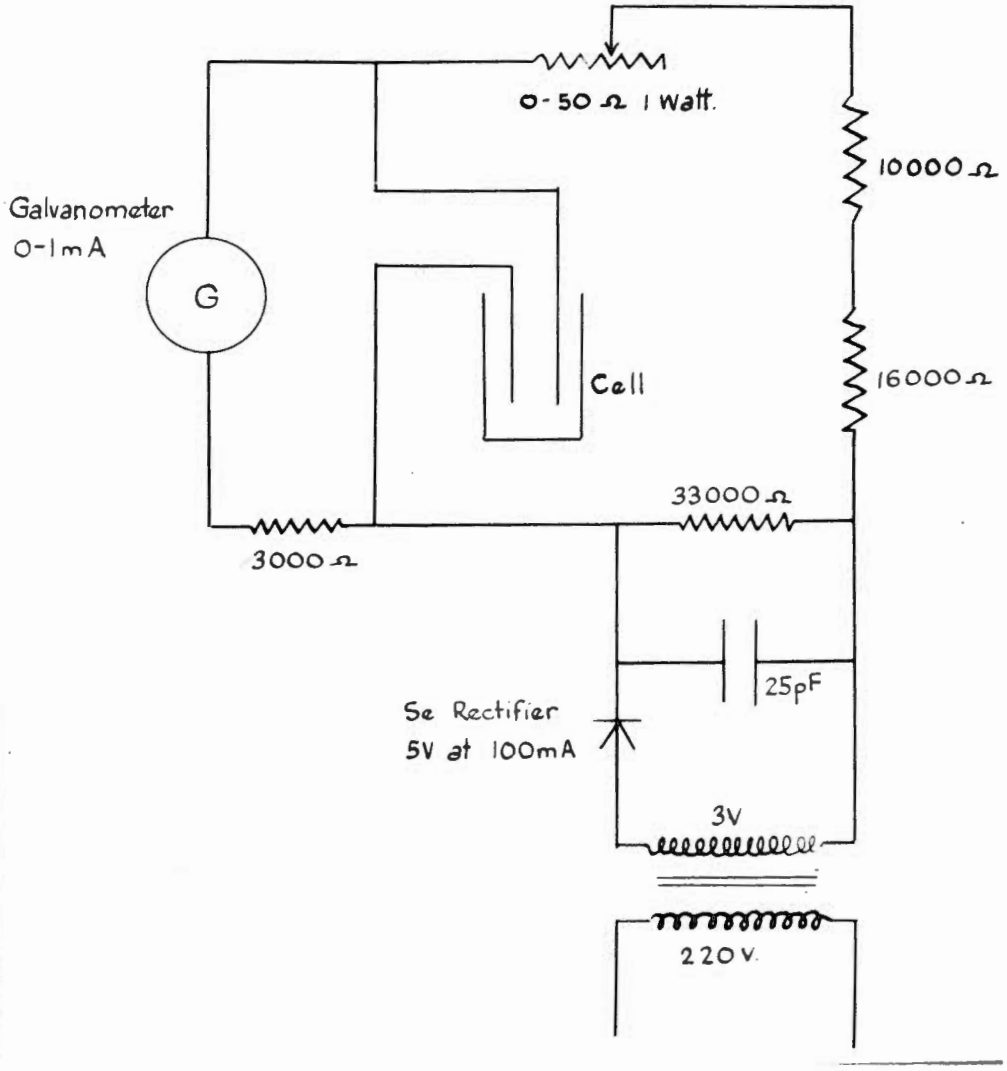


Fig. 28b. CIRCUIT OF TITRIMETER.



of 270 ml. pyridine, 668 ml. benzene and 64 g. SO_2.[85] This reagent was standardised with water before use.

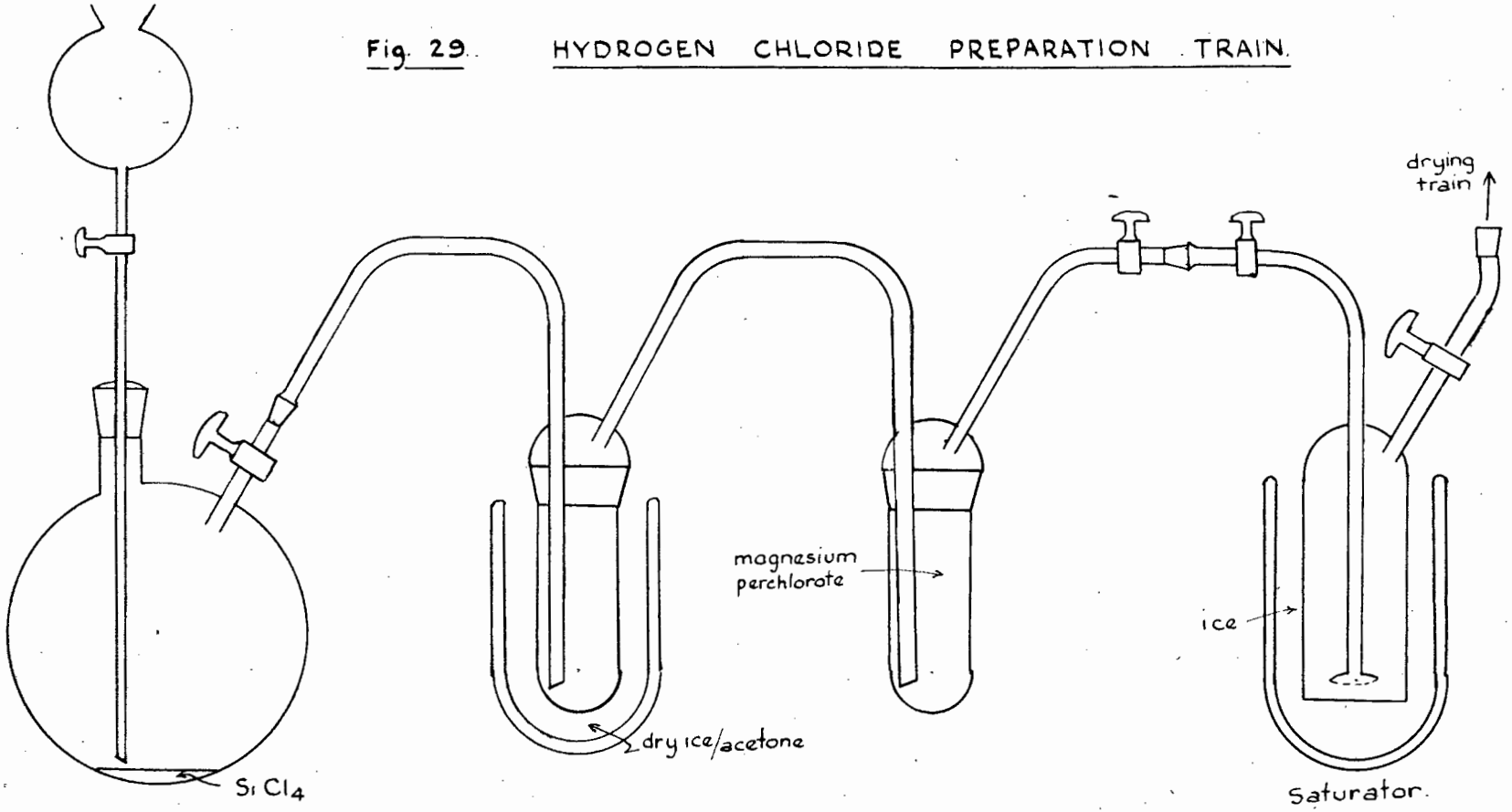
The water content of the acetone used in this work was found to vary between 0.08 - 0.13%.

3. The Preparation and Analysis of Hydrogen Chloride Solutions.

Hydrogen chloride of high purity was prepared by treating silicon tetrachloride with distilled water. The gas was dried by passing it through a magnesium perchlorate tower and a trap immersed in a dry-ice-acetone freezing mixture, after which it was allowed to bubble through an ice-cooled acetone saturator, which had been filled in the drybox (see fig. 29). After about ten minutes the stopcocks were closed and the saturator disconnected and replaced in the drybox. Several samples were then transferred to 50 ml. volumetric flasks with a calibrated 5 ml. pipette. On being removed from the drybox, about 30 ml. distilled water was added to each flask, the contents quantitatively transferred to a 250 ml. beaker, and chloride determined gravimetrically with silver nitrate.

Solutions of the required concentrations were then prepared in the drybox by the method of successive dilution, the concentration of each being checked by titration with standard sodium hydroxide. The last sample of each series was analysed gravimetrically, and if satisfactory agreement with the titration was not obtained, the results for the whole series were ignored.

Fig. 29. HYDROGEN CHLORIDE PREPARATION TRAIN.



Although solutions of hydrogen chloride in acetone turned brown on standing, no appreciable changes in the conductance or the potential were observed over periods of up to twelve hours (see Table XIV); all solutions were accordingly used on the day of preparation. Two batches of acetone were prepared, and two solutions of hydrogen chloride were made from each batch for the conductance studies.

TABLE XIV.

Stability of hydrogen chloride solutions in acetone.

c x 10^4 moles l^{-1}	Initial potential mV	Potential after 8 hours mV	Initial specific cond. x 10^6 mho $cm.^{-1}$	Specific cond. x 10^6 after 12 hours mho $cm.^{-1}$
2.752	-	-	1.7981	1.7979
7.440	-	-	3.5645	3.5641
56.2	50.3	50.4	-	-
183.0	106.5	106.2	-	-

4. Conductance Measurements on Solutions of Hydrogen Chloride in Acetone.

The conductances of solutions of hydrogen chloride in anhydrous acetone were measured on the Jones bridge at 25°C, using the Daly and Smith cell with grey platinum electrodes. It was unfortunately not possible to use the potentiometric method for any work in this solvent, as the prototype potentiometer described in § II.3.2 (page 29) was not suitable for the measurement of high resistances,

and measurements in acetone solution would have required the construction of cells too large to be made in this laboratory.

Equivalent conductances were calculated from the measurements (see Table XV), and plotted against the square root of the concentration (fig. 30), and a graphical extrapolation to infinite dilution gave an approximate value for the limiting conductance of 210 ohm^{-1} $cm.^2$ (cf. Sackur[86] 12.7 ohm^{-1} $cm.^{-1}$; Ross Kane[31] 199 ohm^{-1} $cm.^2$).

TABLE XV.

The conductance of hydrogen chloride in anhydrous acetone - Fuoss Plot

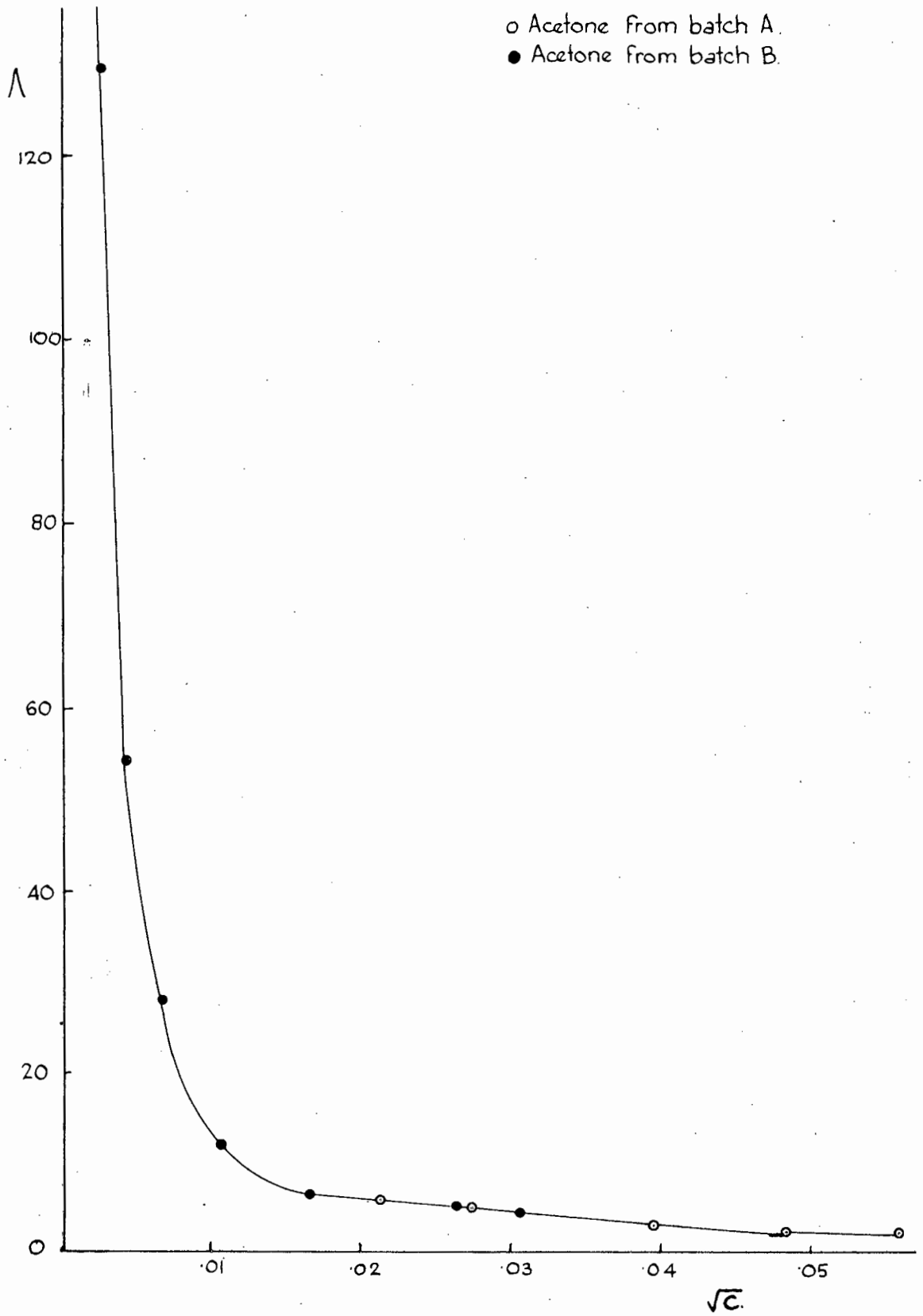
Λ_0 ' assumed 210 mho $cm.^2$

Series	$c \times 10^4$ mole l^{-1}	Specific cond. $\times 10^6$ mho $cm.^{-1}$	Λ mho $cm.^2$	$F(x)$	f^2	$\frac{F(x)}{\Lambda}$	$\frac{C\Lambda f^2}{F(x)} \times 10^3$
B 2	0.0704	0.9111	129.3	0.99630	0.96394	0.0077	0.8815
B 2	0.1761	0.9527	54.10	0.99620	0.96316	0.0184	0.9211
A 1	0.4402	1.2274	27.88	0.99569	0.95822	0.0357	1.181
B 2	1.103	1.3775	12.49	0.99539	0.95580	0.0797	1.323
B 1	2.752	1.7891	6.501	0.99479	0.94980	0.1530	1.708
A 2	4.464	2.5239	5.654	0.99378	0.94062	0.1758	2.389
B 1	6.881	3.4488	5.012	0.99277	0.93092	0.1981	3.234
A 1	7.440	3.5645	4.791	0.99257	0.92980	0.2072	3.340
B 2	9.329	3.9649	4.250	0.99217	0.92608	0.2334	3.701
A 1	15.52	4.7050	3.032	0.99147	0.91972	0.3270	4.365
A 2	23.25	5.5970	2.407	0.99076	0.91274	0.4116	5.156
A 2	30.97	6.9139	2.231	0.98964	0.90350	0.4436	6.308

Series letters refer to batch of acetone, numbers to the HCl solutions.

Least sq. on these data gives $K_D = 2.6859 \times 10^{-7}$ using Λ_0 as 225.0.

FIG 30. HYDROGEN CHLORIDE IN ACETONE.
EQUIVALENT CONDUCTANCE.



Although Braude[42] claimed that hydrogen chloride was "largely or completely dissociated" in acetone, the shape of this curve indicates that it is a very weak acid, calculation from the conductance ratio producing a dissociation constant of 2.82×10^{-7}. This compares reasonably well with the dissociation constants measured by Ross Kane (3.15×10^{-7}), Mackor (10^{-6}) and Sparnaay ($10^{-7} - 10^{-8}$). Braude stated that $\frac{\Lambda}{\Lambda_0} - k\sqrt{\alpha c}$, where k is the Onsager limiting slope, should be an approximate measure of the degree of dissociation, and he based his calculations of this quantity on Sackur's limiting slope, as Ross Kane's results had never been published in detail. However, Sackur was obviously deceived by the apparent linearity of the curve in a region of quite moderate concentration, and did not extend his measurements to sufficiently high dilutions, so that both his limiting slope and limiting equivalent conductance are incorrect. While Braude's conclusions as to the degree of dissociation are fallacious, his use of the acidity function to calculate the proton accepting strengths of ether, alcohol, water and acetone has established the existence of the Me_2COH^+ ion.

For a weak uni-univalent electrolyte the Onsager equation takes the form

$$\Lambda = \alpha \left[\Lambda_0 - (A + B\Lambda_0)\sqrt{\alpha c}\right] \qquad \text{(III.1)}$$

where A and B are constants respectively defined by

$$A = \frac{1.546 \times 10^{-7}}{6\pi\eta}(z_1 + z_2)\left(\frac{8\pi \mathcal{N} e^2}{1000\,\varepsilon k T}\right)^{1/2} = \frac{82.4}{(\varepsilon T)^{1/2}\eta} \qquad \text{(III.1a)}$$

and $$B = \frac{z_1 z_2 e^2}{3 \varepsilon k T} \cdot \frac{(8 \pi \mathcal{N} e^2)^{1/2} q}{(1000 \varepsilon k T)^{1/2} (1 + \sqrt{q}}$$

where $$q = \frac{z_1 z_2}{z_1 + z_2} \cdot \frac{\lambda_1^0 + \lambda_2^0}{z_2 \lambda_1^0 + z_1 \lambda_2^0}$$

$= 1/2$ for symmetrical electrolytes where $z_1 = z_2$, whence B simplifies to

$$B = \frac{8.20 \times 10^5}{(\varepsilon T)^{3/2}} \qquad \text{(III.1b)}$$

While equation (III.1) holds reasonably well for solutions of dielectric constant greater than 30, the limiting slopes have increasingly lower values than those predicted, as the dielectric constant is reduced below this figure. This is due to the formation of ion pairs and ions of greater complexity so that the assumptions regarding the activities of the ions become invalid. Fuoss and Kraus[35] therefore established a method for the determination of both the limiting equivalent conductance and the dissociation constant which is based on a solution of the above equation below the concentration at which association into groups containing more than two ions becomes appreciable. This critical concentration has been stated by Fuoss[35] to be equal to $3.2 \times 10^{-7} \varepsilon^3$, and for acetone it has the value 2.8×10^{-3} mole l^{-1}.[33]

Fuoss modified equation (III.1) to

$$\alpha = \frac{\Lambda}{\Lambda_0 F(x)} \qquad \text{(III.2)}$$

where x is the variable

$$x = \frac{(A + B\Lambda_0)\sqrt{c\Lambda}}{\Lambda_0^{3/2}} \qquad \text{(III. 3)}$$

and $F(x)$ is the continued fraction

$$F(x) = 1 - x(1 - x(1 - x(1 - \ldots)^{-1/2})^{-1/2})^{-1/2}. \qquad \text{(III. 4)}$$

Values of this function have been determined by Fuoss[35], and tabulated to facilitate the calculations.

The dissociation constant is given by

$$K = \frac{\alpha^2 c}{1 - \alpha} \cdot \frac{f_+ f_-}{f_m} \qquad \text{(III. 5)}$$

but if the activity coefficient of the undissociated molecules f_m is taken as unity, this expression becomes

$$K = \frac{\alpha^2 c}{1 - \alpha} f_\pm^2 \qquad \text{(III. 6)}$$

where $f_\pm$ is the mean ionic activity coefficient. Fuoss substituted the value of α given by equation (III. 2) in equation (III. 6) and on rearrangement obtained

$$\frac{F(x)}{\Lambda} = \frac{1}{K\Lambda_0^2} \cdot \frac{c\Lambda f_\pm^2}{F(x)} + \frac{1}{\Lambda_0} \qquad \text{(III. 7)}$$

so that a plot of $\frac{F(x)}{\Lambda}$ against $\frac{c\Lambda f_\pm^2}{F(x)}$ should be a straight line of slope $\frac{1}{K\Lambda_0^2}$ and intercept at infinite dilution $\frac{1}{\Lambda_0}$.

This treatment has been shown to be satisfactory for several salts in acetone and other solvents of low dielectric constant, and as all but two of the measurements on hydrogen chloride were made

on solutions which were below the Fuoss critical concentration, an interpretation of the results by this method was attempted (see Table XV and fig. 31).

