TRANSFERENCE NUMBER STUDIES BY THE DIRECT MOVING BOUNDARY METHOD

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ABSTRACT

This thesis is concerned with transference number measurements by the moving boundary method in ethylenediamine (ED) and in water at 25° C.

No transference work has previously been carried out in amines. Since conductance data are available for amine solutions (including metal solutions which contain solvated electrons), the determination of transference numbers would lead to individual ionic conductances (including that of the electron). ED was chosen as a suitable amine solvent because it is liquid at 25° C.

A number of methods of solvent purification was tested and the technique finally adopted was to reflux and distil ED over CaH_2 in an atmosphere of dry N_2. An improved method was also developed for analysing traces of water in the solvent. Visible and stable anion and cation boundaries were observed for the electrolytes $AgNO_3$ and NaI leading, the first time boundaries had been seen in a solvent of such low dielectric constant. From the exploratory runs approximate transference numbers and ionic conductances were determined. More accurate work had to be discontinued because the writer became highly sensitised to traces of ED.

An aqueous project was then undertaken. The bi-bivalent electrolyte $MgSO_4$ was chosen in order to provide data for testing recent theories, and much more accurate data were obtained than those available from a previous study. Both cation boundaries ($Mg^{2+} \longleftarrow NBu_4^{+}$) and anion boundaries ($SO_4^{2-} \longleftarrow IO_3^{-}$, $SO_4^{2-} \longleftarrow PhSO_3^{-}$) were followed over a range of currents and

initial indicator concentrations, to provide transference numbers at 0.005, 0.01, 0.025 and 0.05 molar.

The experimentally found concentration dependence was then compared with the predictions of two Fuoss-Onsager and the Pitts interionic attraction theories. These were written in the transference form for Z:Z valent electrolytes, and the comparison carried out by computer fitting. The results show that the Fuoss-Onsager theories fit the experimental transference numbers for $MgSO_4$ better than the Pitts theory, using three parameters as criteria : the minimum standard deviation of the fit, the distance of closest approach, and the value of the limiting cation transference number.

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CHAPTER I

1. TRANSFERENCE NUMBERS AND THEIR DETERMINATION

1.1 Definition of transference number

Two definitions of transference or transport number have been given in the literature. The most commonly used in textbooks is "The transference number t_i of an ionic species i is the fraction of the total current carried by that species when the solution is electrolysed". This definition has however little practical applicability except in the cases in which the electrolyte is completely dissociated into two ions only, although even for strong electrolytes we have no meters to measure "current fractions". When the solution forms complex ions, the transport number cannot be determined by any experimental method. The other definition makes the transference number obtainable directly from the experiment and has been given by Spiro (1) as "The transference number t_R of a cation or anion-constituent R is the net number of faradays carried by that ion-constituent in the direction of the cathode or anode respectively across an imaginary plane in the solution, fixed relatively to the solvent, when one faraday of electricity passes across that plane".

The term ion-constituent means the ion-forming portion of an electrolyte without reference to the extent to which it actually exists in a dissociated state. For example, in aqueous oxalic acid solution, the hydrogen ion-constituent is present as free H^+ ions, $HC_2O_4^-$ ions and $H_2C_2O_4$ molecules. Thus in the moving boundary method, used in the present work, one measures the velocity of the boundary due to an ion-constituent and not that due to a free ion.

It is clear from the above definition that

$$\sum_R t_R = 1$$

t_R can be either positive, zero or negative and its numerical value coincides with that of the ionic transference number for strong electrolytes, where the ion-constituent exists only in the form of solvated ion. In terms of the molarities C_i and the molar conductances λ_i of the ionic species i, the transference number of an ion-constituent R can be expressed as

$$t_R = \frac{\sum_i \left(Z_R/Z_i\right) N_{R/i} \lambda_i C_i}{\sum_i \lambda_i C_i} \qquad (1\text{-}1\text{-}1)$$

where Z_i and Z_R are the algebraic charge numbers of the species i and R respectively and $N_{R/i}$ is the number of moles of ion-constituent R contained in one mole of ion i. For a solution of an electrolyte which dissociates into only two ions

$$t_R = \frac{\lambda_R C_R}{\sum_i \lambda_i C_i} = \frac{\lambda_R C_R}{\Lambda C} = \frac{\lambda_R}{\Lambda} \qquad (1\text{-}1\text{-}2)$$

1.2 Methods of measuring transference numbers

There are various experimental methods for measuring transference numbers, but the three principal methods are: the Hittorf, the e.m.f. and the moving boundary methods.

(i) Hittorf method

This method, named after its discoverer in 1853, involves determination of the concentration changes of the solution under investigation after it has been electrolysed in a cell which has been divided into physically separable anodic, cathodic and middle compartments.

On a passage of one faraday through the cell, t_+ equivalent of cation-constituent migrate into the cathode compartment and t_- equivalent of anion-constituent migrate into the anode compartment. It is clear that the composition of the middle section should be the same after the run as before it, and only those of the electrode compartments should change. To ensure that all concentration changes take place only in the electrode sections and that no intermixing occurs, the middle section is usually divided into three parts. Analysis of the solutions in the two electrode compartments before and after the experiment gives the change of the total number of moles and hence the transference number. The electrode reactions have also to be taken into account if they involve the ion-constituent in question, as in the case of the electrolysis of a NaCl solution with a Ag/AgCl cathode and a Ag anode. The method does not need any volume correction as the change in the number of equivalents of the ion-constituent is referred to a constant mass of solvent, as required by the definition. However a solvent correction is necessary to allow for the fraction of current carried by impurity and solvent ions. The method is subject to analytical errors because the concentrations changes are relatively small. Although the accuracy could be improved by passing a sufficient current to produce appreciable changes of concentration, there is then the danger of interdiffusion of the anode and cathode solutions with the middle compartment.

(ii) E.m.f. method

This method involves the measurement of the e.m.f. of a concentration cell with transference, E_t , and the e.m.f. of a corresponding cell without transference, E . A cell with transference has a liquid junction between two solutions of the same salt at two different concentrations. The cell reaction involves the transfer of ion-constituents across the liquid junction, and therefore the e.m.f. is a function of their transference numbers and their activity coefficients. The relationship between t_R and the cell e.m.f.s, E_t and E, is

$$t_R = dE_t/dE$$

This method requires very accurate e.m.f. measurements, because a small error in either E_t or E causes a relatively big error in t_R.

(iii) Moving boundary method

This is the most accurate technique of measuring transference numbers and it has been used successfully in both aqueous and non-aqueous solvents and for strong and weak electrolytes. For these reasons this method was chosen for the present work.

The method is based on the formation and movement of a boundary between two solutions, when an electric current is passed through them. The solution under investigation is called the leading solution and the other is a solution of a suitable indicator electrolyte and called the following solution. The solutions have an ion in common and the velocity of the boundary is proportional to the transference number of the leading non-common ion.

