

TRANSPERANCE NUMBERS : THEIR DETERMINATION IN
SULPHURIC ACID AND THEIR VARIATION WITH
CONCENTRATION IN OTHER SOLVENTS

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Abstract

This thesis describes the measurement, by the moving boundary method, of cation transference numbers in pure sulphuric acid at 25°C. The hydrogen-bonded structure of this solvent, its high acidity, dielectric constant and viscosity all suggested that interesting data might be derived from such studies. The physical properties of 100% sulphuric acid, and of solutions of electrolytes in it, have been reviewed in the thesis.

A conductometric procedure employing grease-free apparatus was developed to prepare the solvent. Similarly, moving boundary cells were modified to incorporate four-way P.T.F.E. stopcocks which required no lubricant, and after some searching, a non-gassing electrode was found. By a suitable choice of following electrolytes, visible rising as well as falling boundaries were obtained. These allowed the transference numbers of lithium, sodium, potassium, ammonium, silver, barium and protonated water and acetic acid, as their hydrogen sulphates, to be determined. All the cation transference numbers were very small (of the order of 0.01) and the boundary velocities were correspondingly slow. The transference number of the sodium ion was measured at three concentrations and the values obtained were combined with the equivalent conductances of the electrolyte to yield corresponding cation conductances. Use was made of these to determine the limiting conductance of the sodium ion at infinitesimal ionic strength. The conductances of other cations at finite ionic strength were derived and estimates of their limiting values made. Information about the solvation of cations was derived from Stokes' law and compared with aqueous data.

The thesis also contains the results of computer calculations to test the applicability of transference forms of the Pitts and Fuoss-Onsager conductance theories to all the reliable moving boundary data currently available. The theories were found not to account adequately for the variation of transference numbers with concentration, the fit being poor for aqueous systems and the derived parameters often unreasonable in non-aqueous ones.

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CHAPTER ONE

TRANSFERENCE NUMBERS AND THEIR DETERMINATION

Definition

The transference number t_R of a cation-or anion-constituent R in solution is defined (1) as 'the net number of faradays carried by that constituent in the direction of the cathode or anode, respectively, across a reference plane fixed with respect to the solvent, when one faraday of electricity passes across the plane.' t_R is dimensionless and,

$$\sum_R t_R = 1 \quad (1 - 1)$$

The term ion-constituent means the positive or negative ion-forming constituent of the salt without reference to the extent to which it actually exists in a dissociated form. For solutions of strong electrolytes the ion-constituents are present only as the ions themselves. The definition is then equivalent to the more usual text-book definition of the transference number of an ion as 'the fraction of the current carried by that ion when the solution is electrolysed'. As this thesis is primarily concerned with solutions of strong electrolytes, no further reference to ion-constituents will be made.

The transference number t_R of an ion R can be expressed in terms of conductances by,

$$t_R = \frac{\lambda_R c_R}{\sum_i \lambda_i c_i} \quad (1 - 2)$$

where λ is equivalent conductance and c is concentration, in equivalents per dm^3 of the subscripted species. The summation is carried out over all the ions i , in the system, including R. For a solution of a single electrolyte dissociating into only two ions, this becomes,

$$t_+ = \lambda_+ / \Lambda; \quad t_- = \lambda_- / \Lambda \quad (1 - 3)$$

where $\Lambda = \lambda_+ + \lambda_- \quad (1 - 4)$

and is the equivalent conductance of the electrolyte.

Clearly, $t_+ + t_- = 1$ (1 - 5)

The determination of transference numbers

The three principal methods of measuring transference numbers are a) the moving boundary method, b) the Hittorf method, and c) the e.m.f. method. For measurements at 25°C the moving boundary method is superior to the others in precision of measurement and reliability of results but is more limited in its applicability. The present work is concerned mainly with transference numbers obtained by the m.b. technique and consequently it will be fully discussed. The Hittorf method will also be briefly described since it was used in the only previous determinations of transference numbers in sulphuric acid. The e.m.f. method is not relevant to this thesis but has been discussed by MacInnes (2a), Robinson and Stokes (3a), and Spiro (4a).

The Moving Boundary Method (4b, 5, 6)

The method is based on the formation and movement of a boundary between a solution of the electrolyte under investigation, and a solution of a second electrolyte having one ion in common with the first, when current passes through the solutions. The velocity of the boundary is proportional to the transference number of the non-common ion in the leading solution (i.e. the solution ahead of the boundary). The necessary conditions for boundary stability are as follows:

- a) The system must be gravitationally stable; the lighter solution must be placed above the heavier one.
- b) The conductance of the non-common ion in the leading solution must exceed that of the non-common ion in the following solution.
- c) The refractive index gradients of the two solutions must differ if the movement of the boundary is to be followed optically.

The theory of the method will be derived by using as an example the boundary formed between aqueous KCl and LiCl solutions. For reasons of gravitational stability the LiCl solution must be above the KCl solution (see fig. 1 - 1).

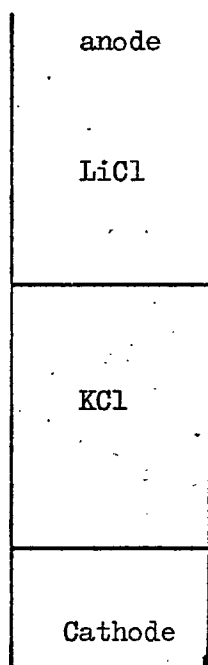


Figure 1.- 1

The very existence of the boundary requires that

$$v_{mb} \text{ (velocity of the boundary)} = v_{Li^+}^{LiCl} = v_{K^+}^{KCl} \quad (1 - 6)$$

The velocity of an ion is proportional to the strength X , of the electric field in which it moves. If the symbol u denotes the ionic mobility (velocity in unit field) then,

$$u_{\text{Li}^+}^{\text{LiCl}} X_{\text{LiCl}} = u_{\text{K}^+}^{\text{KCl}} X_{\text{KCl}} \quad (1 - 7)$$

$$\text{and } \lambda_{\text{Li}^+}^{\text{LiCl}} X_{\text{LiCl}} = \lambda_{\text{K}^+}^{\text{KCl}} X_{\text{KCl}} \quad (1 - 8)$$

$$\text{since } \lambda_i = F u_i \quad (1 - 9)$$

where F is Faraday's constant.

Since $\lambda_{\text{K}^+} > \lambda_{\text{Li}^+}$ the field strengths must be in the inverse ratio, i.e.

$X_{\text{LiCl}} > X_{\text{KCl}}$ (see fig. 1-2). This relation enables a qualitative explanation of boundary stability to be given.

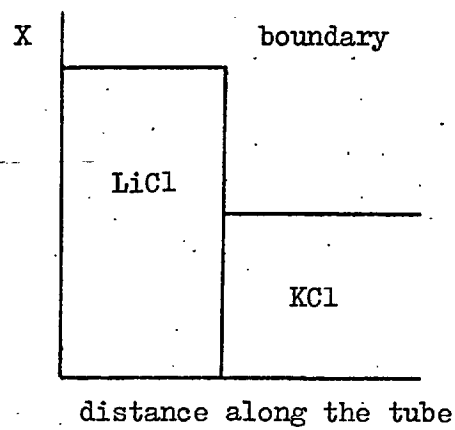


Figure 1 - 2

If a trace of Li^+ diffuses into the KCl solution, it finds itself in a region of lower field strength. Consequently it slows down and the boundary overtakes it. Similarly if a trace of K^+ diffuses into the LiCl solution, it is speeded up by the higher field and eventually overtakes the boundary.

The relation between the transference number and boundary velocity (v_{mb}) may now be derived. Suppose the boundary moves through a volume V in a time t , when a current I passes. The amount of K^+ ion swept out of this volume will be $c_{KCl} V$. This quantity of ion will have crossed an imaginary plane in the leading solution during the passage of It coulombs. By definition the transference number of the K^+ ion is the quantity of K^+ that crosses such a plane when one faraday (F coulombs) passes.

$$\text{Thus } t_{K^+}^{KCl} = \frac{c_{KCl} V F}{It} \quad (1 - 10)$$

Now the volume of KCl solution swept out in time t is given by

$$V = v_{m.b.} A t \quad (1 - 11)$$

where A is the area of the tube in which the boundary moves.

Thus, by combination of (1 - 11) and (1 - 10),

$$t_{K^+}^{KCl} = \frac{c_{KCl} v_{m.b.} A F}{I} \quad (1 - 12)$$

This relation shows that transference number and boundary velocity are proportional to one another at constant current. However, equation (1 - 10) is of more value than (1 - 12) since the times for the boundary to move through known volumes are more easily measured.

Since the current is the same in both solutions, equation (1 - 10) can equally be applied to the Li^+ ion in the $LiCl$ solution.

$$t_{Li^+}^{LiCl} = \frac{c_{LiCl} V F}{It} \quad (1 - 13)$$

$$\text{Then } \frac{t_{Li^+}^{LiCl}}{t_{K^+}^{KCl}} = \frac{c_{LiCl}}{c_{KCl}} \quad (1 - 14)$$

This relationship, known as the Kohlrausch equation, predicts the concentration of the following ($LiCl$) solution which follows the boundary.

Its value is fixed by other parameters in the system: the solution, even if not initially at this concentration adjusts itself to this concentration behind the boundary. The velocity of the boundary is independent of the initial concentration of the following ion over a fairly wide range since Kohlrausch adjustment occurs. The leading (KCl) solution, on the other hand, is of constant and uniform concentration. In moving boundary work it is always the transference number of the leading ion which is obtained and the following ion serves only as an indicator and is often referred to as such. It is usual to check that the transference number measured is independent of indicator electrolyte, indicator concentration, and current.

Two corrections must be applied to the experimental values.

First, a fraction of the current is carried by the ions of the solvent and not by the electrolyte. According to Longworth (5) the corrected transference number t_i is related to the observed value t_{obs} .

by

$$t_i = t_{obs} \left(1 + \frac{\kappa_{solvent}}{\kappa_{solute}} \right) \quad (1 - 15)$$

where $\kappa_{solvent}$ and κ_{solute} are the appropriate specific conductances.

The second correction is due to volume changes at one of the electrodes.

In the definition of transference number, it is implied that boundary movement should be measured with reference to a plane in the leading solution fixed with respect to the solvent. However, the transference numbers are observed relative to a plane fixed with respect to the cell. In moving boundary work one of the electrodes is always closed to avoid bulk movement of solution. The solvent is then displaced only by volume changes at the closed electrode. For the KCl/LiCl system,

$$t_{K^+}^{KCl} (corr.) = t_{K^+}^{KCl} (obs) \pm c_{KCl} \Delta V \quad (1 - 16)$$

Where ΔV is the volume increase, in dm^3 per faraday passed, between the closed electrode and a plane in the leading solution which the boundary does not cross. The plus or minus sign refers to the boundary moving toward or away from the closed electrode, respectively. As a simple example, consider an Ag/AgCl closed cathode in the KCl/LiCl system,

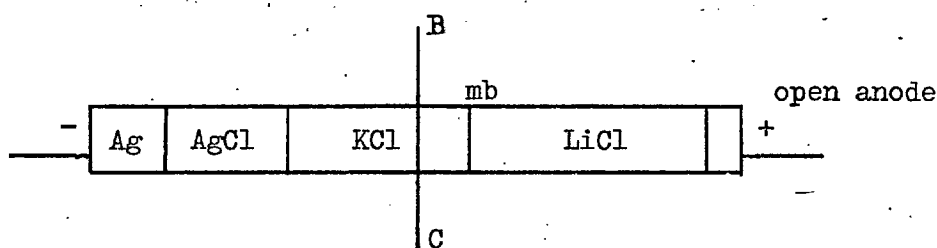


Figure 1 - 3

BC is the plane fixed with respect to the solvent in the leading solution. The changes produced between BC and the cathode by the passage of 1 faraday are as follows:

- Gain of one equiv. of Ag(s) and one equiv. of Cl^- and loss of one equiv. of AgCl(s) due to the electrode reaction.
- Gain of $t_{\text{K}^+}^{\text{KCl}}$ equiv. of K^+ and loss of $t_{\text{Cl}^-}^{\text{KCl}}$ equiv. of Cl^- due to migration across BC

Thus there is a net gain of $t_{\text{K}^+}^{\text{KCl}}$ equivalents of KCl and one equivalent of Ag and a loss of one equiv. of AgCl. So,

$$\Delta V = +V_{Ag(s)} - \bar{V}_{AgCl(s)} + t_{K^+} \frac{KCl}{KCl} \bar{V}_{KCl} \quad (1 - 17)$$

where V and $\bar{V}$ are molar and partial molar volumes, respectively.

In the present work with sulphuric acid as solvent, a closed Ag^+/Ag cathode was used. For NH_4HSO_4 as the leading electrolyte and $H_2OAc.HSO_4$ as following electrolyte, the system is simply represented as

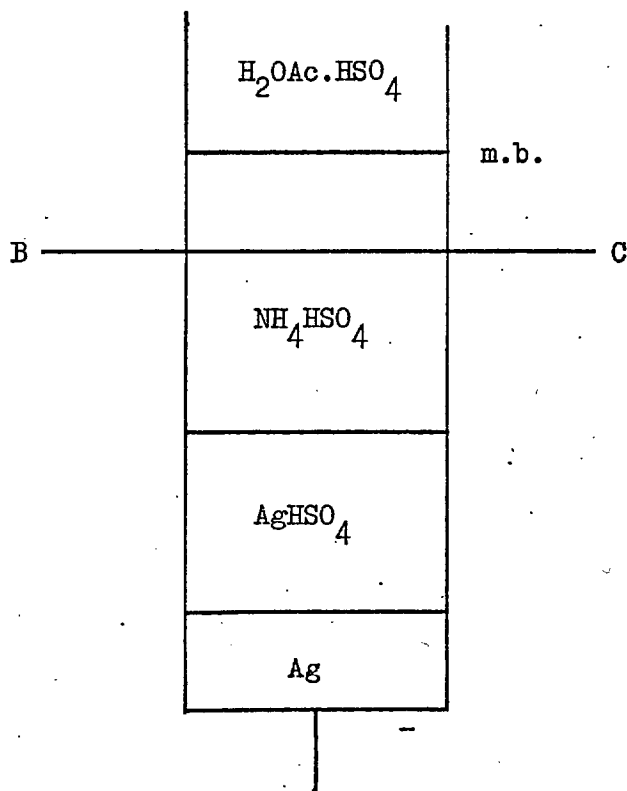


Figure 1 - 4

The volume changes between the electrode and BC are as follows:

- Gain of 1 equiv. of $Ag(s)$ and loss of 1 equiv. of Ag^+ by the electrode reaction.
- Gain of t_+ equiv. of NH_4^+ and loss of t_- equiv. of HSO_4^- by migration across BC.
- Gain of 1 equiv. of HSO_4^- in the NH_4HSO_4 solution and loss of 1 equiv. of HSO_4^- in the $AgHSO_4$ solution by migration across the Ag^+/NH_4^+ boundary since $t_+ + t_- = 1$

(1 - 18)

$$\Delta V = +V_{Ag(s)} - \bar{V}_{AgHSO_4} + t_+ \bar{V}_{NH_4HSO_4} \quad (1 - 19)$$

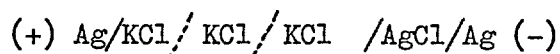
However, this particular volume change is complicated by other reduction processes and will be discussed in greater detail later.

It is interesting to note that the solvent correction becomes more important as the concentration is decreased whilst volume corrections are more significant the higher the concentration. Thus the most precise moving boundary results can only be obtained within a fairly limited range where the corrections are small and the effects of uncertainties in them are minimised.

Unfortunately the moving boundary method has its limitations. It is not always possible to see the boundaries at low concentrations or in solvents where the refractive indices of the leading and following solutions are very similar. Other methods of following the boundaries are then available, including measurement of changes in electrical resistance and potential due to passage of the boundary, a radioactive tracer method, and a thermal method (4). A more serious limitation, especially for non-aqueous work, is that suitable closed electrodes and indicator electrolytes cannot always be found.

The Hittorf Method

This technique has been very adequately described in the literature (2b, 3b, 4c, 7) and the treatment given here will be brief. The essence of the method is the measurement of the amount of electrolyte in the region of the electrodes before and after a current is passed. A Hittorf cell consists of at least three compartments (one for each electrode and also a middle section, the contents of which must be the same before and after the passage of current). As a simple example, consider the cell used by MacInnes and Dole (7) to measure the K^+ transference number of an aqueous KCl solution.



After one faraday was passed the following changes had occurred in the anode compartment solution:

- a) Gain of 1 equiv. of Ag^+ by the electrode reaction. This was precipitated as AgCl leading to a net loss of 1 equivalent of Cl^- in the solution.
- b) Gain of t_- equivalents of Cl^- by migration into the anode compartment from the middle section and a loss to t_+ equivalents of K^+ by migration in the reverse direction.

Thus there was a net loss of t_+ equivalents of KCl in the anode compartment after passage of one faraday. A similar analysis for the cathode compartment shows a net gain of t_+ equivalents of KCl . After analysis, the changes brought about by the passage of It coulombs were measured and consequently the transference number found by simple proportion. A solvent correction similar to that employed in the moving boundary method was applied.

The method is subject to analytical errors since the concentration changes brought about are necessarily small. If large amounts of charge are passed it is difficult to confine the changes to the electrode compartments. Consequently the precision of the method is relatively low and the moving boundary method is preferred whenever it can be applied.

CHAPTER TWO

THE CONCENTRATION DEPENDENCE OF TRANSFERENCE NUMBERS

The interpretation of the variation of the conductance of solutions of strong electrolytes with concentration has been a source of attention since the Debye-Hückel-Onsager treatment was proposed in 1927. They postulated that an ion in a solution is surrounded by an ionic 'atmosphere' of opposite net charge to the central ion, its existence being a consequence of the interplay of electrostatic interactions between the ions and thermal forces. The effect of the atmosphere is to slow down the motion of the ion under an external electric field and it does this in two separate ways. First, the opposite sign of charge between the atmosphere and the central ion means that they will move in opposite directions on application of the external field. The ion is then no longer at the centre of its atmosphere and thus experiences an electrostatic force opposing the applied field. This retarding contribution to the motion of the ion is known as the asymmetry or relaxation effect. Second, the solvent molecules associated with the atmosphere ions cause a local flow in the opposite direction to the central ion and so decrease its velocity. This contribution to the reduction of ionic mobility is known as the electrophoretic effect.

The Debye-Hückel-Onsager (D-H-O) theory treats the ions as point charges and the solvent as a continuum. It consequently ignores the short range repulsive interactions which are introduced when the size and shape of ions are taken into account. The latter effects may only be neglected in extremely dilute solutions where the D-H-O equation holds reasonably well. It is for this reason that the equation has come to be known as the limiting law. The equation may be stated:

$$\text{For a single univalent ion } \lambda_i = \lambda_i^0 - (B_1 \lambda_i^0 + \frac{1}{2} B_2) \sqrt{c} \quad (2 - 1)$$

For a 1:1 electrolyte $\Lambda = \Lambda^0 - (B_1 \Lambda^0 + B_2) \sqrt{c}$ (2 - 2)

where λ_i , Λ represent molar conductances in the units $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ at finite concentrations and λ_i^0 , Λ^0 the hypothetical limiting molar conductances at infinitesimal ionic strength, c is the concentration in mol dm^{-3} , and B_1 and B_2 are parameters given by:

$$B_1 = \frac{8.205 \times 10^5}{(\epsilon T)^{3/2}} \quad \text{mol}^{-1/2} \text{dm}^{3/2} \quad (2 - 3)$$

$$B_2 = \frac{82.46}{\eta (\epsilon T)^{1/2}} \quad \text{cm}^2 \text{ohm}^{-1} \text{mol}^{-3/2} \text{dm}^{3/2} \quad (2 - 4)$$

Here ϵ is the dielectric constant of the solvent, η its viscosity in poise and T is the absolute temperature. The functions B_1 and B_2 represent the contribution to the conductance from the asymmetry and electrophoretic effects respectively.

In an attempt to explain the variation of conductance of strong electrolytes with concentration at higher concentrations, Fuoss and Onsager (8) proposed that:

$$\lambda_i = (\lambda_i^0 - \lambda_i^e) \left(1 + \frac{\Delta X_i}{X}\right) \quad (2 - 5)$$

where λ_i^e represents the electrophoretic contribution to the conductance, X is the applied field and ΔX_i is the additional field at the ion due to asymmetry. An expression for $\Delta X/X$ was obtained by a series of successive approximations yielding terms of different order in c which contribute to the relaxation field. As ΔX_i and X are in opposite direction the sign of $\Delta X_i/X$ is negative and the effect of $(1 + \Delta X_i/X)$ is to reduce the conductance.

For a simple 1:1 electrolyte:

$$\Delta X_+ = \Delta X_- \quad (2 - 6)$$

$$\lambda_+^e = \lambda_-^e = \lambda_{\pm}^e = \frac{1}{2} \Lambda^e \quad (2 - 7)$$

$$\text{and } \Lambda = (\Lambda^0 - \Lambda^e) \left(1 + \frac{\Delta X}{X}\right) \quad (2-8)$$

It may be seen that the limiting law is a special case of this equation in which $\Lambda^e = B_2 \sqrt{c}$, $\Delta X_i/X = -B_1$ and the cross-product of electrophoretic and asymmetric terms is neglected. Fuoss and Onsager allowed for the finite size of ions and introduced a closest distance of approach between cation and anion, symbolised by a . They then deduced that the electrophoretic contribution is given by

$$\Lambda^e = \frac{B_2 \sqrt{c}}{(1 + \kappa a)} \quad (2-9)$$

$$\text{where } \kappa = \sqrt{\frac{4 \pi e^2}{\epsilon k T} \sum n_{i\infty} Z_i^2} \quad (2-9a)$$

Here $n_{i\infty}$ is the bulk concentration of ions of species i , e is the electronic charge and k is Boltzmann's constant. For a fully dissociated 1:1 electrolyte,

$$\kappa = 50.291 \sqrt{\frac{c}{\epsilon T}} \text{ \AA}^{-1} \quad (2-10)$$

With $\kappa a = y$, the equation for a 1:1 strong electrolyte, (2-8) becomes:

$$\Lambda = \left\{ \Lambda^0 - \frac{B_2 \sqrt{c}}{(1+y)} \right\} \left\{ 1 + \frac{\Delta X}{X} \right\} \quad (2-11)$$

However, in a more detailed treatment of the electrophoretic term (9) in 1963, Fuoss and Onsager proposed that a more exact form of Λ^e is.

$$\Lambda^e = B_2 \sqrt{c} - B_3 \quad (2-9b)$$

$$\text{where } B_3 = \frac{2}{3} \frac{N^2 e^6}{\gamma(\epsilon k T)^2} \cdot c \cdot F(b) \times 10^{-3} \quad (2-9c)$$

and $F(b)$ is a complicated function of a , ϵ and T . They stated that the form of Λ^e given in (2-9) is a close approximation to (2-9b) and consequently employed the more approximate form. Calculations of Λ^e by both relations have been carried out by the writer and the details are given in Appendix I

where the validity of the approximation is also discussed.

The form of the conductance equation with the more exact electrophoretic term is then,

$$\Lambda = (\Lambda^0 - (B_2 \sqrt{c} - B_3))(1 + \frac{\Delta X}{X}) \quad (2 - 11a)$$

An extended form of equation (2 - 11) was obtained by Fuoss and Onsager (8) on expanding (2 - 8) with a more detailed derivation of the relaxation field. When terms beyond those in $c^{3/2}$ were ignored the form of the equation is:

$$\Lambda = \Lambda^0 - S \sqrt{c} + Ec \log_e c + J_1 c - J_2 c^{3/2} \quad (2 - 12)$$

$$\text{where} \quad S = B_1 \Lambda^0 + B_2 \quad (2 - 13)$$

E is a function only of the solvent properties and J_1 and J_2 depend on the solvent properties and on a .

The original Fuoss-Onsager equation proved to be more successful at higher concentrations than the limiting law. An arbitrary limit of 0.2 for y was proposed, above which the equation is no longer accurately obeyed. The treatment has been further developed by Fuoss and Hsia (10) and by Murphy and Cohen (11). These modifications involve a recalculation of the relaxation field retaining terms which had previously been neglected.

In 1953, Pitts (12) derived an equation which, although based on a similar model, differs from the Fuoss and Onsager treatment in three ways. First, the Pitts equation takes into account the effect of the asymmetric potential on the local velocities of the solvent near the ions. Second, the two treatments employ different boundary conditions. Fuoss and Onsager considered that perturbed potentials and electric fields are continuous whereas Pitts considered that perturbations could be neglected at distances from the ion greater than a . Third, the theories differ in their approaches to the effect of the asymmetry of the ionic atmosphere upon the central ion. These differences have been fully discussed by Pitts, Tabor and Daly (13, 14) and

by Fernández-Prini (15); the former group (13) somewhat modified the original Pitts equation. For ease of algebraic manipulation the modified equation can be put into the following forms:

For a single ion,

$$\lambda_i^\circ - \lambda_i = \lambda_i^\circ Y_1 - \frac{\lambda_i^\circ}{\Lambda^\circ} Y_2 + \frac{1}{2} Y_3 \quad (2 - 14)$$

For a completely dissociated 1:1 electrolyte,

$$\Lambda^\circ - \Lambda = \Lambda^\circ Y_1 - Y_2 + Y_3 \quad (2 - 15)$$

$$\text{where } Y_1 = \left\{ \frac{e^2 \kappa}{3\epsilon kT(1+\sqrt{2})(1+y)(\sqrt{2}+y)} + \frac{e^4 \kappa^2 S_1}{3\epsilon^2 k^2 T^2} \right\} \quad (2 - 16)$$

$$Y_2 = \frac{(\sqrt{2}-1)}{(\sqrt{2}+y)(1+y)^2} \left\{ \frac{N}{3\pi\eta_0} \right\} \left\{ \frac{e^4 \kappa^2}{3\epsilon kT} \right\} \quad (2 - 17)$$

$$Y_3 = \frac{e^2 \kappa}{(1+y)} \left\{ \frac{N}{3\pi\eta_0} \right\} \left\{ 1 - \frac{e^2 \kappa T_1}{3\epsilon kT} \right\} \quad (2 - 18)$$

Here S_1 and T_1 are numerically evaluated functions of y and N is the Avogadro number.

A comparison of the performances of the Fuoss-Onsager and Pitts equations for fully dissociated electrolytes, in both aqueous and non-aqueous solvents, is of interest. Pitts, Tabor and Daly (14) have shown that, for aqueous systems, the three-parameter version of the Fuoss-Onsager equation, involving Λ° , $\underline{a}$ and an association constant can be closely fitted to the experimental data but such a fit necessitates unreasonably small values of $\underline{a}$ and some negative association constants which are not physically meaningful. They claim, however, that the Pitts theory, involving only Λ° and $\underline{a}$, can be fitted closely to experiment for reasonable values of $\underline{a}$. Fernández-Prini (15) has shown that both the Fuoss-Hsia and Pitts equations account adequately for results in dimethyl formamide and propylene carbonate, the Pitts equation being marginally more successful. However, in methanol the Fuoss-Hsia equation is more satisfactory. By inspection of the full forms of these

equations, it is seen that, for a given electrolyte, Pitts' equation predicts smaller interionic effects and a larger molar conductance. The small values of α predicted by the Pitts equation for a methanol solution may be attributed to a small degree of ion association which is more satisfactorily allowed for in the Fuoss-Hsia equation with an association constant and a more plausible value of α is obtained. The Pitts equation is likely to be equally successful for methanol if association is taken into account.

In view of the success of these equations when applied to conductance data it was decided to test their applicability, in suitable form, to transference data. Compared with the conductance field, there is a paucity of reliable transference data with which the equations may be tested. For most aqueous systems that have been studied, conductances have been measured at many concentrations less than 0.1N whereas the maximum number of corresponding transference measurements is six and a more usual number is three (0.01, 0.02, 0.05N). Moreover, accurate transference measurements have been carried out in far fewer solvents than have accurate conductance measurements. Consequently the theoretical equations have been tested using all the reliable transference data available for both aqueous and non-aqueous systems.

Derivation of the transference forms of the theoretical equations

Transference numbers of completely dissociated electrolytes are defined in terms of conductances by the relations

$$t_i = \frac{\lambda_i}{\Lambda} \quad (2 - 19)$$

$$t_i^\circ = \frac{\lambda_i^\circ}{\Lambda^\circ} \quad (2 - 20)$$

The Debye-Hückel-Onsager equation in transference form

Combining equations (2 - 1), (2 - 2), (2 - 19) and (2 - 20) we obtain

$$t_i = \frac{\lambda_i^{\circ} - (B_1 \lambda_i^{\circ} + \frac{1}{2} B_2) \sqrt{c}}{\Lambda^{\circ} - (B_1 \Lambda^{\circ} + B_2) \sqrt{c}} \quad (2 - 21)$$

$$t_i = t_i^{\circ} + \frac{(t_i^{\circ} - 0.5) B_2 \sqrt{c}}{\Lambda^{\circ} - (B_1 \Lambda^{\circ} + B_2) \sqrt{c}} \quad (2 - 22)$$

As with the conductance form of this equation, (2 - 22) applies only in extremely dilute solutions. It may be rearranged to read

$$t_i^{\circ} = \frac{t_i \Lambda + \frac{1}{2} B_2 \sqrt{c}}{\Lambda + B_2 \sqrt{c}} \quad (2 - 23)$$

At moderate concentrations t_i° so calculated is not constant and henceforth is called $t_i^{\dagger}$. Longworth (5) found that $t_i^{\dagger}$ varies linearly with concentration.

$$t_i^{\dagger} = t_i^{\circ} + bc \quad (2 - 24)$$

This enables a reasonable limiting transference number t_i° to be obtained by extrapolation to zero concentration. It will be shown later that this is a suitable first approximation for an iterative procedure to fit transference data to the Pitts equation.

The Fuoss-Onsager equation in transference form

Combining equations (2 - 5), (2 - 7), (2 - 8) and (2 - 19) gives

$$t_i = \frac{\lambda_i^{\circ} - \frac{1}{2} \Lambda^e}{\Lambda^{\circ} - \Lambda^e} \quad (2 - 25)$$

It was first pointed out by Stokes (16) that the relaxation term cancels out completely so that the transference number depends on the electrophoretic terms alone. Kay and Dye (17) have, in fact attempted to use the variation of t_i with concentration to determine Λ^e . Equation (2 - 25) may be combined with equation (2 - 20) to give

$$t_i = t_i^{\circ} + \frac{(t_i^{\circ} - 0.5) \Lambda^e}{\Lambda^{\circ} - \Lambda^e} \quad (2 - 26)$$

After multiplication by $(\Lambda^o - \Lambda^e)$ and rearrangement

$$t_i = t_i^o + \frac{(t_i - 0.5)\Lambda^e}{\Lambda^o} \quad (2 - 27)$$

When the form of Λ^e proposed by equation (2 - 9) is employed, (2 - 27) becomes

$$t_i = t_i^o + \frac{(t_i - 0.5) B_2 \sqrt{c}}{\Lambda^o (1 + \kappa a)} \quad (2 - 28)$$

or

$$t_i^o = t_i - \frac{(t_i - 0.5) B_2 \sqrt{c}}{\Lambda^o (1 + \kappa a)} \quad (2 - 29)$$

When the more exact electrophoretic term given by (2 - 9b) is used (2 - 27) becomes

$$t_i^o = t_i - \frac{(t_i - 0.5)(B_2 \sqrt{c} - B_3)}{\Lambda^o} \quad (2 - 29a)$$

The forms of the equation employed in the present calculations are (2 - 29) and (2 - 29a). The results of calculations using the former are designated $(F - 0)_1$ and those using the latter $(F - 0)_2$.

The Pitts equation in transference form

Combining equations (2 - 14), (2 - 15), (2 - 19) and (2 - 20) we obtain

$$t_i - t_i^o = \frac{\lambda_i^o - \lambda_i^o Y_1 + \lambda_i^o \left(\frac{Y_2}{\Lambda^o} \right) - \frac{1}{2} Y_3}{\Lambda^o - \Lambda^o Y_1 + Y_2 - Y_3} - \frac{\lambda_i^o}{\Lambda^o} \quad (2 - 30)$$

After algebraic manipulation this becomes

$$\frac{t_i - t_i^o}{t_i^o - 0.5} = \frac{Y_3}{\Lambda^o - \Lambda^o Y_1 + Y_2 - Y_3} = \frac{Y_3}{\Lambda'} \quad (2 - 31)$$

$$\text{or } t_i^{\circ} = \frac{t_i + 0.5 \left\{ \frac{Y_3}{\Lambda'} \right\}}{\left\{ 1 + \frac{Y_3}{\Lambda'} \right\}} \quad (2 - 32)$$

or, on rearrangement,

$$t_i^{\circ} - t_i = \frac{Y_3 (0.5 - t_i^{\circ})}{\Lambda'} \quad (2 - 33)$$

It will be shown in the next section that equations (2 - 32) and (2 - 33) are the forms of the equation which are most suitable for testing how well the theory describes the concentration dependence of transference numbers.

The effects of ion association

All the conductance and derived transference equations may be modified to incorporate ion association where it is thought to be significant. For a 1:1 electrolyte dissociating according to



the equilibrium concentrations of M^{+} , A^{-} and MA are αc , αc and $(1-\alpha)c$ respectively where α is the degree of dissociation. The ion-pair association constant K_A is given by

$$K_A = \frac{(1 - \alpha)}{\alpha^2 c \gamma_{\pm}^2} \quad (2 - 34)$$

A rearranged version reads

$$\frac{1}{\alpha} = 1 + K_A \alpha c \gamma_{\pm}^2 \quad (2 - 35)$$

Here $\gamma_{\pm}$ is the mean activity coefficient of the free ions at concentration αc . The D-H-O equation, (2 - 2), now becomes

$$\frac{\Lambda}{\alpha} = \Lambda^{\circ} - (B_1 \Lambda^{\circ} + B_2) \sqrt{\alpha c} \quad (2 - 36)$$

The Fuoss-Onsager equation in its extended form, (2 - 12) becomes

$$\frac{\Lambda}{\alpha} = \Lambda^{\circ} - S \sqrt{\alpha c} + E(\alpha c) \log_e (\alpha c) + J_1 (\alpha c) - J_2 (\alpha c)^{3/2} \quad (2 - 37)$$

Combination of (2 - 35) with (2 - 37) gives

$$\Lambda = \Lambda^0 - S\sqrt{\alpha c} + E(\alpha c) \log_e(\alpha c) + J_1(\alpha c) - J_2(\alpha c)^{3/2} - K_A \Lambda_{\pm}^0{}^2(\alpha c) \quad (2 - 38)$$

The Pitts equation (2 - 15) becomes

$$\Lambda^0 - \frac{\Lambda}{\alpha} = \Lambda^0 Y_1 - Y_2 + Y_3 \quad (2 - 39)$$

with αc replacing c in the equation for Λ , (2 - 9).

When the transference forms of these amended equations are derived they become identical with those obtained previously except that the quantity αc replaces c wherever it occurs.

In the calculations performed here, ion association has been taken into account for a number of systems. Where the original workers have given values of α , these have been used, but for most systems only a value of K_A was available and the following successive approximations method was used. Equation (2 - 34) was written in the form

$$\alpha_{n+1} = 1 - \alpha_n^2 c K_A \gamma_{\pm}^2 \quad (2 - 40)$$

As a rough first approximation to α , α_0 was set equal to one and α_1 was calculated from equation (2 - 40). This new improved value was then substituted into the right-hand side of the equation and a better approximation, α_2 , was obtained. The procedure was repeated, usually about six times, until α_n and α_{n+1} did not differ significantly. Values of α were calculated for all the concentrations at which transference data were available.

The values of the stoichiometric activity coefficients $\gamma_{\pm}$ were obtained from the Debye-Hückel equation, for 1:1 electrolytes

$$\log_{10} \gamma_{\pm} = \frac{-A_1 \sqrt{\alpha c}}{(\epsilon T)^{3/2} \left(1 + \frac{A_2 a \sqrt{\alpha c}}{(\epsilon T)^{1/2}}\right)} \quad (2 - 40a)$$

where A_1 , A_2 are constants and in the absence of any other value for a , the 'best' conductance values were taken.

Methods of comparing theory with experiment

Two approaches have been developed to test the fit of experimental transference data to the theoretical equations. The first, method A, is based on the fact that if the theory is satisfied for a given value of $\underline{a}$, t_i^0 as calculated is invariant to concentration. The measured transference numbers and corresponding concentrations were substituted into equation (2 - 32) for a test of the Pitts theory, or equation (2 - 29) to test the Fuoss-Onsager theory, for a series of values of $\underline{a}$. That value of $\underline{a}$ was then found which made the standard deviation of calculated t_i^0 values from their average a minimum over a specified concentration range. However, the data were only deemed to fit the equation adequately if the distribution of the calculated t_i^0 values showed no monotonic trend with increasing concentration. The method is limited for the Pitts equation to those values of $\underline{a}$ which render

$$0.01 \leq y \leq 0.50 \quad (2 - 41)$$

since values of the functions S_1 and T_1 are only available for values of y within this range (12, 18). However, various polynomials have been developed to serve as interpolation functions of y for S_1 and T_1 in the computer programme (see below) and these functions permitted estimation of S_1 and T_1 outside this range of y although this is not strictly valid. In the absence of proper calculations of S_1 and T_1 outside this range their behaviour is unknown. The interpolation polynomials, which were derived by a 'least squares' curve-fitting technique, are as follows.

For S_1 at $y \leq 0.12$,

$$\frac{1}{S_1} = 37.64 y + 1.0 \quad (2 - 42)$$

For S_1 at $y > 0.12$

$$\frac{1}{S_1} = 226.35y^3 - 48.654y^2 + 49.229y + 0.25 \quad (2 - 43)$$

For T_1 at $y \leq 0.14$

$$\frac{1}{T_1} = 5.742y + 2.045y^{\frac{1}{2}} + 0.431 \quad (2 - 44)$$

For T_1 at $y > 0.14$

$$\frac{1}{T_1} = 7.324y^2 + 6.359y + 0.974 \quad (2 - 45)$$

There are no such limitations on the values of $\underline{a}$ which may be used in equation (2 - 29) to test the Fuoss-Onsager equation although values which fall appreciably outside the range

$$2.5 \text{ \AA} < \underline{a} < 7 \text{ \AA} \quad (2 - 46)$$

are not physically meaningful as a distance of closest approach.

In more detail, for method A, a computer programme was devised to calculate t_i^0 for each concentration c , now written as $t_i^0(c)$. The average of $t_i^0(c)$ over all the concentrations taken, $\langle t_i^0 \rangle$, and the standard deviation of the values of $t_i^0(c)$ from this average were then found. The calculation was performed for all positive integral values of $\underline{a}$ from $1.0 \text{ \AA}$ to $20.0 \text{ \AA}$. The value of $\underline{a}$ for which the standard deviation of $t_i^0(c)$ values was a minimum, was selected and designated $\underline{a}_3$. In cases where the standard deviations progressively increased with increasing $\underline{a}$, showing no minimum, negative values of $\underline{a}$ were tried. This was only possible in testing the Fuoss-Onsager equation. These negative values of $\underline{a}$ have, of course, no physical significance. The calculation was repeated for values of $\underline{a}$ from $\underline{a}_3 - 1$ to $\underline{a}_3 + 1$ at intervals of $0.1 \text{ \AA}$ and that value of $\underline{a}$, $\underline{a}_4$, corresponding to the new minimum standard deviation was chosen.

Since there are reasons for believing that both theories are most likely to break down at high concentrations, the whole series of calculations was repeated but this time without the data for the highest concentration. The next highest concentration was then excluded and so on until the computation was carried out on data corresponding to only three concentrations. At this

stage the calculations were terminated. These results enable one to judge fairly easily if, and at what concentration, the theories break down.

The second approach, method B, is similar to that used by Pitts, Tabor and Daly (14) to test the fit of experimental conductance data to theoretical equations. It has been applied here only to the transference form of the Pitts equation. The method pre-supposes a knowledge of the approximate value of t_i^o and it is assumed that this value differs from the true value by a parameter δ which is initially unknown. If the approximate value is $t_i^\dagger$, the true value is given by

$$t_i^o = t_i^\dagger + \delta \quad (2 - 47)$$

Since both δ and $\underline{a}$ are initially unknown, a series of iterations is performed to find the best values for these parameters. By analogy with the conductance treatment, the method of making the approximations can best be understood by examination of a plot of $(t_i^o - t_i)_{kj}$ against $c_j^{\frac{1}{2}}$. Here $(t_i^o - t_i)_{kj}$ is that value calculated from equation (2 - 33) at a specified value of $\underline{a}$, $\underline{a}_k$, and at concentration C_j .

In figure 2-1 below $(t_i^o - t_i)$ is represented by Z . The value of Z at concentration c_j , calculated using $\underline{a} = \underline{a}_1$, is designated Z_{1j} . Using $\underline{a} = \underline{a}_2$ it becomes Z_{2j} . The points marked X represent values of w_j , equal to $(t_i^\dagger - t_i)_j$ which is the difference between the initial approximation for t_i^o and the measured transference number at that concentration. The points marked o represent the same values displaced by δ , i.e. the difference between the 'true' value of t_i^o corresponding to the value of $\underline{a}$, $\underline{a}^*$, for which the data best fit the equation, and the experimental values. The Pitts (14) criterion for a fit to the theory is that the function f given by

$$f = \frac{(Z_{2j} - (w_j + \delta))}{(Z_{2j} - Z_{1j})} \quad (2 - 48)$$

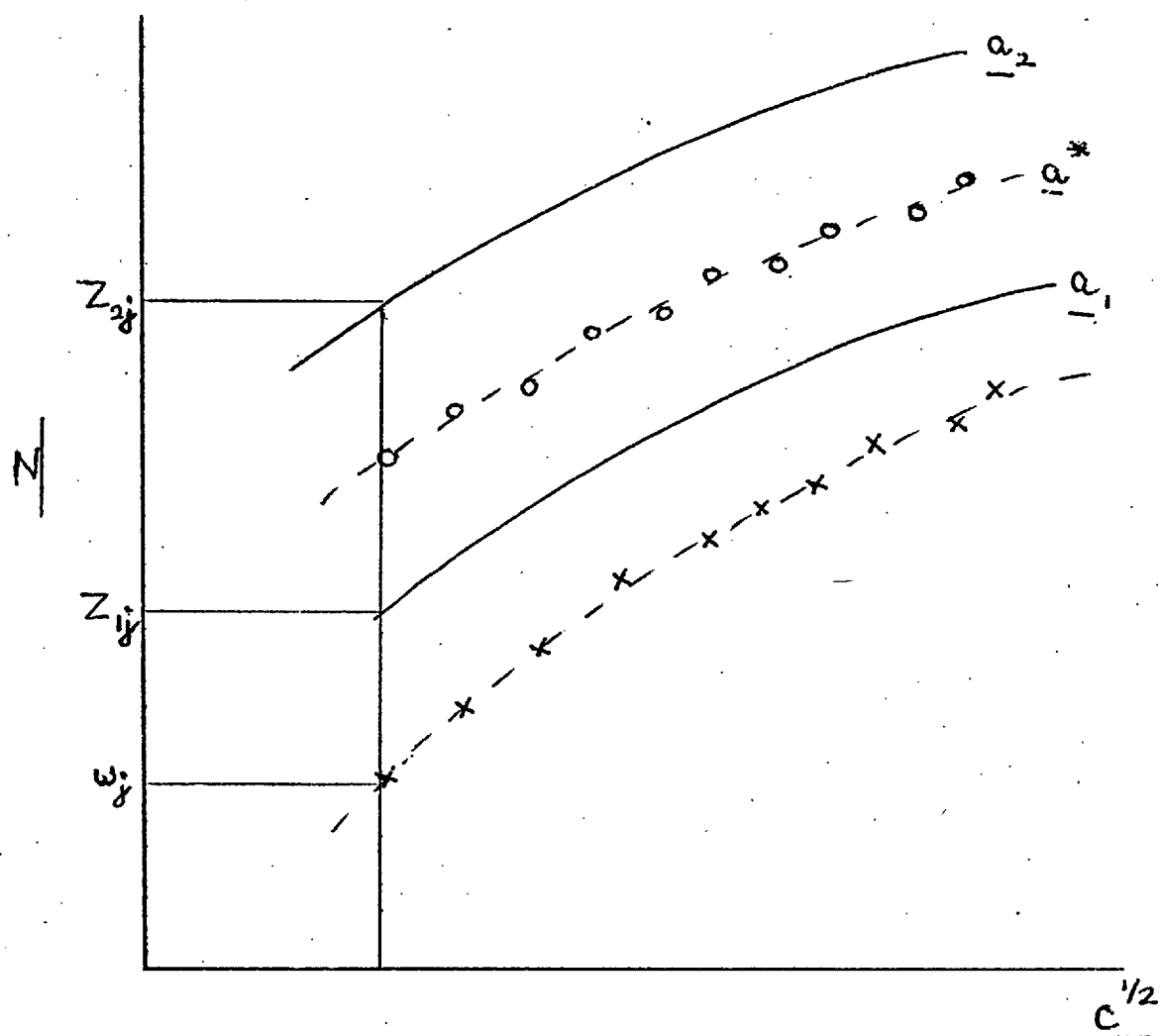


FIGURE 2-1

should be a numerical constant. However, since the experimental values are subject to error and the initial approximations for $\underline{a}_1$, $\underline{a}_2$ and t_i^0 may be far from the true values, the function f may well vary with the initial values chosen for these parameters. By adopting a least squares procedure the best fit to the Pitts equation is for those values of f and δ which minimise the function M

$$M = \sum_1^n \left[\frac{Z_{2j} - (\omega_j + \delta)}{(Z_{2j} - Z_{1j})} - f \right]^2 \quad (2 - 49)$$

The summation extends over all the n transference numbers lying within the concentration range chosen.

By differentiating M with respect to δ and f and equating the resulting expressions to zero, the values of δ and f which make M a minimum are:

$$\delta = \frac{(nT - RS)}{(nU - S^2)} \quad (2 - 50)$$

$$f = \frac{(RU - ST)}{(nU - S^2)} \quad (2 - 51)$$

$$\text{where } R = \sum_1^n \frac{Z_{2j} - \omega_j}{Z_{2j} - Z_{1j}} \quad (2 - 52)$$

$$S = \sum_1^n \frac{1}{Z_{2j} - Z_{1j}} \quad (2 - 53)$$

$$T = \sum_1^n \frac{Z_{2j} - \omega_j}{(Z_{2j} - Z_{1j})^2} \quad (2 - 54)$$

$$U = \sum_1^n \frac{1}{(Z_{2j} - Z_{1j})^2} \quad (2 - 55)$$

The first approximation to the 'best' value of $\underline{a}$ is given by

$$a^* = a_2 + (a_1 - a_2) f \quad (2 - 56)$$

and the first approximation to the value of t_i° is

$$t_i^{\circ} = t_i^{\dagger} + \delta \quad (2 - 57)$$

In the present work, the initial values of $\underline{a}_1$ and $\underline{a}_2$ were chosen arbitrarily although previous calculations using method A enabled reasonable choices to be made. The initial value of $t_i^{\dagger}$ taken was obtained from the Longsworth plots discussed earlier. When these calculations had been performed, they were repeated using for $\underline{a}_1$ and $\underline{a}_2$ the values

$$a_1 = a^* + \frac{(a_1 - a_2)}{4} \quad (2 - 58)$$

$$a_2 = a^* - \frac{(a_1 - a_2)}{4} \quad (2 - 59)$$

and for $t_i^{\dagger}$ the value of t_i° given by (2 - 47).

This procedure was continued until sufficient approximations had been made to render $(\underline{a}_1 - \underline{a}_2)$ less than $0.01\overset{\circ}{\text{\AA}}$. Usually about six approximations were found necessary although this depended on the amount by which the initial values of $\underline{a}_1$ and $\underline{a}_2$ differed. When the best values of t_i° and $\underline{a}$ had been obtained, the Pitts equation in the form of (2 - 33) was used to calculate t_i for all the concentrations at which measurements had been made. These calculated values were then compared with the experimental ones. As a criterion of fitting the difference between these quantities, Δ_B should show no monotonic trend with increasing concentration. As with method A, the calculations were repeated several times excluding, in turn, all the concentrations above the lowest three.

The essential difference between the two methods is one of approach. In method A the experimental transference numbers were first taken and the 'best' average limiting value was calculated. In method B a 'best' value was first

found for the limiting transference number. This was then used to calculate the theoretical transference numbers at finite concentrations in order to compare them with the experimental values.

The Imperial College C.D.C. 6400 computer was employed for these calculations. The computer programmes were written in Fortran IV and are given in Appendices II, III, IV, V and VI.

Summary of Results

The results of applying method A to all the available reliable data are summarized in tables 2, 4 and 6. The abbreviations P_A and F-O indicate the results obtained by application of method A using the Pitts and Fuoss-Onsager theories respectively. The results of calculations using the two forms of the Fuoss-Onsager transference equations (2 - 29) and (2 - 29a) are designated $(F-O)_1$ and $(F-O)_2$ respectively. The quantity $\sigma_{\min}$ is the minimum standard deviation of the calculated $t_i^0(c)$ values from their average over the concentration range specified. The last column of the table describes the distribution of $t_i^0(c)$ values about their average. As explained earlier this should be non-systematic for a true fit of the data to the equation. The results for non-aqueous systems, where ion association is thought to be negligible, are given in table 4. For systems in which ion association is thought to be appreciable, an allowance for it has been made in the calculations and the results are given in table 6. The results of applying method B to the same data are summarized in tables 3 and 5.

References to the sources of the experimental data, together with the appropriate association data are given in table 1.

TABLE 1. SOURCES OF TRANSFERENCE AND ASSOCIATION DATA AT 25°C.

<u>Solvent</u>	<u>Electrolyte</u>	<u>t_+^0(lit.)</u>	<u>Ref.</u>	<u>Association Data</u>	<u>Assn. Ref.</u>
Water	LiCl	0.3368	20		
	NaCl ^a	0.3963	20, 21		
	KCl ^a	0.4906	20, 22		
	HCl	0.8210	20		
	HClO ₄	0.840 ₂	23		
	AgNO ₃	0.4642	24		
50 mol % methanol-water	NaCl	0.4437	25		
	KCl	0.5068	25		
Methanol	LiCl ^b	0.4296	27		
	NaCl ^c	0.4633	26, 27		
	KCl	0.5001	26		
Methanol(10°C)	NaCl	0.4607	27		
	Bu ₄ NBr	0.4085	27		
Ethanol	LiCl	0.4393	28	∞ in transf. paper	28
	NaCl	0.4813	28	∞ in transf. paper	28
Ethylene glycol	KCl	0.4766	29		
Acetone	KCNS	0.376 ₃	30	∞ in transf. paper	30
Formamide	KCl	0.427 ₀	31		
Acetonitrile	Me ₄ NClO ₄	0.4768	32	$K_A = 7.0 \text{ dm}^3 \text{ mol}^{-1}$, $a = 3.13 \text{ \AA}$	33
Nitromethane	Me ₄ NCl	0.4674	34	$K_A = 45.0 \text{ dm}^3 \text{ mol}^{-1}$, $a = 4.0 \text{ \AA}$	33
	Me ₄ NBr	0.4663	34	$K_A = 31.0 \text{ dm}^3 \text{ mol}^{-1}$, $a = 4.1 \text{ \AA}$	33
	Et ₄ NCl	0.4320	34	$K_A = 2.0 \text{ dm}^3 \text{ mol}^{-1}$, $a = 3.4 \text{ \AA}$	33
	Et ₄ NBr	0.4314	34	$K_A = 1.7 \text{ dm}^3 \text{ mol}^{-1}$, $a = 3.3 \text{ \AA}$	33
	Bu ₄ NCl	0.3526	34		
	Bu ₄ NBr	0.3513	34		

- a The data from the two references were combined to give a joint set.
- b The results at around $3.7 \times 10^{-4}\text{N}$ and $10.0 \times 10^{-4}\text{N}$ were averaged and treated as two points only, to avoid over-weighting.
- c The data from the two references were analysed separately.

TABLE 2. APPLICATION OF METHOD A TO AQUEOUS DATA

electrolyte	theory	concn.range, $10^3 M$	best $\frac{O}{a}$	$10^4 \sigma_{\min}$	$\langle t_+^O \rangle$	highest y	trend in $t_+^O(c)$
LiCl	P_A	9.8 - 100	4.7	1.9	0.3365	0.49	see fig. 2-2
	$(F-O)_1$	9.8 - 100	5.0	1.8	0.3366	0.52	see fig. 2-2
	$(F-O)_2$	9.8 - 100	3.9	1.2	0.3371	0.33	see fig. 2-2
	P_A	9.8 - 64	4.4	1.8	0.3366	0.37	see fig. 2-2
	$(F-O)_1$	9.8 - 64	4.8	1.7	0.3367	0.40	see fig. 2-2
	$(F-O)_2$	9.8 - 64	4.0	1.0	0.3370	0.33	see fig. 2-2
	P_A	9.8 - 50	3.9	1.0	0.3368	0.29	see fig. 2-2
	$(F-O)_1$	9.8 - 50	4.3	0.9	0.3367	0.32	see fig. 2-2
	$(F-O)_2$	9.8 - 50	3.8	0.6	0.3371	0.29	see fig. 2-2
	P_A	9.8 - 33	3.3	0.3	0.3369	0.20	see fig. 2-2
	$(F-O)_1$	9.8 - 33	3.9	0.3	0.3370	0.23	see fig. 2-2
	$(F-O)_2$	9.8 - 33	3.7	0.2	0.3372	0.22	see fig. 2-2
	P_A	9.8 - 19	2.9	0.3	0.3370	0.13	see fig. 2-2
	$(F-O)_1$	9.8 - 19	3.6	0.3	0.3371	0.16	see fig. 2-2
	$(F-O)_2$	9.8 - 19	3.6	0.3	0.3372	0.16	see fig. 2-2
NaCl	P_A	10 - 100	5.7	1.4	0.3960	0.59	see fig. 2-3
	$(F-O)_1$	10 - 100	6.0	1.4	0.3961	0.62	see fig. 2-3
	$(F-O)_2$	10 - 100	4.2	2.0	0.3965	0.44	see fig. 2-3
	P_A	10 - 100 excl. 20	5.5	0.9	0.3962	0.57	see fig. 2-4
	$(F-O)_1$	10 - 100 excl. 20	5.8	0.9	0.3962	0.60	see fig. 2-4
	$(F-O)_2$	10 - 100 excl. 20	4.1	1.7	0.3966	0.43	see fig. 2-4
	P_A	10 - 60	6.1	1.5	0.3960	0.49	see fig. 2-3
	$(F-O)_1$	10 - 60	6.4	1.4	0.3960	0.52	see fig. 2-3
	$(F-O)_2$	10 - 60	4.7	1.1	0.3963	0.38	see fig. 2-3

FIGURE 2-2

APPLICATION OF METHOD A TO AQUEOUS LiCl

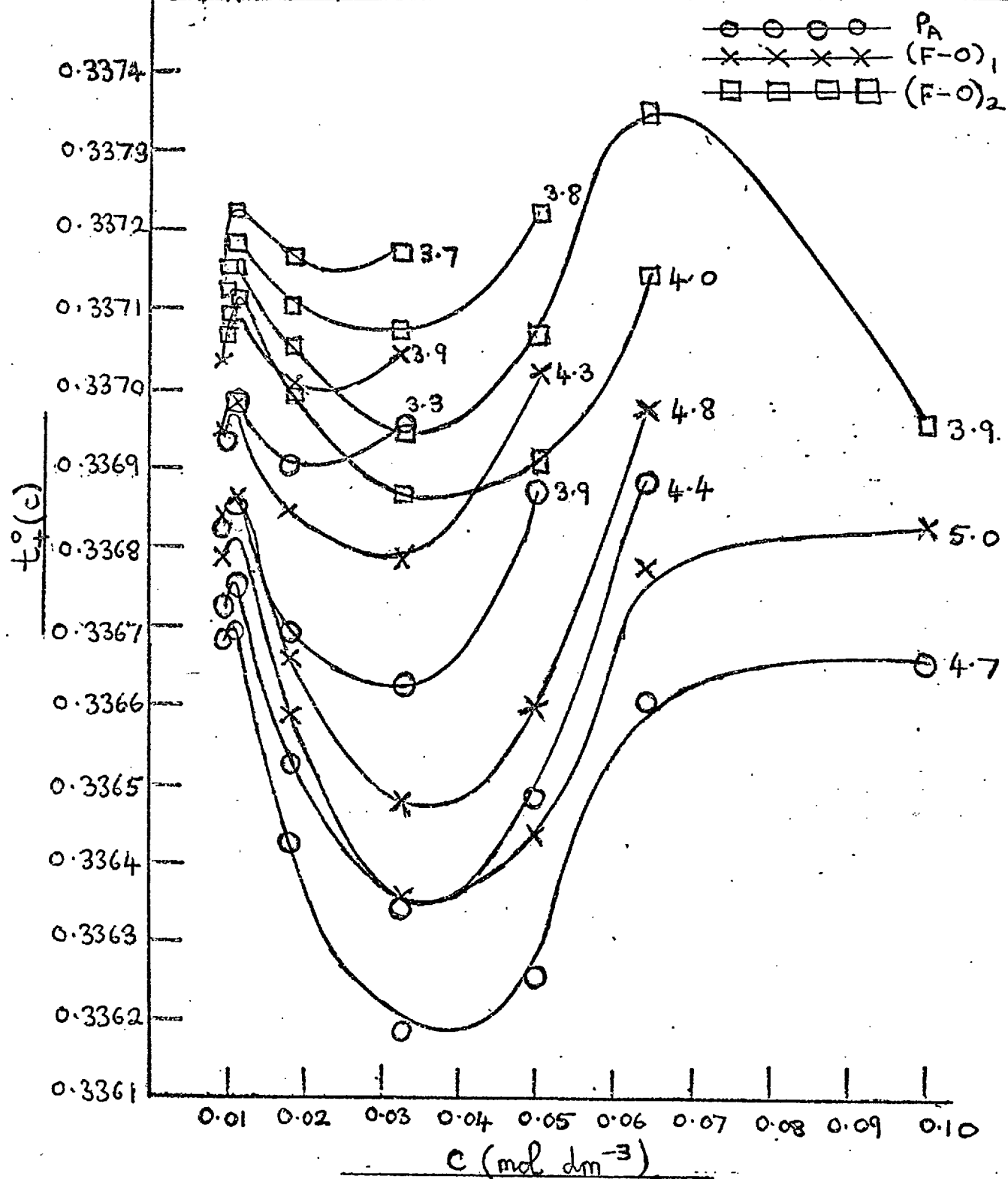


FIGURE 2-3a

APPLICATION OF METHOD A TO AQUEOUS NaCl
(INCLUDING $C = 0.02$)

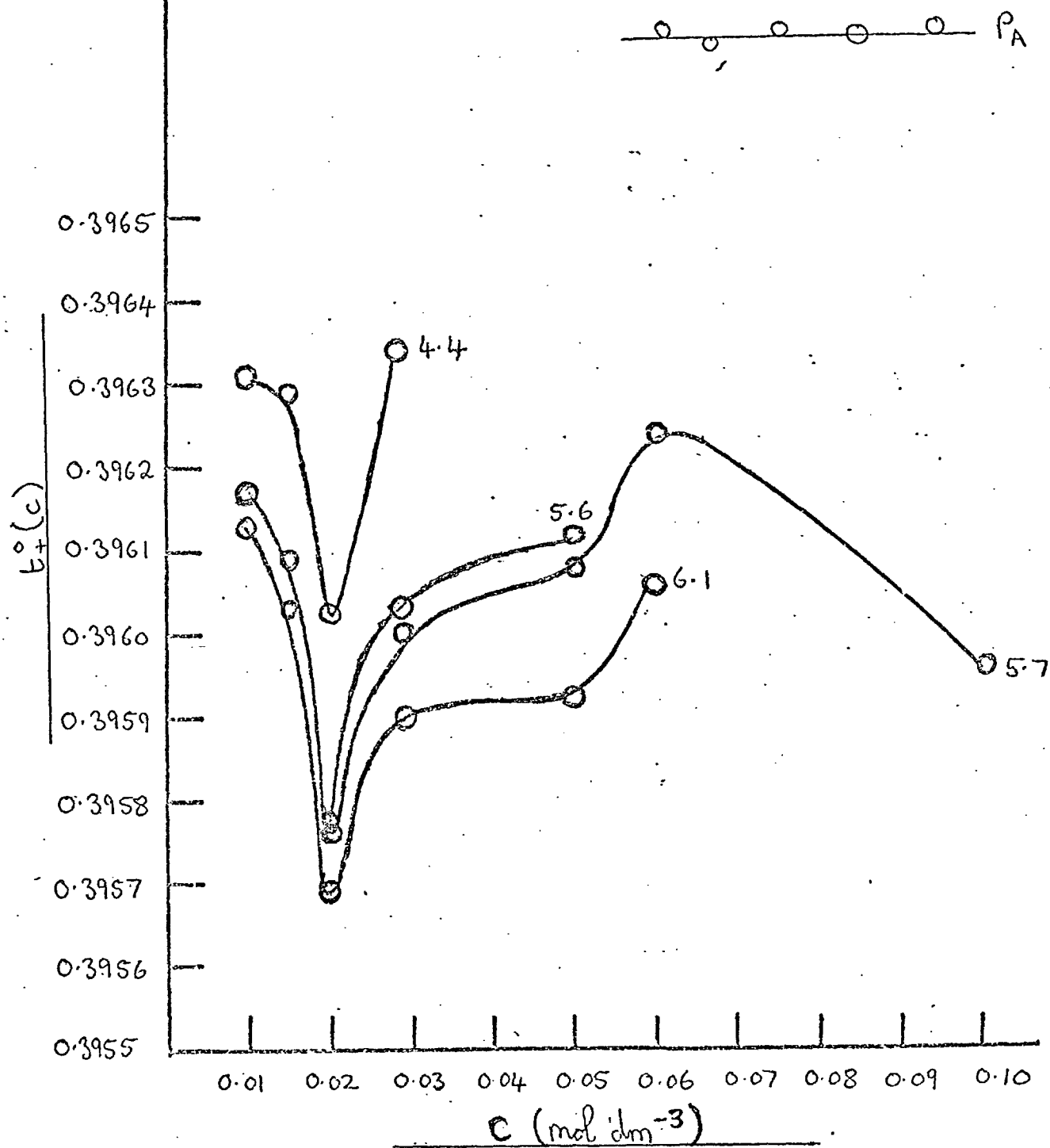


FIGURE 2-3B

APPLICATION OF METHOD A TO AQUEOUS NaCl
(INCLUDING $C = 0.02$)

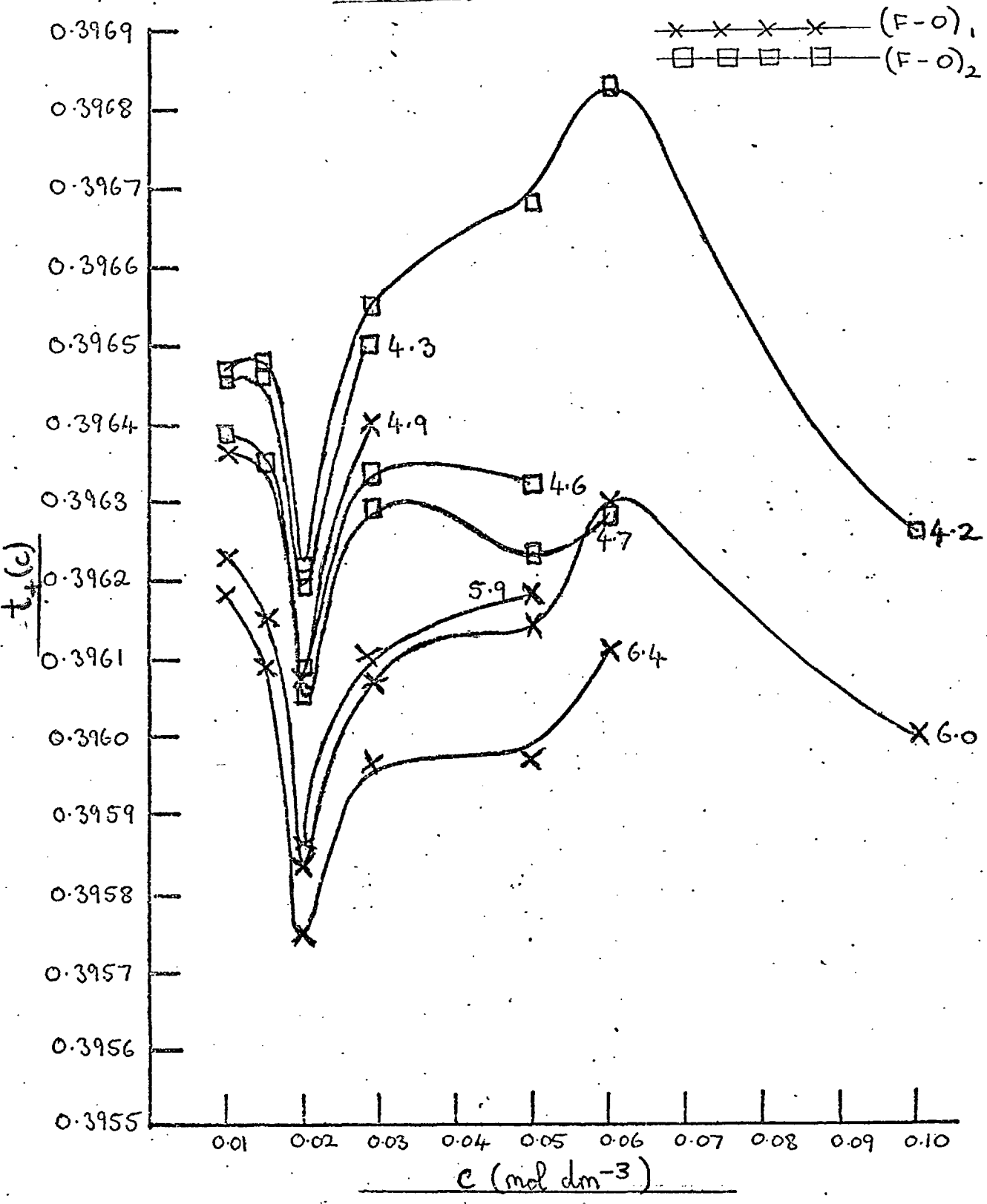
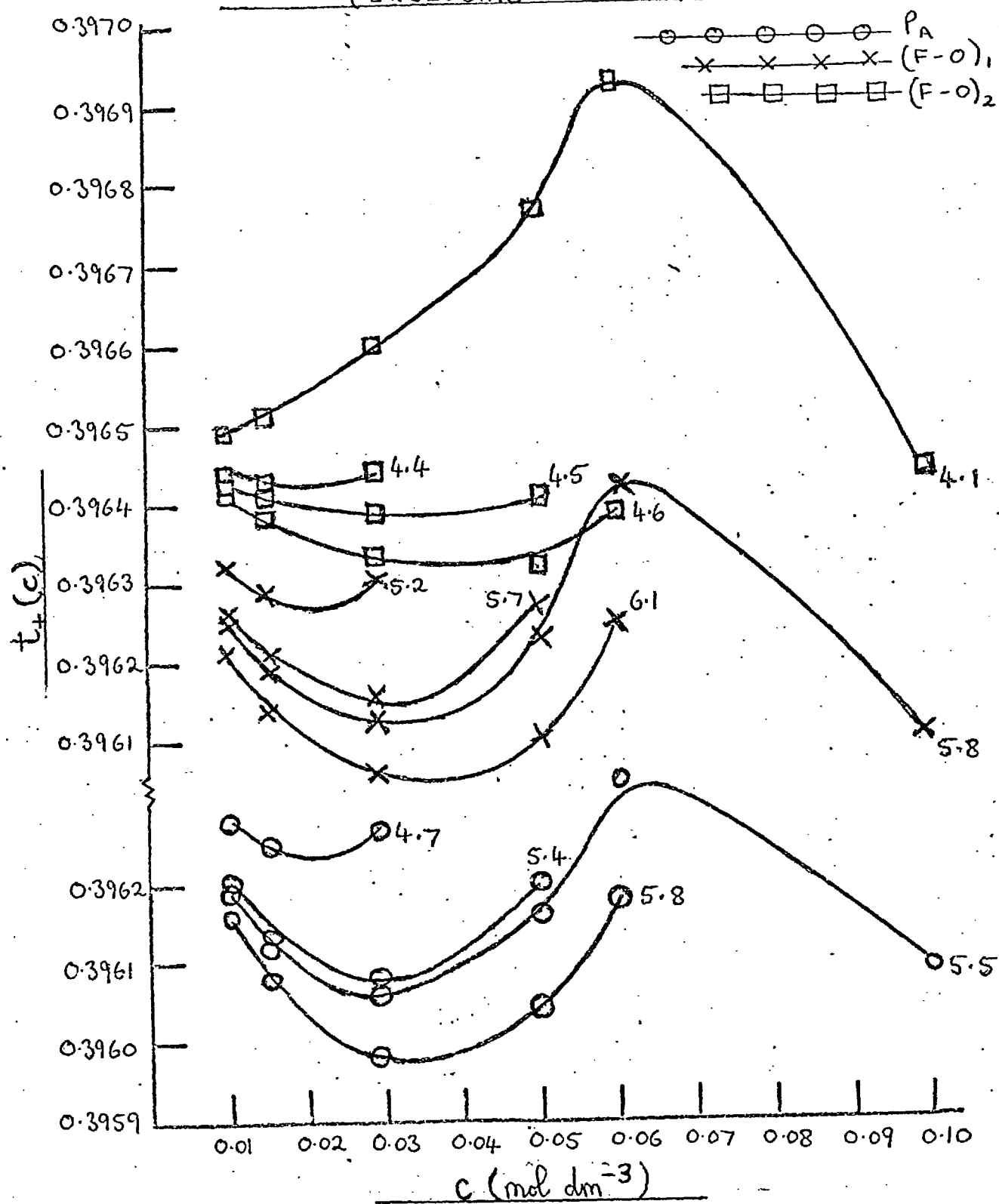


FIGURE 2-4.