The Fuoss plot shows marked changes of slope in the concentration range from 2.5×10^{-4} mole $l.^{-1}$ to 9.5×10^{-4} mole $l.^{-1}$, and extrapolation leads to an impossible value for the limiting equivalent conductance. The dissociation constant calculated from the conductance ratio was found to be fairly constant at $(2.8 \pm 0.3) \times 10^{-7}$ over this concentration range, but calculation from the slopes of the Fuoss plot, assuming Λ_0 to be 210, gave values of 3.1×10^{-7} over the higher range of concentration, 8.7×10^{-7} over the intermediate, and 1.45×10^{-7} in the lower concentration region. Furthermore, according to the treatment given by Kortüm and Bockris[99], in the case of a weak acid in a solvent of low dielectric constant, the interionic forces are relatively small, so that $f_{\pm}$ may be taken as unity and equation (III.6) reduces to the classical form of the Ostwald dilution law

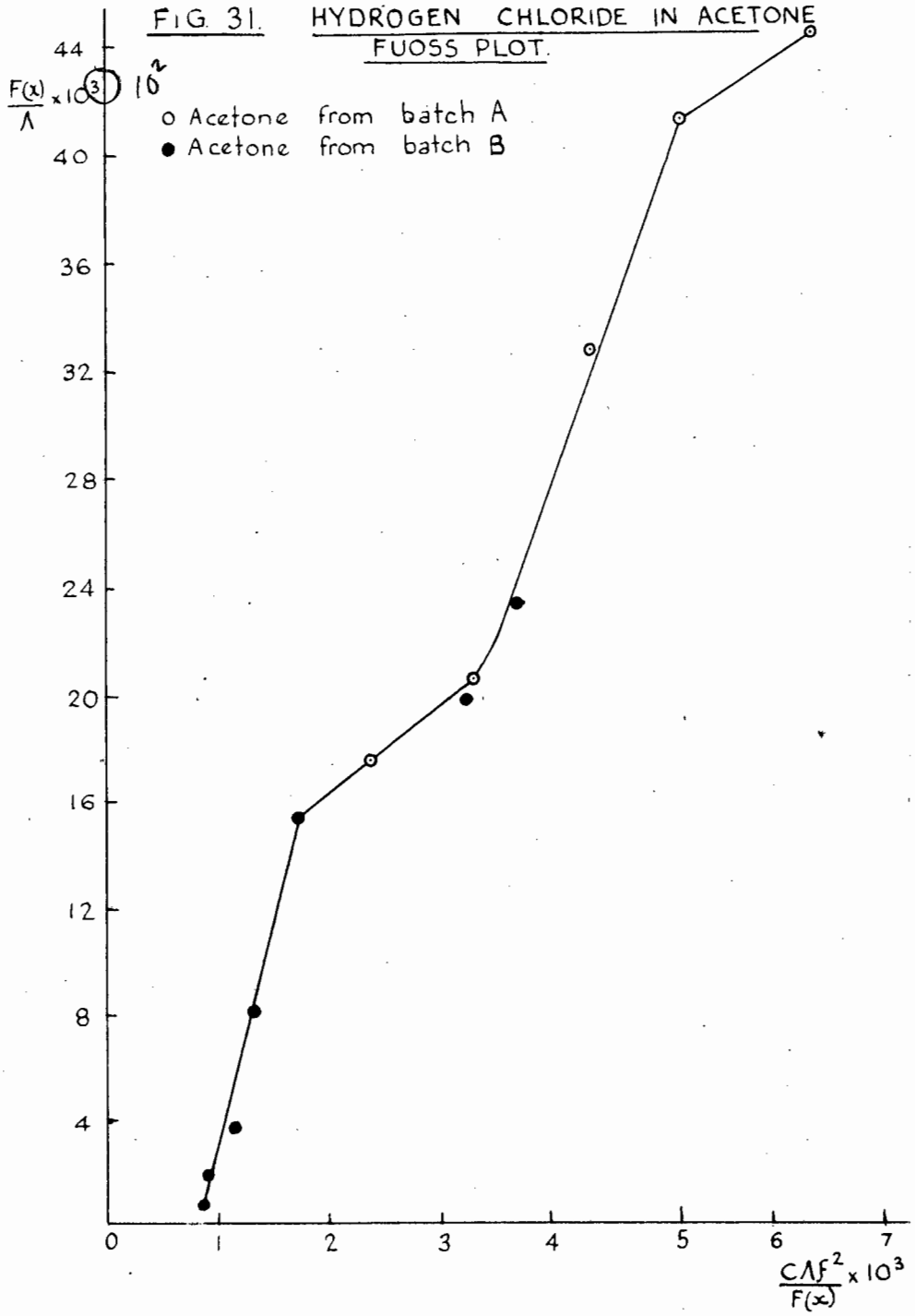
$$K = \frac{\alpha^2 c}{1 - \alpha} \qquad \text{(III.8)}$$

However, if the dissociation constant is very small, $(1 - \alpha)$ will also approximate to unity, and the dissociation constant will be given by

$$K \approx \alpha^2 c \qquad \text{(III.9)}$$

$$\approx \frac{\Lambda^2}{\Lambda_0^2} c \qquad \text{(III.9a)}$$

FIG. 31. HYDROGEN CHLORIDE IN ACETONE
FUOSS PLOT.



On taking logarithms the expression becomes

$$\log \Lambda = \tfrac{1}{2} \log K \Lambda_0^2 - \tfrac{1}{2} \log c. \qquad \text{(III.10)}$$

Log Λ should therefore be a linear function of log c, and at low dilutions, where only ion pair formation is expected, the straight line should have a slope of -0.5. Values of log Λ and log c for hydrogen chloride in acetone are given in Table XVI and the plot shown in fig. 32, whence the slope is found to be -0.8.

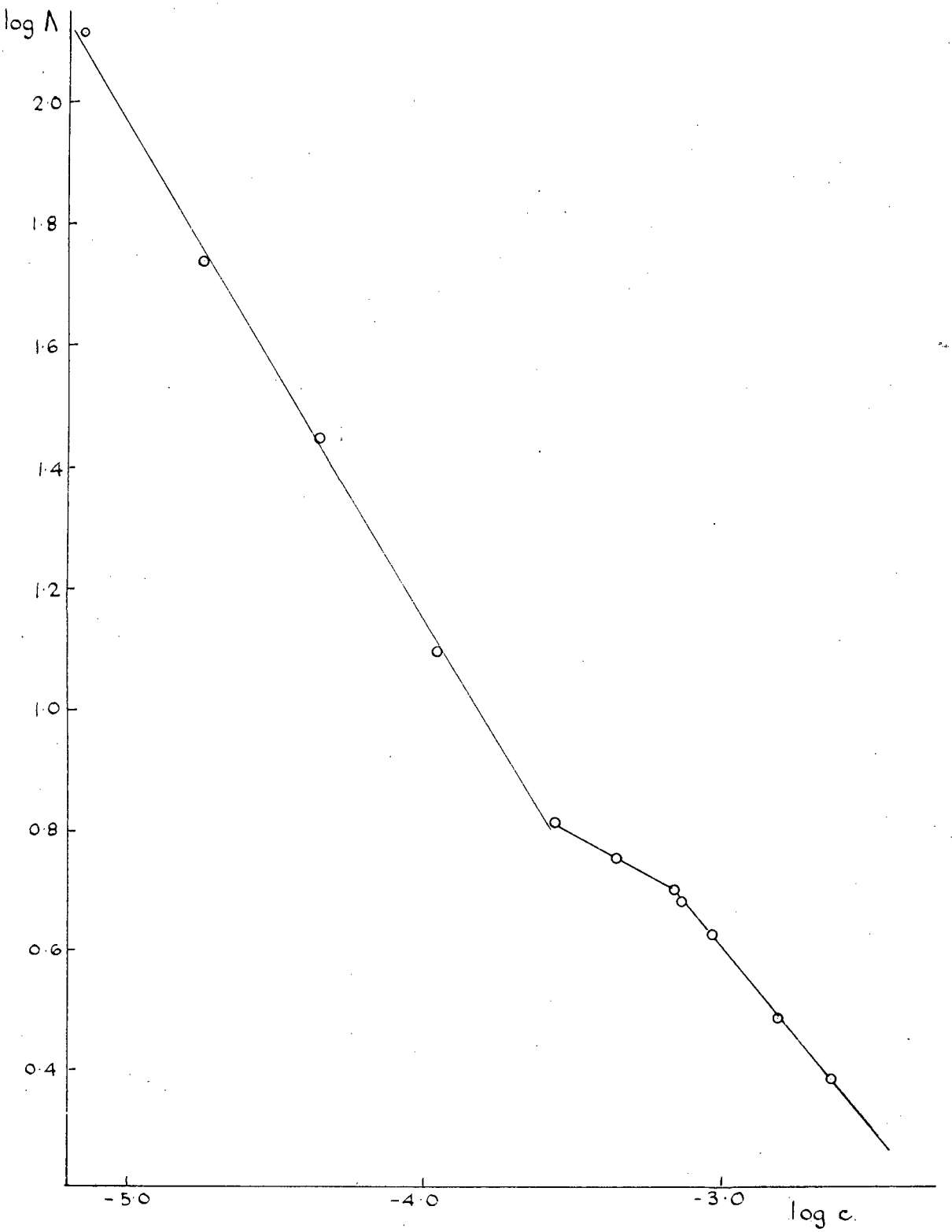
TABLE XVI.

c x 10^4 mole l^{-1}	- log c	log Λ
0.0744	5.1522	2.1116
0.1761	4.7543	1.7332
0.4402	4.3563	1.4453
1.103	3.9575	1.0965
2.752	3.5604	0.8130
4.464	3.3503	0.7523
6.881	3.1623	0.7000
7.440	3.1284	0.6804
9.329	3.0302	0.6284
15.52	2.8091	0.4817
23.25	2.6336	0.3814

It is therefore quite clear that hydrogen chloride does not behave as a simple acid in acetone, and both Mackor[47] and Sparnaay[47] appear to have reached similar conclusions, but neither published details of their work. Mackor has stated that his results might

FIG 32. HYDROGEN CHLORIDE IN ACETONE

log Λ against log C.



indicate a dimerisation of HCl in acetone, but while it seems evident from the present work that association must occur, the aggregates appear to be much larger than dimers. French and Roe[43] have explained the variation of the conductance of picric acid in acetone on the basis of triple ion formation, but due to the shape and size of the picrate ion, their treatment is not applicable in the case of hydrogen chloride.

It has been mentioned that Sackur[86] was deceived by the approach to linearity of the plot of the equivalent conductance against the square root of the concentration at quite moderate concentrations. However, this linearity indicates the presence of an electrolyte which obeys the Onsager equation, i.e.

$$(HCl)_x + Me_2CO \rightleftharpoons Me_2COH^+ + (H_{x-1}Cl_x)^-, \qquad (III.11)$$

although this equilibrium will be complicated by dissociation of the hydrogen chloride polymers into simpler aggregates. Ross Kane has calculated the limiting conductance of the "hydrogen ion" in acetone to be about 88*, and a plausible value for the limiting conductance of the large anion would seem to be about 12, so that Λ_0 might be expected to be about 100. Sackur's extrapolated value for the limiting equivalent conductance of hydrogen chloride was 12.7, and extrapolation of the intermediate concentration section of the Fuoss plot (fig. 31) shows Λ_0 to be about 12.4, indicating that possibly

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* All limiting conductances are expressed in $ohms^{-1} cm^2$.

eight molecules might be associated over this range of concentration.

If the polymerised hydrogen chloride molecules are ionising according to reaction (III. 11), the equivalent conductances should be calculated for molecules of equivalent weight 36.49ω. If a Fuoss plot is made using the values in the concentration range 2.75×10^{-4} to 9.3×10^{-4} mole l^{-1} assuming that the polymer consists of eight molecules, the limiting conductance is found to be 80.6, an impossible value since it is below Ross Kane's value for the limiting conductance of the hydrogen ion. Calculation on the basis of the association of ten molecules provides a value of 101.5 for Λ_0 and a dissociation constant of 3.2×10^{-5}, while the assumption of twelve molecules results in values of 119 for the limiting equivalent conductance and 2.9×10^{-5} for the dissociation constant (Table XVII, fig. 33). As the observed dissociation constant decreases with increasing limiting conductance, it seems that the hydrogen chloride polymer consists more probably of ten molecules than twelve. However, since association is almost certainly due to hydrogen bonding, the aggregates would be expected to be chains of indeterminate length, so that this treatment may only produce an average or most probable estimate of the number of molecules, and the changes of slope in the Fuoss plot may represent changes in this quantity.

TABLE XVII.

Fuoss Plot data for hydrogen chloride polymers; Λ_0 assumed to be 100 mho cm.^{2}.

(a) Polymer consisting of eight molecules ($H_8Cl_8 \rightleftharpoons H^+ + H_7Cl_8^-$)

c x 10^4 mole l^{-1}	Λ mho cm.^{2}	$F(x)$	f^2	$\frac{F(x)}{\Lambda}$	$\frac{c\Lambda f^2}{F(x)}$ x 10^3
0.3440	52.01	0.97344	0.9273	0.01872	1.704
0.5580	45.23	0.96840	0.9142	0.02141	2.383
0.8601	40.10	0.96291	0.9000	0.02402	3.224
0.9300	38.33	0.96229	0.8984	0.02511	3.328
1.166	34.00	0.96021	0.8930	0.02824	3.687

(b) Polymer consisting of ten molecules ($H_{10}Cl_{10} \rightleftharpoons H^+ + H_9Cl_{10}^-$)

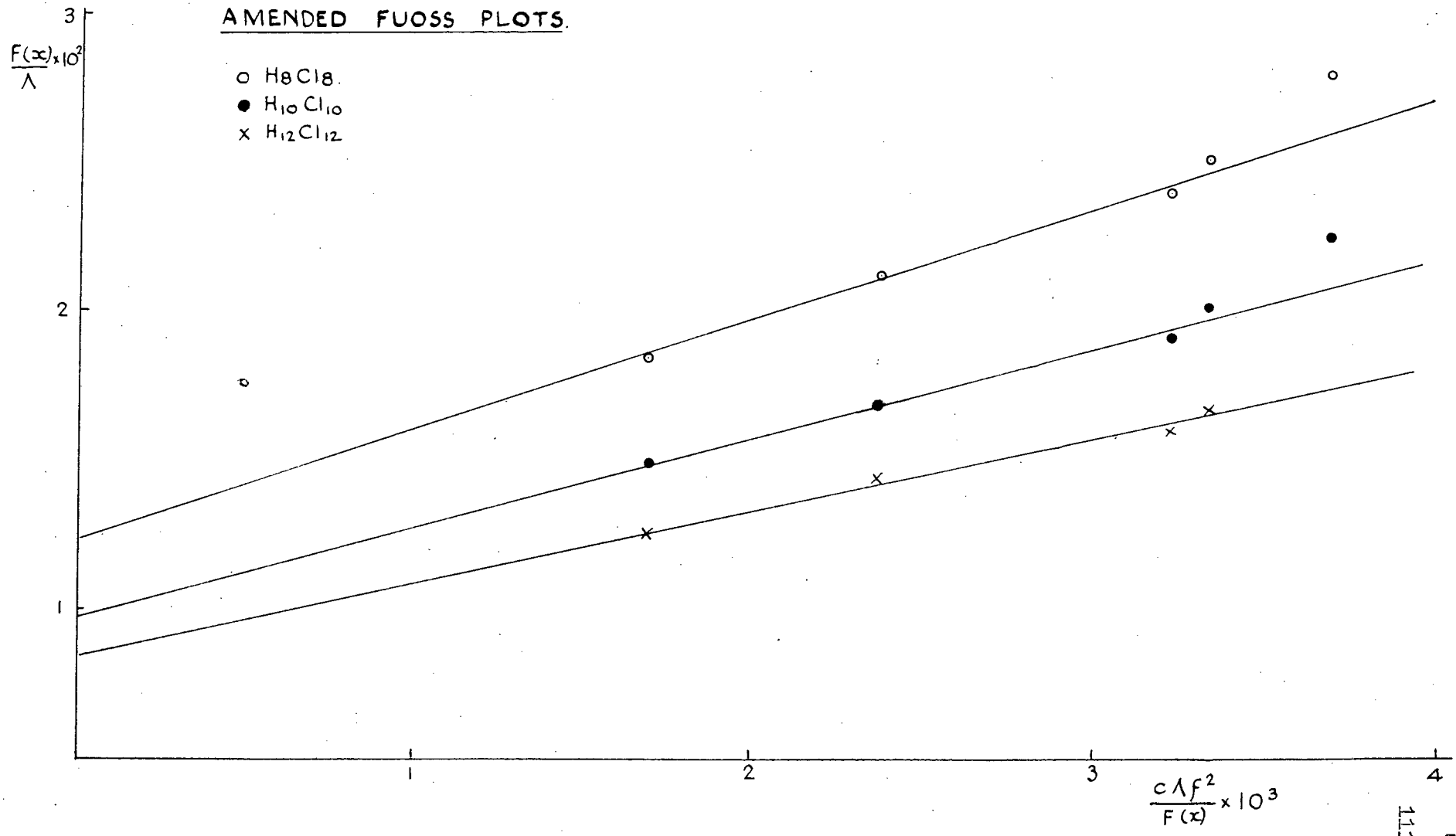
c x 10^4 mole l^{-1}	Λ mho cm.^{2}	$F(x)$	f^2	$\frac{F(x)}{\Lambda}$	$\frac{c\Lambda f^2}{F(x)}$ x 10^3
0.2752	65.01	0.97344	0.9272	0.01497	1.704
0.4464	56.54	0.96840	0.9142	0.01713	2.383
0.6881	50.12	0.96291	0.9000	0.01921	3.224
0.7440	47.91	0.96229	0.8984	0.02009	3.328
0.9329	42.50	0.96021	0.8930	0.02259	3.687

(c) Polymer consisting of twelve molecules ($H_{12}Cl_{12} \rightleftharpoons H^+ + H_{11}Cl_{12}^-$)

c x 10^4 mole l^{-1}	Λ mho cm.^{2}	$F(x)$	f^2	$\frac{F(x)}{\Lambda}$	$\frac{c\Lambda f^2}{F(x)}$ x 10^3
0.2293	78.01	0.97344	0.9272	0.01248	1.704
0.3720	67.85	0.96840	0.9142	0.01427	2.383
0.5734	60.14	0.96291	0.9000	0.01601	3.224
0.6200	57.49	0.96229	0.8984	0.01674	3.328
0.7774	51.00	0.96021	0.8930	0.01883	3.687

FIG 33. HYDROGEN CHLORIDE IN ACETONE.

AMENDED FUOSS PLOTS.



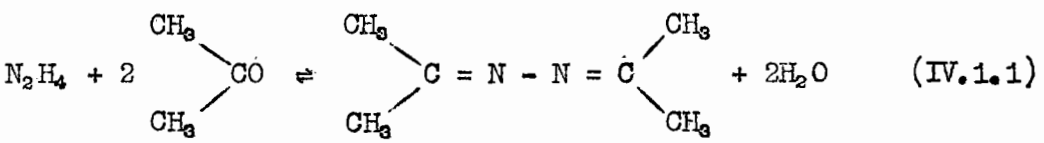
PART IV.

POTENTIOMETRIC EXPERIMENTS IN MOIST AND ANHYDROUS ACETONE.

1. Introduction.

Prior to 1952, dimethylketazine was thought to be too weak a base to form salts, and the preparation by Pugh and his co-workers[8-18] of salts which appeared to contain a dimethylketazinium ion resulted in speculation as to their true nature.

The base is extensively hydrolysed by small traces of moisture, but Gilbert[29] has shown that in excess acetone the equilibrium



(IV.1.1)

lies well over on the azine side, so that conversion of hydrazine to ketazine is almost complete. It appeared that some measure of the order of magnitude of the ionisation constant could be obtained from the half neutralisation point of potentiometric titrations of dimethylketazine with a suitable acid in acetone solution[92], in spite of the fact that the validity of the Henderson equation

$$-\log[H^+] = -\log K_b + \log \frac{[\text{salt}]}{[\text{base}]} \qquad \text{(IV.1.2)}$$

in non-aqueous solvents is uncertain. Furthermore, comparison of the titration curve of dimethylketazine in acetone with those of other bases in the same solvent might be expected to provide some

information as to its relative strength.

Potentiometric titrations of dimethylketazine with solutions of hydrogen chloride in moist acetone were therefore performed, and the results compared with those of titrations of 1:2:3:4-tetrahydroquinoline, 1:2:3:4-tetrahydroisoquinoline and piperidine which had been carried out in connection with another research project in progress in this laboratory. While these titrations indicated the presence of a basic substance of low ionisation constant, this constant could not be determined accurately. Since no standard potentionals for the electrodes used were available, it was apparent that more comprehensive investigations on solutions of hydrogen chloride in anhydrous acetone were necessary, and the succeeding pages describe (i) E.M.F. measurements on solutions of hydrogen chloride in acetone, using the calomel and chloranil electrodes, (ii) potentiometric titrations of tetrahydroquinoline, tetrahydroisoquinoline and piperidine with HCl in moist acetone, and finally (iii) potentiometric titrations of dimethylketazine in moist and anhydrous acetone.

2. E.M.F. Measurements on Solutions of Hydrogen Chloride in Acetone.

Ulich and Spiegel[51] studied several metal-metal halide electrodes in acetone, and found that most of them gave unstable potentials which were not reproducible. They explained this by postulating the formation of complex ions of the type $M_aX_b^{(b-a)-}$, and cited as evidence the fact that the addition of lithium halides increased

the solubility in acetone of the corresponding mercury and silver halides.

Contradictory results were obtained by Arthur and Lyons[52], who constructed cells consisting of two saturated lithium chloride calomel electrodes, and demonstrated their suitability for polarographic work in acetone. The cell $Hg, Hg_2Cl_2 | LiCl || LiCl | Hg_2Cl_2, Hg$ had zero emf. to within one millivolt both before and after the passage of a current of 50 microamps for one hour, and a cell consisting of one freshly prepared electrode and one several weeks old still showed no difference of potential between the electrodes. Current through the cell was found to be a linear function of the applied voltage over a range from 0 to 2 volts. These tests showed that the electrode is reversible, stable and reproducible. These authors also showed that when acetone saturated with lithium chloride is brought into contact with calomel, some of the mercurous ions are reduced to metallic mercury, and some oxidised to a mercury complex which is soluble in acetone, the system reaching equilibrium very rapidly. The water content of their acetone was determined by Karl Fischer titrations and was found to be slightly less than 0.1%. The addition of acetic anhydride to remove the last traces of moisture did not affect their polarographic results, which they interpreted to mean that the presence of water is not essential to the electrode reaction. Since Arthur and Lyons made no attempt to measure the potential of the lithium chloride saturated/calomel electrode against

a standard hydrogen electrode in acetone, no standard potentials were available.