Consider fig. 1-2-1 which shows a rising (a) and a falling (b) direct moving boundary. LZ is the leading and FZ the following electrolyte. The boundary moves in the direction of the arrow, and it is rising (fig. 1-2-1(a)) or falling (fig.1-2-1(b)) if the following solution is respectively denser or lighter than the leading solution. When n faradays of electricity pass through the system, the boundary moves along the tube from position m-b to m′-b′ sweeping out a volume V (litres) in doing so. Consequently $C_L^{LZ}V$ moles of ion-constituent L will migrate across the imaginary plane X-Y which the boundary never reaches, C_L^{LZ} being the molarity of the leading ion. Per faraday, the number of moles will be $C_L^{LZ}V/n$ and hence by the definition of transference number

$$t_L^{LZ} = \frac{C_L^{LZ}|Z_L|V}{n} = \frac{C_L^{LZ}|Z_L|VF}{It} \qquad (1\text{-}2\text{-}1)$$

Fig. 1-2-1

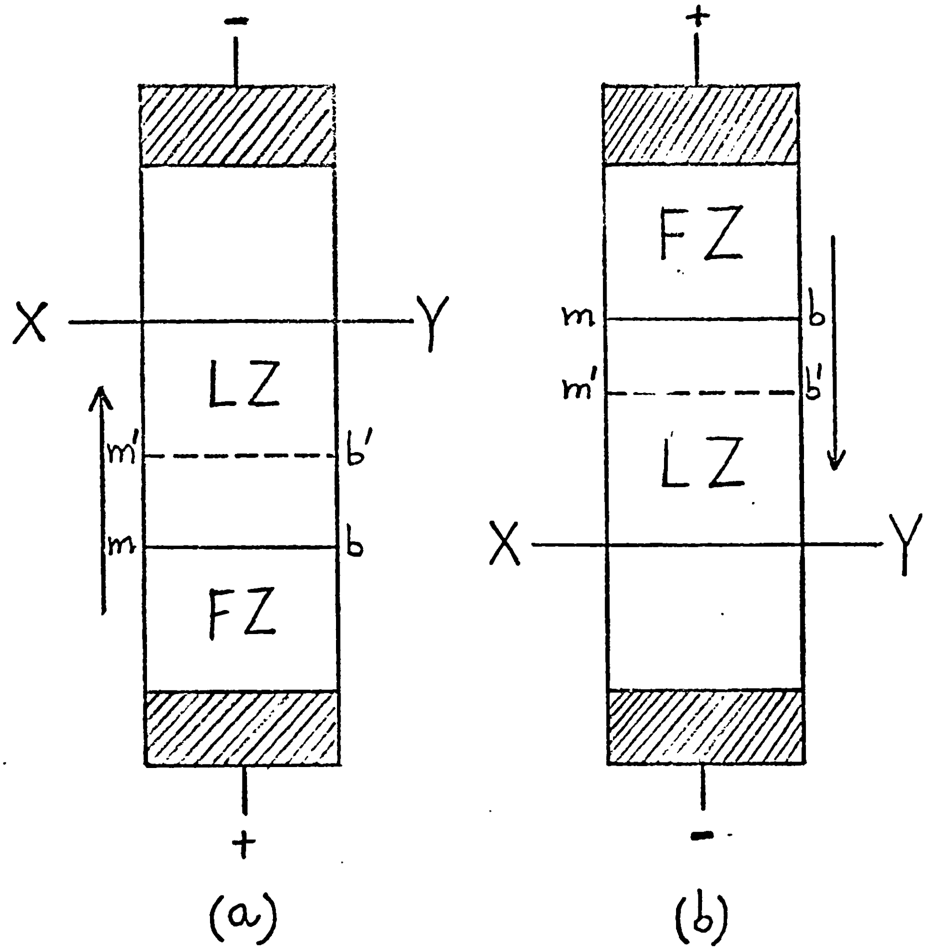
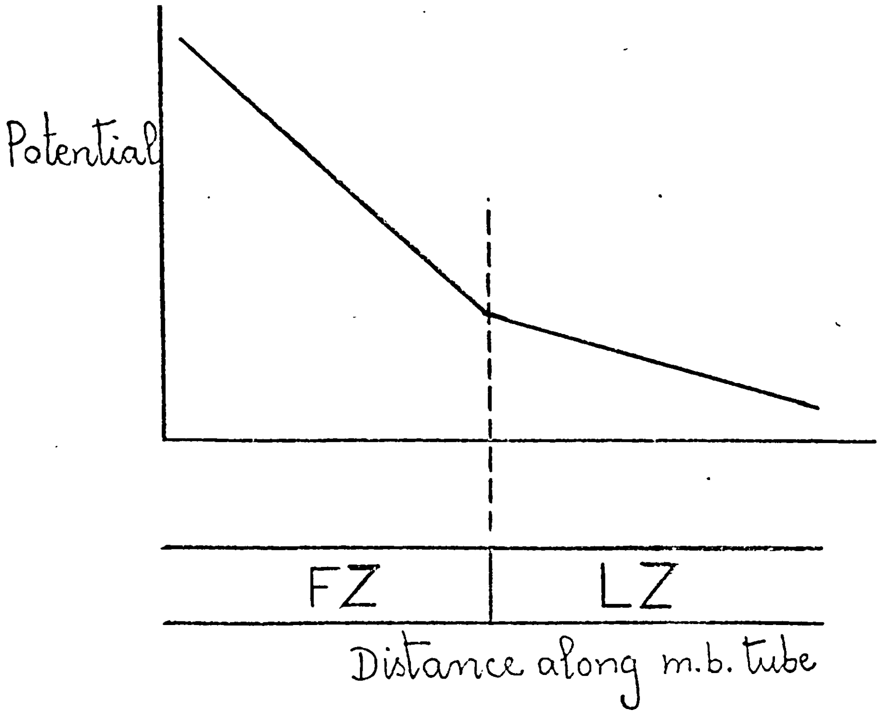


Fig. 1-2-2



where Z_L is the algebraic charge number of the leading ion-constituent L, I the current in amperes passed for a time interval t seconds and F is Faraday's constant.

The existence of the boundary (m.b.) requires that

$$v_{m.b.} = v_L^{LZ} = \mu_L(dE/dX)_{LZ} = v_F^{FZ} = \mu_F(dE/dX)_{FZ}$$

where v is the velocity and μ the mobility of the subscripted ion-constituent, and (dE/dX) the potential gradient of the subscripted solution. Since

$$\lambda_L = F\mu_L|Z_L| \qquad \text{and} \qquad \lambda_F = F\mu_F|Z_F|$$

where λ is the molar conductance of the subscripted ion-constituent and Z its algebraic charge number

$$\lambda_L^{LZ}(dE/dX)_{LZ}\Big/|Z_L| = \lambda_F^{FZ}(dE/dX)_{FZ}\Big/|Z_F|$$

A major condition for boundary stability is that the conductance of the leading ion-constituent must exceed that of the following ion-constituent and therefore

$$(dE/dX)_{LZ} < (dE/dX)_{FZ}$$

Thus when some ion-constituent L diffuses into the FZ solution, it will be subject to a higher potential gradient, move faster than the ion-constituent F, and so overtake the boundary again. Likewise, if an ion F diffuses into the LZ solution, it will find itself in a region of lower potential gradient and so it will be overtaken by the boundary. This is shown in fig. 1-2-2 where the potential is plotted against distance along the m.b. tube. This electrical restoring effect thus counteracts diffusion between the solutions and maintains the boundary sharp.