APPLICATION OF METHOD A TO AQUEOUS NaCl
(EXCLUDING $c = 0.02$)



	P_A	10 - 60 excl. 20	5.8	0.8	0.3961	0.47	see fig. 2-4
	$(F-O)_1$	10 - 60 excl. 20	6.1	0.8	0.3962	0.49	see fig. 2-4
	$(F-O)_2$	10 - 60 excl. 20	4.6	0.3	0.3964	0.37	see fig. 2-4
	P_A	10 - 50	5.6	1.4	0.3960	0.41	see fig. 2-3
	$(F-O)_1$	10 - 50	5.9	1.4	0.3961	0.43	see fig. 2-3
	$(F-O)_2$	10 - 50	4.6	1.1	0.3963	0.34	see fig. 2-3
	P_A	10 - 50 excl. 20	5.4	0.5	0.3962	0.40	see fig. 2-4
	$(F-O)_1$	10 - 50 excl. 20	5.7	0.5	0.3962	0.42	see fig. 2-4
	$(F-O)_2$	10 - 50 excl. 20	4.5	0.1	0.3964	0.33	see fig. 2-4
	P_A	10 - 29	4.4	1.3	0.3962	0.25	see fig. 2-3
	$(F-O)_1$	10 - 29	4.9	1.3	0.3963	0.28	see fig. 2-3
	$(F-O)_2$	10 - 29	4.3	1.2	0.3964	0.24	see fig. 2-3
	P_A	10 - 29 excl. 20	4.7	0.1	0.3963	0.26	see fig. 2-4
	$(F-O)_1$	10 - 29 excl. 20	5.2	0.1	0.3963	0.29	see fig. 2-4
	$(F-O)_2$	10 - 29 excl. 20	4.4	0.0	0.3964	0.25	see fig. 2-4
KCl	P_A	10 - 100	>20				
	$(F-O)_1$	10 - 100	>20				
	$(F-O)_2$	10 - 100	7.0	1.4	0.4905	0.73	see fig. 2-5
	P_A	10 - 100 excl. 14	13.1	0.8	0.4905	1.35	see fig. 2-6
	$(F-O)_1$	10 - 100 excl. 14	13.2	0.8	0.4905	1.37	see fig. 2-6
	$(F-O)_2$	10 - 100 excl. 14	5.8	0.8	0.4906	0.60	similar to fig. 2-6

FIGURE 2-5
RESULTS OF THE APPLICATION OF METHOD A TO
AQUEOUS POTASSIUM CHLORIDE DATA INCLUDING $C = 0.014M$

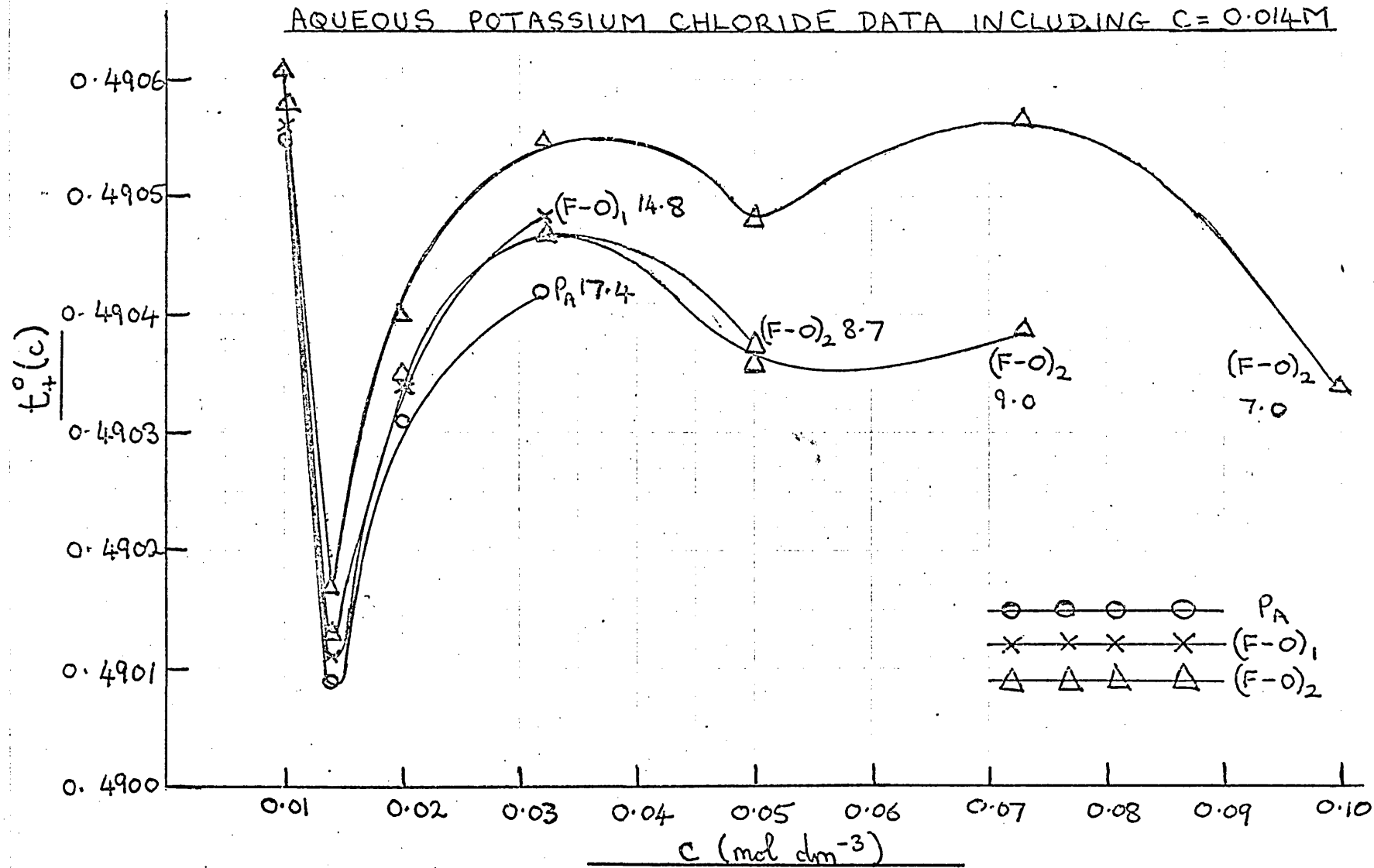
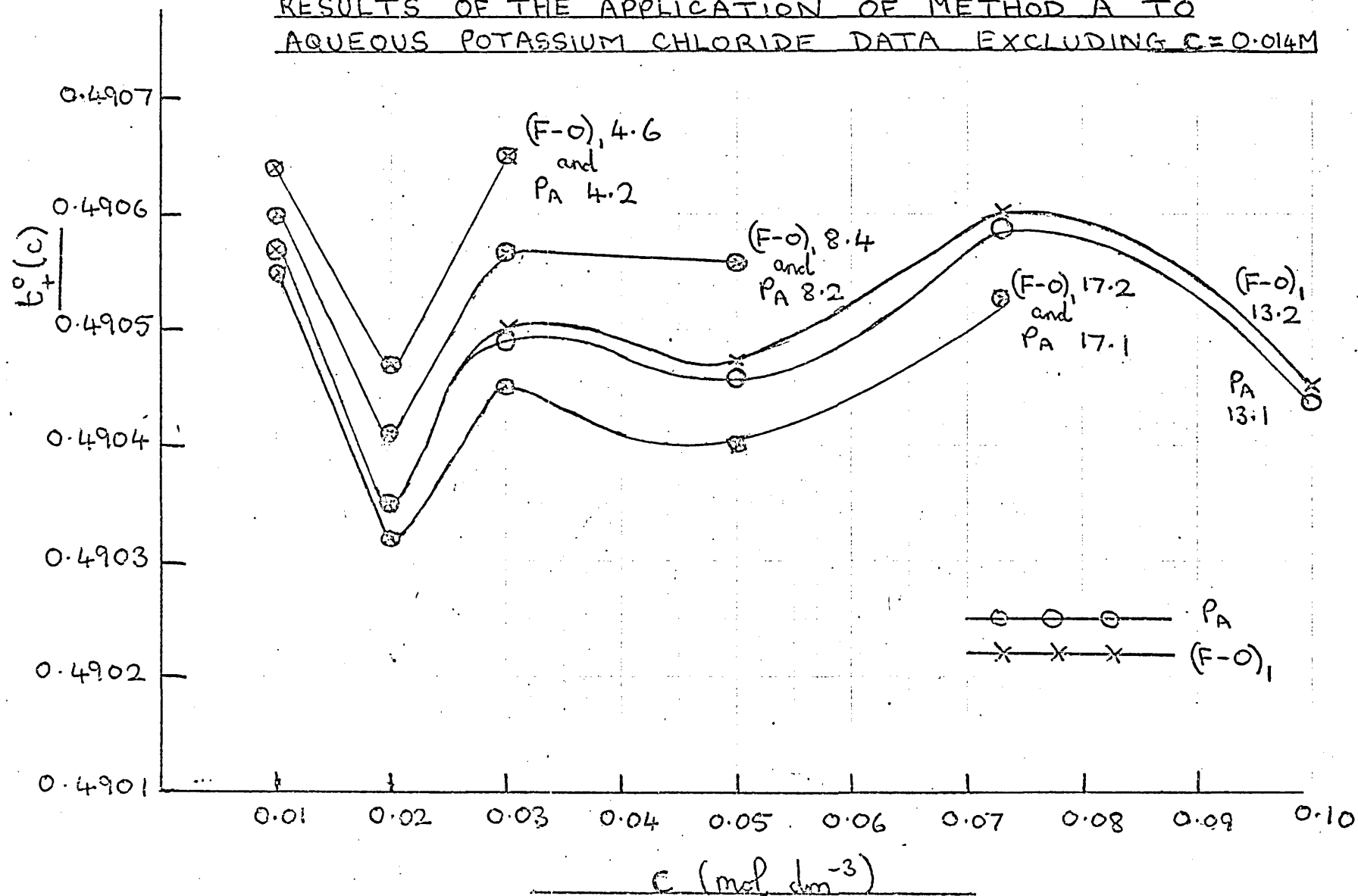


FIGURE 2-6

RESULTS OF THE APPLICATION OF METHOD A TO
AQUEOUS POTASSIUM CHLORIDE DATA EXCLUDING $C=0.014M$



	P _A	10 - 73	>20				
	(F-O) ₁	10 - 73	>20				
	(F-O) ₂	10 - 73	9.0	1.4	0.4904	0.80	see fig. 2-5
	P _A	10 - 73	17.1	0.9	0.4905	1.35	see fig. 2-6
		excl. 14					
	(F-O) ₁	10 - 73	17.2	0.9	0.4905	1.53	see fig. 2-6
		excl. 14					
	(F-O) ₂	10 - 73	7.2	0.7	0.4905	0.64	similar to fig. 2-6
		excl. 14					
	P _A	10 - 50	>20				
	(F-O) ₁	10 - 50	>20				
	(F-O) ₂	10 - 50	8.7	1.5	0.4904	0.64	see fig. 2-5
	P _A	10 - 50	8.2	0.7	0.4905	0.60	see fig. 2-6
		excl. 14					
	(F-O) ₁	10 - 50	8.4	0.7	0.4905	0.62	see fig. 2-6
		excl. 14					
	(F-O) ₂	10 - 50	5.8	0.7	0.4906	0.43	similar to fig. 2-6
		excl. 14					
	P _A	10 - 30	17.4	1.7	0.4904	1.03	see fig. 2-5
	(F-O) ₁	10 - 30	14.8	1.7	0.4904	0.85	see fig. 2-5
	(F-O) ₂	10 - 30	9.9	1.7	0.4904	0.59	see fig. 2-5
	P _A	10 - 30	4.2	0.8	0.4906	0.24	see fig. 2-6
		excl. 14					
	(F-O) ₁	10 - 30	4.6	0.8	0.4906	0.26	see fig. 2-6
		excl. 14					
	(F-O) ₂	10 - 30	5.3	0.8	0.4906	0.31	similar to fig. 2-6
		excl. 14					
HCl	P _A	10 - 100	3.9	1.1	0.8212	0.41	none
	(F-O) ₁	10 - 100	4.2	1.1	0.8211	0.44	none
	(F-O) ₂	10 - 100	3.5	1.1	0.8209	0.36	none
	P _A	10 - 50	3.4	1.1	0.8211	0.25	none
	(F-O) ₁	10 - 50	3.8	1.1	0.8210	0.30	none
	(F-O) ₂	10 - 50	3.5	1.3	0.8209	0.26	none

HClO ₄	P _A	10 - 300	5.5	0.9	0.8402	0.99	none
	(F-O) ₁	10 - 300	5.7	1.0	0.8401	1.03	none
	(F-O) ₂	10 - 300	3.4	4.3	0.8393	0.61	max. by 0.0005 at 0.1M
	P _A	10 - 100	5.5	1.0	0.8402	0.59	none
	(F-O) ₁	10 - 100	5.7	1.0	0.8401	0.61	none
	(F-O) ₂	10 - 100	4.0	2.1	0.8398	0.42	max. by 0.0003 at 0.048M
	P _A	10 - 48	6.1	0.9	0.8403	0.44	none
	(F-O) ₁	10 - 48	6.4	1.0	0.8403	0.46	none
	(F-O) ₂	10 - 48	4.7	1.3	0.8400	0.34	none
AgNO ₃	P _A	10 - 100	>20				
	(F-O) ₁	10 - 100	>20				
	(F-O) ₂	10 - 100	16.0	1.7	0.4658	1.7	max. by 0.0003 at 0.05M
	P _A	10 - 50	>20				
	(F-O) ₁	10 - 50	>20				
	(F-O) ₂	10 - 50	18.2	0.7	0.4656	1.3	none

TABLE 3. APPLICATION OF METHOD P_B TO AQUEOUS DATA

electrolyte	concn. range, $10^3 M$	final $\bar{a}^*$	final t_+^0	no. of iterations, n	trend in Δ_B
LiCl	9.8 - 100	4.22	0.3367	8	see fig. 2-7
	9.8 - 64	3.99	0.3368	8	see fig. 2-7
	9.8 - 50	3.61	0.3369	8	see fig. 2-7
	9.8 - 33	3.23	0.3370	8	see fig. 2-7
	9.8 - 19	3.02	0.3370	8	see fig. 2-7
NaCl	10 - 100	5.56	0.3961	8	see fig. 2-8
	10 - 100 excl. 20	5.43	0.3962	8	see fig. 2-9
	10 - 60	5.57	0.3961	8	see fig. 2-8
	10 - 60 excl. 20	5.46	0.3962	8	see fig. 2-9
	10 - 50	5.54	0.3961	8	see fig. 2-8
	10 - 50 excl. 20	5.11	0.3962	8	see fig. 2-9
	10 - 29	5.53	0.3961	8	see fig. 2-8
	10 - 29 excl. 20	4.60	0.3963	8	see fig. 2-9
HCl	10 - 100	4.07	0.8212	9	none
	10 - 50	4.14	0.8212	9	none
HClO ₄	10 - 300	5.93	0.8404	8	none
	10 - 100	6.14	0.8404	8	none
	10 - 48	6.81	0.8404	8	none

FIGURE 2-7
RESULTS OF THE APPLICATION OF METHOD P_B
TO AQUEOUS LITHIUM CHLORIDE DATA

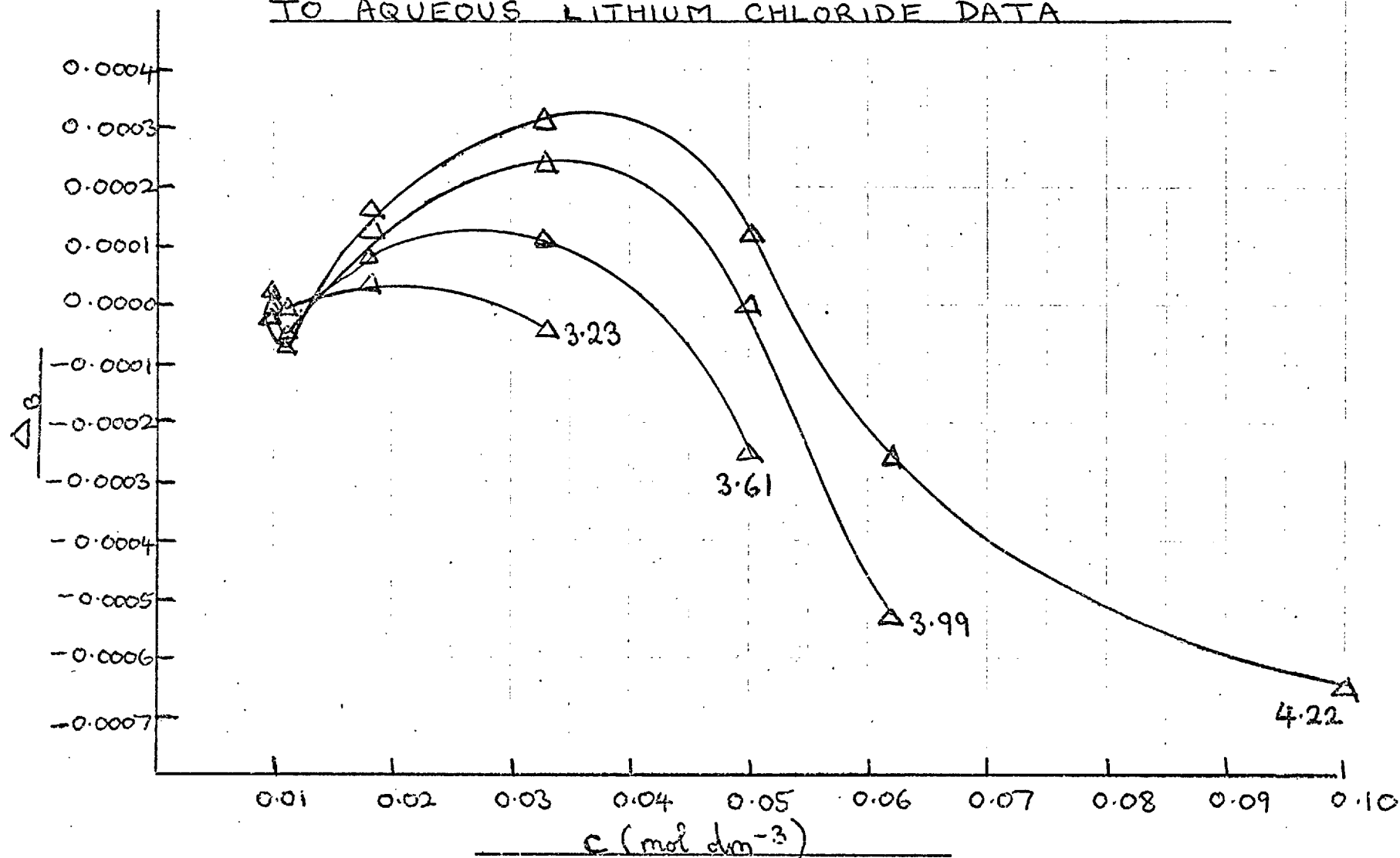


FIGURE 2-8

APPLICATION OF METHOD P_B TO AQUEOUS NaCl
(INCLUDING $C = 0.02$)

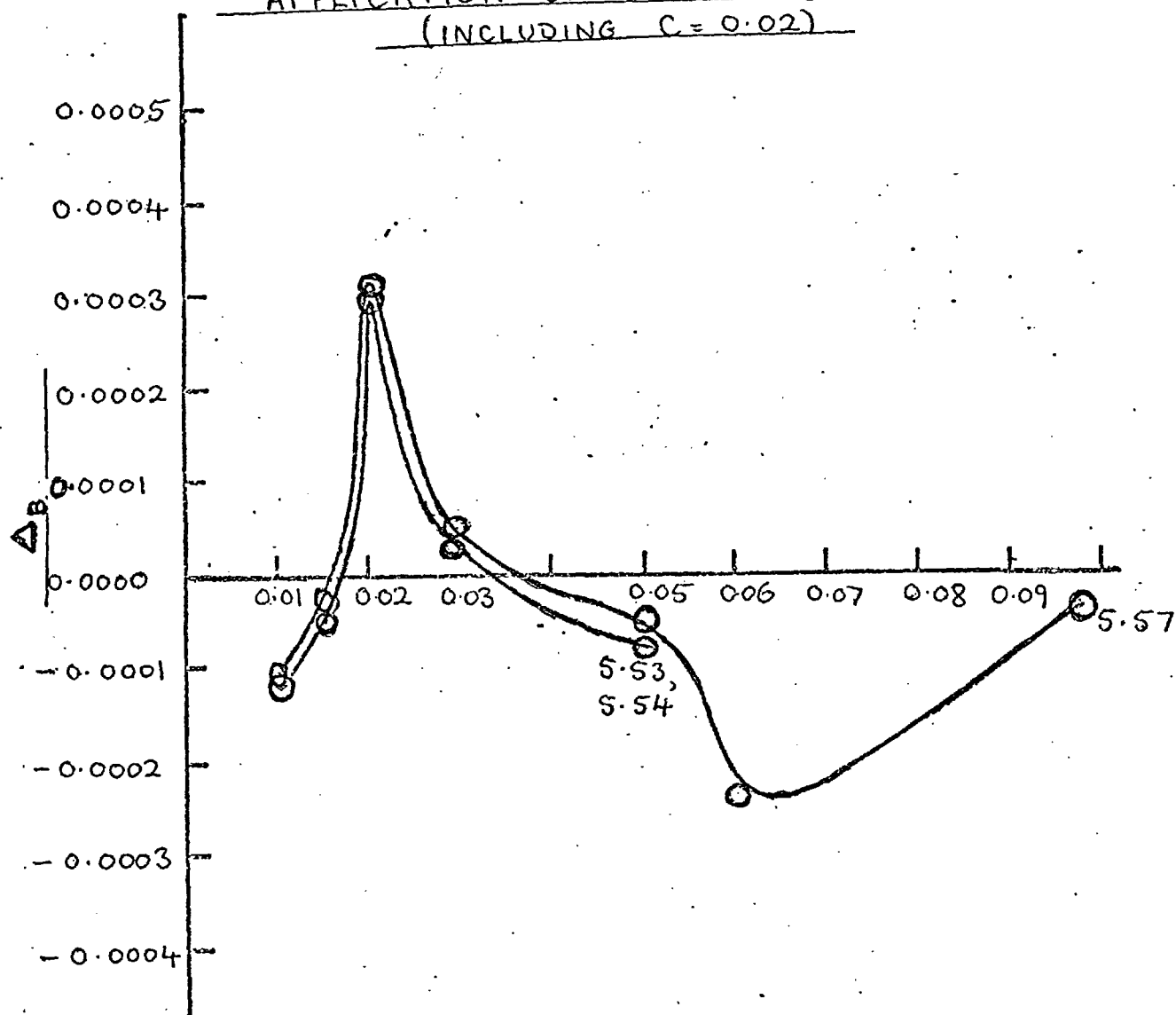


FIGURE 2-9

RESULTS OF THE APPLICATION OF METHOD P_B TO
 AQUEOUS SODIUM CHLORIDE DATA EXCLUDING $C = 0.02 \text{ mol dm}^{-3}$

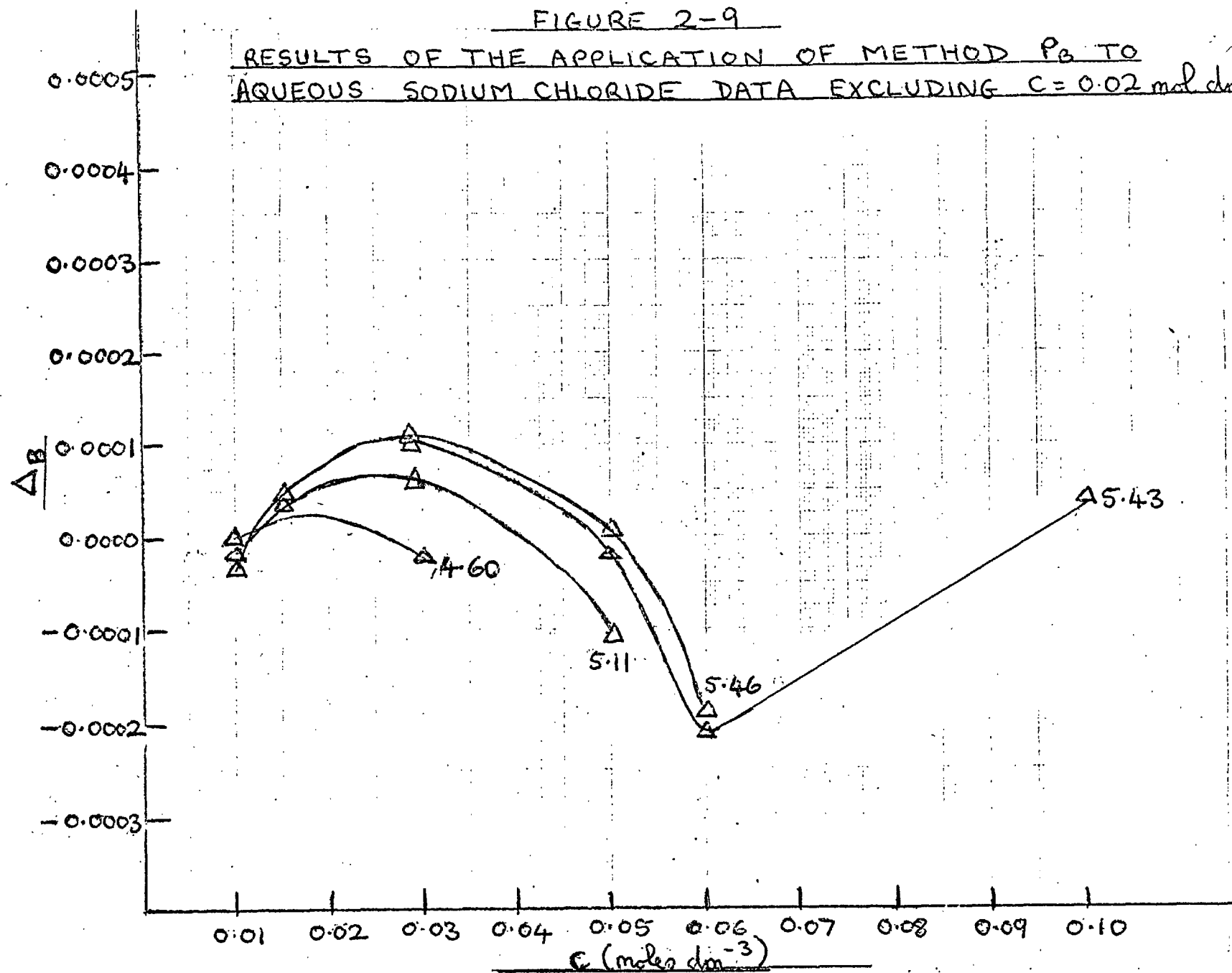


TABLE 4. APPLICATION OF METHOD A TO NON-AQUEOUS DATA (COMPLETE DISSOCIATION ASSUMED)

solvent	salt	theory	concn. range, $10^3 M$	best $\underline{a}$	$10^4 \epsilon_{\min}$	$\langle t_+^0 \rangle$	highest y	trend in $t_+^0(c)$
50 mol % methanol-water	NaCl	P_A	5 - 80	15.3	4.2	0.4440	1.79	max. by 0.0005 at 0.02M
		$(F-O)_1$	5 - 80	15.7	4.2	0.4440	1.84	max. by 0.0005 at 0.02M
		$(F-O)_2$	5 - 80	6.0	6.9	0.4451	0.70	max. by 0.0008 at 0.02M
		P_A	5 - 50	>20			>1.85	
		$(F-O)_1$	5 - 50	>20			>1.85	
		$(F-O)_2$	5 - 50	7.4	5.3	0.4446	0.68	max. by 0.0007 at 0.02M
		P_A	5 - 30	>20			>1.43	
		$(F-O)_1$	5 - 30	>20			>1.43	
		$(F-O)_2$	5 - 30	9.9	2.6	0.4439	0.71	max. by 0.0004 at 0.02M
		P_A	5 - 20	>20			>1.16	
		$(F-O)_1$	5 - 20	>20			>1.16	
		$(F-O)_2$	5 - 20	12.0	0.9	0.4436	0.70	none
		P_A	5 - 80	<0				
		$(F-O)_1$	5 - 80	-4.2	3.3	0.5074	-0.49	max. at 0.05M
50 mol% methanol-water	KCl	$(F-O)_2$	5 - 80	0.3	5.1	0.5077	0.04	max. at 0.05M
		P_A	5 - 50	<0				
		$(F-O)_1$	5 - 50	-5.8	1.6	0.5071	-0.53	max. at 0.02-0.03M
		$(F-O)_2$	5 - 50	0.3	4.9	0.5076	0.03	rises with incr. concn.
		P_A	5 - 30	<0				
		$(F-O)_1$	5 - 30	-7.3	0.9	0.5070	-0.52	max. at 0.02M
		$(F-O)_2$	5 - 30	0.3	3.3	0.5074	0.02	rises with incr. concn.
		P_A	5 - 20	<0				
		$(F-O)_1$	5 - 20	-8.7	0.1	0.5069	-0.51	none
		$(F-O)_2$	5 - 20	0.3	2.5	0.5072	0.02	rises with incr. concn.
		P_A	0.4 - 9.9	6.0	1.5	0.4232	0.36	none
		P_A						
		P_A						
		P_A						
methanol	LiCl	P_A	0.4 - 9.9	6.0	1.5	0.4232	0.36	none

		(F-O) ₁	0.4 - 9.9.	7.2	1.6	0.4292	0.37	none
		(F-O) ₂	0.4 - 9.9	6.9	2.0	0.4294	0.35	none
		P _A	0.4 - 8.1	6.5	1.4	0.4291	0.37	none
		(F-O) ₁	0.4 - 8.1	7.6	1.5	0.4292	0.35	none
		(F-O) ₂	0.4 - 8.1	7.2	1.8	0.4293	0.33	none
		P _A	0.4 - 7.4	6.7	1.5	0.4291	0.37	none
		(F-O) ₁	0.4 - 7.4	7.9	1.6	0.4292	0.35	none
		(F-O) ₂	0.4 - 7.4	7.4	1.9	0.4293	0.33	none
		P _A	0.4 - 4.9	7.1	1.6	0.4291	0.41	none
		(F-O) ₁	0.4 - 4.9	8.4	1.7	0.4291	0.30	none
		(F-O) ₂	0.4 - 4.9	7.9	1.9	0.4292	0.28	none
		P _A	0.4 - 3.0	10.5	1.2	0.4289	0.37	none
		(F-O) ₁	0.4 - 3.0	11.6	1.2	0.4290	0.32	none
		(F-O) ₂	0.4 - 3.0	10.0	1.3	0.4291	0.28	none
methanol	NaCl (data from ref. 27)	P _A	0.5 -14.7	0.6	1.4	0.4630	0.04	none
		(F-O) ₁	0.5 -14.7	3.4	1.9	0.4631	0.21	none
		(F-O) ₂	0.5 -14.7	4.9	2.0	0.4631	0.30	none
		P _A	0.5 - 9.8	3.4	0.7	0.4630	0.17	none
		(F-O) ₁	0.5 - 9.8	5.0	0.8	0.4630	0.25	none
		(F-O) ₂	0.5 - 9.8	5.8	0.8	0.4630	0.29	none
methanol	NaCl 10°C	P _A	1 -10	0.9	1.0	0.4604	0.05	none
		(F-O) ₁	1 -10	3.3	1.2	0.4605	0.17	none
		(F-O) ₂	1 -10	4.8	1.2	0.4605	0.24	none
		P _A	1 - 5	0.5	0.9	0.4604	0.02	none
		(F-O) ₁	1 - 5	4.2	1.1	0.4605	0.18	none
		(F-O) ₂	1 - 5	5.4	1.2	0.4605	0.23	none
methanol	Bu ₄ NBr 10°C	P _A	1 - 5	9.1	0.9	0.4082	0.32	none
		(F-O) ₁	1 - 5	10.0	0.9	0.4083	0.35	none
		(F-O) ₂	1 - 5	8.6	1.1	0.4084	0.30	none
		P _A	1 - 4	9.8	0.9	0.4081	0.31	none
		(F-O) ₁	1 - 4	10.7	0.9	0.4082	0.34	none
		(F-O) ₂	1 - 4	9.1	1.0	0.4083	0.29	none
		P _A	1 - 2.9	10.5	1.0	0.4081	0.28	none

methanol (data from ref.26)	NaCl	(F-O) ₁	1 - 2.9	11.4	1.0	0.4081	0.31	none
		(F-O) ₂	1 - 2.9	9.7	1.1	0.4083	0.26	none
		P _A	3 -10	5.5	1.1	0.4631	0.28	none
		(F-O) ₁	3 -10	6.4	1.0	0.4632	0.33	none
		(F-O) ₂	3 -10	6.4	0.9	0.4632	0.33	none
		P _A	3 - 7	0.7	0.3	0.4633	0.03	none
		(F-O) ₁	3 - 7	3.7	0.4	0.4634	0.16	none
		(F-O) ₂	3 - 7	5.1	0.4	0.4635	0.22	none
methanol	KCl	P _A	3 -10	<0				
		(F-O) ₁	3 -10	-15.2	0.8	0.5005	-0.77	none
		(F-O) ₂	3 -10	0.4	1.3	0.5005	0.02	rises with incr. concn.
		P _A	3 - 7	<0				
		(F-O) ₁	3 - 7	-17.9	0.7	0.5004	-0.76	none
		(F-O) ₂	3 - 7	0.4	0.9	0.5005	0.02	rises with incr. concn.
		P _A	5 -50	8.9	0.4	0.4766	0.91	none, see fig. 2-11
		(F-O) ₁	5 -50	9.3	0.4	0.4766	0.95	none, see fig. 2-11
ethylene glycol	KCl	(F-O) ₂	5 -50	5.9	0.2	0.4767	0.60	none, see fig. 2-11
		P _A	5 -20	5.1	0.1	0.4767	0.33	none, see fig. 2-11
		(F-O) ₁	5 -20	5.7	0.1	0.4767	0.37	none, see fig. 2-11
		(F-O) ₂	5 20	5.4	0.1	0.4767	0.35	none, see fig. 2-11
		P _A	10 -100	9.2	0.9	0.4267	0.81	none, see fig. 2-10
		(F-O) ₁	10 -100	9.3	0.9	0.4267	0.82	none, see fig. 2-10
		(F-O) ₂	10 -100	5.3	1.7	0.4271	0.47	see fig. 2-10
		P _A	10 - 80	9.1	1.0	0.4267	0.72	none, see fig. 2-10
formamide	KCl	(F-O) ₁	10 - 80	9.3	1.0	0.4267	0.73	none, see fig. 2-10
		(F-O) ₂	10 - 80	5.5	1.8	0.4271	0.43	see fig. 2-10
		P _A	10 - 50	10.7	0.5	0.4266	0.67	none, see fig. 2-10
		(F-O) ₁	10 - 50	10.9	0.5	0.4266	0.68	none, see fig. 2-10
		(F-O) ₂	10 - 50	6.5	0.9	0.4268	0.40	none, see fig. 2-10
		P _A	0.2 - 10	2.5	0.6	0.3526	0.12	none
		(F-O) ₁	0.2 - 10	4.2	0.3	0.3528	0.20	none
		(F-O) ₂	0.2 - 10	5.2	0.5	0.3528	0.25	none
nitromethane	Bu ₄ NCl	P _A	0.2 - 5	1.8	0.4	0.3526	0.06	none

FIGURE 2-10

RESULTS OF THE APPLICATION OF METHOD A
TO DATA FOR KCl IN FORMAMIDE

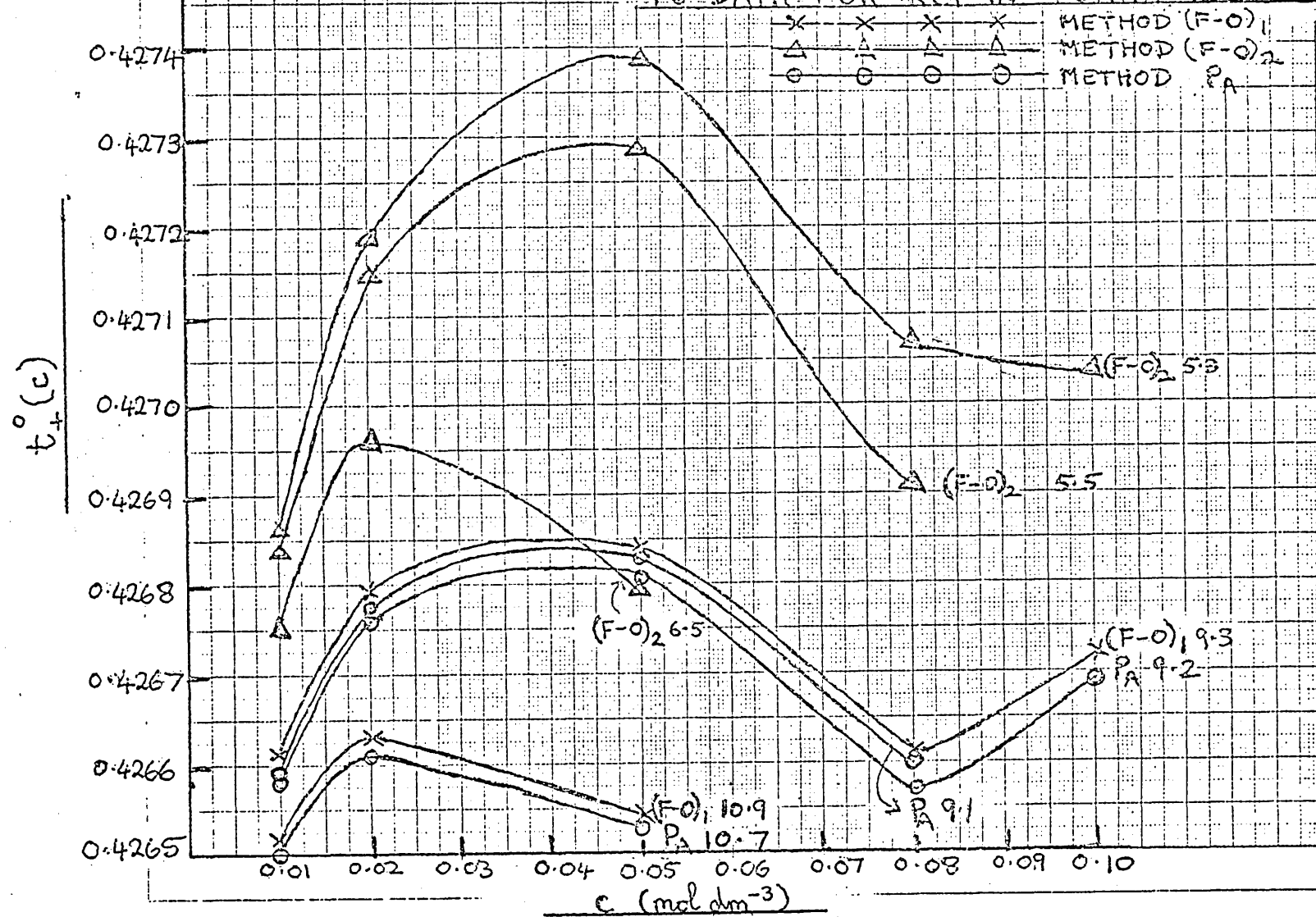
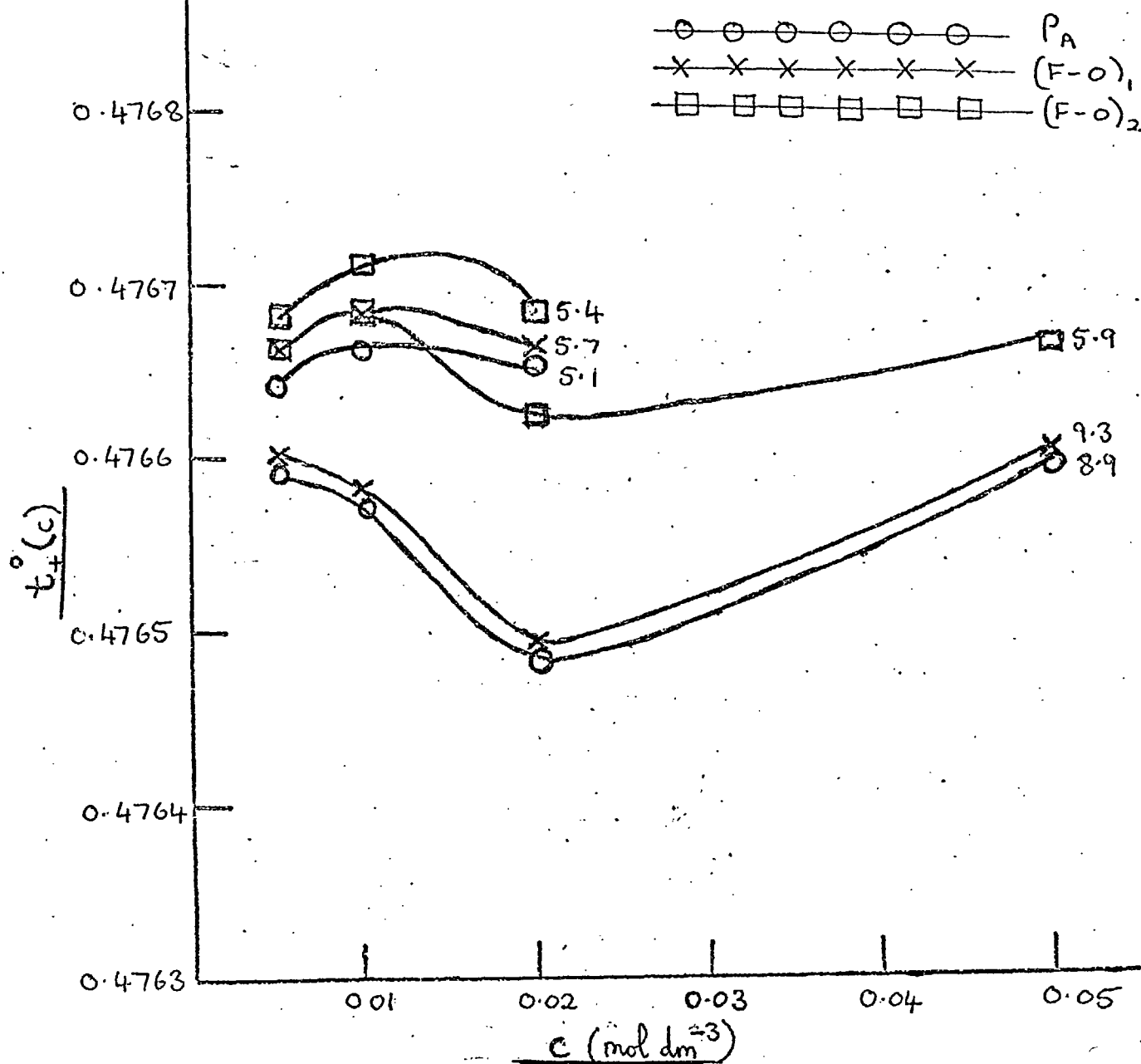


FIGURE 2-11
APPLICATION OF METHOD A TO KCL/ETHYLENE GLYCOL



		(F-O) ₁	0.2 - 5	4.2	0.3	0.3528	0.14	none
		(F-O) ₂	0.2 - 5	5.3	0.4	0.3528	0.18	none
		P _A	0.2 - 2	1.6	0.5	0.3526	0.04	none
		(F-O) ₁	0.2 - 2	4.5	0.3	0.3527	0.10	none
		(F-O) ₂	0.2 - 2	5.7	0.4	0.3528	0.12	none
		P _A	0.2 - 1	1.8	0.5	0.3527	0.03	none
		(F-O) ₁	0.2 - 1	4.9	0.4	0.3527	0.07	none
		(F-O) ₂	0.2 - 1	6.1	0.4	0.3527	0.09	none
nitromethane	Bu ₄ NBr	P _A	0.2 - 10	3.5	0.6	0.3512	0.17	none
		(F-C) ₁	0.2 - 10	5.0	0.4	0.3513	0.24	none
		(F-O) ₂	0.2 - 10	5.6	0.6	0.3513	0.27	none
		P _A	0.2 - 5	3.1	0.5	0.3512	0.05	none
		(F-O) ₁	0.2 - 5	4.9	0.4	0.3513	0.11	none
		(F-O) ₂	0.2 - 5	5.8	0.4	0.3513	0.20	none
		P _A	0.2 - 2	2.4	0.6	0.3512	0.05	none
		(F-O) ₁	0.2 - 2	5.1	0.5	0.3513	0.11	none
		(F-O) ₂	0.2 - 2	6.1	0.4	0.3513	0.13	none
		P _A	0.2 - 1	1.7	0.6	0.3512	0.03	none
		(F-O) ₁	0.2 - 1	3.5	0.3	0.3513	0.05	none
		(F-O) ₂	0.2 - 1	5.0	0.3	0.3513	0.08	none

TABLE 5. APPLICATION OF METHOD P_B TO NON-AQUEOUS DATA (ASSUMING COMPLETE DISSOCIATION)

solvent	salt	concn. range, $10^3 M$	final $\underline{a}^*$	final t_+^0	no. of iterations	trend in Δ_B
methanol	NaCl	0.5 - 14.7	4.62	0.4629	8	none
(data from ref. 27)		0.5 - 9.8	6.98	0.4629	8	none
methanol	NaCl	3 - 10	4.31	0.4632	8	none
(data from ref. 26)		3 - 7	2.59	0.4633	8	none
ethylene glycol	KCl	5 - 50	7.39	0.4766	9	none
		5 - 20	5.62	0.4766	9	none
formamide	KCl	10 - 100	9.90	0.4266	9	none
		10 - 80	10.15	0.4266	9	none
		10 - 50	11.49	0.4265	9	none

TABLE 6. APPLICATION OF METHOD A TO NON-AQUEOUS DATA (ION ASSOCIATION ALLOWED FOR)

solvent	salt	theory	concn. range $10^3 M$	best $\frac{0}{a}$	$10^4 \sigma_{\min}$	$\langle t_+^0 \rangle$	highest y	trend in $t_+^0(c)$
ethanol	LiCl	P_A	0.9 - 2.5	<0				
		$(F-O)_1$	0.9 - 2.5	-4.5	0.0	0.4392	-0.13	none
		$(F-O)_2$	0.9 - 2.5	1.2	0.0	0.4392	0.03	none
ethanol	NaCl	P_A	1 - 2.5	<0				
		$(F-O)_1$	1 - 2.5	-8.9	0.6	0.4812	-0.25	none
		$(F-O)_2$	1 - 2.5	0.6	0.9	0.4810	0.02	none
		P_A	1 - 2	<0				
		$(F-O)_1$	1 - 2	-6.3	0.3	0.4811	-0.16	none
		$(F-O)_2$	1 - 2	0.6	0.3	0.4810	0.02	none
acetone	KCNS	P_A	1.1 - 2.4	<0				
		$(F-O)_1$	1.1 - 2.4	-12.2	0.9	0.3754	-0.35	none
		$(F-O)_2$	1.1 - 2.4	0.8	6.5	0.3734	0.02	rises with incr. concn.
		P_A	1.1 - 2.0	<0				
		$(F-O)_1$	1.1 - 2.0	-12.2	1.0	0.3754	-0.32	none
		$(F-O)_2$	1.1 - 2.0	0.8	5.0	0.3736	0.02	rises with incr. concn.
		P_A	1.1 - 1.9	<0				
		$(F-O)_1$	1.1 - 1.9	-12.8	0.4	0.3756	-0.33	none
		$(F-O)_2$	1.1 - 1.9	0.8	5.3	0.3736	0.02	rises with incr. concn.

acetonitrile	Me_4NClO_4	P_A	0.63 -12.4	0.7	1.6	0.4769	0.04	risers with incr. concn. but anomal- ously low at high- est concn.
		$(F-O)_1$	0.63 -12.4	2.9	1.7	0.4770	0.15	"
		$(F-O)_2$	0.63 -12.4	4.3	1.7	0.4770	0.23	"
		P_A	0.63 - 8.0	8.2	0.3	0.4768	0.35	none
		$(F-O)_1$	0.63 - 8.0	9.0	0.3	0.4768	0.39	none
		$(F-O)_2$	0.63 - 8.0	7.8	0.4	0.4768	0.33	none
		P_A	0.63 - 5.0	9.3	0.3	0.4768	0.31	none
		$(F-O)_1$	0.63 - 5.0	10.2	0.3	0.4768	0.34	none
		$(F-O)_2$	0.63 - 5.0	8.9	0.3	0.4768	0.30	none
		P_A	0.63 - 2.5	4.5	0.2	0.4768	0.11	none
		$(F-O)_1$	0.63 - 2.5	6.1	0.2	0.4768	0.15	none
		$(F-O)_2$	0.63 - 2.5	6.8	0.2	0.4768	0.16	none
nitromethane	Me_4NCl	P_A	0.2 -10	3.0	0.4	0.4674	0.13	none
		$(F-O)_1$	0.2 -10	4.5	0.4	0.4674	0.20	none
		$(F-O)_2$	0.2 -10	5.4	0.3	0.4674	0.24	none
		P_A	0.2 - 5	1.6	0.4	0.4674	0.05	none
		$(F-O)_1$	0.2 - 5	3.9	0.4	0.4674	0.13	none
		$(F-O)_2$	0.2 - 5	5.1	0.3	0.4674	0.16	none
		P_A	0.2 - 2	1.6	0.4	0.4674	0.04	none
		$(F-O)_1$	0.2 - 2	1.8	0.3	0.4674	0.04	none
		$(F-O)_2$	0.2 - 2	3.8	0.3	0.4674	0.08	none

nitromethane	Me ₄ NBr	P _A	0.2 - 1	1.7	0.4	0.4674	0.03	none
		(F-O) ₁	0.2 - 1	0.7	0.4	0.4674	0.01	none
		(F-O) ₂	0.2 - 1	3.0	0.4	0.4674	0.04	none
		P _A	0.2 -10	1.3	0.6	0.4663	0.06	none
		(F-O) ₁	0.2 -10	2.8	0.4	0.4664	0.13	none
		(F-O) ₂	0.2 -10	4.3	0.4	0.4664	0.19	none
		P _A	0.2 - 5	1.4	0.7	0.4663	0.05	none
		(F-O) ₁	0.2 - 5	1.9	0.4	0.4664	0.06	none
		(F-O) ₂	0.2 - 5	3.8	0.4	0.4664	0.12	none
		P _A	0.2 - 2	1.5	0.4	0.4663	0.03	none
		(F-O) ₁	0.2 - 2	3.7	0.4	0.4664	0.08	none
		(F-O) ₂	0.2 - 2	5.1	0.4	0.4664	0.11	none
nitromethane	Et ₄ NCl	P _A	0.2 - 1	10.4	0.2	0.4663	0.15	none
		(F-O) ₁	0.2 - 1	11.9	0.2	0.4663	0.18	none
		(F-O) ₂	0.2 - 1	11.1	0.2	0.4663	0.17	none
		P _A	0.2 - 10	3.6	0.5	0.4320	0.17	none
		(F-O) ₁	0.2 - 10	5.0	0.4	0.4321	0.24	none
		(F-O) ₂	0.2 - 10	5.6	0.4	0.4321	0.27	none
		P _A	0.2 - 5	3.6	0.5	0.4320	0.12	none
		(F-O) ₁	0.2 - 5	5.2	0.4	0.4321	0.17	none
		(F-O) ₂	0.2 - 5	6.0	0.4	0.4321	0.20	none

nitromethane	Et ₄ NBr	P _A	0.2 - 2	1.6	0.4	0.4320	0.03	none
		(F-O) ₁	0.2 - 2	3.2	0.1	0.4321	0.07	none
		(F-O) ₂	0.2 - 2	4.7	0.1	0.4321	0.10	none
		P _A	0.2 - 1	1.7	0.2	0.4321	0.07	none
		(F-O) ₁	0.2 - 1	4.1	0.1	0.4320	0.03	none
		(F-O) ₂	0.2 - 1	5.4	0.1	0.4321	0.08	none
		P _A	0.2 - 10	1.3	0.4	0.4313	0.06	none
		(F-O) ₁	0.2 - 10	3.4	0.1	0.4314	0.16	none
		(F-O) ₂	0.2 - 10	4.7	0.1	0.4314	0.23	none
		P _A	0.2 - 5	1.4	0.5	0.4313	0.05	none
		(F-O) ₁	0.2 - 5	3.4	0.1	0.4314	0.12	none
		(F-O) ₂	0.2 - 5	4.8	0.1	0.4314	0.16	none
		P _A	0.2 - 2	1.6	0.3	0.4313	0.04	none
		(F-O) ₁	0.2 - 2	3.5	0.1	0.4314	0.08	none
		(F-O) ₂	0.2 - 2	4.9	0.1	0.4314	0.11	none
		P _A	0.2 - 1	1.7	0.1	0.4314	0.03	none
		(F-O) ₁	0.2 - 1	4.4	0.1	0.4314	0.07	none
		(F-O) ₂	0.2 - 1	5.7	0.1	0.4314	0.09	none

Discussion

Inspection of the tables shows that, in general, the values of $\langle t_i^0 \rangle$ calculated by the Pitts, P_A , and the Fuoss-Onsager, $(F-O)_1$, theories agree within 0.0001. Furthermore the 'best' values of t_i^0 obtained by method P_B always agree within 0.0002 with those of $\langle t_i^0 \rangle$ obtained by method P_A . However, the values of $\langle t_i^0 \rangle$ calculated from the 1963 $(F-O)_2$ theory usually differ from the $(F-O)_1$ values by several units in the fourth decimal place in water, in 50% methanol-water and in formamide (all high dielectric constant solvents) and by as much as 0.002 in acetone. The values obtained from the two theories are in closer agreement in methanol, ethanol, ethylene glycol, acetonitrile and nitromethane.

In many cases, especially in aqueous solutions, the 'best' values of $\underline{a}$ obtained by the P_A and $(F-O)_1$ theories for the same concentration range are similar. The former usually leads to $\underline{a}$ values smaller by several tenths of an angstrom than those derived from the latter. There are, however, exceptions to these generalizations notably for results in nitromethane and methanol, where they are often smaller by several angstroms. Some of the P_A and $(F-O)_1$ results for $\underline{a}$ are unreasonably high (KCl , $AgNO_3$ in water, $NaCl$ in 50% methanol water, Bu_4NBr in methanol, KCl in formamide), whilst others are negative. For the latter, the values calculated from theory $(F-O)_2$ are always positive although often unreasonably small. For many protic, high dielectric constant solvents (water, ethylene glycol, formamide) the $(F-O)_2$ values are smaller and, in several cases, more realistic than the high P_A or $(F-O)_1$ results.

The trends in $t_i^0(c)$ and the standard deviations from $\langle t_i^0 \rangle$ obtained by the P_A and $(F-O)_1$ theories are very similar. The degree of fit of the $(F-O)_2$ equation to the data is as good as the fits of P_A and $(F-O)_1$ for many systems but is appreciably worse for others, particularly $HClO_4$ in water, $NaCl$ and KCl in 50% methanol-water, KCl in methanol, KCl in formamide and

KCNS in acetone. It is unfortunate that these include some of the systems for which $(F-O)_2$ leads to a more physically meaningful $\underline{a}$ value and it would seem as if the price to be paid for more realism in $\underline{a}$ is apt to be a poorer fit to the data.

The effects on the calculations of the progressive exclusion of the higher concentrations is worthy of comment. The theories would be expected to apply better at lower concentrations and the tables do indeed show a definite tendency for the minimum standard deviations to decrease as the higher concentrations are excluded. There is generally less change in the best $\underline{a}$ value for $(F-O)_2$ than for P_A and $(F-O)_1$ when the concentration range narrows (exceptions are $HClO_4$ in water and Me_4NCl , Et_4NCl and Bu_4NCl in nitromethane).

In view of the different nature of the results of the calculations for aqueous and non-aqueous systems, these two classes of solvent will be discussed separately. Aqueous data often fit the theories less well than do non-aqueous data, but the latter often produce unreasonable values of $\underline{a}$.

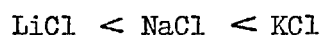
Calculations using Method A for Aqueous Systems

The most notable feature of the calculations for $LiCl$, $NaCl$ and KCl is the occurrence of a minimum in the plots of $t_i^0(c)$ against c for those values of $\underline{a}$ at which σ is a minimum. For $NaCl$ this minimum is well-pronounced at a concentration of 0.02M (Figure 2-3a) In view of this it was suspected that the experimental measurement at this concentration may have been in error and consequently the calculations were repeated with its exclusion. Although this significantly reduced the value of σ , the minimum in the values of $t_i^0(c)$ still remains (Figure 2-4) albeit in a more shallow form, and the values of $\underline{a}$ and $\langle t_i^0 \rangle$ are only very slightly changed. Even when an upper limit of $c = 0.029M$ is placed on the calculations, the shallow minimum still appears. For $LiCl$ the occurrence of a minimum is again very much in evidence (Figure 2-2) It is as well to point out, at this stage, that

all the plots are on an exaggerated scale and errors of 0.0002 or 0.0003 in the experimental values, t_i , would explain all these minima. For LiCl and NaCl the three theories predict reasonable, but slightly different values of $\underline{a}$ although the trends in $t_i^0(c)$ are virtually identical. The average values of t_i^0 , $\langle t_i^0 \rangle$, usually agree within 0.0003 with the Longsworth values in table 1. In the case of LiCl, the P_A and $(F-0)_1$ values rise gradually as the higher concentrations are successively excluded and pass through the Longsworth value on the way. The $(F-0)_2$ figure is consistently higher than that in table 1. Except for the lowest concentration range, the NaCl $\langle t_i^0 \rangle$ values are below the Longsworth figure for P_A and $(F-0)_1$ and above it for $(F-0)_2$. All the limiting transference numbers are raised when the 0.02M data point is left out of the calculations.

The values of $\underline{a}$ obtained by application of the theory to potassium chloride data are high but the transference numbers are very close to 0.5. Inspection of equations (2 - 29) and (2 - 33) reveals that in such a case the calculated values of t_i^0 are insensitive to concentration and the chosen value of $\underline{a}$. The sharp minimum at 0.014M is considerably reduced but not excluded by the omission of the data at this concentration from the computations. The standard deviation after the omission is correspondingly smaller. There can be no doubt that the results of calculations by method $(F-0)_2$ are much more reasonable than those of the other two theories for this system.

It is worth commenting that, whichever theory is employed, the distances of closest approach rise in the sequence



which is the opposite of that expected from the sizes of the hydrated ions. It is also the opposite of that found (14) in the analysis of the corresponding conductances although the mean conductance $\underline{a}$ values fall by only 0.15 in going from LiCl to KCl.

The $\underline{a}$ values obtained by all theories for aqueous silver nitrate are very large and, unlike KCl, $(F-O)_2$ is only slightly superior to the other two theories. The value of the $(F-O)_2$ mean limiting transference number is in poor agreement with the value calculated from limiting ionic conductances (0.4642, (35)). It should be remembered that a high value of $\underline{a}$ leads to a large value for the highest $y(=\kappa \underline{a})$ and all the theories lose their validity when y exceeds certain limits.

The data for HCl and $HClO_4$ fit all the theories at plausible values of $\underline{a}$. The calculated values of $\langle t_i^0 \rangle$ for HCl and $HClO_4$ are in reasonable agreement with the Longworth values (0.8209 (20) and 0.1600 (23) respectively).

Calculations using Method A for non-aqueous systems

Inspection of the results for non-aqueous systems shows that, for the majority, unreasonable values of $\underline{a}$ are required although the minima which manifest themselves in aqueous systems are not found. Figure 2 - 11 illustrates a fairly typical set of data.

Undoubtedly the worst correlations between the theories and the experimental data occur in the 50 mol % methanol-water calculations. For both NaCl and KCl in this solvent, systematic maxima and unreasonable values of $\underline{a}$ are obtained. The $(F-O)_2$ calculations, for this system, are substantially different from those of the other two theories but the $\underline{a}$ values obtained are still physically meaningless and the trends in $t_i^0(c)$ are disconcerting and suggest that true fits of the theory to the data have not been obtained.

For solutions in methanol, the LiCl, NaCl and Bu_4NBr data fit all the theories without a trend in $t_i^0(c)$. However, the $\underline{a}$ values are, in general, unreasonably large and particularly so for LiCl. Furthermore they become larger and less realistic as the higher concentrations are excluded. It is notable that the P_A theory, applied to NaCl, provides a surprising exception to this generalization. Here the $\underline{a}$ values for several sets of data are very small ($< 1\text{\AA}$) and a parallel may be drawn with the low values of $\underline{a}$ yielded

when the Pitts conductance theory is applied to methanolic conductance data. (15) The two independent sets of NaCl transference data yield values of $\langle t_1^0 \rangle$ which agree within 0.0003, with the $\underline{a}$ values corresponding to the older set (26) rather higher.

The data for LiCl and NaCl in ethanol can be fitted to the (F-0) theories only if $\underline{a}$ is negative in the case of (F-0)₁, and if $\underline{a}$ is small and positive for (F-0)₂. An even more unreasonable $\underline{a}$ value ($-12\text{\AA}$) is obtained when the (F-0)₁ theory is applied to the data for KCNS in acetone. The (F-0)₂ theory, for this system, gives very small positive values for $\underline{a}$, but the trends in $t_1^0(c)$ indicate very poor fits of theory to data.

The results for ethylene glycol suggest a reasonable correlation between theories and data when the upper concentration limit is reduced from 0.05M to 0.02M. In the case of KCl in formamide, the (F-0)₂ theory leads to realistic distances of closest approach but the fits to the data are poorer than for the other two theories which lead to unrealistically high $\underline{a}$ values. For Me_4NClO_4 in acetonitrile, the trends in $t_1^0(c)$ are only eliminated if data at concentrations greater than 0.0025M are excluded. Over the whole concentration range the (F-0) theories lead to reasonable values of $\underline{a}$ while P_A , as for NaCl in methanol, requires a tiny value less than $1\text{\AA}$. However, when the highest concentration (0.012M) is excluded, the $\underline{a}$ values, calculated by all the theories, rise to physically unreasonable magnitudes, even though the trends in $t_1^0(c)$ are eliminated.

Several sets of experimental data are available for quaternary ammonium halides in nitromethane and, for the smaller sized cations the degree of association has been allowed for. All the fits are good and no trends were found. The least satisfactory aspects of the results are the small values of $\underline{a}$ which method P_A yields for most of the systems and the fact that these values become smaller as the higher concentrations are excluded. The (F-0)₂ $\underline{a}$ values are always bigger than the (F-0)₁

distances and are in fair agreement with the sum of the ionic radii.

On balance, however, the values of $\underline{a}$ obtained for salts in non-aqueous solvents have little or no meaning in terms of ionic size and we are forced to the conclusion that equations (2 - 29) and (2 - 33) fail to represent adequately the concentration dependence of transference numbers in such solvents.

The agreements of the $\langle t_i^0 \rangle$ values with the Longworth values given in the original data sources, for NaCl in methanol, NaCl and LiCl in ethanol, KCl in ethylene glycol and Me_4NClO_4 in acetonitrile are all good to within 0.0002. Particularly good agreements are also found for all the tetra-alkyl salts in nitromethane. However, the values of $\langle t_i^0 \rangle$ which the theories yield for KCl in methanol, NaCl and KCl in a 50 mol% aqueous methanol mixture and KCNS in acetone are all greater than the Longworth values (0.5001, 0.4437, 0.5068 and 0.3763 respectively). The value obtained for KCl in formamide is less than the Longworth value (0.4270). There appears to be no obvious correlation between the reasonableness of the $\underline{a}$ values obtained and the extent of divergence of $\langle t_i^0 \rangle$ from the Longworth value.

Comparison of methods A and B

Although the same trends in the value of $\underline{a}$ are found in methods P_A and P_B when the highest concentrations are progressively excluded, the absolute values of $\underline{a}$ differ by varying amounts up to $1.5\overset{\circ}{A}$ according to the system and the concentration range under test. This is attributable to the different criteria of fitting. For aqueous LiCl and NaCl the values of $\underline{a}$ for method P_B are lower than for method P_A , although the values obtained by the two methods converge as the high concentration limit is reduced. For aqueous HCl the two methods yield similar values of $\underline{a}$. Method P_B predicts higher values, by between $0.5\overset{\circ}{A}$ and $1\overset{\circ}{A}$, of $\underline{a}$ than does method P_A for aqueous HClO_4 and KCl in formamide at all the concentration

ranges considered. A less dramatic fall in $\underline{a}$ is predicted by P_B for NaCl in methanol and KCl in ethylene glycol when the highest concentration is excluded. It is shown below that, on the whole, the results by P_B agree more reasonably with conductance $\underline{a}$ values than do those by P_A . These observations lead the writer to suggest that method P_B is superior to P_A as a means of fitting the Pitts equation to the data for those systems in which the values of $\underline{a}$ are physically meaningful.

It is worthwhile considering the trends in the deviations of theory and experiment, Δ_B , for the results of calculations using method B. This quantity is defined by

$$\Delta_B = t_i(\text{calc}) - t_i(\text{expt}) \quad (2 - 60)$$

The general form of these trends (figures 2-7, 2-8, 2-9) is clearly the inverse of trends in Δ_A where

$$\Delta_A = t_i^0(c) - \langle t_i^0 \rangle \quad (2 - 61)$$

However, the quantities, Δ_A and Δ_B are not exactly equal in magnitude at a given value of $\underline{a}$, as may be seen from the following analysis.

Combination of (2 - 60) with (2 - 33) yields

$$\Delta_B = t_i^0 - (0.5 - t_i^0) \frac{Y_3}{\Lambda'} - t_i(\text{expt}) \quad (2 - 62)$$

Here the value of t_i^0 is the 'best' value obtained after the series of successive approximations. For method A, using (2 - 33),

$$\begin{aligned} \Delta_A &= t_i^0(c) - \langle t_i^0 \rangle \\ &= \frac{t_i(\text{expt}) + 0.5Y_3/\Lambda'}{1 + Y_3/\Lambda'} - \langle t_i^0 \rangle \end{aligned} \quad (2 - 63)$$

which after rearrangement gives

$$- \Delta_A = \left\{ \langle t_i^0 \rangle - (0.5 - t_i^0(c)) \frac{Y_3}{\Lambda'} - t_i(\text{expt}) \right\} \quad (2 - 64)$$

Since the value of t_i^0 calculated in method B is seldom different from $\langle t_i^0 \rangle$ calculated in method A, the principal difference between the

expressions (2 - 62) and (2 - 64) for Δ lies in the value of t_i^0 used in the term $(0.5 - t_i^0) Y_3/\Lambda^1$. At a concentration where this value calculated by method A differs significantly from that calculated in method B, there is also an appreciable numerical discrepancy between Δ_A and Δ_B . Such cases are usually at high concentrations or at the minimum in $t_i^0(c)$ found for aqueous systems with method A.

Comparison of conductance and transference parameters

It is interesting to compare the 'best' values of a for fits to the conductance and transference forms of the equations. The Pitts conductance formula is expressed in equation (2 - 15), the Fuoss-Onsager analogue is that in equation (2 - 11). The Pitts and (F-0) conductance results for aqueous systems are the mean values of the calculations of Pitts, Tabor and Daly (using method B) and those for non-aqueous systems, except methanol, come from the compilation of Fernández-Prini (33). In the case of methanol the latter used experimental data (36) which the writer considers to be less reliable than those (37) analysed by Kay (38), and therefore Kay's methanol analyses have been preferred. The Pitts conductance results for methanol were those calculated by Fernandez-Prini and Prue (39). In table 7 the values, in $\overset{0}{A}$, are compared for various concentration ranges, the upper limits of which are such that a is less than 0.29 but as close to 0.29 as possible.