Everett and Rasmussen[48] investigated the cell $Pt, H_2 (1\ atm) | HCl | AgCl, Ag$ and found that the silver-silver chloride electrode behaved satisfactorily in dilute solutions in acetone, and they calculated the standard potential by the following procedure:

Since hydrogen chloride is a weak electrolyte in solution in acetone, the e.m.f. of the cell $Pt, H_2 | HCl | AgCl, Ag$ should be given by

$$E = E^{\circ} - \frac{2RT}{F} \ln \alpha\, m_{HCl}\, \gamma_{\pm} \qquad (IV.2.1)$$

in which α is the degree of dissociation, m_{HCl} the stoicheiometric molality of hydrogen chloride, and $\gamma_{\pm}$ the mean activity coefficient of the ions. Introducing the dissociation constant

$$K_a = \frac{\alpha^2 m_{HCl}}{1 - \alpha} \cdot \frac{\gamma_{\pm}^2}{\gamma_{HCl}} \qquad (IV.2.2)$$

into equation (IV.2.1), Everett and Rasmussen obtained

$$E + \frac{RT}{F} \ln m_{HCl} = E^{\circ} - \frac{RT}{F} \ln K_a - \frac{RT}{F} \ln (1 - \alpha) - \frac{RT}{F} \ln \gamma_{HCl} \qquad (IV.2.3)$$

which reduces to

$$E + \frac{RT}{F} \ln m_{HCl} = E^{\circ} - \frac{RT}{F} \ln K_a - \frac{RT}{F} \ln \gamma_{HCl} \qquad (IV.2.4)$$

because $(1 - \alpha)$ may be taken as unity. They assumed γ_{HCl} to vary

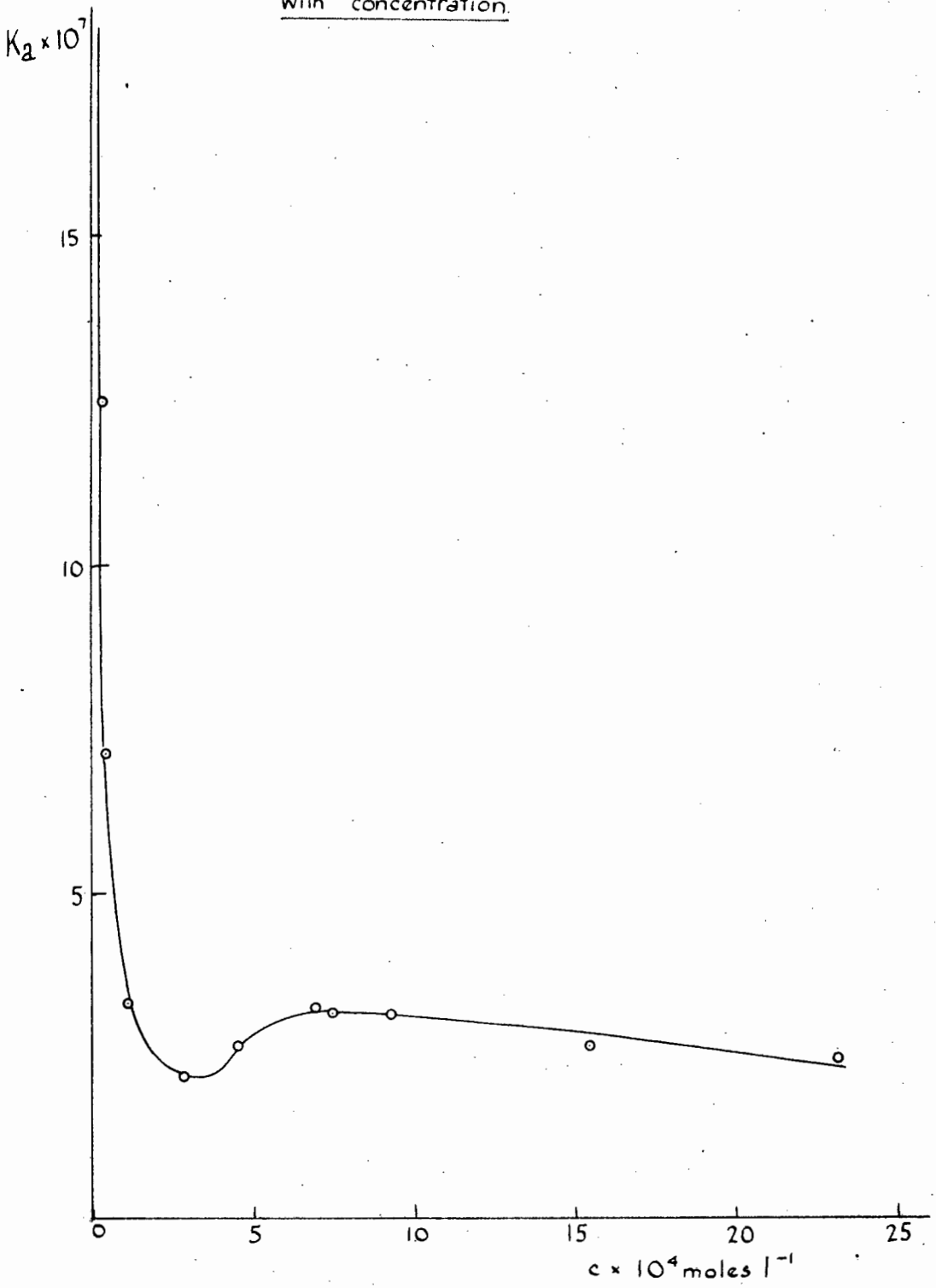
linearly with the molality of hydrogen chloride, so that a plot of $E + \frac{RT}{F} \ln m_{HCl}$ against m_{HCl} might be expected to be linear, having an intercept of $E^{\circ} - \frac{RT}{F} \ln K_a$ and a slope representing the variation of γ_{HCl} with m_{HCl}. This assumption was justified since Everett and Rasmussen's points for concentrations above 0.01 molal were found to lie on such a straight line, but two points measured below this concentration were above the line.

The fact that the plot of $E + \frac{RT}{F} \ln m_{HCl}$ against the molality is linear, indicates either (i) that the apparent K_a is effectively constant over the concentration range in which measurements were made and that γ_{HCl} varies linearly with the molality, or (ii) that the apparent dissociation constant varies and γ_{HCl} is not linear with the molality, but that the variation of the two combined provides a linear function. The latter possibility seems most improbable, and evidence for the former is provided by the shape of the graph of the apparent dissociation constant against the concentration of hydrogen chloride measured in the present work, which is almost parallel to the concentration axis over part of the concentration range concerned (fig. 34).

Using Mackor's value for the dissociation constant of hydrogen chloride in acetone (10^{-8}), Everett and Rasmussen obtained a standard potential for the silver-silver chloride electrode of -0.53 volts. Their treatment should be applicable to all cells of

FIG 34. HYDROGEN CHLORIDE IN ACETONE.

Variation of Apparent Dissociation Constant with concentration.



the type $Pt,H_2|HCl|MCl,M$ in acetone, irrespective of the metal used.

In solutions containing dimethylketazine, the silver-silver chloride electrode did not function satisfactorily, and since the use of a hydrogen electrode in a direct potentiometric titration would have complicated the design of the cell, the chloranil and lithium chloride saturated/calomel electrodes were selected for the present work.

The quinhydrone electrode had been used by Izmailov and Zabara[93] in acetone-water mixtures, but quinhydrone appeared to be too soluble in anhydrous acetone. Previous use of the chloranil electrode in this solvent could not be traced, and no standard potentials of the calomel electrode had been recorded; accordingly the cells

$$Pt,H_2|HCl\|LiCl|Hg_2Cl_2,Hg$$

$$Pt,\text{chloranil}|HCl\|LiCl|Hg_2Cl_2,Hg \quad \text{and}$$

$$Hg,Hg_2Cl_2|LiCl\|HCl|AgCl,Ag$$

were investigated to facilitate the interpretation of the potentiometric titration.

3. Studies on the Calomel and Chloranil Electrodes in Acetone.

In cells with liquid junction, diffusion between the solutions in contact must be reduced to a minimum, but the conventional gel-type salt bridges are soluble in acetone, and the use of saturated solutions for this purpose must await the measurement of transference

numbers in this solvent. The problem of diffusion between the calomel electrode and the hydrogen chloride solution was overcome by constructing an H-shaped vessel in which the calomel compartment was separated from the hydrogen chloride solution by a sintered glass disc of low porosity. (See fig. 35). A platinum wire was sealed into the solution compartment for use with the chloranil electrode during potentiometric titration, and the B14 ground glass joint so arranged to take either a specially designed burette or a platinum plated glass rod for the hydrogen electrode. A nozzle was provided to supply either hydrogen for the electrode or nitrogen for stirring during the titration.

The saturated lithium chloride/calomel electrode was prepared in the following manner: a paste of acetone, calomel, lithium chloride and mercury was made by mixing and grinding the dried constituents in an agate mortar in the drybox, and poured on to a pool of redistilled electrolytically purified mercury in the smaller limb of the cell. This was covered with acetone which had previously been saturated with calomel and lithium chloride, and contact with the mercury pool was made by means of a platinum wire sealed into a glass tube internally sealed into a B14 ground glass joint, by means of which this limb of the cell was closed, thus preventing evaporation. The wire was pressed through the paste into the mercury, and electrical contact made through a mercury cup formed by pouring the metal down the tube.

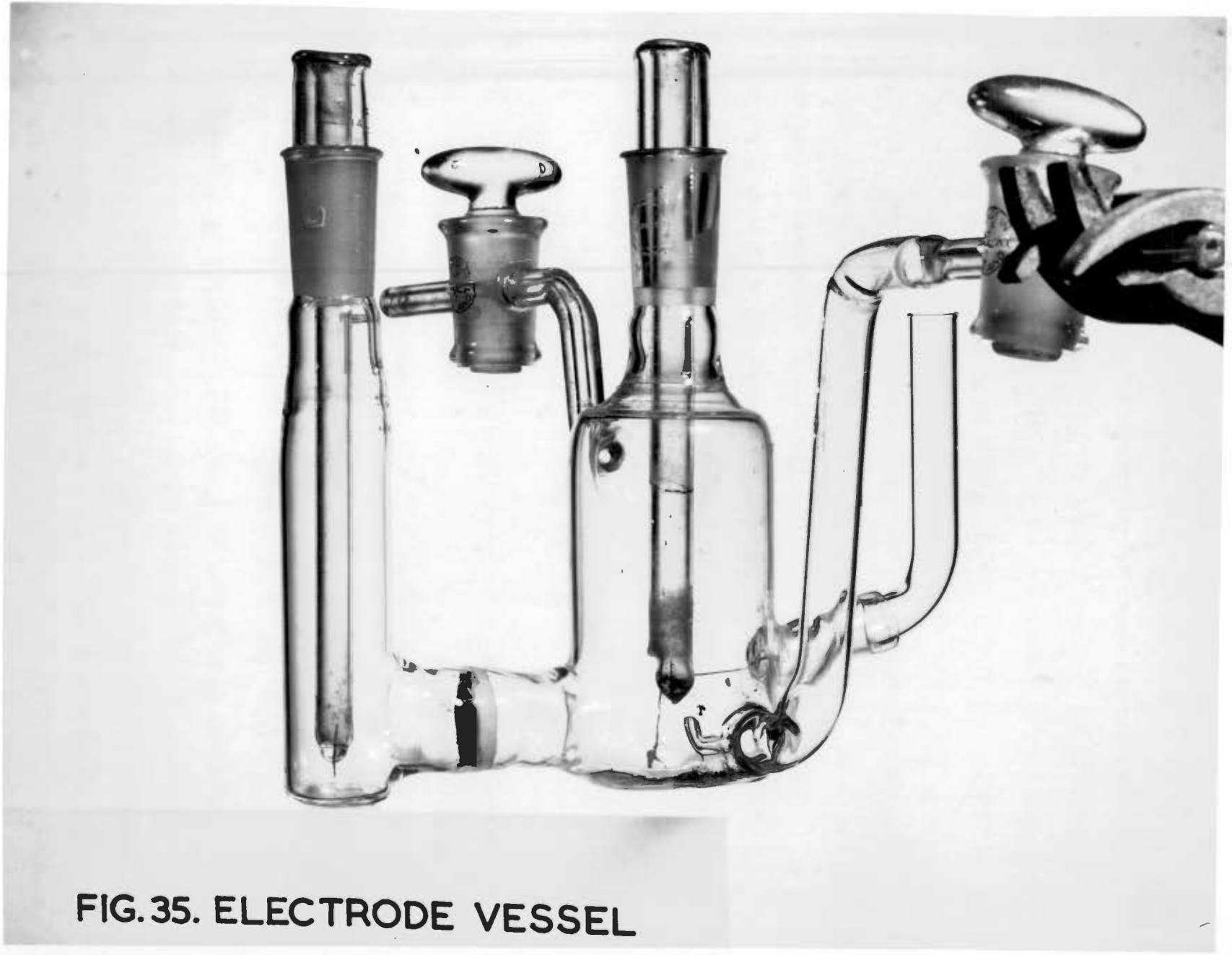


FIG. 35. ELECTRODE VESSEL

The hydrogen electrode consisted of a glass tube joined to a B14 ground joint at one end, with a platinum contact sealed at the other. Platinum was plated on to the glass by the usual reduction method, heated until it just glowed, and stored in a hydrogen-filled desiccator until used. Hydrogen was prepared by the electrolysis of aqueous sodium hydroxide solution and passed through drying tubes containing indicating silica gel and magnesium perchlorate, after which it was allowed to bubble through an acetone saturator immersed in the thermostat. Following the recommendation of Everett and Rasmussen[48], the volume of the saturator was about three times that of the cell. The gas outlet was protected from atmospheric moisture by tubes of magnesium perchlorate and silica gel.

Tetrachlorohydroquinone was prepared from tetrachloroquinone (chloranil) by reduction with sulphur dioxide. A mixture consisting of equimolar proportions of chloranil and the reduced form was dried by storing in a vacuum desiccator over phosphorus pentoxide for three weeks. Enough to saturate the solution (about 2.5 gm.) was placed in the cell before the solution was poured in, and the electrode system completed by connecting the platinum wire, sealed into the vessel, to the potentiometer.

The silver-silver chloride electrode was prepared by first plating the platinum wire with silver, and then making it the anode for the electrolysis of dilute hydrochloric acid. The cell was then

washed thoroughly with acetone and dried in a stream of nitrogen.

Since it was easier to prepare solutions of known molarity than of known molality, a molarity-molality conversion curve was constructed from the results of gravimetric analyses of a series of solutions of hydrogen chloride in acetone. Solutions were then made by the method of successive dilution, analysed as described in § III.3, (page 96), and the corresponding molality read off the graph. Owing to the high resistances of the solutions, it was not possible to measure the potentials of cells containing hydrogen chloride solutions of concentration less than 2×10^{-3} molal.

The cells $Pt,H_2|HCl\|LiCl|Hg_2Cl_2,Hg$ were made and sealed in the drybox, all joints and stopcocks being lubricated with "Nonaq" grease. Two separate batches of acetone were used for the work on these cells. The vessel was then placed in a water thermostat maintained at $25 \pm 0.02^{\circ}C$, care being taken to keep the "Nonaq" sealed joints away from the water, and the potentials measured, first on a Pye Universal pH and millivoltmenter and then with a Cambridge slide wire potentiometer and a Cambridge d'Arsonval reflecting galvanometer, which gave a deflection of 1000 mm. for one microamp at a distance of one metre. This procedure enabled accurate measurements to be made without drawing large currents from the cells.

TABLE XVIII.

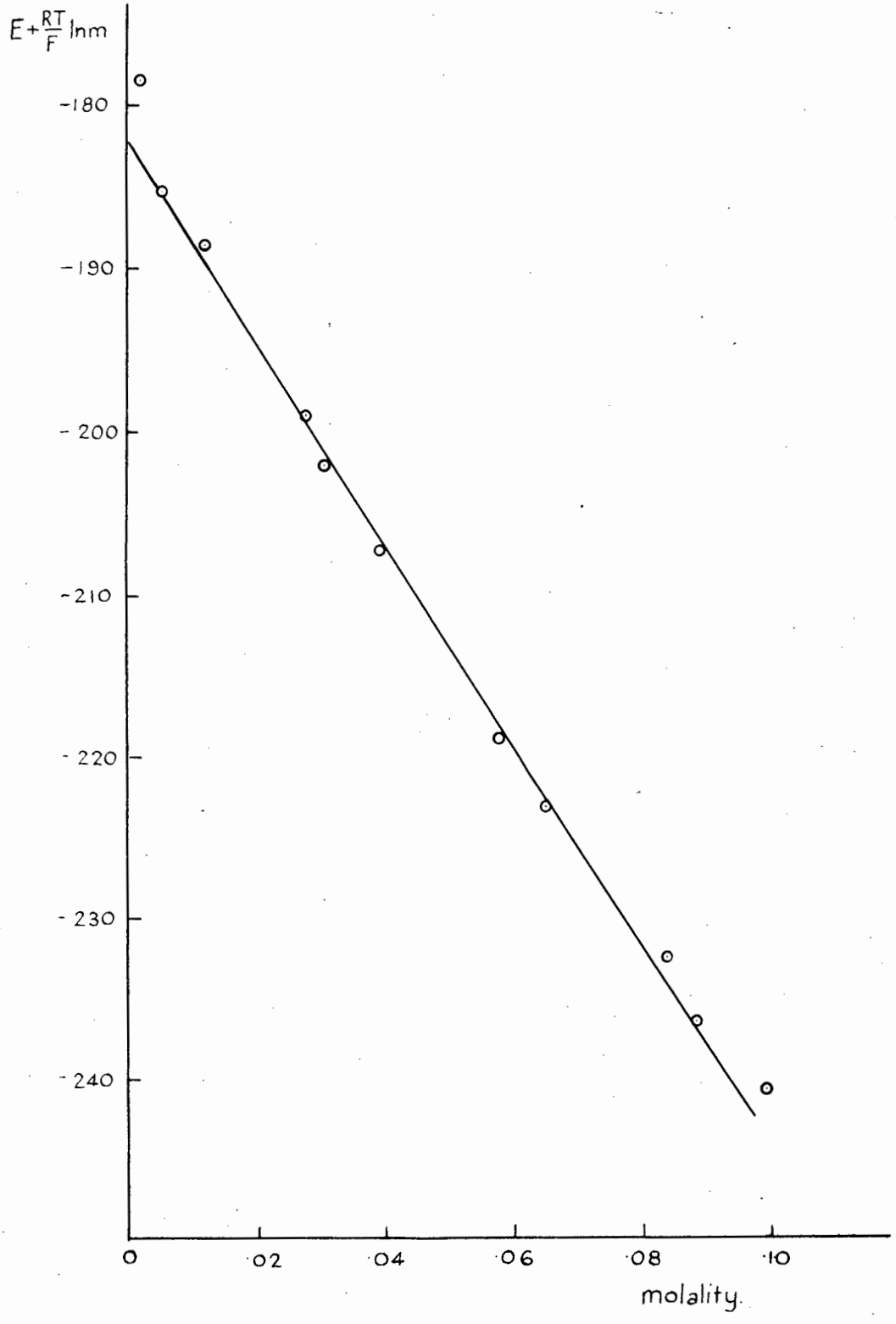
The cell $Pt,H_{2\,(1\ atm)}|HCl\|LiCl|Hg_2Cl_2,Hg$ *

Series	Molality	E millivolts	$-(E + \frac{RT}{F} \ln m)$	$-(E + \frac{2RT}{F} \ln m)$
A	0.0020	-18.8	178.5	338.1
A	0.0051	-50.3	185.3	321.4
A	0.0122	-75.4	188.6	301.8
A	0.0274	-106.5	198.9	291.3
B	0.0305	-112.2	201.9	291.5
B	0.0392	-124.0	207.2	290.4
A	0.0580	-145.6	218.8	291.9
B	0.0650	-152.8	223.1	293.3
B	0.0840	-168.8	232.5	296.1
A	0.0883	-174.1	236.5	298.8
B	0.0995	-181.4	240.7	299.9

The potentials of the $Pt,H_2|HCl\|LiCl|Hg_2Cl_2,Hg$ cells for differing molalities are given in table XVIII. The results were investigated by Everett and Rasmussen's method, when the graph of $E + \frac{RT}{F} \ln m_{HCl}$ against the molality, shown in fig. 36, provided a standard potential for the calomel electrode of -0.654 volts. This value is based on Mackor's dissociation constant (10^{-8}) for ease of comparison with Everett and Rasmussen's results, since this is near enough to the value calculated in the present work (3×10^{-7}) to

* The sign of all potentials is that of the right hand electrode of the cells as written.

FIG 36 THE CELL $Pt, H_2 / HCl // LiCl / Hg_2Cl_2, Hg$



make no significant differences. While the use of apparent dissociation constants based on the conductance ratio might seem out of line with the treatment given in § III.4, it was not possible to make any estimates of true dissociation constants, because in this concentration range the equilibrium between solvated protons, polymeric ions and molecular polymers would be very complicated; moreover, since the potential depends on the molality of protons, the apparent constant provides a sufficiently good approximation, and its constancy has been shown by the discussion given in § IV, 2, page 116).