If the movement of the following solution is treated as was that of the leading solution, we obtain for the transference number of the following ion-constituent

$$t_F^{FZ} = \frac{C_F^{FZ}|Z_F|V}{n} = \frac{C_F^{FZ}|Z_F|VF}{It} \qquad (1\text{-}2\text{-}2)$$

Hence

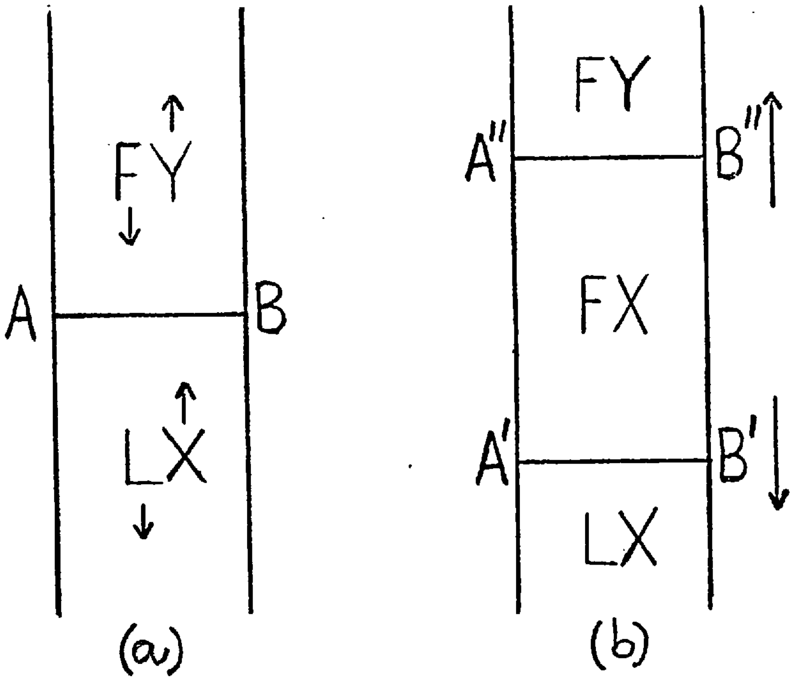
$$\frac{t_L^{LZ}}{t_F^{FZ}} = \frac{|Z_L|C_L^{LZ}}{|Z_F|C_F^{FZ}} \qquad (1\text{-}2\text{-}3)$$

This is the Kohlrausch equation, which relates the transference numbers and concentrations of the leading and following ion-constituents. For a given leading solution, the concentration of the indicator solution adjusts itself automatically behind the boundary to the Kohlrausch value. Another but slow and diffuse "concentration" boundary then forms between the initial and the adjusted following solutions. In practice, it is usual to make the initial concentration of the following solution a few per cent higher than the Kohlrausch value for rising boundaries and a few per cent lower for falling boundaries to ensure gravitational stability. An important feature of the method is that the velocity of the boundary depends only on the properties of the leading solution and should be independent on the type and initial concentration of the following solution.

It is not essential for the leading and following solutions to have an ion-constituent in common, as it is possible to form the appropriate Kohlrausch solution when the current is passed. This is the case of the $MgSO_4$ runs in which the boundary is followed by $H_2C_2O_4$, $PhSO_3Na$ and $\underline{n}$-Bu_4NCl (see later). Consider fig. 1-2-3(a) where LX and FY are the leading and the following solutions respectively (e.g., LX = $MgSO_4$, FY = $\underline{n}$-Bu_4NCl, $H_2C_2O_4$, $PhSO_3Na$). If L in LX and Y in FY move away from the junction AB, on passage of a current, a solution of FX will automatically form between the solutions FY and LX giving rise to a falling boundary $A'B'$ with FX following LX, as shown in fig. 1-2-3(b). This figure shows that there is also another boundary $A''B''$ (rising) between the FY and FX solutions, which moves in the opposite direction to that of $A'B'$. The appropriate initial concentration of the following solution is calculated by combining two Kohlrausch relationships

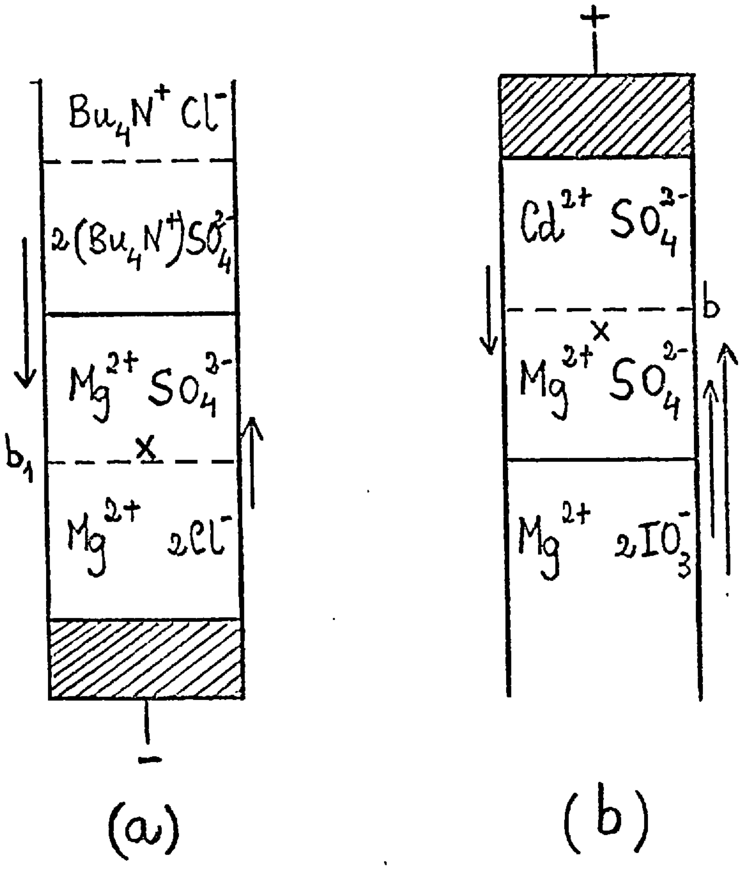
$$C_Y^{FY} = \frac{C_X^{FX}|Z_X|t_Y^{FY}}{t_X^{FX}|Z_Y|} = \frac{C_L^{LX}|Z_L|t_F^{FX}t_Y^{FY}}{t_L^{LX}t_X^{FX}|Z_Y|} \qquad (1\text{-}2\text{-}4)$$

Fig. 1-2-3



(a) (b)

Fig. 1-4



(a) (b)

In using this equation later, limiting transference numbers, obtained from limiting conductivities (2a), were always used in the absence of information on their concentration dependences.