It is clear from table 7 that there is very little correlation between the best values of a for conductance and transference, particularly for non-aqueous data. It would be expected that better agreement with the (F-0) conductance values would be obtained for the $(F-0)_1$ than for the $(F-0)_2$ values since the former are derived from an equation based on the same electrophoretic term as the conductance theory.

TABLE 7. COMPARISON OF CONDUCTANCE AND TRANSFERENCE α VALUES ($y \leq 0.29$)

solvent	electrolyte	$r_+ + r_-$	conductance		transference				comments
			P	F-O	P_A	P_B	$(F-O)_1$	$(F-O)_2$	
water	LiCl	2.4	3.13	3.18	3.9	3.2 ₃	3.9	3.8	
	NaCl	2.8	3.15	3.24	4.4	5.5 ₃	4.9	4.3	$y=0.31$ for P_B
	KCl	3.1	3.00	3.10	4.2		4.6		transference data exclude 0.014M
	HCl		3.76	3.39	3.4	4.1 ₄	3.8	3.5	$y=0.30$ for $(F-O)_1$
	HClO ₄		3.87	3.54	6.1	6.8 ₁	6.4	4.7	$y \leq 0.46$ for transference
methanol	LiCl	2.4	2.92	3.73			8.4	7.9	$y=0.30$ for $(F-O)_1$
	NaCl	2.8	2.78	4.04	3.4	4.6 ₂	5.0	5.8	transference data from ref.30
					5.5	2.5 ₉	3.7	5.1	transference data from ref.31
	KCl	3.1	2.16	3.40	<0			0.4	
ethanol	LiCl	2.4		4.4	<0		-4.5	1.2	
	NaCl	2.8		4.0	<0		-8.9	0.6	
ethylene glycol	KCl	3.1		3.78	5.1	5.6 ₂	5.7	5.4	$y \leq 0.37$ for transference
acetonitrile	Me ₄ NClO ₄			3.13	4.5		2.9	4.3	
nitromethane	Me ₄ NCl	4.6		4.0	3.0		4.5	5.4	
	Me ₄ NBr	4.8		4.1	10.4		11.9	4.3	
	Et ₄ NCl	5.2		3.4	3.6		5.0	5.6	
	Et ₄ NBr	5.3		3.3	1.3		3.4	4.7	
	Bu ₄ NCl	6.0		4.12	2.5		4.2	5.2	
	Bu ₄ NBr	6.1		3.19	3.5		5.0	5.6	

However, except for most of the nitromethane systems, the conductance a figures usually agree better with $(F-O)_2$ transference results. For aqueous LiCl and NaCl in methanol the results of method P_B show a greater correlation with conductance data than do the results of P_A . This is to be expected since the same criterion of fitting (method B) has been used in P_B as in the conductance calculations. However, for HCl and $HClO_4$, in aqueous solutions the results of P_A are in better agreement with the conductance figures. It is tempting to suggest that this observation is connected with the different conducting mechanism for the hydrogen ion, the so-called 'proton-jumping' mechanism. However, Robinson and Stokes (40) and Pitts et al. (14) have argued that this should affect only the value of Λ^0 and, as far as the concentration dependence is concerned, such proton jumping ions should behave as if conduction were by simple migration.

Evaluation of the theories

It is indeed surprising that the two theories should describe the variation of conductance of these systems with concentration so adequately and yet break down so dramatically when applied to their transference properties. Reasons must now be sought for these discrepancies.

(1) Errors in the experimental data

One possible explanation for the discrepancy between theory and experiment is that the experimental transference numbers are in error. If this were the case it would not be a question of any particular series of measurements being incorrect. In order to explain the unreasonable results obtained for a wide variety of systems the error would have to be inherent in the moving boundary method of measuring transference numbers. In view of the various independent tests, such as insensitivity to following electrolyte, following electrolyte concentration and to current, described elsewhere in this thesis (p. 6), and summation of t_+ and t_- ($t_+ + t_- = 1$) which are passed by all reliable transference data, such an error would appear unlikely. However, the effect of raising and lowering the experimental transference number corresponding

to the lowest concentration, by 0.0001, on calculations using method P_A , for three selected systems, has been investigated. The results are shown in table 8.

In the case of aqueous KCl the changes caused in $\underline{a}$ are substantial. However, as has been mentioned earlier, the standard deviation, for this system is insensitive to changes in $\underline{a}$ over a wide range of values. For the other systems the changes are fairly small ($\leq 0.7A^0$) and therefore unlikely to make unreasonable values of $\underline{a}$ more meaningful. As one would expect the effect of raising or lowering the transference number corresponding to the lowest concentration causes a larger change in the best values of $\underline{a}$ as the higher concentrations are excluded. In general, the fewer data points that are involved in the analysis, the more sensitive are the results to small changes in each. (Conductance analyses possess the advantage of including much larger numbers of data points and so suffer much less from the effects of random experimental errors).

TABLE 8 THE EFFECT OF POSSIBLE EXPERIMENTAL ERRORS^a ON CALCULATIONS BY METHOD P_A

solvent	salt	concn. range, 10 ³ M	$\frac{a}{L}$	$\frac{a}{\text{exp}}$	$\frac{a}{R}$	$\langle t_+^0 \rangle_L$	$\langle t_+^0 \rangle_{\text{exp}}$	$\langle t_+^0 \rangle_R$
water	NaCl	10 - 100	5.8	5.7	5.6	0.3960	0.3960	0.3961
		10 - 60	6.3	6.1	5.9	0.3959	0.3960	0.3960
		10 - 50	5.8	5.6	5.4	0.3960	0.3960	0.3961
		10 - 29	4.9	4.4	3.9	0.3961	0.3962	0.3964
water	KCl	10 - 100 excl. 14	18.2	13.1	9.9	0.4904	0.4905	0.4906
		10 - 73 excl. 14	>20	17.1	11.5		0.4905	0.4905
		10 - 50 excl. 14	14.8	8.2	4.4	0.4904	0.4905	0.4906
		10 - 30 excl. 14	13.8	4.2	0.8	0.4904	0.4906	0.4907
formamide	KCl	10 - 100	9.5	9.2	8.9	0.4266	0.4267	0.4268
		10 - 80	9.5	9.1	8.8	0.4266	0.4267	0.4268
		10 - 50	11.5	10.7	10.1	0.4264	0.4266	0.4266

^aSubscript L means that the value of the experimental transference number at the lowest concentration has been lowered by 0.0001, subscript R means that the same transference number has been raised by 0.0001.

(2) Viscosity or obstruction factors

It would seem reasonable that tests of the conductance - concentration and transference - concentration relationships should all be relative to the same solution viscosity. Thus, the application of Waldens rule gives

$$\lambda_i (\text{exp}) = \lambda_i \frac{\eta_o}{\eta_i} \quad (2 - 65)$$

$$\text{and } \Lambda (\text{exp}) = \Lambda \frac{\eta_o}{\eta} \quad (2 - 66)$$

where λ_i , Λ are the conductances calculated from the Pitts or Fuoss-Onsager equations, η is the viscosity of the solution, η_i is the viscosity in the vicinity of the ion, i , and η_o is the viscosity of the solvent. The ratio η_o/η is obtainable from the well known Jones-Dole (41) equation

$$\eta/\eta_o = 1 + A \sqrt{c} + Bc \quad (2 - 67)$$

where A is a positive computable constant and B is an empirical constant. In the concentration region between 0.002M and 0.10M, within which lie almost all the transference measurements concerned in the present calculations, neglect of the $A\sqrt{c}$ term is justifiable. Thus the viscosity-corrected forms of the Fuoss-Onsager equations (2 - 8) and (2 - 5) are

$$\lambda_i = (\lambda_i^o - \lambda_i^e) \left(1 + \frac{\Delta X_i}{X}\right) / (1 + B_i c) \quad (2 - 68)$$

$$\text{and } \Lambda = (\Lambda^o - \Lambda^e) \left(1 + \frac{\Delta X}{X}\right) / (1 + Bc) \quad (2 - 69)$$

Fuoss and Onsager included the term $(1 + B_+ c)$, which they called $(1 + Fc)$, in their equation and in their earlier papers (42, 43) attributed it to the above viscosity effect. However, in their later ones (10, 19) they interpreted it as a cation-anion obstruction effect. If B_i represents an obstruction effect it will always be positive and larger the greater the ionic radius. If, on the other hand, B_i arises from a change in the solution

viscosity when the ions are added, it can be positive or negative. For noble gas type ions in water, it will be positive for small ions (structure-makers) and negative for large ions (structure-breakers). Assuming B_+ and B_- are different then

$$t_+(\text{exp}) = \frac{\lambda_+}{\lambda_+ + \lambda_-} = \frac{(\lambda_+^0 - \frac{1}{2}\Lambda^e)(1 + B_-c)}{(\lambda_+^0 - \frac{1}{2}\Lambda^e)(1 + B_-c) + (\lambda_-^0 - \frac{1}{2}\Lambda^e)(1 + B_+c)}$$

$$= \frac{t_+(1 + B_-c)}{t_+(1 + B_-c) + t_-(1 + B_+c)} \quad (2 - 70)$$

t_+ and t_- stand for the theoretically evaluated transference numbers. It may be rearranged to give

$$t_+ = \frac{t_+(\text{exp})(1 + B_+c)}{t_+(\text{exp})(1 + B_+c) + t_-(\text{exp})(1 + B_-c)} \quad (2 - 71)$$

The right hand side of this equation now replaces $t_i(\text{exp})$ in equations like (2 - 29) and (2 - 29a). Some calculations to test the effect of a viscosity correction were carried out using for B_+ and B_- the B_η values tabulated by Kaminsky (44). The results suggest that $\langle t_i^0 \rangle$ is affected only slightly whereas $\underline{a}$ is changed by several angstroms, as table 9 makes clear. The correction substantially increases the best values of $\underline{a}$ for aqueous LiCl and NaCl and makes them physically less reasonable. The same trends in $t_+^0(c)$ were again obtained for both salts. The results for aqueous HCl are lowered and possibly also made less reasonable.

TABLE 9

THE EFFECT ON $\underline{a}$ OF APPLYING A VISCOSITY CORRECTION

Solvent	Salt	Concentration Range	$\underline{a}$	$\overset{0}{A}$	$\underline{a}$	$\overset{0}{A}$
			10^3 mol dm^{-3}	Without correction	With correction	
Water	LiCl	9.8 - 100		4.7	7.6	
		9.8 - 64		4.4	6.9	
		9.8 - 50		3.9	6.1	
		9.8 - 33		3.3	5.3	
		9.8 - 19		2.9	4.8	
	NaCl (excl. c=0.02M)	10 - 100		5.5	9.6	
		10 - 60		5.8	9.4	
		10 - 50		5.4	8.6	
		10 - 29		4.7	7.4	
	KCl (excl. 0.014M)	10 - 100		13.1	< 0	
		10 - 73		17.1	< 0	
		10 - 50		8.2	< 0	
		10 - 30		4.2	< 0	
	HCl	10 - 100		3.9	2.4	
		10 - 50		3.4	2.1	
Formamide	KCl	10 - 100		9.2	7.9	
		10 - 80		9.1	7.7	
		10 - 50		10.7	9.3	

No definite conclusions can be drawn about the dramatic change in $\underline{a}$ upon applying the correction to aqueous KCl since the transference numbers are very close to 0.5 and correspondingly insensitive to $\underline{a}$. The results of applying the correction to the calculations for KCl in formamide show a shift in $\underline{a}$ to a more meaningful value although the results are still physically unreasonable.

It seems justifiable to conclude therefore that the difficulties in interpreting the unreasonable values of $\underline{a}$ and trends in $t_1^0(c)$ obtained by applying method A to the transference data cannot be resolved by the application of a viscosity correction. The situation is not helped by the uncertainty in the physical interpretation of the $(1 + Bc)$ terms.

(3) Errors in the theories

The Fuoss-Onsager theory may be faulted in that it is unreasonable for the transference numbers to be dependent purely on electrophoretic factors and not at all on relaxation effects. However, no such criticism can be levelled against the Pitts theory and yet the results are broadly the same. It is therefore improbable that the Fuoss-Hsia (10) and Murphy and Cohen (11) equations, which are improvements on the original Fuoss-Onsager equation, would fare any better for transference. These observations have led Spiro (45) to suggest that the sum of the individual ion conductances cancels some additional factor which remains when the conductance ratio is taken for the transference numbers. One such effect to which he draws attention is that the conductance of the electrolyte is independent of the frame of reference with respect to which the ions move. On the other hand the individual ion mobilities, and consequently the transference numbers, depend very strongly upon the chosen frame of reference. The one on which transference numbers in the literature are based is the solvent as a whole. Carman (46) has suggested that interionic

theories really apply to 'true' transference numbers based on movement relative to the 'free' unsolvated solvent molecules only. However, as Spiro (45) has shown, this does not resolve the discrepancy between theory and experiment because the solvation numbers required to bring about a fit are physically unreasonable.

It is clearly impossible on the basis of the considerations of this chapter to choose between the Fuoss-Onsager and Pitts theories. Both are entirely adequate for the interpretation of conductance data but, on balance, they are unsuccessful when applied to transference. It must be hoped that further developments in the theories of ionic migration will help to resolve the discrepancies.

CHAPTER THREE

SULPHURIC ACID AS A SOLVENT

Introduction

Although sulphuric acid is one of the most widely-known and commonly-used inorganic compounds, relatively few of the physico-chemical properties of solutions in the acid have been studied. This is indeed surprising when some of its advantages, as a solvent, listed below are considered.

- (a) The high acidity of the acid enhances the basic nature of many solutes and permits the study of many bases, such as ketones and nitrocompounds, which are too weak to study in aqueous solution.
- (b) The high acidity also reduces the acidity of many solutes. In particular solutes such as NO_2^+ and carbonium ions, which are too strongly acidic to exist in water, are stable in sulphuric acid.
- (c) The basic properties of solutes which are weakly acidic in water can be investigated in sulphuric acid. In the present work, use has been made of acetic acid which accepts a proton from sulphuric acid to become $\text{CH}_3\text{COOH}_2^+$.
- (d) The ionic nature of the pure acid and correspondingly high dielectric constant means that the dissolution of most ionic solutes is accompanied by complete dissociation.
- (e) Sulphuric acid, being a liquid at room temperature, is relatively easy to handle. In many ways sulphuric acid resembles water because of the extensive hydrogen bonding in the structures of both liquids.

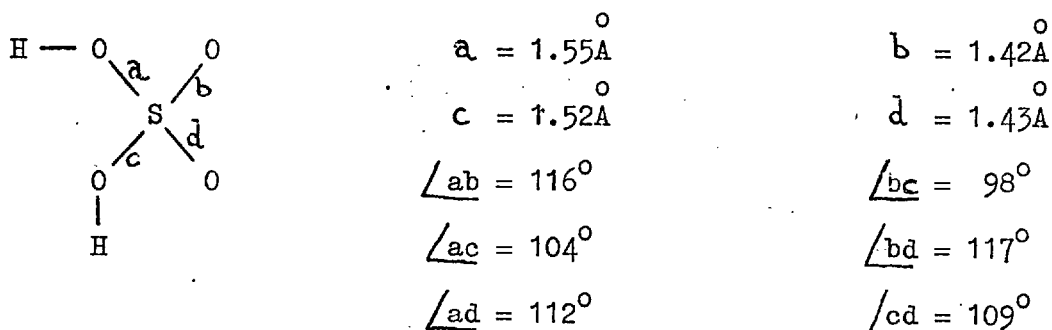
The main disadvantages of sulphuric acid as a solvent are its highly corrosive nature, its strong affinity for water and, from a preparative viewpoint, its high boiling point.

Previous investigations of the properties of solutions in pure sulphuric acid fall into three distinct periods; Hantzsch's between 1907 and 1911, Hammett's between 1932 and 1937 and those of Gillespie and his school since 1950. The latter has published several reviews (47 - 51) of the subject.

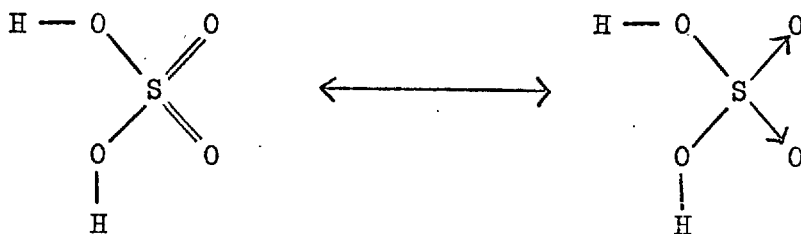
Other reviews are by Audrieth and Kleinberg (52), Sisler (53), Lee (54) and Jander and Lafrenz (55).

Structure of sulphuric acid

X-ray analysis shows that crystalline sulphuric acid (56) consists of an approximately tetrahedral arrangement of two oxygen atoms and two O-H groups about the sulphur atom. The S-O bond lengths and O-S-O bond angles are as follows:



The dimensions of bonds b and d indicate considerable shortening and double-bond character.



The high boiling point, viscosity and surface tension listed below indicate that sulphuric acid is highly associated through hydrogen bonding. The X-ray study of the solid by Pascard (56) indicated a layer-like structure in which each sulphuric acid molecule is hydrogen-bonded to four others. The liquid structure may well be similar to this. X-ray studies (59) of 97% aqueous sulphuric acid have demonstrated the existence of hydrogen bonds of length $2.85\text{\AA}$.

Physical properties of sulphuric acid

Freezing Point

Sulphuric acid of composition H_2SO_4 represents only one point in the complex $\text{H}_2\text{O}-\text{SO}_3$ system at which neither of these two components is in excess.

On one side of this point water is present as H_3O^+ and there is no free SO_3 . On the other side SO_3 is in excess, most probably as $\text{H}_2\text{S}_2\text{O}_7$. The system exhibits a maximum freezing point of 10.371°C (57, 58) at composition H_2SO_4 . This is to be expected since conductance measurements indicate that the number of ions present at this composition is also a minimum. It is well-known that the effect of introducing more ions into a system is to depress its freezing point.

Boiling Point

Pure sulphuric acid boils, with decomposition, at about 273°C (59, 60). Sulphur trioxide is evolved, the acid becomes progressively richer in water and the boiling point rises until a constant boiling mixture of strength 98.3% H_2SO_4 is obtained at 338°C .

Density and Viscosity

Gillespie and Wasif (61) found the density to be $1.8269 \text{ kg dm}^{-3}$ at 25°C and the viscosity 24.54 centipoise. It is interesting to compare these values with the corresponding ones for water (density = 0.997 kg dm^{-3} . Viscosity = 0.8903 centipoise) indicating just how strongly hydrogen-bonded the sulphuric acid structure is.

Dielectric constant

The dielectric constant of sulphuric acid at 25°C is 100 (62 - 64). This high value indicates that most solutes will be fully dissociated in solution.

Thermal data

The heat of fusion at 10.371°C of the acid was found by Rubin and Giaque (65) to be $1.07 \times 10^4 \text{ J mol}^{-1}$. The heat capacity, according to Kunzler and Giaque (66) is $1.41 \text{ J deg}^{-1} \text{ g}^{-1}$.

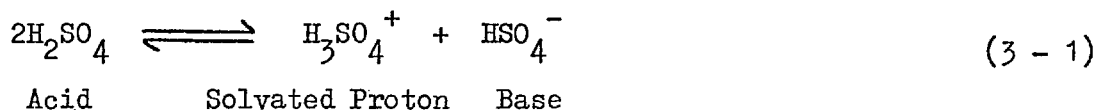
Conductance

The specific conductance of the acid at the composition H_2SO_4 is $1.0439 \times 10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1}$ (67). The behaviour of the conductance with changes in the composition of H_2O and SO_3 in the system is discussed

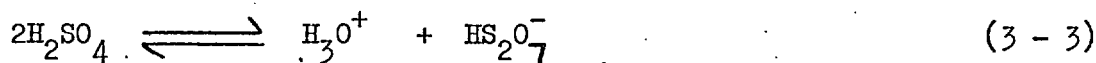
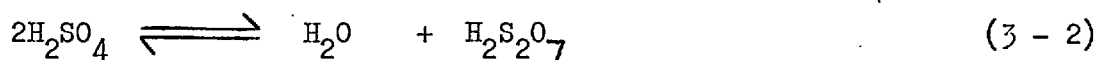
more fully in the following chapter.

The self-dissociation of sulphuric acid

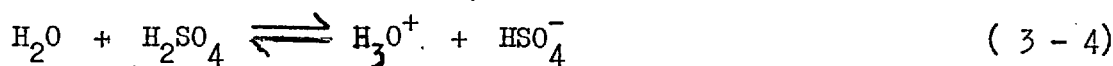
In addition to the normal 'acid-base' type dissociation of a conventional protonic solvent,



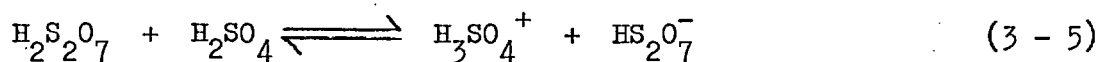
sulphuric acids exhibits a number of other self-dissociation reactions. In particular the disproportionation reactions.



give rise to other molecular and ionic species in solution. However, water does not exist appreciably as free H_2O but is protonated thus:



and disulphuric acid, $\text{H}_2\text{S}_2\text{O}_7$, is also partially dissociated.



Gillespie (48) defines the concentrations of these species in terms of the following equilibrium constants.

$$K_{ap} = [\text{H}_3\text{SO}_4^+][\text{HSO}_4^-] = 3.7 \times 10^{-4} \text{ mol}^2 \text{ kg}^{-2} \quad (3-6)$$

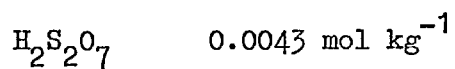
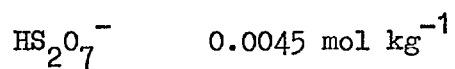
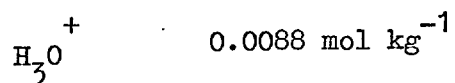
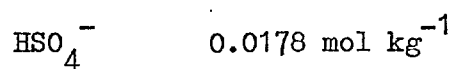
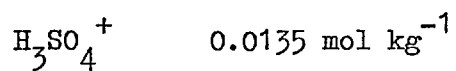
$$K_{id} = [\text{H}_3\text{O}^+][\text{HS}_2\text{O}_7^-] = 5.1 \times 10^{-5} \text{ mol}^2 \text{ kg}^{-2} \quad (3-7)$$

$$K_a = [\text{H}_3\text{SO}_4^+][\text{HS}_2\text{O}_7^-]/[\text{H}_2\text{S}_2\text{O}_7] = 1.4 \times 10^{-2} \text{ mol kg}^{-1} \quad (3-8)$$

$$K_b = [\text{H}_3\text{O}^+][\text{HSO}_4^-]/[\text{H}_2\text{O}] = 1 \text{ mol kg}^{-1} \quad (3-9)$$

The values (at 25°C) quoted were calculated by Gillespie, Robinson and Solomons (68), and revised by Gillespie and Robinson (50), from freezing point and conductance measurements in solutions of metal hydrogen sulphates, water and disulphuric acid. The equilibrium molalities of

the various species are given (69) as,



The thermodynamic functions for the self-dissociation reactions have been investigated by Kirkbride and Wyatt (70) and by Gillespie, Robinson and Solomons (68).

CHAPTER FOUR

SOLUTIONS IN SULPHURIC ACID

The high acidity of sulphuric acid means that most solutes behave as bases. However, certain solutes do function as acids and acid-base reactions have been carried out in the solvent (48, 71).

Solutions of bases

A solute functioning as a base in sulphuric acid yields an excess of HSO_4^- ions.



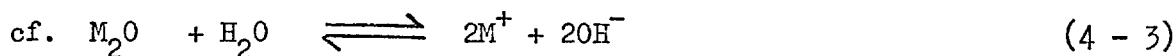
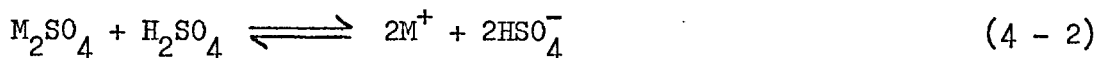
Basic solutions may be formed in four ways:

- (i) from metal sulphates,
- (ii) by solvolysis of salts of acids weaker than sulphuric acid,
- (iii) by simple protonation of the solute molecule, and
- (iv) by dehydration of the solute molecule.

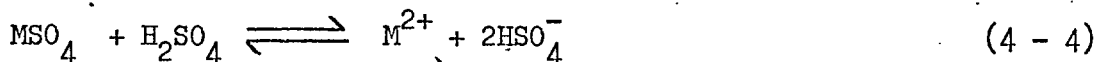
These will now be discussed in turn.

(i) Basic solutions of metal sulphates

Normal sulphates, when soluble, are converted quantitatively to their hydrogen sulphates. This is formally analogous to the addition of metal oxides to water. For the sulphate of a univalent ion,



For the sulphate of a divalent ion,



The hydrogen sulphates, MHSO_4 , behave as fully dissociated binary electrolytes and are formally analogous to the hydroxides in water.



The investigation of the properties of such solutions is limited by solubility factors for all but a few sulphates. The results of solubility measurements by Kendall and Landon (72) and Kendall and Davidson (73) on the sulphates of the most common metals are as follows.

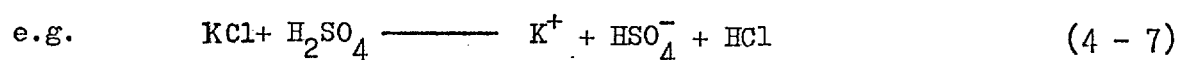
Table 4a

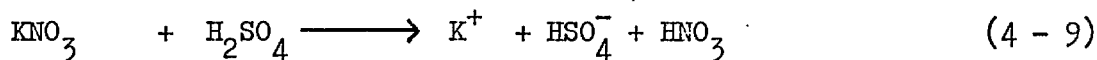
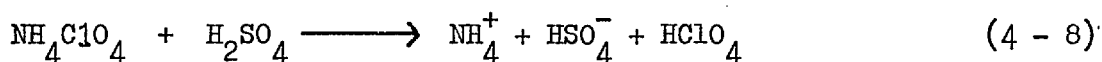
<u>Sulphate</u>	<u>mol % solubility at 25°C</u>
Li_2SO_4	14.28
K_2SO_4	9.24
Ag_2SO_4	9.11
BaSO_4	8.85
Na_2SO_4	5.28
CaSO_4	5.16
Hg_2SO_4	0.78
MgSO_4	0.18
FeSO_4	0.17
$\text{Fe}_2(\text{SO}_4)_3$	0.17
ZnSO_4	0.17
CuSO_4	0.08
$\text{Al}_2(\text{SO}_4)_3$	< 0.01

Thus, of the sulphates studied, only those of silver, barium, calcium and the alkali metals are sufficiently soluble for moderately concentrated ($\sim 0.1\text{M}$, 1.7 mol %) solutions to be prepared. In addition, ammonium, thallium and strontium sulphates are all quite soluble (51) although no measurements of their solubilities are available.

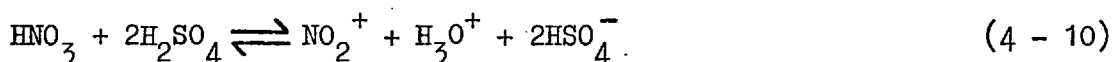
(ii) Basic solutions obtained by solvolysis

Although some salts of other inorganic acids (e.g. AgCl , AlCl_3 , CuBr_2) are insoluble (51) in sulphuric acid, those which do dissolve undergo complete solvolysis and regenerate the parent acid.



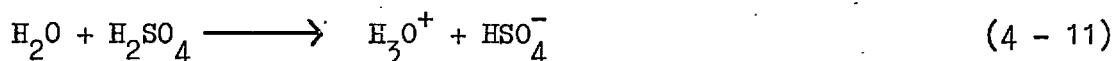


The parent acids are all weaker than sulphuric acid. Hydrogen chloride is only sparingly soluble and is unionised (48), whilst perchloric is exceedingly weak (74) and nitric acid actually behaves as a base, undergoing a dehydration reaction (75).

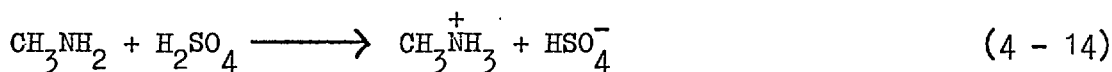
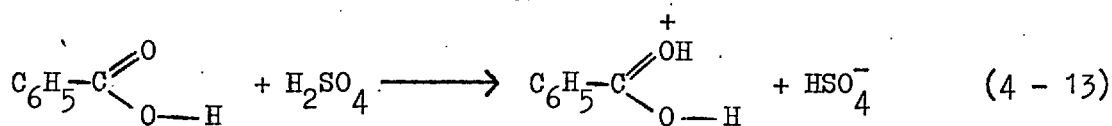
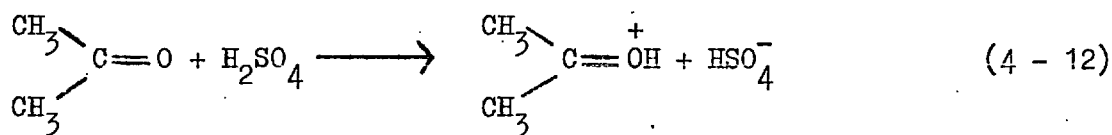


(iii) Basic solutions obtained by protonation of the solute

Solute molecules containing a potentially basic site, e.g. a lone pair of electrons or an unsaturated system, usually exist in their protonated form in sulphuric acid. The most important example of such a species is water.



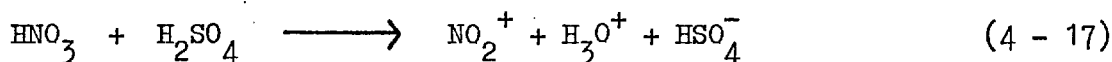
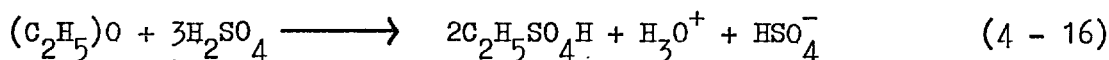
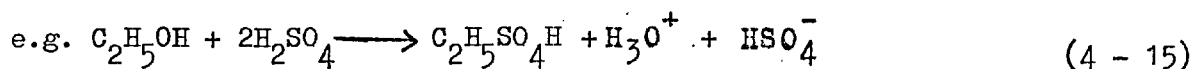
Most ketones, carboxylic acids, amines, amides and esters function as bases in this way (47, 50).



The experimental part of this thesis involves the determination of the transference numbers of a selection of cations and the protonated forms of water, acetic acid and benzoic acid proved to be useful species in this respect. The nomenclature of the last two compounds is unfortunate since, although they both function as acids in water, only their basic properties are in evidence in sulphuric acid.

(iv) Basic solutions obtained by dehydration of the solute

The removal of the elements of water from oxy- and hydroxy- compounds by sulphuric acid yields basic solutions containing the hydroxonium ion, H_3O^+ (75-77).

Solutions of acids

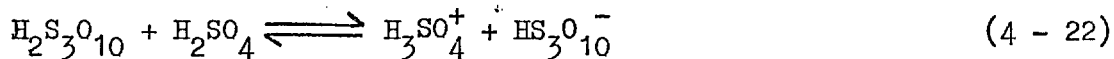
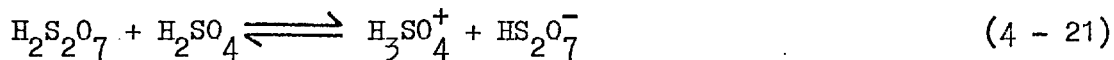
The simplest example of the amphoteric nature of sulphuric acid is found in the autoprotolysis reaction.



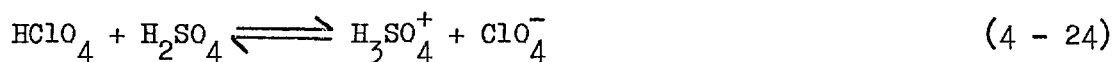
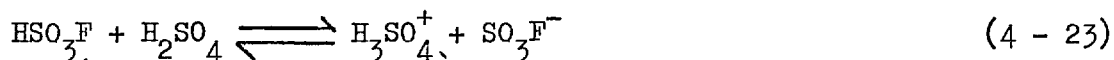
in which one molecule functions as an acid and the other functions as a base. For a solute to be considered an acid, it should react with the solvent to produce an excess of H_3SO_4^+



Disulphuric acid, $\text{H}_2\text{S}_2\text{O}_7$ and the higher polysulphuric acids present in oleum solutions function as weak acids in sulphuric acid (50, 78)

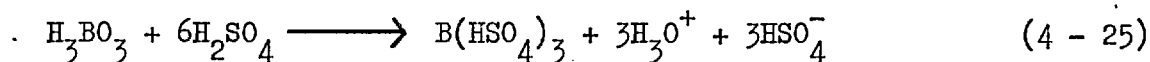


Fluorosulphuric acid and perchloric acid also behave as very weak acids.

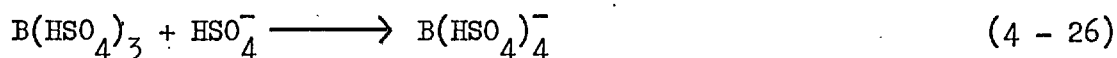


The only solute, so far discovered, that behaves as a strong acid in sulphuric acid is the complex tetrahydrogensulphatoboric acid $\text{HB}(\text{HSO}_4)_4$ obtained by dissolution of boric acid (79, 71, 80). This solute behaves initially as a

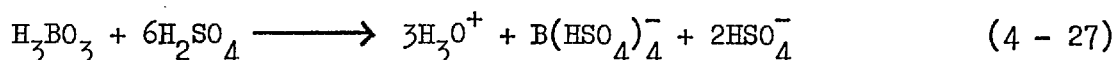
complex base undergoing protonation and three dehydration reactions.



However, the species, $\text{B}(\text{HSO}_4)_3$, then behaves as a strong acid and neutralizes an HSO_4^- ion



The overall reaction is therefore,



Since the $\text{B}(\text{HSO}_4)_4^-$ ion exists in solution (71) without undergoing solvolysis, (unlike the ions in equations (4 - 7) - (4 - 9)), the parent acid $\text{HB}(\text{HSO}_4)_4$ must be a strong acid in the H_2SO_4 solvent system. Other complex acids including $\text{H}_2\text{Sn}(\text{HSO}_4)_6$ and $\text{H}_2\text{Pb}(\text{HSO}_4)_6$ have been found in sulphuric acid solution (81) but they appear to be weaker than their boron analogue.

Solutions of water and sulphur trioxide

These two compounds are particularly interesting and important solutes in sulphuric acid. This is because all the ions they yield after dissolution and ionization are also obtained by the self-dissociation of the acid itself.

The basic solutions of $\text{H}_3\text{O} \cdot \text{HSO}_4$ obtained by adding water to sulphuric acid are in many respects similar to solutions of the metal hydrogen sulphates. The latter ionize to yield HSO_4^- ions which suppress the solvent self-dissociation reaction,

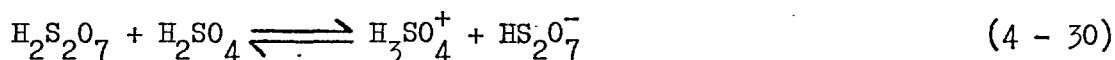


and so do solutions of water. In addition, however, hydroxonium ions are also produced and these lead to suppression of a further self-dissociation reaction,



This additional suppression leads to fewer ions arising from the solvent and its contribution to the conductance of the solution is thereby considerably reduced when water is the solute.

Solutions of sulphur trioxide in sulphuric acid are acidic and are known as oleums. The cryoscopic evidence (51) suggests that the SO_3 is almost totally converted to disulphuric acid which is incompletely ionized:



The production of these two ionic species leads to suppression of both the self-dissociation reactions (4 - 28) and (4 - 29) whereas a solution of a normal acid solute, such as $\text{HB}(\text{HSO}_4)_4$, only suppresses reaction (4 - 28).

It has already been mentioned that acid-base neutralization reactions may be carried out in sulphuric acid. The addition of a solution of water in H_2SO_4 to an oleum provides an excellent example of such a reaction which is essentially the combination of H_3SO_4^+ and HSO_4^- .



in water. Despite the formal analogy, reaction (4 - 32) always yields a solution of a salt at the neutralization point whereas the combination of H_3O^+ and HS_2O_7^- ,



results in the pure solvent only and forms a useful means of its preparation (see Chapter 5).

As the neutralization point is approached the total number of ionic species in solution falls and one would expect the reaction to be capable of being monitored conductometrically, as is the case for aqueous acid-base systems. This is indeed possible, and forms the basis of a most sensitive method of preparing accurately 100% sulphuric acid. However, unlike the aqueous systems, the minimum in the conductance does not occur exactly at the point of neutralization and two reasons have been proposed for this (51). First, the complex nature of the sulphuric acid self-dissociation reactions means that the concentrations of the two main conducting species, H_3SO_4^+ and

HSO_4^- , are not equal at the point of neutralization. Second, these two ions differ considerably in mobility and it has been deduced (69) that the H_3SO_4^+ ion is some 1.45 times more mobile than HSO_4^- ($\lambda_{\text{H}_3\text{SO}_4^+}^0 = 247 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$, $\lambda_{\text{HSO}_4^-}^0 = 171 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$). As a consequence of these two factors, a slightly lower specific conductance (69) is found just on the aqueous side of the neutralization point (0.0019 moles of H_2O per kg of solution) where there is a slight excess of HSO_4^- and a slight deficit of H_3SO_4^+ ions relative to their concentrations in the pure solvent. The composition of the system in the region of the minimum conductance has been the subject of several papers (66, 67, 69, 79, 82-89). In all except the most recent investigation (67) the techniques used were unable to resolve the composition of minimum conductivity from the 100% H_2SO_4 composition. However, assuming the correspondence of the latter with the maximum freezing point of the system, Gillespie, Oubridge and Solomons (67) analysed their solutions very carefully and obtained the following results.

Specific conductance at composition, $\text{H}_2\text{SO}_4 = 0.010439 \pm 0.0005 \text{ ohm}^{-1} \text{ cm}^{-1}$
 Minimum specific conductance of system = $0.010432 \pm 0.0005 \text{ ohm}^{-1} \text{ cm}^{-1}$
 Molality of water at composition of minimum conductance = $0.0019 \pm 0.0005 \text{ mol}^{-1} \text{ kg}^{-1}$

Their conductivity-composition and freezing point-composition plots are reproduced here as figure 4-1. Their values for the specific conductances of dilute solutions of H_2O and $\text{H}_2\text{S}_2\text{O}_7$ in sulphuric acid outside the region of the minimum are plotted here as figure 4-2. The greater extent of dissociation of $\text{H}_3\text{O}^+ \cdot \text{HSO}_4^-$ relative to $\text{H}_2\text{S}_2\text{O}_7$ is demonstrated by a steeper slope to its arm of the conductivity curve.

FIGURE 4-1 : SPECIFIC CONDUCTANCES AND FREEZING POINTS
IN THE VICINITY OF THE 100% H_2SO_4 COMPOSITION

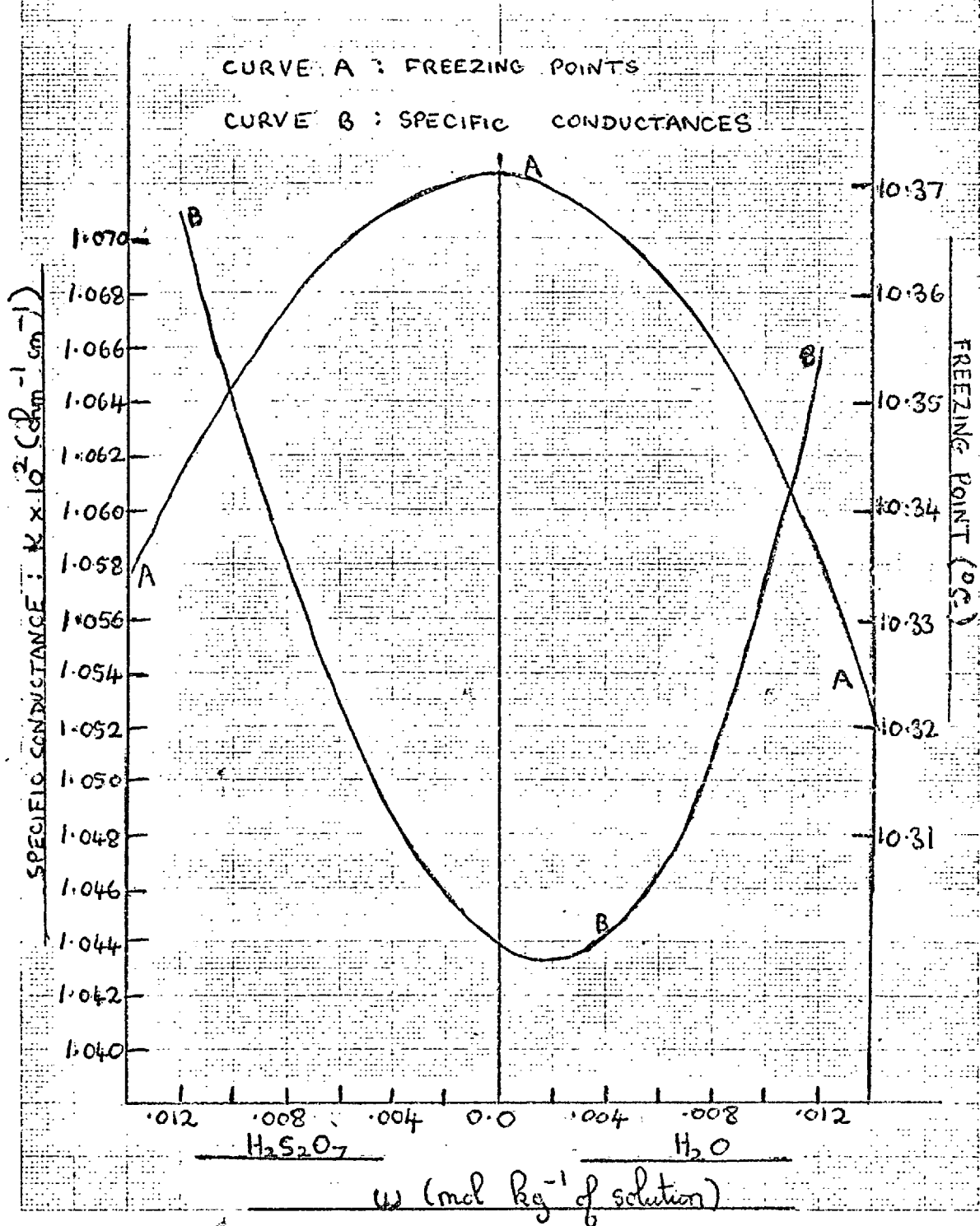
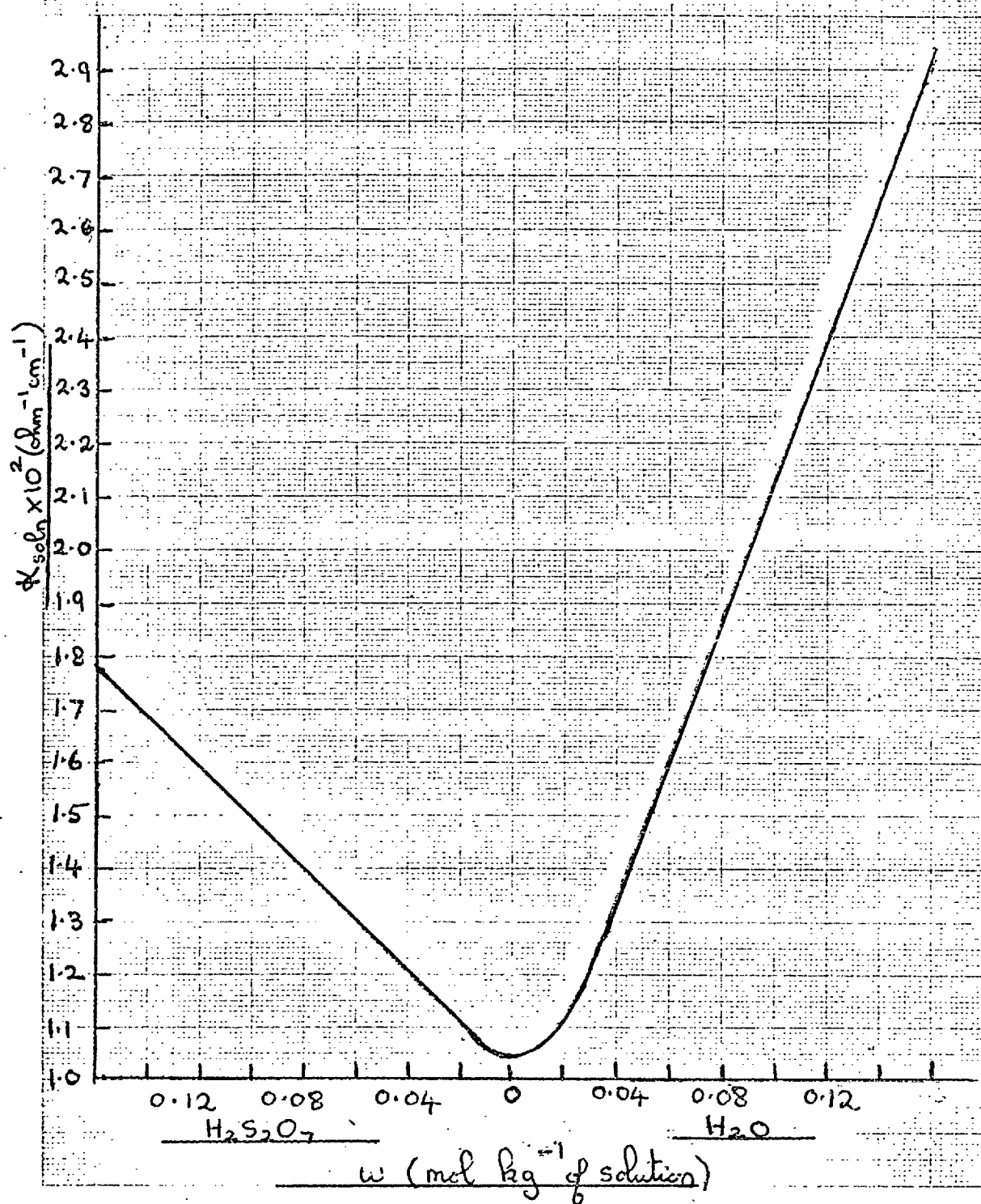


FIGURE 4-2: SPECIFIC CONDUCTANCES OF SOLUTIONS OF
SULPHUR TRIOXIDE AND WATER IN SULPHURIC ACID



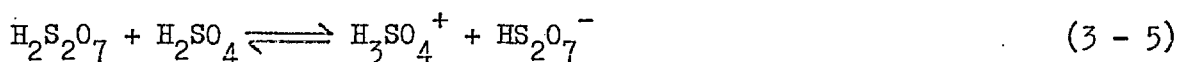
Cryoscopic properties of solutions

Hantzsch (79) in 1907 first used sulphuric acid as a cryoscopic solvent when he studied the behaviour of weak bases. Unfortunately he did not realise that the presence of solutes suppresses the self-dissociation of the acid and the proximity of his acid to the composition 100% H_2SO_4 is questionable.

Interest in sulphuric acid was revived in 1933 when Hammett and Deyrup (90) carried out freezing point measurements using sulphuric acid to which a small amount of water had been added to repress the self-dissociation.

(a) Determination of the equilibrium constants of self-dissociation

The cryoscopic behaviour of the pure acid was first studied in 1950 by Gillespie, Hughes and Ingold (91) who showed that the depression of the freezing point of the acid by the added solute was a measure not only of the number of particles produced by dissolution of the solute but also of the deviations of the solution from ideality. They assumed that reactions (3 - 4) and (3 - 5),



proceed to completion such that $K_a = K_b = \infty$. This enabled them to deduce values of K_{ap} and K_{id} .

These calculations were later refined and updated in the light of more accurate freezing point data (92) by Bass, Gillespie and Robinson (78). The assumptions made previously were replaced in a complicated procedure involving the following steps:

- 1) The existence of hypothetical undissociated sulphuric acid was first assumed. Pure sulphuric acid was then considered to be a solution in this medium in which the species resulting from self-dissociation function as the solute.

- 2) A relationship was derived between the freezing point depression of a solution relative to this hypothetical solvent, the total concentration of all the solute species and the molal osmotic coefficient of the solution.
- 3) Values were assumed for the four equilibrium constants of self-dissociation and, assuming ideal behaviour in the pure acid, the concentrations of all the self-dissociation species were obtained from equations (3-6), (3-7), (3-8) and (3-9).
- 4) The relationship derived in step 2 was used in conjunction with an assumed molal osmotic coefficient (0.98) to calculate the freezing point depression of the pure acid relative to the hypothetical undissociated solvent. Since the freezing point of the former (10.371°C) was known, that of the latter was calculated.
- 5) The assumed values of the equilibrium constants were used to calculate the concentrations of all the solute species in a large number of solutions of sodium, potassium and ammonium sulphates, of water and of disulphuric acid.
- 6) Molal osmotic coefficients of all these solutions were calculated from the relationship derived in step 2, from their measured freezing points (92) and from the total concentrations of solute species determined in step 5.
- 7) Values for the osmotic coefficients of the same solutions were calculated from the Debye-Hückel interionic attraction theory, suitably modified for sulphuric acid.
- 8) The two sets of data obtained in 6) and 7) were compared for all the solutions of the five different solutes.
- 9) New values of the equilibrium constants were chosen and steps 3) to 8) were repeated until the best correlations between the two sets of osmotic coefficients were found. (The 'best' value for the f.p. of the hypothetical solvent was 10.625°C).

The theoretical basis of the above procedure will now be discussed in more detail. For a solute that produces ideal solutions and no species in common with the solvent self-dissociation species, the freezing point depression θ (relative to the pure solvent) is given by thermodynamics as

$$\theta = \gamma R_c m \quad (4 - 34)$$

where γ is the number of moles of all species produced in solution by dissolution of one mole of solute, R_c is the cryoscopic constant ($6.12 \text{ deg mol}^{-1} \text{ kg}$ for H_2SO_4 (93)) and m is the stoichiometric molality of the solute. In the case of sulphuric acid it is also necessary to take into account the repression of the self-dissociation, the variation of the latent heat of fusion with temperature, the non-ideality of the solutions and the change in the number of moles of solvent due to reaction with the solute. The last-mentioned is significant only in that disappearance of solvent leads to changes in the concentrations of all solutes. A suitably modified form of equation (4 - 34) is

$$\theta (1 + 0.002 \theta) = R_c \phi \sum m_i \quad (4 - 35)$$

where the bracketted term allows for changes in the latent heat of fusion, the molal osmotic coefficient ϕ allows for deviations from ideality and the repression of the self-dissociation and changes in the amount of solvent present are taken into account within the summation of concentrations of all the solute species. Equation (4 - 35) is the relationship discussed in step 2) and used in steps 4) and 6).

The Debye-Hückel interionic attraction theory has been discussed at length by Robinson and Stokes (94). These authors combined the Gibbs-Duhem equation, the Debye-Hückel theory and the definition of osmotic coefficient in terms of activity coefficients and deduced the relation for a solution containing a single uni-univalent electrolyte,

$$\phi = 1 - \frac{\alpha \sqrt{m}}{3} \sigma(\beta \sqrt{m}) \quad (4 - 36)$$

where α and β are constants from the Debye-Hückel theory and

$$\sigma(x) = \frac{3}{x^3} \left[(1+x) - 2\ln(1+x) - 1/(1+x) \right] \quad (4 - 37)$$

By assuming this equation holds equally well for solutions containing appreciable concentrations of species obtained by self-dissociation, Bass et al. (78) deduced the relation for sulphuric acid,

$$\phi = 1 - 0.223 I_s^{\frac{1}{2}} \cdot \frac{c}{m \rho} \cdot \sigma(0.273 a I_s^{\frac{1}{2}}) + b \sum m_i \quad (4 - 38)$$

where c is the molar concentration of the electrolyte, m its molal concentration ρ is the density of the solution and I_s is the ionic strength equal to $\frac{1}{2} \sum c_i z_i^2$ in which c_i is the molar concentration of the ion, i , z_i its valency and the summation is taken over all the ions in the solution, The term $b \sum m_i$, where b is an arbitrary constant, is empirical and was included to take account of ionic solvation. The term is small and only significant at high ionic strengths ($I_s > 0.1$). The values of b required are either zero or less than 0.1. A value of $10 \text{ \AA}$ was taken for a , the distance of closest approach of anion and cation. The reasons for this choice are discussed in part (c) of this section. Equation (4 - 38) is the relationship used to calculate osmotic coefficients in step 7) of the procedure discussed previously in this section.

It has been pointed out by Wyatt (95) that this 'trial and error' procedure involves many estimates and assumptions about the nature of solutions in sulphuric acid. He suggests that the concentrations of too many species are variable for this system to be completely interpreted in terms of cryoscopic data and questions the values obtained for the equilibrium constants. In particular, values of K_{ap} up to 70% greater than the value given ($2.4 \times 10^{-4} \text{ mol}^2 \text{ kg}^{-2}$) still lead to osmotic coefficients consistent with the theoretical ones. Wyatt favours the higher estimates of the concentrations of H_3SO_4^+ and

Table 4bEstimates of K_{ap}

<u>Method</u>	<u>$K_{ap} \times 10^4 \text{ mol}^2 \text{ kg}^{-2}$</u>			<u>Reference</u>
	<u>10°C</u>	<u>25°C</u>	<u>40°C</u>	
Cryoscopy	1.7			125
"	1.56			126
"	1.7			78
" and conductance	1.7	2.9		127
" " "	1.7	2.4	3,2	68
"	2.85	4.5		95
Conductance		2.3		97
Thermochemical		3.4		70
Acidity function		7.3		128
" "		5.4		96
" "		5.5		97

HSO_4^- made by Hammett and Dejrup (90) and by Brand, Jarvie and Horning (96) from acidity function measurements. However the accuracy of this method is questionable in view of the sensitivity of activity coefficients to ionic strength. The linearity of the freezing point - molality curves for $\text{H}_3\text{O}^+\cdot\text{HSO}_4^-$ and MHSO_4 beyond 0.1 molal suggests that autoprotolysis is largely suppressed at these solute concentrations and is consistent with the original estimates of K_{ap} by Bass et al. Furthermore a recent conductometric estimate of K_{ap} by Liler (97) is in good agreement with Bass's value (see table 4b).

(b) Determination of modes of ionization

Once the equilibrium constants have been obtained, cryoscopy is most useful in determining the mode of ionization of a particular solute. The number of moles of all species, γ , produced by dissolution of one mole of solute, is given by a rearranged form of (4 - 35), (50) ,

$$\gamma = \frac{\vartheta(1 + 0.002\vartheta - 0.098m_s)}{6.12m} - \frac{m_d}{m} \quad (4 - 39)$$

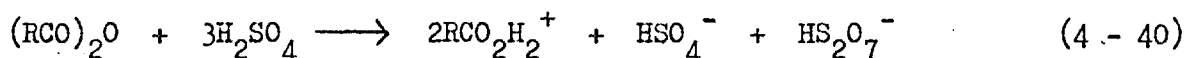
where ϑ is the freezing point depression relative to the hypothetical undissociated acid, m_d the total molality of the solvent self-dissociation species, and s the number of moles of solvent used up in dissolution of one mole of solute.

Consistent with equations (4 - 2), (4 - 4), (4 - 5), (4 - 10), (4 - 11), (4 - 15), (4 - 16) and (4 - 27), the appropriate values of γ for the various solutes (48) are

M_2SO_4	4	H_2O	2
$\text{M}'\text{SO}_4$	3	$\text{C}_2\text{H}_5\text{OH}$	3
MHSO_4	2	$(\text{C}_2\text{H}_5)_2\text{O}$	4
HNO_3	4	H_3BO_3	6

Before the cryoscopic theory had been developed to the level appropriate to equation (4 - 39), the practice (90) had been to add small quantities of water or other bases to the solvent to repress the self-dissociation so that

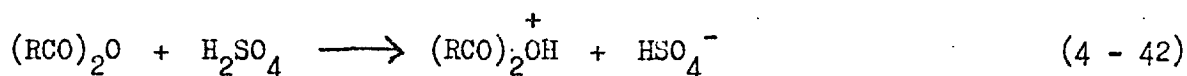
equation (4 - 34) held approximately. The procedure can be criticized on the grounds that the self-dissociation cannot be completely suppressed and the value of γ obtained is not necessarily the value appropriate to the solute's mode of ionization in the pure solvent. For example, in the pure solvent, the freezing point depression for carboxylic acid anhydrides corresponds to $\gamma = 4$ and the dissolution reaction is thought to be



However, in slightly aqueous acid, the HS_2O_7^- produced causes an elevation of the freezing point owing to the reverse of the self-ionization reaction.



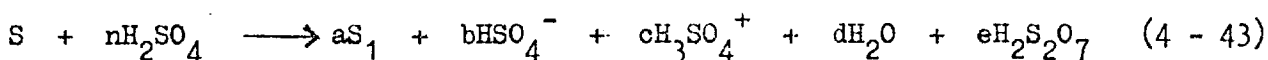
Two solute species are removed from solution by this reaction and the appropriate value of γ is 2. On the basis of this value it might have been wrongly concluded that the dissolution was accompanied only by simple protonation.



On the other hand it is also possible to take advantage of the difference in cryoscopic behaviour of a solute in sulphuric acid to which small amounts of electrolytes have been added. Leisten (98,99) has suggested an ingenious use of the following cryoscopic mixtures;

- (i) sulphuric acid containing water, i.e. H_3O^+ , HSO_4^-
- (ii) sulphuric acid containing $\text{H}_2\text{S}_2\text{O}_7$, HS_2O_7^-
- (iii) sulphuric acid containing HS_2O_7^- , HSO_4^-
- (iv) sulphuric acid containing H_3SO_4^+ , H_3O^+
- (v) sulphuric acid containing H_3SO_4^+ , HS_2O_7^-

The dissolution of any solute, S, can be thought of in terms of the equation,



The effects of producing one mole of the species H_2O , $\text{H}_2\text{S}_2\text{O}_7$, HSO_4^- , or H_3SO_4^+ on the total number of particles in each of these cryoscopic mixtures are

summarized as follows. Positive values imply an increase and negative values a decrease in the number of moles of solute.

	(i)	(ii)	(iii)	(iv)	(v)
H ₂ O	2	-1	0	0	-1
HSO ₄ ⁻	1	0	1	-1	-1
H ₂ S ₂ O ₇	-2	1	0	0	1
H ₃ SO ₄ ⁺	-1	0	-1	1	1

Thus the cryoscopic behaviour of any given solute will be different in at least three of the five solvent mixtures. The nature of the self-dissociation of the solvent is such that either b or c and either d or e must be zero. It follows that the use of three appropriate cryoscopic mixtures enables a, b, c, d, and e, and hence the mode of dissolution, to be determined for any solute.

(c) Information derived from osmotic coefficients

Accurate freezing point measurements (92) of solutions of a variety of solutes have been used (100) to calculate the corresponding osmotic coefficients, ϕ , using equation (4 - 35) with the equilibrium constants determined by Bass et al. (78). The values of the parameters, $\underline{a}$ and b, which give the best fits of the results obtained for ϕ to equation (4 - 38) have also been found. The method of fitting was as follows. Equation (4 - 38) may be re-written,

$$\phi - \phi_1 = 1 + b \sum m_i \quad (4 - 44)$$

where the second term on the right hand side, involving the parameter $\underline{a}$, has been replaced by ϕ_1 . A plot of $(\phi - \phi_1)$ against $\sum m_i$ should be a straight line of slope, b, and intercept 1.0 and, for each series of solutions of a given solute, such a graph was plotted. For all electrolytes, except H₃O.HSO₄ and AgHSO₄, a value of 10 Å for $\underline{a}$ was required for straight lines extrapolating satisfactorily to 1.0. Although the plots for other values of $\underline{a}$ were not straight lines over the whole of the concentration range, their linear portions all had very nearly the same slope so that the value of b could be determined almost independently of $\underline{a}$. The following table indicates the results of the calculations for electrolytes relevant to the present work.

Cation	<u>a</u>	<u>b</u>	Cation	<u>a</u>	<u>b</u>
Ba ²⁺	10	0.32	NH ₄ ⁺	10	0.015
Na ⁺	10	0.14	Ag ⁺	2	0
Li ⁺	10	0.08	H ₃ O ⁺	2	0
K ⁺	10	0.07			

The value of $10 \text{ \AA}$ for a is considerably higher than the corresponding values in aqueous solutions (usually within the range $2.5 \leq \underline{a} \leq 7 \text{ \AA}$). However it is not unreasonable if it is assumed (101) that, for unassociated electrolytes, there is always at least one solvent molecule between anion and cation when they collide. Bass et al. (100) have indeed calculated such values from the sum of the crystal radius of the cation and estimated radii of a sulphuric acid molecule and a hydrogen sulphate ion. The interpretation of the low value of a ($2 \text{ \AA}$) obtained for $\text{H}_3\text{O}.\text{HSO}_4$ and AgHSO_4 is less straightforward and it has been necessary to postulate (100) that these electrolytes are incompletely dissociated in dilute solution in sulphuric acid. When a dissociation constant of unity is assumed for these electrolytes, smaller values of $\sum m_i$ ensue and the osmotic coefficients calculated from (4 - 35) then fit (4 - 38) with a equal to $10 \text{ \AA}$ and b equal to 0.06 for $\text{H}_3\text{O}.\text{HSO}_4$ and 0.07 for AgHSO_4 .

Information about the solvation of ions has been derived from the values of the parameter b (100). By thermodynamic considerations (3) of osmotic coefficients in terms of the chemical potential of the solvent, Bass et al. (100) showed that, for sulphuric acid solutions, b could be expressed in terms of the solvation number s of an electrolyte by the expression

$$\underline{b} = (2s - \gamma) / 40.8 \quad (4 - 45)$$

When the entropy of mixing of the solvent molecules and the solvated ions (141) is taken into account, a modified form of this equation is

$$\underline{b} = \frac{(r + s)^2}{40.8} - \frac{r \gamma}{20.4} \quad (4 - 46)$$

where r is the ratio of the apparent molar volume of the unsolvated electrolyte to the molar volume of solvent. The following values of s were obtained,

<u>Cation</u>	<u>i.</u>	<u>ii.</u>	<u>iii.</u>
Ba ²⁺	11.5	6.5	3.0
Na ⁺	3.8	3.0	2.0
Li ⁺	2.6	2.3	3.4
K ⁺	2.4	2.1	0.6
NH ₄ ⁺	1.2	1.2	0.2
H ₃ O ⁺	-	-	4.0

i. solvation numbers calculated from equation (4 - 45).

ii. " " " " " (4 - 46).

iii. aqueous solvation numbers (102).

All the solutes studied do, of course, have the common anion HSO₄⁻; and consequently the values represent the relative solvation numbers of the cations. Furthermore the large hydrogen sulphate ion may well be unsolvated in which case these values represent the solvation numbers of the cations. For barium, equation (4 - 46) yields a smaller and more reasonable solvation number than does (4 - 45) whereas the two treatments yield similar values for the other ions. Their magnitude is reasonable for primary solvation numbers and, lithium excepted, show the expected trend with changes in the charge/radius ratio. It has been suggested (103) that the coordination number for the lithium ion for sulphuric acid molecules is only three whilst that of sodium is four. Consequently steric factors and not charge/radius considerations limit the extent of solvation of the lithium ion. The sulphuric acid solvation numbers are, in general, larger than the aqueous ones and this may be attributed to the greater polarity of the H₂SO₄ molecule.

A review, incorporating experimental details of the cryoscopic method and the information derived from it for sulphuric acid, has recently been published by Gillespie and Robinson (105).

Electrical conductances of solutions

From general considerations of conductances and mobilities, particularly in aqueous solutions, two main mechanisms by which ionic conduction takes place have been proposed. The reader is referred to reviews by Conway (106) and by Spiro (45), and references therein, for a full discussion of the evidence for, and the underlying theories of, the two mechanisms. Only a brief discussion will be given here.

The first, by which all ionic species are thought to conduct, is simple migration of the ion through the medium. On the assumptions that the ion was a large sphere of radius, r_i , and the solvent was a continuous incompressible fluid of viscosity, η , Stokes (107) derived hydrodynamically the steady state velocity, v_i , achieved by the ion when subjected to a force F ,

$$v_i = F / 6\pi\eta r_i \quad (4 - 47)$$

provided the liquid immediately adjacent to the interface 'wets' the sphere and so moves along with it. Modifications of the formula to take into account slipping between the surface of the sphere and the fluid have been made (45). The force usually arises from the application of a potential gradient, X , and the sphere possesses a charge $|z_i|e$,

$$F = |z_i|eX \quad (4 - 48)$$

from which it may be shown (45) that

$$\lambda_i^0 = \frac{z_i^2 F^2}{6\pi N \eta r_i} \quad (4 - 49)$$

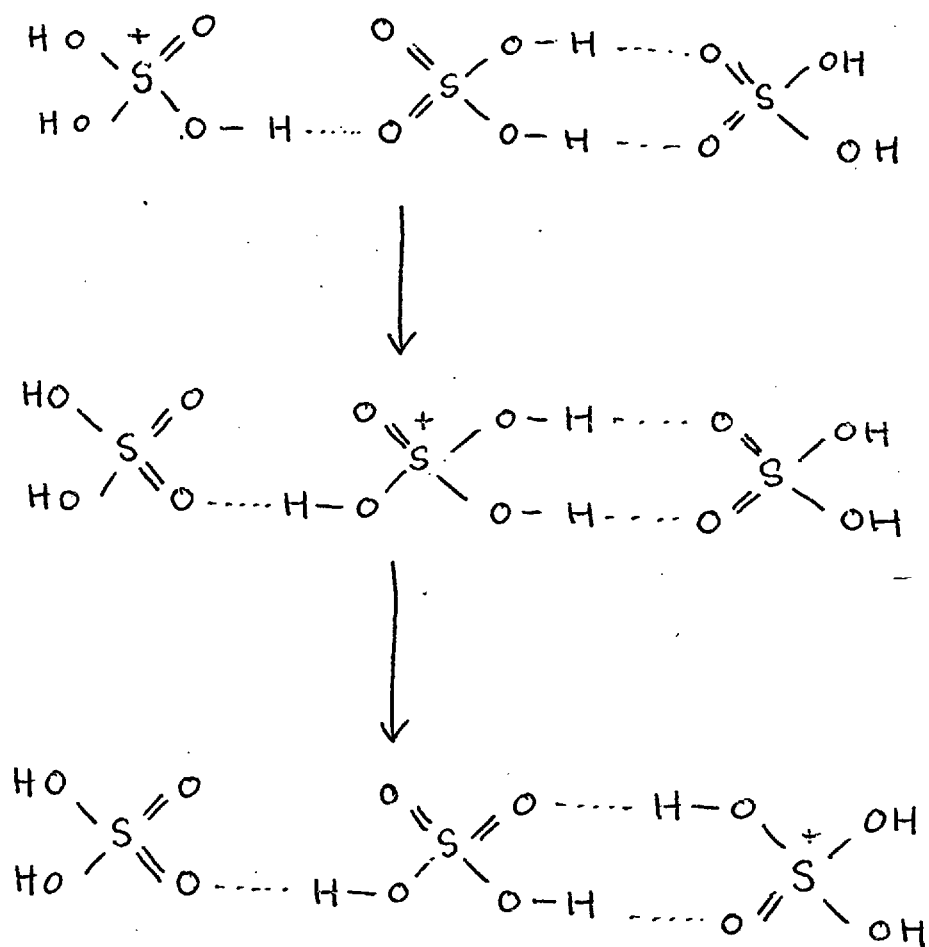
This equation, usually known as Stokes' law, implies that, for a given ion, λ_i^0 is inversely proportional to the viscosity of the solvent and, for a given solvent, λ_i^0 is inversely proportional to the radius of the ion.

The second approach to the theory of ionic conduction is from the so-called proton transfer mechanism. In certain hydrogen-bonded solvents the hydrogen ion is unusually mobile in comparison with K^+ or other alkali metal ions whilst, in water, H_3O^+ and OH^- have considerably higher mobilities than other ions which

arise from the dissolution of solutes. It is generally thought (106) that this is attributable to a mechanism involving the successive transfer of protons through the hydrogen-bonded network of the solvent without necessitating actual translatory motion of the ions. The mechanism is often referred to as 'proton-jumping' between favourably oriented solvent molecules and the conducting ions. There has been much speculation about the nature of the rate-determining step (45, 118-122) in this process but it seems likely, for water at least, that rotation of the solvent molecules, into an orientation for proton transfer to occur, is slower than the actual proton jump itself. In general, the only ions likely to take part in proton transfer are derived from the autoprotolytic self-dissociation of the solvent and it must be emphasised that these ions also conduct by normal migration.