The limiting slope at low hydrogen ion concentrations of the plot of $E + \frac{2RT}{F} \ln m_{HCl}$ against the square root of the molality was found to be 0.60 (fig. 37), a value which agrees reasonably well with that of 0.51 obtained by Everett and Rasmussen for the cell $Pt,H_2|HCl|AgCl,Ag$ (fig. 38), but the curve differs from theirs in having a pronounced maximum. This occurs at 0.03 molal, but Everett's results showed no maximum up to a concentration of 0.15 molal.

While no adequate explanation for this effect can be given, the discussion in § III.4 might indicate that it is caused by the association of a larger number of hydrogen chloride molecules, but neither of the cells $Pt,chloranil|HCl\|LiCl|Hg,Cl_2,Hg$ nor $Hg,Hg_2Cl_2|LiCl\|HCl|AgClAg$ exhibit this feature (see figs. 39 and 40). Nevertheless in all cases, including Everett's work,

FIG 37 THE CELL $Pt, H_2 / HCl // LiCl / Hg_2Cl, Hg$.

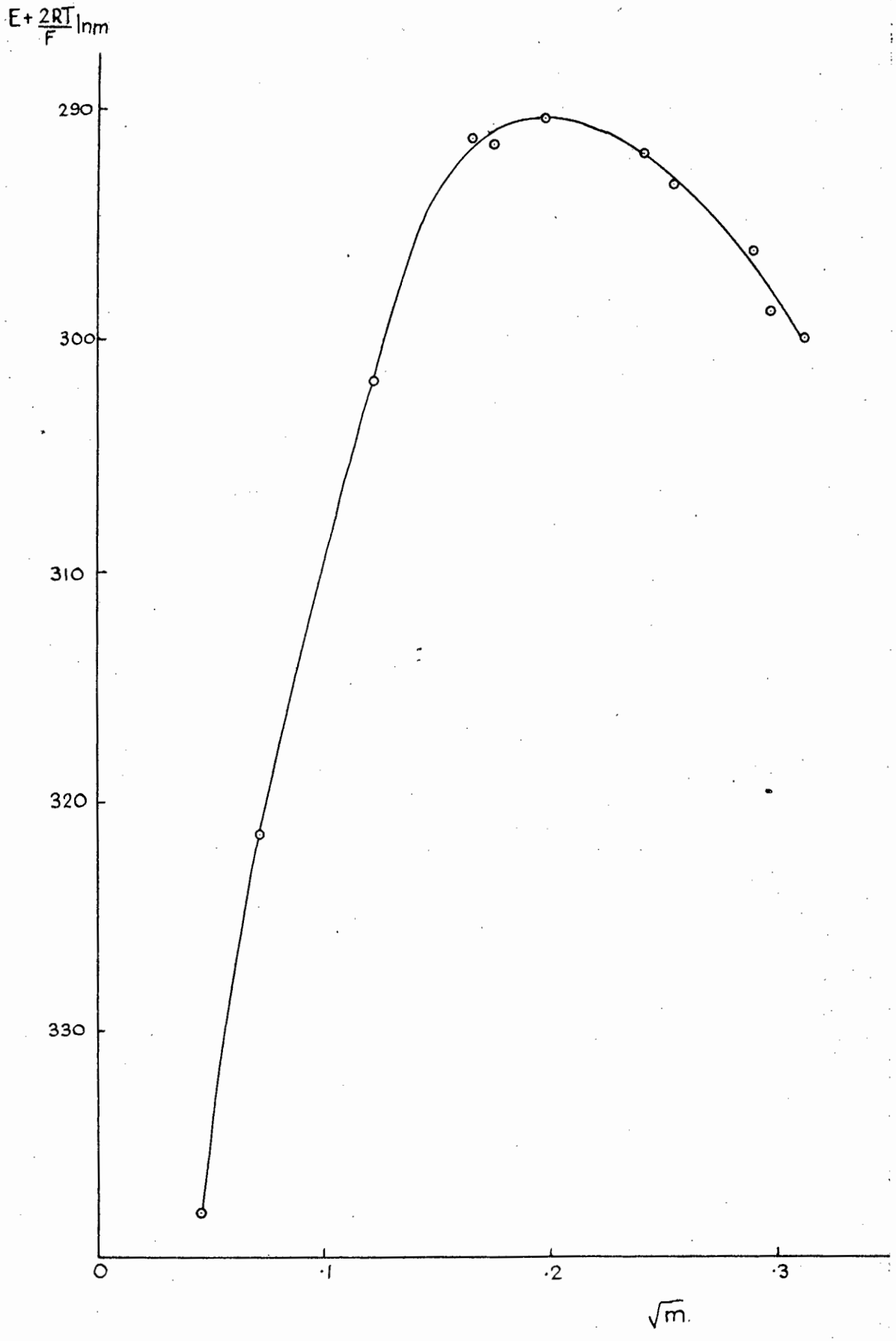
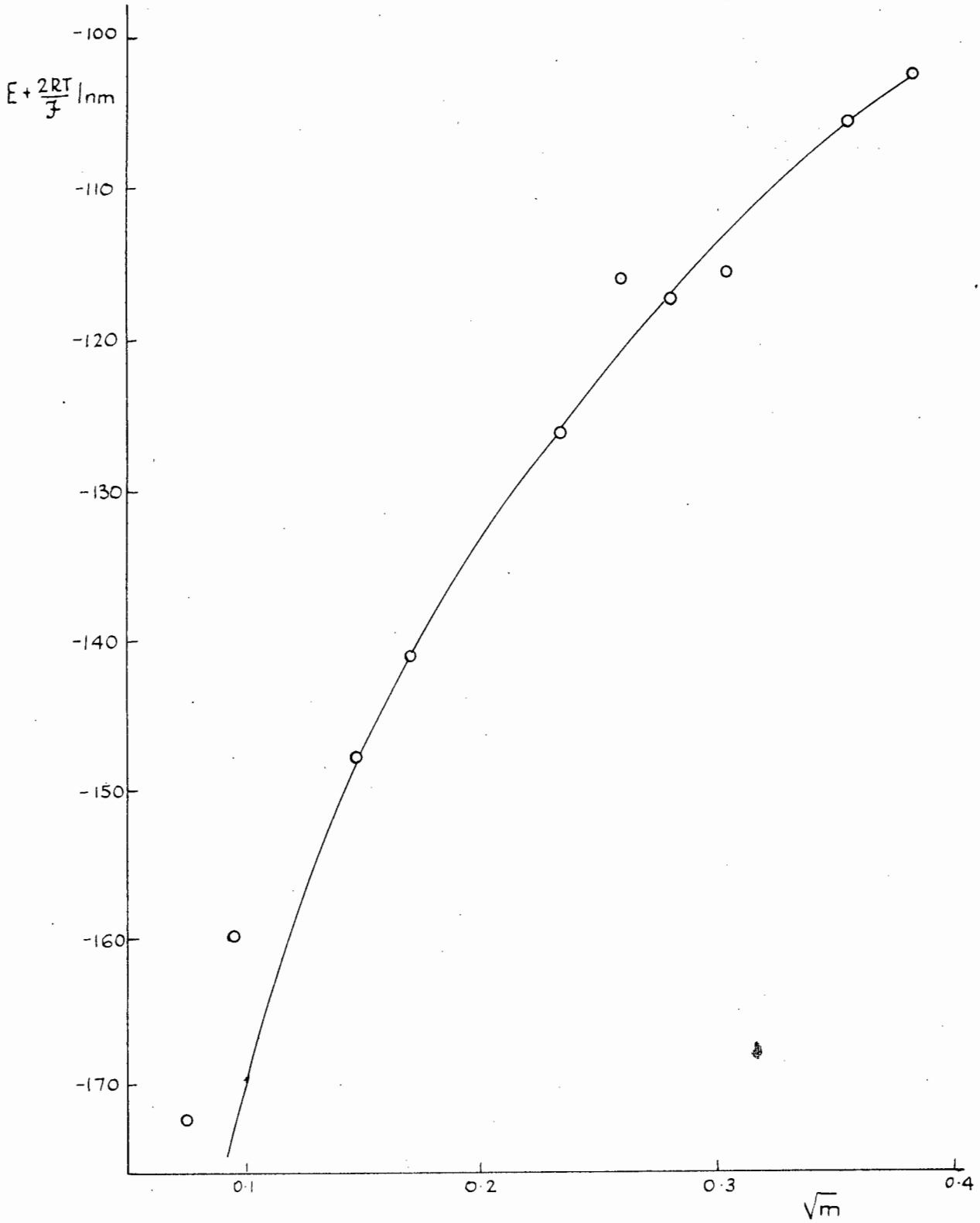


FIG 38. THE CELL Pt, H_2 / H Cl / Ag Cl, Ag

(after Everett and Rasmussen)



points at concentrations below 0.01 molal lie above the straight line plot of $E + \frac{RT}{F} \ln m$ against the molality; this may well be caused by the onset of polymer dissociation, leading to a higher apparent dissociation constant.

TABLE XIX.

The cell Pt, chloranil | HCl || LiCl | Hg_2Cl_2, Hg

Molality	E millivolts	$-(E + \frac{RT}{F} \ln m)$	$-(E + \frac{2RT}{F} \ln m)$
0.0023	-518.0	674.1	830.2
0.0088	-557.2	678.9	800.6
0.0168	-576.2	681.2	786.2
0.0332	-595.9	683.5	771.1
0.0683	-620.6	689.6	758.6
0.1037	-633.5	693.6	753.7

TABLE XX.

The cell Hg, Hg_2Cl_2 | LiCl || HCl | AgCl, Ag

Molality	E millivolts	$-(E + \frac{RT}{F} \ln m)$	$-(E + \frac{2RT}{F} \ln m)$
0.0023	543.5	381.1	218.7
0.0060	511.2	379.8	248.4
0.0145	484.6	375.9	267.1
0.0287	464.9	373.6	282.4
0.0427	450.7	369.7	288.7
0.0611	437.8	366.0	294.2
0.1032	411.8	358.2	304.6

FIG 39. THE CELL Chloranil/HCl//LiCl/Hg_2Cl_2, Hg.

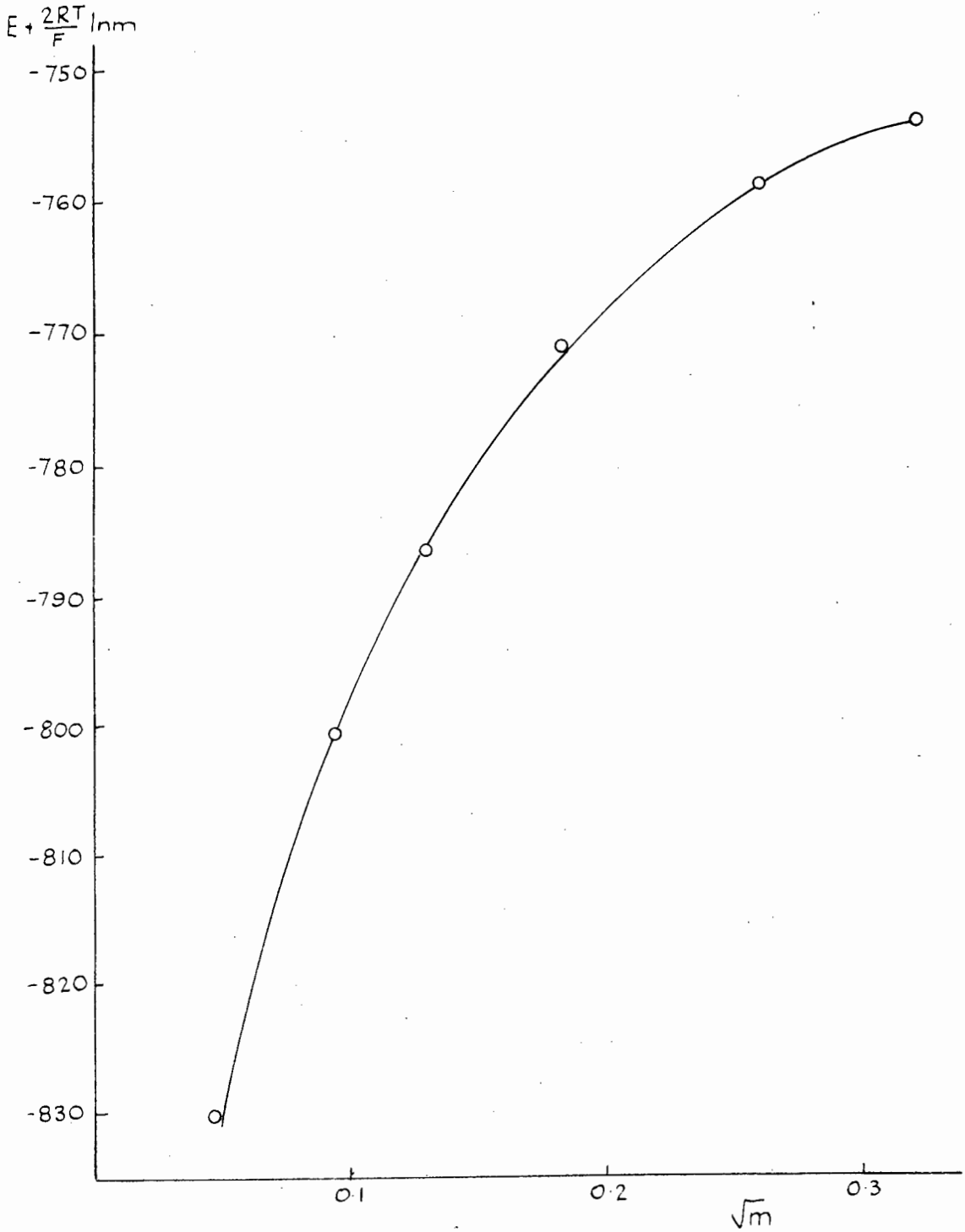
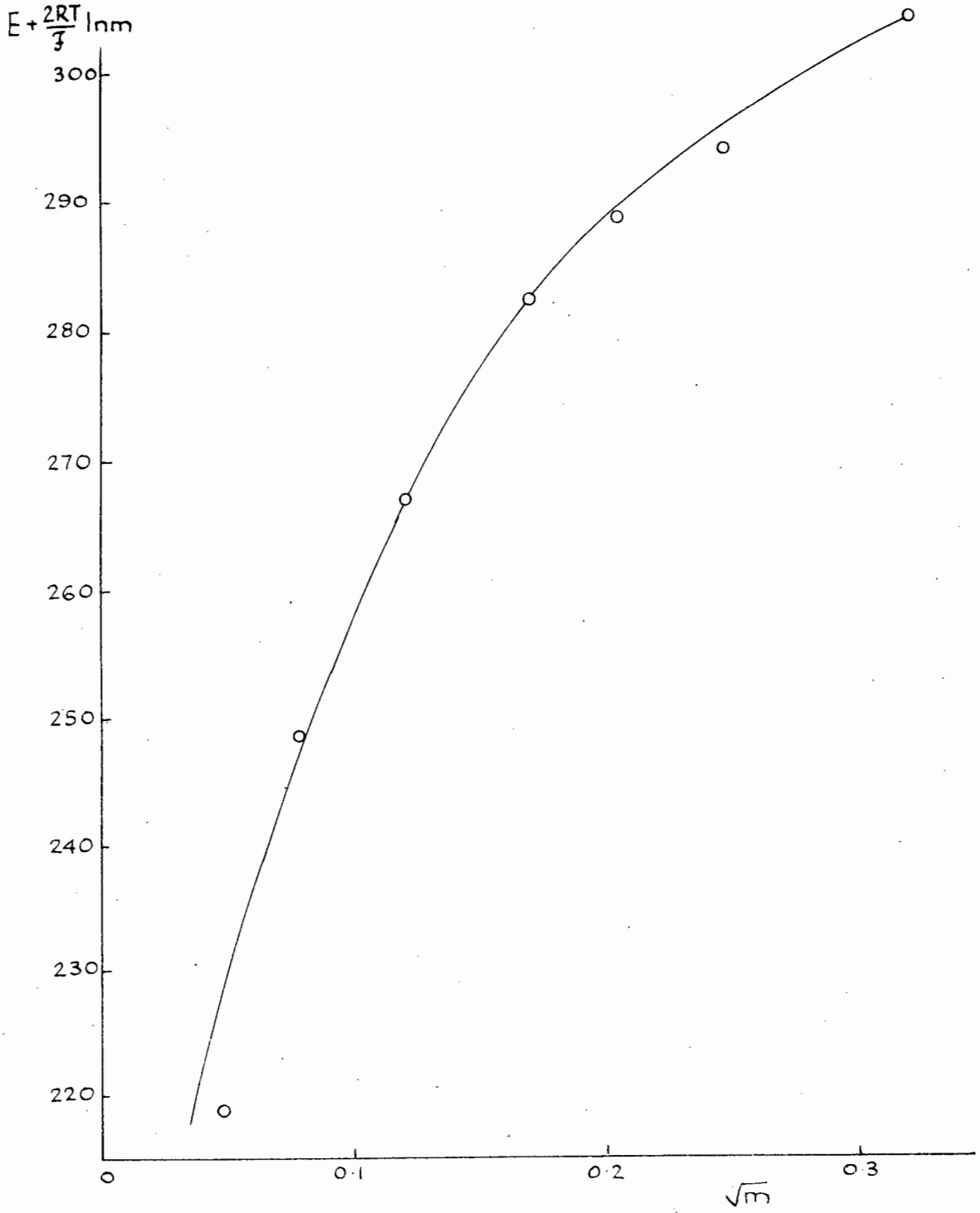


FIG 40. THE CELL $Hg, Hg_2Cl_2 / LiCl // HCl / AgCl, Ag$.



The potentials of the cells Pt,chloranil|HCl||LiCl|Hg_2Cl_2,Hg and Hg,Hg_2Cl_2|LiCl||HCl|AgCl,Ag are given in tables XIX and XX. The results were analysed by Everett and Rasmussen's procedure, their standard emf's being -1.151 volts and -.092 volts respectively (see figs. 41 and 42). The standard potential of the Ag,AgCl electrode found by comparison with the calomel electrode is -0.56 volts, which is in reasonable agreement with Everett and Rasmussen's value (-0.53 volts).

4. Potentiometric Titrations of 1:2:3:4-Tetrahydroquinoline, 1:2:3:4-Tetrahydroisoquinoline and Piperidine in Moist Acetone.

Karrer and Schmid[94] quoted measurements made by Schwarzenbach of the ionisation constants of 1:2:3:4-tetrahydroquinoline and 1:2:3:4-tetrahydroisoquinoline by potentiometric titration of the hydrochlorides of the bases with sodium hydroxide in solution in water and 79% ethanol. No details of the electrodes used were given; moreover, the reading of the pH meter was apparently used to calculate values for the ionisation constant in alcohol, neglecting the changes in the activities of the ions, and no allowance was made for the extremely low solubility of tetrahydroisoquinoline in water.