In the derivation of the m.b. equation (1-2-1), it is assumed that the following solution FZ does not contain any leading ion-constituent L. A more general equation has been derived (3) for the cases in which L is present in both solutions

$$t_L^{LZ} - t_L^{FZ} = V(C_L^{LZ} - C_L^{FZ})|Z_L|F/It \qquad (1\text{-}2\text{-}5)$$

It is clear that equation (1-2-5) reduces to equation (1-2-1) when the following solution is free of the leading ion-constituent, because in this case t_L^{FZ} and C_L^{FZ} are both zero.

1.3 Electrodes

In the moving boundary method one of the electrode compartments must be open to allow for expansion or contraction of the whole system during a run. The other should be kept completely closed with a non-gassing electrode of known electrode reaction. This prevents the movement of the bulk solutions in either direction and allows the volume correction (section 1.4) to be calculated. No foreign ions resulting from the electrode reaction should reach the boundary, as this progressively slows down its velocity.

1.4 Volume correction

In the m.b. method the boundary movement is measured with respect to the etch marks of the m.b. tube (which are fixed relative to the cell), whereas from the definition of transference number the boundary movement should be determined with respect to a plane fixed relative to the solvent. Since volume changes occur due to the electrode reactions and ionic movements, the displacement of the solvent relative to the m.b. cell must be worked out. This is possible from a knowledge of the volume changes taking place between the closed electrode and a point in the leading solution, which the boundary never passes. If ΔV is the volume increase in this region in dm^3 per faraday of electricity, the corrected transference number is given by

$$t_L^{LZ}(\mathrm{corr}) = t_L^{LZ}(\mathrm{obs}) \pm C_L^{LZ}|Z_L|\Delta V \qquad (1\text{-}4\text{-}1)$$

The plus and minus signs refer to the boundary moving towards or away from the closed electrode, respectively. In the present work with $MgSO_4$ solutions, the boundary moved towards the closed compartment in the anion runs and in cation runs in which Ag/AgCl was used as closed electrode, and away from the closed compartment in the cation runs with a closed Ag anode.

a) Cation transference number runs

Fig. 1-4-a shows the case of the cation $MgSO_4$ boundary followed by n-Bu_4NCl, which formed a "synthetic"

Kohlrausch solution of $(\underline{n}\text{-Bu}_4N)_2SO_4$ behind the boundary, with a Ag/AgCl closed electrode. Traditionally the volume changes have been calculated by using partial molar volumes, but recent work (4) has proved that apparent molar volumes should be used instead. The volume changes per faraday taking place between a point x in the $MgSO_4$ solution and the Ag/AgCl cathode during the run are :

1. Electrode reaction

$$AgCl(s) + e^- \longrightarrow Ag(s) + Cl^-$$

(i) loss of 1 equiv. AgCl(s)
(ii) gain of 1 equiv. Ag(s)
(iii) gain of 1 equiv. Cl^- in $MgCl_2$ solution

$$\therefore \Delta V_1 = V_{Ag(s)} + \phi^{MgCl_2}_{Cl^-} - V_{AgCl(s)}$$

where V is the molar volume of the subscripted solid and ϕ is the apparent molar volume in the superscripted solution.

2. Transfer across b_1

(i) loss of 1 equiv. Mg^{2+} from $MgSO_4$ solution
(ii) gain of 1 equiv. Mg^{2+} in $MgCl_2$ solution

$$\therefore \Delta V_2 = -\tfrac{1}{2}\phi^{MgSO_4}_{Mg^{2+}} + \tfrac{1}{2}\phi^{MgCl_2}_{Mg^{2+}}$$

3. Transfer across reference point x

(i) loss of $t_{SO_4^{2-}}^{MgSO_4}$ equiv. SO_4^{2-}

(ii) gain of $t_{Mg^{2+}}^{MgSO_4}$ equiv. Mg^{2+}

$$\therefore \Delta V_3 = -\tfrac{1}{2} t_{SO_4^{2-}}^{MgSO_4} \times \phi_{SO_4^{2-}}^{MgSO_4} + \tfrac{1}{2} t_{Mg^{2+}}^{MgSO_4} \times \phi_{Mg^{2+}}^{MgSO_4}$$

The total volume increase will therefore be

$$\Delta V = V_{Ag(s)} - V_{AgCl(s)} + \tfrac{1}{2}\phi_{MgCl_2}^{MgCl_2} - \tfrac{1}{2} t_{SO_4^{2-}}^{MgSO_4} \times \phi_{MgSO_4}^{MgSO_4} \qquad (1\text{-}4\text{-}2)$$

In a similar way one can deduce that, for the cation runs in which the boundary moved away from a closed Ag anode, the volume increase ΔV is given by

$$\Delta V_{total} = - V_{Ag(s)} + V_{AgCl(s)} - \phi_{Bu_4NCl}^{Bu_4NCl} + \tfrac{1}{2}\phi_{(Bu_4N)_2SO_4}^{(Bu_4N)_2SO_4} - \tfrac{1}{2} t_{Mg^{2+}}^{MgSO_4} \times \phi_{MgSO_4}^{MgSO_4} \qquad (1\text{-}4\text{-}3)$$

b) Anion transference number runs

Fig. 1-4-b shows one of the anion runs in which $MgSO_4$ is followed by $Mg(IO_3)_2$, with the boundary moving towards a closed Cd anode.

The volume increases per faraday are :

1. Electrode reaction

$$\tfrac{1}{2}Cd \longrightarrow \tfrac{1}{2}Cd^{2+} + 1e^-$$

(i) loss of 1 equiv. Cd(s)

(ii) gain of 1 equiv. Cd^{2+} in $CdSO_4$ solution

$$\therefore \Delta V_1 = -\tfrac{1}{2}V_{Cd(s)} + \tfrac{1}{2}\phi_{Cd^{2+}}^{CdSO_4}$$

2. Transfer across b

(i) loss of 1 equiv. SO_4^{2-} from $MgSO_4$ solution

(ii) gain of 1 equiv. SO_4^{2-} in $CdSO_4$ solution

$$\therefore \Delta V_2 = -\tfrac{1}{2}\phi_{SO_4^{2-}}^{MgSO_4} + \tfrac{1}{2}\phi_{SO_4^{2-}}^{CdSO_4}$$

3. Transfer across reference point x

(i) loss of $t_{Mg^{2+}}^{MgSO_4}$ equiv. Mg^{2+}

(ii) gain of $t_{SO_4^{2-}}^{MgSO_4}$ equiv. SO_4^{2-}

$$\therefore \ \Delta V_3 = -\tfrac{1}{2}t^{MgSO_4}_{Mg^{2+}} \times \phi^{MgSO_4}_{Mg^{2+}} + \tfrac{1}{2}t^{MgSO_4}_{SO_4^{\ 2-}} \times \phi^{MgSO_4}_{SO_4^{\ 2-}}$$

Therefore ΔV_{total} will be

$$\Delta V_{total} = -\tfrac{1}{2}V_{Cd(s)} + \tfrac{1}{2}\phi^{CdSO_4}_{CdSO_4} - \tfrac{1}{2}t^{MgSO_4}_{Mg^{2+}} \times \phi^{MgSO_4}_{MgSO_4} \qquad (1\text{-}4\text{-}4)$$

It is important to note that the volume corrections $C|Z|\Delta V$ are more significant as the concentration increases, and the uncertainties in them limit the accuracy of the moving boundary method at higher concentrations.