The experimental conductance data for solutions in sulphuric acid have been interpreted in terms of these two mechanisms. There have been several investigations of the conductances of solutions of water and sulphur trioxide (66, 69, 67, 79, 82-89, and see earlier in this chapter). A few studies of the conductometric behaviour of other solutes were reported by the early workers (79, 85, 87, 108, 110) but the first detailed investigations were by Gillespie and Wasif (76) and by Gillespie and his school (111, 69) in 1960. The specific conductances of all the metal sulphates that are appreciably soluble in sulphuric acid have been measured and solutions of several organic bases have also been investigated. The conclusions drawn about the nature of ionic conduction were based on two independent sets of experimental observations as follows,

- 1) The specific conductances of solutions of metal hydrogen sulphates (see fig. 4-4) obtained by Flowers et al. (69) were almost independent of the nature of the cation at concentrations below 0.1N.
- 2) The transference measurements of Gillespie and Wasif (112), discussed later in this chapter, indicated that the cations in MH_2SO_4 solutions contributed 3% or less to the total conductance of the solutions. The measurements reported in this thesis suggest that an upper limit of 1% is more appropriate.



PROTON TRANSFER BY H_3SO_4^+

FIGURE 4-3

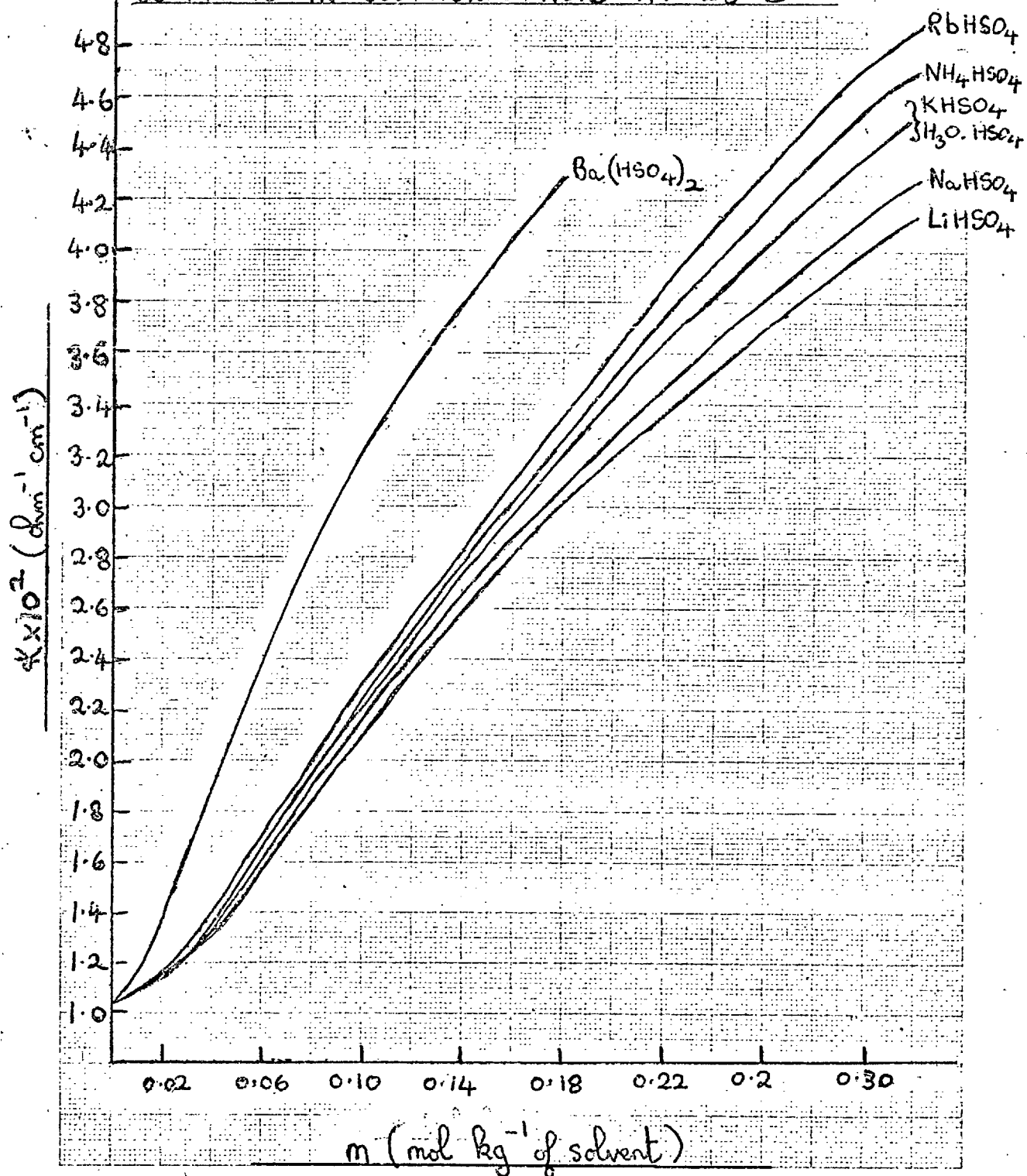
Both observations suggest that conduction in these solutions is due almost entirely to the HSO_4^- ion with the cation contributing only to a minor extent. Several workers (113, 112, 69) have proposed that conduction by HSO_4^- and H_3SO_4^+ is by proton transfer, in addition to normal migration, whilst other ions conduct only by migration. Proton transfer by H_3SO_4^+ is shown schematically in figure 4-3 .

A comparison of the mobilities of ions conducting by proton transfer with those by normal migration is of interest both for solutions in water and in sulphuric acid. The limiting ion conductances of H_3O^+ and OH^- in water are ca. 350 and 200 $\text{ohm}^{-1}\text{cm}^2\text{equiv}^{-1}$, respectively, whereas the values for ions conducting by normal migration lie in the range 20 to 70 $\text{ohm}^{-1}\text{cm}^2\text{equiv}^{-1}$ (114). Thus conduction by proton transfer is five to ten times faster than normal ionic migration. In sulphuric acid solutions, however, the ratio would appear to be an order of magnitude higher. The vast difference in the effectiveness of the two conduction mechanisms is attributable to the very high viscosity of the medium (some 27.6 times greater than that of water). The latter exerts a severe retarding effect on ions conducting by normal migration, as can be seen from Stokes' law, but proton transfer, which involves no actual translatory motion of the ions, is much less affected by viscosity.

Equivalent conductances in sulphuric acid

In figure 4-4 the specific conductances κ_{soln} of solutions of MHSO_4 and water are plotted against concentration. All the curves have the same general shape, commencing convex to the concentration axis as a result of repression of the self-dissociation and then becoming concave to this axis at high concentrations. This suggests that the mobility of the hydrogen sulphate ion decreases with increasing concentration and the divergence of the curves for different electrolytes indicates that it decreases to varying extents depending on the accompanying cation.

FIGURE 4-4 : SPECIFIC CONDUCTANCES OF SOLUTIONS IN SULPHURIC ACID AT 25°C



Before equivalent conductances of electrolytes can be calculated from these data, it is necessary to take into account the contribution to the conductance from the ions introduced by the self-dissociation of the solvent (the 'solvent ions'). This cannot be done, as is usual, by simply subtracting the specific conductance of the pure solvent since the self-dissociation is repressed to a greater extent as the concentration of the solute increases. This difficulty can be overcome in three ways as follows.

Approach A :

The specific conductance due to the solvent ions only is calculated at every concentration and subtracted from the measured value of κ_{soln} . For solutions of MHSO_4 in sulphuric acid we have

$$\kappa_{\text{soln}} = 10^{-3} (c_{\text{H}_3\text{SO}_4^+} \lambda_{\text{H}_3\text{SO}_4^+} + c_{\text{HSO}_4^-} \lambda_{\text{HSO}_4^-} + c_{\text{H}_3\text{O}^+} \lambda_{\text{H}_3\text{O}^+} + c_{\text{HS}_2\text{O}_7^-} \lambda_{\text{HS}_2\text{O}_7^-} + c_{\text{M}^+} \lambda_{\text{M}^+}) \quad (4 - 50)$$

and

$$\kappa_{\text{solv}} = 10^{-3} (c_{\text{H}_3\text{SO}_4^+} \lambda_{\text{H}_3\text{SO}_4^+} + c_{\text{HSO}_4^-}^{\text{I}} \lambda_{\text{HSO}_4^-} + c_{\text{H}_3\text{O}^+} \lambda_{\text{H}_3\text{O}^+} + c_{\text{HS}_2\text{O}_7^-} \lambda_{\text{HS}_2\text{O}_7^-}) \quad (4 - 50a)$$

where $c_{\text{HSO}_4^-}$ is the total concentration of HSO_4^- in the solution, $c_{\text{HSO}_4^-}^{\text{I}}$ is the contribution of HSO_4^- arising from the self-dissociation of the acid and

$$c_{\text{HSO}_4^-} - c_{\text{HSO}_4^-}^{\text{I}} = c_{\text{M}^+} \quad (4 - 51)$$

The quantity κ_{solv} is that part of the conductance of this solution, which is attributable to the solvent ions and is not the conductance of the pure solvent because of repression of the self-dissociation. The concentrations of all the species in solution are known or may be calculated from the equilibrium constants. Values of $\lambda_{\text{HSO}_4^-}$ and $\lambda_{\text{H}_3\text{SO}_4^+}$ are required before this correction may be applied and these are first obtained from approach B or C. Once found, κ_{solv} may be evaluated and subtracted from κ_{soln} , the experimental value, to yield κ_{solute} . This form of correction must be applied to data obtained in

transference measurements.

Approach B :

This is the method proposed by Flowers et al. (69) . The following series of steps indicates the procedure adopted by these workers.

(a) It is convenient to define a quantity κ' which excludes the contribution to the total conductance from all the ions that do not conduct by the proton transfer mechanism.

$$\kappa' = \kappa_{\text{soln}} - 10^{-3}(c_{\text{H}_3\text{O}^+}\lambda_{\text{H}_3\text{O}^+} + c_{\text{HS}_2\text{O}_7^-}\lambda_{\text{HS}_2\text{O}_7^-} + c_{\text{M}^+}\lambda_{\text{M}^+}) \quad (4-52)$$

The bracketed term in (4 - 52) represents only a small correction since the ionic conductances involved are all very small compared to $\lambda_{\text{H}_3\text{SO}_4^+}$ and $\lambda_{\text{HSO}_4^-}$. Flowers et al. assigned a value of $5 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ to the ionic conductances of all univalent ions moving by simple migration and a value of $1.5 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ to λ for divalent ions such as Ba^{2+} . The present work indicates that these were overestimates and the correction term is even smaller.

(b) Values of κ' were calculated from equation (4 - 52) and the experimental specific conductance. The concentrations of H_3O^+ and HS_2O_7^- were calculated from the self-dissociation equilibrium constants. The concentration of M^+ was the equivalent concentration of the solute.

(c) The ratio of the mobilities of the H_3SO_4^+ and HSO_4^- ions has been calculated over a wide range of concentrations by Gillespie, Robinson and Solomons (68). In essence, the procedure they adopted was to consider the values of κ' , designated $(\kappa')^{\text{ol}}$ and $(\kappa')^{\text{aq}}$, for two solutions of disulphuric acid and of water, having equal ionic strengths. Then, from charge balance relations,

$$c_{\text{HSO}_4^-}^{\text{aq}} = c_{\text{H}_3\text{SO}_4^+}^{\text{ol}} \quad c_{\text{H}_3\text{SO}_4^+}^{\text{aq}} = c_{\text{HSO}_4^-}^{\text{ol}} \quad (4-53)$$

$$c_{\text{H}_3\text{O}^+}^{\text{aq}} = c_{\text{HS}_2\text{O}_7^-}^{\text{ol}} \quad c_{\text{HS}_2\text{O}_7^-}^{\text{aq}} = c_{\text{H}_3\text{O}^+}^{\text{ol}} \quad (4-54)$$

where the superscripts 'ol' and 'aq' refer to the disulphuric acid and water solutions respectively. It further follows that,

$$(\kappa')^{ol} = 10^{-3}(c_{H_3SO_4^+}^{ol}\lambda_{H_3SO_4^+} + c_{HSO_4^-}^{ol}\lambda_{HSO_4^-}) \quad (4-55)$$

$$(\kappa')^{aq} = 10^{-3}(c_{H_3SO_4^+}^{aq}\lambda_{H_3SO_4^+} + c_{HSO_4^-}^{aq}\lambda_{HSO_4^-}) \quad (4-56)$$

Since all the concentrations could be calculated from equilibrium constants the ratios $(\kappa')^{ol}/(\kappa')^{aq}$ and $\lambda_{H_3SO_4^+}/\lambda_{HSO_4^-}$ could be determined. A value of 1.45 was obtained for the latter and it was found to be independent of the ionic strengths of the solutions, over the range $I_s = 0.019$ to $0.038 \text{ mol kg}^{-1}$, from which it had been calculated.

(d) Returning to the $MHSO_4$ solutions, κ' could then be written,

$$\kappa' = \lambda_{HSO_4^-}(1.45c_{H_3SO_4^+} + c_{HSO_4^-}) \quad (4-57)$$

and hence values of $\lambda_{HSO_4^-}$ were determined at all solute concentrations. Flowers et al. plotted $\lambda_{HSO_4^-}$ against $c_{HSO_4^-}$ for NH_4HSO_4 solutions and extrapolated the straight line obtained to $c_{HSO_4^-} = 0$ to give $\lambda_{HSO_4^-} = 170 \text{ ohm}^{-1}\text{cm}^2\text{mol}^{-1}$. Similar plots for $KHSO_4$, $NaHSO_4$, and $LiHSO_4$ all yielded the same limiting value. A conventional Debye-Hückel-Onsager plot (see chapter two) of $\lambda_{HSO_4^-}$ against $\sqrt{c_{HSO_4^-}}$ was found to be S-shaped and could not be extrapolated. This is not altogether surprising when it is remembered that even in the pure solvent $c_{HSO_4^-} = 0.0325M$, a concentration already beyond the limit for the limiting D-H-O equation to be applicable. However it is still surprising that $\lambda_{HSO_4^-}$ should vary linearly with concentration.

(e) The same procedure was adopted for acidic solutions of $HB(HSO_4)_4$ and $H_2S_2O_7$ to calculate $\lambda_{H_3SO_4^+}$ from

$$\kappa' = \lambda_{H_3SO_4^+}(c_{H_3SO_4^+} + c_{HSO_4^-}/1.45) \quad (4-58)$$

The former solute yielded a limiting value of $245 \text{ ohm}^{-1}\text{cm}^2\text{mol}^{-1}$. This was in good agreement with a value of 247 obtained from $\lambda_{H_3SO_4^+}^o/\lambda_{HSO_4^-}^o = 1.45$ when a value of 170 was used for the HSO_4^- ion. For disulphuric acid solutions, a value of 232 was obtained but the presence of higher polysulphuric acids, which

are stronger than $\text{H}_2\text{S}_2\text{O}_7$, may have led to an underestimate of $c_{\text{H}_3\text{SO}_4^+}$ and an overestimate of $c_{\text{HSO}_4^-}$ in these solutions.

The writer wishes to question this procedure on the following three counts

- 1 On the basis of the Fuoss-Onsager conductance equation, discussed in chapter two, the ratio $\lambda_{\text{H}_3\text{SO}_4^+}^0 / \lambda_{\text{HSO}_4^-}^0$ should be equal to $(\lambda_{\text{H}_3\text{SO}_4^+}^0 - \lambda^e) / (\lambda_{\text{HSO}_4^-}^0 - \lambda^e)$. The electrophoretic term, λ^e , is independent of the ion but depends on concentration. Since $\lambda_{\text{H}_3\text{SO}_4^+}^0$ is greater than $\lambda_{\text{HSO}_4^-}^0$, the conductance ratio should increase with increasing concentration.
- 2 In different MHSO_4 solutions of the same ionic strength, the specific conductances vary with the solute. As the mobilities of the cations are very low, this means that $\lambda_{\text{HSO}_4^-}$ varies with the nature of the cation. It seems rather unlikely, therefore, that the ratio $\lambda_{\text{H}_3\text{SO}_4^+} / \lambda_{\text{HSO}_4^-}$ should remain constant with both changes in concentration and changes in solute.
- 3 The derivation of the value of this ratio depends on measurements of the conductance of oleums. Since the nature of these polysulphuric acids, the extents to which they are present and the extents to which they are dissociated are all uncertain, considerable doubts about the calculated ionic strengths of these solutions must be expressed. The poor agreement between the values of $\lambda_{\text{H}_3\text{SO}_4^+}^0$ obtained by Flowers et al. (69) for disulphuric acid solutions and for $\text{HB}(\text{HSO}_4)_4$ solutions lends support to these doubts.

Approach C :

In this approach, developed by the writer, $\lambda_{\text{H}_3\text{SO}_4^+}$ and $\lambda_{\text{HSO}_4^-}$ are calculated separately for any basic solution of known concentration and consequently of known ionic strength. It should be superior to approach B for two reasons. First, it makes no assumptions about the ratios of the mobilities of the proton-jumping ions and, second, it uses as reference the acid solutions of $\text{HB}(\text{HSO}_4)_4$. This electrolyte is a stronger acid than disulphuric acid and is not complicated by polymeric species. Complete dissociation of both $\text{HB}(\text{HSO}_4)_4$ and the basic solute whose solution is being considered, is assumed. It is also assumed that a proton-

jumping ion has the same ionic mobility in a solution of an acid as in a solution of a base if the solutions have the same total ionic strength. The following series of steps indicates the procedure adopted.

a) The ionic strength, I_s , of the basic solution is calculated from its concentration using the tables of concentrations of species in strong base - sulphuric acid systems given by Flowers et al. (69) and from the relation,

$$I_s = \frac{1}{2} (c_{\text{HSO}_4^-} + c_{\text{H}_3\text{SO}_4^+} + c_{\text{H}_3\text{O}^+} + c_{\text{HS}_2\text{O}_7^-} + c_{\text{M}^+}) \quad (4 - 59)$$

b) The specific conductance, κ_{acid} , of a solution of $\text{HB}(\text{HSO}_4)_4$ of the same ionic strength is interpolated from a plot of κ_{acid} against I_s using the data of Bass et al. (111) and the tables of concentrations of species in strong acid - sulphuric acid systems given by Flowers et al. (69).

c) The concentrations of all the species in the $\text{HB}(\text{HSO}_4)_4$ solution are found from the same tables or plots based on the tables.

d) Values of κ' for the basic solution, κ'_{base} , and for the $\text{HB}(\text{HSO}_4)_4$ solution, κ'_{acid} , are found from the measured conductance of the former, κ_{base} , the interpolated conductance, κ_{acid} , and the relations below

$$\kappa'_{\text{base}} = \kappa_{\text{base}} - 10^{-3} (c_{\text{H}_3\text{O}^+}^{\text{base}} \lambda_{\text{H}_3\text{O}^+}^{\text{base}} + c_{\text{HS}_2\text{O}_7^-}^{\text{base}} \lambda_{\text{HS}_2\text{O}_7^-}^{\text{base}} + c_{\text{M}^+}^{\text{base}} \lambda_{\text{M}^+}^{\text{base}}) \quad (4 - 60)$$

$$\kappa'_{\text{acid}} = \kappa_{\text{acid}} - 10^{-3} (c_{\text{H}_3\text{O}^+}^{\text{acid}} \lambda_{\text{H}_3\text{O}^+}^{\text{acid}} + c_{\text{HS}_2\text{O}_7^-}^{\text{acid}} \lambda_{\text{HS}_2\text{O}_7^-}^{\text{acid}} + c_{\text{B}(\text{HSO}_4)_4}^{\text{acid}} \lambda_{\text{B}(\text{HSO}_4)_4}^{\text{acid}}) \quad (4 - 61)$$

Equation (4 - 60) employs the concentrations appropriate to the basic solution obtained in a) and (4 - 61) employs those obtained for the $\text{HB}(\text{HSO}_4)_4$ solution in c). A value of $1 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ is considered reasonable for the conductances of ions moving by simple migration, i.e. for all values of λ in the bracketted terms.

d) Values of $\lambda_{\text{H}_3\text{SO}_4^+}$ and $\lambda_{\text{HSO}_4^-}$ are calculated from the relations

$$10^3 \kappa'_{\text{base}} = c_{\text{H}_3\text{SO}_4^+}^{\text{base}} \lambda_{\text{H}_3\text{SO}_4^+}^{\text{base}} + c_{\text{HSO}_4^-}^{\text{base}} \lambda_{\text{HSO}_4^-}^{\text{base}} \quad (4 - 62)$$

$$10^3 \kappa'_{\text{acid}} = c_{\text{H}_3\text{SO}_4^+}^{\text{acid}} \lambda_{\text{H}_3\text{SO}_4^+} + c_{\text{HSO}_4^-}^{\text{acid}} \lambda_{\text{HSO}_4^-} \quad (4 - 63)$$

where superscripts to the concentrations apply as in d).

An example of the application of this procedure to determine $\lambda_{\text{H}_3\text{SO}_4^+}$, $\lambda_{\text{HSO}_4^-}$ and the transference number solvent correction for 0.126N NaHSO_4 in sulphuric acid will now be given. The molality of this solution is $0.0687 \text{ mol kg}^{-1}$, its specific conductance is $1.71 \times 10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1}$ and its density is 1.831 kg dm^{-3} .

a) The total molality of ionic species is 0.157 which means that the ionic strength calculated from (4 - 59), is $0.144 \text{ mol dm}^{-3}$.

b) The $\text{HB}(\text{HSO}_4)_4$ solution having this ionic strength is 0.071 molal, has a specific conductance of $1.83 \times 10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1}$ and a density of 1.833 kg dm^{-3} .

c) Interpolation of the data of Flowers et al. (69) yields the following molalities of ions in these solutions.

	<u>0.0687 molal NaHSO_4</u>	<u>0.071 molal $\text{HB}(\text{HSO}_4)_4$</u>
H_3SO_4^+	0.0033	0.0620
HSO_4^-	0.0725	0.0039 ₅
H_3O^+	0.0071	0.0147
HS_2O_7^-	0.0056	0.0027
Na^+	0.0687	0.0
$\text{B}(\text{HSO}_4)_4^-$	0.0	0.0710

d) Assuming values of $1 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ for λ for all ions except H_3SO_4^+ and HSO_4^- , substitution in equations (4 - 60) and (4 - 61) yields

$$\begin{aligned} \kappa'_{\text{base}} &= 1.71 \times 10^{-2} - 1.831 \times 10^{-3}(0.0071 + 0.0056 + 0.0687) \\ &= 1.69_5 \times 10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1} \end{aligned}$$

$$\begin{aligned} \kappa'_{\text{acid}} &= 1.83 \times 10^{-2} - 1.833 \times 10^{-3}(0.0147 + 0.0027 + 0.0710) \\ &= 1.81 \times 10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1} \end{aligned}$$

e) Insertion of these values of κ'_{base} and κ'_{acid} into (4 - 62) and (4 - 63) yields $\lambda_{\text{H}_3\text{SO}_4^+} = 151.9 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ and $\lambda_{\text{HSO}_4^-} = 120.8 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$.

It will be recalled, from (4 - 50) and (4 - 51), that the part of the conductance of a basic solution, κ_{solv} , which is attributable to the solvent ions alone is

$$\kappa_{\text{solv}} = 10^{-3} (c_{\text{H}_3\text{SO}_4^+} \lambda_{\text{H}_3\text{SO}_4^+} + c_{\text{HSO}_4^-} \lambda_{\text{HSO}_4^-} + c_{\text{H}_3\text{O}^+} \lambda_{\text{H}_3\text{O}^+} + c_{\text{HS}_2\text{O}_7^-} \lambda_{\text{HS}_2\text{O}_7^-}) \quad (4 - 50a)$$

where $c_{\text{HSO}_4^-}$ is the contribution of HSO_4^- arising from the self-dissociation of the acid and

$$c_{\text{HSO}_4^-} - c_{\text{HSO}_4^-} = c_{\text{M}^+} \quad (4 - 51)$$

For this NaHSO_4 solution,

$$\begin{aligned} \kappa_{\text{solv}} &= 1.831 \times 10^{-3} ((0.0033 \times 151.9) + (0.0038 \times 120.8) + 0.0071 + 0.0056) \\ &= 1.78 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1} \end{aligned}$$

The reader may recall, from chapter one, that transference numbers measured by the Hittorf or moving boundary methods are corrected for the effects of the solvent by multiplication by $(1 + \kappa_{\text{solv}} / \kappa_{\text{soln}})$. This quantity, henceforth referred to as the solvent correction factor, has the value

$$\left\{ 1 + \frac{1.78 \times 10^{-3}}{1.71 \times 10^{-2}} \right\} = 1.10_4$$

for this 0.126N NaHSO_4 solution.

The concentration dependence of $\lambda_{\text{HSO}_4^-}$

The values of λ_- , equal to $\lambda_{\text{HSO}_4^-}$, for a series of concentrations (molalities) of MHSO_4 solutions have been calculated (69), using approach B, after interpolation of the specific conductance - concentration curves in figure 4-4. These values are listed in table 4c below.

Table 4c

Molality	$\lambda_- \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$					
	LiHSO_4	NaHSO_4	KHSO_4	RbHSO_4	NH_4HSO_4	$\text{H}_3\text{O} \cdot \text{HSO}_4^{\text{a}}$
0.00 ^b	151.2	151.2	151.2	151.2	151.2	151.2
0.01	148.5	149.0	149.0	-	149.0	149.8
0.02	143.0	143.6	144.0	-	144.8	146.5
0.04	129.9	130.2	131.7	135.5	132.8	131.7
0.06	118.3	119.4	121.5	125.3	122.3	121.8
0.12	98.5	99.8	102.7	106.9	104.6	101.7

a. Assuming $K_b = \infty$ and complete dissociation of $\text{H}_3\text{O} \cdot \text{HSO}_4$.

b. The values of λ_- at $m = 0.00$ are not the same as values of λ_-^0 . The former are appropriate to the pure acid whereas the latter refer to the hypothetical medium in which $c_{\text{HSO}_4^-} = 0$.

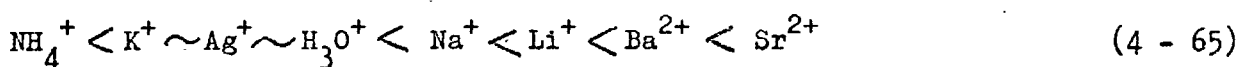
By ignoring the contribution of the cation and equating $\lambda_{\text{HSO}_4^-}$ to Λ for the MHSO_4 electrolyte, Flowers et al. (69) attempted to fit the above data to the Robinson and Stokes conductance equation (115). This is a modification of the Debye-Hückel-Onsager equation to include finite ion size and a Boltzmann distribution, of the ions in the atmosphere, in the relaxation term. The form of the equation employed was

$$\Lambda = \left\{ \Lambda^0 - \frac{B_2 \sqrt{c}}{(1+y)} \right\} \left\{ 1 - \frac{B_1 \sqrt{c}}{(1-y)} \cdot \frac{\exp(0.2929y) - 1}{0.2929y} \right\} \quad (4-64)$$

where all the symbols are defined in chapter two. For a values between 2 Å and

10 Å, and over the range of molality given in this table, equation (4 - 64) predicted a fall in $\lambda_{\text{HSO}_4^-}$ (or Λ) of between 5 and 15 conductance units (depending on whether the chosen value of a was high or low). This is much less than the decrease in conductance found experimentally in table 4b. It would be necessary to insert negative values of a into the equation to obtain a fit to the data. The following explanations have been put forward to account for this rapid fall of $\lambda_{\text{HSO}_4^-}$ with concentration (76, 69) :

i) To play its part in the chain-transfer conduction mechanism, a solvent molecule will usually have to undergo a rotation into a suitable orientation. It has been suggested (76) that the rotation of solvent molecules involved in solvation of the ions will be restricted and such molecules will be unable to play as great a role in chain conduction as those in the 'free' solvent. Thus the greater the extent of ion solvation, the greater will be the decrease in $\lambda_{\text{HSO}_4^-}$. If a solvation number of four is assumed, then in a 0.1M solution, the amount of free solvent would be expected to decrease by 0.4 moles per dm^3 . Sulphuric acid contains approximately 10 moles per dm^3 of H_2SO_4 and so a decrease of about 4% in $\lambda_{\text{HSO}_4^-}$ might be expected. The actual decreases are, however, much bigger (about 20%). Since HSO_4^- is common to all the electrolytes considered, its solvation need not be taken into account. Assuming that there is a direct correlation between the polarising power of an ion and the extent to which it is solvated, the order of increasing extent of solvation is



and this is exactly the order of decrease of $\lambda_{\text{HSO}_4^-}$ at a given concentration. The restriction in the motion of solvent molecules when they are coordinated to an ion should lead to an increase in the viscosity of the solution and it has been found (61) that the order of increasing viscosity of sulphuric acid solutions likewise follows the sequence (4 - 65). Gillespie and Wasif (76) found that, at a given concentration, the specific conductances of a series of sulphuric acid solutions of MHSO_4 solutes, were inversely proportional to the square roots

of their viscosities. They plotted $\kappa(\eta/\eta_0)^{\frac{1}{2}}$, where η is the solution viscosity and η_0 that of the solvent, against concentration and found that the differences in κ between solutes were almost completely eliminated and the results for all the electrolytes fell on the same curve. It is worth commenting that Stokes' law (107) predicts that the conductance should depend on $1/\eta$, and not $1/\eta^{\frac{1}{2}}$, but this law is based on conduction by normal migration and there is no reason to expect it to hold for ions conducting by a chain-transfer mechanism.

ii) Gillespie and Wasif also proposed that the mobility of the HSO_4^- ion depends on the frequency with which conducting chains collide. They attempted to justify this proposal by considering the situation that arises when two HSO_4^- ions simultaneously arrive at positions adjacent to an H_2SO_4 molecule. The last-mentioned can participate in a chain transfer conduction process with only one of these ions at a time and the second ion must wait until the H_2SO_4 molecule has re-oriented itself into an appropriate position before a further proton transfer can take place. In effect, the time of rotation of the sulphuric acid molecule has increased relative to the second ion and the average mobility of the HSO_4^- has decreased due to competition for the same H_2SO_4 . This effect will clearly become more significant as the concentration of HSO_4^- in the solution increases. Furthermore it is independent of the cation and so, although it explains the general decrease in $\lambda_{\text{HSO}_4^-}$ with concentration, it does not resolve the differences between solutes.

Both explanations i) and ii) are conditional on molecular rotation being the rate-determining step in chain transfer conduction.

iii) The ions derived from the solute must occupy sites in the liquid structure that would otherwise be occupied by sulphuric acid molecules. Consequently, when an HSO_4^- ion arrives at an adjacent site, no proton is available for transfer and the chain conduction is hindered. Both the solute cation and the HSO_4^- ion itself will function in this way since no proton transfer can take place between M^+ and HSO_4^- ions or between two HSO_4^- ions. This effect would be expected to

acquire greater importance as the concentration and number of sites occupied by the solute increase and should lead to a fall in the average mobility of the HSO_4^- ion.

All the factors i), ii) and iii) would be expected to apply to chain conduction by H_3O^+ and OH^- in water as well as to MHSO_4 solutions in sulphuric acid. However, Λ for aqueous solutions of hydrochloric acid changes by about 2% over the concentration range 0.0 to 0.1 molal (116) and the experimental data satisfactorily obey the Robinson and Stokes equation. Three important differences between aqueous solutions and solutions in sulphuric acid, which may account for the observed behaviour, will now be pointed out. First, there is a significant contribution from normal migration to the ionic mobilities of H_3O^+ (ca. 20%) and OH^- (ca. 33%) in water whereas the contribution to the conductances of HSO_4^- and H_3SO_4^+ from this mechanism is probably negligible. Second, if viscosity-dependent molecular rotation is the rate-determining step of chain conduction in both solvents, the time for which a proton transferring ion must wait, while a solvent molecule takes up an appropriate orientation, will be much smaller in factors i) and ii) above for water than for sulphuric acid because of the great difference in the viscosities of the two solvents. A third possible reason is that there is a much greater contribution from asymmetric autoprotolysis, discussed below, for sulphuric acid solutions than for aqueous ones.

iv) Wyatt (117) has suggested that there is a special contribution to conductance from asymmetric dissociation for any liquid dissociating by an autoprotolytic mechanism. When an electric field is applied there is a bias towards the movement of protons in the direction of the field and consequently, although they move in all directions, a slight excess moves with the field and a slight deficit against it. The chain transfer conduction by the ions derived from autoprotolysis is interpreted as the movement of protons from solvent cations to neutral molecules and from neutral molecules to solvent anions when an

external field is applied. Wyatt now suggests that there will also be a slight bias towards the movement of protons from neutral molecules to their neutral neighbours i.e. towards dissociation in the direction of the field, and that this additional effect will contribute to the conductance. It is important to appreciate that no net increase in the extent of ionization is envisaged but the self-dissociation merely becomes asymmetrical. The number of protons formed per unit time in the direction of the field is slightly increased and the number in the opposite direction is slightly decreased. For a solvent HA dissociating according to



the contribution of the asymmetric autoprotolysis to the specific conductance of the solvent has been derived (117) as

$$\kappa_D = 3.733 \times 10^{-11} k_R [H_2A^+] [A^-] \left\{ \frac{\chi_a^2}{F} \right\} \quad (4 - 67)$$

where k_R is the rate of recombination of the autoprotolysis ions and χ is the effective internal field for an external applied field of 1 volt cm^{-1} . Although k_R and χ are not known with certainty, Wyatt showed that for sulphuric acid this factor might contribute as much as 30% of the conductance of the pure solvent. Since the ionic product, $[H_3O^+] [OH^-]$, is very much smaller than $[H_3SO_4^+] [HSO_4^-]$, asymmetric autoprotolysis is unlikely to be a significant contribution to the conductance of aqueous solutions. Equation (4 - 57) has been modified by Gillespie and Robinson (50) to include the contribution from this effect. They showed that

$$10^3 \kappa' = \rho \lambda_{HSO_4^-} (\mu m_+ + m_-) + 10^3 \kappa_D \quad (4 - 68)$$

where m_+ and m_- are the molalities of $H_3SO_4^+$ and HSO_4^- respectively, μ is the ratio $\lambda_{H_3SO_4^+} / \lambda_{HSO_4^-}$, and ρ the density of the solution. Graphs of $10^3 \kappa'$ against $(\mu m_+ + m_-)$, using $\mu = 1.5$, were plotted (50) for various metal hydrogen sulphates at 25°C and found to be straight lines up to 0.1 molal with

intercepts of $\kappa_D = 0.38 \times 10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1}$ and slopes that gave $\lambda_{\text{HSO}_4^-} = 166 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$. As κ_D depends on the ionic product, $[\text{H}_3\text{SO}_4^+][\text{HSO}_4^-]^4$, which is a constant, it is not a function of concentration and has the same value in the pure solvent as in solutions. This value represents a contribution of 36% to the conductance of the pure solvent. The writer feels there is little justification for such a plot since it is unreasonable to expect $\lambda_{\text{HSO}_4^-}$, the density and the ratio of the mobilities to remain constant over such a concentration range. However the allowance for asymmetric autoprotolysis has eliminated the large variations in $\lambda_{\text{HSO}_4^-}$ with concentration obtained by Flowers et al.

v) The mobilities calculated for $\lambda_{\text{H}_3\text{SO}_4^+}$ and $\lambda_{\text{HSO}_4^-}$ from equations (4 - 57) and (4 - 58) or from (4 - 62) and (4 - 63) depend on the values taken for $c_{\text{H}_3\text{SO}_4^+}$ and $c_{\text{HSO}_4^-}$ which in turn depend on the value of the autoprotolysis constant K_{ap} . It is clear that an underestimate of K_{ap} must lead to an overestimate of the mobilities of these two ions. If the higher estimates of K_{ap} , from acidity function measurements, are used, the large variation of $\lambda_{\text{HSO}_4^-}$ with concentration is eliminated, since such high mobilities as were calculated by Flowers et al., using the lower estimates from cryoscopy, are no longer appropriate in the region of the pure acid and dilute solutions. Table 4b, given earlier in this chapter, shows all the currently available data for K_{ap} at 10°C, 25°C and 40°C.

The determination of χ from conductivity measurements

The fact that almost all the conductance of a basic solution in sulphuric acid can be ascribed to the HSO_4^- ion enables the number of moles of this ion, χ , produced by one mole of electrolyte, to be conveniently determined. One might expect that, at a given electrolyte concentration, the conductivity of a dihydrogen sulphate would be twice that of a monohydrogen sulphate but at low concentrations this is not the case because of different extents of repression of the self-

dissociation. However, if the concentration of a standard monohydrogen sulphate (e.g. KHSO_4) which produces a given specific conductance is compared with the concentration of any other base giving the same conductance, the value of χ is given by their ratio. This is because the HSO_4^- concentration and the extent of repression of the self-dissociation are the same for the two solutions if their conductances are equal. The value of χ from conductivity measurements, together with ν from cryoscopy, often enables the mode of ionization of a given solute to be unambiguously determined. The values of χ obtained are not always exact integers since the conductances do not depend entirely on $c_{\text{HSO}_4^-}$ and are influenced to a minor extent by the electrolyte chosen as reference. There is seldom any ambiguity, however, about the appropriate integer to be deduced from a calculated value of χ .

It is worth noting, at this point, that the conductances of solutions of $\text{H}_3\text{O}^+.\text{HSO}_4^-$ and AgHSO_4 are such as to render $\chi = 1$ and provide no evidence of the incomplete dissociation that must be postulated to explain the osmotic coefficient data for these electrolytes. It has been suggested (50) that water is fully ionized as $\text{H}_3\text{O}^+.\text{HSO}_4^-$ but that the ions are not completely separated. Such incomplete dissociation would not influence the conductance of the solution if the life-time of the ion-pair were shorter than the average time between successive chain transfers.

Transference numbers in sulphuric acid

Three previous papers have reported the measurement of cation transference numbers in sulphuric acid, all by the Hittorf method (see chapter one). Hammett and Lowenheim (113), in 1934, found the transference number of the barium ion in $\text{Ba}(\text{HSO}_4)_2$ solutions to be 0.007 ; they recognised, however, that its precision was limited by the very small changes in concentration involved, the difficulties of stopcock lubrication, and the rather cumbersome gravimetric technique by which the solutions were analysed. However, their results were useful in that they demonstrated a very small but definite migration of the barium ion towards the cathode. Hantzsch (79) had previously suggested that no migration could be demonstrated in sulphuric acid.

More recently, Gillespie and Wasif (112) and Wasif (129) have measured the cation transference numbers of a variety of hydrogen sulphates. They used a Hittorf technique (4) comprising three compartments (each of capacity about 50 cm^3) connected to each other by narrow bent tubes to minimise convection and diffusion from one compartment to the next. Platinum electrodes were employed and the currents passed were 20 - 25 mA. Most solutions were analysed gravimetrically. Barium and strontium were determined as their sulphates by diluting a weighed portion of solution with a large excess of water or 1:1 water - alcohol mixture. Silver determinations were carried out by dilution with water and slow precipitation of silver chloride with excess HCl. Sodium, potassium and lithium solutions were analysed by slowly driving off the sulphuric acid, leaving a residue of the hydrogen sulphate, which was heated to constant weight at 600°C . The ammonium analysis involved the direct addition of 30% sodium hydroxide solution to the solution in sulphuric acid and estimation of the evolved ammonia. Acetic acid analysis necessitated a more complicated procedure and the sulphuric acid was neutralized with sodium carbonate so that the solution contained only sodium hydrogen sulphate and acetic acid. The latter was then distilled, under partial vacuum, into a known amount of standard alkali, the

Table 4d

Hittorf cation transference results in sulphuric acid (112, 129)

Solute	Molality ^d	t_c	t_a	t	Reference
LiHSO_4	0.5562	0.015	0.012	0.013	112
NaHSO_4	0.7918	0.022	0.020	0.021	112
KHSO_4	0.6244	0.030	0.030	0.030	112
	1.2262	0.025	0.025	0.025	112
AgHSO_4	0.2490	0.028	0.024	0.026	112
	0.3056	0.022	0.022	0.022	112
NH_4HSO_4	0.4766	0.031	0.030	0.030 ₅	129
	0.7836	0.036	0.031	0.033 ₅	129
	0.9780	0.034	0.040	0.037	129
$\text{CH}_3\text{CO}_2\text{H}$	0.5723	0.022	0.022	0.022	129
$\text{Ba}(\text{HSO}_4)_2$	0.1738	0.009	0.009	0.009	112
	0.1969	0.009	0.009	0.009	112
	0.2073	0.009	0.007	0.008	112
	0.2292	0.010	0.009	0.010	112
	0.2418	0.008	0.007	0.008	112
	0.3062	0.008	0.008	0.008	112
	0.5391	0.005	0.005	0.005	112
	0.7981	0.004	0.004	0.004	112
$\text{Sr}(\text{HSO}_4)_2$	0.2111	0.008	0.007	0.007	112
	0.2788	0.008	0.007	0.007	112
	0.5819	0.005	0.004	0.005	112
	0.8247	0.003	0.003	0.003	112

t_c are transference numbers determined from analysis of the cathode compartment.

t_a " " " " " " " " " "

t is the mean of t_c and t_a .

d. molality is moles per kg of solvent

excess of which was titrated with standard hydrochloric acid. The transference numbers obtained in both these studies are given in table 4d.

The techniques by which these data were obtained can be criticized on the following counts:

- 1) The changes in concentration during a Hittorf experiment are invariably small and consequently the reliability of the results is strongly dependent on the sensitivity of the analytical techniques employed. The very low cation transference numbers in sulphuric acid result from very small differences between initial and final concentrations, and correspondingly low precision is to be expected. On the the assumption that each analysis is accurate to 0.1% (and consequently an overall inaccuracy of 0.2% per run), the writer has calculated that the uncertainty in the concentration changes obtained by Gillespie and Wasif would be between 5 and 10%, depending on the electrolyte and the particular run concerned. The corresponding uncertainties in the transference numbers lie between 0.001 and 0.002. The methods of analysis employed were cumbersome, often involving a complicated series of operations resulting in several possible sources of error, and it is not unreasonable to suppose that the 0.1% uncertainty is an underestimate. Unfortunately the original workers do not state the quantity of solution analysed and it is therefore impossible to make a well-founded estimate of the errors due to weighing, titrations etc.
- 2) The difference in the transference numbers obtained by analysis of the changes that take place in the anode and cathode compartments, t_a and t_c respectively, is on average 0.002 - 0.003 and is for one system, NH_4HSO_4 , as high as 0.006. Not only does this rather poor agreement lead to appreciable uncertainty in the overall transference number but it also casts further doubts on the reliability of the analytical techniques.
- 3) It is uncertain whether the products of the electrode reactions complicate the analyses. On the basis of the experiments described in chapter six, part I, of this thesis, the formation of colloidal sulphur and the discharge of hydrogen would be expected in the cathode compartment. It is possible that the anodic process in the other electrode compartment leads to the discharge of oxygen and

the formation of sulphur trioxide, which would almost certainly re-dissolve causing appreciable volume and density changes.

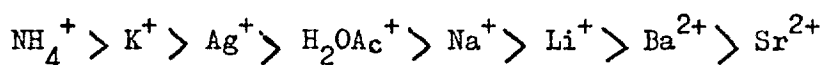
4) No solvent corrections were applied to the data by the original workers.

However, the concentrations employed were high (> 0.25 molal, $> 0.46M$) and the self-dissociation of the solvent was severely repressed. The writer has calculated, using approach B (see p. 89), that at 0.25 molal the solvent correction has a 1.1% effect on the transference number of the silver ion (a change of 0.0003) and at higher concentrations the effect is even smaller.

The results of these Hittorf measurements are compared later with the moving boundary data obtained in the present work. It is worth pointing out, at this stage, that the concentrations employed in the Hittorf technique are necessarily much higher than those in the latter because of the analytical difficulties discussed above.

The decrease in the transference number of the barium, strontium and potassium ions with increasing concentration, obtained by Gillespie and Wasif, was attributed to the effects of the increasing viscosities of the solutions. If the molecular rotations involved in the proton transfers of HSO_4^- are influenced to a lesser extent than the cation mobility by a rise in viscosity, then the cationic transference number would be expected to fall. It may be noted that the viscosity of ammonium hydrogen sulphate solutions is almost constant (perhaps because of a structure - breaking effect) and that the transference number of the NH_4^+ ion rises with increasing concentration.

Before a strict comparison of the transference numbers of the various different ions can be made, they should all be measured at the same concentration. The results in table 4d suggest that, at a given concentration, the cation transference numbers would decrease in the sequence,



It is therefore probable that the sequence of increasing solvation is the inverse order.

Densities and molar volumes of solutions

Two sets of measurements of the densities of solutions in sulphuric acid have been reported (61, 124). Since solutions in sulphuric acid are most conveniently made up by weight, accurate density data are essential for the calculation of molarities and normalities. Concentrations have been expressed in the literature in three different sets of units as follows.

<u>Symbol</u>	<u>Name</u>	<u>Unit</u>
w	molon	moles of solute per kg of solution
m	molal	moles of solute per kg of solvent
c	molar	moles of solute per dm ³ of solution

The concentrations are inter-related as follows,

$$c = wQ \quad (4 - 69)$$

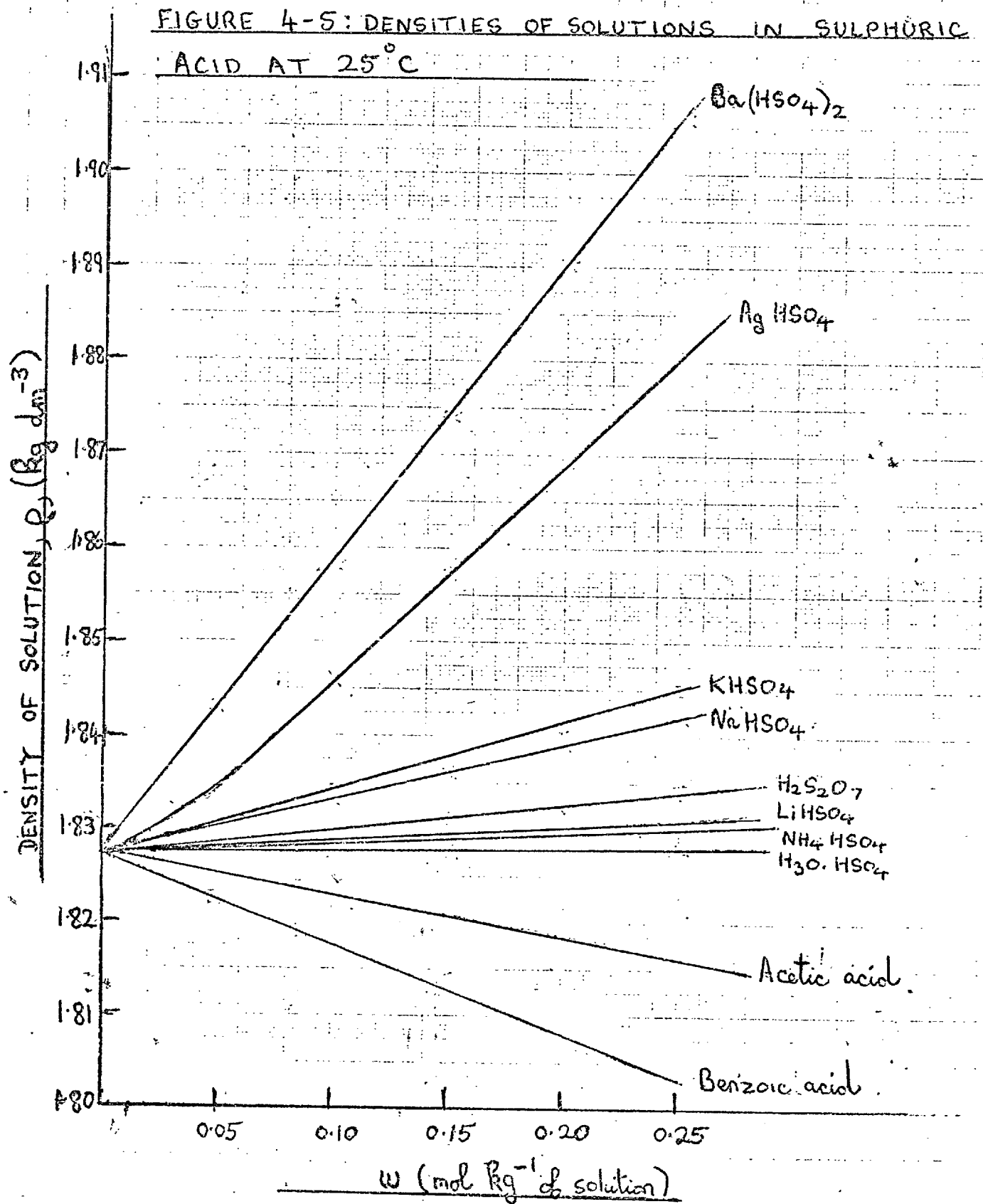
where Q is the density of the solution in kg dm⁻³, and

$$w = \frac{1000m}{1000 + mW} \quad (4 - 70)$$

where W is the molecular weight of the solute.

Figure 4-5 shows plots of the available density data for solutes of particular relevance to the present thesis. The density of the pure solvent is 1.8269 kg dm⁻³ (124) at 25°C. All solutions of MHSO_4 and $\text{M' (HSO}_4)_2$ show increases in density relative to the pure solvent which are approximately proportional to the concentration of solute. The increases are greater for $\text{M' (HSO}_4)_2$ than for MHSO_4 at the same equivalent concentration and this suggests that densities reflect the extent of cation-solvent interaction. Solvation of cations involves electrostriction and hence volume contraction. Large organic solutes such as benzoic acid cause decreases in density on dissolution, presumably due to disruption of the hydrogen - bonded network of the solvent (structure - breaking). Solutions of NH_4HSO_4 show only small changes in density relative to pure H_2SO_4 , indicating that the NH_4^+ cation fits closely into the structure of the solvent and does not significantly alter the extent of hydrogen-bonding.

FIGURE 4-5: DENSITIES OF SOLUTIONS IN SULPHURIC ACID AT 25°C



Density changes of solutions are commonly interpreted by means of two derived quantities:

1) The partial molar (or molal) volume, $\bar{V}_a$, of a component, a, in a solution present at molality m defined by

$$\bar{V}_a = \left(\frac{\partial V}{\partial m_a} \right)_{T, b, c, \dots} \quad (4-71)$$

in which V is the volume of the solution. The concentrations of other components of the solution, b , c , etc., and the temperature are kept constant.

2) The apparent molar (or molal) volume of the solute, ϕ_v , defined by

$$\phi_v = \frac{V - V_0}{m} \quad (4-72)$$

where V is the volume of an m molal solution (i.e. one containing m moles of solute in 1 kg of solvent) and V_0 is the volume of 1 kg of solvent. The partial and apparent molal volumes of the solute are related (2) by

$$\bar{V} = m \frac{\partial \phi_v}{\partial m} + \phi_v \quad (4-73)$$

It has been standard procedure to use the partial molar volumes in the volume correction to moving boundary transference number measurements (see chapter one) but Gwyther (23) has recently shown that ϕ_v should be used. It is usual, in aqueous solutions, to calculate ϕ_v at different concentrations and to extrapolate ϕ_v against $m^{\frac{1}{2}}$ to $m = 0$ to obtain $\bar{V}^0$.

A convenient method of calculating ϕ_v from density data is obtained by combining (4-69), (4-70), and (4-72) to yield

$$\phi_v = \frac{W}{\rho^0} + 10^3 \left\{ \frac{1}{\rho} - \frac{1}{\rho^0} \right\} / w \quad (4-74)$$

where W is the molecular weight of the solute, ρ is the density of the solution and ρ^0 that of the solvent. Flowers, Gillespie and Robinson (124) have performed such calculations for solutions in sulphuric acid, based on their own density

Table 4e

Apparent molal volumes in sulphuric acid ($\text{cm}^3 \text{mol}^{-1}$)

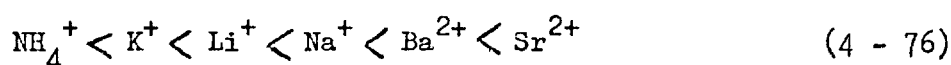
<u>Solute</u>	<u>ϕ_v</u>	<u>ϕ_v^+</u>	<u>$\bar{v}^+ (\text{H}_2\text{O})$</u>	<u>δv</u>
LiHSO_4	47	-7	-7.0	-8
NaHSO_4	46	-8	-7.5	-10
KHSO_4	53	-1	1.7	-7
AgHSO_4	53	-1	-7.0	-5
NH_4HSO_4	59	5	-	-3
$\text{H}_3\text{O}^+\text{HSO}_4$	61	7	12.0	-1
$\text{Sr}(\text{HSO}_4)_2$	87	-21	-30.2	-27
$\text{Ba}(\text{HSO}_4)_2$	96	-12	-24.3	-19
$\text{H}_2\text{OAc}.\text{HSO}_4$	96	42	-	-
$\text{H}_2\text{OBz}.\text{HSO}_4$	149	96	-	-

measurements. At concentrations below $w = 0.1$ they were unable to measure the densities with sufficient precision to yield reliable values of $(1/\rho - 1/\rho^0)$ and at concentrations between $w = 0.1$ and $w = 0.5$ they were unable to demonstrate any significant dependence of ϕ_v on concentration. No determinations of $\bar{V}^0$ were therefore carried out.

If the assumption is made (124) that the apparent molal volume of the HSO_4^- ion is the same as the molal volume of the sulphuric acid molecule (54 cm^3), then the apparent molal volumes of the cations, ϕ_v^+ , are given by

$$\phi_v^+ = \phi_v - 54 \quad (4 - 75)$$

This assumption is valid if the HSO_4^- ion is unsolvated and causes little disturbance in terms of the extent of hydrogen bonding, to the structure of the solvent on dissolution. Values of ϕ_v^+ calculated on this basis are given in table 4e where the corresponding partial molal volumes of the cations in water, calculated by Couture and Laidler (130) from derived relations between $\bar{V}^+$ and the ionic radii, are also stated. The values of $-\delta V$ are the contractions produced in the sulphuric acid by the cation and were determined (124) by subtracting the volume of the bare cation from ϕ_v^+ . The cations were assumed to be spherical and their volumes were calculated from their crystallographic radii. It is reasonable to suggest that the greater the contraction produced, the greater is the extent of ion - solvent interaction. If this is the case the order of increasing solvation of the ions is



which is the same order as was obtained by Flowers et al. (69) from determinations of $\lambda_{\text{HSO}_4^-}$ and by Gillespie and Wasif (112) from transference measurements, except that the positions of Li^+ and Na^+ are reversed.

Viscosities of solutions

Viscosities of sulphuric acid solutions have been measured by Gillespie and Wasif (61). The solvent itself has a high viscosity (24.54 centipoise at 25°C, 27.6 times that of water), and most solutes cause larger increases in viscosity than in their corresponding aqueous solutions. Figure 4-6 shows viscosity - concentration plots for a number of solutes.

It is usual to express relative viscosities, η / η^0 , where η is the viscosity of the solution and η^0 that of the solvent, in terms of the well-known Jones-Dole equation (41)

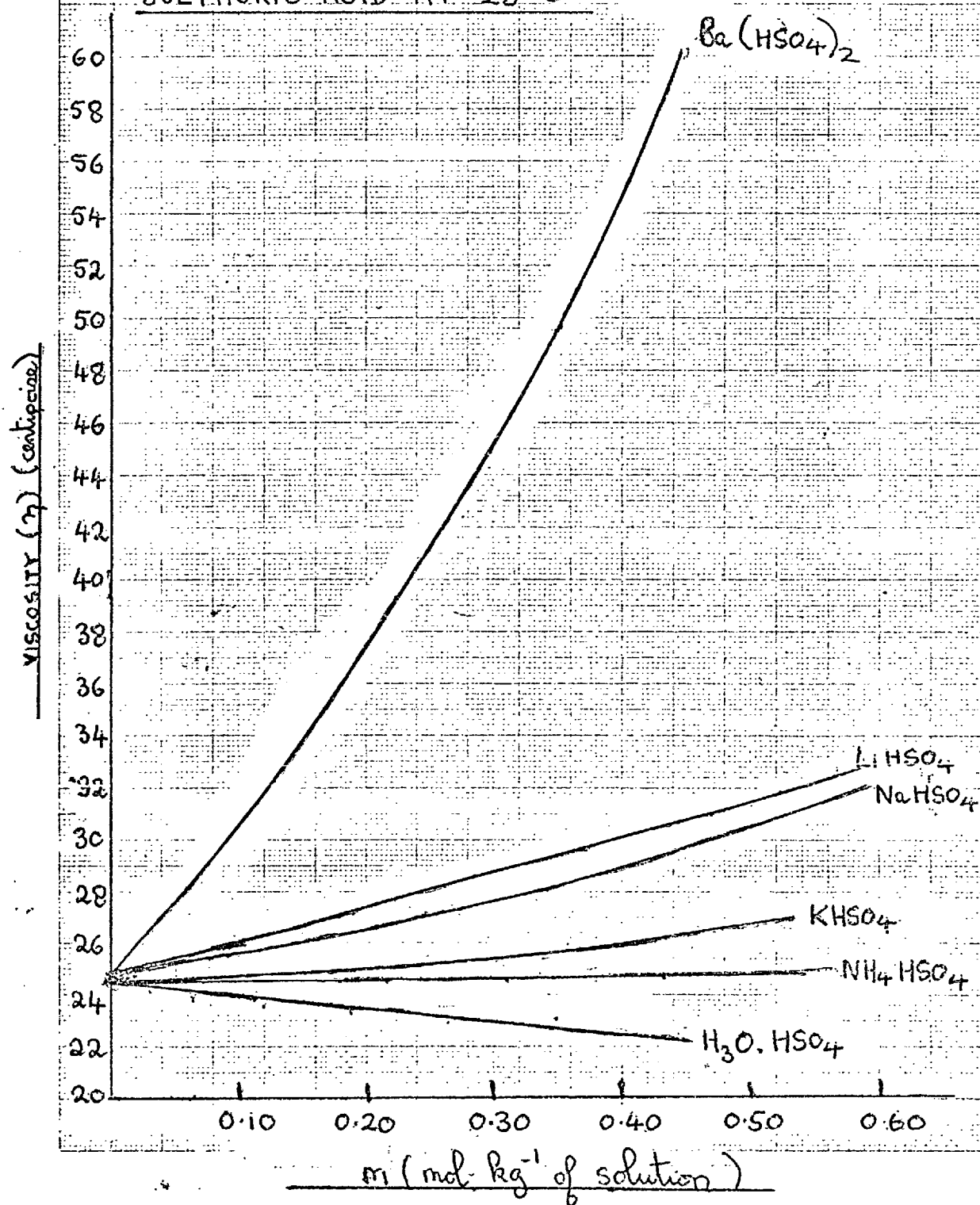
$$\eta / \eta^0 = 1 + A c^{\frac{1}{2}} + B c \quad (4 - 77)$$

A is a positive computable parameter that allows for ionic atmosphere effects and is of such a magnitude in sulphuric acid as to make $A c^{\frac{1}{2}}$ negligible. The quantity, B, is an empirical constant, values of which for sulphuric acid solutions and aqueous solutions are as follows (50)

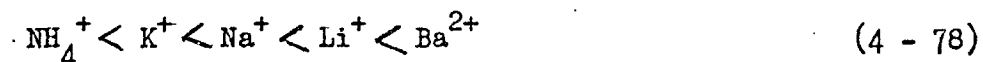
<u>Solute</u>	<u>B (kg mol⁻¹)</u>	
	<u>H₂SO₄</u>	<u>H₂O</u>
H ₃ O.HSO ₄	-0.4	0.07
NH ₄ HSO ₄	-0.1	-0.01
KHSO ₄	0.2	-0.007
NaHSO ₄	0.8	0.09
LiHSO ₄	1.0	0.15
Ba(HSO ₄) ₂	4.4	0.22

If the HSO₄⁻ ion is taken as having a negligible effect on the solvent viscosity, then the above values in sulphuric acid may be attributed to the effects of the cation on the solvent structure. It is generally believed (131)

FIGURE 4-6 : VISCOSITIES OF SOLUTIONS IN
SULPHURIC ACID AT 25°C



that ion - solvent interaction leads to positive values of B whereas negative values imply structure - breaking. The extents of solvation of the cations are then seen to increase in the order



which is the same order as Flowers et al. found from conductance calculations.

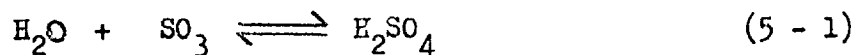
The apparent molar volume and B coefficient for $\text{H}_3\text{O}^+.\text{HSO}_4^-$ suggest that the H_3O^+ ion exerts a net structure - breaking effect in sulphuric acid.

CHAPTER FIVE

THE PREPARATION OF PURE SULPHURIC ACID

In Chapter four, it was pointed out that the neutralization point of the titration of an acid solution of SO_3 with a basic solution of H_2O , in sulphuric acid, corresponds to the composition 100% H_2SO_4 . This chapter is concerned with the practical details of the preparation of the pure solvent by this reaction. The method adopted was fundamentally the same as that of Gillespie and Wasif (88) and Gillespie, Oubridge and Solomons (67) but differed in the design of the conductivity cells, the stirring arrangements and the initial strength of the commercial oleum used as a source of sulphur trioxide. The reader's attention will be drawn to these differences at the appropriate points in the following account. The preparation could be conveniently represented by the following series of stages.

I. Distillation of sulphur trioxide, from a commercial cleum, into Analar sulphuric acid (the composition of which is approximately 98% H_2SO_4 , 2% H_2O) until all the water had been taken up by the reaction



and SO_3 was in excess.

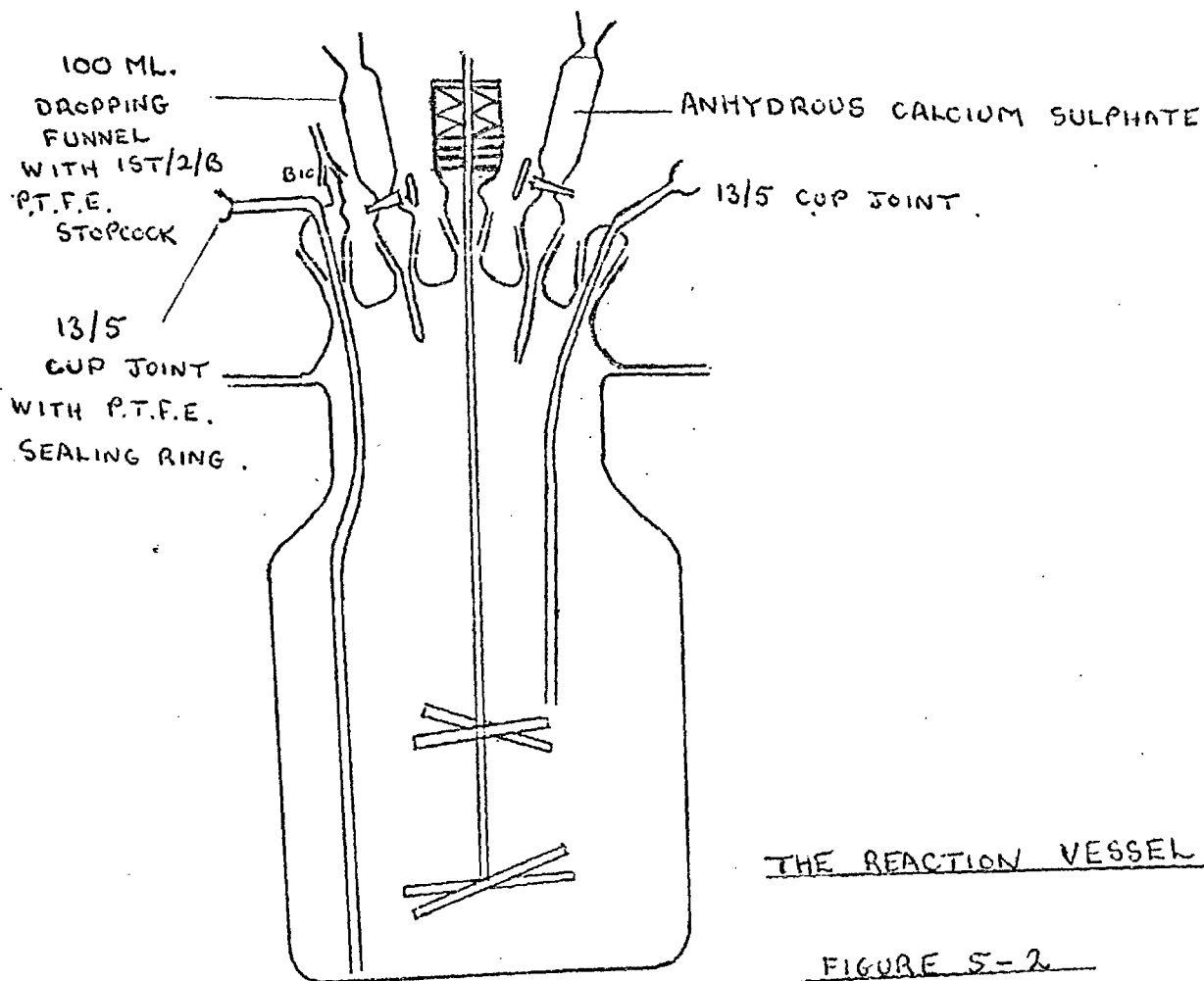
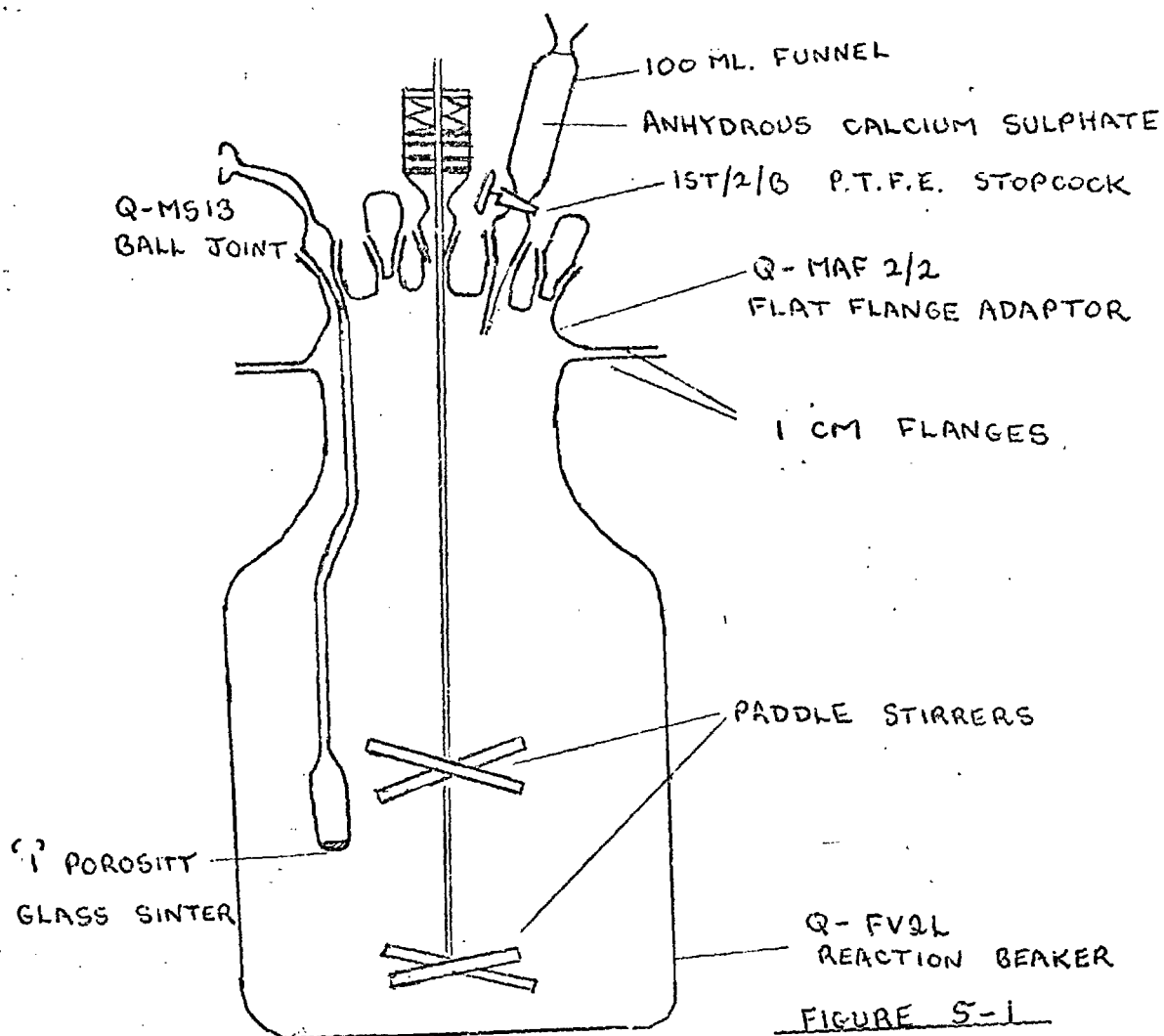
II(a). The weak oleum obtained in stage I was titrated with Analar sulphuric acid, at 25°C , until a minimum in the specific conductance of the solution ($0.010432 \text{ ohm}^{-1}\text{cm}^{-1}$) was obtained.