Potentiometric titrations of 1:2:3:4-tetrahydroquinoline, 1:2:3:4-tetrahydroisoquinoline and piperidine with hydrogen chloride in acetone were performed, using a glass electrode in conjunction with an acetone/saturated lithium chloride/calomel electrode and

FIG 41. THE CELL Chloranil /HCl // LiCl / Hg_2Cl_2, Hg

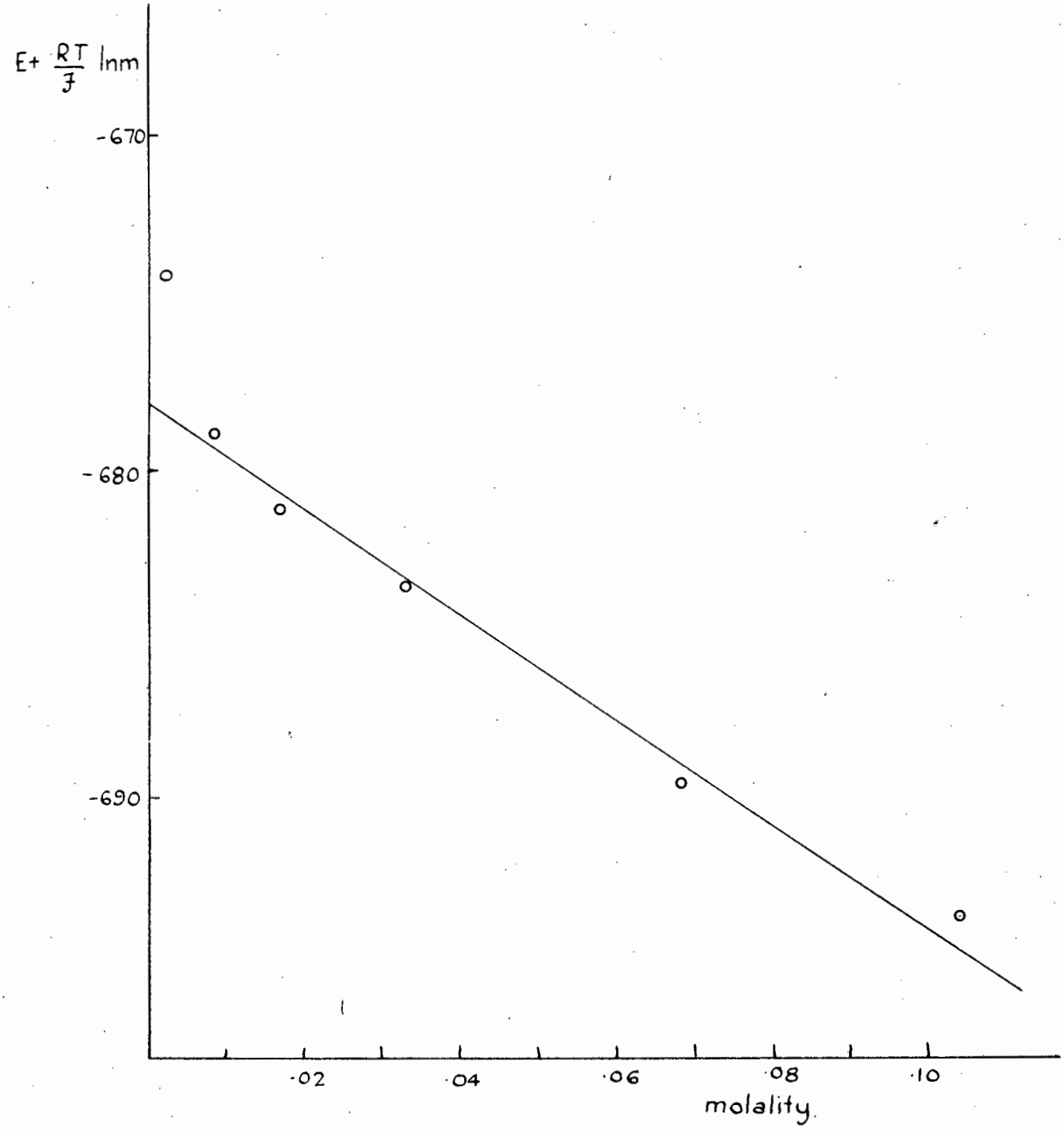
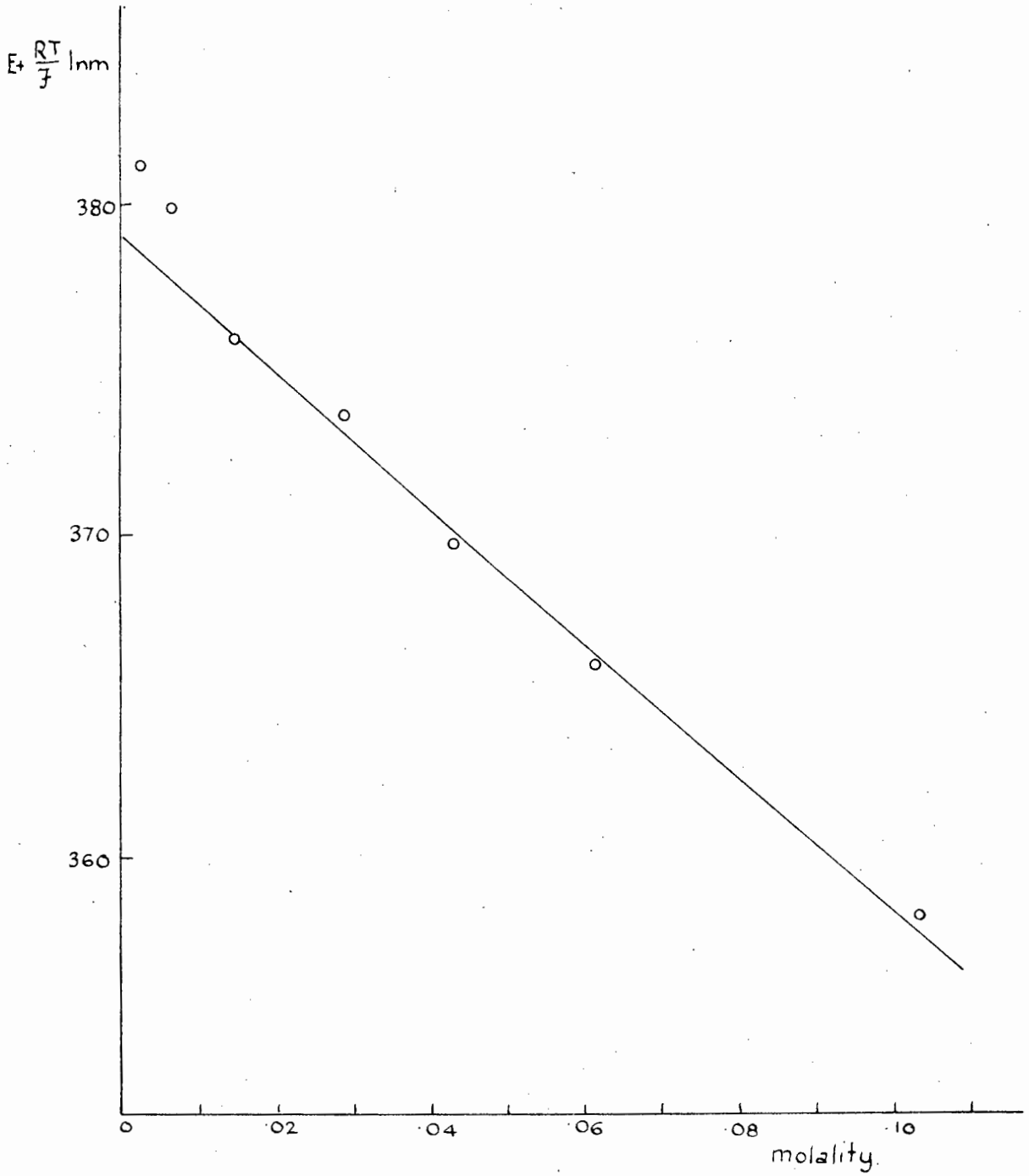


FIG 42. THE CELL $Hg.Hg_2Cl_2/LiCl//HCl/AgCl,Ag$.



a Marconi type TF 717 pH meter. "Analar" grade acetone was used, but no further drying was attempted, so that while the moisture content was fairly low (probably about 0.5%), it was somewhat uncertain.

Titration curves were constructed by plotting the reading of the pH meter against the calculated percentage neutralisation of the base. The curve for tetrahydroisoquinoline was found to be very close to that obtained for the titration of piperidine with hydrogen chloride in moist acetone, and it seemed reasonable to suggest that the ionisation constants of these bases were of similar magnitude (about 10^{-3} in water). These curves are plotted in fig. 43 and detailed results given in appendix IV.1.

The solubility of 1:2:3:4-tetrahydroquinoline in water is sufficient to allow potentiometric titration of its hydrochloride with aqueous sodium hydroxide (fig. 44), leading to a value of $K_b = 1.09 \times 10^{-9}$ (Karrer and Schmid 1.07×10^{-9}), but tetrahydroisoquinoline is only sparingly soluble and the titration curve of its hydrochloride is not easily interpreted. Nevertheless, Karrer and Schmid calculated an ionisation constant from its half neutralisation point of 3×10^{-5}, a value considerably lower than that indicated from the titration of the base in acetone.

Since the buffering effect of a weak acid such as tetrahydroquinoline hydrochloride is low, a rapid change of pH is expected to

FIG. 43 POTENTIOMETRIC TITRATION OF VARIOUS BASES IN MOIST ACETONE.

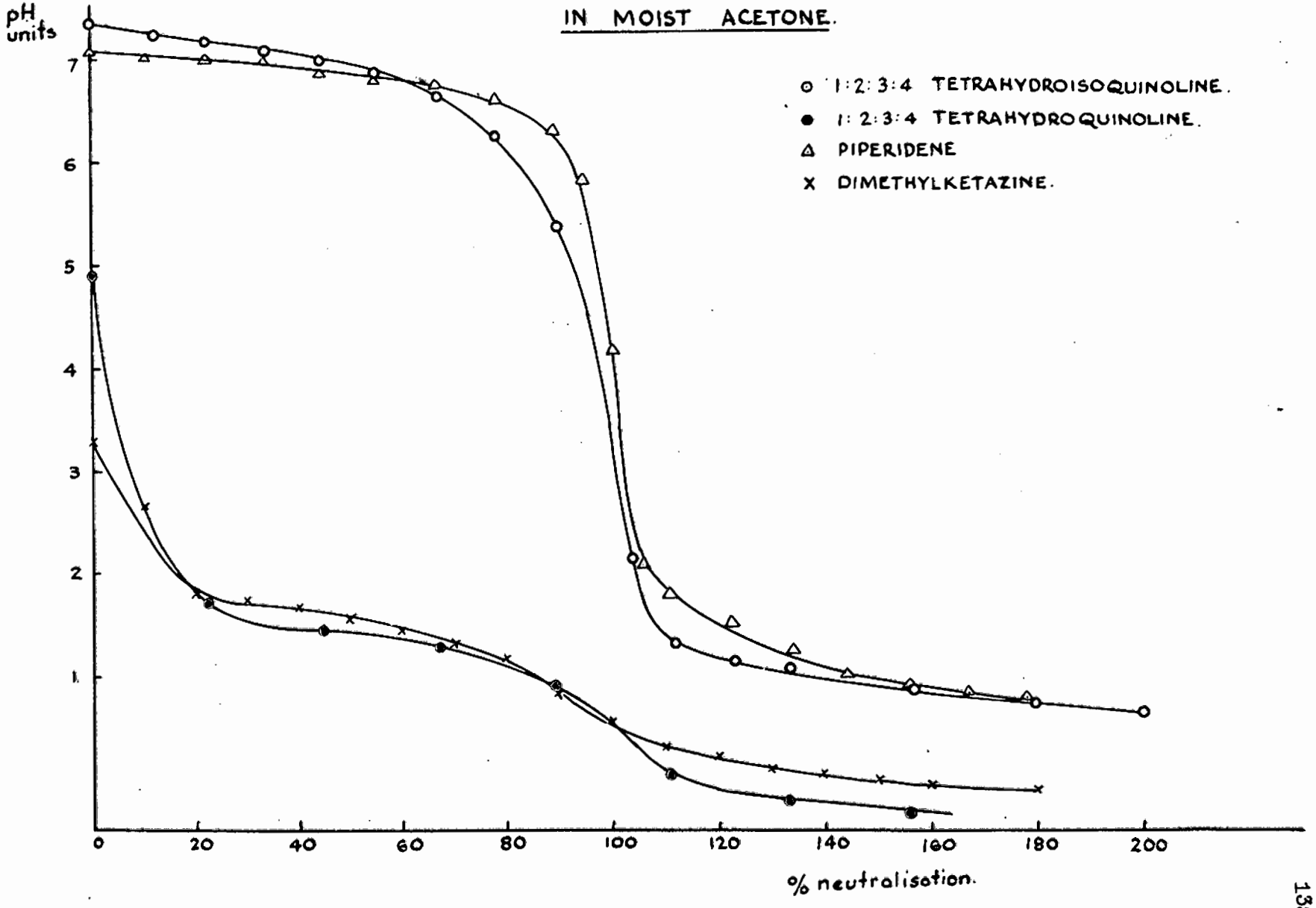
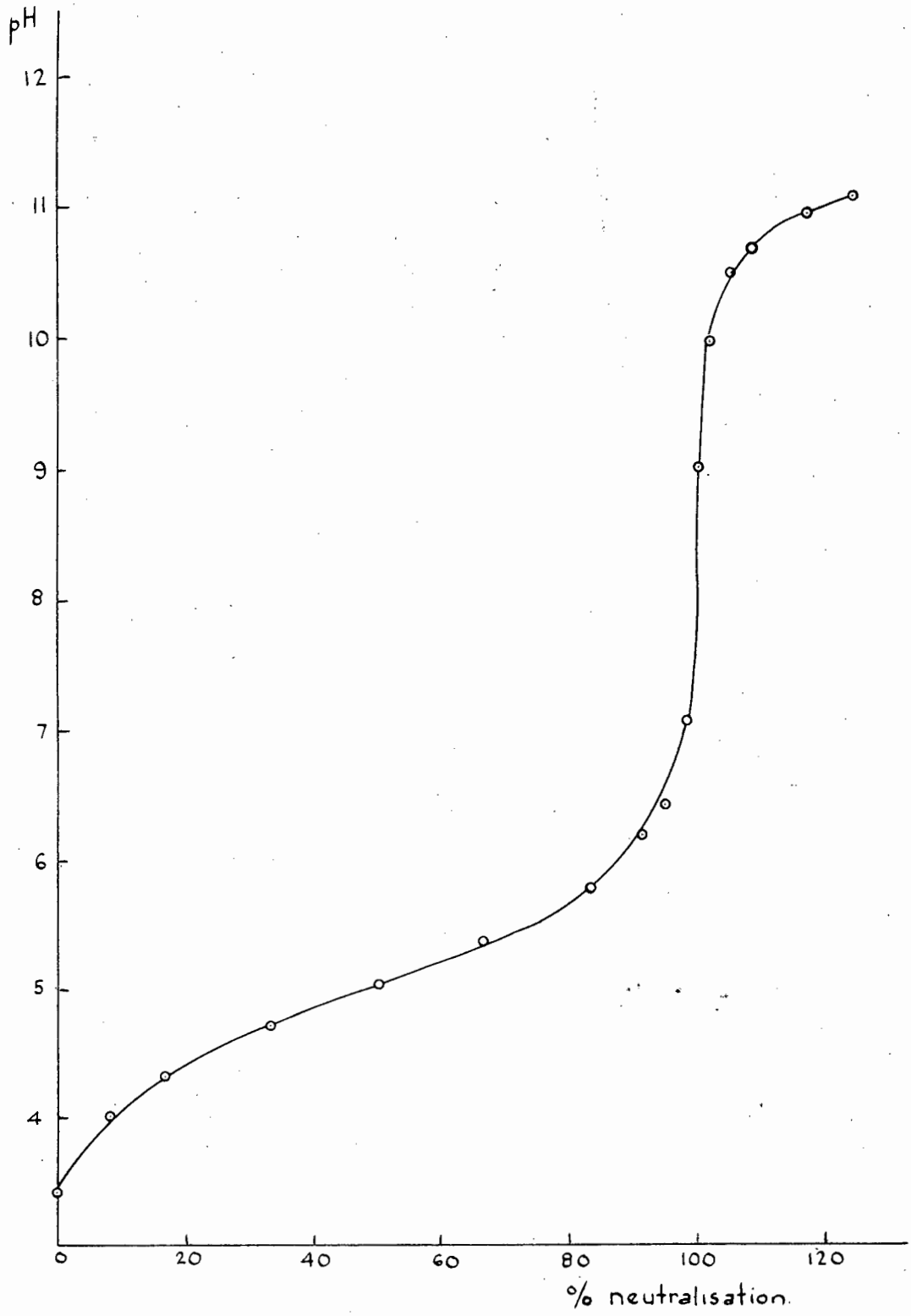


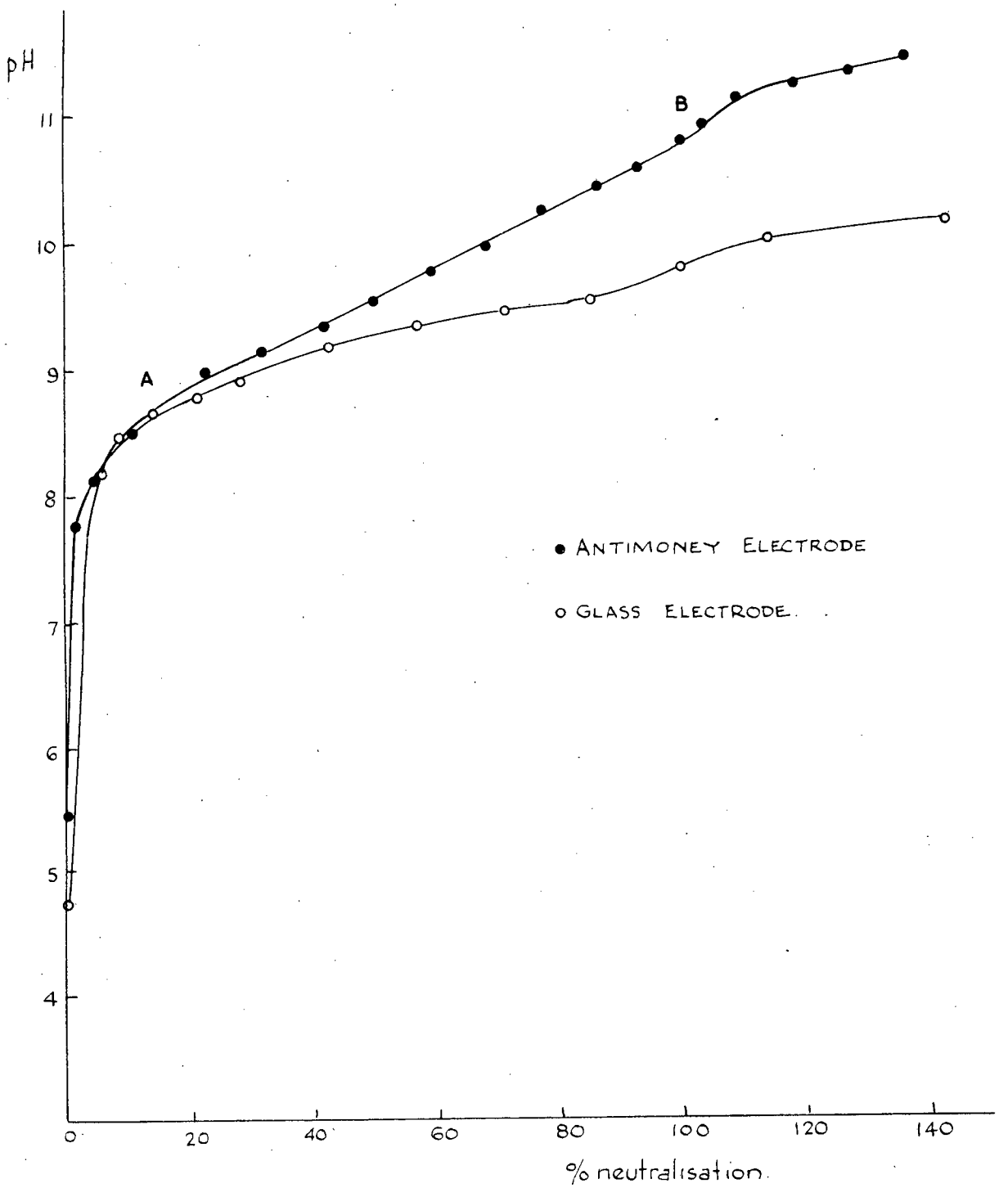
FIG 44. POTENTIOMETRIC TITRATION OF 1:2:3:4-TETRAHYDROQUINOLINE WITH AQUEOUS SODIUM HYDROXIDE.



occur on the first addition of sodium hydroxide. Thereafter the pH should increase more slowly, but the curves obtained with both the antimony and the glass electrodes show an abrupt inflexion at the point A in fig. 45. This is believed to be caused by saturation of the solution with the liberated base, although no precipitation was ever observed, but the base may either be colloidally dispersed or adsorbed on the electrode. The latter possibility might account for both the difference in slope between the curves obtained with the glass and antimony electrodes and the failure of the hydrogen electrode to reach equilibrium beyond 30% neutralisation. [cf. the effect of tetrahydroquinoline and piperidine on the activity of platinum and palladium as hydrogenation catalysts[95].] The small inflexion B occurs at the point corresponding to complete neutralisation.

The solubility of the base was estimated from inflexion A, and this value (0.075 g. litre^{-1}) was used to calculate the point where the concentrations of ion and base in solution were equal. From the pH at this point the ionisation constant, K_b, was found to lie between 10^{-3} (antimony electrode) and 10^{-4} (glass electrode), which is somewhat lower than expected from the acetone titration, but this may be a further consequence of adsorption on the electrodes. These two values are, nevertheless, not inconsistent, and it is therefore suggested that an approximate estimate of the ionisation constant of a base which is insoluble in, or hydrolysed by, water can be

FIG 45. POTENTIOMETRIC TITRATION OF TETRAHYDROISOQUINOLINE HYDROCHLORIDE WITH SODIUM HYDROXIDE.



obtained by potentiometric titration in a suitable solvent, provided that a reference substance of known ionisation constant is available for comparison.

5. An Investigation of the Basic Character of Dimethylketazine.

5.1 The preparation of dimethylketazine (N:N'-diisopropylidene-hydrazine).

18 c.c. 60% hydrazine hydrate was cooled in an ice-salt freezing mixture and 27 c.c. acetone added slowly, the temperature being kept below 10°C. Anhydrous potassium carbonate was added until the mixture became pasty, when the container was stoppered and allowed to stand in the dark for several days. The azine was then extracted with ether, which was distilled off, and the residue fractionated. The fraction boiling between 128°C and 133°C was redistilled, and the 131° - 132°C fraction finally collected. The azine, contained in a flask closed with a ground glass stopper lubricated with "Nonaq", was stored in a deep freeze and redistilled before use. The hydrazine content shown by iodate titration was 28.3% (dimethylketazine requires 28.6%) and the refractive index n_D^{25} was 1.444 (Beilstein, "Handbuch" quotes $n_D^{24.5}$ 1.45102).

5.2 Potentiometric titrations of dimethylketazine with hydrogen chloride in moist acetone.

In order to demonstrate the basic character of dimethylketazine, potentiometric titrations of solutions of the azine with hydrogen chloride in moist acetone were performed, using a glass electrode in conjunction with an acetone/saturated lithium chloride/

calomel electrode. The results of this work are tabulated in Appendix IV.2.

When the reading of the pH scale of the meter was plotted against the percentage neutralisation calculated on the assumption that the azine is a monoacid base, a distinct inflexion occurred in the region of 100% neutralisation (fig. 43). The titration curve was found to lie close to that obtained for the titration of 1:2:3:4-tetrahydroquinoline with hydrogen chloride in acetone, the treatment given in § IV, 4 (page 137) indicating that the ionisation constant of dimethylketazine in water is of the order 10^{-9}. Although it is not possible to calculate the ionisation constant in acetone by this procedure, it does show the presence of a basic substance in this solvent and provides an indication of its relative strength.