1.5 Solvent correction

This correction allows for the fraction of the current carried by the solvent due to the ions formed by its self-dissociation and dissolved impurities. The correction becomes more important as the concentration of the solute decreases. The corrected (5) transference number, t_{corr}, is related to the observed value, t_{obs}, by the equation

$$t_{corr} = t_{obs}(1 + K_{solvent}/K_{solute}) \qquad (1\text{-}5\text{-}1)$$

where K stands for specific conductivity. The conductivity of the doubly distilled water used in the present work was

$0.98_4 \times 10^{-6} \Omega^{-1} cm^{-1}$, which was mainly due to dissolved carbon dioxide which forms H^+ and HCO_3^- by ionisation.

CHAPTER II

2. THE CONCENTRATION DEPENDENCE OF CONDUCTANCE AND TRANSFERENCE NUMBERS

2.1 Introduction

The interpretation of the variation of the electrical conductance of an electrolyte solution with concentration has been a source of attention since the beginning of the 20th century. According to the classical ionic theory of Arrhenius, the decrease of equivalent conductance with increase of concentration was attributed to a diminution of the extent to which the electrolyte was dissociated into its ions. Arrhenius considered that the ionic mobilities were independent of the concentration, and so that the equivalent conductance was proportional to the number of ions present in the solution. According to him, the degree of dissociation α, of an electrolyte was given by

$$\alpha = \Lambda/\Lambda^0$$

where Λ is the equivalent conductance at the concentration in question and Λ^0 is the limiting value where the electrolyte is completely dissociated into its ions.

The Arrhenius theory was shown to be approximately correct for weak electrolytes, but not for strong ones. For instance the variation of transference numbers with concentration could not be explained by this theory for either class of electrolyte.

In the previous chapter molar rather than equivalent conductances have been used in the m.b. equations, as recommended by McGlashan (6). However in the literature, the Fuoss and Pitts conductance equations have all been given in "equivalent" units and this practice has been continued in this chapter to allow direct comparisons with literature equations. Were conversions to molar quantities to be applied in future, one would need to write for a Z:Z valent electrolyte

$$\Lambda(\text{molar}) = |Z|\Lambda(\text{equiv})$$

and for a single ion or ion-constituent

$$\lambda_{\pm}(\text{molar}) = |Z|\lambda_{\pm}(\text{equiv})$$

The transference numbers for a Z:Z valent electrolyte are accordingly independent of this choice, since $|Z|$ cancels between numerator and denominator.

It should also be explicitly stated that all the parameters in the theoretical conductance or transference-concentration relations will be quoted in c.g.s. units, again in order to permit direct comparison with literature forms.

2.2 Variation of conductance with concentration

Later work showed that strong electrolytes are completely dissociated in solution at all reasonable concentrations, and therefore that the decrease of equivalent conductance with concentration must be attributed to a decrease of ionic mobility with concentration. This fact was explained quantitatively by the interionic theory of Debye, Hückel and Onsager (2b,7). They stated that due to interionic attractions and repulsions, a positive ion, over a time average, has in its vicinity more negative than positive ions, and vice-versa. This can be pictured by an "ionic atmosphere" distributed with radial symmetry around the central ion and with an equal and opposite charge. The change of equivalent conductance of a strong electrolyte with concentration is due to this ionic atmosphere, which modifies the motion of the ions through the solution by the electrophoretic and relaxation effects.

Under the influence of an external electrical field, the ionic atmosphere moves in the opposite direction to the central ion, as it carries an opposite charge to that of ion itself. The ion thus moves against a flow of oppositely charged ions and of the solvent molecules associated with them. The result is a reduction of the mobility of the ion, called the electrophoretic effect.

When no external electrical field is applied, the ion is at the centre of its ionic atmosphere. On application of an external electrical field, the ion and the ionic atmosphere will move in opposite directions. The ion is then no longer at the centre of its atmosphere, and the adjustment of the atmosphere to the new condition will take place rapidly but not instantaneously. Therefore the ion experiences an electrostatic force, which opposes the applied field and the effect is a retardation of its motion, called the relaxation effect.

Both effects will clearly be zero at infinitesimal ionic strength, where the separation of the ions tends to infinity.

Debye, Hückel and Onsager (D-H-O) $^{(2b)}$ treated these effects quantitatively. Their theory treats the solvent as a continuum and the ions as point charges. The theory therefore applies only to extremely dilute solutions and for this reason is known as the limiting law. For a symmetrical electrolyte it can be expressed by the equation

$$\Lambda/\alpha = \Lambda^0 - (B_1\Lambda^0 + B_2)\sqrt{\alpha C} \qquad (2\text{-}1\text{-}1)$$

where B_1 is the relaxation term given by

$$B_1\sqrt{\alpha C} = \frac{Z_+Z_-e^2}{3\varepsilon KT}\cdot\frac{q\,\chi}{1+\sqrt{q}} \qquad (2\text{-}1\text{-}2)$$

where e is the charge of the proton, ε the dielectric constant of the medium, K the Boltzmann constant, T the absolute temperature, and Z_+ and Z_- the algebraic charge number of the cation and anion respectively. q is given by

$$q = \frac{|Z_+Z_-|}{|Z_+| + |Z_-|} \cdot \frac{\lambda^0_+ + \lambda^0_-}{|Z_-|\lambda^0_+ + |Z_+|\lambda^0_-} \tag{2-1-3}$$

where λ^0_+ and λ^0_- are the individual equivalent ionic conductivities of the cation and anion at infinitesimal ionic strength. $\mathcal{K}$, the inverse of the Debye length, is given by

$$\mathcal{K} = \left(\frac{8\pi Ne^2 I}{1000\varepsilon KT}\right)^{\frac{1}{2}} \tag{2-1-4}$$

where N is the Avogadro number and I, the ionic strength, is defined as

$$I = \frac{1}{2}\sum_i C_i Z_i^2 \tag{2-1-5}$$

C_i being the molarity of the ions of algebraic charge number Z_i. The electrophoretic effect is given by

$$B_2 \sqrt{\alpha C} = \frac{e^2 \mathcal{K} N}{6\pi\eta_0}(|Z_+| + |Z_-|) \tag{2-1-6}$$

where η_0 is the viscosity of the medium. For a symmetrical electrolyte where $|Z_+| = |Z_-| = Z$, $q = \frac{1}{2}$ and the electrophoretic term B_2 becomes

$$B_2 \sqrt{\alpha C} = \frac{2Ze^2 \mathcal{K} N}{6\pi\eta_0} \tag{2-1-7}$$

If the constants are replaced in equations (2-1-2), (2-1-4) and (2-1-6), they will become in c.g.s. units for a Z:Z electrolyte,

$$B_1 = 82.0460\text{x}10^4 Z^3 \big/ (\varepsilon T)^{3/2} \big/ \text{mol}^{-\frac{1}{2}}.\text{dm}^{3/2}$$

$$B_2 = 82.487 Z^2 \big/ \eta_o (\varepsilon T)^{\frac{1}{2}} \big/ \Omega^{-1}\text{cm}^2.\text{mol}^{-3/2}.\text{dm}^{3/2}$$

$$\kappa = 50.29\text{x}10^8 (Z^2 \alpha C / \varepsilon T)^{\frac{1}{2}} \big/ \text{cm}^{-1}$$