II(b) Further addition of Analar acid until the specific conductance of the 100% acid ($0.010439 \text{ ohm}^{-1}\text{cm}^{-1}$) was reached.

III. Transfer of the acid to an air-tight blackened vessel to ensure that no changes in its composition occurred on storage.

The reaction vessel.

Steps I and II, above, were carried out in the reaction vessel shown in figures 5-1 and 5-2. It was simply a 2-litre pyrex beaker the rim of which was a circular ground glass flange, 1 cm in width. Its lid was an adaptor consisting of five B19 sockets and a flange identical with that on the beaker. The two flanges, lubricated with a few drops of Analar sulphuric acid, were held firmly together

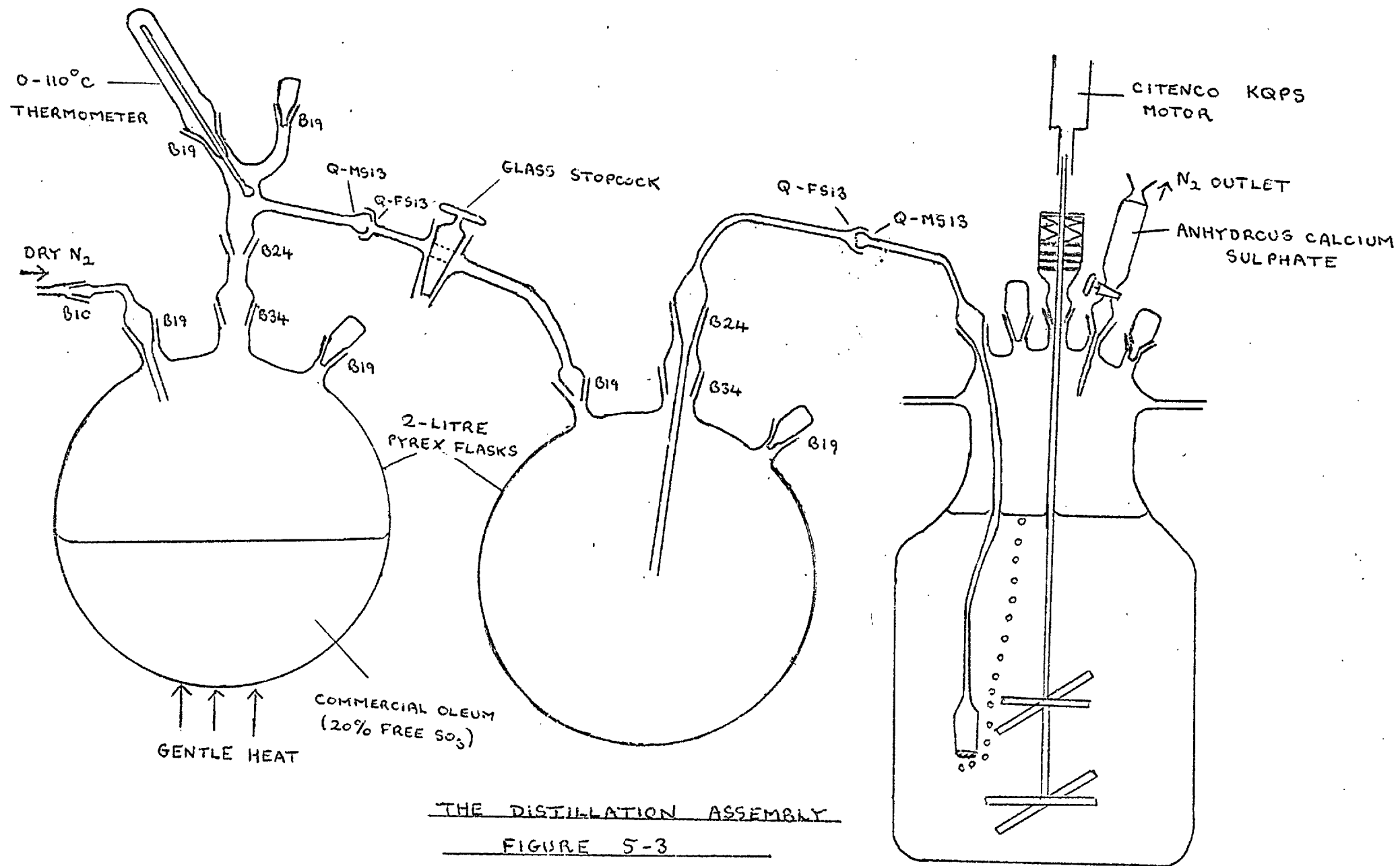


in a light circular aluminium cage to form a pressure-tight seal. Figure 5-1 shows the reaction vessel with the accessories necessary for the distillation stage whilst figure 5-2 is appropriate to the titration assembly. The function of the glass sinter was to disperse the sulphur trioxide, which was carried over in a stream of dry nitrogen, into small bubbles to increase reaction efficiency. The anhydrous calcium sulphate guard tube excluded moisture and provided an outlet for the nitrogen and unreacted SO_3 . The Q-MS13 ball was a Quickfit ground glass joint but the 13/5 cups were Sovirel Rotulex joints which formed pressure-tight seals with 13/5 ball joints when a P.T.F.E. sealing ring was employed. The more expensive Rotulex joints were preferred since they have greater flexibility and required no lubricant other than the sealing ring but the Quickfit joint was used in the distillation since a P.T.F.E. aerosol lubricant (see below) was already being used in other joints in this set-up. Both types of joint required strong metal clips to hold ball and cup firmly together. The centre socket of the lid carried a Sovirel, 4-588-07 stirrer. This was particularly suitable in the present work since it provided pressure-tight stirring without the requirement of an external lubricant which would almost certainly have been a source of contamination in the presence of the highly corrosive SO_3 . The pressure-tight seal was maintained by four P.T.F.E. sealing chevrons between the stirrer shaft and the glass walls. These were held firmly in place with a spring, a washer and a polyamide screwed plug. The stirrer shaft was made of ground glass and carried, at its base, pyrex paddles in the reaction mixture. The diagram on p.39 of the Sovirel catalogue shows this arrangement in three dimensions. Different stirrer motors were employed for the distillation and the titration assembly and are described below as appropriate. All the B19 cones and sockets were lubricated with a few drops of the Analar acid and were held firmly together with glass hooks and metal springs.

Stage I : Distillation.

Previous distillations have been reported (88,67) in connection with the preparation of pure sulphuric acid but no practical details were given. Gillespie and Wasif (88) distilled sulphur trioxide from an oleum containing 65% free SO_3 under reduced pressure whilst Gillespie, Oubridge and Solomons (67) warmed a similar oleum at atmospheric pressure. No oleum of this strength was available for the present work and one containing 20% free SO_3 supplied by Fisons Ltd., was used instead. Since the boiling point of sulphur trioxide is 44.8°C (59) it was only necessary to warm the oleum to generate a plentiful supply. A slow steady flow was maintained by using a current of dry nitrogen as a carrier gas for the sulphur trioxide. The absorption of sulphur trioxide by sulphuric acids of different strengths has been discussed by Pearce (132) who states that optimum absorption conditions are achieved in the azeotrope containing 98.3% H_2SO_4 which is the composition of the Analar acid.

The distillation assembly employed here is shown in figure 5-3. The intermediate 2-litre flask was incorporated, as a safety trap, to ensure that explosive contact between the warm oleum and the Analar acid would be avoided in the event of the latter sucking back due to some arrest or blockage in the flow of dry nitrogen. During the course of the distillation, some liquid sulphur trioxide condensed in this flask but, when gently warmed, it soon boiled and was absorbed in the usual way. The reaction mixture in the 2-litre beaker was stirred at a speed fast enough to give efficient mixing and yet not so fast that vibrational strain in the assembly was produced. The Sovirel stirrer was driven by a Citenco KQPS motor. Apart from the flanges and the B19 necks of the lid of the reaction vessel, where Analar acid was used, all the joints of the apparatus were lubricated with a Hilflon P.T.F.E. aerosol which consisted of finely dispersed particles of P.T.F.E. in a petroleum solvent. The last-mentioned evaporated quickly when sprayed on to ground glass joints to leave a thin dry P.T.F.E. film

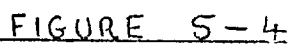


which formed an excellent inert seal . The use of a film lubricant, however, was limited to the gas phase since it was readily removed by contact with liquids. Leakage of sulphur trioxide from any of the joints was easily spotted by the readiness with which it combines with water vapour in the air to form dense white sulphuric acid fumes. That the absorption reaction was efficient could be deduced from the almost complete absence of these fumes when one of the stoppers was removed from the reaction vessel.

The course of the first few distillations carried out was monitored by measuring the conductances of samples taken from the reaction mixture at intervals of 20 minutes. The desired free sulphur trioxide content of the oleum obtained by the absorption reaction was governed by two factors. First, it should have been sufficiently weak in SO_3 to require only a relatively small amount of Analar acid (200-300 ml per 1500 ml of the weak oleum) to bring the composition to 100% H_2SO_4 . Second, it should have been sufficiently rich in SO_3 to maintain the composition on the oleum side of the pure acid after allowance for the absorption of atmospheric moisture during modification of the reaction vessel for the titration assembly. A steady distillation at $40-60^\circ\text{C}$, for about $2\frac{1}{2}$ hours, into 1500 ml of initially 98% acid was found to give the optimum strength of product. At this point the nitrogen flow was stopped, the heating was ceased and, when no more bubbles emerged from the sinter, the reaction vessel and contents were transferred to the titration assembly (see fig. 5-7).

The conductivity cell.

This is shown in figure 5-4. Its design was such that it could be filled and emptied under pressure of dry nitrogen without exposing the solutions to the moist atmosphere. Apart from the P.T.F.E. double oblique IDO/2/B stopcock and the electrodes, the cell was made entirely of pyrex glass. The doubly bent capillary, within which most of the resistance of the solution was contained, had an internal diameter of 2 mm. The bright platinum electrodes were supplied by Johnson Matthey and Co., and had cross-section areas of 1 cm^2 each.



The resistance, R , of the conductivity cell containing a solution is related to the latter's specific conductance κ_{soln} by

$$R\kappa_{\text{soln}} = \ell/a \quad (5 - 2)$$

where ℓ/a is the cell constant. In order that the specific conductances of the sulphuric acid solutions could be calculated from the measured resistances, it was necessary to calibrate the cell with a solution for which κ was accurately known. Such a solution is 0.1 demal aqueous potassium chloride which contains one tenth of a gram molecule of KCl per cubic decimetre of solution at 0°C (133). However it is more convenient to make up this solution by weight, and Robinson and Stokes (134) have stated that its composition is 7.4191 g of KCl per 1000 g of solution and its specific conductance, at 25°C is $1.2856 \times 10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1}$. Two batches of this solution were prepared, quite independently, and the resistances were 37,142 ohms and 37,135 ohms corresponding to values for ℓ/a of 477.5 cm^{-1} and 477.4 cm^{-1} respectively. The agreement of these values to within 0.025% was considered satisfactory and within the limits of experimental error usually associated with conductance measurements.

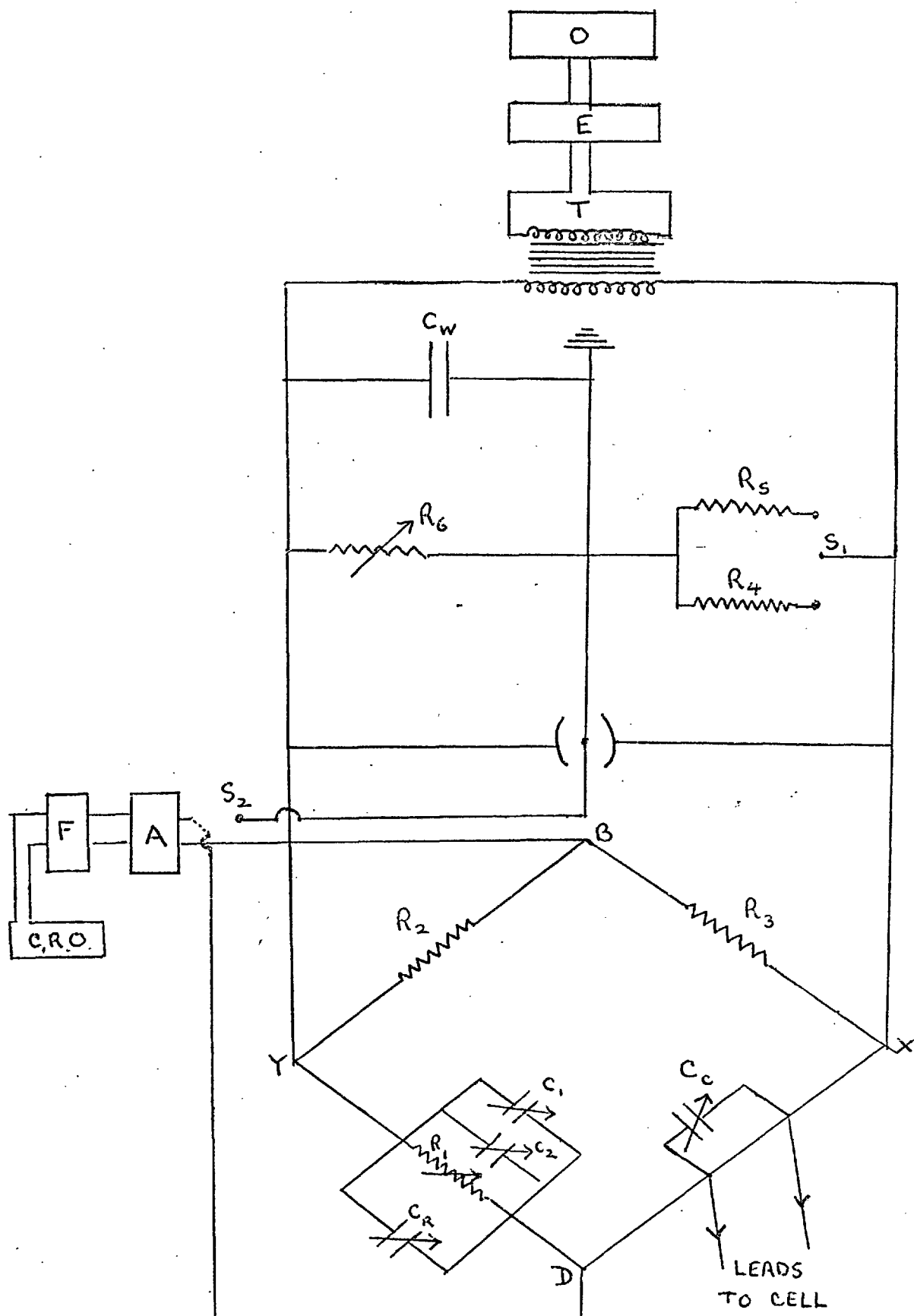
The measurement of resistances

The resistance of the conductivity cell and contents was measured using the alternating current bridge whose circuit is shown in figure 5-5. It was built by O.D.E.S. Ibrahim (135) based on the design of Draper, whose thesis (136) should be consulted for the principles of operation and fuller specifications of the functions of its various components. Its most notable feature is a simple Wagner earth to improve the sharpness of the balance point. Only its use to measure resistances of the order of 10 000 - 50 000 ohms, encountered in the present work, will be described here. The following settings were found to give maximum sensitivity for unknown resistances of this order.

$$R_2 = R_3 = 1000 \text{ ohms}$$

$$\text{A.C. frequency} = 2\text{kHz}$$

$$C_1 = C_2 = 0$$



THE ALTERNATING CURRENT BRIDGE

FIGURE 5-5

Table 5aComponents of the A.C. bridge (see figure 5-5)

R_1 , Sullivan 6-dial decade box (0 to 99 999.9 ohms)

R_2 and R_3 , Sullivan ratio arms

R_4 = 10 000 ohms , R_5 = 1000 ohms

R_6 , Pye 5-dial decade box (0 to 9 999.9 ohms)

S_1 and S_2 , Yaxley switches

O , Advance variable frequency oscillator (type J1)

E , Sullivan decade attenuator (600 ohms)

T , Sullivan balanced and screened transformer

C.R.O. , Telequipment cathode ray oscilloscope (type D43)

C_w , Sullivan air condenser (C. 8591S), 61pF

C_1 , Sullivan mica decade condenser (C. 2099) , $1\mu\text{F}$

C_2 , Sullivan air condenser (C. 500D) , 1290pF

A , amplifier

F , filter (parallel - T)

C_c , Sullivan air condenser (C. 8551S), 390pF

Oscilloscope sensitivity = 0.2v per cm , with $\times 10$ Y gain = 0.02v per cm

The balancing procedure was as follows :

- 1) R_1 and C_R were set to values for which the signal on the C.R.O. screen was a minimum. This was an approximate first balance. The S_2 switch was in the dotted position in figure 5-5 whilst this operation was carried out.
- 2) S_2 was thrown to the Wagner earth position and a balance, corresponding again to minimum signal on the C.R.O. screen, was obtained by adjustment of R_6 and C_w .
- 3) S_2 was thrown back to its original position and a more sensitive balance was obtained by simultaneous balancing of the bridge and the Wagner earth for both capacitance and resistance as in steps 1) and 2).

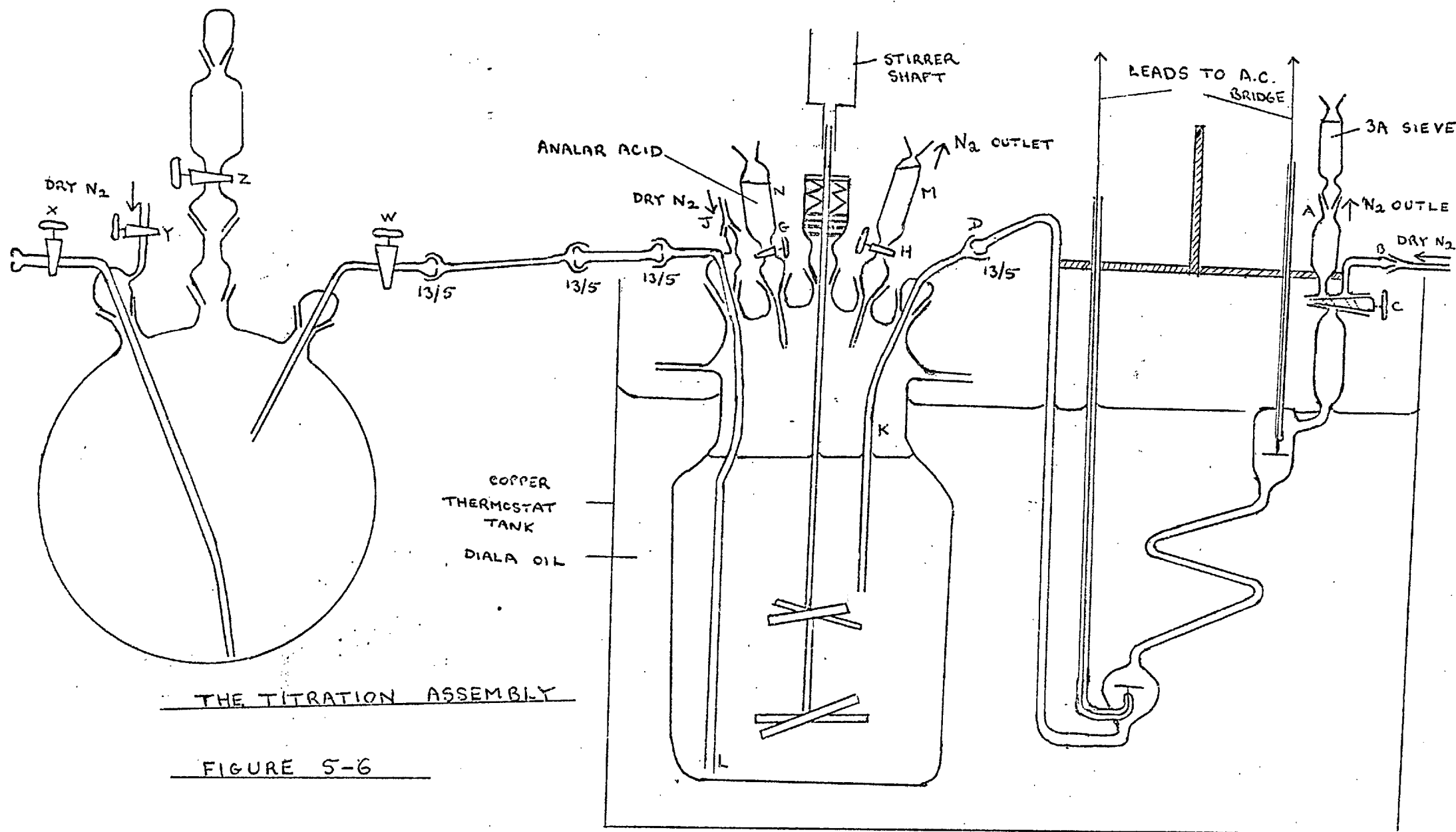
The resistance of the cell was given at the balance point by

$$R = \frac{R_3 R_1}{R_2} \quad (5 - 3)$$

A sensitivity of $2 \text{ in } 10^5$ (0.02%) was achieved and the precision of the measurement was checked using standard resistances. The applied signal was not greater than 0.5v r.m.s. so as to minimise heating effects by the electrical energy dissipated in the solutions. The specific conductance, κ_{soln} , of the solution was obtained from (5 - 2).

Stage II: Titration

The titration assembly is shown in figure 5-6. Its three basic components, the storage flask, reaction vessel, and conductivity cell were all linked in such a way that solution could be transferred from one to another without exposure to atmospheric moisture. This was achieved by the use of interconnecting glass tubes carrying Rotulex 13/5 flexible ball and cup joints with P.T.F.E. sealing rings, and Springham's IST/2/B P.T.F.E. stopcocks to regulate the flows of solution and dry nitrogen. The reaction vessel carried the accessories shown in figure 5-2 and discussed at the beginning of this chapter. The conductivity cell has been described above and the storage flask is shown in greater detail in figure 5-8. All cones and sockets were held together with hooks and springs



THE TITRATION ASSEMBLY

FIGURE 5-6

whilst stainless steel spring clips were used for ball and cup joints. The guard tubes on the storage flask and conductivity cell contained Linde molecular sieve 3A which had previously been heated for several hours at 360°C in an electric furnace through which ultra - dry nitrogen from a liquid nitrogen source was passing. The nitrogen used to transfer solutions in the titration assembly was obtained from a cylinder (British Oxygen 'OFN') and was dried by passing it through several towers containing the freshly regenerated 3A sieve. A three - speed gearbox on a 1:1 ratio setting, linked to a d.c. motor and Servomex MC 43 controller and attached to a paddle stirrer via a hollow vertical stainless steel shaft, enabled the reaction mixture to be stirred at 200 r.p.m. The reaction vessel and conductivity cell were thermostated in a copper tank containing Shell Diala oil. The temperature was accurately maintained at 25°C by a mercury - toluene thermoregulator similar to the one used in the tank for the moving boundary measurements to be described in the next chapter.

Analar acid was added to the weak oleum obtained after distillation and the course of the reaction was monitored by measuring the resistance of samples of the solution which were transferred from the reaction vessel to the cell. In order that the acid was not prematurely transferred to the storage flask the arrangement, for the inlet of nitrogen, shown below was devised.

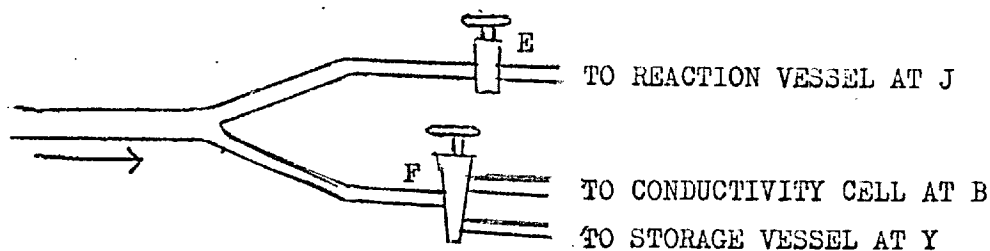


FIGURE 5-7

The titration procedure was as follows.

- 1) All taps were initially closed except for Y and W which were open throughout.
- 2) A small amount, usually less than 5 ml, of Analar acid was admitted from N by opening G . The displaced nitrogen above the solution was allowed to escape through M by opening H. G was then closed and a few minutes were allowed to

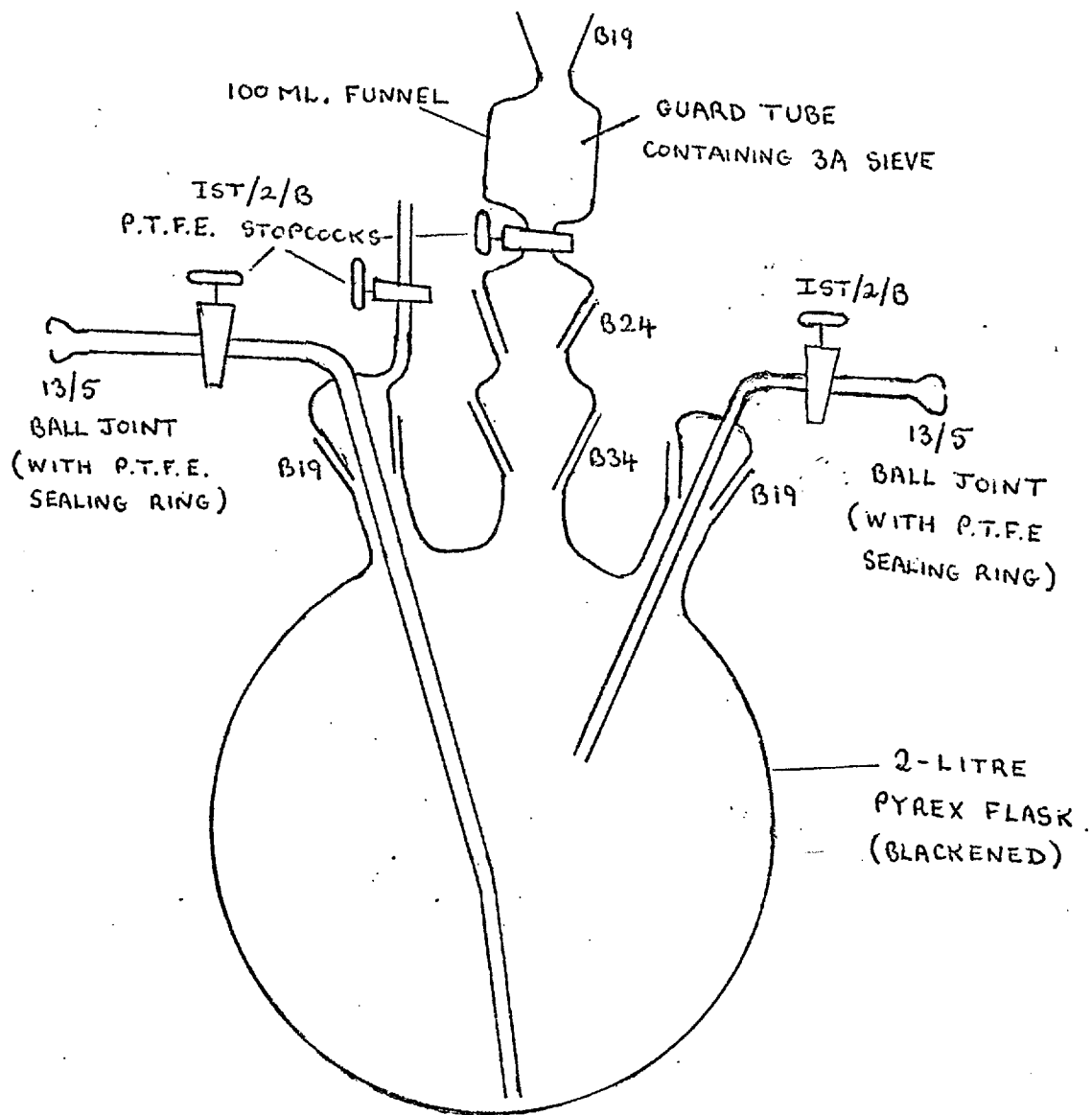
elapse to ensure complete mixing.

- 3) Tap E (see fig. 5-7) was opened, F was opened to Y and nitrogen was admitted to the reaction vessel through J and L, and allowed to escape through H and M.
- 4) Tap C was opened to A, H was closed and solution was then transferred to the cell through K under the pressure of nitrogen built up in the reaction vessel.
- 5) When the level of liquid in the cell was just above the level of oil in the tank, C was closed and H was opened thus releasing the pressure above the solution
- 6) The resistance of the cell was measured using the A.C. bridge.
- 7) Tap E was closed and F and C were both opened to B so that nitrogen was admitted to the cell and the sample of solution was returned to the reaction vessel.
- 8) When the cell was empty, C and F were both closed.
- 9) Steps 3) to 8) were repeated until the same resistance was obtained on successive fillings of the cell. The first two fillings served only to wash the cell with solution and it was necessary to fill and empty the cell some three to four times to achieve the required reproducibility of the resistance.
- 10) If the solution did not have the maximum resistance corresponding to the minimum conductance ($\kappa = 0.010432 \text{ ohm}^{-1} \text{ cm}^{-1}$, $R = 45\,763 \text{ ohms}$) a further addition of Analar acid was made, steps 3) to 9) were repeated and the new resistance was measured. When an addition caused a fall in resistance the titration was continued with 1 ml aliquots of Analar acid until the conductance of the 100% acid ($\kappa = 0.010439 \text{ ohm}^{-1} \text{ cm}^{-1}$, $R = 45\,730 \text{ ohms}$) was reached whereupon the transfer to the storage vessel described below was carried out.

Stage III. Storage

The method of transferring the 100% acid to the storage vessel was as follows

- i) Taps Y and H were closed, E and Z were opened and F and C were both opened to B. The pressure built up by the nitrogen now entering the reaction vessel through F and K forced the acid through tube L into the storage flask.
- ii) When the transfer was complete all the taps were closed and the nitrogen



THE STORAGE FLASK

FIGURE 5-8

was turned off at the cylinder.

The storage vessel is shown in detail in figure 5-8. The cone and socket joints were all lubricated with P.T.F.E. sleeves supplied by Fisons Ltd. It was found that the acid, which was initially colourless, gradually turned yellow on standing and, after several days, its conductance was found to have risen slightly. This was thought to be due to a polymerisation reaction yielding disulphuric acid and other higher acids. Fortunately this decomposition did not seem to occur when the flask was painted black suggesting that the reaction was light - catalysed or light - initiated. The acid then remained colourless and its conductance, which was periodically checked, did not change.

CHAPTER SIX

MOVING BOUNDARY MEASUREMENTS IN PURE SULPHURIC ACID

PART I : EXPERIMENTAL

The preparation of solutions

Solutions of ammonium hydrogen sulphate and all the metal hydrogen sulphates, except $\text{Ba}(\text{HSO}_4)_2$, were obtained by dissolution of the appropriate Analar sulphates. These were carefully dried as follows:

$(\text{NH}_4)_2\text{SO}_4$	-	heated at 150°C for two days in an oven and stored under vacuum
K_2SO_4	"	" " " " " " " " " " " " " "
Na_2SO_4	"	" " 180°C " " " " " " " " " " " "
Ag_2SO_4	"	" " " " " " " " " " " " " "

Li_2SO_4 The Analar material was supplied as $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ which was fiercely heated to constant weight in a crucible (ensuring that the weight loss was equal to, or greater than, that corresponding to water of crystallisation). It was stored in a vacuum dessicator and solutions were prepared as soon after drying as possible.

Barium sulphate was not supplied as an Analar material. Preliminary runs in which the final corrected transference number was negative, suggested that the transference number was influenced by the presence of impurities. Attempts were then made to prepare the sulphate by precipitation from Analar BaCl_2 and Analar sulphuric acid in dilute solution. However, co-precipitation of barium chloride could not be avoided and was evidenced by the formation of a trace of AgCl whenever solutions in sulphuric acid of AgHSO_4 and $\text{Ba}(\text{HSO}_4)_2$, obtained from BaSO_4 prepared in this way, were mixed. Finally, pure BaSO_4 was obtained by slow precipitation at 100°C from excess aqueous sulphuric acid and a dilute aqueous solution of barium hydroxide. The last - mentioned was first filtered to remove barium carbonate obtained by reaction with atmospheric carbon dioxide. After filtration and washing, the BaSO_4 was dried in an oven at 700°C for three days and stored under vacuum dessication.

Benzoic acid was supplied as a volumetric standard reagent by Hopkin and

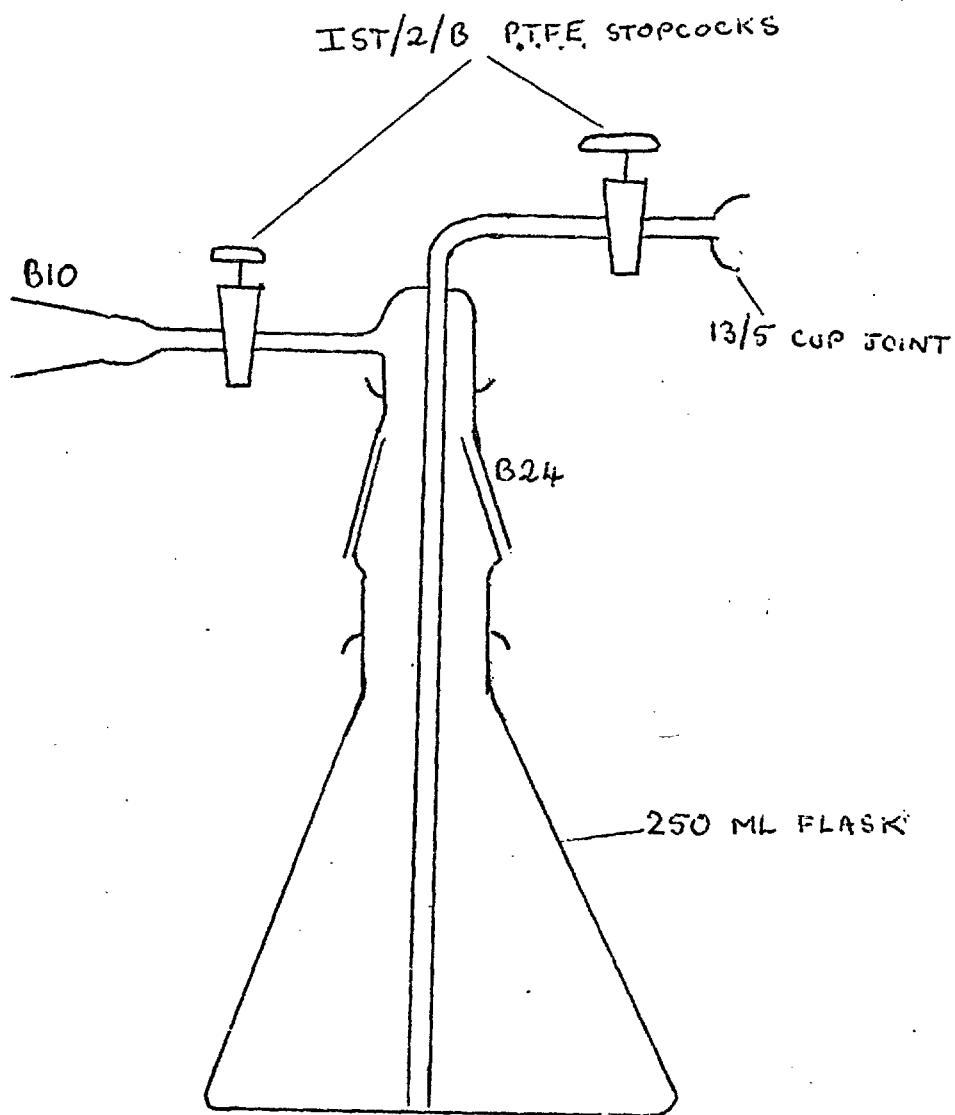
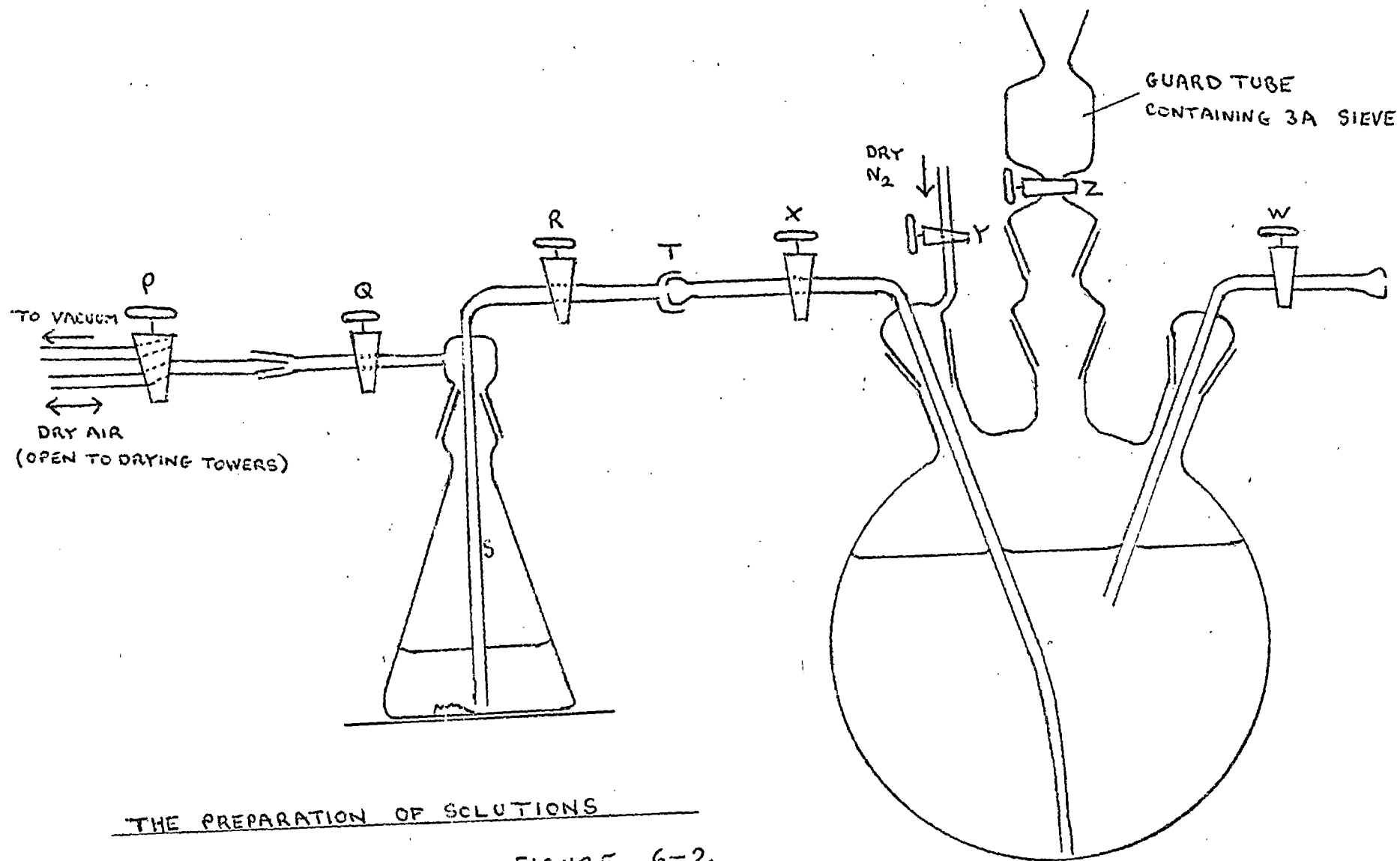


FIGURE G-1

Williams. Although the suppliers guaranteed the dryness of this material, it was stored for several days under vacuum in a dessicator before use. Acetic acid was the Aristar material and water was doubly distilled (conductivity water), the second distillation from alkaline potassium permanganate to remove all oxidizable impurities.

The method of preparation of solutions from all the solutes, except acetic acid and water, was as follows. A quantity of solute was weighed directly into a conical flask such as that shown in figure 6-1. This had been previously cleaned with chromic acid, copiously rinsed with distilled water and doubly distilled water and dried overnight in an oven at 110°C . This cleansing procedure was used throughout for all non-calibrated glassware. Immediately after weighing, a P.T.F.E. sleeve was fitted to the B24 joint and the lid was tightly placed on the flask hooks and springs being used to ensure an air-tight seal. The flask, plus its accessories and contents, was then weighed, after which it was attached to the storage vessel and nitrogen line in the manner shown in figure 6-2., with all the taps initially closed. The remaining stages in the preparation of the solutions were as indicated below.

- 1) Tap Q was opened and P was opened to the vacuum pump so that the flask was evacuated.
- 2) P was switched to the drying towers so that dry air was admitted to the flask
- 3) Y and Z were opened and dry nitrogen was passed over the sulphuric acid in the storage flask.
- 4) Z was closed, R and X were opened and the acid was transferred, under the pressure generated, from the storage flask into the conical flask until the required amount had been taken.
- 5) R, X, Y and Z were all closed. P was switched to the vacuum pump so that mixing of the acid in the tube S with the main body of the liquid was achieved. The solution was shaken to hasten mixing and dissolution.
- 6) P was switched to the drying towers so that dry air was admitted to the flask whereupon Q and then P were closed.



THE PREPARATION OF SOLUTIONS

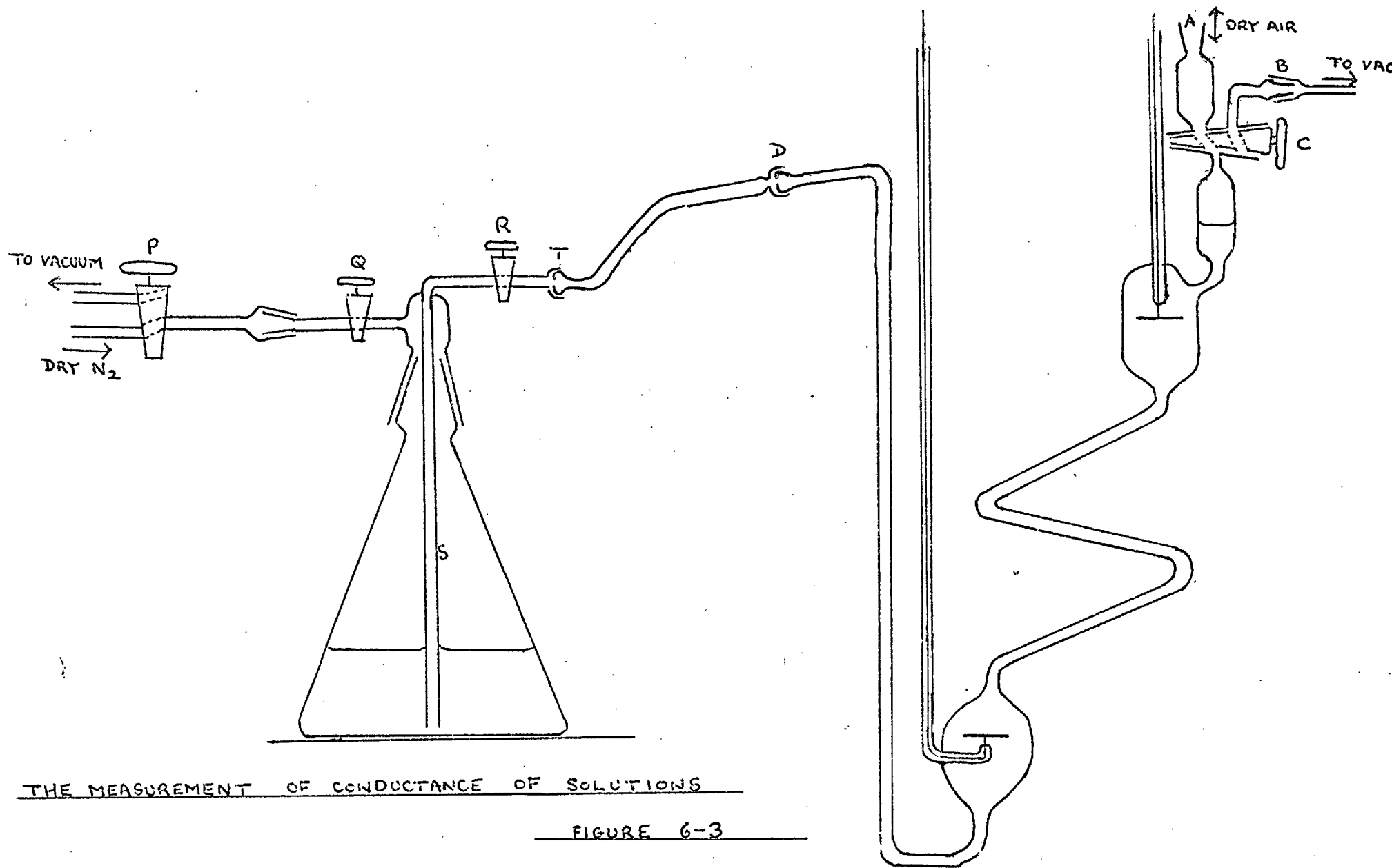
FIGURE 6-2

- 7) The flask and contents were detached from the storage vessel at T and the tube between R and T was copiously rinsed with Analar acetone and dried under suction
- 8) The flask, accessories and contents were re-weighed so that the total mass of solvent, and hence the total mass of solution, could be found. The concentration was then obtained by interpolation of the density data of Flowers et al. (124).

Two procedures were developed for the preparation of solutions of water and acetic acid. Both involved taking a quantity of solvent alone by the above method, placing the flask and contents in a dry bag (A polythene bag which was inflated with dry nitrogen and had glove ports similar to a dry box) and adding the solute directly to the acid. The procedures differed only in the physical state in which the solute was added. One method was to add the required amount of solute from a syringe and quickly replace the lid. However, solute may have been lost due to heat of solution and subsequent evaporation. The second and more satisfactory method was to freeze out a weighed amount of solute in a small stoppered bottle which was then added to the acid in the flask. After replacement of the lid the flask and contents were shaken until the sample bottle and its stopper were separated and thorough mixing of solute and solvent was achieved.

All the methods of preparation of solutions described above ensured no contact between the hygroscopic sulphuric acid and the moist laboratory atmosphere. The solutions, once prepared, showed no change in mass on storage indicating that the seals were air-tight.

It was necessary to measure the specific conductances of the leading solutions employed in the moving boundary runs. Figure 6-3 shows the arrangement for transferring solution to the conductivity cell, which was first filled with dry air by manipulation of tap C between the vacuum pump and the drying towers. The solution had previously been degassed under suction through P, with vigorous



shaking before connection to the cell at D. Taps Q and R were opened, P was switched to the nitrogen line and the cell was filled under nitrogen pressure, allowing the displaced air to escape through A. When the level of solution in the cell was that shown in figure 6-3, all the taps were closed. The cell was detached, sealed at D and immersed in the thermostat at 25°C. The resistance was then measured with the A.C. bridge in the usual way.

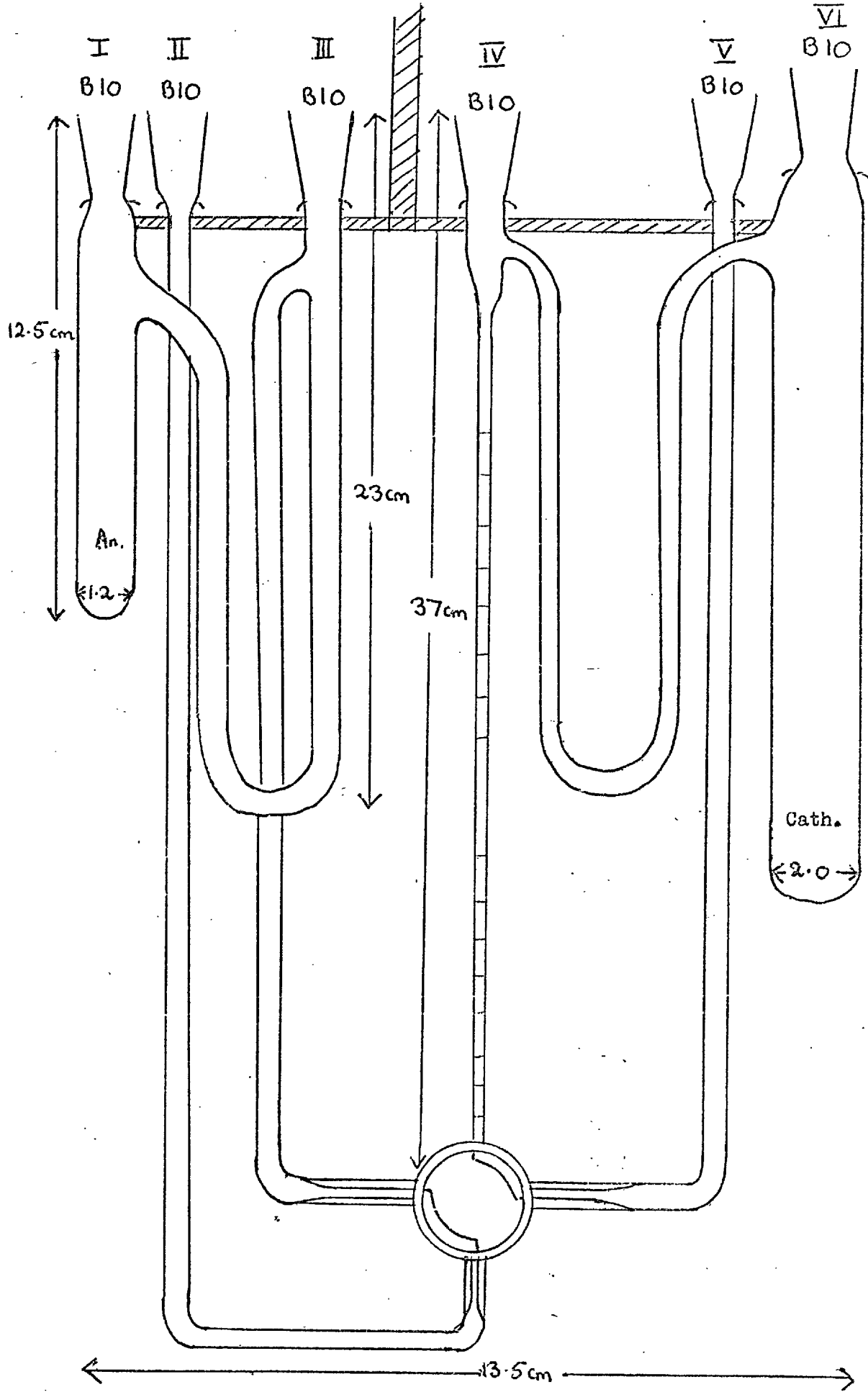
Moving boundary cells

It was stated, in chapter one, that a condition of formation of a moving boundary between leading and indicator solutions is that the lighter solution should be above the heavier one. It will be appreciated that both rising and falling boundaries may be formed in this way depending on the relative densities of the two solutions. In the present work, the condition of ensuring gravitational stability resulted in the observation of both types of boundary and two cells, of different design, were specially made and employed for this purpose.

The rising cell

The cell, which was of the sheared boundary type (4d), is shown in figure 6-4. It was made entirely of pyrex apart from a P.T.F.E. stopcock and all the tubes except the calibrated moving boundary (m.b.) tube and the electrode compartments had an internal diameter of 6mm. The m.b. tube itself had an internal diameter of 2mm and a wall thickness of 1mm.

It has been usual in m.b. cells to employ a suitably lubricated hollow glass tap of the type described by Spiro (4d) and by Notley (137). For sulphuric acid this was not possible since a lubricant, that did not react in some way with the acid, could not be found. The following lubricants were tested and the reasons for their unsuitability are given.



THE RISING CELL

FIGURE 6-4

<u>Lubricant</u>	<u>Reason for unsuitability</u>
Silicone greases	rapidly dissolve in the acid
Vaseline greases	" " " " "
Apiezon greases	react to form a black mass of carbon
Voltalef fluorocarbon greases	slowly dissolve turning brown
Hilflon P.T.F.E. aerosol	leakage of solutions around barrel of tap
P.T.F.E. sleeves into which	" " " " " "
appropriately placed holes	
had been cut.	

It was finally decided that no suitable work could be done with glass taps and four - way P.T.F.E. stopcocks were specially made by G. Springham and Co., Harlow, Essex. It was not possible to make hollow keys similar to the glass ones due to the difficulty of drilling bends in P.T.F.E. The alternative arrangement was that shown in the tap in figure 6-4 in which grooves were cut in the outside of the key. The principal advantage of hollow glass stopcocks is circulation of the thermostat liquid through the key and efficient cooling of the solution inside the cell which is being warmed by Joule heating effects. In the arrangement employed here, the heating of the solutions was minimised, although less efficiently, by having the solution on the outside of the key and in direct contact with the glass barrel. If the solution had been remote from the barrel and contained within the key, the low thermal conductivity of P.T.F.E. would have resulted in very poor heat dissipation.

The moving boundary tube had two sets of eight calibration marks, although only the lower set were used, etched on to it in a manner similar to that described by Notley (137). Before it was sealed into the cell, the tube was coated with a 50:50 mixture of paraffin wax and beeswax. Fine lines were cut in the wax by rotating the tube against a metal scriber, with a very fine point, at the places where the calibration marks were required. The tube was etched by suspending a few drops of a 40% aqueous solution of hydrogen fluoride on the tube where it had been scribed, and slowly rotating it for thirty minutes. The acid

was washed away and the wax was removed by melting. The tube was then cleaned with carbon tetrachloride leaving a series of fine circular lines about 0.01 cm broad. The tube itself was at least eight years old to prevent changes in volume of the glass due to ageing. It was then sealed into the rest of the cell.

In order that the cell could be calibrated with precision, a moving boundary system in which the transference number of the leading non-common ion-constituent is accurately known, was required. Such a system is 0.1N KCl followed by 0.065N KIO_3 in aqueous solution, which has been studied in considerable detail (20, 22, 138-140) and for which $t_{\text{Cl}^-} = 0.5100$. This value, however, is corrected for volume and solvent effects and had to be 'uncorrected' before it could be related to the speed of the boundary. The appropriate value of t_{Cl^-} (uncorr), 0.5108, was then substituted into the equation

$$t_{\text{Cl}^-} = \frac{V F c_{\text{KCl}}}{I t} \quad (6 - 1)$$

and, by timing the boundary between etch marks, the corresponding volumes, V , were accurately determined. The two salts, KCl and KIO_3 , were both Analar materials, twice recrystallised from doubly distilled water, thoroughly dried at 110°C and stored over H_2SO_4 in a vacuum dessicator. A closed cadmium anode and an open AgCl/Ag cathode were employed and, after satisfactory evidence of reproducibility and invariance to current, the following values were obtained:

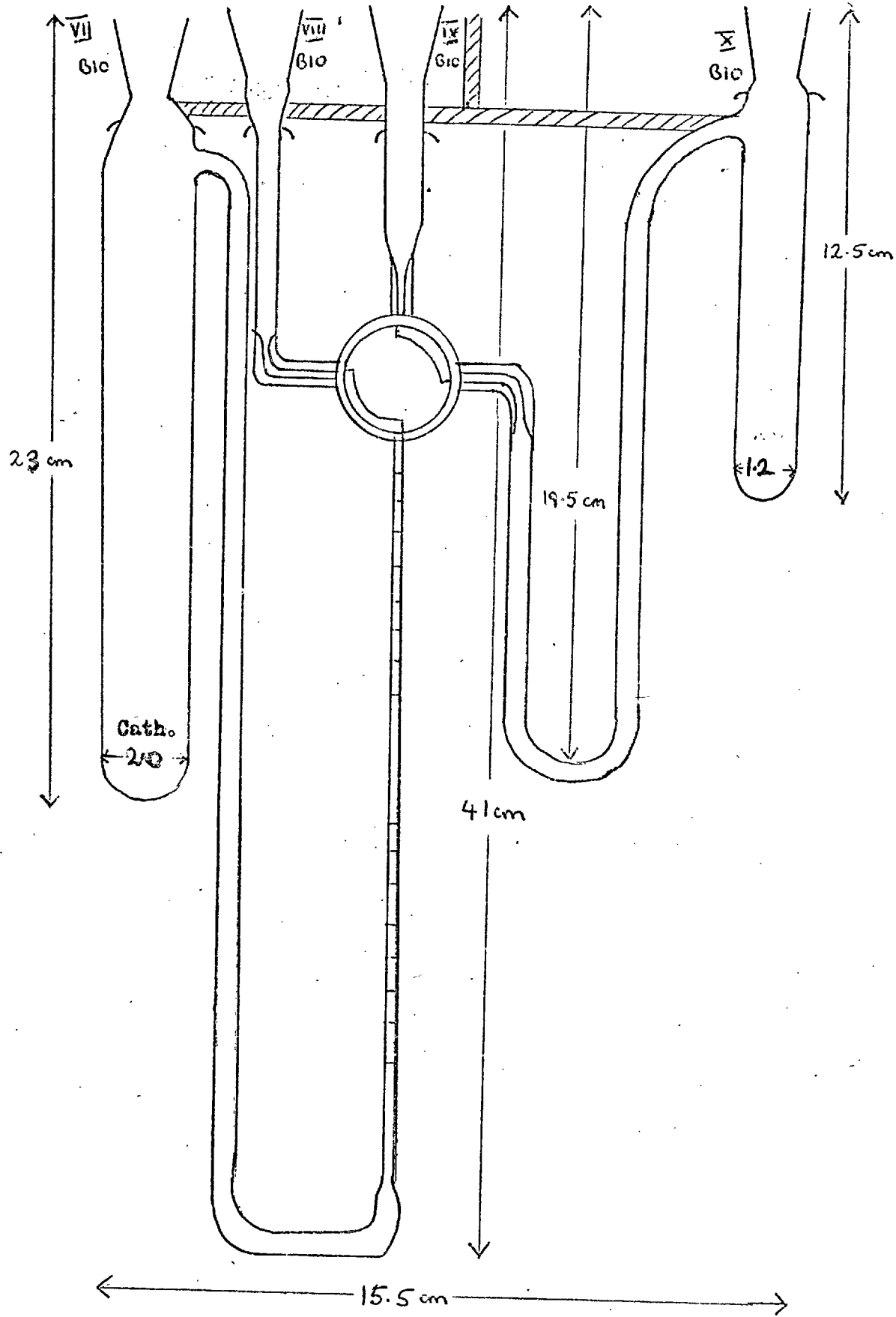
<u>Etch marks concerned</u>	<u>Volume cm^3</u>
1 $\rightarrow$ 5	0.193
2 $\rightarrow$ 6	0.184
3 $\rightarrow$ 7	0.193
4 $\rightarrow$ 8	0.189 ₅
1 $\rightarrow$ 2	0.0546
2 $\rightarrow$ 3	0.0402
3 $\rightarrow$ 4	0.0543
4 $\rightarrow$ 5	0.0436
5 $\rightarrow$ 6	0.0453
6 $\rightarrow$ 7	0.0498
7 $\rightarrow$ 8	0.0509

The etch marks are numbered from the moving boundary tap i.e. in the order in which they were passed by the boundary.

The falling cell

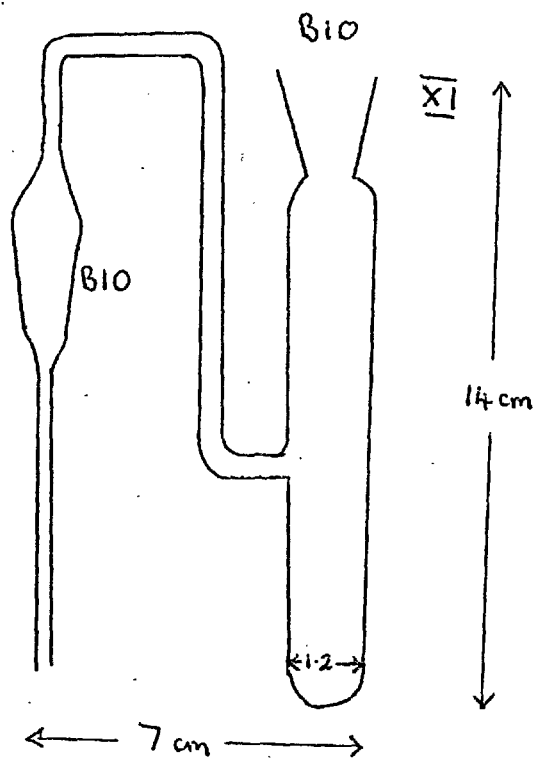
The cell used to study systems where falling boundaries were obtained is shown in figure 6-5. The tube diameters, ground glass joints and P.T.F.E. stopcock are identical with those in the rising cell. An extended anode section, shown in figure 6-6, was fitted in neck X in sulphuric acid runs to ensure that no electrode product reached the boundary. The calibrated tube was etched as before and the calibration was carried out using the system 0.1N KCl/ 0.062N LiCl in aqueous solution for which $t_{K^+} = 0.4900$ and, employing a cadmium anode, $t_{K^+} (\text{uncorr}) = 0.4892$. The lithium chloride used was supplied by B.D.H., specially purified for atomic absorption spectroscopic work. It was dried by fusion in an atmosphere of dry nitrogen and stored under vacuum dessication. The calculated volumes, after satisfactory evidence of reproducibility and invariance to current, were:

<u>Etch marks concerned</u>	<u>Volume cm³</u>
1 → 5	0.204
2 → 6	0.213
3 → 7	0.211
4 → 8	0.218
1 → 2	0.0554
2 → 3	0.0483
3 → 4	0.0509
4 → 5	0.0487
5 → 6	0.0649
6 → 7	0.0464
7 → 8	0.0577



THE FALLING CELL

FIGURE 6-5



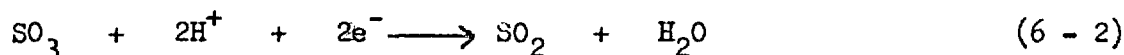
EXTENDED ANODE SECTION

FIGURE 6-6

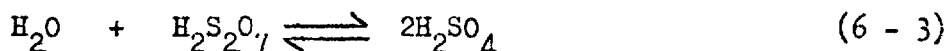
The electrodes

No studies of electrode processes appear to have been carried out in pure sulphuric acid although some cathodic work in oleums (141-144) and in water - sulphuric acid mixtures, primarily in the composition range 85 - 98 % H_2SO_4 (145-149), have been reported.

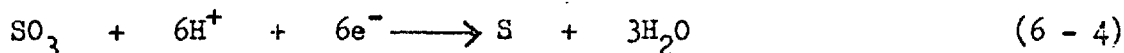
The main conclusion of the oleum studies is that the cathodic reaction at platinum is the reduction of dissolved sulphur trioxide to sulphur dioxide possibly according to



followed by reaction of the water formed with disulphuric acid in oleums,



Some SO_3 is also further reduced to sulphur which forms blue solutions

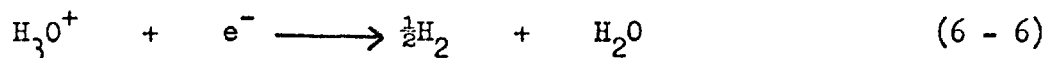


The water once again reacts with $\text{H}_2\text{S}_2\text{O}_7$ to produce H_2SO_4 . These reductions are always accompanied by hydrogen discharge.



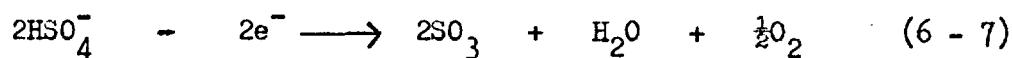
The work in water - sulphuric acid mixtures indicates that it is possible to carry out electroreductions in this medium, but as the proportion of water is reduced, the likelihood of reduction of the acid itself increases. James (145), in 1951, was the pioneer of such studies. He obtained polarographic reduction waves of organic compounds at compositions up to 98% H_2SO_4 beyond which the mercury was chemically attacked by the acid. Other electroreductions, particularly studied in these media, are those of nitrocompounds and the NO/NO^+ couple (146-148). Beck (149) recently concluded that electroreductions can be satisfactorily carried out up to 92% H_2SO_4 , but reduction of the H_2SO_4 molecule is favoured as the proportion of water is gradually reduced further. Cathodic behaviour in the range 85 - 100 % H_2SO_4 was investigated with relation to cathode material and the gradation in discharge potentials with various electrode species followed the usual sequence for hydrogen overpotentials (150). A 'prewave' increased strongly as the pure H_2SO_4 concentration was approached and this was interpreted as the

reduction of solvated SO_3 to SO_2 . At 85% H_2SO_4 the probable electrode reaction was thought to be reduction of H_3O^+ to hydrogen and water



The products of reduction of the acid were thought to be H_2 , H_2S , SO_2 , and colloidal sulphur.

In moving boundary work one of the electrode compartments is open to allow for expansion or contraction of the whole system and the other is closed to permit calculation of the exact volume change occurring. The choice of a suitable open electrode is no problem since any ions produced other than H_3SO_4^+ and HSO_4^- will be very slow and therefore a large or extended electrode section will overcome any tendency of the ions generated to reach the boundary. The choice of a suitable closed electrode is more difficult. The electrode must not 'gas', must be chemically inert, must undergo a known reaction and any ions generated must not reach the boundary during the run. None of the foregoing cathodic work is of value in the search for a closed electrode system in 100% sulphuric acid. Moreover, no anodic studies appear to have been carried out. The writer found that a platinum anode 'gassed' in the pure acid, presumably due to discharge of oxygen and possibly SO_3



or,



The behaviour of a number of possible electrode systems in pure sulphuric acid was investigated with the simple bench cell arrangement shown in figure 6-7. A Farnell stabilised power supply was used to maintain a steady current which was measured with a milliammeter. The test electrode was placed in the extended section shown which had previously been filled to such a level that solution overflowed when the electrode was inserted. In this way any gassing could easily be detected. Where a simple platinum electrode was employed, foil was used in

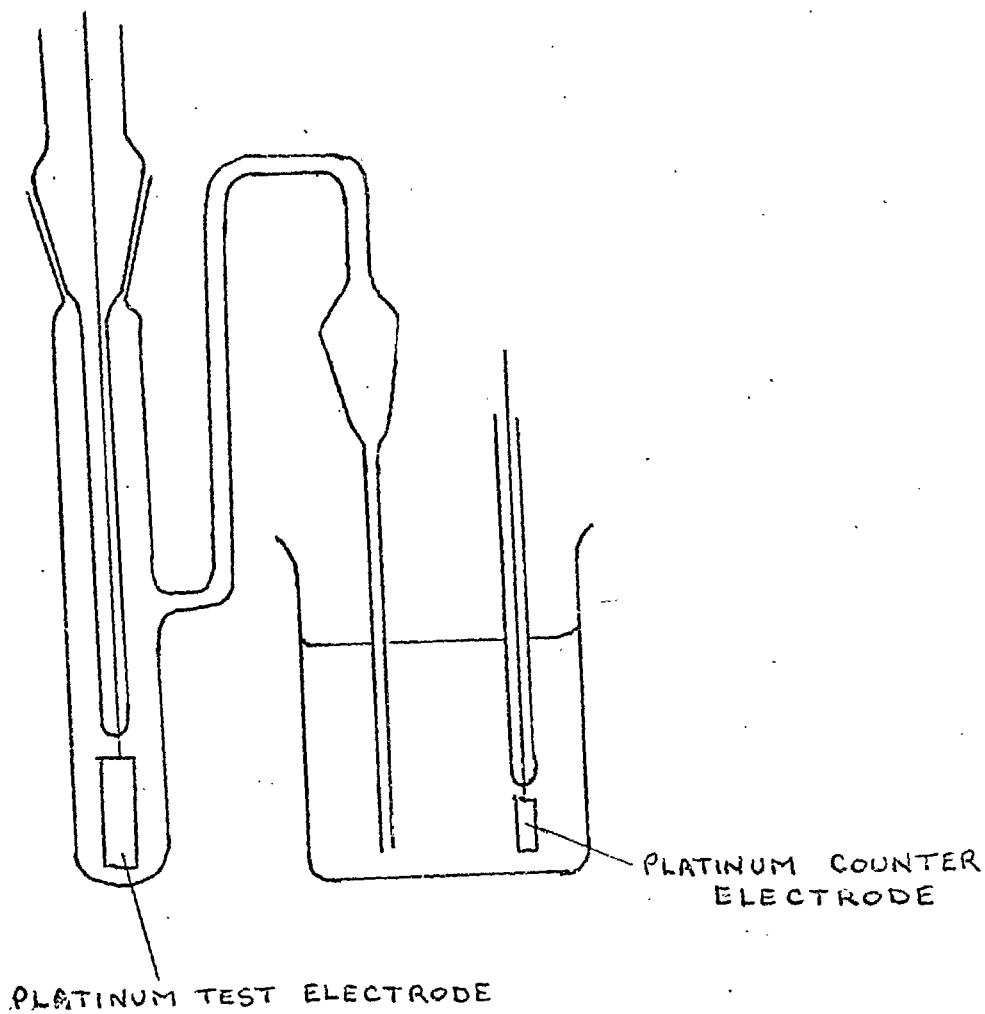
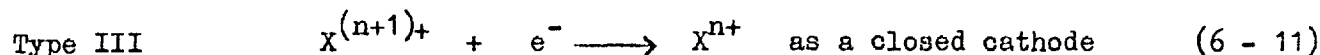
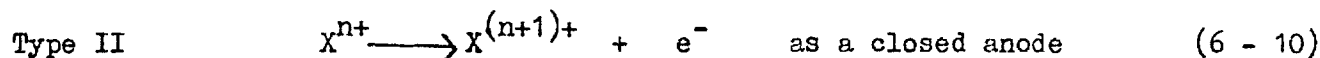


FIGURE 6-7

preference to wire to minimise current density. A platinum counter - electrode was always employed in the solution in the beaker. Four types of electrode reaction



were considered promising, and a variety of chemical substances M and X were investigated.