5.3 Potentiometric Titrations of Dimethylketazine with hydrogen chloride in anhydrous and aqueous acetone.

Although the preliminary measurements indicated the presence of a basic substance, it was not clear whether this was, in fact, dimethylketazine, or hydrazine, or a hydrazone produced by hydrolysis. The titrations were therefore repeated in anhydrous acetone and acetone containing small known amounts of water. Since it was impossible to seal a glass electrode into the titration vessel, the chloranil electrode was used in conjunction with the acetone/saturated lithium chloride/calomel electrode and a Pye Universal pH and millivoltmeter. A special burette which balanced the pressures throughout

the system during addition of the hydrogen chloride solution was designed, and the apparatus was assembled in the drybox. The liquid in the titration vessel was stirred with dry nitrogen after each addition of hydrogen chloride solution.

The potentials measured are listed in Table XXI, and plotted against the calculated percentage neutralisation (assuming the azine to be a monoacid base) in fig. 46, for anhydrous acetone and acetone to which 0.2%, 0.65% and 1% water had been added.

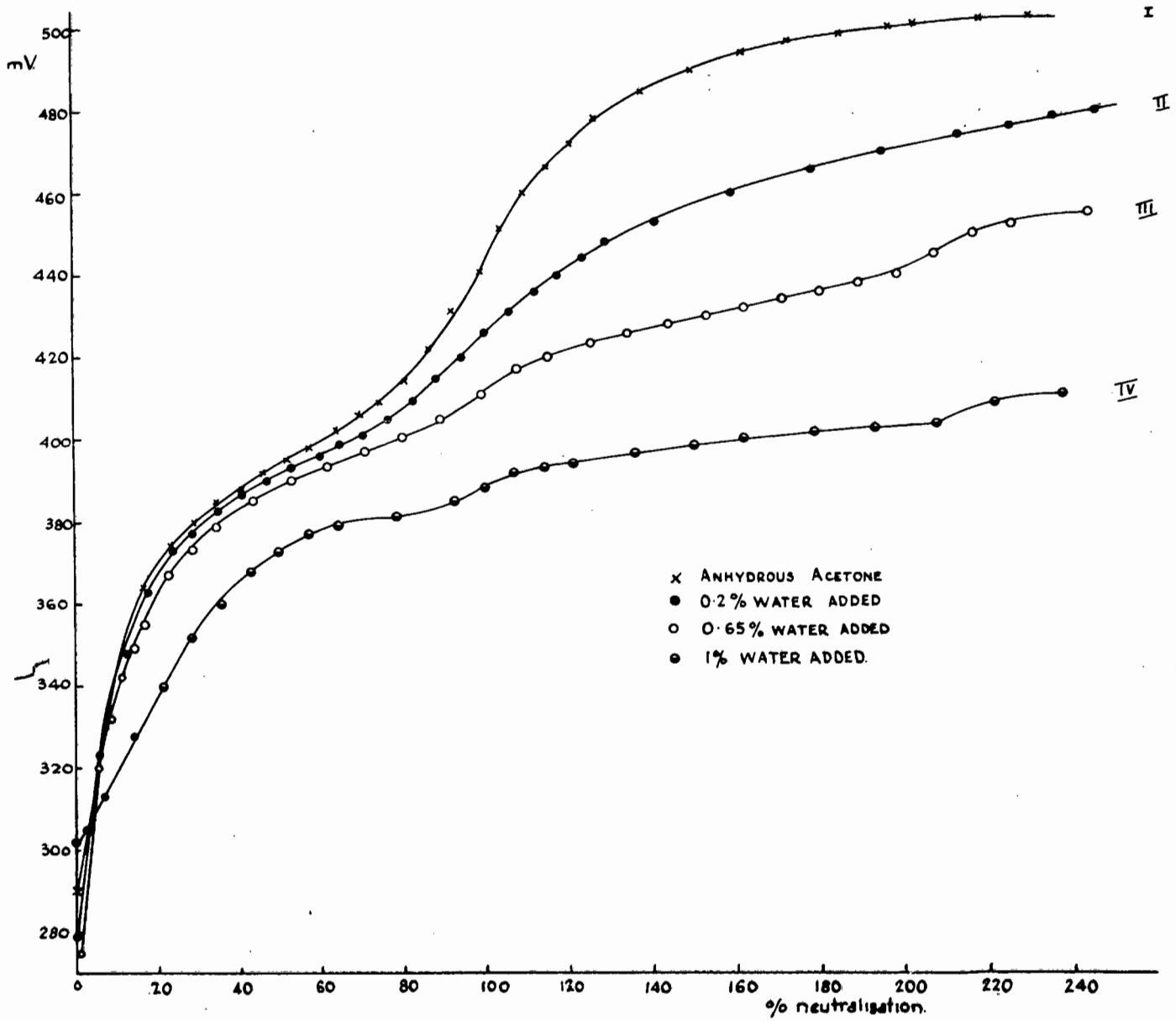
The curve for anhydrous acetone shows an inflexion near 100% neutralisation, and no further inflexion could be obtained even when addition of hydrogen chloride was continued beyond twice the quantity required for neutralisation. The same effect is shown by the curve for 99.8% acetone, although the base appears to be stronger in anhydrous acetone. Acetone hydrazone, which might have been produced by hydrolysis, could be a monoacid base, but would be expected to be stronger than the ketazine, so that its formation does not seem likely here, and the weakness shown by curve II (fig. 46) may well be due to the increased dielectric constant of the solvent. The curves obtained in 99.35% and 99.0% acetone show two inflexions, one near 100% and the other near 200% neutralisation. The first ionisation constant of hydrazine in water is about 10^{-6} and the second approximately 10^{-15}, one of the smallest known (see Table I). The ionisation constant of dimethylketazine appears

TABLE XXI.

Potentiometric titration of solutions of dimethylketazine with HCl in anhydrous and aqueous acetone.

Anhydrous		0.2% water		0.65% water		1% water	
% neut.	mV	% neut.	mV	% neut.	mV	% neut.	mV
0.00	290	0.00	279	0.00		0.00	302
2.87	305	5.98	320	0.91	275	7.14	313
5.75	320	11.76	350	7.30	330	14.3	327
8.62	333	17.64	363	11.8	342	21.4	340
11.5	350	24.0	373	16.4	354	28.6	352
14.4	359	29.4	377	20.9	364	35.7	360
17.3	366	35.3	383	25.4	370	42.8	368
23.0	374	41.2	387	30.0	375	50.0	372
28.8	380	47.1	390	34.6	379	57.2	377
34.5	385	52.9	393	43.6	385	64.3	379
40.3	388	59.8	396	52.7	390	78.6	381
46.0	392	64.7	399	61.8	393	92.8	385
51.7	395	70.6	401	70.9	397	100.0	388
57.5	398	76.5	405	80.1	400	107.1	392
63.8	402	82.4	409	89.2	405	114.3	393
69.3	406	88.2	415	98.3	410	121.5	394
74.7	409	94.2	420	107.5	417	135.8	396
80.4	414	100.0	426	116.4	420	150.0	398
86.2	422	105.9	431	125.5	423	164.3	400
91.9	431	111.8	436	134.6	426	178.5	402
98.8	441	117.6	440	143.8	428	193.0	403
103.4	451	123.5	444	152.8	430	207.4	404
109.2	460	129.3	448	161.9	432	221.5	409
114.9	466	135.2	450	171.0	434	245.8	411
120.7	472	141.2	453	180.0	436		
126.4	478	147.0	456	189.2	438		
138.0	485	158.9	460	198.3	440		
149.6	490			207.3	445		
161.2	494			216.5	450		
172.4	497			222.5	452		
184.4	498			243.4	456		
196.1	500						
202.8	501						
217.9	502						
229.5	503						

FIG 46. POTENTIOMETRIC TITRATION OF DIMETHYLKETAZINE WITH HCl IN ACETONE.



to be of the order 10^{-9} in water (p. 140), so that a second ionisation constant would be too small to measure. In anhydrous acetone only one inflexion is obtained on potentiometric titration with hydrogen chloride, so that the appearance of a second inflexion on the addition of an appreciable amount of water indicates that a mono-acid base has been converted to a diacid base (fig. 46). This is consistent with the hydrolysis of dimethylketazine to hydrazine.

Throughout this work it has been assumed that the presence of a base stronger than acetone would disturb the equilibria between the hydrogen chloride polymer, monomer and ions, and that reaction to form the conjugate acid of the base will take place.

The potentials of half-neutralised weak acids and weak bases in non-aqueous solvents seem to bear a linear relationship to their ionisation constants in aqueous solution, but the slope of the line $\frac{dE_{1/2}}{dpK}$ varies and is generally greater than the theoretical value for aqueous solutions (59 mV. at 25°C for a change of 1pK unit)[100]. The relationship between the mid-titration potentials in non-aqueous solvents of organic bases and their ionisation constants in water has been examined by Hall[102] in glacial acetic acid, Lykken, Porter, Ruliffson and Tuember[101] in benzene/isopropanol and Fritz[92] in acetonitrile, but their comparisons with the aqueous ionisation constants are not relevant to the present work because the object of the investigation was to calculate the ionisation constant of dimethylketazine in acetone. The theoretical value was therefore used for the calculations on solutions in this solvent.

It would appear that assumption of the Henderson equation (IV.1.2) might give some idea of the order of magnitude of the ionisation constant, since at the half-neutralisation point the system here described is assumed to be uncomplicated by the presence of hydrogen chloride polymers (p. 108).

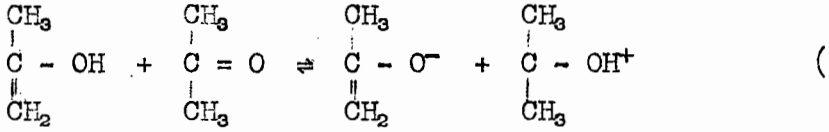
The dissociation constant of the conjugate acid of the azine may then be obtained from the half-neutralisation potential by the equation

$$-\log[H^+] = pK_a = \frac{E_{1/2} - E_{ref}}{59.12}$$

where E_{ref} is the potential of the reference electrode. The half-neutralisation potential interpolated from curve I of fig. 46 is -395 mV., and the potential of the calomel electrode is -654 mV., whence

$$pK_a = \frac{-395 + 654}{59.12}$$

which leads to a value of $K_a = 4.2 \times 10^{-5}$. An estimate of the ionic product of acetone, to enable calculation of a value for the ionisation constant of dimethylketazine, may be obtained by the following procedure. Schwarzenbach[46] has shown that the enol form is present to the extent of about 2.5×10^{-4} percent in acetone. If the conductance of acetone is due to the ionisation of the enol according to



(IV.5.1)

and ionisation is assumed to be complete, the concentration of each

ion will be 4.3×10^{-5} g. ions l^{-1}, and the ionic product given by $(4.3 \times 10^{-5})^2 = 2 \times 10^{-9}$. Complete ionisation, however, would affect the keto-enol equilibrium, so that the ionic product must be considerably lower than this value. Ross Kane[31] has shown the limiting conductance of the solvated proton in acetone to be about 88 ohm^{-1} $cm.^2$, and taking a similar value for the limiting conductance of the anion, because the two ions are about the same size, Λ_o would be about 180 ohm^{-1} $cm.^2$. The limiting equivalent conductance is given by the equation

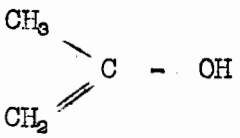
$$\Lambda_o = \frac{1000\ K}{c} \qquad (IV.5.2)$$

and since acetone has a specific conductance of about $10^{-9} ohm^{-1} cm.^{-1}$, the concentration of the ions would be

$$c = \frac{1000\ K}{\Lambda_o} = \frac{10^3 \times 10^{-9}}{180} = 5.6 \times 10^{-9} \text{ mole } l^{-1},$$

leading to an ionic product 3.1×10^{-17}. The conductance of the cation may be due in part to proton transfer, which would make its conductance greater than that of the anion, so that assumption of an equal value for the limiting conductance of the anion may not be justified.

The $\diagdown\!\!\!\diagup C - OH$ group is found both in phenol (K_a = 1.1×10^{-10}) and hydroquinone ($K_a = 1.3 \times 10^{-10}$), and taking the dissociation constant of the enol form,



to be of the same order of magnitude, the expression

$$\frac{\left[H^+\right]\left[\begin{array}{l}CH_3\\ \diagdown\\ \quad C - O^-\\ \diagup\!\!\diagup\\ CH_2\end{array}\right]}{\left[\begin{array}{l}CH_3\\ \diagdown\\ \quad C - OH\\ \diagup\!\!\diagup\\ CH_2\end{array}\right]} = 10^{-10} \qquad \text{(IV.5.3)}$$

is obtained.

In view of the small dissociation constant, the concentration of undissociated acid may be taken as equal to the total enol concentration (4.3×10^{-5} moles l^{-1}), so that the ionic product

$$\left[H^+\right]\left[\begin{array}{l}CH_3\\ \diagdown\\ \quad C - O^-\\ \diagup\!\!\diagup\\ CH_2\end{array}\right] = 4.3 \times 10^{-15}$$

and $$\left[H^+\right] = \left[\begin{array}{l}CH_3\\ \diagdown\\ \quad C - O^-\\ \diagup\!\!\diagup\\ CH_2\end{array}\right] = \sqrt{4.3 \times 10^{-15}} = 6.6 \times 10^{-8} \text{ g. ion } l^{-1}$$

Substitution of this concentration in equation (IV.5.2) leads to a limiting equivalent conductance of 15.2 ohm^{-1} $cm.^2$, which is impossibly low in view of Ross Kane's value for the limiting conductance of the proton, but the dissociation constant of the enol

acid in acetone might be expected to be rather less than 10^{-10}, the constant determined for phenol in water, and the value 4.3×10^{-15} may provide an upper limit for the ionic product with 3.1×10^{-17} as a lower limit.

Taking the ionic product of acetone to be 10^{-16}, the ionisation constant for dimethylketazine in acetone is found to be $K_b \sim 10^{-11}$. This is reasonably consistent with the value of 10^{-9} in water, which was determined by comparison of its titration curve in moist acetone with that obtained for 1:2:3:4-tetrahydroisoquinoline (see § IV, 5.2, page 140).

PART V.

CONDUCTANCE STUDIES ON SOLUTIONS OF DIMETHYLKETAZINE IN ACETONE.

1. The Conductimetric Titration of Dimethylketazine with Hydrogen Chloride in Anhydrous Acetone Solution.

A lower limit for the limiting equivalent conductance of a hydrazinium salt in acetone can be calculated from the equivalent conductance of the salt in aqueous solution by correcting for the solvent viscosity and dielectric constant. Assuming that the ions are spherical and that the macroscopic dielectric constant of the solvent will not affect primary solvation owing to dielectric saturation, the solvation energy of hydrazine is found to be lower in acetone than in water[102]. Solvation in acetone will therefore be less than in water, and this factor will tend to increase the conductance so that Λ_0 will be considerably higher than in water. Owing to the larger size of the cation, the corresponding dimethylketazinium salt will have a lower limiting equivalent conductance in acetone, and it appeared that it might be possible to demonstrate the existence of the dimethylketazinium ion in this solvent by comparison of the measured limiting equivalent conductance of a supposed ketazinium salt with values calculated for both this salt and the hydrazinium salt of the same acid. To this end, the conductances of aqueous solutions of hydrazinium chloroplatinate were measured as described in § II.3 (page 51), but the solubility of dimethyl-

ketazinium chloroplatinate in acetone was found to be too low to allow preparation of a range of solutions of concentrations suitable for conductivity measurements. Although no noticeable dissolution of the salt had occurred, the conductance of a saturated solution was measured, and a calculation based on a reasonable value for Λ_0 indicated that the solubility was of the order 10^{-7} mole l^{-1}. This low solubility is consistent with Pugh's preparation of dimethylketazinium salts by precipitation with acetone[8].

Although efforts to prepare crystalline simple salts of aliphatic azines had been unsuccessful[17], the potentiometric studies described in § IV.5 (page 140) indicated that dimethylketazine was a monoacid base of low ionisation constant. A range of mixtures of varying proportions of dimethylketazine and hydrogen chloride in acetone was therefore examined, the conductance of each being measured at several dilutions. Values of the conductance at three selected azine concentrations were then found by interpolation, and used to construct conductimetric titration curves and find an equivalence point, which would correspond to a solution of the "salt" $C_6H_{13}N_2^+Cl^-$. It was assumed that hydrogen chloride would behave as a simple monobasic acid in its reaction with dimethylketazine since presence of the base would disturb the equilibria between HCl polymers, monomers and ions (see §§ III.4 (p. 108) and IV.5 (p. 144)).

The required amount of dimethylketazine was added to acetone

solutions of hydrogen chloride in a calibrated 50 ml. volumetric flask, which was then filled to the mark with acetone, the entire operation being performed in the drybox. After thorough mixing, a sample was taken for gravimetric chloride analysis. Series of dilutions of the original solutions were then made, and the chloride analysis repeated on the last of each series, the results being disregarded if these did not agree with the calculated values. The resistances of these solutions were then measured on the Jones bridge, and the results are listed in Appendix V.1.

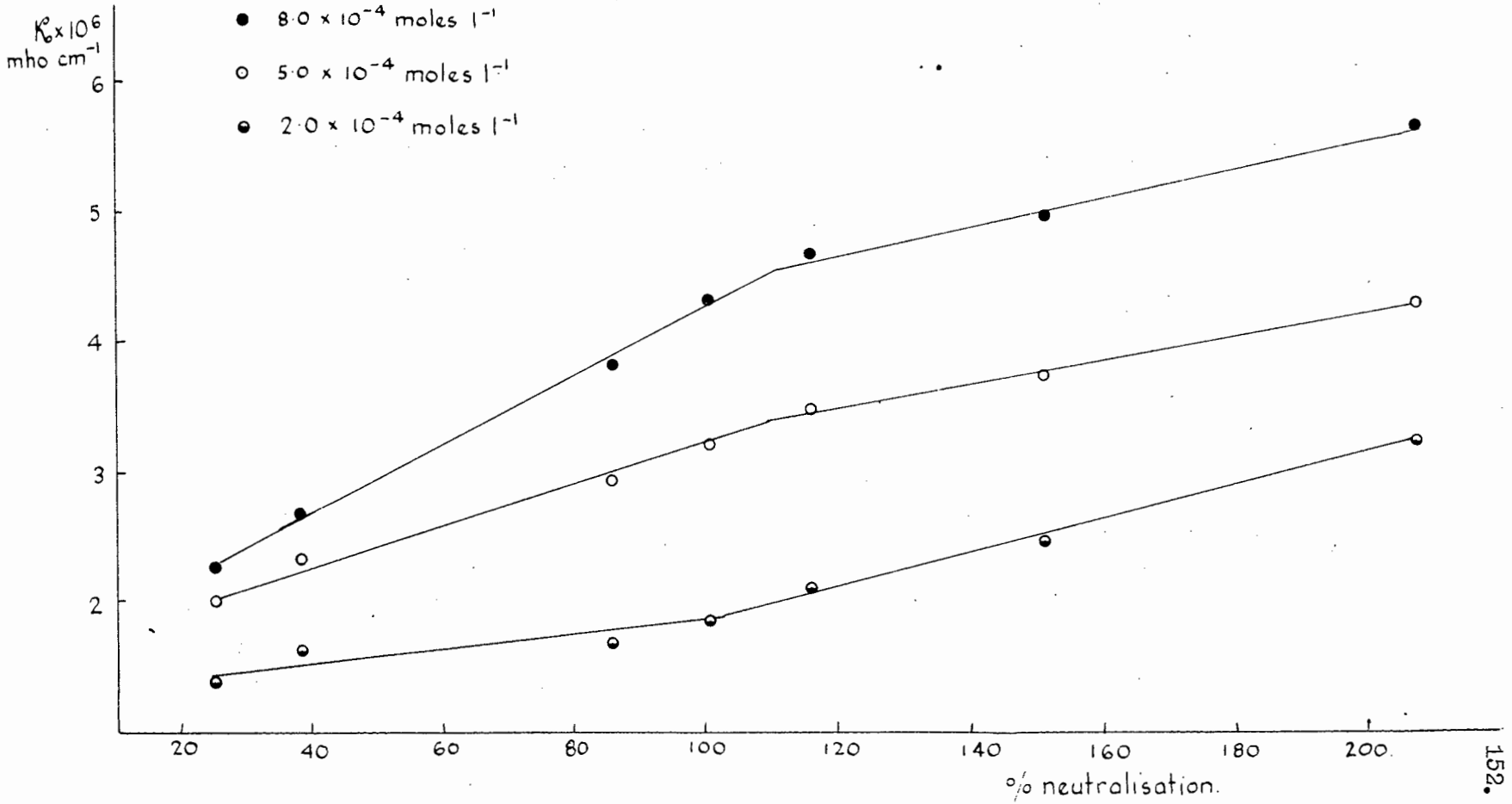
TABLE XXII.

Conductimetric titration of dimethylketazine with hydrogen chloride in acetone interpolated conductances.

Percentage Neutralisation	25.23	38.59	86.09	100.9	116.1	151.4	207.8
$c \times 10^3$ mole l^{-1}	$K \times 10^6$ ohm^{-1} $cm.^{-1}$	$K \times 10^6$ ohm^{-1} $cm.^{-1}$	$K \times 10^6$ ohm^{-1} $cm.^{-1}$	$K \times 10^6$ ohm^{-1} $cm.^{-1}$	$K \times 10^6$ ohm^{-1} $cm.^{-1}$	$K \times 10^6$ ohm^{-1} $cm.^{-1}$	$K \times 10^6$ ohm^{-1} $cm.^{-1}$
2.0	1.42	1.64	1.70	1.87	2.14	2.48	3.25
5.0	2.02	2.36	2.95	3.22	3.50	3.75	4.32
8.0	2.29	2.72	3.85	4.36	4.70	4.98	5.71

The specific conductance for each series of dilutions was plotted against the concentration of dimethylketazine, and interpolated values for 2.0×10^{-3}, 5.0×10^{-3} and 8.0×10^{-3} moles l^{-1} read off. These were plotted against the theoretical percentage neutralisation of the

FIG 47. CONDUCTRIMETRIC TITRATION OF DIMETHYLKETAZINE WITH HYDROGEN CHLORIDE IN ACETONE



azine, and the titration curves shown in fig. 47 were constructed. The interpolated conductances are given in Table XXII.