Very careful conductance measurements on aqueous NaCl, KCl, HCl, $AgNO_3$, $CaCl_2$ and $LaCl_3$ have shown that the limiting law only holds below concentrations of 0.001N (2c) where the parameter κd is small compared with unity, d being the distance of closest approach.

Various empirical and theoretical attempts have been made to produce a D-H-O equation applicable to higher concentrations. In essence these attempts have all led to the limiting law supplemented by additional terms in C, $C^{3/2}$ and ClogC. An often used empirical form was published by Shedlovsky (8), who observed that for strong aqueous 1:1 electrolytes, the value of the limiting conductance, Λ^0, calculated from experimental values of strong electrolytes by equation (2-1-1), varied almost linearly with concentration up to 0.1N. He therefore proposed an extrapolation function $\Lambda^{0\prime}$ defined by

$$\Lambda^{0\prime} = (\Lambda + B_2\sqrt{C}) \big/ (1 - B_1\sqrt{C}) = \Lambda^0 + bC \qquad (2\text{-}1\text{-}8)$$

which gives the true limiting conductance Λ^0 on plotting

$\Lambda^{0\prime}$ against C, b being an empirical coefficient. The Shedlovsky equation has been used in the present work to extrapolate the conductances of $PhSO_3Na$ in water (see later). Fuoss and Onsager (9) have shown that the approximate constancy of b was a fortuitous consequence of the numerical values of certain terms in their more complete theory. In this, they treated the ions as hard spheres with finite dimensions moving in a continuum. They introduced the distance of closest approach, d, between cation and anion and obtained the equation

$$\Lambda/\alpha = (\Lambda^0 - \Lambda^e)(1 + \Delta X/X) \qquad (2\text{-}1\text{-}9)$$

where the electrophoretic term Λ^e is given by

$$\Lambda^e = B_2 \sqrt{\alpha C}/(1 + \kappa d) \qquad (2\text{-}1\text{-}10)$$

where X is the applied electrical field and ΔX is the relaxation field opposed to X. An expression for $\Delta X/X$ was obtained by a series of successive approximations which yielded terms of different order in C, by solving the corresponding differential equations with the boundary conditions appropriate to the model. Combined with the previous value of the electrophoretic term the conductance equation obtained is

$$\Lambda/\alpha = \Lambda^0 - (B_1\Lambda^0 + B_2)(\alpha C)^{\frac{1}{2}} + E(\alpha C)\ln(\alpha C) + J_1(\alpha C) - J_2(\alpha C)^{3/2}\left(1 - B_1(\alpha C)^{\frac{1}{2}}\right) \qquad (2\text{-}1\text{-}11)$$

in which the constants J_1 and J_2 are explicit functions of ion size, Λ^0 and the properties of the solvent and E is independent of ion size.

In 1963 Fuoss and Onsager (10) derived a more exact form of the electrophoretic effect given by the equation

$$\Lambda^e = B_2\sqrt{\alpha C} - B_3 \qquad (2\text{-}1\text{-}12)$$

where for a symmetrical electrolyte,

$$B_3 = \frac{2}{3}\frac{N^2e^6Z^5}{\eta_0(\varepsilon KT)^2}(\alpha C)10^{-3}F(b) \qquad (2\text{-}1\text{-}13)$$

and F(b) is a function of d, ε and T. They stated that the form given in (2-1-10) is a close approximation to (2-1-12). Calculations of Λ^e by both equations were made by Spiro and Sidebottom (11). They showed that the revised form given by (2-1-12) does in fact differ appreciably from the old form (2-1-10) and appears to represent the electrophoretic effect more exactly. Using the revised form, equation (2-1-9) becomes

$$\Lambda/\alpha = \left[\Lambda^0 - (B_2\sqrt{\alpha C} - B_3)\right](1 + \Delta X/X) \qquad (2\text{-}1\text{-}14)$$

This equation has been further improved with a recalculated relaxation term by Fuoss and Hsia (12). In 1975 Fuoss (13) published yet another updated version of his equation, which was modified by Chen (14). This newest equation for associated symmetrical electrolytes is

$$\Lambda/\alpha = \left[\Lambda^0(1 + \Delta X/X) - \Lambda^e\right] \qquad (2\text{-}1\text{-}15)$$

and resulted from a rigorous development of the electrophoretic (Λ^e) and relaxation effects. Contrary to the previous expressions used for the conductance (9,10), in equation (2-1-15) the relaxation term cannot be factorized out.

An independent derivation of a conductance-concentration relation was carried out by Pitts (15) in 1953. His physical model was similar to that employed by Fuoss and Onsager (F) but his treatment (P) differed in certain aspects :

1. In (F) the force of an ion i in the presence of another j includes explicitly a contribution from the ionic atmosphere around i. In (P) this is regarded as implicit in the definition of electrostatic field about the j ion.
2. In (P) the ionic radius is not the same as the closest distance of approach, whereas the (F) theory requires them to be identical.
3. In (F) the net force on a volume element of solvent arises from electrical effects and also from a hypothetical effect of ionic Brownian motion. In (P) only the electrical part is used in the electrophoretic calculation.
4. An approximate electrostatic boundary condition is used in (P) together with hydrodynamic conditions consistent with the model. In (F) an exact electrostatic condition is used, but the remaining conditions refer to relative ionic velocities at closest approach ; these are not correctly calculated from the hydrodynamic equations.
5. The final expression for conductivity in (F) is assembled by a method which is not simply related to the calculated

forces acting on the ions.

These differences have been discussed in detail by Pitts, Tabor and Daly(16,17) and Fernandez-Prini(18). Pitts' equation was slightly modified(16) from its original form and can be written

$$\Lambda/\alpha = (1 - Y_1)\Lambda^0 + Y_2 - Y_3 \qquad (2\text{-}1\text{-}16)$$

where

$$Y_1 = \frac{Z^2e^2\kappa}{3\varepsilon KT(1 + \sqrt{2})(1 + Y)(\sqrt{2} + Y)} + \frac{Z^4e^4S_1\kappa^2}{3(\varepsilon KT)^2} \qquad (2\text{-}1\text{-}17)$$

$$Y_2 = \frac{\sqrt{2} - 1}{(\sqrt{2} + Y)(1 + Y)^2}\cdot\frac{N}{3\pi\eta_0}\cdot\frac{Z^4e^4\kappa^2}{3\varepsilon KT} \qquad (2\text{-}1\text{-}18)$$

$$Y_3 = \frac{Z^2e^2\kappa}{(1 + Y)}\cdot\frac{N}{3\pi\eta_0}\left(1 - \frac{Z^2e^2\kappa\, T_1}{3\varepsilon KT}\right) \qquad (2\text{-}1\text{-}19)$$

where $Y = \kappa d$ and S_1 and T_1 are numerically evaluated functions of Y.