Type I

A metal was required which was chemically inert with respect to the acid but which was stoichiometrically converted to its ions on the passage of current. The more electropositive metals (alkalis and alkaline earths) are chemically attacked, often explosively, by the acid whilst the least electropositive ones (e.g. Pt, Au) are inert to self - dissolution. Cadmium, thallium, mercury, nickel, lead, copper and silver were thought to be the most suitably placed metals in the electrochemical series for the required behaviour to be feasible. Chemical activity was tested for by immersing a weighed segment of the metal in the acid for two to three days and then re-weighing. Cadmium, lead, nickel, copper and thallium exhibited varying degrees of dissolution and were therefore unsuitable. Although James (145) stated that mercury is attacked by 100% sulphuric acid, the reaction appears to be very slow. However a mercury anode, made by dipping a platinum wire into a pool of mercury, gassed readily due to oxidation of the acid and a crust of $HgSO_4$ was observed. Silver appeared more promising. A piece of silver foil, immersed in the acid for four days, showed no change in weight. Moreover, silver dissolution appeared to proceed without gassing when a platinum electrode heavily coated in silver was used as anode. Gassing commenced when some bare platinum became exposed to the solution and, in an attempt to offset this, the experiment was repeated using a heavier coating of silver but the onset of gassing occurred after the passage of a similar amount of charge. It was therefore concluded that the build -

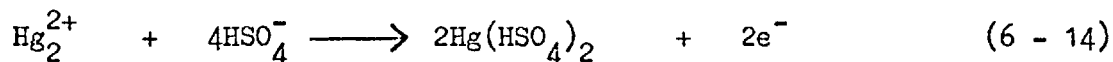
up of silver ions in the vicinity of the electrode was so great that the potential for the required dissolution was greater than the discharge potential for anodic oxidation of the acid. In an effort to reduce the silver ion concentration, a little sodium chloride was initially added to the solution. It was hoped that the HCl and Cl^- generated by solvolysis of the NaCl would facilitate precipitation of AgCl on dissolution of the silver anode. This did indeed occur but two important drawbacks to this electrode system were discovered. First, for complete precipitation of all the silver as AgCl during a typical transference run, an initial concentration of HCl (0.61M) far in excess of its solubility, or else a ludicrously large electrode compartment ($\sim 400\text{ml}$), would be required to provide the required quantity of chloride species. Second, traces of AgCl were seen in the electrode compartment before any current was passed, indicating chemical dissolution. Further reference will be made to this observation in connection with the Ag^+/Ag cathode discussed in a later section of this thesis.

Type II

A species was required which would be oxidized stoichiometrically, and without gassing, at a platinum anode.



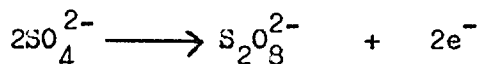
Possible systems such as $\text{Ce}^{\text{III}}/\text{Ce}^{\text{IV}}$, $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$ and $\text{Pb}^{\text{II}}/\text{Pb}^{\text{IV}}$ were all ruled out because of the insolubility of the corresponding sulphates (or hydrogen sulphates). A platinum anode dipping into a solid mass of the lower oxidation state sulphate invariably led to gassing owing to the greater ease with which the acid itself was oxidized. Only Hg_2SO_4 , of the sulphates of metals capable of existing in two positive oxidation states, is even moderately soluble (73), (0.78 mol % solubility). It was thought possible that a feasible process might be



but gassing occurred at a platinum anode dipping into a saturated solution of $\text{Hg}_2(\text{HSO}_4)_2$. With the platinum electrode dipping into a solid mass of this compound, gassing again took place. Thus no suitable electrode, conforming to (6 - 13),

could be found.

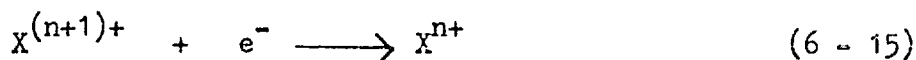
It is well-known that in concentrated aqueous solutions of sulphates, oxidation of sulphate ions to persulphate occurs at a platinum electrode,



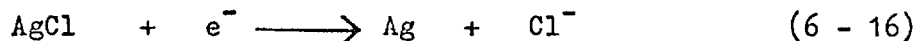
but there is no evidence for the occurrence of this reaction in the pure acid.

Type III

This is the reverse of type II in that a species was required which would be reduced stoichiometrically, without gassing, according to:



Silver chloride is known to be insoluble in sulphuric acid, which suggests that its behaviour as a cathodic material might resemble the reaction undergone in water



An electrode prepared by dipping a platinum wire repeatedly into molten silver chloride was employed as cathode in the usual test apparatus (figure 6-7).

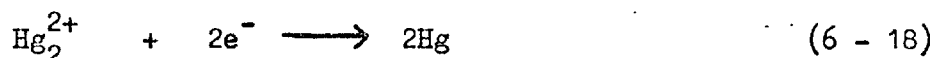
However, gassing readily occurred and colloidal sulphur was formed in the electrode compartment indicating reduction of the acid, accompanied by hydrogen discharge. All the couples involving a single metal in its different oxidation states, discussed above, must be similarly ruled out for solubility reasons when reduction of the higher oxidation state to the lower is considered. A platinum cathode dipping into a solid mass of the higher oxidation state sulphate invariably gassed.

Type IV

One electrode was found which satisfied the non - gassing condition. This consisted of a platinum cathode dipping into a concentrated solution of silver hydrogen sulphate. On passage of current, silver metal was observed to plate out



It is possible that other similar systems might display this behaviour, for example:



is feasible but the limited solubility of mercurous sulphate imposes unsatisfactory limits on the amount of charge which can be passed or necessitates an unreasonably large electrode compartment. Silver sulphate is the most soluble of all the sulphates and the usefulness of this electrode with regard to the amount of charge which can be passed across it is clear.

The reaction at the Ag^+/Ag cathode

In order that the volume correction for this closed electrode can be calculated, the extent of any side reaction, in addition to the reduction of silver ions should be known. The fact that no gassing occurs and no colloidal sulphur is formed suggests that only (6 - 17) is occurring and hydrogen discharge and reduction of the acid are absent.

In several early rising boundary runs (involving NH_4^+ followed by Ba^{2+}) using this electrode, it was observed that some of the deposited silver dropped off the platinum wire during the run. It was therefore decided to weigh the silver to see if the yield was that predicted by Faraday's first law. The theoretical yield in grams, m , is given by

$$m = Q \times 107.9 / F \quad (6 - 19)$$

where Q is the total amount of charge passed in coulombs. The actual yields obtained were :

60 - 70 % of the theoretical yield for rising boundary runs when some silver fell off.
 90 - 93 % of the theoretical yield for falling boundary runs when all the silver adhered.
 Even if the reaction had proceeded completely according to (6 - 17), a yield less than the theoretical would have been expected because:

- 1) The design and geometry of the cells made it very difficult to collect all the silver after the run.
- 2) Although silver foil did not dissolve in the pure acid, finely divided silver is said to dissolve slowly (59) and experiments in which pre-weighed silver grains were allowed to stand in the acid for 2-3 days confirmed this. It was

therefore quite possible that some dissolution occurred in the interval (approx. 20 minutes) between the current being switched off and the silver being removed from the acid prior to washing and weighing.

3) On removal of the silver from the acid it had to be washed with doubly distilled water before being dried and weighed. Considerable heat was generated in this process and this may have enhanced the dissolution of silver.

It was thought probable that the silver plated out on the platinum did not re-dissolve during the run because such a dissolution is an oxidation reaction and the silver should have been cathodically protected. However, if the silver failed to adhere to the electrode, then it might well have re-dissolved. This would explain the different yields obtained in the rising and falling boundary runs. The failure of silver to adhere was later overcome by employing a large area platinum foil as electrode, instead of a single wire, to minimise the current density. Moreover, part of the foil was allowed to lie flat on the bottom of the electrode compartment so that any silver which dropped off the top of the electrode remained in contact and so stayed at the potential of the cathode. Thus it was postulated that the electrode reaction was simply the reduction of silver ions to silver with no dissolution whilst at a cathodic potential. On switching off the current some dissolution was thought to occur before the analysis was carried out. A more reliable procedure than collecting the silver deposited in an actual m.b. run was required and the apparatus shown in figure 6-8 was devised. The glass sinter, clean, dry and empty, and the electrode were both pre-weighed. After passage of a similar amount of charge to that passed in an actual m.b. run, the electrode was removed and plunged into iced water. The sinter was taken out of the beaker and, after removal of the acid solution, quickly placed in an ice bath. Iced water was then poured into the sinter. All the silver no longer attached to the electrode was recovered and transferred to the sinter. After drying, the sinter and contents and the electrode were weighed. This procedure was preferable to the analyses at the end of the transference runs since all the

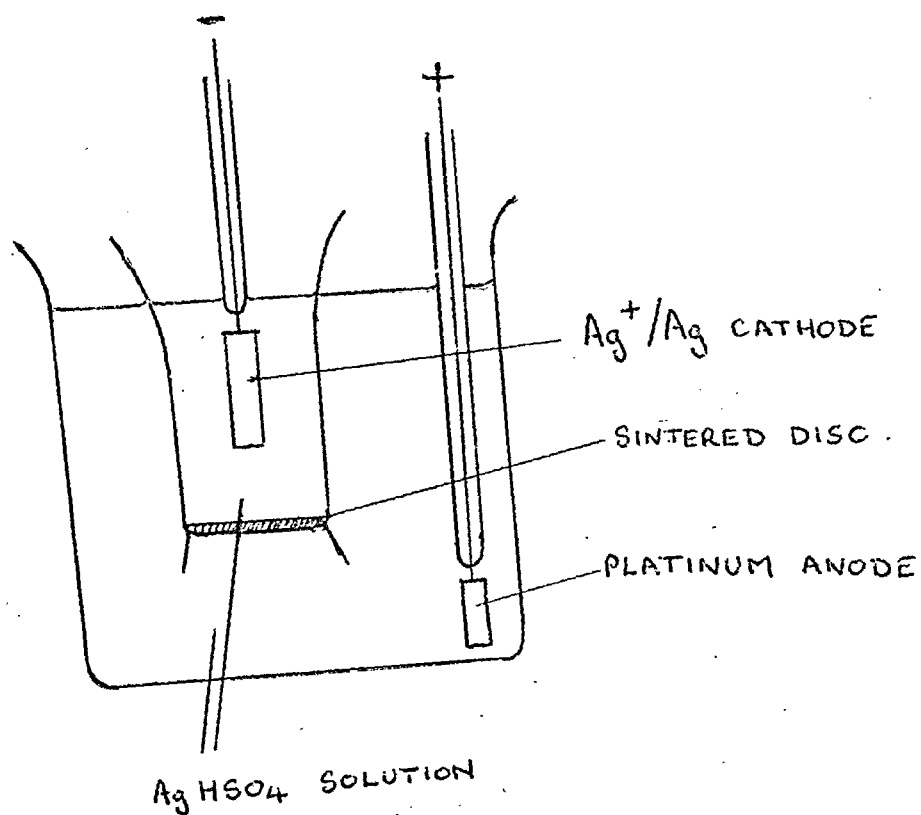


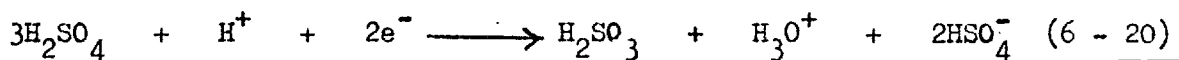
FIGURE 6-8

silver which had not dissolved was recovered, and the swift removal of the electrode from the solution after switching off minimised subsequent dissolution. The use of ice-water and an ice bath minimised the heating effect. Yields of between 90% and 93% were generally obtained by this method. A test for reduction products in the AgHSO_4 solution, removed from the sinter immediately after the current was switched off, was carried out by titration with 0.1N $\text{K}_2\text{Cr}_2\text{O}_7$ solution. After doing a blank titration, reduction products equivalent to 1% of the amount of silver predicted by Faraday's first law were detected. There appears to be no way of deciding whether these products are due to cathodic reduction of the acid or to the reduction of the acid which accompanies dissolution of silver either during or, more likely, after the electrolysis.

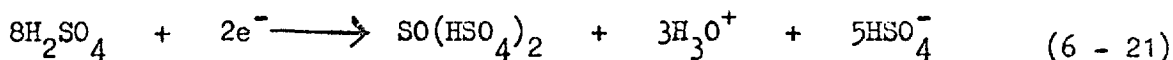
The following conclusions can be drawn from these analyses. It is certain that 93% of the charge passed results in silver plating out on the platinum foil. The remaining 7% may be attributed to one or more of the following:

A Plated silver re-dissolving after the run.

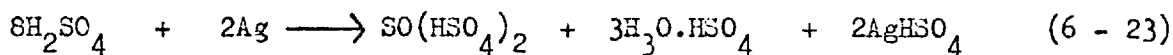
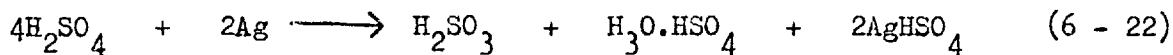
B Reduction of the acid. It is interesting to consider the reaction involved here. One suggestion is



Another is



C Silver plating out and redissolving during the run. The following two reactions are suggested for the dissolution:



The writer considers possibility B the least likely since cathodic reduction in the pure acid is usually accompanied by hydrogen discharge and formation of colloidal sulphur. The oxidation of silver whilst at a cathodic potential, as in C, seems unlikely and A would appear to be the most probable explanation.

The volume change for the Ag^+/Ag cathode

The actual value of ΔV used to compute the volume correction ($c\Delta V$) depends upon which of the suggestions, A, B and C above, is accepted to account for the 'missing' 7% silver.

A Here the volume correction is based simply on 100% reduction of silver ions to silver as in (6 - 17). In chapter one, the volume change appropriate to this reaction, now designated ΔV_{17} , was given as

$$\Delta V_{17} = V_{\text{Ag(s)}} - \bar{V}_{\text{AgHSO}_4} + t_+ \bar{V}_{\text{NH}_4\text{HSO}_4} \quad (6 - 24)$$

The partial molar volumes of the hydrogen sulphates have been given by Flowers, Gillespie and Robinson (124) and are discussed in chapter four of this thesis. The molar volume of silver is $10.3 \text{ cm}^3 \text{ mol}^{-1}$ (153). Insertion of these values into (6 - 24) yields $\Delta V_{17} = -43 \text{ cm}^3 \text{ mol}^{-1}$.

B If the reduction proceeds according to (6 - 20) the volume change in the closed section corresponding to this reaction alone, ΔV_{20} , per faraday passed, is

$$\Delta V_{20} = -2\bar{V}_{\text{H}_2\text{SO}_4} + \frac{1}{2}\bar{V}_{\text{H}_2\text{SO}_3} + t_+ \bar{V}_{\text{NH}_4\text{HSO}_4} + \frac{1}{2}\bar{V}_{\text{H}_3\text{O}^+ \cdot \text{HSO}_4^-} \quad (6 - 25)$$

This expression was derived in the same way as (6 - 24) by considering the changes occurring between the cathode and a reference plane in the leading solution when one faraday passes. No values for the partial molar volume of H_2SO_3 have been given in the literature. Since $\bar{V}_{\text{SO}_3} = 37 \text{ cm}^3 \text{ mol}^{-1}$ and $\bar{V}_{\text{H}_2\text{SO}_4} = 54 \text{ cm}^3 \text{ mol}^{-1}$, an intermediate value of $42 \text{ cm}^3 \text{ mol}^{-1}$ has been chosen for the quantity $\bar{V}_{\text{H}_2\text{SO}_3}$ which, after substitution of the relevant data into (6 - 25), yields $\Delta V_{20} = -56 \text{ cm}^3 \text{ mol}^{-1}$. Now reaction (6 - 20) contributes at most 7% to the overall electrode process and so a maximum numerical value for ΔV is given by

$$\begin{aligned} \Delta V &= \frac{93}{100} \Delta V_{17} + \frac{7}{100} \Delta V_{20} \\ &= -44 \text{ cm}^3 \text{ mol}^{-1} \end{aligned} \quad (6 - 26)$$

If the reduction proceeds according to (6 - 21), then the volume change in the closed section corresponding to this reaction alone, ΔV_{21} , per faraday passed is

$$\Delta V_{21} = -4\bar{V}_{\text{H}_2\text{SO}_4}^{\text{AgHSO}_4} + \frac{1}{2}\bar{V}_{\text{SO}(\text{HSO}_4)_2}^{\text{AgHSO}_4} + \frac{3}{2}\bar{V}_{\text{H}_3\text{O}.\text{HSO}_4}^{\text{AgHSO}_4} + \frac{1}{2}\bar{V}_{\text{NH}_4\text{HSO}_4}^{\text{NH}_4\text{HSO}_4} \quad (6-27)$$

The size of the SO^{2+} ion is probably similar to that of Ba^{2+} and so $\bar{V}_{\text{SO}(\text{HSO}_4)_2}^{\text{AgHSO}_4}$ has been replaced by the value for $\text{Ba}(\text{HSO}_4)_2$ ($96 \text{ cm}^3 \text{ mol}^{-1}$). Substitution of the appropriate data into (6-27) yields $\Delta V_{21} = -74.5 \text{ cm}^3 \text{ mol}^{-1}$. Assuming a 7% contribution from reduction the maximum numerical value for ΔV is

$$\Delta V = \frac{93}{100} \Delta V_{17} + \frac{7}{100} \Delta V_{20} \quad (6-28)$$

$$= -45 \text{ cm}^3 \text{ mol}^{-1} \quad (6-29)$$

C In this case the volume change is based on 100% silver plating and the volume change appropriate if up to 7% of the silver participates in (6-22) or (6-23). The volume changes corresponding to the dissolution of one mole of Ag in each of these reactions are as follows:

$$\Delta V_{22} = -2\bar{V}_{\text{H}_2\text{SO}_4}^{\text{AgHSO}_4} - V_{\text{Ag(s)}} + \frac{1}{2}\bar{V}_{\text{H}_2\text{SO}_3}^{\text{AgHSO}_4} + \frac{1}{2}\bar{V}_{\text{H}_3\text{O}.\text{HSO}_4}^{\text{AgHSO}_4} + \bar{V}_{\text{AgHSO}_4}^{\text{AgHSO}_4} \quad (6-30)$$

$$\Delta V_{23} = -4\bar{V}_{\text{H}_2\text{SO}_4}^{\text{AgHSO}_4} - V_{\text{Ag(s)}} + \frac{1}{2}\bar{V}_{\text{SO}(\text{HSO}_4)_2}^{\text{AgHSO}_4} + \frac{3}{2}\bar{V}_{\text{H}_3\text{O}.\text{HSO}_4}^{\text{AgHSO}_4} + \bar{V}_{\text{AgHSO}_4}^{\text{AgHSO}_4} \quad (6-31)$$

$$\Delta V_{22} = -13.5 \text{ cm}^3 \text{ mol}^{-1}, \quad \Delta V_{23} = -33.5 \text{ cm}^3 \text{ mol}^{-1}$$

Assuming dissolution according to (6-22), the maximum numerical value for ΔV is given by

$$\begin{aligned} \Delta V &= \Delta V_{17} + \frac{7}{100} \Delta V_{22} \\ &= -44 \text{ cm}^3 \text{ mol}^{-1} \end{aligned} \quad (6-32)$$

Similar calculations assuming dissolution according to (6-23) yield a maximum numerical $\Delta V = -45 \text{ cm}^3 \text{ mol}^{-1}$.

Since A is considered a more likely explanation for the 'lost' silver than either B or C, the value of ΔV has been taken as $-43 \text{ cm}^3 \text{ mol}^{-1}$ but the possibility that its magnitude is an underestimate has been remembered in considering the uncertainty in the transference numbers obtained after extrapolation to zero current and application of the solvent and volume corrections

Further uncertainties in ΔV are evident when the changes in silver concentration in the cathode compartment, due to removal of Ag^+ during plating and diffusion effects, are considered. Since the concentration dependences of values of $\bar{V}$ in H_2SO_4 solutions have not been fully studied, no estimates of these uncertainties can be made. However, it would be unreasonable to assume limits to the precision of ΔV less than $\pm 2 \text{ cm}^3 \text{ mol}^{-1}$.

Practical aspects of electrode design

Closed Ag^+ / Ag cathode

The importance of having a platinum foil electrode, part of which sits on the bottom of the electrode compartment, has been discussed above. It is clear that, for the passage of a given amount of charge, the larger the electrode compartment the smaller the initial concentration of AgHSO_4 required. Both the cathode compartments, marked Cath, in figures 6-4 and 6-5, have a volume of $\sim 35 \text{ ml}$ and an initial concentration of 0.35 N was always employed. Sufficient charge to exhaust such quantities of solution of their silver content was never passed. Figure 6-9 shows the platinum electrode employed. Platinum - to - pyrex seals are more prone to leakage than platinum - to - soda glass ones and so a pyrex/ soda graded seal was incorporated as shown.

Open Pt anode

This is shown in figure 6-9. The use of a spiral electrode minimised the current density but, for an open electrode, this is not an important factor and a wire would have sufficed. The most important aspect of the electrode concerns its proximity to the boundary. Extended anode sections, discussed earlier in connection with the moving boundary cells, were important to ensure that no electrode product reached the boundary.

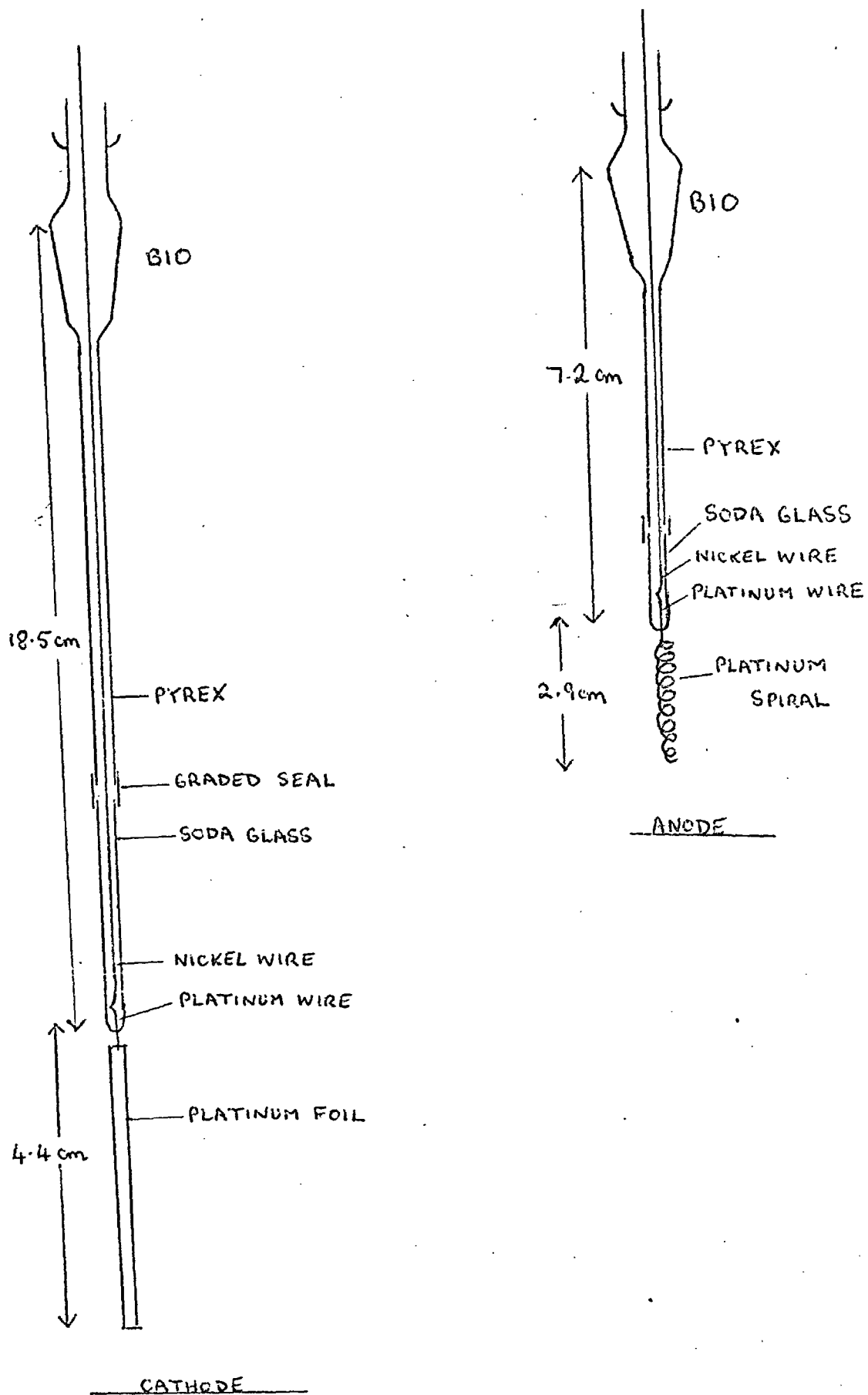
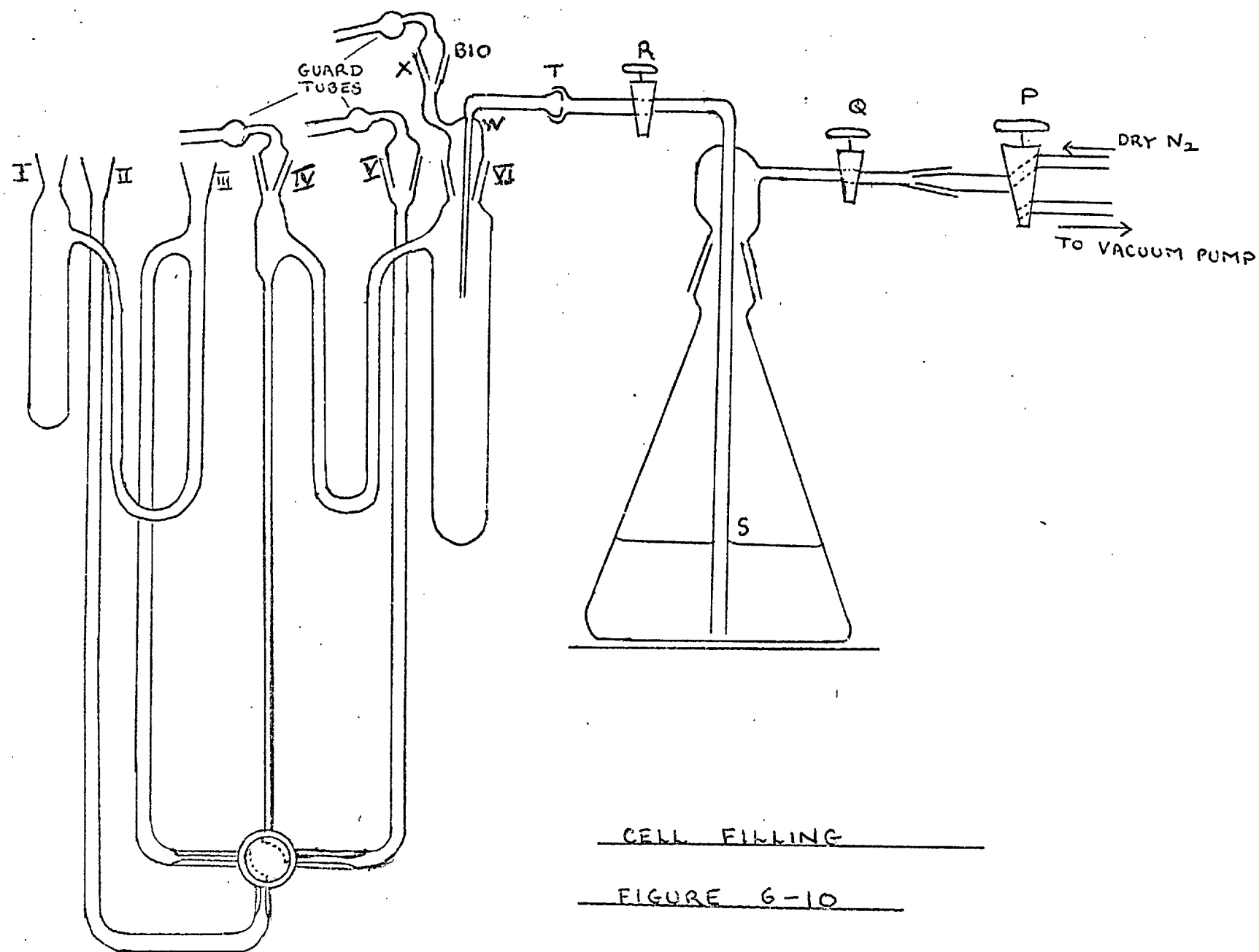


FIGURE 6-9

Cell filling

Before the solutions were transferred to the moving boundary cell they were first degassed. This was done by attaching the flasks to a vacuum pump as shown in figure 6-10 and swirling the solutions around whilst taps Q and P were open and R was closed. The purpose of degassing was to ensure that no dissolved gas came out of solution during the run.

The assembly in figure 6-10 shows the arrangement for filling the cathode compartment of the rising cell with the silver electrode solution ($0.35N \text{ AgHSO}_4$). All the taps were initially closed and dry nitrogen was passed into the cell through V and out through IV and X. The nitrogen was then switched to P, taps Q and R were opened and solution was transferred through S to the cell under the pressure developed above the surface of the solution in the flask. When the cathode compartment was three - quarters full, R and Q were closed and the nitrogen was switched back to V. The transfer device, W, was then removed and replaced by the long platinum cathode shown in figure 6-9, lodged loosely in the neck with a small piece of platinum wire. A clean transfer device was placed in neck V and degassed leading solution was admitted, in a similar manner to that described above, until the U-bend was full and solution overflowed into the electrode compartment. Gas bubbles trapped in the tap were then removed by suddenly 'squeezing and sucking' the solutions with a Pumpette attached to a B10 cone through the joint, X, of the transfer device in V. More leading solution was admitted so that it spilled over into the electrode compartment. Since filling was carried out slowly and the leading solution was always less dense than the Ag electrode solution, the former existed as a layer on top of the latter and very little mixing took place. The platinum wire was removed and the electrode was pushed into its socket so that solution overflowed down the outside of the cell. More leading solution was admitted through V until neck IV was full. The guard tube, containing 3A sieve, was then removed and a long glass stopper was placed in IV so that solution again spilled down the outside of the cell. The electrode



CELL FILLING

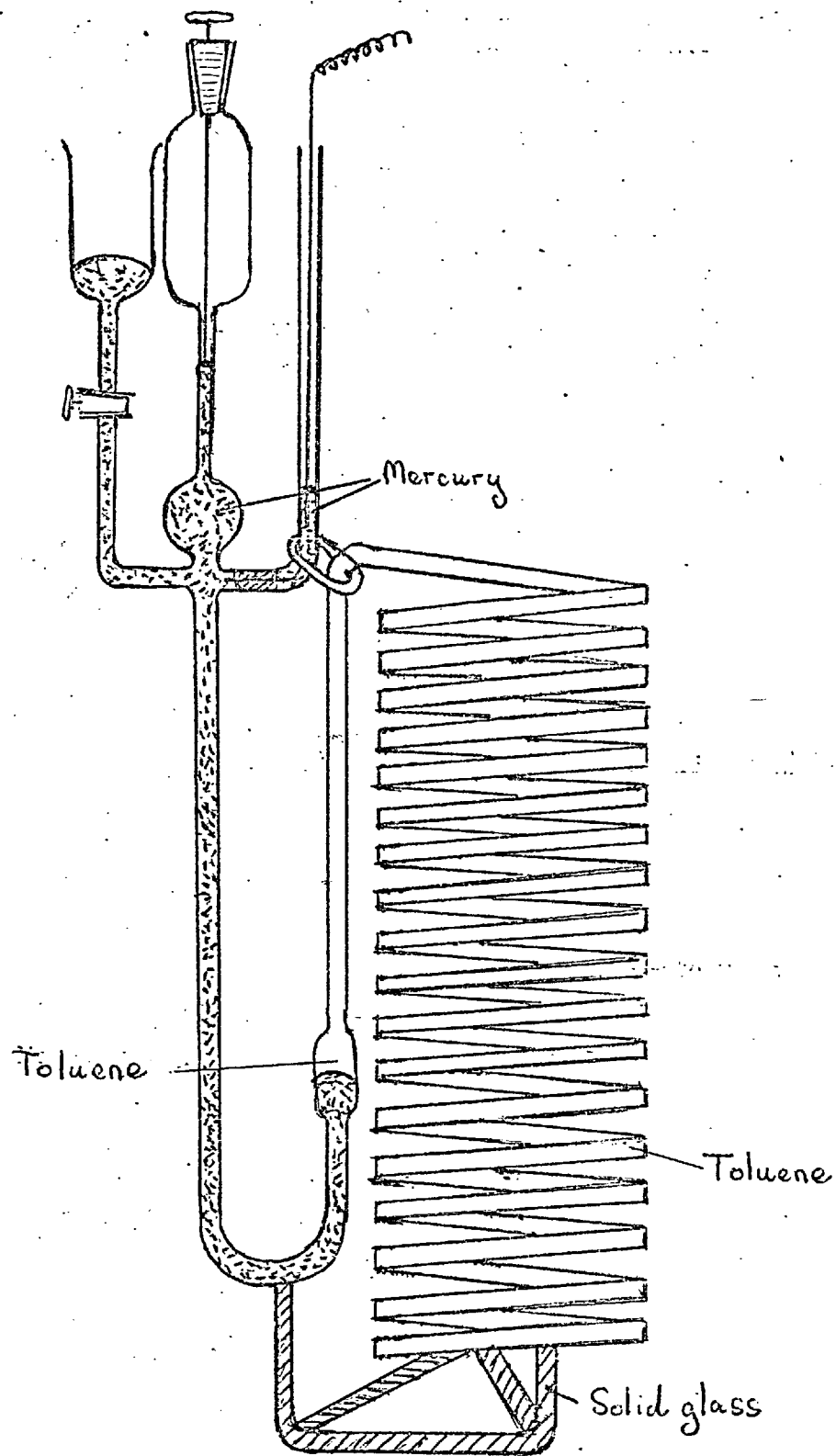
FIGURE 6-10

and the stopper were held firmly in place with hooks and springs. The transfer device in V was replaced with a guard tube to complete the filling of the right hand side of the cell. The cell was filled with following solution through neck II in the same way and the platinum anode was placed in neck I. Since it was the open electrode a platinum wire was slipped between the cone and socket to provide an outlet for expansion and for the oxygen produced when current passed.

The falling cell was filled similarly. With the four-way P.T.F.E. stopcock in the position shown in figure 6-5, leading solution was admitted through VIII and the closed platinum cathode was placed in neck VII and secured in place with hooks and springs. The extended anode section shown in figure 6-6 was placed in neck X with a platinum wire slipped between cone and socket. The following solution was admitted through neck IX and, when the right hand side of the cell was full, the extended section was filled by suction through XI. After the removal of the gas bubbles trapped in the tap by sudden 'squeezing and sucking' of the solutions, the platinum wire was removed and the cone of the extended section was pushed into its socket so that solution spilled down the outside of the cell. The open platinum anode was lodged loosely in neck XI and guard tubes were placed in VIII and IX.

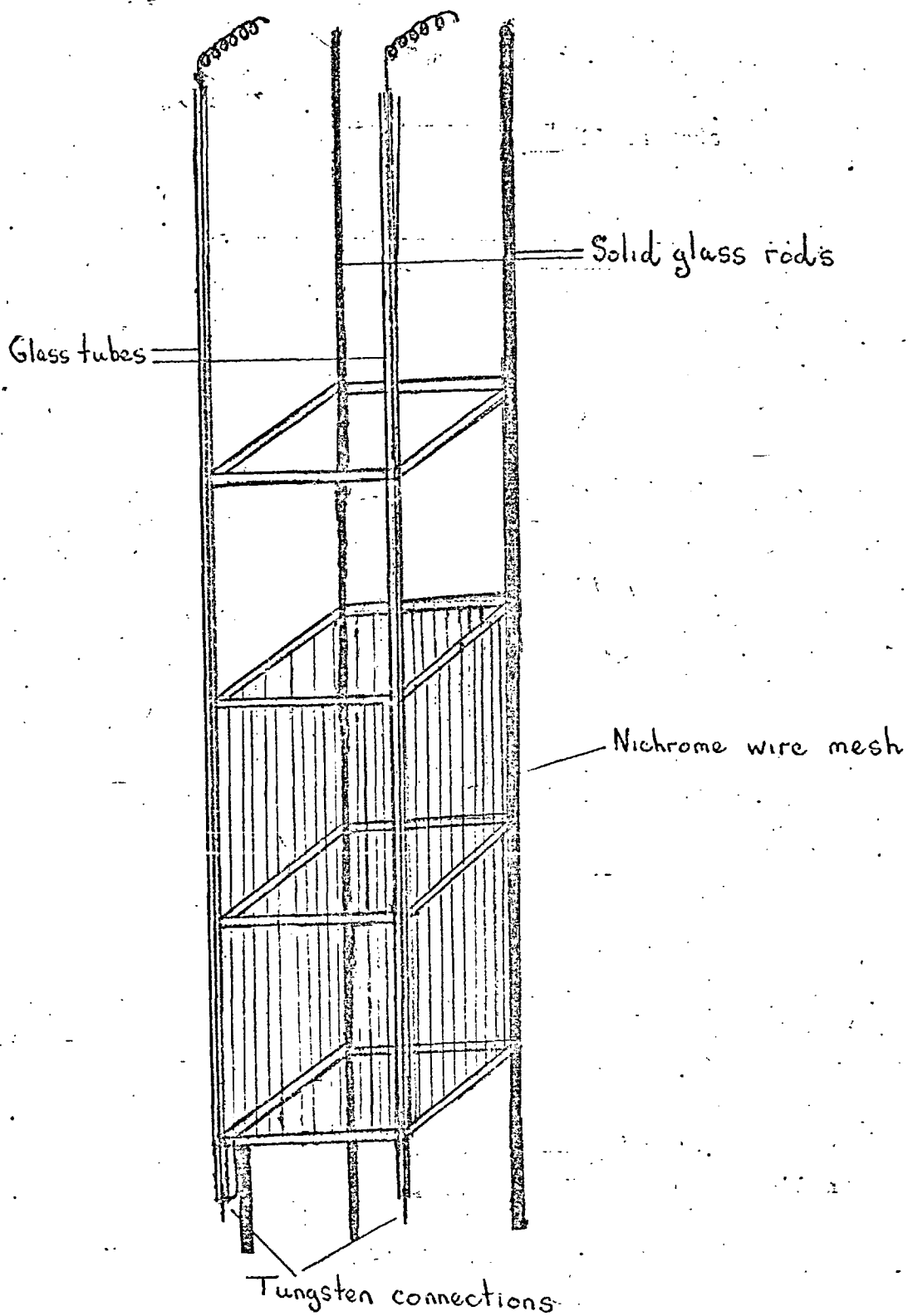
The thermostat

The thermostat tank was 61cm long, 35.6cm wide and 53.3cm deep. Its two largest faces were made of plane glass to enable the cell to be viewed. There was also an end window for inspection of the contents of the tank from the sides. The thermostat fluid, Shell Diala^{BX}/oil, was specially chosen for its transparency, fluidity and high resistance which minimises the risk of current leakage. The oil was vigorously stirred by a $\frac{1}{8}$ H.P. motor which drove two sets of paddle stirrers situated on opposite sides of the tank. The motor and stirrers were mounted on a separate frame from that of the tank to prevent their vibrations from disturbing the boundary. A large helical mercury - toluene thermoregulator, shown in figure 6-11, was used in conjunction with a 150W bare nichrome wire heater, seen here in figure 6-12, to ensure good temperature control. The regulator controlled the



THERMOREGULATOR

FIGURE 6-11



THERMOSTAT HEATER

FIGURE 6-12

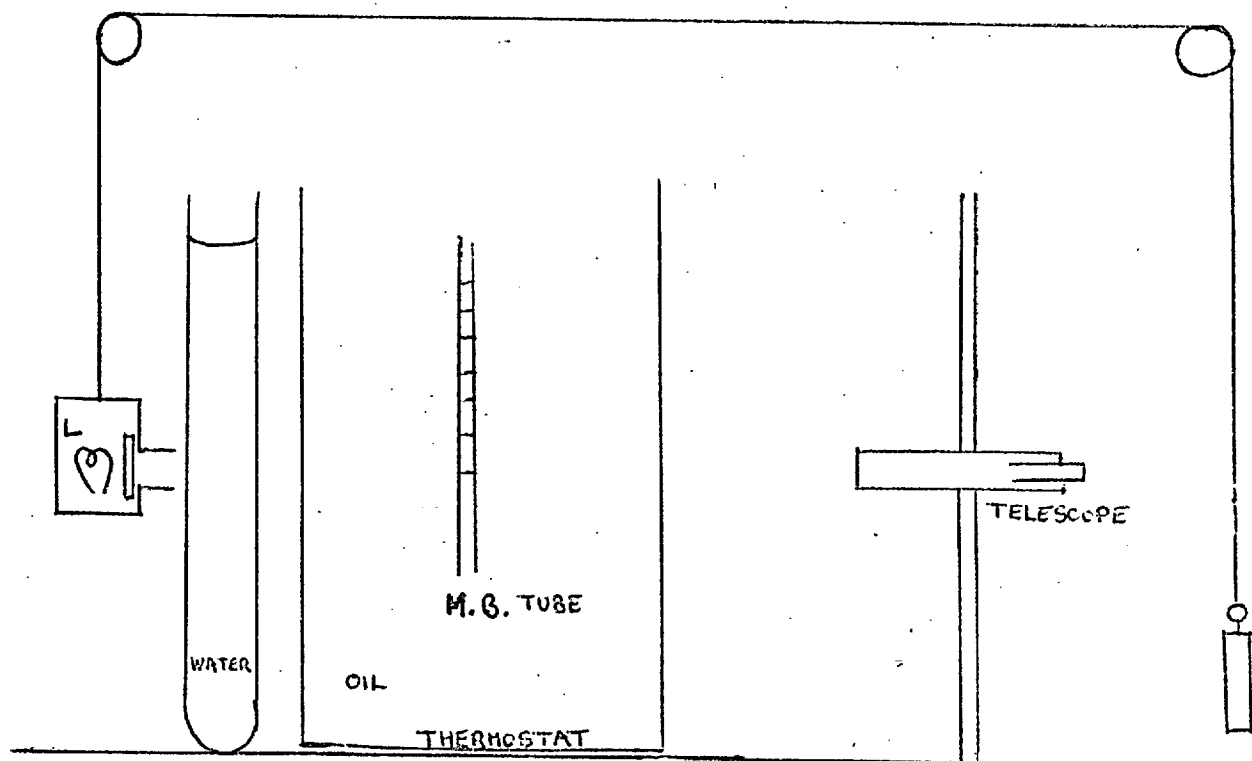
current in the heater via a simple relay, built in the departmental electrical workshop. When the heater was placed within the coils of the helix, maximum sensitivity was achieved and no temperature fluctuations were registered on a Beckmann thermometer graduated to 0.01°C . On hot days when the temperature in the laboratory exceeded 23.5°C the temperature of the oil rose above 25°C due to the extra heat generated by stirring and it was necessary to pass cold water through a copper coil immersed in the oil.

The optical assembly

The arrangement for observation of the boundary is shown in figure 6-13. The light source was a 25W bulb (L) mounted inside a black box, across the front of which was a piece of frosted glass. It could be moved to follow the progress of the boundary up or down the tube by a system of two pulleys, a string and a counter - weight. Between the light source and the back window of the tank there was a glass cylinder full of water, which functioned as a lens. The optimum condition for viewing the boundary and etch marks was against the bottom edge of the light source.

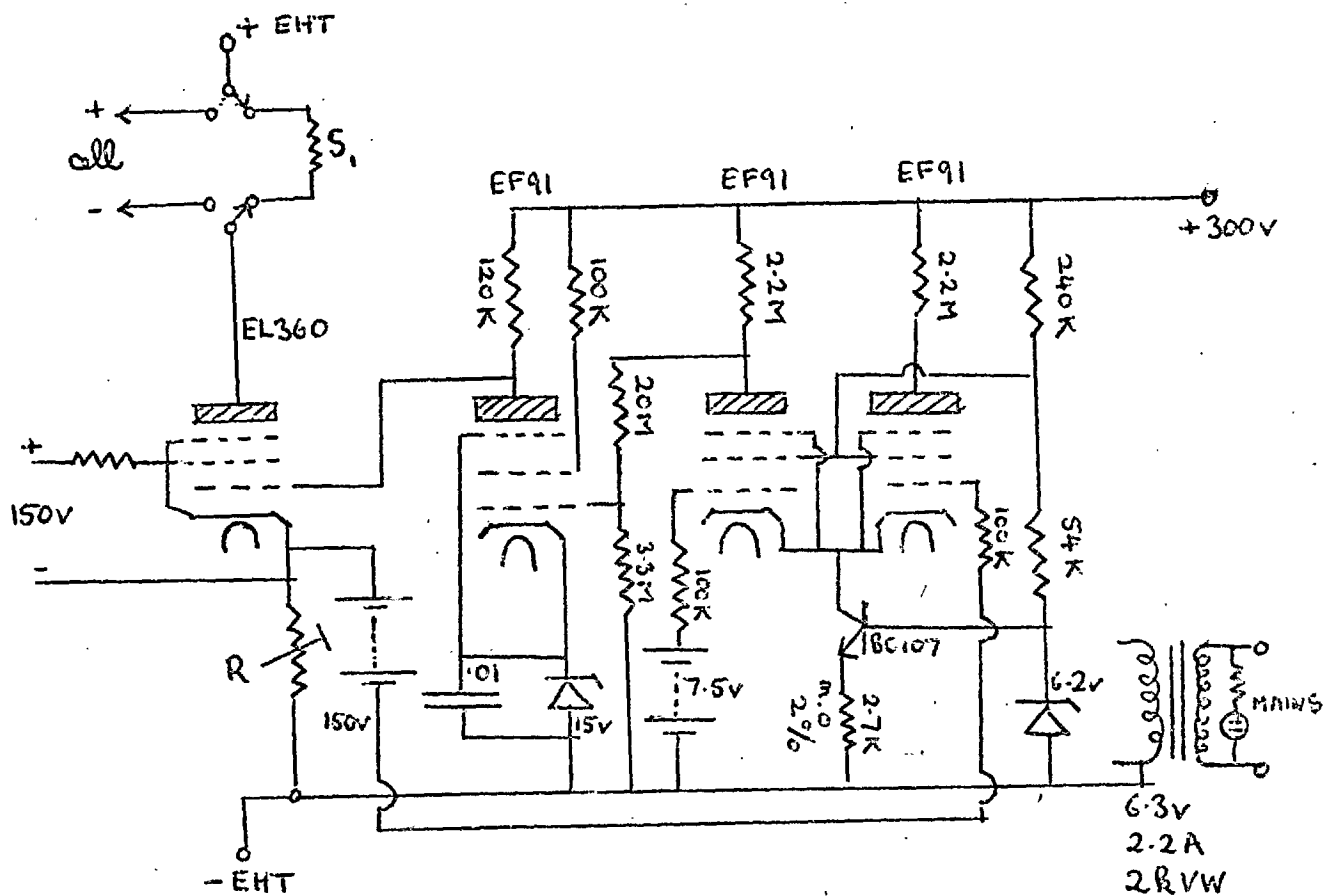
The constant current regulator

In order that transference numbers could be accurately calculated from equation (1 - 10) it was desirable that the current was kept constant throughout the run. Since most of the resistance of the cell was in the moving boundary tube, the replacement of the leading solution by the following one meant that higher voltages had to be supplied as the run proceeded. A high voltage galvanostat designed by Gwyther (151) was particularly suitable for this purpose. Its basic circuit is shown in figure 6-14 from which it can be seen that d.c. input sources of 150v and 300v and a negative EHT supply were required. Figures 6-15 and 6-16 show circuits which provided outputs of all these voltages from 240v A.C. mains inputs. The cathode of the EL360 valve had three banks of resistors in parallel (designated R) between earth and itself to define the current dropping through 150v. The lay - out of resistors and switching arrangements, shown in figure 6-17, enabled stabilised currents between zero



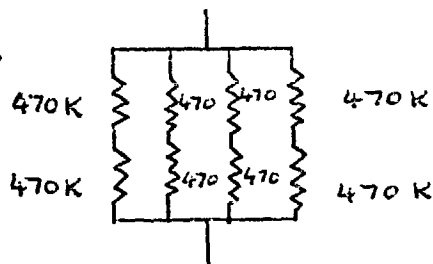
THE OPTICAL ASSEMBLY

FIGURE 6-13



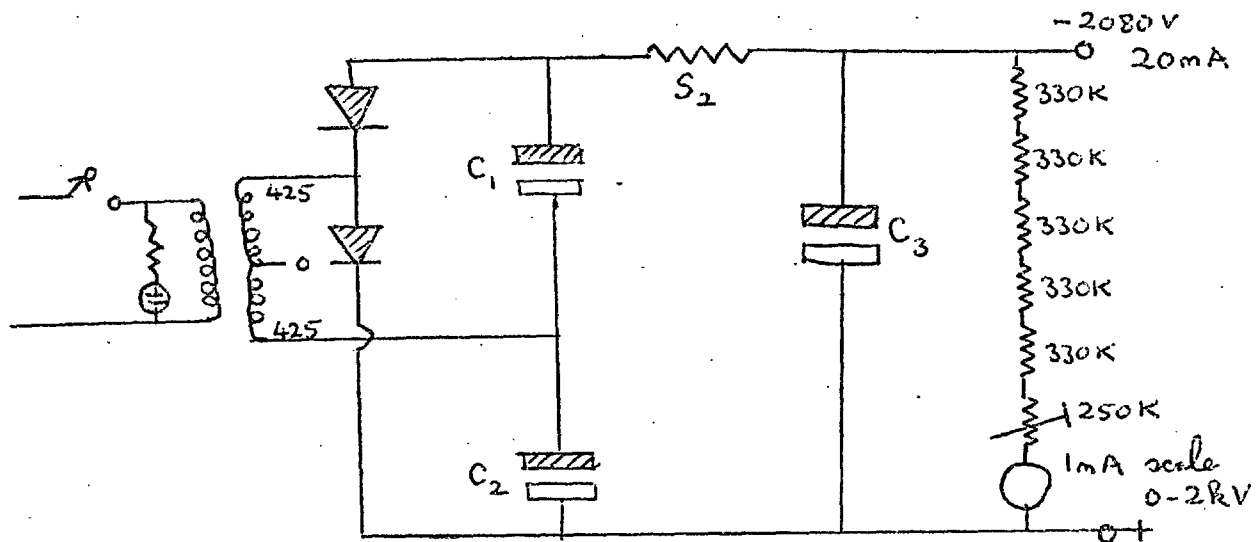
CONSTANT CURRENT SOURCE : CONTROL ELEMENT AND FEEDBACK AMPLIFIER

N.B. 1) THE RESISTOR, S_f , COMPRISES



2) THE RESISTOR, R , IS SHOWN IN FIGURE 6-17

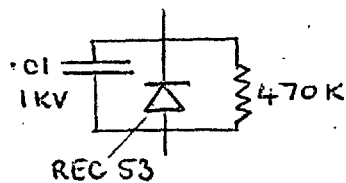
FIGURE 6-14



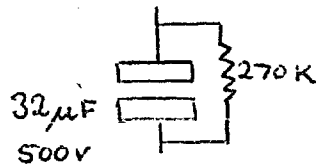
THE EHT SOURCE

N.B.

- 1) EACH DIODE CONSISTS OF 3 UNITS OF:



- 2) C1 AND C2 CONSIST OF 3 UNITS OF:
C3 CONSISTS OF 5 UNITS OF:



- 3) S2 CONSISTS OF:

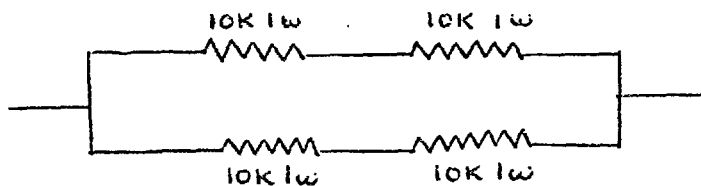
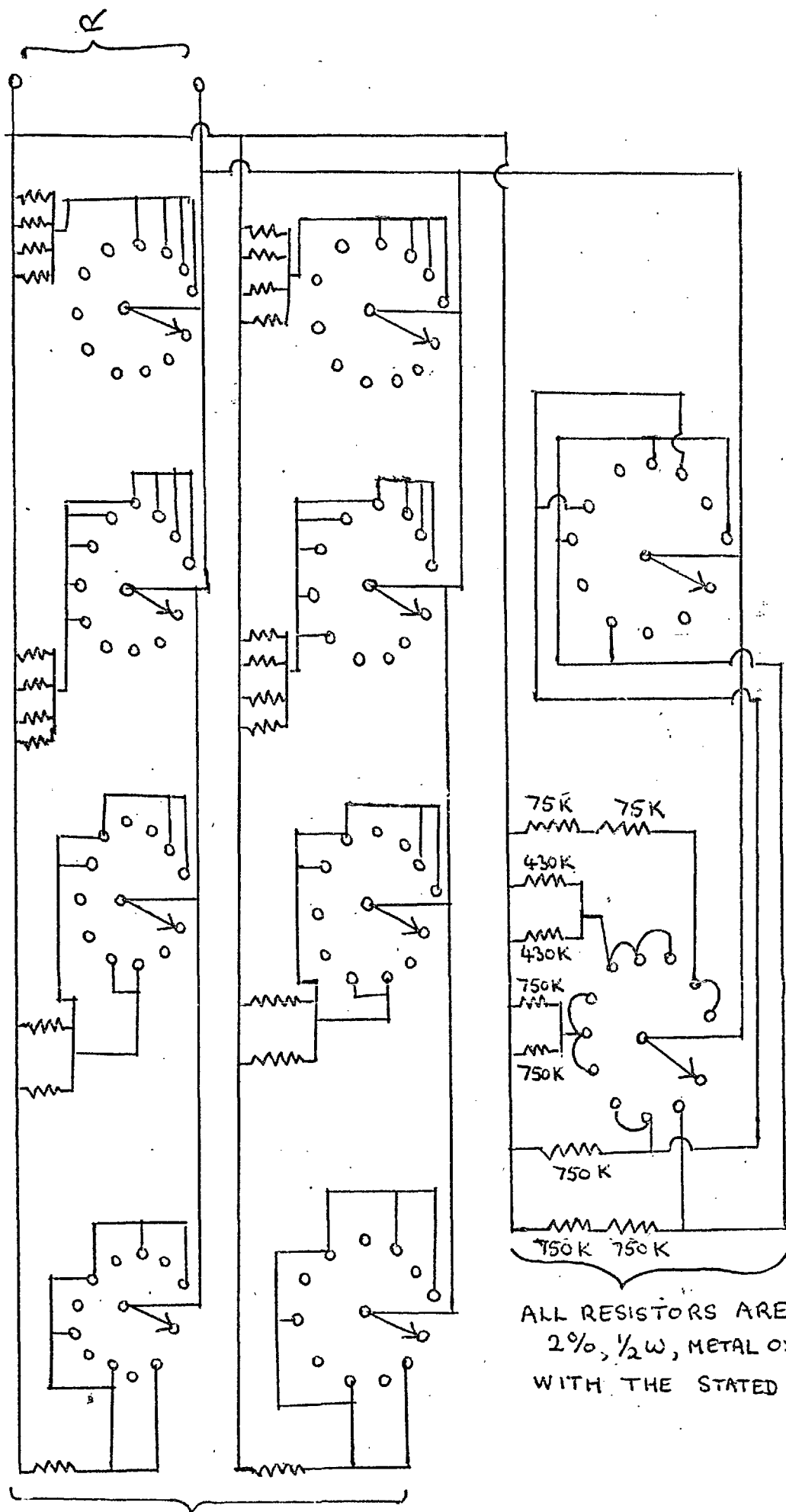


FIGURE 6-16



'THE RESISTOR 'R'

FIGURE 6-17

and 14mA, in steps of 0.1mA, to be selected. Interconnected devices based on all the circuits in figures 6-14, 6-15, 6-16 and 6-17 were all packed together in the same earthed case. Fuller details of the principles of operation of similarly - based regulators and the reasons for the choice of each component have been given by Gwyther (23,152). Summarizing, the important characteristics of this galvanostat are:

Input : 230 - 240v mains A.C. , 50Hz

Output : up to 2kv , 0 -14mA in steps of 0.1mA

Stability : maximum change of 0.01mA during the course of a run ,

The switch - on procedure was 1) switch on filament heaters and wait 30 seconds 2) switch on HT supply and wait 30 seconds 3) switch on EHT, with the regulator switched to the dummy load and the output current set below 10mA 4) switch to cell and 5) adjust the current as required. The switch - off procedure was the reverse of this without the 30 second pauses.

The measurement of current and time

The cell was connected in series with the galvanostat, a milliammeter and a 1000ohms standard resistor, the potential difference across which was measured with a Racal digital voltmeter, model number 9075. This instrument had its own built-in standard cell and temperature compensation arrangement. On the 0-30v range, normally used, it was capable of measuring to 0.001v corresponding to a precision of 0.001mA in the current through the cell. The accuracy of the instrument was periodically checked by connecting it across a Weston standard cell.

Although a Secticon battery-operated clock was employed in the first few runs, most of the boundaries were timed against a Zenith 'Exact Time' clock employing Mallory Duracell mercury batteries. This highly accurate instrument was found to gain by roughly one minute per month (1 in 45 000). It was possible to judge the coincidence of the boundary with the etch marks to between 1 and 2 minutes in the high current runs but the precision fell to between $1\frac{1}{2}$ and $2\frac{1}{2}$ minutes in the lower current runs. The boundary velocity, however, depends not

only on current but also on concentration and transference number and the limits of uncertainty quoted are only average values.

Procedure for carrying out a run

After the cell had been filled the outside was thoroughly wiped with a Kleenex tissue which had previously been soaked in methanol. It was then placed in the thermostat in such a position that the necks were all just above the oil level and the m.b. tube was in the centre of the light beam. A period of one hour was allowed for thermal equilibrium to be established between the cell and the oil after which the stopcock was turned clockwise through 90° and the current regulator was switched from the dummy load to the cell. This rotation of the stopcock of either cell meant that sheared boundaries, which did not have to move through the tap, were formed. It was usual to pass between six and eight milliamperes until the boundary was seen and then reduce the current accordingly.

Cell cleaning and drying

After its removal from the thermostat bath, the cell was well wiped with Kleenex tissues soaked in methanol. The electrodes, stopper and guard tubes were removed and the solutions were poured into large quantities of cold water. The cell was inverted and allowed to drain for a few minutes after which it was swilled with distilled water, methanol to remove traces of oil and again with water to remove methanol. It was then filled with chromic - sulphuric cleaning mixture, left for ten minutes and then copiously rinsed with distilled water (at least eight times). The P.T.F.E. stopcock was removed from the barrel and both were well washed. Two final washings with doubly distilled water were then carried out; the cell was inverted and left to drain for a few hours. The stopcock was replaced and dry nitrogen was passed simultaneously through necks II and V for the rising cell, or VIII and IX for the falling cell. It was usual to pass a slow current of dry nitrogen overnight followed by a more rapid flow for one hour before the cell was filled for the next run.

The cathode, now carrying a deposit of silver which was removed in boiling nitric acid, and the anode were cleaned similarly except that they were dried in an oven at 110°C . The used 3A sieve in the guard tubes was replaced with the freshly regenerated material before further use.

A typical run

Run No. 89 : falling boundary

9th January 1973

NaHSO₄ leading solution : Flask 5

Prepared by dissolving 0.756g of Na₂SO₄ in 256.0g of H₂SO₄. This solution has

$m = 0.0416$ moles of NaHSO₄ per kg of solvent

$w = 0.0414$ " " " " " " solution

density = 1.830 kg dm^{-3} so $c = 0.0758\text{N}$

specific conductance, κ_{soln} , = $1.37 \times 10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1}$

Benzoic acid following solution : Flask 6

Prepared by dissolving 0.612g of solute in 190.9g of H₂SO₄

$w = 0.0263 \text{ mol kg}^{-1}$ of solution

density = 1.826 kg dm^{-3} so $c = 0.0480\text{N}$

Electrodes

cathode : platinum wire in 0.35N AgHSO₄ solution

anode : platinum wire in following solution

Observations

Tap opened at 22-41 with overnight current $I = 3.573\text{mA}$

<u>Etch mark</u>	<u>Day</u>	<u>Time</u>	<u>Current (mA)</u>	<u>Beckmann</u>
1	Wed. 10th Jan	13-13	3.879	24.75
2	" " "	17-47	3.879	24.75
3	" " "	21-43	3.878	24.75
4	missed			
5	missed			
6	Thur. 11th Jan	11-06	3.878	24.75
7	" " "	14-50	3.879	24.75
8	" " "	19-30	3.878	24.75

Results

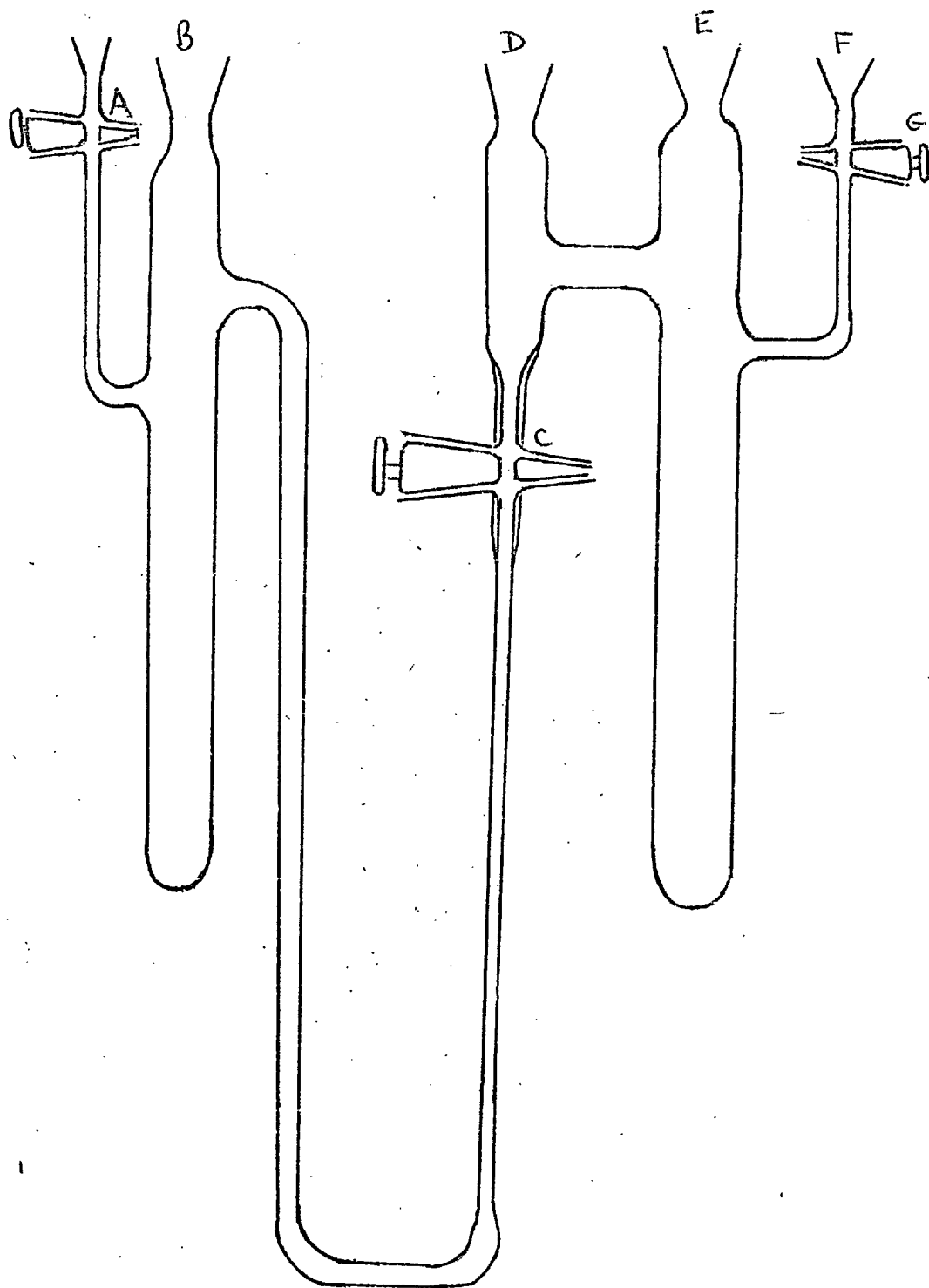
<u>Etch marks concerned</u>	<u>Volume (cm³)</u>	<u>t₊</u>
1 → 2	0.0554	0.0063 ₅
1 → 3	0.1037	0.0064
2 → 3	0.0483	0.0064
1 → 6	0.268	0.0064
2 → 6	0.213	0.0064
3 → 6	0.165	0.0064
1 → 7	0.315	0.0064
2 → 7	0.259	0.0064 ₅
3 → 7	0.211	0.0064 ₅
6 → 7	0.0464	0.0065
1 → 8	0.372	0.0065
2 → 8	0.317	0.0065
3 → 8	0.269	0.0065
6 → 8	0.1041	0.0065
7 → 8	0.0577	0.0065

'Best' value for t₊ = 0.0064₅

Analysis of solutions

A feature of a number of runs, usually employing AgHSO_4 as leading electrolyte, was the occurrence in the m.b. tube of two boundaries. To investigate this strange observation a method of analysing the solutions in the tube, at the end of the run, was required. Although double boundaries were only seen in falling runs the normal falling cell could not be used since there was no satisfactory way of withdrawing samples from the m.b. tube afterwards. Two new cells, both employing two-way stopcocks, instead of four-way ones, and conforming to the design shown in figure 6-18, were made. The cells differed only in the form of lubrication between the key and barrel and the arrangement for dissipation of the heat generated within the tap; one employed a hollow glass stopcock lubricated with Voltalef 90 fluorocarbon grease whilst the other was made of P.T.F.E. (Springham's Interflon IST/4/B) with no special provisions for cooling the solutions. The two side taps, A and G, were both greased with Voltalef 90 and the position of the cell in the thermostat was such that they were above the oil level.

The cell was filled as follows. With all three taps open, leading solution was admitted through B, until it emerged through the top of the main stopcock, C, Tap G was then closed, the cell was stoppered at E and the solution was 'squeezed and sucked' through D using a Pumpette attached to a B10 cone, after which the main stopcock, C, was closed with the leading solution in the bore of the key and above it. The filling of the left hand section of the cell was continued until the level of liquid reached tap A which was then closed. A long platinum electrode was then placed in neck B ensuring that solution overflowed down the side of the cell with no air bubbles trapped inside. The electrode was secured firmly in place with hooks and springs as usual. The leading solution above C was then sucked out using a Pumpette attached to a glass capillary. This part of the cell was then washed several times with following solution removing the washings under suction each time. The right hand side of the cell was filled with following solution through D using a transfer device in the usual way. A platinum anode was



FALLING CELL FOR SAMPLING

FIGURE 6-18

lodged in neck E with a small piece of platinum wire and a guard tube was placed in D. The outside of the cell was wiped clean with methanol and ink marks were made on the m.b. tube at $\frac{1}{2}$ cm intervals. The cell was placed in the thermostat, tap A was opened and the electrodes were connected to the power supply. When thermal equilibrium with the oil had been established, tap A was closed, C opened and current passed.

When the run was over, C was closed and the cell was removed from the tank for analysis of its contents. The solution in the anode compartment was first removed by suction through a capillary attached to a vacuum pump. This was done to prevent overspill during the sampling of the solutions in the m.b. tube. All the solution above C was similarly withdrawn by inserting the capillary through D and placing its tip as close to C as possible. Taking great care not to disturb the solution at A or B the key of C was carefully opened. Solution was then removed from the m.b. tube by suction through a capillary whose tip was placed just below the surface of the liquid. The samples were taken in the form of upper layers of solution with no disturbance of the remainder below. Each sample was taken through a clean capillary and was rapidly transferred to a small previously - weighed flask which was then re-weighed. The mass of sample, which was typically about 0.1g corresponding to a thread of liquid roughly $\frac{1}{2}$ cm long, was thus found. At least ten samples per run were taken in succession and analysed.