2. Discussion.

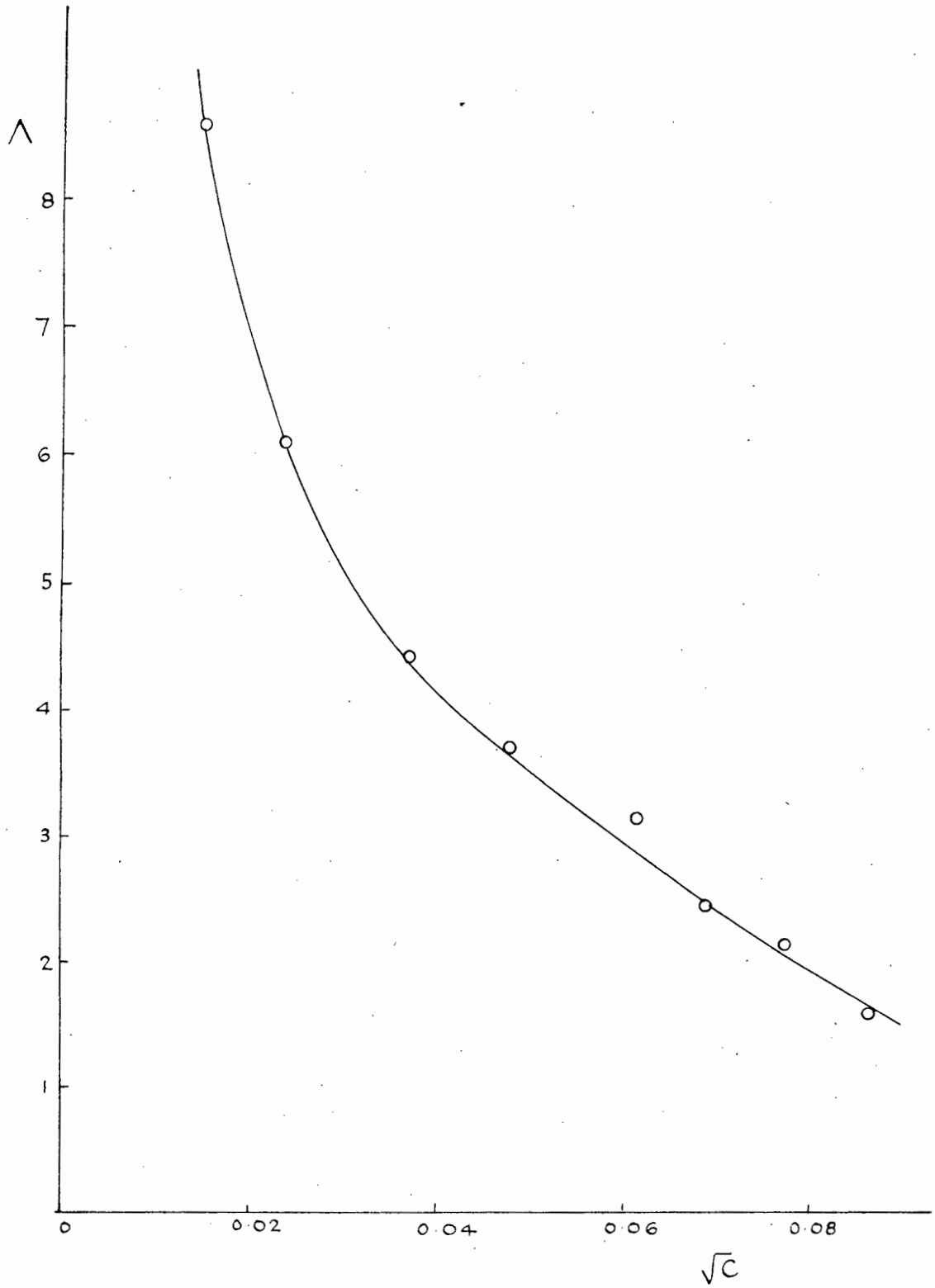
If the dimethylketazinium ion exists, its concentration will be greatest at the equivalence point of the titration curve, where interference from other ionic species is minimal, and the solution should consist of dimethylketazinium chloride, hydrazinium chloride or a mixture of the two, although the emf studies described in § IV.5(p. 144) indicated that the hydrazinium salt is unlikely to be produced in anhydrous acetone. Equivalent conductances were calculated from the series of dilutions of composition nearest to that of the equivalence points (see Table XXIII), and the plot of Λ against the square root of the concentration is shown in fig. 48.

TABLE XXIII.

Equivalent conductance of "dimethylketazinium chloride".

c x 10^3	Specific conductance x 10^6 ohm^{-1} $cm.^{-1}$	Equivalent conductance ohm^{-1} $cm.^2$
7.471	11.842	1.585
5.977	12.850	2.150
4.781	11.715	2.450
3.825	12.168	3.181
2.295	8.498	3.703
1.377	6.066	4.405
0.5508	3.3492	6.081
0.2203	1.8873	8.567

FIG 48. EQUIVALENT CONDUCTANCE OF "DIMETHYLKETAZINIUM CHLORIDE"



As the "salt" appeared to be a weak electrolyte, and measurements could not be carried out at extreme dilutions, extrapolation of this curve to obtain a provisional value for the limiting equivalent conductance was not feasible. Nevertheless, it seemed likely that values for Λ_0 for both dimethylketazinium and hydrazinium chlorides could be calculated, using the observed values of the equivalent conductance in the Falkenhagen equation[87].

$$\Lambda = \left(\Lambda_0 - \frac{41.25\ (z_+ + z_-)\sqrt{I}}{\eta(\varepsilon T)^{1/2}(1 + \kappa a)} \right) \left(1 - \frac{2.801 \times 10^6 (z_+ z_-) q}{(\varepsilon T)^{3/2}\ (1 + \sqrt{q})} \cdot \frac{e^{\kappa a(1 - \sqrt{q})} - 1}{\kappa a\ (1 - \sqrt{q})} \right.$$

$$\left. \cdot \frac{\sqrt{I}}{1 + \kappa a} \right) \qquad (V.1)$$

where κ is defined by

$$\kappa = \left(\frac{8\pi N e^2}{1000\ \varepsilon k T} \right)^{1/2} \sqrt{I}\ , \qquad (V.1a)$$

and the sum of the ionic radii is represented by a, the valences of the ions by z_+ and z_- and the mobility function by q, which is defined by

$$q = \frac{z_+ z_-}{z_+ + z_-} \cdot \frac{\lambda_+^0 + \lambda_-^0}{z_- \lambda_+^0 + z_+ \lambda_-^0}$$

$$= \tfrac{1}{2} \quad \text{for symmetrical electrolytes where } z_+ = z_-.$$

The values of Λ_0 so obtained could then be used in Fuoss plots[35], and it was expected that the curve providing the best straight line

would indicate the ionic species present.

Two sets of calculations using this equation were made, one employing the van der Waals' radii, and the other the crystal radii for the dimethylketazinium and hydrazinium ions. These calculations provided approximately the same values for the limiting equivalent conductances of both the salts, viz.: dimethylketazinium chloride 14.34 and hydrazinium chloride 14.40. Since the limiting conductance of the chloride ion is 111[105], this approach was abandoned.

The lack of diffusion coefficients appeared to close the approach offered by the Nernst-Hartly relation[104]

$$D = \frac{RT}{F^2} \cdot \frac{z_+ + z_-}{z_+ z_-} \cdot \frac{\lambda_+^0 \lambda_-^0}{\lambda_+^0 + \lambda_-^0} \left(1 + \frac{d \ln f}{dc}\right) \qquad (V.2)$$

but Edward[88] has shown the applicability to diffusion in water of a modified Stokes-Einstein equation

$$D = \frac{kT}{5\pi r_w \eta X'} \qquad (V.3)$$

in which r_w is the van der Waals' radius and X' the frictional coefficient to correct for the shapes of non-spherical ions[89]. Although this equation is not valid for solutions in non-aqueous solvents, White[90] has shown that the diffusion coefficients of fatty acids in n-decane at 30°C are represented satisfactorily by

$$D = \frac{kT}{2.9\pi r_M \eta X'}, \qquad (V.4)$$

r_M being the molecular radius, and Edward has altered the form of this expression to

$$D = \frac{\mathcal{R}T}{3.4\pi r_w \eta X^3} \qquad (V.5)$$

the change in the numerical constant accounting for the difference introduced by substitution of the van der Waals' radius for the molecular radius.

If the Nernst-Hartley relation (V.2) is equated with the modified Stokes-Einstein equation (V.5) the equation

$$\frac{RT}{F^2}\ \frac{z_+ + z_-}{z_+ z_-}\ \frac{\lambda_+^0\ \lambda_-^0}{\lambda_+ + \lambda_-}\left(1 + \frac{d\ \ln f}{dc}\right) = \frac{\mathcal{R}T}{3.4\pi r_w \eta X^3} \qquad (V.6)$$

is obtained. Assuming that in dilute solution $\frac{d\ \ln f}{dc} = 0$, this equation becomes

$$\frac{RT}{F^2}\ \frac{z_+ + z_-}{z_+ z_-} \cdot \frac{\lambda_+^0\ \lambda_-^0}{\lambda_+^0 + \lambda_-^0} = \frac{\mathcal{R}T}{3.4\pi r_w \eta X^3}. \qquad (V.7)$$

However, calculation on the basis of Edward's empirical constant produced impossible values for the limiting conductances of both the dimethylketazinium and hydrazinium ions in acetone solution (dimethylketazinium 298; hydrazinium 2713). Edward's empirical constant might be expected to vary from solvent to solvent on account of differing solvation effects, and it therefore seemed reasonable to calculate a new constant from the known conductances of the ammonium[91] and chloride[105] ions in acetone.

On introduction of the numerical constants, temperature and viscosity of acetone, equation (V.7) reduces to

$$\frac{\lambda_+^o \lambda_-^o}{\lambda_+^o + \lambda_-^o} = \frac{8.0850 \times 10^{-6}}{b\, r_w X'} \qquad (V.8)$$

for a uni-univalent electrolyte. For ammonium chloride (V.8) becomes

$$\frac{10530}{205.9} = \frac{8.0850 \times 10^{-6}}{b \times 1.65 \times 10^{-8} \times 1.0}$$

whence b is found to be 9.58, so that Edward's factor $(3.4 \pi r_w \eta X')$ of equation V.5 should be replaced by $(9.58 \pi r_w \eta X')$. This factor might seem large in comparison with the factor (5) for aqueous solutions, but although solvation is greater in water than in acetone, the effective radii of the ions produced will be larger in the latter owing to the size of the solvent molecule.

Substitution of this factor in equation (V.8) produced limiting equivalent conductances of 149.7 for dimethylketazinium chloride and 168.4 for hydrazinium chloride in acetone. Fuoss plots were then made using these figures as provisional values for Λ_0, but both series of points lay close together and no straight line could be drawn through either set (fig. 49). (It might be worthy of remark that a Fuoss plot calculated from the provisional value of 14.4 for Λ_0 provided for the hydrazinium salt by the Falkenhagen Equation, produced points which lie on almost the same curve).

FIG. 49. "DIMETHYLKETAZINIUM CHLORIDE."

FUOSS PLOT

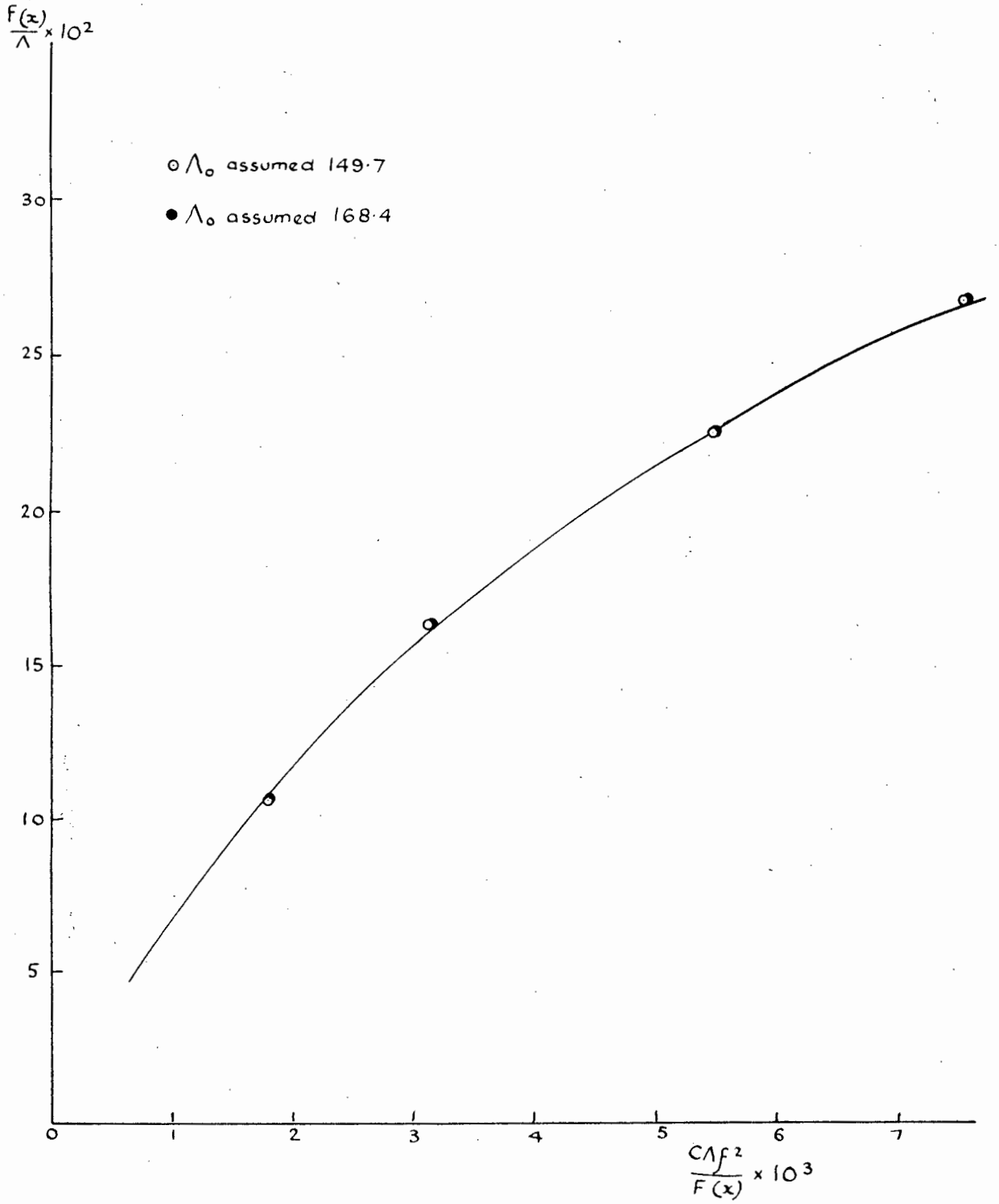


TABLE XXIV.

Fuoss plots for equivalent mixtures of dimethylketazinium and hydrogen chloride in acetone.

(a) Dimethylketazinium chloride Λ_0 assumed 149.7

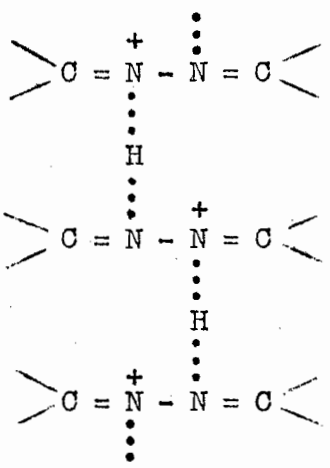
$c \times 10^3$ mole l^{-1}	Λ mho cm.^{2}	$F(x)$	f^2	$\frac{F(x)}{\Lambda}$	$\frac{c\Lambda f^2}{F(x)} \times 10^3$
2.295	3.703	0.98599	0.87498	0.2663	7.541
1.377	4.405	0.98812	0.89339	0.2243	5.485
0.5508	6.081	0.99117	0.91976	0.1630	3.108
0.2203	8.567	0.99338	0.93922	0.1160	1.784

(b) Hydrazinium chloride Λ_0 assumed 168.4.

$c \times 10^3$ mole l^{-1}	Λ mho cm.^{2}	$F(x)$	f^2	$\frac{F(x)}{\Lambda}$	$\frac{c\Lambda f^2}{F(x)} \times 10^3$
2.295	3.703	0.98691	0.88172	0.2666	7.592
1.377	4.405	0.98894	0.89670	0.2245	5.500
0.5508	6.081	0.99187	0.92420	0.1631	3.121
0.2203	8.567	0.99388	0.94278	0.1160	1.790

Handling and analytical difficulties precluded measurements at lower concentrations, but trials with Catalin molecular models indicated that dimethylketazinium ions were sterically capable of associating in groups of six to ten, through the formation of proton bonds between the coordinated hydrogen atom of one ion and the "available" nitrogen atom of another,

i.e.:



The low mobility of the large aggregates so formed would explain the low value of the limiting conductance obtained from the Falkenhagen equation, and variation of the mean size of the groups with concentration may be responsible for the failure of the Fuoss procedure.

The shapes of the conductimetric titration curves are typical of those obtained for neutralisation of a weak base by a weak acid (see fig. 47). Over the portion of the curve where insufficient acid for neutralisation has been added, the conductance depends on the concentration of ions produced by equivalent neutralisation of the base, and the slope would therefore be expected to be steeper at higher concentrations of the base than at lower, as is observed. Beyond the equivalence point, the slope of the curve should be very much lower on account of the low dissociation constant of the acid, but it would be expected to vary with concentration. A plausible explanation of the virtual constancy of this slope with concen-

tration might be provided by the existence of hydrogen chloride polymers as described in § III.4 (p. 108).

PART VI.

CONCLUSION.

Prior to the commencement of this investigation, only the analytical results of Pugh and his co-workers provided any evidence for the existence of salts of dimethylketazine. Consideration of all the results together affords circumstantial support for the existence of the dimethylketazinium ion in solution in acetone, but no single line of approach undertaken was sufficient to prove it conclusively.

Probably the strongest evidence is provided by the curves obtained from the potentiometric titration of dimethyketazine with hydrogen chloride (fig. 46). These not only show that the compound titrated is a monoacid base in anhydrous acetone, but that the addition of small amounts of water produce a diacid base, results which are consistent with the hydrolysis of dimethylketazine. Furthermore, it was possible to calculate that the ionisation constant of the base in anhydrous acetone is of the order 10^{-11}.

The variation of the slopes of those portions of the conductimetric titration curves where insufficient acid for neutralisation had been added showed that the products of the titration were ionic in character, and that dimethylketazine is a weak base in acetone, but it was not possible to determine a limiting

equivalent conductance for the assumed salt.

Much of the argument of this thesis depends for its validity on the assumptions that the acetone used was in fact pure, that its moisture content was the minimum attainable, and that the moisture content remained constant from sample to sample. An independent investigation of these assumptions appears desirable. It appears from the present work that a study of the properties of acids in solution in acetone should be undertaken, and to this end, modification of the circuit of the A.C. potentiometer is projected. It is intended to extend the range of the instrument to enable the measurement of resistances lower than those of which the prototype is capable, and obtain results for solutions of lower concentration than hitherto possible.

Further projected work includes attempts to measure the diffusion coefficients of dimethylketazine using isotopically labelled "ions", and it is hoped that the Department of Physics of this University will shortly commence a crystallographic investigation of dimethylketazinium chlorostannate.

APPENDIX I.

Bibliography.

1. E.C. Gilbert, J. Phys. Chem., 1929, 33, 1235.
2. L.F. Audrieth and B.A. Ogg, The Chemistry of Hydrazine, New York, 1951.
3. W.C.E. Higginson and D. Sutton, J. Chem. Soc., 1953, 1402. W.C.E. Higginson and P. Wright, J. Chem. Soc., 1955, 1551.
4. J.W. Cahn and R.E. Powell, J. Amer. Chem. Soc., 1954, 76, 2568.
*5. S. Vivarelli, Ann. Chim. (Rome), 1951, 41, 415.
6. P.A. Giguère, Trans. Roy. Soc. Canada (III), 1941, 35, 1.
7. G. Schwarzenbach, Helv. chim. Acta, 1936, 19, 178.
8. W. Pugh and A.M. Stephen, J. Chem. Soc., 1952, 4138.
9. W. Pugh and A.M. Stephen, J. Chem. Soc., 1953, 354.
10. W. Pugh, J. Chem. Soc., 1953, 1934.
11. W. Pugh, J. Chem. Soc., 1953, 2491.
12. W. Pugh and M.C.B. Hotz, J. Chem. Soc., 1953, 2493.
13. W. Pugh, J. Chem. Soc., 1953, 3445.
14. W. Pugh, J. Chem. Soc., 1954, 1385.
15. W. Pugh, J. Chem. Soc., 1954, 2423.
16. M. Lamchen, W. Pugh and A.M. Stephen, J. Chem. Soc., 1954, 2429.
17. E.G. Sohn, R.H. Marks and W. Pugh, J. Chem. Soc., 1955, 1753.
18. R.H. Marks, Ph.D. thesis, University of Cape Town, 1957.
19. W. Schaffer, Acta Crystallographica, 1954, 7, 242.
20. O. Tessche, personal communication.
21. I.R. Morrison, quoted by W. Pugh and M.C.B. Hotz, J. Chem. Soc., 1953, 2493.