Both the Pitts and the Fuoss-Onsager equations can be closely fitted to the experimental conductance data, the Pitts' equation being marginally more successful in some cases(17,18).

2.3 Variation of transference numbers with concentration

That transference numbers for both strong and weak electrolytes vary with concentration is confirmed by many experimental results. This fact alone shows that the mobilities of the ions depend on concentration and thus transference number measurements provide a very sensitive test of the interionic theory.

At infinitesimal ionic strength, where ion association is absent, the transference numbers attain their limiting values given by

$$t^0_\pm = \lambda^0_\pm / \Lambda^0 \qquad (2\text{-}1\text{-}20)$$

where $\lambda^0_\pm$ and Λ^0 are the limiting equivalent conductances of the ions and of the whole electrolyte, respectively. For convenience, equations will be given only for the cation-constituent. The same equations apply to the anion-constituent with the appropriate changes. Equation (2-1-9) written for the cation-constituent then takes the form

$$\lambda_+/\alpha = (\lambda^0_+ - \lambda^e_+)(1 + \Delta X_+/X) \qquad (2\text{-}1\text{-}21)$$

For a symmetrical electrolyte (19):

$$\lambda^e_+ = \lambda^e_- = \tfrac{1}{2}\Lambda^e$$

$$\Delta X_+ = \Delta X_- = \Delta X$$

By combining equations (1-1-2), (2-1-9) and (2-1-21) one obtains

$$t_+ = (\lambda^0_+ - \Lambda^e/2) \big/ (\Lambda^0 - \Lambda^e) \qquad (2\text{-}1\text{-}22)$$

Combination with equation (2-1-20) written in the form for the cation transference number, gives

$$t_{+} = t_{+}^{0} + \frac{(t_{+}^{0} - 0.5)\Lambda^{e}}{\Lambda^{0} - \Lambda^{e}} \qquad (2\text{-}1\text{-}23)$$

After multiplication by $(\Lambda^{0} - \Lambda^{e})$ and rearrangement :

$$t_{+} = t_{+}^{0} + \frac{(t_{+} - 0.5)\Lambda^{e}}{\Lambda^{0}} \qquad (2\text{-}1\text{-}24)$$

Inserting Λ^{e} in the form given by equation (2-1-10) then leads to

$$t_{+}^{0} = t_{+} - \frac{(t_{+} - 0.5)B_{2}\sqrt{\alpha C}}{\Lambda^{0}(1 + \chi \partial)} \qquad (2\text{-}1\text{-}25)$$

which is the Fuoss-Onsager equation in its transference form with the old electrophoretic term. After rearrangement, equation (2-1-25) differentiated with respect to $\sqrt{\alpha C}$ gives

$$\left(\frac{dt_{+}}{d\sqrt{\alpha C}}\right)_{\alpha C \to 0} = \frac{(t_{+}^{0} - 0.5)B_{2}}{\Lambda^{0}} \qquad (2\text{-}1\text{-}26)$$

The right-hand side of (2-1-26) is the limiting Onsager slope of the curve obtained by plotting transference number against the square root of ionic concentration. Thus, when t_{+}^{0} is close to 0.5, t_{+} will hardly change with concentration, but it will do so the more t_{+}^{0} differs from 0.5.

With the revised electrophoretic term the F-O equation in its transference form is

$$t_+^0 = t_+ - \frac{(t_+ - 0.5)(B_2\sqrt{\alpha C} - B_3)}{\Lambda^0} \qquad (2\text{-}1\text{-}27)$$

No ionic form of Fuoss' 1975 equation (2-1-15) has yet been published, but it is being developed by Justice and Perie (14). However a form without derivation was announced at the V ICNAS conference in Leeds in July 1976, which for the cation-constituent can be stated by

$$\lambda_+ = \alpha\left[\lambda_+^0(1 + \Delta X_r/X) + t_+^0\Delta X_v/X - 0.5\Lambda^e\right] \qquad (2\text{-}1\text{-}29)$$

where $\Delta X_r/X$ and $\Delta X_v/X$ are the electrostatic and hydrodynamic terms of the relaxation field, respectively. For many years, the complete cancellation of the relaxation term in the derivation of the Fuoss-Onsager transference form had been accepted ; this more recent investigation has shown that part of the relaxation term should be retained as in the transference form of Pitts equation. Since Perie's derivations (14) are being carried out only for 1:1 electrolytes and have not yet been published, these equations cannot be used in the present work. The $MgSO_4$ data will therefore be tested by the previous Fuoss-Onsager transference forms.

The Pitts conductance equation for a cation is (20)

$$\lambda_+/\alpha = \lambda_+^0 - \lambda_+^0 Y_1 + (\lambda_+^0/\Lambda^0)Y_2 - \tfrac{1}{2}Y_3 \qquad (2\text{-}1\text{-}30)$$

Combining this equation with (2-1-16) gives

$$t_+ = t_+^0 + (t_+^0 - \tfrac{1}{2})Y_3 / \Lambda' \qquad (2\text{-}1\text{-}31)$$

where $\Lambda' = \Lambda^0 - \Lambda^0 Y_1 + Y_2 - Y_3$
or, on rearrangement,

$$t_+^0 = (t_+ + \tfrac{1}{2}Y_3/\Lambda') / (1 + Y_3/\Lambda') \qquad (2\text{-}1\text{-}32)$$

This is the Pitts equation in its transference form. M. Perie and Mme. Perie at the Leeds conference in 1976 (14) presented a different version in which the relaxation term $(1 + \Delta X/X)$ is retained, but without giving a derivation.