Barium was detected by the addition of the sample to about 3ml of doubly distilled water. A white precipitate of BaSO_4 confirmed the presence of barium in the sample. The very low solubility of BaSO_4 in aqueous solution (0.2 - 0.3mg per 100ml) meant that very low concentrations of $\text{Ba}(\text{HSO}_4)_2$ in the sulphuric acid could still be detected.

Silver was detected by the addition of the sample to 2 - 3ml of a concentrated aqueous solution of potassium chloride, giving a white precipitate of AgCl . This precipitate was distinguished from BaSO_4 , which would be formed by treating a

sample containing barium ions with almost any aqueous solution, by the addition of ammonia solution in which AgCl is readily soluble but BaSO_4 is not. Quantitative analysis for silver was carried out by the technique of atomic absorption spectroscopy (A.A.S.) which is particularly sensitive and selective for silver. The samples were diluted with water until the Ag concentration was in the range 1 - 10 parts per million (p.p.m.). A 0.1g sample of 0.22N AgHSO_4 in sulphuric acid, when diluted to 250ml gave a solution containing 5.2 p.p.m. Standard silver solutions having concentrations in this range were made up from Analar silver nitrate. Their absorbances at 328.1 nm were measured and a calibration graph (absorbance versus concentration) was drawn. The absorbances of the diluted AgHSO_4 solutions were measured and their concentrations interpolated from this graph. Barium and sulphuric acid only interfere when they are present in aqueous solutions having very much higher concentrations than those encountered here. A check on the concentration of the AgHSO_4 leading solution was also made. The value obtained from analysis was in good agreement with that calculated from the weighings made in its preparation.

The results of the analyses are given at the end of Part II of this chapter.

PART II : RESULTS

The choice of a suitable following electrolyte

In the early runs attempts were made to follow H_3O^+ with Ag^+ but no boundaries were obtained and later work showed that the following ion is faster than the leading one. The Hittorf studies (112,129) suggested that the slowest cations (of electrolytes that were sufficiently soluble) were Ba^{2+} and Sr^{2+} , and consequently these were considered the most promising as following ions. The first system giving a visible boundary was $\text{H}_3\text{O}^+/\text{Ba}^{2+}$ (leading/following), and other leading ions were then tried. Boundaries were seen for NH_4^+ , K^+ , Na^+ , and Ag^+ (but not for Li^+), all followed by Ba^{2+} .

Before performing accurate measurements it was desirable to have a rough knowledge of the Ba^{2+} transference number so that an initial indicator concentration, close to the Kohlrausch concentration, could be made up. To measure $t_{\text{Ba}^{2+}}$ a slower ion than barium was required to follow the boundary. It was thought that a large protonated organic molecule would be suitable. Indeed, a $\text{Ba}^{2+}/\text{H}_2\text{OBz}^+$ (protonated benzoic acid) boundary was seen, thus enabling $t_{\text{Ba}^{2+}}$ to be determined after measurements at two currents and extrapolation to $I = 0$.

In order to test the dependence of m.b. measurements on the nature of the indicator electrolyte, a second following ion was needed. It was thought probable that protonated acetic acid would fill this need. A knowledge of $t_{\text{H}_2\text{OAc}^+}$ was necessary if the initial indicator concentration was to be close to the Kohlrausch value, and it was determined from $\text{H}_2\text{OAc}^+/\text{H}_2\text{OBz}^+$ boundary measurements. Although satisfactory boundaries were obtained when H_2OAc^+ followed K^+ , NH_4^+ and Ag^+ , slower ions such as Na^+ and Li^+ move at speeds comparable to H_2OAc^+ and no boundaries were seen. Furthermore boundaries against acetic acid were not visible at currents below about 5mA and so, for these slower systems, H_2OBz^+ was employed as indicator instead. Excellent boundaries, visible over a wide range of currents ($3.5\text{mA} < I < 8.5\text{mA}$), were obtained. Unfortunately $t_{\text{H}_2\text{OBz}^+}$ was not known (no slower ion could be found), and an estimate of the Kohlrausch concentration was

difficult to make. This disadvantage was, in part, offset by two redeeming features. First, the very existence of an $\text{H}_2\text{OAc}^+/\text{H}_2\text{OBz}^+$ falling boundary meant that $t_{\text{H}_2\text{OAc}^+} > t_{\text{H}_2\text{OBz}^+} \gg \frac{2}{3} t_{\text{H}_2\text{OAc}^+}$. This was deduced as follows. The density of the leading 0.090N H_2OAc^+ solution employed was 1.825 kg dm^{-3} which is also the density of 0.060N $\text{H}_2\text{OBz} \cdot \text{HSO}_4$. Since densities of solutions of organic acids decrease with increasing concentration it follows from the Kohlrausch relation, (1 - 14), that

$$\frac{t_{\text{H}_2\text{OBz}^+}}{t_{\text{H}_2\text{OAc}^+}} = \frac{c_{\text{H}_2\text{OBz}^+}}{c_{\text{H}_2\text{OAc}^+}} \gg \frac{0.06}{0.09} = \frac{2}{3} \quad (6 - 33)$$

for boundary stability. Moreover since the initial H_2OBz^+ concentration in this series of runs was 0.06N, there would have been a density instability in the following solution if the Kohlrausch concentration had been much greater than 0.060N. So, very roughly, $t_{\text{H}_2\text{OBz}^+} = \frac{2}{3} t_{\text{H}_2\text{OAc}^+}$. Second, the results of m.b. measurements for all runs in which H_2OBz^+ was the indicator ion showed very little dependence on the initial indicator concentration. The last-mentioned could be varied by as much as 30% without significant effect on the transference number (extrapolated to zero current) of the leading ion. Thus benzoic acid proved to be a good choice as following solute.

Boundary systems studied

Boundaries were obtained between the solutions of the hydrogen sulphates of the cations specified in table 6a. Certain systems yielded two boundaries in the tube as indicated. The technique of analysis described earlier was used to investigate these systems and the results are discussed later in this chapter.

Dependence on current, indicator electrolyte and indicator concentration

It is a feature of the moving boundary method that the observed transference number should be independent of the current at which the measurement was made. A consideration of equation (1 - 12) reveals that a change in current, I , should be accompanied by a proportional change in boundary velocity, v , and t_i should

Table 6aSystems for which boundaries were seen

<u>Leading cation</u>		<u>Following cation</u>		<u>Comments</u>
1.	Ba^{2+}	H_2OBz^+	falling	Double boundary
2.	H_2OAc^+	H_2OBz^+	falling	
3.	NH_4^+	Ba^{2+}	rising	
4.	NH_4^+	H_2OAc^+	falling	
5.	K^+	Ba^{2+}	rising	Very poor boundaries
6.	K^+	H_2OAc^+	falling	
7.	Na^+	Ba^{2+}	rising	
8.	Na^+	H_2OBz^+	falling	
9.	Li^+	H_2OBz^+	falling	
10.	H_3O^+	Ba^{2+}	rising	
11.	H_3O^+	H_2OBz^+	falling	
12.	Ag^+	Ba^{2+}	falling	Double boundary
13.	Ag^+	H_2OAc^+	falling	Double boundary

Systems 3., 8. and 13. were studied at more than one concentration.

remain unchanged. However, for most of the systems listed in table 6a, the measured transference number varied according to the current passed. With the exception of systems 2, and 11, , where the opposite trend was found, t_+ rose with increasing current for falling runs and fell with increasing current for rising runs.

It seems likely that inefficient dissipation of the electrical or Joule heating generated by the passage of current was the main factor causing a variation in the observed transference number with current. The actual current dependence should be interpreted as the combination of several effects amongst which were the following.

- i) As the solutions were warmed they expanded and the volume of liquid between the electrodes rose. The boundary moved away from the open electrode and towards the closed one and consequently was pushed back by the expansion. Thus a smaller boundary velocity and observed transference number ensued.
- ii) The warming of the leading solution in the m.b. tube led to a fall in its density and its concentration. This should have led to a rise in boundary velocity and consequently in the measured transference number since the original concentration was used in the calculation.
- iii) The amount of Joule heating is directly proportional to I^2 and to the total resistance of the solution (s) between the electrodes. Thus the degree of Joule heating depends on the nature of both leading and following electrolytes and on their concentrations. This point is further discussed below in connection with the dependence on indicator electrolyte and indicator concentration.
- iv) Ionic mobilities and equivalent conductances are considerably increased by a rise in temperature (about 4% per $^{\circ}\text{C}$ for sulphuric acid solutions) but transference numbers, being a ratio of conductances, were only likely to be affected to a slight extent by a speeding up of the ions. A variation in temperature coefficient of ionic mobility between two ions meant they would have been speeded up to different extents by heating of the solutions and, since the HSO_4^- anion was

common to all electrolytes, their transference numbers may have had slightly different temperature dependences.

v) Changes in current and temperature may have led to different distributions of the electrode products in the vicinity of the cathode due to changes in their rates of diffusion. Since the dependence of apparent molar volumes on concentration have not been investigated no reliable estimate of the influence of current variation on the volume correction can be made. An attempt was made to allow for the effects of Joule heating by examining each system at two currents and extrapolating to $I = 0$. The results of these studies are listed in tables 6b to 6o.

If the sensitivity of the measured values to the amount of Joule heating is accepted then their variation with indicator electrolyte at finite concentrations can be explained. Most of the resistance between the electrodes exists in the m.b. tube, and the solution behind the boundary in this tube contains indicator electrolyte at the Kohlrausch concentration. A change in indicator electrolyte would therefore lead to a different specific resistance (or conductance) in the solution following the boundary and hence, for a given current, to a different amount of Joule heating. Moreover, a change of indicator usually necessitated a change from rising to falling cells (or vice versa), and it seems probable that the resistance also depended on the dimensions and geometry of the cells. The different directions of the current dependence are less easily accounted for but the agreement of the values obtained after extrapolation to zero current suggests that these trends were again related to the amount of Joule heating. Although figures 6-20 and 6-21^{show} variations of up to 30% in the observed transference number when changes in indicator electrolyte were made, the close agreements of the zero current values yielded by extrapolation are very satisfying.

As most of the cell resistance resided in the contents of the m.b. tube, changing the initial indicator concentration should have caused no significant alteration in the observed transference number since it is likely that all the

indicator solution behind the boundary in this tube was at the adjusted Kohlrausch concentration. Inspection of tables 6j and 6n, and figures 6-20 and 6-21 shows that this is true within the limits of experimental error.

Treatment of results

Three operations, listed below in the order in which they were performed, were necessary to convert the measured transference numbers to corrected values.

- 1) Extrapolation to zero current as discussed above.
- 2) Application of the volume correction. A full discussion of the value of ΔV and its sign have been given earlier in this chapter. As the boundary always moved towards the closed electrode, the volume correction, $c\Delta V$, was added to the observed transference number (by analogy with equation (1 - 16)). Since $\Delta V = -43 \text{ cm}^3 \text{ mol}^{-1}$ ($-0.043 \text{ dm}^3 \text{ mol}^{-1}$), this entailed, for a 0.1N solution, the subtraction of 0.0043 from the extrapolated value for t_+ .
- 3) Multiplication by the solvent correction factor. The detailed calculation of this quantity for 0.126N NaHSO_4 was given in the conductance section of chapter four. Values for other leading solutions were calculated similarly.

The results for all the systems studied are listed in tables 6b to 6o. The uncertainties quoted were estimated after consideration of two contributing sources of error as follows.

- a) The limitations in the precision of the measured transference numbers. Within any given run, slightly different values were usually obtained over different sets of etch marks. The choice of the "best" value was arbitrary and an uncertainty of at least ± 0.0001 was usually assumed.
- b) The length of the extrapolation to zero current. This depended upon the current values at which the m.b. measurements were made. For systems in which the following ion was H_2OAc^+ the poor visibility of the boundaries below 5mA led to longer extrapolations and greater uncertainties than those in systems employing H_2OBz^+ and Ba^{2+} as following ions where the boundaries were visible over a wider range of currents. Figure 6-19 shows the extrapolation uncertainty

for the system $0.090N\ H_2OAc.HSO_4 / 0.060N\ H_2OBz.HSO_4$.

The factors which limit the precision of the solvent and volume corrections have already been discussed and estimated in the appropriate sections of chapter four and part I of this chapter.

Table 6bCation transference numbers in 0.034N Ba(HSO₄)₂ solution

<u>Run number</u>	<u>Following solution</u>	<u>Current</u>	<u>Measured t₊</u>
64	0.052N H ₂ O Bz.HSO ₄	5.41 ^a	0.0048
63	ditto	8.17 ^a	0.0049

Uncorrected zero current transference number = 0.0046 ± 0.0002

Volume correction = -0.0036

Solvent correction factor = 1.20

Corrected zero current transference number = 0.0012 ± 0.0004 Ionic strength of leading solution = $0.147 \text{ mol dm}^{-3}$ $\lambda_{\text{HSO}_4^-}$ in leading solution = $140 \text{ ohm}^{-1} \text{ cm}^2 \text{ equiv}^{-1}$

a. Two boundaries were seen in these runs. They were very close together throughout and timing both of them yielded the same value of t₊. The leading boundary was sharper than the following one.

Table 6cCation transference numbers in 0.090N $\text{H}_2\text{OAc.HSO}_4$ solution

<u>Run number</u>	<u>Following solution</u>	<u>Current (mA)</u>	<u>Measured t_+</u>
61	0.060N $\text{H}_2\text{OBz.HSO}_4$	3.45	0.0064
62	ditto	5.53	0.0056

Uncorrected zero current transference number = $0.0077 \pm 0.0002_5$

Volume correction = -0.0039

Solvent correction factor = 1.189

Corrected zero current transference number = $0.0045 \pm 0.0004_5$ Ionic strength of leading solution = $0.110 \text{ mol dm}^{-3}$ $\lambda_{\text{HSO}_4^-}$ in leading solution = $135 \text{ ohm}^{-1} \text{ cm}^2 \text{ equiv}^{-1}$ The transference number of H_2OBz^+

The density considerations discussed at the beginning of Part II of this chapter enabled the following estimate to be made.

 $t_{\text{H}_2\text{OBz}^+}$ in 0.060N $\text{H}_2\text{OBz.HSO}_4$ solution $\simeq \underline{0.0030}$

FIGURE 6-19

EXTRAPOLATION TO ZERO CURRENT OF THE
CATION TRANSFERENCE NUMBER IN

0.090N $\text{H}_2\text{OAc} \cdot \text{H}_2\text{SO}_4$

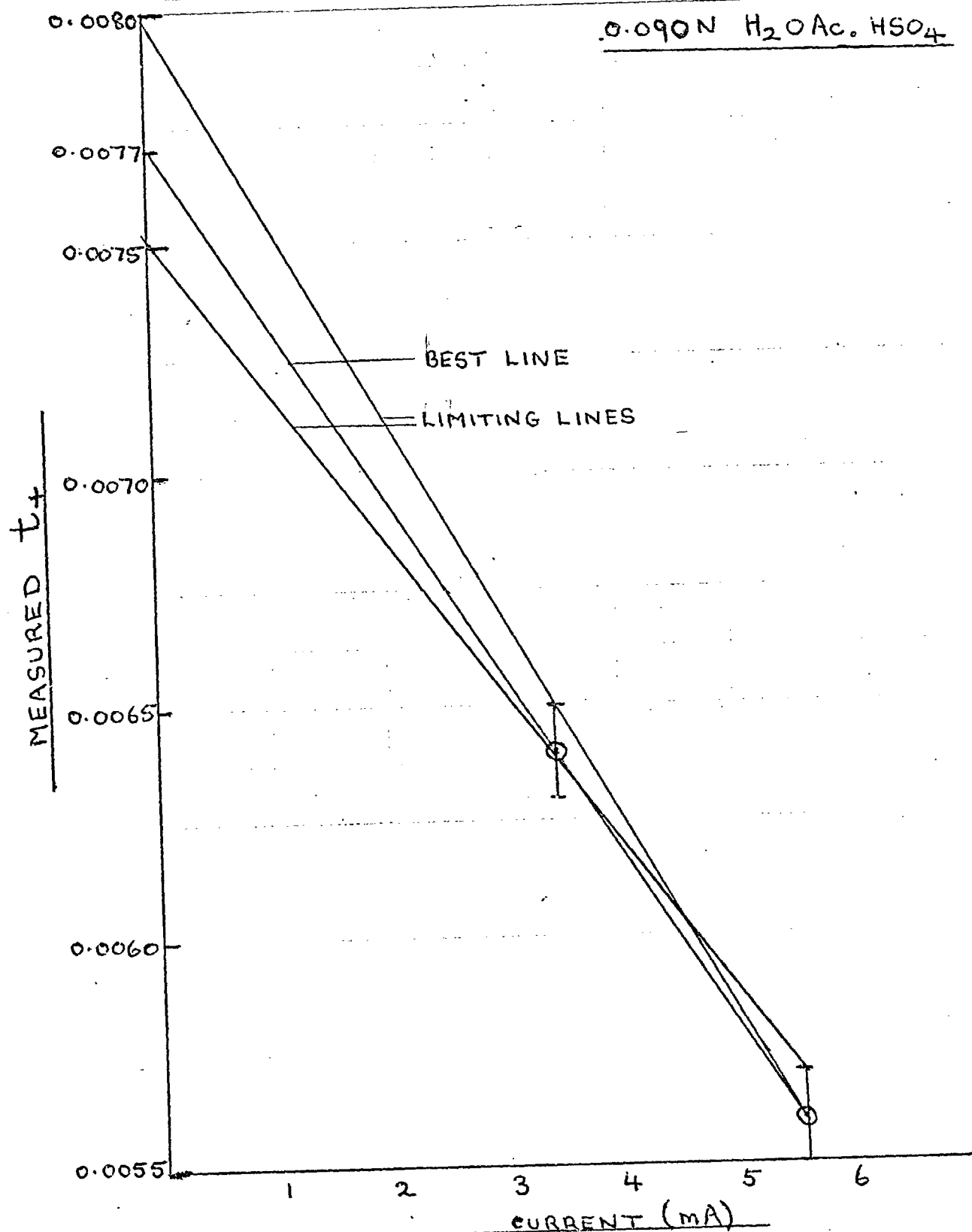


Table 6dCation transference numbers in 0.0623N NH_4HSO_4 solution

In these runs some of the silver, deposited at the cathode, dropped off and dissolved during the run. The results must be regarded as unreliable and are included only to illustrate the approximate magnitude of t_+ and to compare its variation with concentration with that of t_+ for solutions of NaHSO_4 and AgHSO_4 .

<u>Run number</u>	<u>Following solution</u>	<u>Current (mA)</u>	<u>Measured t_+</u>
52	0.030N $\text{Ba}(\text{HSO}_4)_2$	3.93	0.0060
51	ditto	5.56	0.0057

Uncorrected zero current transference number = 0.0068 ± 0.0002

Correction term for Ag dissolution (estimated as 30%) = 0.0001_5

Volume correction = -0.0027

Solvent correction factor = 1.30

Corrected zero current transference number = 0.0055 ± 0.0004

Ionic strength of leading solution = $0.086 \text{ mol dm}^{-3}$

$\lambda_{\text{HSO}_4^-}$ in leading solution = $148 \text{ ohm}^{-1} \text{ cm}^2 \text{ equiv}^{-1}$

Table 6e

Cation transference numbers in 0.111N NH_4HSO_4 solution

These results are again unreliable because of partial re-dissolution of the silver.

<u>Run number</u>	<u>Following solution</u>	<u>Current (mA)</u>	<u>Measured t_+</u>
49	0.052N $\text{Ba}(\text{HSO}_4)_2$	3.84	0.0094
50	ditto	6.85	0.0088

Uncorrected zero current transference number = 0.0102 ± 0.0002

Correction term for Ag dissolution (estimated as 30%) = 0.0003

Volume correction = -0.0048

Solvent correction factor = 1.14

Corrected zero current transference number = 0.0065 ± 0.0005

Ionic strength of leading solution = $0.130 \text{ mol dm}^{-3}$

$\lambda_{\text{HSO}_4^-}$ in leading solution = $129 \text{ ohm}^{-1} \text{ cm}^2 \text{ equiv}^{-1}$

Table 6f

Cation transference numbers in 0.19N NH_4HSO_4 solutionsLeading solution : 0.187N

<u>Run number</u>	<u>Following solution</u>	<u>Current (mA)</u>	<u>Measured t_+</u>
72	0.066N $\text{Ba}(\text{HSO}_4)_2$	4.60	0.0118
73	ditto	8.15	0.0115

Uncorrected zero current transference number = $0.0122 \pm 0.0001_5$

Volume correction = -0.0081

Solvent correction factor = 1.05

Corrected zero current transference number = 0.0043 ± 0.0005 Leading solution : 0.193N

43	0.0120N $\text{H}_2\text{OAc.HSO}_4$	5.22	0.0131
42	ditto	7.09	0.0134

Uncorrected zero current transference number = 0.0123 ± 0.0002

Volume correction = -0.0083

Solvent correction factor = 1.04

Corrected zero current transference number = 0.0042 ± 0.0005 Leading solution : 0.193N

44	0.090N $\text{H}_2\text{OAc.HSO}_4$	5.22	0.0129
45	ditto	7.31	0.0133

Uncorrected zero current transference number = 0.0120 ± 0.0002 Corrected zero current transference number = 0.0039 ± 0.0005 Ionic strength of 0.187N leading solution = $0.204 \text{ mol dm}^{-3}$ $\lambda_{\text{HSO}_4^-}$ in 0.187N leading solution = $112 \text{ ohm}^{-1} \text{ cm}^2 \text{ equiv}^{-1}$ Ionic strength of 0.193N leading solution = $0.210 \text{ mol dm}^{-3}$ $\lambda_{\text{HSO}_4^-}$ in 0.193N leading solution = $111 \text{ ohm}^{-1} \text{ cm}^2 \text{ equiv}^{-1}$

FIGURE 6-20
EXTRAPOLATION TO ZERO CURRENT OF THE CATION TRANSFERENCE
NUMBER IN 0.19N NH_4HSO_4 SOLUTIONS

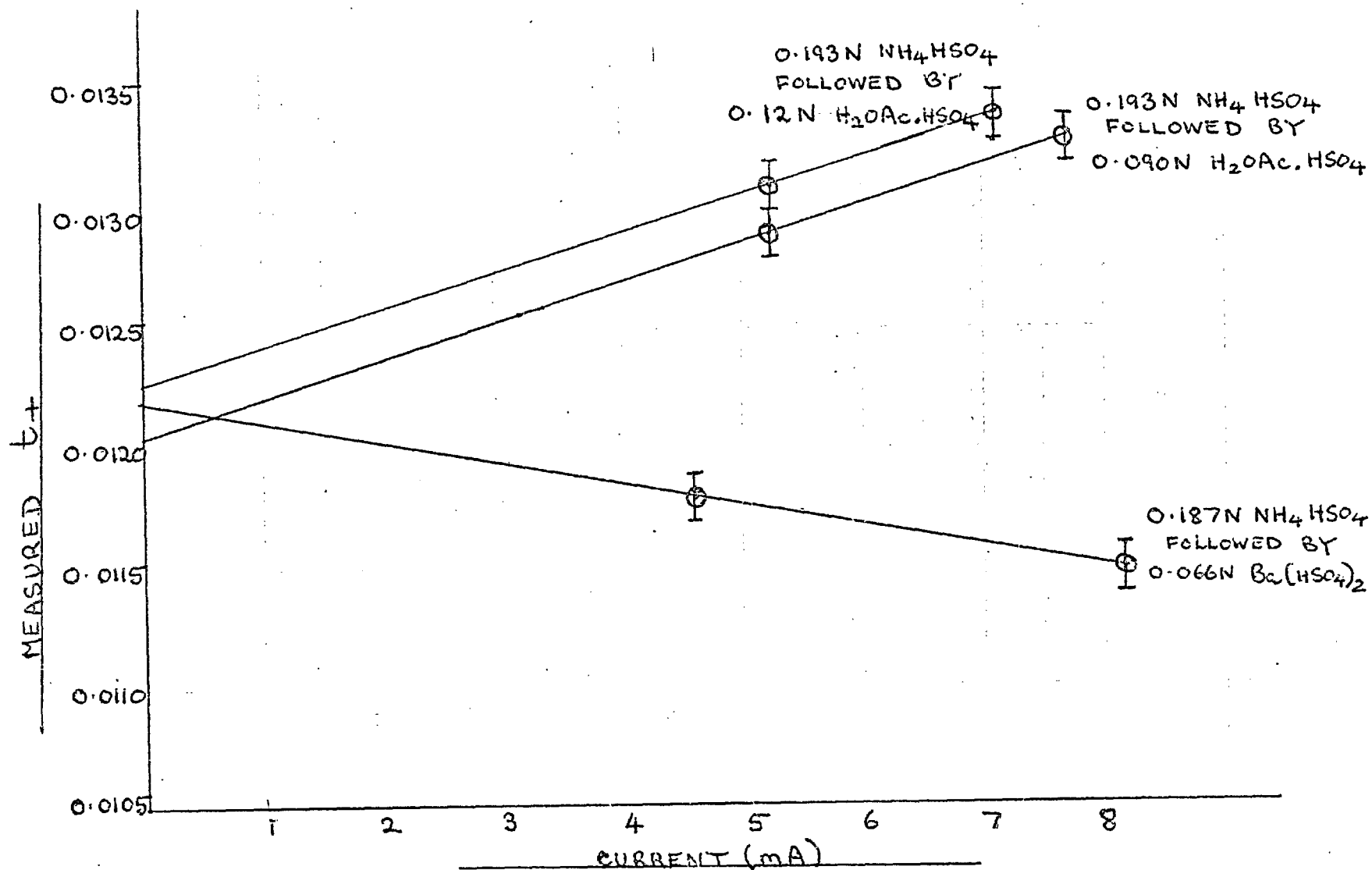


Table 6gCation transference numbers in 0.123N KHSO_4 solution

<u>Run number</u>	<u>Following solution</u>	<u>Current (mA)</u>	<u>Measured t_+</u>
78	0.103N $\text{H}_2\text{OAc.HSO}_4$	6.1	0.0117
76	ditto	8.2	0.0118

Uncorrected zero current transference number = 0.0114 ± 0.0003

Volume correction = -0.0053

Solvent correction factor = 1.12

Corrected zero current transference number = 0.0069 ± 0.0005 Ionic strength of leading solution = $0.139 \text{ mol dm}^{-3}$ $\lambda_{\text{HSO}_4^-}$ in leading solution = $122 \text{ ohm}^{-1} \text{cm}^2 \text{equiv}^{-1}$

Table 6hCation transference numbers in 0.0758N NaHSO₄ solution

<u>Run number</u>	<u>Following solution</u>	<u>Current (mA)</u>	<u>Measured t₊</u>
89	0.048N H ₂ O Bz.HSO ₄	3.88	0.0064 ₅
88	ditto	8.02	0.0066

Uncorrected zero current transference number = $0.0063 \pm 0.0001_5$

Volume correction = -0.0033

Solvent correction factor = 1.24

Corrected zero current transference number = 0.0037 ± 0.0003 Ionic strength of leading solution = 0.098 mol dm⁻³ $\lambda_{\text{HSO}_4^-}$ in leading solution = 136 ohm⁻¹cm²equiv⁻¹

Table 6jCation transference numbers in 0.126N NaHSO₄ solution

<u>Run number</u>	<u>Following solution</u>	<u>Current (mA)</u>	<u>Measured t₊</u>
80	0.107N Ba(HSO ₄) ₂	3.44	0.0081
82	ditto	8.04	0.0071

Uncorrected zero current transference number = $0.0088_5 \pm 0.0001_5$

Volume correction = -0.0053

Solvent correction factor = 1.10

Corrected zero current transference number = 0.0039 ± 0.0004

86	0.071N Ba(HSO ₄) ₂	3.80	0.0080
86	ditto	8.03	0.0073

Uncorrected zero current transference number = 0.0086 ± 0.0002 Corrected zero current transference number = $0.0036 \pm 0.0004_5$

83	0.080N H ₂ O ₂ .HSO ₄	3.90	0.0090
81	ditto	8.03	0.0092 ₅

Uncorrected zero current transference number = $0.0088 \pm 0.0001_5$ Corrected zero current transference number = $0.0038_5 \pm 0.0004$

87	0.063N H ₂ O ₂ .HSO ₄	3.55	0.0089
85	ditto	8.02	0.0091

Uncorrected zero current transference number = $0.0087_5 \pm 0.0001_5$ Corrected zero current transference number = 0.0038 ± 0.0004 Ionic strength of leading solution = 0.144 mol dm⁻³ $\lambda_{\text{HSO}_4^-}$ in leading solution = 121 ohm⁻¹cm²equiv⁻¹

FIGURE 6-21

EXTRAPOLATION TO ZERO CURRENT OF THE CATION TRANSFERENCE
NUMBER IN 0.126 N NaHSO_4 SOLUTIONS

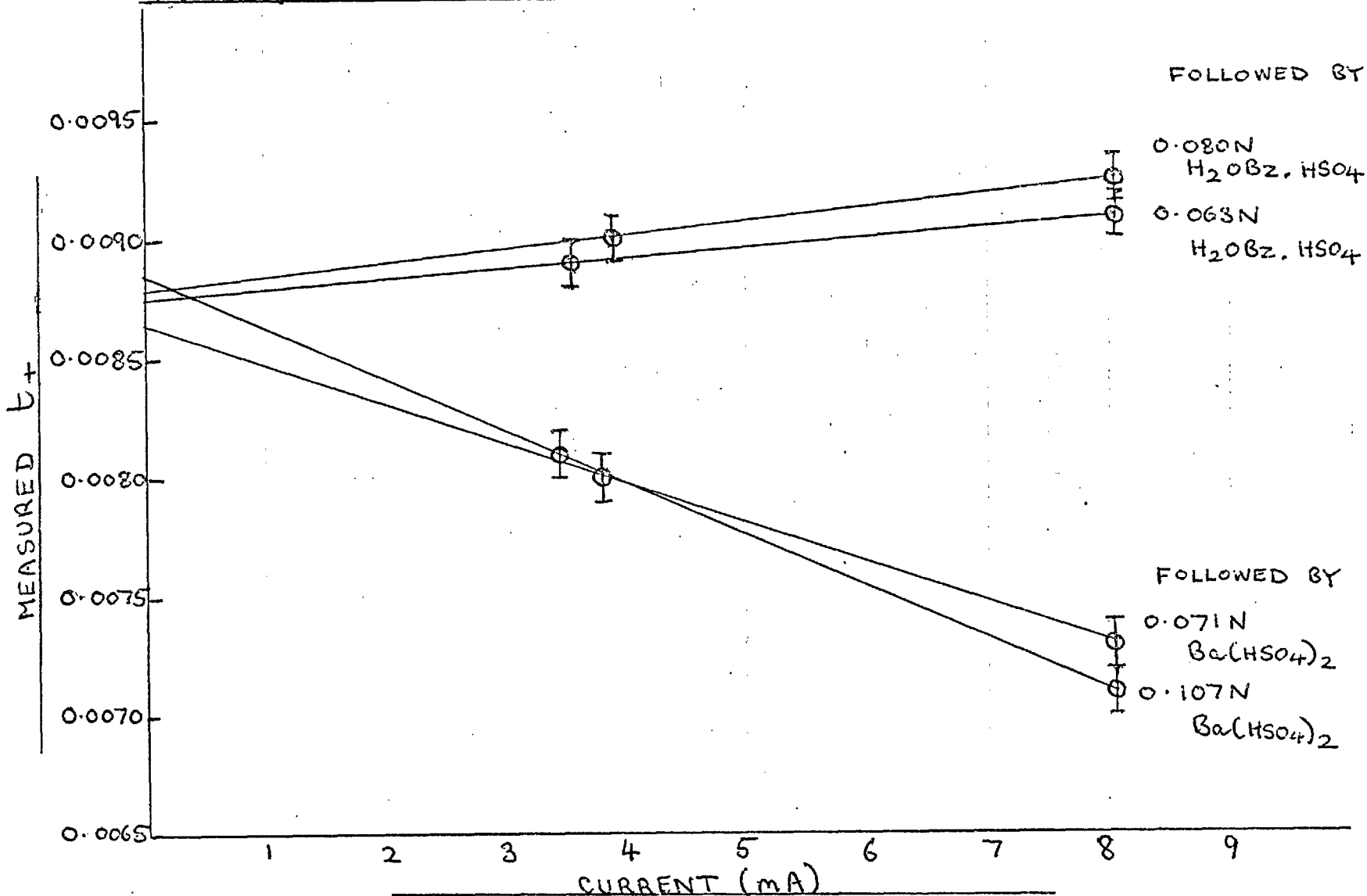


Table 6kCation transference numbers in 0.194N NaHSO₄ solution

<u>Run number</u>	<u>Following solution</u>	<u>Current (mA)</u>	<u>Measured t_+</u>
91	0.128N H ₂ OBr.HSO ₄	4.00	0.0104
90	ditto	8.34	0.0105 ₅

Uncorrected zero current transference number = 0.0103 ± 0.0002

Volume correction = -0.0083

Solvent correction factor = 1.04

Corrected zero current transference number = 0.0021 ± 0.0005 Ionic strength of leading solution = $0.212 \text{ mol dm}^{-3}$ $\lambda_{\text{HSO}_4^-}$ in leading solution = $107 \text{ ohm}^{-1} \text{ cm}^2 \text{ equiv}^{-1}$

Table 6lCation transference numbers in 0.127N LiHSO_4 solution

<u>Run number</u>	<u>Following solution</u>	<u>Current (mA)</u>	<u>Measured t_+</u>
93	0.106N $\text{H}_2\text{OBz.HSO}_4$	3.90	0.0083
92	ditto	8.11	0.0085 ₅

Uncorrected zero current transference number = $0.0081 \pm 0.0001_5$ Volume correction = -0.0054_5

Solvent correction factor = 1.10

Corrected zero current transference number = 0.0029 ± 0.0004 Ionic strength of leading solution = $0.145 \text{ mol dm}^{-3}$ $\lambda_{\text{HSO}_4^-}$ in leading solution = $120 \text{ ohm}^{-1} \text{cm}^2 \text{equiv}^{-1}$

Table 6mCation transference numbers in 0.118N $\text{H}_3\text{O}^+\text{HSO}_4^-$ solution

<u>Run number</u>	<u>Following solution</u>	<u>Current (mA)</u>	<u>Measured t_+</u>
95	0.062N $\text{H}_2\text{OBz}^+\text{HSO}_4^-$	4.03	0.0104
94	ditto	7.97	0.0101 ₅

Uncorrected zero current transference number = $0.0106_5 \pm 0.0002$

Volume correction = -0.0051

Solvent correction factor = 1.04_5 Corrected zero current transference number = 0.0057 ± 0.0004 Ionic strength of leading solution = $0.127 \text{ mol dm}^{-3}$ $\lambda_{\text{HSO}_4^-}$ in leading solution = $130 \text{ ohm}^{-1} \text{cm}^2 \text{equiv}^{-1}$

Table 6nCation transference numbers in 0.0915N AgHSO_4 solution

<u>Run number</u>	<u>Following solution</u>	<u>Current (mA)</u>	<u>Measured t_+</u>
58	0.055N $\text{H}_2\text{OAc.HSO}_4$	4.73	0.0124
57	ditto	7.51 ^b	0.0126

Uncorrected zero current transference number = $0.0121 \pm 0.0002_5$

Volume correction = -0.0039

Solvent correction factor = 1.19

Corrected zero current transference number = 0.0097 ± 0.0004

60	0.031N $\text{H}_2\text{OAc.HSO}_4$	4.96	0.0120
59	ditto	7.49 ^b	0.0121

Uncorrected zero current transference number = $0.0118_5 \pm 0.0002_5$ Corrected zero current transference number = 0.0095 ± 0.0004 Ionic strength of leading solution = $0.112 \text{ mol dm}^{-3}$ $\lambda_{\text{HSO}_4^-}$ in leading solution = $132 \text{ ohm}^{-1} \text{ cm}^2 \text{ equiv}^{-1}$

b. Double boundary runs. The leading one was the sharper and was timed. The second one caught up with the first in the early stages and the two continued to move together for the remainder of the run.

Table 6o

Cation transference numbers in 0.218N AgHSO_4 solution

<u>Run number</u>	<u>Following solution</u>	<u>Current (mA)</u>	<u>Measured t_+</u>
68	0.039N $\text{Ba}(\text{HSO}_4)_2$	4.60	0.0166
65	ditto	8.05 ^c	0.0169

Uncorrected zero current transference number = $0.0160 \pm 0.0002_5$

Volume correction = -0.0094

Solvent correction factor = 1.04

Corrected zero current transference number = 0.0069 ± 0.0006

69	0.128N $\text{H}_2\text{OAc.HSO}_4$	4.96 ^d	0.0160
70	ditto	8.14 ^e	0.0161

Uncorrected zero current transference number = 0.0158 ± 0.0003 Corrected zero current transference number = $0.0067_5 \pm 0.0006_5$ Ionic strength of leading solution = $0.234 \text{ mol dm}^{-3}$ λ_{HSO_4} - in leading solution = $105 \text{ ohm}^{-1} \text{ cm}^2 \text{ equiv}^{-1}$

c. A double boundary run in which the leading boundary was weaker than the following one. The latter closed up on the former in the early stages and they continued to move at the same rate with the one slightly ahead of the other throughout. The calculation of t_+ was based on this rate.

d. Two boundaries of approximately equal strength were seen. The leading one was the faster and the separation between them increased. The quoted transference number is the mean of those calculated for each boundary.

e. Two boundaries of comparable strength and the same speed were obtained. The leading one was approximately $\frac{1}{2}$ cm ahead of the other throughout the run.

Results of double boundary analyses.

The unexpected occurrence of two boundaries in runs employing silver as leading ion was further investigated using the techniques of analysis described at the end of Part I of this chapter. Two cells, both conforming to the design shown in figure 6-18 but differing in the nature of the two-way stopcock at which the sheared boundary was formed, were used. One cell employed a P.T.F.E. stopcock and no further lubricant whilst a hollow glass key lubricated with Voltalef 90 fluorocarbon grease was used in the other. Unfortunately no boundaries at all were seen in either cell when the runs listed in table 6p were carried out and separate explanations, for each cell, of this disappointing result are now suggested.

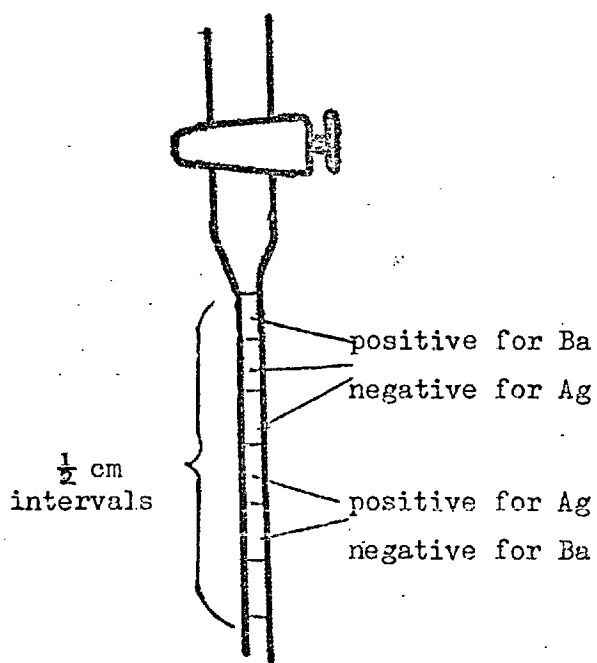
(a) Poor heat dissipation is a well-known characteristic of P.T.F.E. and the efficiency of cooling of the solution inside the bore of the key was low. Thus the boundaries may well have been destroyed as a result of Joule heating. In the m.b. cells employing four-way P.T.F.E. stopcocks the heating was minimised by having the solution on the outside of the key and in direct contact with the glass barrel which was surrounded by the thermostat oil. However this arrangement was not possible for the straight-through two-way stopcock required for runs in which samples could be withdrawn for analysis.

(b) Voltalef 90 was rapidly attacked by the sulphuric acid. Dissolution of the grease in the acid was observed and a black deposit, probably carbon, was seen around the ends of the bore of the hollow key. Leakage of the solutions into the barrel of the tap then occurred and the absence of a boundary might then be attributed to movement of the solutions as a whole, instead of just ion migration, within the m.b. tube. Destruction of the boundary by Joule heating was unlikely since the glass key was hollow to permit circulation of the thermostat oil and so dissipate the heat generated.

Although no boundaries were seen, samples for analysis were still taken from the m.b. tubes at the ends of the runs in the hope that the results would enable the position of the boundary to be located and the concentration(s) of silver in its vicinity to be determined. The results of these investigations are summarized in table 6p overleaf. The findings at the end of run 98, shown in figure 6-22

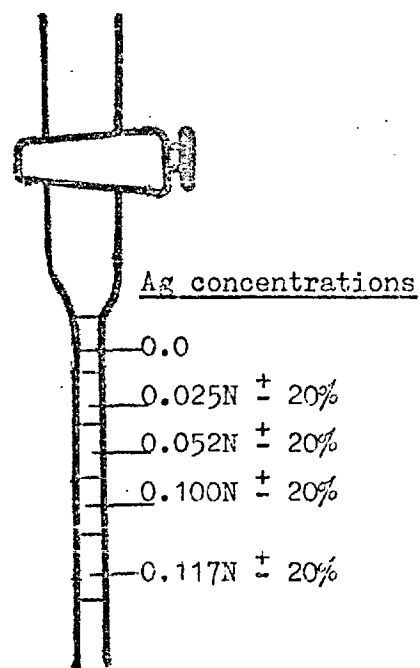
Table 6pAnalysis of suspected double boundary systems

<u>Run number</u>	<u>Leading solution</u>	<u>Indicator solution</u>	<u>Lubricant</u>	<u>Analysis</u>
96	0.223N AgHSO_4	0.0414N $\text{Ba}(\text{HSO}_4)_2$	P.T.F.E.	-
97	ditto	ditto	Voltalef 90	-
98	ditto	ditto	ditto	see fig. 6-22
99	0.114N AgHSO_4	0.060N $\text{H}_2\text{OAc.HSO}_4$	ditto	see fig. 6-23



Tested for Ag with aqueous KCl solution

Tested for Ba with aqueous H_2SO_4 solution

Figure 6-22

Analysis for Ag by atomic
absorption spectroscopy

Figure 6-23

lead to the conclusion that a sharp boundary between silver and barium solutions existed in the m.b. tube although it was not seen during the run. No evidence to indicate the existence of a second boundary was found.

The results of run no.99, shown in figure 6-23, suggest that there was no abrupt change in silver concentration and the results might be taken to indicate that the leading boundary separated two silver solutions, the leading one having a higher concentration than the following one. The second boundary would then have separated a silver solution with a concentration smaller than that of the "bulk" leading solution in the cathode section of the cell from the acetic acid indicator solution at the Kohlrausch concentration. A possible explanation for such a situation is that the initial indicator concentration was much lower than the Kohlrausch value and so, in addition to self-adjustment of the indicator concentration, some adjustment in the leading solution also occurred to maintain the ratio required by equation (1-14). An objection which might be levelled against the hypothesis is that the silver ion transference number appears to decrease with increasing concentration, in which case the silver ions in the solution ahead of the leading boundary should have been moving more slowly than those immediately behind it. Such a situation would have led to mixing and boundary instability and it is necessary to postulate a higher transference number at the higher concentration if this explanation is to be accepted. An attempt to investigate this possibility further was made by performing a run in which the whole of the normal falling cell (figure 6-5) was filled with 0.223N AgHSO_4 solution but no boundary was seen. This experiment rules out extraneous reasons (such as leakage of solution or the presence of impurities like water in the leading solution) for the existence of the second boundary. If a series of further experiments employing leading and following AgHSO_4 solutions of different concentrations were to be carried out, then a boundary might be seen, but it seems more likely that the presence of a solution of the following ion would be required to perpetuate the difference in Ag^+ concentrations and prevent mixing.

Any hypothesis involving a third ionic species such as a silver complex is difficult to accept since an equilibrium with either the leading or following ion would be expected and a boundary between ions in equilibrium seems improbable. If a little water was absorbed by the solutions during cell filling, then a third cation, H_3O^+ would then have been introduced and the situation depicted in figure 6-24 might be considered as a possible explanation of the double boundary. Only

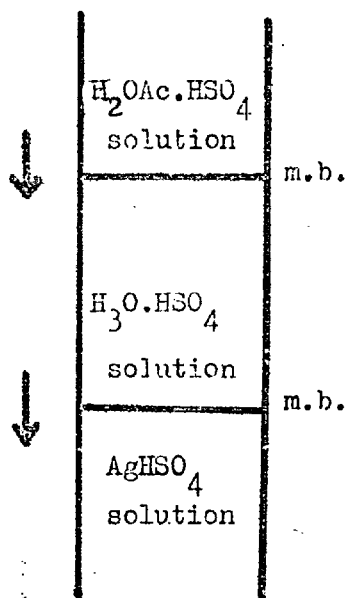


Figure 6-24

absorption into the indicator solution could have resulted in this species migrating to a position in the m.b. tube between leading and indicator solutions. Since it must have been absorbed at one of the openings of the cell, the time required for this to take place would have been long and much greater than the interval between opening the tap and observing the two boundaries in the early stages of the run. Furthermore it is unlikely that the concentration of H_3O^+ would have been high enough for any boundary its solution formed

with silver or barium solutions to be seen. If one or both of the leading and indicator solutions contained a small amount of H_3O^+ before the cell was filled, this would have been evenly dispersed through one half or the whole of the cell and much charge would have to be passed to resolve the ions into separate solutions of their hydrogen sulphates. It thus seems unlikely that the occurrence of the double boundary can be interpreted in terms of figure 6-24. Therefore no really satisfactory explanation of the formation of two boundaries can be given without proper analysis of the solutions immediately ahead of, and behind, each one. Before this can be done, however, a cell employing a P.T.F.E. two-way stopcock with adequate arrangements for dissipating the heat generated within the key, must be designed.

PART III : DISCUSSION

The magnitude of t_+

Table 6q lists the cation transference numbers obtained by both Hittorf and moving boundary methods. A true comparison of the two sets of results can only be made when they both relate to the same ionic strength (I_s) but transference numbers, being ratios of conductances, tend to vary to a much smaller extent with I_s than do the conductances themselves. Moreover, the results reported here for Na^+ , NH_4^+ , and Ag^+ suggest that beyond 0.1N the transference numbers fall with increasing I_s and so the effect of correcting the values from the two methods to the same ionic strength would be to accentuate the difference between them. If this factor is ignored, the Hittorf values are between 3 and 10 times (and mostly 5 times) greater than the newer moving boundary ones. Moving boundary results are usually preferred to Hittorf ones (4). The criticisms made in chapter four of the sulphuric acid Hittorf studies suggest that the method is particularly unreliable for this solvent. The moving boundary transference numbers presented in tables 6b to 6o are less precise in percentage terms than values obtained by the m.b. method in other solvents. This is a consequence of the very small magnitudes of the cation transference numbers in sulphuric acid. Their absolute precision may also be somewhat lower than usual because of the relatively large, and slightly uncertain, solvent and volume corrections in this solvent. Nevertheless, the m.b. results are almost certainly much more reliable than the Hittorf ones.

The very small cation transference numbers obtained confirm the conclusions of previous workers (113, 112, 69) that almost all of the current passed through solutions of hydrogen sulphates in sulphuric acid is conducted by the HSO_4^- ion. Thus the results lend further support to the proposal that some special conducting mechanism such as proton transfer exists for this anion (113, 112, 69, see also chapter four of this thesis). The results presented now provide no new evidence for the nature of such a mechanism. However, the above comparison of the transference numbers determined previously (112, 129) with those reported here suggests that there is an even greater difference between the mobilities of cation

Table 6g

Cation transference numbers measured by different methods

Solute	<u>Hittorf (112,129)</u>		<u>Moving boundary (present study)</u>	
	Concentration (mol dm ⁻³)	t ₊	Concentration (mol dm ⁻³)	t ₊
LiHSO ₄	1.01	0.013	0.127	0.0029
NaHSO ₄	1.47	0.021	0.076	0.0037
			0.126	0.0038
			0.194	0.0021
KHSO ₄	1.17	0.030	0.123	0.0069
	2.33	0.025		
AgHSO ₄	0.47	0.026	0.091 ₅	0.0096
	0.58	0.022	0.218	0.0068
NH ₄ HSO ₄	0.86	0.030 ₅	0.062	0.0055
	1.44	0.033 ₅	0.111	0.0065
	1.81	0.037	0.19	0.0042
CH ₃ CO ₂ H	1.04	0.022	0.090	0.0045
Ba(HSO ₄) ₂	0.38	0.009	0.042	0.0012
	0.37	0.009		
	0.39	0.008		
	0.43	0.010		
	0.46	0.008		

and anion and, therefore, between the efficiencies of the conducting mechanisms than was at first believed (69). The grounds on which the estimates were made have been discussed in chapter four.

Cation conductances

It was pointed out in chapter four that the excess of HSO_4^- ions over M^+ ions in MHSO_4 solutions, and the increasing repression of the solvent self-dissociation with rising concentration, make the calculation of Λ_{MHSO_4} , and hence of λ_{M^+} , very complicated. The difficulty may be overcome by rearranging equation (1-3) into the form

$$\lambda_+ = \frac{t_+ \lambda_-}{t_-} \quad (6 - 34)$$

This equation enables the cation conductance, λ_+ , to be determined from the corrected experimental transference number, t_+ , the conductance of the HSO_4^- ion, λ_- calculated in the estimation of the solvent correction, and the transference number of the HSO_4^- ion, t_- , given by,

$$t_- = 1 - t_+ \quad (6 - 35)$$

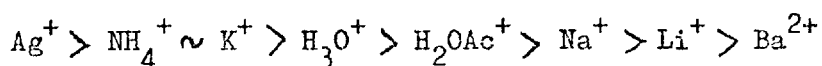
Values of λ_+ for the solutions in which boundary measurements were made are listed in table 6r.

Conductances of different ions can only properly be compared when they refer to solutions of the same ionic strength. In other solvents, values at infinitesimal ionic strength are often derived before any comparison is made. It will be shown below that the extrapolation procedure is difficult and unreliable for sulphuric acid solutions and a sequence of decreasing cation conductances, calculated for solutions with ionic strengths in the range $0.11 \leq I_g < 0.15$ (mol dm^{-3}) has been worked out instead. It is realised that λ_+ for each cation would be changed slightly by relating all the calculations to exactly the same ionic strength (e.g. 0.13 mol dm^{-3}), if this could be done with confidence, but it is unlikely that the sequence of cations would be affected. The cation conductances were found to decrease in the order

Table 6r

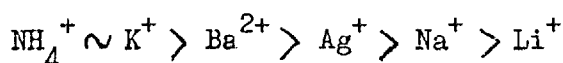
Cation conductances in sulphuric acid solutions

<u>$0.11 < I_s < 0.15$</u>					<u>At other I_s values</u>			
<u>Cation</u>	<u>I_s</u>	<u>t_+</u>	<u>λ_+</u>	<u>λ_-</u>	<u>I_s</u>	<u>t_+</u>	<u>λ_+</u>	<u>λ_-</u>
	<u>mol dm⁻³</u>		<u>ohm⁻¹ cm² equiv⁻¹</u>		<u>mol dm⁻³</u>		<u>ohm⁻¹ cm² equiv⁻¹</u>	
Ba ²⁺	0.147	0.0012	0.17	140				
H ₂ OAc ⁺	0.110	0.0045	0.61	135				
NH ₄ ⁺	0.130	0.0065	0.85	129	0.086	0.0055	0.82	148
					0.207	0.0041	0.46	111
K ⁺	0.139	0.0069	0.85	122				
Na ⁺	0.144	0.0038	0.49	121	0.098	0.0037	0.51	136
					0.212	0.0021	0.23	107
Li ⁺	0.145	0.0029	0.35	120				
H ₃ O ⁺	0.127	0.0057	0.75	130				
Ag ⁺	0.112	0.0096	1.27	132	0.234	0.0069	0.72	105



As λ_+ decreases, the size of the solvated ion and the degree of solvation increase. This order is the same as that found by Gillespie and Wasif (112) from transference measurements and by Flowers et al. (69) from $\lambda_{\text{HSO}_4^-}$ considerations (see discussion in chapter four) except for the position of the silver ion.

In aqueous solution H_2OAc^+ does not exist and the mobility of H_3O^+ is abnormally high due to proton transfer. The aqueous conductances of the remaining cations (154) are listed in table 6s and decrease in the order



It may reasonably be concluded that solvation in sulphuric acid is similar to hydration in aqueous solutions in its dependence on the charge/radius ratio of the ion, although Ba^{2+} appears to be more heavily solvated than expected in H_2SO_4 . A more quantitative comparison in terms of solvation numbers will be made later in this chapter.

The conductance of the silver ion in sulphuric acid ($1.27 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ at $I_s = 0.112 \text{ mol dm}^{-3}$) seems surprisingly high and its position in the sequence is anomalous when the crystal radii of the bare ions and the limiting ion conductances in aqueous solution, given in table 6s, are examined. It is tempting to suggest that the low osmotic coefficients (100) of AgHSO_4 solutions in H_2SO_4 discussed in chapter four, the occurrence of double boundaries when this electrolyte is employed in m.b. runs, and the high cation conductance may have a common explanation. Although the equivalent conductances indicated complete dissociation of the electrolyte, Bass, Gillespie and Oubridge (100) showed that the osmotic coefficients were not anomalous if some ion association was assumed. If the true concentration of Ag^+ ions was αc , ($\alpha < 1$), t_{Ag^+} should have been unaffected because ion-constituent transference numbers are obtained by experiment and since the conductances Λ have the expected values, the high results for λ_+ cannot be satisfactorily explained. Moreover, the assumption of some ion association leads to higher estimates of λ_- (see equation (4 - 62)) and

Table 6sCrystal radii of cations and their equivalent conductances in water and

<u>Ion</u>	<u>crystal radius, r_x, (104)</u>	<u>sulphuric acid</u>	
		<u>sulphuric acid</u>	<u>water</u>
		<u>λ_+</u>	<u>λ_+^0</u>
		($0.11 < I_s < 0.15$)	($I_s = 0$)
	<u>$\text{\AA}$</u>	<u>$\text{ohm}^{-1} \text{cm}^2 \text{equiv}^{-1}$</u>	
Ba ²⁺	1.35	0.17	63.6
NH ₄ ⁺	1.48	0.85	73.6
K ⁺	1.33	0.85	73.5
Na ⁺	0.95	0.49	50.1
Li ⁺	0.60	0.35	38.7
H ₃ C ⁺	-	0.75	349.8
Ag ⁺	1.26	1.27	61.9

consequently even higher values of λ_+ than those listed in table 6r. Thus incomplete dissociation cannot satisfactorily explain the high cation conductances. Nor is it possible to explain the occurrence of a second boundary in terms of ion association, unless the degree of dissociation varied down the m.b. tube giving two AgHSO_4 solutions with different concentrations of silver ion. This seems most unlikely although a boundary velocity appropriate to a lower concentration of Ag^+ than that of the bulk of the leading solution would have led to overestimates of t_{Ag^+} and λ_{Ag^+} .

Limiting cation conductances

The variation of the transference numbers of three ions NH_4^+ , Ag^+ and Na^+ with concentration was investigated. The uncertainty about the extent of silver dissolution after plating at the cathode in the NH_4^+ runs, and the anomalous nature of data for AgHSO_4 solutions, make the validity of the experimental results for these two ions somewhat suspect. The Na^+ values are likely to be more trustworthy and four approaches to the determination of $\lambda_{\text{Na}^+}^0$ have been tried.

In chapter two it was shown that, in most solvents, conductance data fit the available theories more closely than do the corresponding transference ones. In the first two approaches, the values of λ_+ calculated from t_+ at each of three concentrations, were used in the estimation of λ_+^0 . The other two employ the experimental transference numbers themselves to determine t_+^0 from which λ_+^0 is then found. The four approaches will now be discussed in turn.

I. The starting point is the Debye - Hückel - Onsager limiting law for a single univalent ion,

$$\lambda_i = \lambda_i^0 - (B_1 \lambda_i^0 + \frac{1}{2} B_2) \sqrt{I_s} \quad (6 - 36)$$

Equation (6 - 36) differs from (2 - 1) in that $\sqrt{I_s}$ has replaced $\sqrt{c}$ on the right hand side. The original theory was derived in terms of ionic strengths but since the number of ions arising from the solvent self-dissociation is negligible for most systems, the equation is normally quoted in terms of concentration. For sulphuric acid solutions, the ionic strengths and concentrations differ

significantly, as can be seen in the foregoing tables of results, and the replacement of I_s by c is no longer valid. Moreover, as Spiro (155) has pointed out, λ_i^0 is the value of λ_i at infinitesimal ionic strength ($I_s \rightarrow 0$) and not the value at infinite dilution ($c \rightarrow 0$). Whilst the difference between these reference states is academic in many solvents, it is significant in sulphuric acid. A solution of infinitesimal ionic strength is one which approaches closely to the hypothetical undissociated acid discussed in chapter four, whilst a solution of infinite dilution approaches closely to the pure solvent which contains appreciable quantities of ions arising from the self-dissociation. (The ionic strength of pure 100% H_2SO_4 is $0.039 \text{ mol dm}^{-3}$).

The D-H-O limiting law, (6 - 36), is usually only applicable below $I_s = 0.01$ and is consequently of little value for H_2SO_4 solutions. Shedlovsky (156) proposed a form of extrapolation similar to the Longworth one for transference numbers. He suggested that the function λ_i^+ obtained as λ_i^0 in a rearranged form of (6 - 36)

$$\lambda_i^+ = \frac{\lambda_i + \frac{1}{2}B_2\sqrt{I_s}}{1 - B_1\sqrt{I_s}} \quad (6 - 37)$$

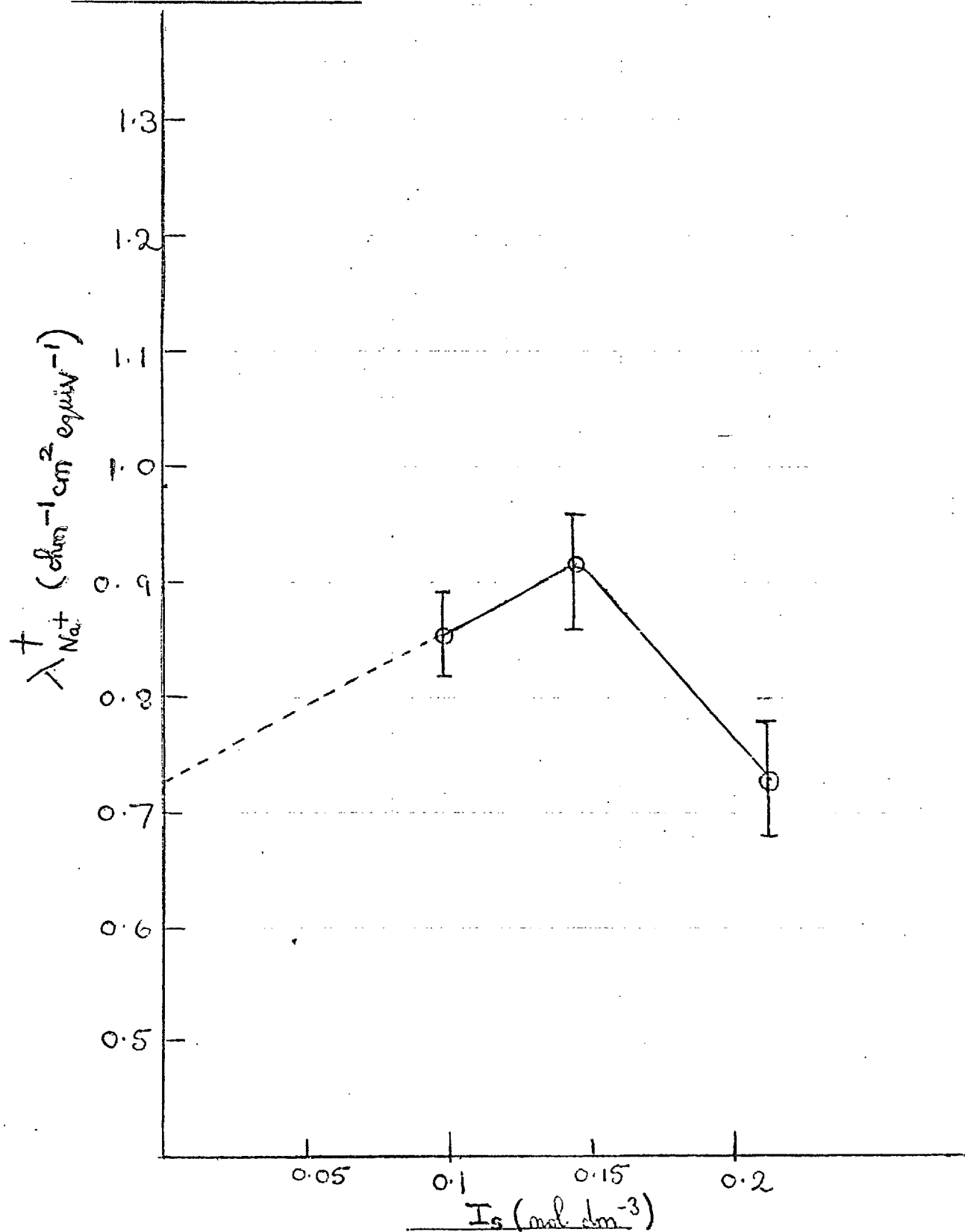
varied linearly with ionic strength,

$$\lambda_i^+ = \lambda_i^0 + bI_s \quad (6 - 38)$$

and that a reasonable value of λ_i^0 could be obtained by extrapolation of a plot of λ_i^+ , so calculated, against I_s to zero ionic strength. Figure 6-25 shows such a plot for the Na^+ results and it can be seen that no satisfactory straight line through the three calculated values of $\lambda_{Na^+}^+$ can be drawn, even when estimated error limits are included. If these limits are extended by ± 0.01 a line extrapolating to a value of 0.98 for $\lambda_{Na^+}^0$ can be drawn but there seems little justification for assuming that all the errors reinforce to raise $\lambda_{Na^+}^0$ at the highest and lowest ionic strengths and to lower it at the intermediate one.

The Robinson and Stokes (115) extension to the limiting law was next tried. For a single univalent ion their equation is

FIGURE 6-25: SHEDLOVSKY PLOT OF $\lambda_{Na^+}^+$ CALCULATED FROM THE DEBYE-HÜCKEL-ONSAGER EQUATION, AGAINST IONIC STRENGTH



$$\lambda_i = \lambda_i^o - \frac{(B_1 \lambda_i^o + \frac{1}{2} B_2) \sqrt{I_s}}{(1 + \kappa a)} \quad (6-39)$$

and only differs from the D-H-O equation by the inclusion of the $(1 + \kappa a)$ term which allows for finite ion size. A series of Shedlovsky extrapolations of $\lambda_{Na^+}^+$ values obtained from

$$\lambda_{Na^+}^+ = \frac{\left\{ \lambda_{Na^+} + \frac{1}{2} \frac{B_2 \sqrt{I_s}}{(1 + \kappa a)} \right\}}{\left\{ 1 - \frac{B_1 \sqrt{I_s}}{(1 + \kappa a)} \right\}} \quad (6-40)$$

was carried out at different chosen integral values of a and the plots obtained are shown in figure 6-26. It will be seen that a satisfactory straight line through the three calculated values of $\lambda_{Na^+}^+$ is obtained only when a physically meaningless value of $-5 \text{ \AA}$ is chosen. This line yields, at $I_s = 0$,

$$\lambda_{Na^+}^o = 0.50 \pm 0.10 \quad (6-41)$$

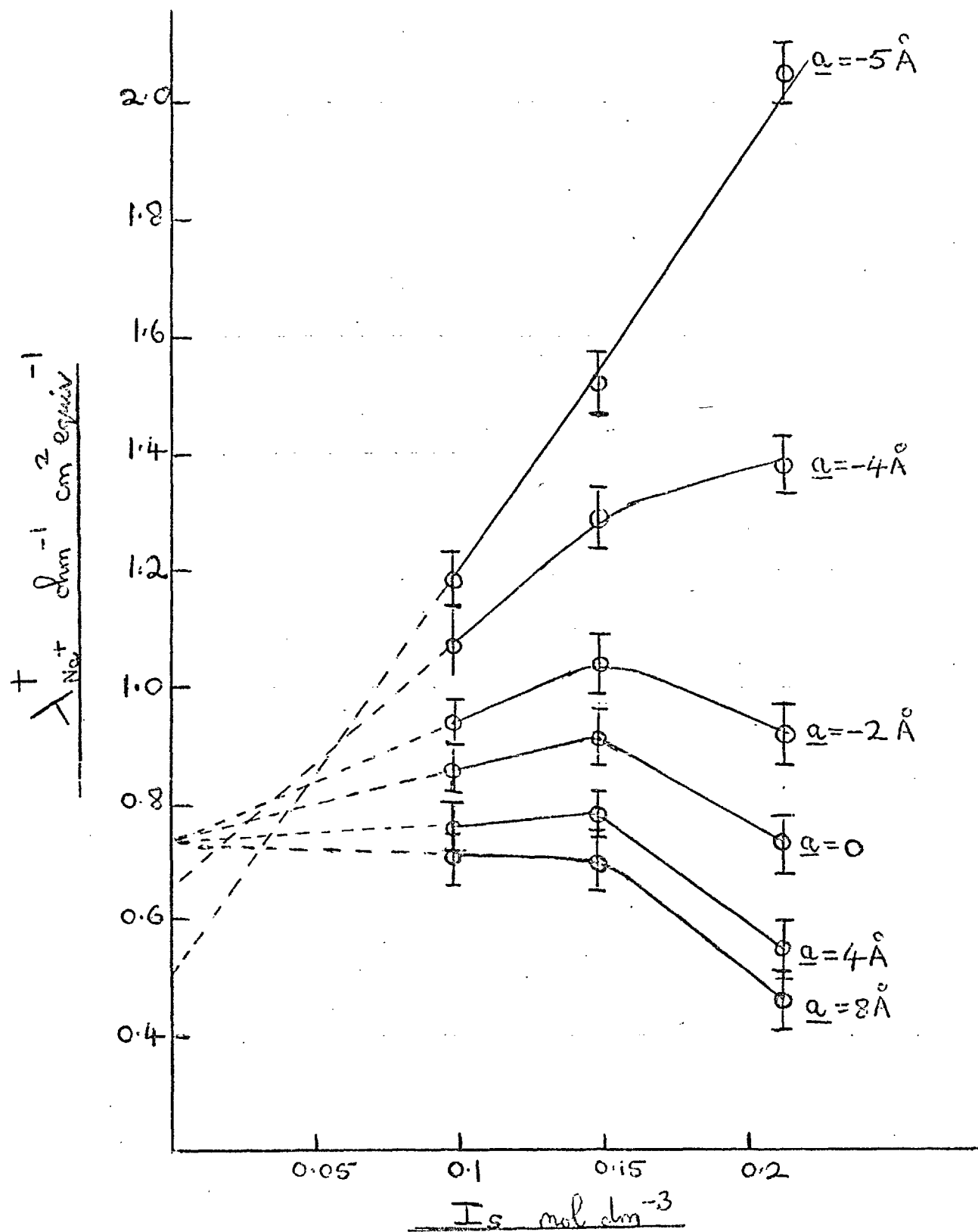
When the results at the highest ionic strength ($0.212 \text{ mol dm}^{-3}$) are excluded from the calculation, straight lines through the two calculated values of λ_i^+ for chosen a values of $-2 \text{ \AA}$, zero (where the Robinson and Stokes equation becomes identical with the limiting law), and positive values less than $8 \text{ \AA}$ all extrapolate to

$$\lambda_{Na^+}^o = 0.74 \pm 0.08 \quad (6-42)$$

Since the theories are more likely to break down at high ionic strengths it is suggested that this value, yielded by calculations at reasonable values of a , is the more reliable.

II Calculations similar to the method A transference ones in chapter two were carried out to try to fit the values of λ_{Na^+} to the Robinson and Stokes equation. A value of a was chosen and the three cation conductances and corresponding ionic strengths were inserted, in turn, into equation (6-39) and values of $\lambda_{Na^+}^o$ (c) calculated. The mean of these, $\langle \lambda_{Na^+}^o \rangle$, and their standard deviation, σ , from the mean were then found. The calculations were repeated employing all integral values of a between $-6 \text{ \AA}$ and $10 \text{ \AA}$ and a minimum value of σ was 0.05_2

FIGURE 6-26. SHEDLOVSKY PLOTS OF $\lambda_{Na^+}^+$, FROM THE ROBINSON AND STOKES EQUATION, AGAINST IONIC STRENGTH.



at $\underline{a}$ equal to $-2 \text{ \AA}$. The mean $\lambda_{\text{Na}^+}^{\circ}$ was

$$\langle \lambda_{\text{Na}^+}^{\circ} \rangle = 0.97 \pm 0.08 \quad (6-43)$$

The actual values of $\lambda_{\text{Na}^+}^{\circ}$ (c) calculated from equation (6-39) are identical with those of $\lambda_{\text{Na}^+}^{\dagger}$ in the Shedlovsky plots shown in figure 6-26.