22. G. Schwarzenbach and A. Zobrist, Helv. chim. Acta, 1952, 35, 1291.

23. R.L. Rebertus, H.A. Laitinen and J.C. Bailar, J. Amer. Chem. Soc., 1953, 75, 3051.

24. E.G. Sohn, Ph.D. thesis, University of Cape Town, 1957.

25. L.P. Hammett and A.J. Deyrup, J. Amer. Chem. Soc., 1932, 54, 2721.

26. G. Bredig, Z. physikal. Chem., 1894, 13, 191.

27. E.C. Gilbert, J. Amer. Chem. Soc., 1931, 53, 3956.

28. R.P. Seward, J. Amer. Chem. Soc., 1955, 77, 905.

29. E.C. Gilbert, J. Amer. Chem. Soc., 1929, 51, 3394.

30. P. Walden, H. Ulich and G. Busch, Z. physikal. Chem., 1926, 123, 429.

31. N.L. Ross Kane, see D.M. Murray-Rust, O. Gatty, W.A. Macfarlane and H. Hartley, Ann. Rep., 1930, 27, 326.
H. Hartley and D.L. Hughes, Phil. Mag., 1933, 15, 610.

32. F. Accascina and S. Schiavo, Ann. Chim. (Rome), 1953, 43, 695.

33. M.B. Reynolds and C.A. Kraus, J. Amer. Chem. Soc., 1948, 70, 1709.

34. P. van Rysselberghe and R.M. Fristrom, J. Amer. Chem. Soc., 1945, 67, 680.

35. R.M. Fuoss, J. Amer. Chem. Soc., 1935, 57, 488.
C.A. Kraus, J. Franklin Institute, 1938, 225, 687.

36. D.L. Fowler and C.A. Kraus, J. Amer. Chem. Soc., 1940, 62, 2237.

37. J.F.J. Dippy and S.R.C. Hughes, J. Chem. Soc., 1954, 953.

38. N. Bjerrum, Kgl. Dansk Videnskab. Selsk., 1926, 7, 9.

39. M.J. McDowell and C.A. Kraus, J. Amer. Chem. Soc., 1951, 73, 3293.

40. R.M. Fuoss and T. Shedlovsky, J. Amer. Chem. Soc., 1949, 71, 1496.
H.M. Daggett, J. Amer. Chem. Soc., 1951, 73, 4977.

41. T. Shedlovsky, J. Franklin Institute, 1938, 225, 739.

42. E.A. Braude, J. Chem. Soc., 1971. cf. Sackur, Ber., 1902, 35, 1248.

43. C.M. French and I.G. Roe, Trans. Faraday Soc., 1953, 49, 314.

44. R.M. Fuoss and C.A. Kraus, J. Amer. Chem. Soc., 1933, 55, 2387; 1935, 57, 1.

45. V.S. Griffiths, and K.S. Lawrence, Research, 1955, 8, S51.

46. G. Schwarzenbach and E. Felder, Helv. chim. Acta, 1944, 27, 1044. G. Schwarzenbach and C. Wittwer, Helv. chim. Acta, 1947, 30, 659, 669.

47. E. Mackor quoted by (D.H. Everett and S.E. Rasmussen. M.J. Sparnaay " " (J. Chem. Soc., 1954, 2812.

48. D.H. Everett and S.E. Rasmussen, J. Chem. Soc., 1954, 2812.

49. T. Erdey-Gruz, Z. physikal. Chem., 1927, 131, 81.

50. W. Birkenstock, Z. physikal. Chem., 1928, 138, 432.

51. H. Ulich and G. Spiegel, Z. physikal. Chem., 1936, 177A, 103.

52. P. Arthur and H. Lyons, Analyt. Chem., 1952, 24, 1422.

53. D. Feakins and C.M. French, J. Chem. Soc., 1957, 2581.

54. M.G. Flora, Ph.D. Thesis, University of Cape Town, 1957.

55. G.R. Nash and C.B. Monk, J. Chem. Soc., 1955, 1899.

56. V.S. Griffiths, J. Chem. Soc., 1954, 686.

57. J. Daly and C.G. Smith, J. Chem. Soc., 1953, 2779.

58. E. Mackor, Rec. Trav. chim., 1951, 70, 457.

59. K.J. Mysels, J. Phys. Chem., 1947, 51, 708.

60. D.H. Everett, personal communication.

61. J.L. Eck, Ann. physique, 1949, [12], 4, 12.

62. F.P. Anderson, R.W. Guelke, M.C.B. Hotz and A.H. Spong, Chem. and Ind., 1957, 732.

63. P. Bender, W.J. Biermann and A.G. Winger, J. Chem. Educ., 1950, 27, 212.

64. E. Newbery, J. Chem. Soc., 1918, 113, 701.
H.E. Gunning and A.R. Gordon, J. Chem. Phys., 1942, 10, 126.

65. L. Elias and H.I. Schiff, J. Phys. Chem., 1956, 60, 595.

66. D.J.G. Ives and S. Swaroopa, Trans. Faraday Soc., 1953, 49, 788.

67. F.A. Wenner, Sci. Pap. U.S. Bur. Stand., 1916, No. 258.
O.H. Gish and W.J. Rooney, Terr. Magn. atmos. Elect., 1925, 30, 161.

68. H.C. Parker, J. Amer. Chem. Soc., 1923, 45, 1366, 2017.

69. S. Jacobs, Chem. and Ind., 1955, 944.

70. G. Jones and B.C. Bradshaw, J. Amer. Chem. Soc., 1933, 55, 1780.

71. A. Gutbier and K. Neundlinger, Z. physikal. Chem., 1913, 84, 203.

72. G. Jaffé, Ann. Physik, 1933, 16, 217, 249.
G. Jaffé and J.A. Rider, J. Chem. Phys., 1952, 20, 1077.

73. H.-C. Chang and G. Jaffé, J. Chem. Phys., 1952, 20, 1071.

74. M. Shaw and A.E. Remick, J. Electrochem. Soc., 1950, 97, 324.

75. A.E. Remick and H.W. McCormick, J. Electrochem. Soc., 1955, 102, 534.

76. D.C. Grahame, J. Electrochem. Soc., 1952, 99, 370C.

77. D.C. Grahame, J. Chem. Phys., 1955, 23, 1725.

78. L. Thomas and E. Marum, Z. physikal. Chem., 1929, 143A, 191.

79. H.M. Daggett, E.J. Bair and C.A. Kraus, J. Amer. Chem. Soc., 1951, 73, 799.

80. J.H. Jones, J. Amer. Chem. Soc., 1945, 67, 855.

81. J.F.J. Dippy, H.O. Jenkins and H.E. Page, J. Chem. Soc., 1939, 1386.

82. A. Lannung, Z. physikal. Chem., 1932, 161A, 255.

83. J. Mitchell and D.M. Smith, "Aquametry", New York, 1948.

84. J.B. Wiggill, personal communication.

85. C.W. Ehmke, personal communication.

86. O. Sackur, Ber., 1902, 35, 1242.

87. H. Falkenhagen, M. Leist and G. Kelbg, Ann. Phys., Lpz. [6], 1952, 11, 51.

88. J.T. Edward, Sci. Proc. Roy. Dublin Soc., 1957, 27, 287.

89. E.J. Cohn and J.T. Edsall, Proteins, Amino Acids and Peptides, New York, 1943.

90. J.R. White, J. Chem. Phys., 1955, 23, 2247.

91. M.J. McDowell and C.A. Kraus, J. Amer. Chem. Soc., 1951, 73, 3293.

92. J.S. Fritz, Analyt. Chem., 1953, 25, 407.

*93. Izmailov and I. Zabara, J. Phys. Chem. U.S.S.R., 1946, 20, 165.

94. P. Karrer and H. Schmid, Helv. chim. Acta, 1946, 29, 1853.

95. K. Kindler, E. Schärfe and P. Henrich, Annalen, 1949, 565, 51.

96. J. Thiele, Annalen, 1892, 270, 1.

97. A.I. Vogel, Textbook of Quantitative Inorganic Analysis, Second Edition, London, 1951, page 365.

98. A.I. Vogel, Textbook of Quantitative Inorganic Analysis, Second Edition, London, 1951, page 258.

99. G. Kortum and J. O'M. Bockris, Textbook of Electrochemistry, Amsterdam, 1951.

100. H.T.S. Britton, Hydrogen Ions, London, 1955.

101. L. Lykken, P. Porter, H.D. Ruliffson and F.D. Tuemmler, Ind. Eng. Chem., Anal. Ed., 1944, 16, 219.

102. R.A. Robinson and R.H. Stokes, Electrolyte Solutions, London, 1955.

103. N.F. Hall and J.B. Conant, J. Amer. Chem. Soc., 1927, 49, 3047.
N.F. Hall and T.H. Werner, J. Amer. Chem. Soc., 1928, 50, 2367.
N.F. Hall, J. Amer. Chem. Soc., 1930, 52, 5115.

104. W. Nernst, Z. physikal. Chem., 1888, 2, 613.
G.S. Hartley, Phil. Mag., 1931, 12, 473.

105. M.J. McDowell and C.A. Kraus, J. Amer. Chem. Soc., 1951, 73, 3293.

* Denotes references available only in abstract.

APPENDIX II.1

Dihydrazinium Chloroplatinate.

Typical data for the variation of resistance with time measured on the Jones Bridge at 25°C.

Concentration: 3.936×10^{-4} mole l^{-1}

Time (minutes)	Resistance (ohms)
16.0	1068.0
18.0	1058.6
21.0	1046.1
23.0	1033.5
24.0	1028.0
26.0	1014.0
27.0	1006.2
30.0	992.8
32.0	979.3
39.0	949.1
45.0	922.2
51.0	899.4
56.0	883.9
65.0	854.8
74.0	837.2
83.0	821.4
89.0	819.5
96.0	813.2
103.0	814.0
110.0	815.6
118.0	817.9
125.0	820.2
136.0	823.0

APPENDIX II.2

Dihydrazinium Chloroplatinate.

Typical data for the variation of pH with time at 25°C.

(a) With added platinum.
Concentration: 4.34 mole l^{-1}

Time (minutes)	pH
8.0	2.97
10.0	2.88
12.0	2.85
15.5	2.85
18.0	2.84
21.0	2.84
24.0	2.84
27.0	2.83
30.0	2.83
34.0	2.82
38.0	2.82
42.0	2.82
46.0	2.82
50.0	2.82
60.0	2.82
65.0	2.80
69.0	2.76
82.0	2.70
86.0	2.67
88.0	2.65
92.0	2.63
100.0	2.63
166.0	2.62
217.0	2.61
242.0	2.60

(b) No platinum added.
Concentration: 4.62 mole l^{-1}

Time (minutes)	pH
10.0	2.84
12.0	2.73
29.0	2.76
49.0	2.81
60.0	2.81
77.0	2.79
95.0	2.79
105.0	2.80
125.0	2.79
137.0	2.79
180.0	2.79
217.0	2.78
240.0	2.76
270.0	2.71
280.0	2.67
294.0	2.64
309.0	2.62
314.0	2.60
324.0	2.60
329.0	2.57
353.0	2.56
362.0	2.55
376.0	2.53
390.0	2.52
411.0	2.51
455.0	2.49

APPENDIX II.3

Dihydrazinium Chloroplatinate.

Typical data for the variation of resistance with time measured on the potentiometer at 25°C.

Concentration: 1.619×10^{-4} moles l^{-1}

Time (minutes)	Resistance (ohms)
12.0	406.0
14.0	398.7
15.0	395.5
16.0	393.0
18.0	387.5
20.0	379.4
22.0	374.6
24.0	371.1
25.0	369.5
27.0	368.0
29.0	366.7
31.0	366.1
33.0	365.5
35.0	365.1
38.0	364.8
41.0	363.5
45.0	362.9
49.0	362.6
55.0	361.6
60.0	361.6
65.0	361.0
70.0	360.6
80.0	360.4

APPENDIX II.4

Dihydrazinium chloroplatinate.

Rates of change of specific conductance with time at 31.70°C and 20.69°C measured on the Jones Bridge at frequencies of 1000 c./sec. and 80 c./sec.

(a) 31.70°C.

$c \times 10^4$ mole l^{-1}	Frequency c./sec.	$\frac{d\kappa}{dt} \times 10^6$	$\frac{d\kappa'}{dt} \times 10^7$
2.330	1000	3.52	3.36
3.638	1000	4.19	4.33
7.803	1000	6.42	15.4
9.120	1000	7.03	26.5
2.584	80	2.95	2.03
4.658	80	3.68	2.61
8.764	80	5.18	8.20

(b) 20.69°C.

$c \times 10^4$ mole l^{-1}	Frequency c./sec.	$\frac{d\kappa}{dt} \times 10^6$	$\frac{d\kappa'}{dt} \times 10^7$
2.891	80	0.874	0.317
4.990	80	0.998	0.391
6.662	80	1.14	0.550
8.610	80	1.32	0.928
2.814	1000	1.11	0.586
5.136	1000	1.26	0.944
6.562	1000	1.33	1.57
8.818	1000	1.64	4.64

APPENDIX II.5

Dihydrazinium Chloroplatinate.

Variation of $\frac{d\Lambda}{dt}$ and $\frac{d \log \kappa}{dt}$ with concentration at 25°C.

(a) Measured on Jones bridge, frequency 1000 c./sec.

c x 10^4 mole l^{-1}	$\frac{d \log \kappa}{dt}$ x 10^3	$\frac{d\Lambda}{dt}$ x 10^3
2.579	13.3	7.14
3.529	11.1	5.64
3.936	10.5	5.26
4.500	9.77	4.67
5.115	9.51	4.38
6.170	9.03	3.87
8.596	7.73	3.15
24.26	5.60	1.75
39.08	5.04	1.44

(b) Measured on potentiometer, frequency 1000 c./sec.

c x 10^4 mole l^{-1}	$\frac{d \log \kappa}{dt}$ x 10^3	$\frac{d\Lambda}{dt}$ x 10^4
1.619	3.34	15.1
2.603	2.59	11.1
4.297	1.85	7.33
6.282	1.56	5.60
9.167	1.61	5.34
11.88	1.44	4.61

APPENDIX II.6

Hydrazinium Perchlorate.

Variation of $\frac{d \log \kappa}{dt}$ with concentration at 25°C.

(a) Measured on potentiometer, frequency 1000 c./sec.

c x 10^4 mole l^{-1}	$\frac{d \log \kappa}{dt}$ x 10^4
4.859	5.490
8.075	2.308
15.53	0.8990
23.51	0.4924
30.18	0.2545
42.51	0.1778
53.65	0.0929

(b) Measured on Jones Bridge, frequency 1000 c./sec.

c x 10^4 mole l^{-1}	$\frac{d \log \kappa}{dt}$ x 10^4
7.699	0.4473
7.916	0.4179
10.73	0.3184
13.34	0.3035
17.67	0.2150
20.39	0.2061
24.68	0.1093
37.84	0.0540

APPENDIX IV.1

Potentiometric titrations of organic bases with hydrogen chloride in moist acetone.

(a) 1:2:3:4-Tetrahydroquinoline.

% neutralisation	pH units
0.00	4.89
22.6	1.70
44.5	1.44
67.0	1.28
89.0	0.90
111.0	0.05
133.2	-0.21
156.0	-0.35

(b) 1:2:3:4-Tetrahydroisoquinoline.

% neutralisation	pH units
0.0	7.33
11.0	7.22
22.1	7.15
33.8	7.07
44.6	6.99
55.0	6.87
67.0	6.64
78.0	6.26
90.1	5.36
104.0	2.15
112.0	1.33
123.0	1.15
133.5	1.08
156.7	0.86
179.2	0.74
200.0	0.65

(c) Piperidine.

% neutralisation	pH units
0.0	7.05
11.0	7.01
22.1	7.00
33.8	6.91
44.6	6.86
55.0	6.79
66.9	6.75
78.1	6.60
89.0	6.30
94.5	5.81
100.0	4.15
105.8	2.06
111.0	1.78
122.5	1.50
134.0	1.25
144.0	1.01
156.2	0.90
167.0	0.84
178.3	0.79

(d) Dimethylketazine.

% neutralisation	pH units
0.0	3.28
10.0	2.64
20.0	1.78
30.0	1.71
40.0	1.64
50.0	1.54
60.0	1.42
70.0	1.30
80.0	1.16
90.0	0.84
100.0	0.55
110.0	0.30
120.0	0.22
130.0	0.10
140.0	0.06
150.0	-0.00
160.0	-0.08
170.0	-0.10
180.0	-0.22

APPENDIX IV.2

Potentiometric titrations of aqueous solutions of hydrochlorides with sodium hydroxide.

(a) 1:2:3:4-Tetrahydroquinoline hydrochloride (glass electrode).

% neutralisation	pH
0.0	3.41
8.3	4.00
16.7	4.32
25.0	4.52
33.4	4.73
41.6	4.88
50.0	5.03
58.4	5.20
66.6	5.36
75.0	5.51
83.4	5.79
91.6	6.20
95.0	6.43
98.4	7.07
100.1	9.01
101.8	9.98
103.2	10.30
105.0	10.50
106.8	10.61
108.3	10.68
112.5	10.84
116.8	10.95
124.9	11.10

(b) 1:2:3:4-Tetrahydroisoquinoline hydrochloride (hydrogen electrode).

% neutralisation	pH
0.0	4.25
5.0	7.91
10.0	8.50
15.0	8.73
20.0	8.82
30.0	8.99
40.0	8.46

(c) 1:2:3:4-Tetrahydroisoquinoline hydrochloride (glass electrode).

% neutralisation	pH
0.0	4.75
5.7	8.17
8.6	8.40
14.3	8.65
21.4	9.76
28.6	8.89
42.8	9.15
57.1	9.34
71.4	9.42
85.6	9.54
100.0	9.80
114.2	10.00
142.9	10.15

(d) 1:2:3:4-Tetrahydroisoquinoline hydrochloride (antimony electrode)

% neutralisation	pH
0.0	5.45
1.8	7.71
2.7	7.90
4.5	8.12
10.9	8.50
13.6	8.64
18.2	8.77
20.9	8.85
22.8	8.96
27.3	9.00
31.8	9.12
36.4	9.25
41.9	9.33
45.5	9.40
50.0	9.52
54.6	9.64
59.1	9.75
63.6	9.85
68.3	9.95
72.8	10.10
77.3	10.24
81.9	10.33
86.4	10.42
90.9	10.50
93.4	10.55
100.0	10.77
102.0	10.85
103.7	10.90
105.5	11.00
107.2	11.05
109.1	11.11
113.8	11.17
118.2	11.22
127.3	11.31
136.5	11.43

APPENDIX V.1

Conductimetric titration of dimethylketazine with hydrogen chlorine in anhydrous acetone at various concentrations.

Note: Concentrations refer to dimethylketazine.
HCl added to azine.

25.23% neutralised.
Azine 7.471 x 10^{-3} g. mole l^{-1}
HCl 1.885 x 10^{-3} g. mole l^{-1}

c x 10^4 mole l^{-1}	Sp. cond. x 10^6 mho cm.$^{-1}$
74.71	4.6578
59.77	4.9552
35.86	4.2239
21.52	3.1759
12.91	2.9183
5.164	2.0337
3.098	2.2455

38.59% neutralised.
Azine 7.471 x 10^{-3} g. mole l^{-1}
HCl 2.883 x 10^{-3} g. mole^{-1}

c x 10^4 mole l^{-1}	Sp. cond. x 10^6 mho cm.$^{-1}$
74.71	4.5267
59.77	5.0899
35.86	4.7463
21.52	4.0195
12.91	3.3761
5.164	2.3830
3.098	2.1915

86.09% neutralised.
Azine 7.471 x 10^{-3} g. mole l^{-1}
HCl 6.432 x 10^{-3} g. mole l^{-1}

c x 10^4 mole l^{-1}	Sp. cond. x 10^6 mho cm.$^{-1}$
74.71	6.9540
59.77	7.2621
35.86	6.0218
21.52	4.7318
12.91	4.1376
5.164	2.9424
3.098	1.9160

100.9% neutralised.
Azine 7.471 x 10^{-3} g. mole l^{-1}
HCl 7.541 x 10^{-3} g. mole l^{-1}

c x 10^4 mole l^{-1}	Sp. cond. x 10^6 mho cm.$^{-1}$
74.71	11.842
59.77	12.850
47.81	11.715
38.25	12.168
22.95	8.4975
13.77	6.0662
5.508	3.3492
2.203	1.8873

116.1% neutralised.
Azine 7.471×10^{-3} g. mole l^{-1}
HCl 8.672×10^{-3} g. mole l^{-1}

c x 10^4 mole l^{-1}	Sp. cond. x 10^6 mho cm.$^{-1}$
74.71	11.115
59.77	10.844
35.68	11.080
21.52	8.3320
12.91	6.7389
5.164	4.1742
2.066	2.7641

151.4% neutralised.
Azine 7.412×10^{-3} g. mole l^{-1}
HCl 11.22×10^{-3} g. mole l^{-1}

c x 10^4 mole l^{-1}	Sp. cond. x 10^6 mho cm.$^{-1}$
74.12	13.732
44.77	10.648
26.30	8.5385
15.38	6.4934
9.228	5.2120
3.691	3.0860
1.476	1.8118

207.8% neutralised.
Azine 7.471×10^{-3} g. mole l^{-1}
HCl 15.53×10^{-1} g. mole l^{-1}

c x 10^4 mole l^{-1}	Sp. cond. x 10^6 mho cm.$^{-1}$
74.71	24.112
29.88	13.858
11.95	7.5622
7.172	5.6729
4.303	3.9959