III A Longworth transference plot, of $t_{\text{Na}^+}^{\dagger}$ against I_s , using equations (2-23) and (2-24) is shown in figure 6-27. Once again, no satisfactory straight line can be drawn through the points even when error limits are included. Exclusion of the result at the highest ionic strength and extrapolation of the values of $t_{\text{Na}^+}^{\dagger}$ at the lower concentrations yields,

$$t_{\text{Na}^+}^{\circ} = 0.0044 \pm 0.0005 \text{ giving, } \lambda_{\text{Na}^+}^{\circ} = 0.75 \pm 0.08 \quad (6-44)$$

Proceeding along similar lines to the first approach, an extension of this treatment is a series of calculations, at different values of $\underline{a}$, of $t_{\text{Na}^+}^{\dagger}$ using the $(F-0)_1$ equation,

$$t_{\text{Na}^+}^{\dagger} = t_{\text{Na}^+} - \frac{(t_{\text{Na}^+} - \frac{1}{2}) B_2 \sqrt{c}}{\Lambda^{\circ} (1 + K \underline{a})} \quad (6-45)$$

followed by extrapolation of the plots of $t_{\text{Na}^+}^{\dagger}$ against I_s to zero ionic strength.

Figure 6-28 shows the results of these calculations when values of $\underline{a}$ between $-5.5 \text{ \AA}$ and $8 \text{ \AA}$ were chosen. The shapes of the plots obtained closely resemble those in figure 6-26 and yield, on extrapolation, the following values,

With all three data points included and $\underline{a}$ equal to $-5.5 \text{ \AA}$,

$$t_{\text{Na}^+}^{\circ} = 0.0034 \pm 0.0007 \text{ giving, } \lambda_{\text{Na}^+}^{\circ} = 0.58 \pm 0.11 \quad (6-46)$$

With the highest data point excluded and $-2 \text{ \AA} < \underline{a} < 8 \text{ \AA}$,

$$t_{\text{Na}^+}^{\circ} = 0.0043 \pm 0.0005 \text{ giving, } \lambda_{\text{Na}^+}^{\circ} = 0.73 \pm 0.08 \quad (6-47)$$

IV. The performance of the method A computer calculations on the experimental transference numbers yields the following results. The symbols were defined in chapter two.

FIGURE 6-27 LONGSWORTH PLOT OF $t_{Na^+}^+$ CALCULATE
FROM THE DEBYE - HÜCKEL - ONSAGER EQUATION, AGAINST
IONIC STRENGTH

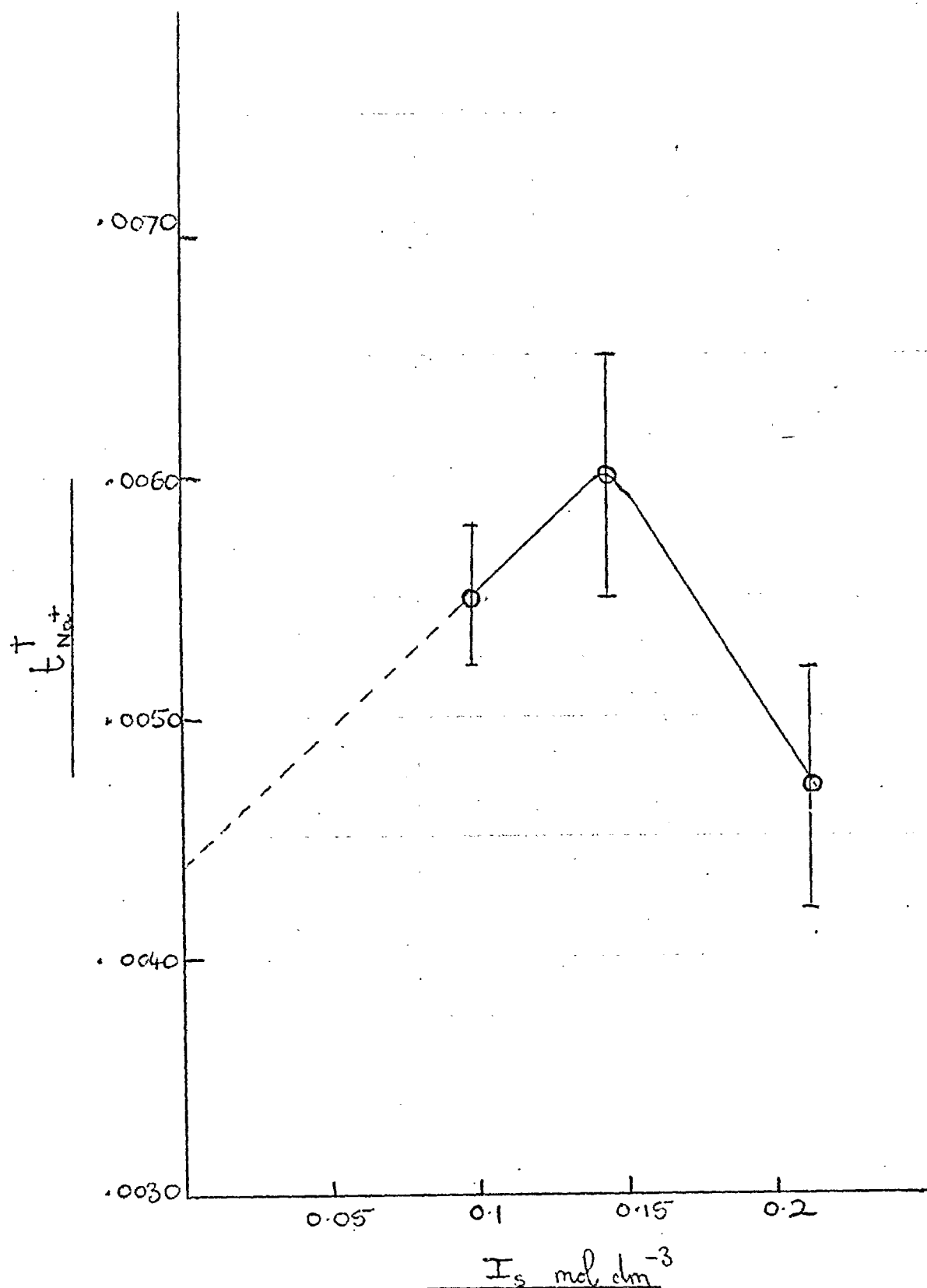
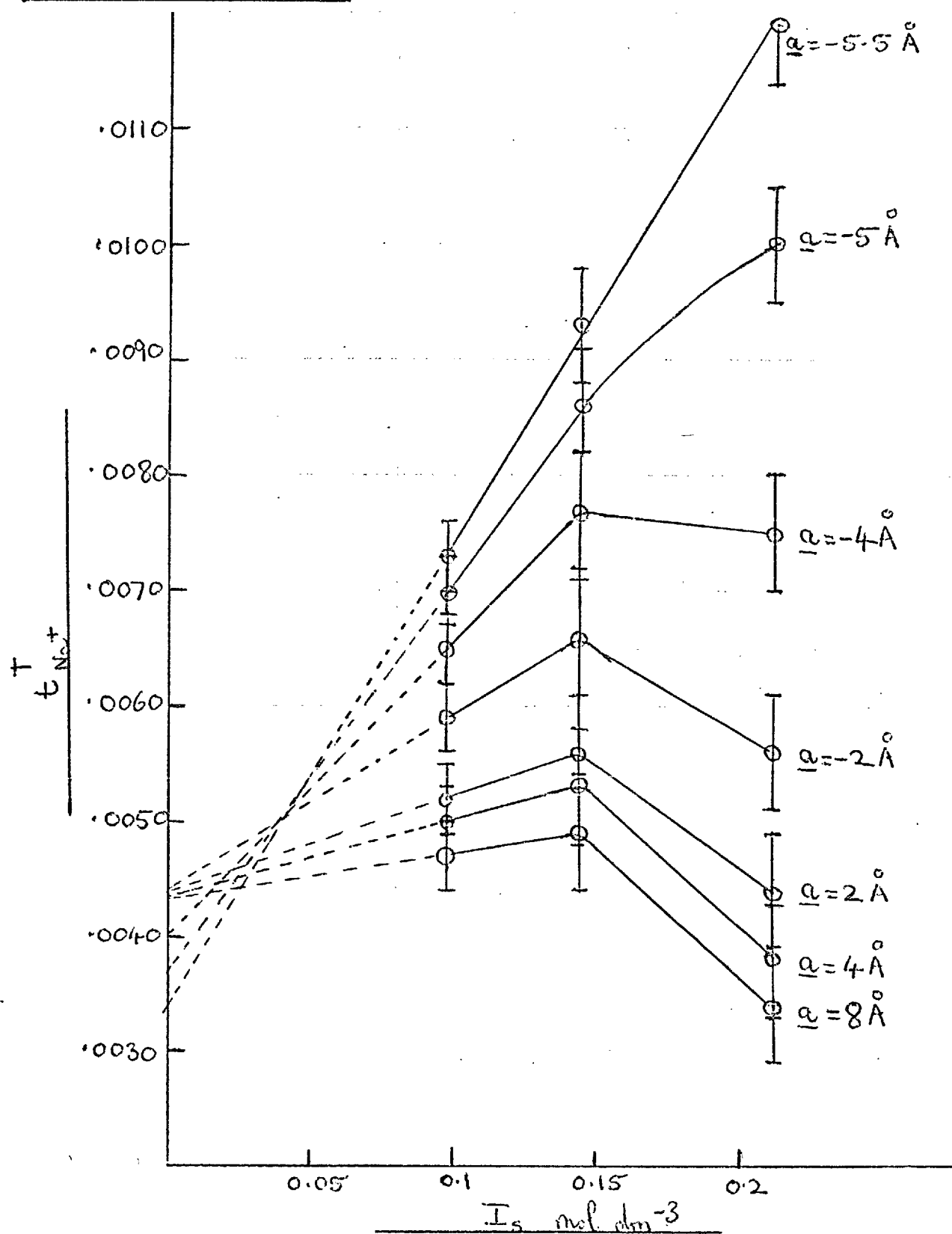


FIGURE 6-28 LONGSWORTH PLOTS OF $t_{Na^+}^+$,
FROM THE FUOSS-ONSAGER THEORY ((F-O)_i), AGAINST
IONIC STRENGTH



theory	I_s range	best $\underline{a}$	$10^4 \sigma_{\min}$	$\langle t_{Na^+}^o \rangle$	trend in $t_{Na^+}^o$ (c)
P_A	0.098 - 0.212	< 0			
$(F-O)_1$	0.098 - 0.212	-2.7	3.5	0.0064	fig. 6-29
$(F-O)_2$	0.098 - 0.212	0.2	4.3	0.0058	fig. 6-29
P_A	0.098 - 0.144	> 20			
$(F-O)_1$	0.098 - 0.144	> 20			
$(F-O)_2$	0.098 - 0.144	6.8	0.0	0.0045	fig. 6-29

The limiting cation conductances obtained from the above values of $\langle t_{Na^+}^o \rangle$

are,

theory	I_s range	$\lambda_{Na^+}^o$
$(F-O)_1$	0.098 - 0.212	1.09
$(F-O)_2$	0.098 - 0.144	0.76

The Longworth and Shedlovsky extrapolations and method A transference $(F-O)_2$ calculations all yield values between 0.73 and 0.76 $\text{ohm}^{-1} \text{cm}^2 \text{equiv}^{-1}$ for $\lambda_{Na^+}^o$ at plausible values of $\underline{a}$ when the highest data point is excluded. Both the higher and lower results for $\lambda_{Na^+}^o$ were obtained from calculations employing all three ionic strengths and involve negative or an exceedingly small positive value of $\underline{a}$. Therefore a value of 0.75 has been taken as the best $\lambda_{Na^+}^o$. Insertion of this value, together with those of λ_{Na^+} and I_s , into equation (6 - 39) yield for $\underline{a}$,

$$\begin{aligned} \text{At } I_s &= 0.098 & \underline{a} &= 4.8 \text{ \AA} \\ \text{At } I_s &= 0.144 & \underline{a} &= 5.4 \text{ \AA} \\ \text{mean } \underline{a} &= 5.1 \text{ \AA} \end{aligned}$$

The standard procedure in other solvents (45, 137, 153) was to combine $\lambda_{M^+}^o$, determined from a Longworth extrapolation of t_{M^+} , with the value of Λ_{MX}^o for the electrolyte, MX, and so determine $\lambda_{X^-}^o$,

$$\lambda_{X^-}^o = \Lambda_{MX}^o - \lambda_{M^+}^o \quad (6 - 48)$$

Since the value applies to infinitesimal ionic strength it is independent of the

FIGURE 6-29 PLOT OF $\epsilon_{Na^+}^{\circ}(c)$, CALCULATED BY METHOD (F-O)₁, AGAINST IONIC STRENGTH

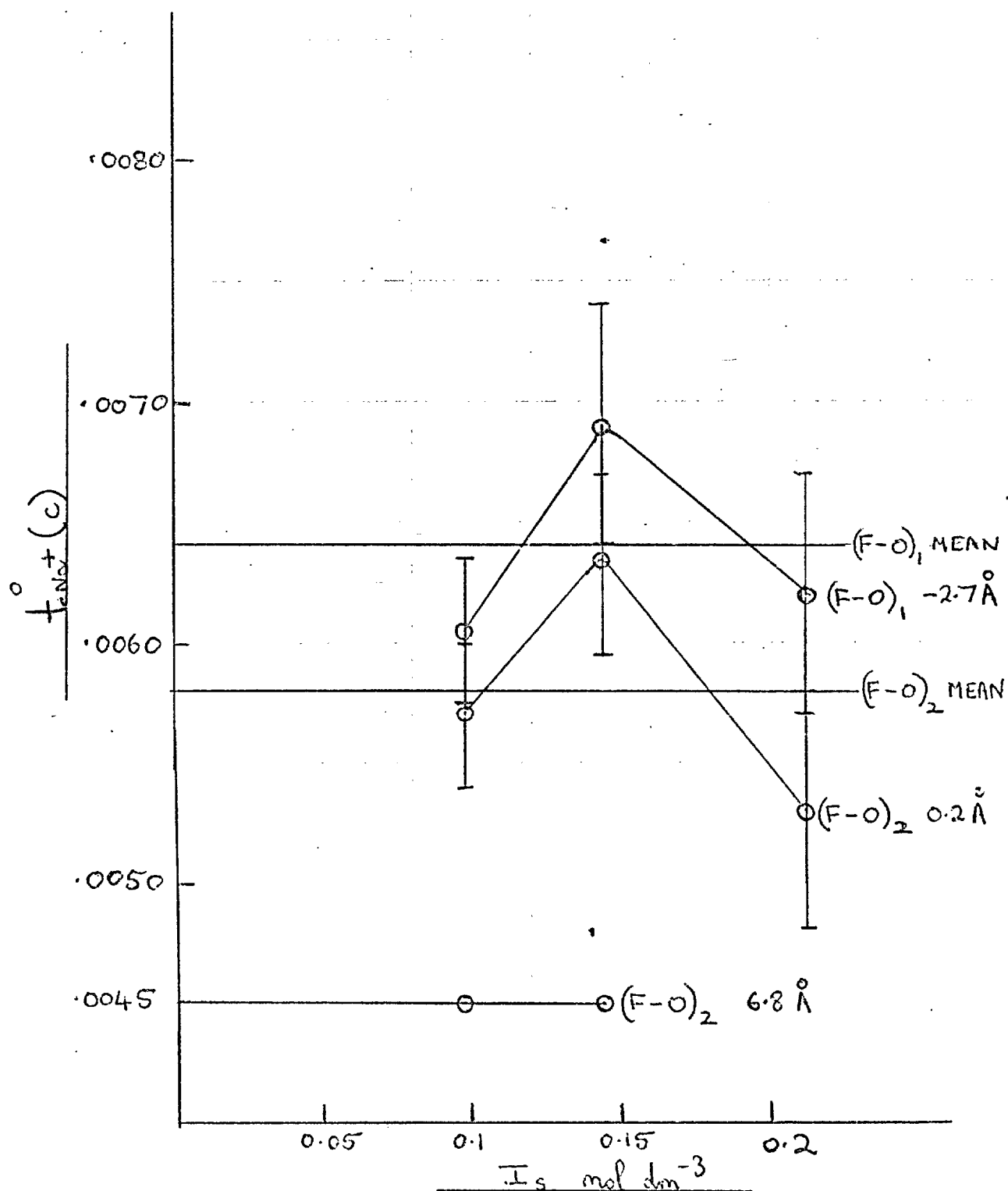


Table 6tLimiting cation conductances in sulphuric acid

<u>Ion</u>	<u>λ_+^0</u>	<u>λ_+</u>
		($0.11 < I_s < 0.15$) <u>$\text{ohm}^{-1} \text{cm}^2 \text{equiv}^{-1}$</u>
Ba ²⁺	0.42	0.17
H ₂ OAc ⁺	0.86	0.61
NH ₄ ⁺	1.12	0.85
K ⁺	1.13	0.85
Na ⁺	0.76	0.49
Li ⁺	0.61	0.35
H ₃ O ⁺	1.01	0.75
Ag ⁺	1.54	1.27

cation and so values of $\lambda_{M^+}^{\circ}$ were determined by combination of $\lambda_{X^-}^{\circ}$ with $\Lambda_{M'X}^{\circ}$ for other electrolytes, $M'X$, in the solvent. This approach is not possible for electrolytes in sulphuric acid since no values of $\Lambda_{MHSO_4}^{\circ}$ are available and, even if they were, the uncertainties in them would be comparable with the values of $\lambda_{M^+}^{\circ}$ themselves.

Instead it has been assumed that all the cation conductances obey the Robinson and Stokes equation. In the absence of a more satisfactory procedure the value of $5.1 \text{ \AA}$ for a , derived above for $NaHSO_4$, has been used for all the hydrogen sulphates. Some justification for this step comes from the fact that $\lambda_{Na^+}^{\circ}$ was virtually independent of a in the Longworth and Shedlovsky extrapolations using only the lowest two data points. Insertion of the appropriate values of λ_{Na^+} and I_s ($0.11 < I_s < 0.15$) into equation (6-39) yields the limiting cation conductances given in table 6t. These decrease in the same sequence as those at finite ionic strengths discussed earlier.

Clearly a more trustworthy extrapolation of λ_{Na^+} to infinitesimal ionic strength is required but, first, the variation of the transference numbers with concentration must be more thoroughly examined, particularly below $I_s = 0.1$. There are two problems here; boundaries cannot be seen at ionic strengths significantly below this value and the extensive self-dissociation of the solvent means that very dilute solutions of $MHSO_4$ still have appreciable ionic strengths. It is possible that the first difficulty might be partly offset if the boundaries were followed by some other means such as the measurement of changes in electrical potential or resistance mentioned in chapter one and discussed by Spiro (4).

Solvation of ions in sulphuric acid

Solvation numbers have seldom been satisfactorily derived from limiting ion conductances although a variety of attempts has been made (45). The starting point for such calculations is Stokes' law, equation (4-49), which may be expressed in the following form for ions in sulphuric acid.

$$r_s = 3.35 / \lambda_i^{\circ} \text{ \AA} \quad (6-49)$$

Table 6uStokes radii of cations in sulphuric acid and water

<u>Cation</u>	<u>Crystal radius, r_x, (104)</u>	<u>Stokes radius, r_s</u>	
		<u>Å</u>	
		<u>sulphuric acid</u>	<u>water</u>
Ba ²⁺	1.35	7.9	2.89
H ₂ OAc ⁺	-	3.9	-
NH ₄ ⁺	1.48	3.0	1.25
K ⁺	1.33	2.9	1.25
Na ⁺	0.95	4.4	1.84
Li ⁺	0.60	5.5	2.38
H ₃ O ⁺	-	3.3	-
Ag ⁺	1.26	2.2	1.49

H₂OAc⁺ does not exist in water or in the crystalline state whilst H₃O⁺ conducts by proton transfer as well as normal migration in aqueous solution and so Stokes law cannot be applied.

By inspection of the values listed in table 6u, it may be seen that the Stokes radii, r_s , obtained are all greater than the crystal radii of the ions and this may be taken as evidence for solvation.

Several writers (157,45) have drawn attention to the limitations of Stokes' law which centre on its derivation from a model of a spherical particle moving in an ideal hydrodynamic continuum. The law is therefore least valid for a small ion moving in a real medium where its size is comparable to that of the solvent molecules. Robinson and Stokes (157) have proposed an empirical correction to Stokes' law for aqueous solutions and their approach has been extended to other solvents (45). They assumed that a number of selected tetraalkyl ammonium ions are unsolvated. Their radii, r_c , were calculated from bond lengths or molar volumes of related hydrocarbons and their Stokes radii determined from their limiting ion conductances. The ratio r_c/r_s was then plotted against r_s and, from the plot, a correction factor at an intermediate Stokes radius for some other ion could be obtained. Multiplication of the Stokes radius by this factor yields an effective value for the radius of the solvated ion (r_{eff}). This procedure is difficult to carry out for solutions in sulphuric acid since no conductances of tetraalkyl ammonium ions are available. A very crude approximation is to assume Walden's rule for a given ion,

$$\lambda_i^0 \eta = \text{constant} \quad (6 - 50)$$

holds for water and sulphuric acid. In spite of similarities between these solvents, both being protonic and extensively hydrogen-bonded, they differ greatly in viscosity and doubts must be expressed about the applicability of (6 - 50). Walden's rule is an extension of Stokes' ^{law} and has the same limitations. By applying it to the tetraalkyl ammonium ions, from Me_4N^+ to Am_4N^+ , a Robinson and Stokes correction plot can be drawn (fig. 6-30) and correction factors r_c/r_s read off. Values of r_{eff} for ions in sulphuric acid are listed in table 6v.

The solvation number, n_i , is found by dividing the volume of the solvation shell (equal to the volume of the solvated ion less that of the bare ion)

FIGURE 6-30

CORRECTION FACTORS TO STOKES' LAW FOR
IONS (BASED ON AQUEOUS DATA)

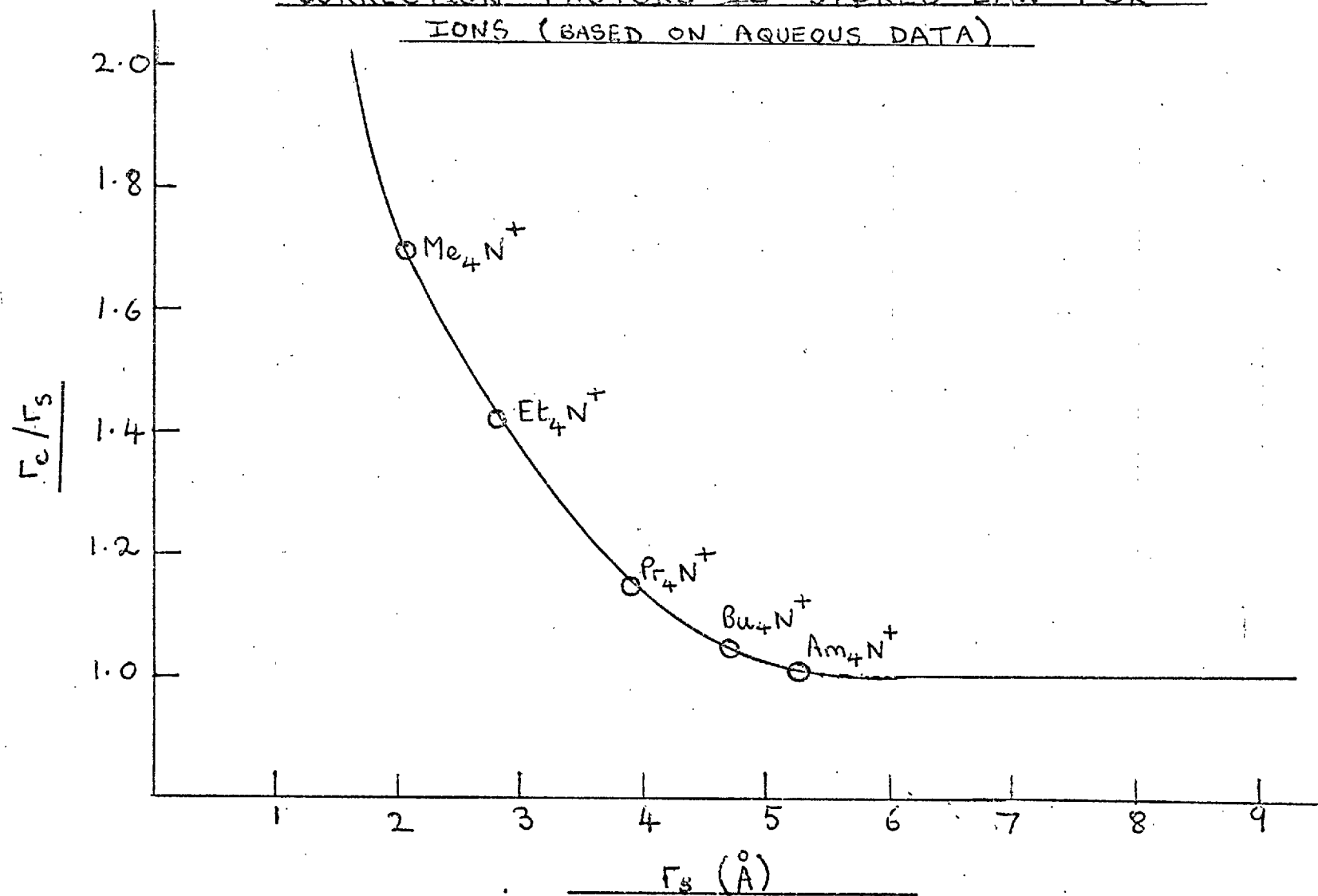


Table 6vA comparison of solvation numbers in sulphuric acid and water

<u>Cation</u>	<u>sulphuric acid</u>				<u>water</u>
	<u>r_s</u>	<u>r_c/r_s</u>	<u>r_{eff}</u>	<u>n_i</u>	<u>n_i</u>
	<u>Å</u>		<u>Å</u>		
Ba ²⁺	7.9	1.0	7.9	23.4	9 - 10
NH ₄ ⁺	3.0	1.37	4.1	3.1	2
K ⁺	2.9	1.39	4.0	2.9	2
Na ⁺	4.4	1.08	4.7 ₅	4.9 ₅	5
Li ⁺	5.5	1.0	5.5	7.7 ₅	7
Ag ⁺	2.2	1.61	3.5	1.9	2

by the average volume of a sulphuric acid molecule, V_s .

$$n_i = \frac{4}{3}\pi(r_{\text{eff}}^3 - r_x^3) / V_s \quad (6 - 51)$$

A value for V_s of $8.95 \times 10^{-23} \text{ cm}^3$ was estimated by dividing the molar volume of sulphuric acid by the Avogadro number. It is pleasing, if surprising, to note that these calculations yield reasonable solvation numbers, listed in table 6v. Too much significance should not be attached to them in view of the many assumptions and approximations made in their derivation. To summarize the weaknesses of the treatment ; (i) the uncertain extrapolation of λ_{Na^+} to $\lambda_{\text{Na}^+}^0$, (ii) the assumption that λ_{M^+} obeys the Robinson and Stokes equation and the same value of a is required for all the hydrogen sulphates, (iii) the use of Stokes' law for this system where solute and solvent particles are of comparable size and the law is least likely to hold, (iv) the use of empirical aqueous correction factors for a non-aqueous system, and (v) the neglect of electrostriction effects in estimating V_s . Nevertheless there is a striking similarity between the two sets of solvation numbers in sulphuric acid and water. A smaller solvation number for sulphuric acid might have been expected in view of the larger H_2SO_4 molecule but the solvent is more polar and so has a greater tendency to solvate the ions. The high value of n_i for Ba^{2+} may well be a consequence of more secondary coordination beyond the primary solvation shell than this ion undergoes in aqueous solution. The solvation numbers obtained here are slightly larger than the ones obtained from osmotic coefficients (see p. 82) but, unlike the last-mentioned, show the expected decrease on going from Li^+ to Na^+ .

APPENDIX I

The Fuoss-Onsager conductance equation: Electrophoretic term

In 1963, Fuoss and Onsager (9) derived the electrophoretic contribution Λ^e to the conductance of a symmetrical electrolyte. After conversion of their equation '61' from ion velocity to conductance form, Λ^e becomes

$$\Lambda^e = B_2 \sqrt{c} - B_3 \quad (\text{I} - 1)$$

where
$$B_3 = \frac{2}{3} \frac{N^2 e^6}{\eta (\epsilon R T)^2} \cdot c \cdot F(b) \times 10^{-3} \quad (\text{I} - 2)$$

and $F(b)$ is a complicated function of a, ϵ , and T .

In a review published in 1968 (19), Fuoss states that the simpler more usual form of Λ^e

$$\Lambda^e = \frac{B_2 \sqrt{c}}{(1 + \frac{1}{2} a)} \quad (\text{I} - 3)$$

is a very close approximation to the more exact form (I - 1). In view of the overall failure of the transference form of the Fuoss-Onsager equation, employing the simple form of Λ^e , to fit the experimental transference data, (calculations $(F-0)_1$), it was decided to employ the fuller form of Λ^e in (I - 1). The calculation of $F(b)$ is a complicated procedure and it is listed below in stepwise form.

1. b is given by
$$b = \frac{e^2}{a \epsilon k T} \quad (\text{I} - 4)$$

with e in e.s.u. of charge and a in Å.

2.
$$E_n(b) = \int_b^{\infty} \exp(-t) \frac{dt}{t} \quad (\text{I} - 5)$$

3.
$$E_p(b) = \int_{-\infty}^b \exp(t) \frac{dt}{t} \quad (\text{I} - 6)$$

4. Euler's constant, $\Gamma = 0.577216 \quad (\text{I} - 7)$

5.
$$j_n(b) = E_n(b) + \ln b + \Gamma \quad (\text{I} - 8)$$

6.
$$j_p(b) = E_p(b) - \ln b - \Gamma \quad (\text{I} - 9)$$

7.
$$F_n(b) = \left(\frac{1}{2} j_n(b) - 1 + (1 - \exp(-b))/b \right) \quad (\text{I} - 10)$$

8.
$$F_p(b) = \left(\frac{1}{2} j_p(b) + 1 - (\exp(b) - 1)/b \right) \quad (\text{I} - 11)$$

9.
$$T_1(b) = \exp(-b) \left(1 + b + b^2/2 \right) \quad (\text{I} - 12)$$

10.
$$T_2(b) = \exp(b) \left(1 - b + b^2/2 \right) \quad (\text{I} - 13)$$

11.
$$M = T_2 / (T_2 - 1) \quad (\text{I} - 14)$$

TABLE Ia: COMPARISON OF Λ^e FOR $(F-O)_1$ AND $(F-O)_2$ THEORIES

<u>a</u>	<u>b</u>	<u>F(b)</u>	<u>c</u>	<u>$B_2 \sqrt{c}$</u>	<u>B_3</u>	<u>Λ_2^e</u>	<u>Λ_1^e</u>	<u>$\Lambda_2^e - \Lambda_1^e$</u>
0.50	14.3150	-.74454						
			.001	1.91784	-0.02659	1.94443	1.90791	0.03652
			.010	6.06474	-0.26589	6.33063	5.96655	0.36408
			.100	19.17838	-2.65892	21.83731	18.22967	3.60763
1.00	7.1575	-.20073						
			.001	1.91784	-0.00717	1.92501	1.89808	0.02692
			.010	6.06474	-0.07169	6.13642	5.87148	0.26494
			.100	19.17838	-0.71686	19.89524	17.37040	2.52484
1.50	4.7717	.23981						
			.001	1.91784	0.00856	1.90927	1.88836	0.02092
			.010	6.06474	0.08564	5.97910	5.77940	0.19970
			.100	19.17838	0.85640	18.32198	16.58849	1.73350
2.00	3.5788	.61799						
			.001	1.91784	0.02207	1.89577	1.87873	0.01704
			.010	6.06474	0.22070	5.84404	5.69016	0.15388
			.100	19.17838	2.20696	16.97142	15.87393	1.09749
2.50	2.8630	.95789						
			.001	1.91784	0.03421	1.88363	1.86920	0.01443
			.010	6.06474	0.34208	5.72265	5.60364	0.11902
			.100	19.17838	3.42083	15.75755	15.21840	0.53915
3.00	2.3858	1.27477						
			.001	1.91784	0.04552	1.87231	1.85977	0.01255
			.010	6.06474	0.45525	5.60949	5.51971	0.08978
			.100	19.17838	4.55247	14.62591	14.61486	0.01106
3.50	2.0450	1.57721						
			.001	1.91784	0.05633	1.86151	1.85043	0.01108
			.010	6.06474	0.56326	5.50148	5.43825	0.06323
			.100	19.17838	5.63255	13.54583	14.05736	-0.51153
4.00	1.7894	1.87012						
			.001	1.91784	0.06679	1.85105	1.84118	0.00987
			.010	6.06474	0.66786	5.39688	5.35916	0.03771
			.100	19.17838	6.67858	12.49980	13.54084	-1.04104
4.50	1.5906	2.15646						
			.001	1.91784	0.07701	1.84083	1.83203	0.00880
			.010	6.06474	0.77012	5.29462	5.28235	0.01227
			.100	19.17838	7.70117	11.47721	13.06092	-1.58371
5.00	1.4315	2.43811						
			.001	1.91784	0.08707	1.83077	1.82297	0.00780
			.010	6.06474	0.87070	5.19404	5.20770	-0.01366
			.100	19.17838	8.70701	10.47138	12.61387	-2.14249

TABLE Ia (contd:)								
a	b	F(b)	c	$B_2 \sqrt{c}$	B_3	Λ_2^e	Λ_1^e	$\Lambda_2^e - \Lambda_1^e$
5.50	1.3014	2.71628	.001	1.91784	0.09700	1.82083	1.81399	0.00684
			.010	6.06474	0.97004	5.09470	5.13513	-0.04043
			.100	19.17838	9.70039	9.47799	12.19640	-2.71841
6.00	1.1929	2.99181	.001	1.91784	0.10684	1.81099	1.80511	0.00589
			.010	6.06474	1.06844	4.99630	5.06456	-0.06826
			.100	19.17838	10.68435	8.49403	11.80568	-3.31165
6.50	1.1012	3.26528	.001	1.91784	0.11661	1.80123	1.79631	0.00492
			.010	6.06474	1.16610	4.89864	4.99590	-0.09726
			.100	19.17838	11.66100	7.51739	11.43922	-3.92183
7.00	1.0225	3.53716	.001	1.91784	0.12632	1.79152	1.78760	0.00392
			.010	6.06474	1.26319	4.80155	4.92908	-0.12753
			.100	19.17838	12.63191	6.54647	11.09482	-4.54835
7.50	0.9543	3.80773	.001	1.91784	0.13598	1.78186	1.77897	0.00289
			.010	6.06474	1.35982	4.70492	4.86402	-0.15910
			.100	19.17838	13.59817	5.58021	10.77055	-5.19034
8.00	0.8947	4.07723	.001	1.91784	0.14561	1.77223	1.77042	0.00181
			.010	6.06474	1.45606	4.60867	4.80066	-0.19198
			.100	19.17838	14.56064	4.61774	10.46470	-5.84696
8.50	0.8421	4.34586	.001	1.91784	0.15520	1.76264	1.76196	0.00068
			.010	6.06474	1.55200	4.51274	4.73892	-0.22618
			.100	19.17838	15.51995	3.65843	10.17574	-6.51731
9.00	0.7953	4.61378	.001	1.91784	0.16477	1.75307	1.75357	-0.00050
			.010	6.06474	1.64767	4.41706	4.67876	-0.26169
			.100	19.17838	16.47675	2.70164	9.90232	-7.20068
9.50	0.7534	4.88105	.001	1.91784	0.17431	1.74353	1.74527	-0.00174
			.010	6.06474	1.74312	4.32161	4.62010	-0.29848
			.100	19.17838	17.43124	1.74714	9.64320	-7.89605
10.00	0.7158	5.14780	.001	1.91784	0.18384	1.73400	1.73704	-0.00304
			.010	6.06474	1.83839	4.22635	4.56289	-0.33654
			.100	19.17838	18.38386	0.79453	9.39729	-8.60276

$$12. A = -T_1 / (1 - T_1) \quad (I - 15)$$

$$13. F_1(b) = MF_n(b) + AF_p(b) \quad (I - 16)$$

$$14. F_x = (1 / (1 - T_1) - 1 / (T_2 - 1)) \quad (I - 17)$$

$$15. F(b) = 2/b + bF_x/4 - F_1(b) \quad (I - 18)$$

A series of computer calculations was performed to calculate Λ^e by both equations (I - 1) and (I - 3) for values of a between 0.5 and 10 Å at intervals of 0.5 Å. Table Ia lists the results obtained for aqueous systems. the values of Λ^e obtained using equation (I - 1) are designated Λ_2^e and those obtained using (I - 3) are designated Λ_1^e . the subscripts are to maintain consistency with the methods (F-0)₁ and (F-0)₂. The calculations were performed at three concentrations 0.001N, 0.01N, and 0.1N. Inspection of the results shows that Λ_1^e and Λ_2^e only correspond closely at one particular value of a for each concentration. Thus for 0.01N the terms only correspond closely for values of a between 4.5 Å and 5 Å and when a has the fairly plausible value of 3.5 Å the discrepancy between them is of the order of 1.1 %. In his 1968 review, cited above (19), Fuoss states that the difference between the terms divided by Λ^o for KCl in 0.1N is of the order of 0.2 %. The present set of calculations indicate that this is indeed the case if a is of the order of 3.3 Å. However the numerical difference increases the further the chosen value of a is from this value as the following table makes clear.

Table Ib

a (Å)	$\frac{\Lambda_2^e - \Lambda_1^e}{\Lambda^o}$ as %
1	1.27
2	0.73
3	0.02
4	-0.70
5	-1.43
6	-3.64

APPENDIX II

This is the computer programme appropriate to the application of method A to the Pitts transference equation (P_A). In addition to the main programme SUBROUTINE AVTLIM computes the average limiting transference number, SUBROUTINE STDEV computes the standard deviation of the calculated limiting transference numbers from their average value, SUBROUTINE PITTS calculates S_1 and T_1 from the interpolation polynomials and SUBROUTINE FRED calculates αc from the association constant. If association data is included in the calculations, a CALL FRED card is required between the cards 102L=M and 100L=L-1 .

Specimen data

No association

Column	14	15	16	17	18	19	22	23	24	25	26	27	28	29	33	34	35	36	37	38
ϵ, γ, T	3	2	.	6	2		0	.	0	0	5	4	2	8	2	9	8	.	1	6
	9	1	.	7	7															
$t_{i,c}$	0	.	4	2	4	4	0	.	0	0	1	9	9	6						
$t_{i,c}$	0	.	4	2	3	7	0	.	0	0	2	9	7	0						
$t_{i,c}$	0	.	4	2	1	9	0	.	0	0	4	9	4	5						
final card	1	.	0				0	.	0											

Association data, if appropriate, follows the last data card of the above set

Specimen association data,

	13	14	15	16	31	32	33
K_A, a	4	5	.	0	4	.	0

```

C THE CONCENTRATION DEPENDENCE OF TRANSFERENCE NUMBERS
  PROGRAM FIRST (INPUT, OUTPUT, TAPE5=INPUT, TAPE6=OUTPUT )
C APPLICATION OF THE PITTS CONDUCTANCE EQUATION TO TRANSFERENCE
C   MAIN PROGRAMME FOR PITTS TRANSFERENCE DATA
  DIMENSION T(20),C(20),TLIM(20),COND(20),Y(20),S1(20),T1(20),
  1ALPHA(20),GAMMA(20),
  COMMON Y,S1,T1,R,Q,I,L,TLIM,TAVG,SIGMA,NC,SIGMN,B,A,J,C,COND,U,W,
  1CONLIM,DC,VIS,TEM,T,ALPHA,NB,M,GAMMA
  KI=0
708  I=0
  READ (5,1000) DC, VIS, TEM
1000 FORMAT ( 10X, F10.4, F10.7, F10.4 )
  READ (5,1001) CONLIM
1001 FORMAT (10X, F10.4)
10  I = I+1
  READ (5,1002) T(I),C(I)
1002 FORMAT (10X,F10.5,F10.7)
  IF (C(I).NE.0.0) GO TO 10
  NB = 1
  M = I
102  L = M
100  L = L-1
  A = 0.0
  SIGMN = 1.0
  U = 1.0
  WRITE (6,3000)
3000 FORMAT (8X,'J',8X,'A',10X,'SIGMA',9X,'TLIM',11X,'C',12X,'LAMDA')
  WRITE (6,4000)
4000 FORMAT (84X,'Y',13X,'S1',12X,'T1',4X,'TAVG')
  CALL AVTLIM
  A = B -1.0
  IF (A.NE.0.0) GO TO 106
  WRITE (6,9000)
9000 FORMAT (10X,'SUSPECT NEGATIVE A MAY BE REQUIRED:')
  WRITE (6,9100)
9100 FORMAT (10X,'Y MAY LIE BELOW 0.01 AND OUTSIDE RANGE, CHECK')
106  U = 0.1
  CALL AVTLIM
  IF (L.GT.3) GO TO 100
  IF (NB.EQ.1) GO TO 101
9199 WRITE (6,9200)
9200 FORMAT (10X,'NOW INCLUDE ION ASSOCIATION')
  GO TO 102
101 STOP
  END

```

```

SUBROUTINE FRED
  DIMENSION T(20),C(20),TLIM(20),COND(20),Y(20),S1(20),T1(20),
  1ALPHA(20),GAMMA(20)
  COMMON Y,S1,T1,R,O,I,L,TLIM,TAVG,SIGMA,NC,SIGMN,B,A,J,C,COND,U,W,
  1CONLIM,DC,VIS,TEM,T,ALPHA,NB,M,GAMMA
  THIS SUBPROGRAMME CALCULATES ALPHA FROM ASSOCIATION CONSTANTS
  BY SUCCESSIVE APPROXIMATIONS
  THE VALUE OF 'A' USED TO COMPUTE ACTIVITY COEFFICIENTS IS THE CONDUCTANCE 'A'
  READ (5,3601) ASSCON, AA
3601 FORMAT (10X,F10.5,10X,F6.4)
  MN = M-1
  DO 40 I = 1,MN      *AA
  DENOM = (50.291*(C(I)**0.5)/((DC*TEM)**0.5)) + 1.0
  DHF = -(1824600.0*(C(I)**0.5)/(((DC*TEM)**1.5)*DENOM))
  GAMMA(I) = 10**DHF
  ALPHA(I) = 1.0
  NK = 1
  DO 42 NK = 1,6
  ALPHA(I) = 1.0 - ((ALPHA(I)**2)*C(I)*ASSCON*(GAMMA(I)**2))
  42 CONTINUE
  C(I) = ALPHA(I)*C(I)
  40 CONTINUE
  WRITE (6,3602)
3602 FORMAT(10X,'GAMMA',10X,'ALPHA')
  WRITE (6,3603) (GAMMA(I), ALPHA(I), I = 1,MN)
3603 FORMAT (10X, F5.4,10X,F5.4)
  NB = 1
  RETURN
END

```

```

SUBROUTINE AVTLIM
  DIMENSION T(20),C(20),TLIM(20),COND(20),Y(20),S1(20),T1(20)
  COMMON Y,S1,T1,R,Q,I,L,TLIM,TAVG,SIGMA,NC,SIGMN,B,A,J,C,COND,U,W,
1CONLIM,DC,VIS,TEM,T
  J = 0
12  NC = 0
    TSUM = 0.0
    A = A + U
    J = J + 1
    IF (J.GT.20 .AND. U.EQ.1.0) RETURN
    IF (J.GT.20 .AND. U.EQ.0.1) A=B
    IF (J.GT.21) RETURN
    DO 13 I = 1,L
      CAPA = 50.291*((C(I)/(DC*TEM))**0.5)
      Y(I) = CAPA*A
      NC = NC + 1
      R = 1.0 + Y(I)
      Q = 2.0**0.5 + Y(I)
      CALL PITTS
      Y1 = (77.3714*CAPA)/(DC*R*Q) + 104672.0*S1(I)*((CAPA/DC)**2)
      Y2 = (((CAPA/R)**2)*126.713)/(DC*VIS*Q)
      Y3 = ((1.0-(186.791*CAPA*T1(I)/DC))*1.6398*CAPA)/(VIS*R)
      COND(I) = ((1.0-Y1)*CONLIM)+Y2-Y3
      TLIM(I) = (T(I)+((0.5*Y3)/COND(I)))/(1+(Y3/COND(I)))
      TSUM = TSUM + TLIM(I)
      TAVG = TSUM/NC
13  CONTINUE
    CALL STDEV
    GO TO 12
    RETURN
    END

```

```

SUBROUTINE STDEV
  DIMENSION T(20),C(20),TLIM(20),COND(20),Y(20),S1(20),T1(20)
  COMMON Y,S1,T1,R,Q,I,L,TLIM,TAVG,SIGMA,NC,SIGMN,B,A,J,C,COND,U,W,
  1CONLIM,DC,VIS,TEM,T
  D2 = 0.0
  DO 35 I = 1,L
    D2 = D2 + ((TAVG - TLIM(I))**2)
35  CONTINUE
    SIGMA = (D2/NC)**0.5
    IF (SIGMA.GT.SIGMN) GO TO 36
    SIGMN = SIGMA
    B = A.
36  WRITE (6,1005) J,A,SIGMA,TAVG
1005 FORMAT (6X,I3,6X,F6.3,6X,F10.8,80X,F8.5)
    IF (J.EQ.21) GO TO 141
    RETURN
141 WRITE (6,1006) (TLIM(I),C(I),COND(I),Y(I),S1(I),T1(I), I = 1,L)
1006 FORMAT (40X,F8.5,6X,F8.6,6X,F8.3,6X,F6.4,8X,F6.4,8X,F6.4)
    RETURN
  END

```

```

SUBROUTINE PITTS
  DIMENSION Y(20),S1(20),T1(20)
  COMMON Y,S1,T1,R,Q,I,L,TLIM,TAVG,SIGMA,NC,SIGMN,B,A,J,C,COND,U,W,
  1CONLIM,DC,VIS,TEM,T
  C INTERPOLATION FUNCTIONS FOR S1 AND TU FROM Y
  IF (Y(I).LT.0.12) GO TO 333
  S2=226.35*(Y(I)**3) - 48.654*(Y(I)**2) + (49.229*Y(I)) + 0.25
  GO TO 334
333 S2 = 37.64*Y(I) + 1.0
334 S1(I) = 1.0/S2
  IF (Y(I).LT.0.14) GO TO 335
  T2 = 7.324*(Y(I)**2) + (6.359*Y(I)) + 0.974
  GO TO 336
335 T2 = 5.7418*Y(I) + 2.0455*(Y(I)**0.5) + 0.4311
336 T1(I) = R/T2
  RETURN
  END

```

APPENDIX III

This is the programme appropriate to the application of method B to the Pitts transference equation (P_B) for unassociated systems.

Specimen data

No association data is included; the data is the same as for P_A (Appendix II) with the addition of the last card containing the initial values of $\underline{a}_1$, $\underline{a}_2$, and t_1^0 . Such a card is,

Column	16 17 18	26 27 28	34 35 36 37 38 39
	6 . 0	9 . 9	0 . 4 2 9 2

```

PROGRAM DAVE (INPUT, OUTPUT, TAPES=INPUT, TAPE6=OUTPUT )
C THE CONCENTRATION DEPENDENCE OF TRANSFERENCE NUMBERS
C APPLICATION OF PITTS SUCCESSIVE APPROXIMATIONS TREATMENT
  DIMENSION T(20),C(20),COND(20),Y(20),S1(20),T1(20),Z(5,20),
  1ZX(20),DEV(20),TCALC(20),ALPHA(20),GAMMA(20)
  COMMON Y,S1,T1,R,Q,I,L,A1,A2,TLIM,NB,M,J,DC,VIS,TEM,T,Z,ZX,ASTAR,
  1DEV,ALPHA,GAMMA,TLCOR,CONLIM,JL,C
  I = 0
  READ (5,1000) DC, VIS, TEM
1000 FORMAT ( 10X, F10.4, F10.7, F10.4 )
  READ (5,1001) CONLIM
1001 FORMAT (10X, F10.4)
10  I = I+1
C KAYS NEW DATA FOR LiCl IN METHANOL AT 25
  READ (5,1002) T(1),C(1)
1002 FORMAT (10X,F10.5,F10.7)
  IF (T(1).GT.0.5) T(1) = 1.0-T(1)
  IF (T(1).NE.0.0) GO TO 10
  READ (5,1221) B2,B1,TLIM
1221 FORMAT (10X,F10.3,F10.3,F10.5)
  NB = 1
  M = 1
102  L = M
100  L = L-1
  WRITE (6,1927)
1927 FORMAT (10X,'REPEAT WITH ONE LESS CONCENTRATION')
  IF (TLIM.GT.0.5) TLIM = 1.0-TLIM
  TLCOR=TLIM
  JL=0
  A1=B1
  A2=B2
  WRITE (6,3000)
3000 FORMAT (8X,'JL',4X,'A1',5X,'A2',4X,'ASTAR',3X,'TLCOR',5X,'TCALC',
  17X,'T')
  CALL ARTHUR
  IF (L.GT.3) GO TO 100
  IF (NB.EQ.1) GO TO 101
9199 WRITE (6,9200)
9200 FORMAT (10X,'NOW INCLUDE ION ASSOCIATION')
  CALL FRED
  GO TO 102
101 STOP
END

```

```

SUBROUTINE ARTHUR
C THIS SUBPROGRAMME USES AN ITERATIVE PROCEDURE TO FIND THE BEST TLIM
C AND THE BEST VALUE OF A
  DIMENSION T(20),C(20),COND(20),Y(20),S1(20),T1(20),Z(5,20),
  1ZX(20),DEV(20),TCALC(20),ALPHA(20),GAMMA(20)
  COMMON Y,S1,T1,R,Q,I,L,A1,A2,TLIM,NB,M,J,DC,VIS,TEM,T,Z,ZX,ASTAR,
  1DEV,ALPHA,GAMMA,TLCOR,CONLIM,JL,C
77  RSUM=0.0
  PSUM=0.0
  SSUM=0.0
  USUM=0.0
  J=0
  A=A1
73  J=J+1
  DO 13 I = 1,L
    CAPA = 50.291*((C(I)/(DC*TEM))**0.5)
    Y(I) = CAPA*A
    R = 1.0 + Y(I)
    Q = 2.0**0.5 + Y(I)
    CALL PITTS
    Y1 = (77.3714*CAPA)/(DC*R*Q) + 104672.0*S1(I)*((CAPA/DC)**2)
    Y2 = (((CAPA/R)**2)*126.713)/(DC*VIS*Q)
    Y3 = ((1.0-(186.791*CAPA*T1(I)/DC))*1.6398*CAPA)/(VIS*R)
    COND(I) = ((1.0-Y1)*CONLIM)+Y2-Y3
    Z(J,I)=((0.5-TLCOR)*Y3)/COND(I)
    TCALC(I)=TLCOR-Z(J,I)
    DEV(I)=TCALC(I) - T(I)
    IF (J.NE.3) GO TO 13
    WRITE (6,3123) TCALC(I),T(I),DEV(I),C(I),COND(I)
3123 FORMAT (4X,F11.6,F9.6,2X,F8.6,10X,F6.4,10X,F7.3)
13  CONTINUE
    IF (J.EQ.2) GO TO 71
    IF (J.EQ.3) RETURN
    A=A2
    GO TO-73
71  DO 75 I=1,L
    ZX(I)=TLIM-T(I)
    XY=(Z(2,I)-Z(1,I))
    G=(Z(2,I)-ZX(I))/XY
    RSUM=RSUM+G
    S=1.0/XY
    SSUM=SSUM+S
    P=G/XY
    PSUM=PSUM+P
    U=S/XY
    USUM = USUM+U
75  CONTINUE
    DELLA=(L*USUM-(SSUM**2))
    DELTA=(L*PSUM-RSUM*SSUM)/DELLA
    F=(RSUM*USUM-(SSUM*PSUM))/DELLA
    JL=JL+1
    TLCOR=TLIM+DELTA
    ASTAR=A2+(A1-A2)*F
    WRITE (6,6789) JL,A1,A2,ASTAR,TLCOR
6789 FORMAT (7X,I3,F8.3,F7.3,F8.3,F9.6)
    ADIF=A1-A2
    A1=ASTAR+(ADIF/4.0)
    A2=ASTAR-(ADIF/4.0)
    IF (JL.LT.15) GO TO 77

```

```

A=ASTAR
WRITE (6,1928)
1928 FORMAT (10X,'BEST VALUES FOR THIS CONCENTRATION RANGE')
WRITE (6,1925) ASTAR,TLCOR
1925 FORMAT (10X,'ASTAR = ',F5.3,10X,'TLIM = ',F7.5)
GO TO 73
END

```

```

SUBROUTINE FRED
C THIS SUBPROGRAMME CALCULATES ALPHA FROM ASSOCIATION CONSTANTS
C BY SUCCESSIVE APPROXIMATIONS
C THE VALUE OF 'A' USED TO COMPUTE ACTIVITY COEFFICIENTS IS THE CONDUCTANCE
DIMENSION T(20),C(20),COND(20),Y(20),SI(20),T1(20),Z(5,20),
1ZX(20),DEV(20),TCALC(20),ALPHA(20),GAMMA(20)
COMMON Y,S1,T1,R,0,1,L,A1,A2,TLIM,NB,M,J,DC,VIS,TEM,T,Z,ZX,ASTAR,
1DEV,ALPHA,GAMMA,TLCOR,CONLIM,JL,C
READ (5,3601) ASSCON, AA
3601 FORMAT (10X,F10.5,10X,F6.4)
MN = M-1
DO 40 I = 1,MN
DENOM = (50.291*(C(I)**0.5)/((DC*TEM)**0.5)) + 1.0
DHF = -(1824600.0*(C(I)**0.5))/(((DC*TEM)**1.5)*DENOM)
GAMMA(I) = 10**DHF
ALPHA(I) = 1.0
NK = 1
DO 42 NK = 1,6
ALPHA(I) = 1.0 - ((ALPHA(I)**2)*C(I)*ASSCON*(GAMMA(I)**2))
42 CONTINUE
C(I) = ALPHA(I)*C(I)
40 CONTINUE
WRITE (6,3602)
3602 FORMAT(10X,'GAMMA',10X,'ALPHA')
WRITE (6,3603) (GAMMA(I), ALPHA(I), I = 1,MN)
3603 FORMAT (10X, F5.4,10X,F5.4)
NB = 1
RETURN
END

```

SUBROUTINE PITTS

C INTERPOLATION FUNCTIONS FOR S1 AND T1 FROM Y

```

    DIMENSION T(20),C(20),COND(20),Y(20),S1(20),T1(20),Z(5,20),
    1ZX(20),DEV(20),TCALC(20),ALPHA(20),GAMMA(20)
    COMMON Y,S1,T1,R,Q,I,L,A1,A2,TLIM,NB,M,J,DC,VIS,TEM,T,Z,ZX,ASTAR,
    1DEV,ALPHA,GAMMA,TLCOR,CONLIM,JL
    IF (Y(I).LT.0.0) Y(I)=0.0
    IF (Y(I).LT.0.12) GO TO 333
    S2=226.35*(Y(I)**3) - 48.654*(Y(I)**2) + (49.229*Y(I)) + 0.25
    GO TO 334
333 S2 = 37.64*Y(I) + 1.0
334 S1(I) = 1.0/S2
    IF (Y(I).LT.0.14) GO TO 335
    T2 = 7.324*(Y(I)**2) + (6.359*Y(I)) + 0.974
    GO TO 336
335 T2 = 5.7418*Y(I) + 2.0455*(Y(I)**0.5) + 0.4311
336 T1(I) = R/T2
    RETURN
    END

```

APPENDIX IV

This is the computer programme which calculates the electrophoretic terms by methods $(F-0)_1$ and $(F-0)_2$ and their difference. I am grateful to Professor R.M. Fuoss for supplying subroutines SUBEN(X,EN) and SUBEP(BX,EP) from which the positive and negative exponential integrals are computed. Only the first data card, containing dielectric constant, viscosity and temperature from the previous set is required.

```

C  COMPARISON OF OLD AND NEW ELECTROPHORETIC TERMS
  PROGRAM FROG (INPUT,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT)
  DIMENSION C(5)
  READ (5,1000) DC,VIS,TEM
1000 FORMAT (10X,F10.4,F10.7,F10.4)
  C(1) = 0.001
  C(2) = 0.01
  C(3) = 0.10
  A=0.0
  B2 = 82.5/(VIS*((DC *TEM)**0.5))
 86  A = A + 0.5
  BE = 167098.5/(A*DC*TEM)
C  THIS PROGRAMME CALCULATES F(B) - ELECTROPHORETIC CORRECTION TERM
  ENN=0.0
  EPP =0.0
  CALL SUBEN (BE,ENN)
  CALL SUBEP (BE,EPP)
  EUL = 0.577216
  AJNB = ENN+EUL + ALOG(BE)
  AJPB = EPP - EUL -ALOG(BE)
  EB =-BE
  FNB = ((1.0-EXP(EB))/BE) + (0.5*AJNB) -1.0
  FPB = (0.5*AJPB) - ((EXP(BE)-1.0)/BE) +1.0
  T1B = (1.0+BE+((BE**2)*0.5))*EXP(EB)
  T2B = (1.0-BE +((BE**2)*0.5))*EXP(BE)
  EM=T2B/(T2B-1.0)
  EMA = -T1B/(1.0-T1B)
  F1B = (EM*FNB) + (EMA*FPB)
  FX = (1.0/(1.0-T1B)) - (1.0/(T2B-1.0))
  FB = (2.0/BE) + ((BE*FX)/4.0) - F1B
  WRITE (6,5550) A,BE,FB
5550 FORMAT (8X,F7.3,7X,F9.4,7X,F11.5)
  DO 88 I=1,3
  B2RC = B2*(C(1)**0.5)
  CAPA = 50.291*((C(1))/(DC*TEM))**0.5)
  YZ = (CAPA*A) + 1.0
  B5 = B2RC/YZ
  B31 = (17329.0*C(1))/(VIS*((DC*TEM)**2))
  B3 = 10000.0*B31*FB
  B4=(B2RC - B3)
  B6 = B4 - B5
  WRITE (6,5551) C(1),B2RC,B3,B4,B5,B6
5551 FORMAT (55X,F7.4,2X,F10.5,4X,F9.5,3X,F9.5,1X,F9.5,2X,F9.5)
 88  CONTINUE
  IF (A.NE.10.0) GO TO 86
  STOP
  END

```

```

SUBROUTINE SUBEN (X,EN)
CON = -ALOG(X) - 0.577216
FN = 0.0
TOT = 0.0
30  FN = FN + 1.0
    IF ((FN-1.0)-0.1) 31,31,32
31  FNTH = X
    GO TO 33
32  FNTH = -(FNTH*X*(FN-1.0))/(FN*FN)
33  TOT = TOT + FNTH
    TEST = ABS(0.0001*TOT)
    IF (TEST-ABS(FNTH)) 30,30,41
41  EN = CON+TOT
    RETURN
END

```

```

SUBROUTINE SUBEP (BX,EP)
CON = ALOG(BX) + 0.577216
FN = 0.0
TOT = 0.0
30  FN = FN+1.0
    IF ((FN-1.0)-0.1) 31,31,32
31  FNTH = BX
    GO TO 33
32  FNTH= (FNTH*BX*(FN-1.0))/(FN*FN)
33  TOT = TOT + FNTH
    TEST = 0.00001*TOT
    IF (TEST - FNTH) 30,30,41
41  EP = CON + TOT
    RETURN
END

```

APPENDIX V

This is the programme appropriate to the application of Method A to the Fuoss-Onsager equation with the original electrophoretic term, $(F-0)_1$. In addition to the main programme SUBROUTINE CYRIL computes the average limiting transference number, SUBROUTINE HORACE computes the standard deviation of the calculated limiting transference numbers from their average value and SUBROUTINE FRED calculates α_c from the association constant. If association data is included a CALL FRED card is required between the cards 102L=M and 100L=L-1. The data lay-out is exactly as for P_A (Appendix II).

```

PROGRAM FUOSS (INPUT,OUTPUT, TAPE5 = INPUT, TAPE6= OUTPUT)

C THE CONCENTRATION DEPENDENCE OF TRANSFERENCE NUMBERS

C APPLICATION OF THE FUOSS-ONSAGER CONDUCTANCE EQUATION

C OLD ELECTROPHORETIC TERM

  DIMENSION T(20),C(20),TLIM(20),Y(20),ALPHA(20),GAMMA(20)

  COMMON Y,R,I,L,TLIM,TAVG,SIGMA,NC,SIGMN,B,A,J,C,U,W,CONLIM,DC,VIS,
  1TEM,T,ALPHA,NB,M,GAMMA

706 I = 0

  READ (5,1000) DC,VIS,TEM
1000 FORMAT (10X,F10.4,F10.7,F10.4)

  READ (5,1001) CONLIM
1001 FORMAT (10X,F10.4)

  10 I = I + 1

  READ (5,1002) T(I),C(I)
1002 FORMAT (10X,F10.5,F10.7)

  IF (T(I).NE.1.0) GO TO 10

  M = I

102 L = M

100 L = L - 1

  A = 0.0

  U = 1.0

  SIGMN = 1.0

  WRITE (6,3000)

3000 FORMAT (8X,'J',8X,'A',10X,'SIGMA',9X,'TLIM',11X,'C',10X,'Y')

  CALL CYRIL

  IF (B.GT.3.0) GO TO 104

  A = 0.0

  U = -1.0

  CALL CYRIL

104 A = B - 1.0

```

U = 0.1

CALL CYRIL

IF (L.GT.3) GO TO 100

STOP

END

SUBROUTINE CYRIL

DIMENSION T(20),C(20),TLIM(20),Y(20),ALPHA(20),GAMMA(20)

COMMON Y,R,I,L,TLIM,TAVG,SIGMA,NC,SIGMN,B,A,J,C,U,W,CONLIM,DC

J = 0

12 NC = 0

TSUM = 0.0

A = A + U

J = J + 1

IF (J.GT.20 .AND. U.EQ.1.0) RETURN

IF (J.GT.20 .AND. U.EQ.0.1) A = B

IF (J.GT.21) RETURN

DO 13 I=1,L

CAPA = 50.291*((C(I)/(DC*TEM))**0.5)

Y(I) = CAPA*A

NC = NC + 1

B2 = 82.5/(VIS*((DC*TEM) **0.5))

R = 1.0 + Y(I)

B2RC = B2*(C(I)**0.5)

ZA = (T(I)-0.5)*B2RC

ZB = CONLIM*R

TLIM(I) = T(I) - ZA/ZB

TSUM = TSUM + TLIM(I)

TAVG = TSUM/NC

13 CONTINUE

CALL HORACE

GO TO 12

RETURN

END

SUBROUTINE HORACE

DIMENSION T(20),C(20),TLIM(20),Y(20),ALPHA(20),GAMMA(20)

COMMON Y,R,I,L,TLIM,TAVG,SIGMA,NC,SIGMN,B,A,J,C,U,W,CONLIM,DC,VIS,

ITEM,T,ALPHA,NB,M,GAMMA

D2 = 0.0

DO 35 I = 1,L

D2 = D2 + ((TAVG - TLIM(I))**2)

35 CONTINUE

SIGMA = (D2/NC)**0.5

IF (SIGMA.GT.SIGMN) GO TO 36

SIGMN = SIGMA

B = A

36 WRITE (6,1005) J,A,SIGMA,TAVG

1005 FORMAT (6X,I3,6X,F6.3,6X,F10.8,42X,F8.5)

IF (J.EQ.21) GO TO 141

RETURN

WRITE (6,1006) (TLIM(I),C(I),Y(I), I=1,L)

1006 FORMAT (40X,F8.5,6X,F8.6,6X,F6.4)

RETURN

END

SUBROUTINE FRED

APPENDIX VI

This is the computer programme appropriate to the application of method A to the Fuoss-Onsager transference equation with the fuller electrophoretic term $(F-0)_2$. The subroutines required are those in Appendix V but the calculation of the extended electrophoretic term requires additional subroutines, FUNCB(EPS,ETA,THETA,DIS,FB), SUBEN(X,EN) and SUBEP(BX,EP). The last two are given in Appendix IV. SUBROUTINE FUNCB(EPS,ETA,THETA,DIS,FB) comprises all the cards in PROGRAM FROG between and including $BE = 167098.5 / (DIS * EPS * THETA)$ and $FB = (2.0 / BE) + ((BE * FX) / 4.0) - FIB$ followed by appropriate RETURN and END cards. The data lay-outs are identical with those in Appendices I and V

```

PROGRAM FMOD (INPUT,OUTPUT, TAPE5=INPUT, TAPE6=OUTPUT)
C THE CONCENTRATION DEPENDENCE OF TRANSFERENCE NUMBERS
C APPLICATION OF THE FUOSS-ONSAGER CONDUCTANCE EQUATION
C NEW ELECTROPHORETIC TERM

  DIMENSION T(20),C(20),TLIM(20),Y(20),ALPHA(20),GAMMA(20)
  COMMON Y,R,I,L,TLIM,TAVG,SIGMA,NC,SIGMN,B,A,J,C,U,W,CONLIM,DC,VIS,
  1TEM,T,ALPHA,NB,M,GAMMA

706 I = 0

  READ (5,1000) DC,VIS,TEM
1000 FORMAT (10X,F10.4,F10.7,F10.4)

  READ (5,1001) CONLIM
1001 FORMAT (10X,F10.4)

  10 I = I + 1

  READ (5,1002) T(I),C(I)
1002 FORMAT (10X,F10.5,F10.7)

  IF (T(I).NE.1.0) GO TO 10

  M = I

102 L = M

100 L = L - 1

  A = 0.0

  U = 1.0

  SIGMN = 1.0

  WRITE (6,3000)

3000 FORMAT (8X,'J',8X,'A',10X,'SIGMA',9X,'TLIM',11X,'C',10X,'Y')

  CALL CYRIL

104 A = B - 1.0

  U = 0.1

  CALL CYRIL

```

```

IF (L.GT.3) GO TO 100

STOP

END

SUBROUTINE CYRIL

DIMENSION T(20),C(20),TLIM(20),Y(20),ALPHA(20),GAMMA(20)

COMMON Y,R,I,L,TLIM,TAVG,SIGMA,NC,SIGMN,B,A,J,C,U,W,CONLIM,DC

J = 0

12 NC = 0

TSUM = 0.0

A = A + U

J = J + 1

IF (J.GT.20 .AND. U.EQ.1.0) RETURN

IF (J.GT.20 .AND. U.EQ.0.1) A=B

IF (J.GT.21) RETURN

CALL FUNCB(DC,VIS,TEM,A,FBB)

DO 13 I=1,L

CAPA = 50.291*((C(I)/(DC*TEM))**0.5)

Y(I) = CAPA*A

NC = NC + 1

B2 = 82.5/(VIS*((DC*TEM)**0.5))

B31 = (17329.0+C(I))/(VIS*((DC*TEM)**2))

B2RC = B2*(C(I)**0.5)

B4 = (B2RC - B3)

ZA = (T(I)-0.5)*B4

ZB = CCNLIM

TLIM(I) = T(I) - ZA/ZB

TSUM = TSUM + TLIM(I)

TAVG = TSUM/NC

13 CONTINUE

```

CALL HORACE

GO TO 12

RETURN

END

SUBROUTINE HORACE

DIMENSION T(20),C(20),TLIM(20),Y(20),ALPHA(20),GAMMA(20)

COMMON Y,R,I,L,TLIM,TAVG,SIGMA,NC,SIGMN,B,A,J,C,U,W,CONLIM,DC,VIS,

ITEM,T,ALPHA,NB,M,GAMMA

D2 = 0.0

DO 35 I=1,L

D2 = D2 + ((TAVG-TLIM(I))**2)

35 CONTINUE

SIGMA = (D2/NC)**0.5

IF (SIGMA.GT.SIGMN) GO TO 36

SIGMN = SIGMA

B = A

36 WRITE (6,1005) J,A,SIGMA,TAVG

1005 FORMAT (6X,I3,6X,F6.3,6X,F10.8,42X,F8.5)

IF (J.EQ.21) GO TO 141

RETURN

141 WRITE (6,1006) (TLIM(I),C(I),Y(I), I=1,L)

1006 FORMAT (40X,F8.5,6X,F8.6,6X,F6.4)

RETURN

END

SUBROUTINE FRED

SUBROUTINE FUNCB(EPS,ETA,THETA,DIS,FB)

SUBROUTINE SUBEN(X,EN)

SUBROUTINE SUBEP(BX,EP)

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