Equations (2-1-25), (2-1-27) and (2-1-32) have been used to test how well the theory describes the concentration dependence of transference numbers of 1:1 electrolytes in various solvents (21). The interionic effects are of course much larger for 2:2 electrolytes, and the first test with reliable 2:2 electrolyte transference data will be described in chapter VII. The 1:1 electrolyte calculations were carried out by two different types of computer fitting, and in the present thesis, Sidebottom and Spiro's method A will be employed. It is based on the fact that if the theory is fitted by a given value of $\underline{d}$, t_+^0 as calculated should be independent of concentration. The measured transference numbers and corresponding ionic concentrations (αC) were inserted into equations (2-1-25), (2-1-27) and (2-1-32), for a series of values of $\underline{d}$. That value of $\underline{d}$, d_1, was then found which made the standard deviation of the calculated t_+^0 values from their average, a minimum over a specified concentration range. A computer programme has been written by Sidebottom (21a) in FORTRAN IV for the Imperial College CDC 6400 computer for uni-univalent electrolytes. This programme was rewritten by Kumarasinghe (22) and then revised, to calculate t_+^0 for symmetrical electrolytes of any order, and was used in the present work to calculate t_+^0 of $MgSO_4$ from the experimentally found transference numbers. The calculation was carried out for all positive integral values of d from 1.0 Å to 20.0 Å. The calculation was repeated for values of d ranging from $d_1 - 1$ to $d_1 + 1$ (d_1 being the selected value in the first calculation) at intervals of 0.1 Å and that value of d corresponding to the new minimum standard deviation was chosen. Since the theories are likely to break down at high concentrations, the whole series of calculations was repeated, but this time the highest concentration was excluded. As a result this latter computation was performed on three data points only.

CHAPTER III

3. ETHYLENEDIAMINE AS A SOLVENT

3.1 Introduction

Although accurate conductance measurements have been carried out on a large number of non-aqueous solvents, only in a few have transference numbers been measured. A combination of both conductances and transference numbers is needed to derive individual ionic conductances. So far, no transference work has been reported for amines, and ethylenediamine (ED) was chosen for the present work as it can be handled at room temperature and conductances in it are known (23-26). A further reason for this research was to obtain accurate transference data in a solvent of low dielectric constant, where ionic association occurs even at ordinary concentrations. Yet another reason for choosing ED for the present work, was that ED is one of the few organic solvents which dissolves metals to produce highly conducting solvated electrons. A knowledge of the conductivity of the solvated electron is of great interest; such knowledge is possible in ED from the known conductances of its metal solutions only if transference data are also available in this solvent.

Although this chapter deals mainly with ethylenediamine, some transference data from the literature for liquid ammonia are also included due to the similarity of this solvent to ethylenediamine. Comparison will also be occasionally made between the properties of both solvents.

3.2 Properties of the solvent

Ethylenediamine is a colourless liquid which fumes strongly in air and smells like ammonia. It is a slightly stronger base than ammonia when dissolved in water (25). As a pure liquid it is appreciably more viscous than either ammonia or water and has a much lower dielectric constant (see Table 3-2-1). It readily absorbs water and carbon dioxide from the air and it does so more rapidly than it evaporates, so that it leaves a residue of ethylenediamine carbamate ($NH_2CH_2CH_2NH_3^+ \ ^-OOCNH_2$), a white solid subliming at 170° C. The high basicity of ED makes it extremely difficult to work with and its conductance due to absorbed carbon dioxide becomes an appreciable factor in the conductance of solutions at low concentrations. Anhydrous ethylenediamine is somewhat corrosive to the skin and mucous membranes.

The following table summarizes the values at 25° C (unless otherwise stated) of the most important properties of ED. Its molecular weight is 66.08.

Noticeable in the values here tabulated is the big difference between the specific conductance measured by the different workers. This shows how the purity of ethylenediamine depends on the purification method used, but mainly it depends on the care in its handling, due to its very high reactivity. The relatively high value for the heat of vaporization indicates considerable association in the liquid state.

From the table, the values for the viscosity η_0, relative dielectric constant ε and density ρ chosen for this work are

Table 3-2-1

Property	Value	Reference
Boiling point at 760 mmHg	116.2° C	27
	117.2° C	28
	117.0° C	25
	118-121° C	29
	116-117° C	30
	116.7° C	31
Vapour pressure at 20° C	10.7 mmHg	25
	10.0 mmHg	28
	10.0 mmHg	27
Heat of vaporization	161 cal/g = 10.6 kcal/mol	28
	167 cal/g = 11.0 kcal/mol	27
	11.2 kcal/mol at 20° C	32
Freezing point	10.8° C	28
	11.0° C	27
	11.0° C	25
	11.0° C	32
Heat of fusion	77 cal/g = 5.0 kcal/mol	33
Refractive index	1.4540 at 20° C	34
	1.4565	28
Viscosity	0.0160 poise	28
	0.0154 poise	35
	0.0154 poise	25
	0.01725 poise	32
	0.0152 poise at 20° C	36
Dielectric constant	12.5	31
	12.5	37,38
	12.9	23
	12.9	32

Table 3-2-1 (cont.)

Property	Value	Reference
Density	0.8995 at 20° C	28
	0.895	25
	0.891	23
	0.8994 at 20° C	27
	0.8970 at 20° C	31
	0.893 at 20° C	36
	0.8935	39
	0.891	32
	0.907 at 17° C	30
	0.896 at 20.7° C	40
	0.8923	*
Ionization constant (in water)	8.5×10^{-5} mol.dm^{-3}	25
	7.1×10^{-5} mol.dm^{-3}	41
Specific conductance $\times 10^7$	0.2-0.5 Ω^{-1}.cm^{-1}	25
	10-30 Ω^{-1}.cm^{-1}	42
	2 Ω^{-1}.cm^{-1}	24
	0.9 Ω^{-1}.cm^{-1}	23
	14 Ω^{-1}.cm^{-1}	32
	5-20 Ω^{-1}.cm^{-1}	43,44
	2.4 Ω^{-1}.cm^{-1}	*

* Values determined by the writer

respectively:

$\eta_0 = 0.0154$ poise (1 poise = 1 $g.cm^{-1}.s^{-1}$ = 1 $dyn.s.cm^{-2}$)

$\varepsilon = 12.7 \pm 0.2$

$\rho = 0.893\ g.cm^{-3}$

3.3 Electrolyte solutions in ethylenediamine

3.3.1 Alkali metal solutions in ethylenediamine

As mentioned in section (3-1), ED forms metal solutions in which highly conducting solvated electrons are produced. Dissolved electrons are not a recent discovery but were observed more than a hundred years ago on dissolving alkali metals in liquid ammonia (45). Many of the physical properties of these metal solutions have been established (46); they constitute a link between electrolytes (dilute solutions) and metals (concentrated solutions). Dilute metal solutions in both ED and NH_3 exhibit a dark blue colour as a result of the high light absorption in the red to infrared region of the spectrum by the dissolved electrons. The electrons exist in this state only at low concentrations, as at higher concentrations electron pairs are formed (47). If the concentration of the electrons can be further increased, the solutions will assume a metal-like character with high conductivities and metallic lustre. These transitions can be followed readily in solutions of alkali metals in liquid ammonia where their solubility is considerably higher than in ED (47). Dewald and Dye (48) have determined the solubility of the alkali metals in ED at room temperature and found that the most soluble is lithium (solubility $0.287 \pm 0.015\ mol.l^{-1}$)

and the least soluble is sodium (solubility $2.39 \pm 0.04 \times 10^{-3}$ mol.l^{-1}).

Conductance measurements of the alkali metals in ED as a function of concentration have also been made by Dewald and Dye (48), although the results for lithium are only semiquantitative. The general form of the conductance curves for K, Rb and Cs in ED is similar to that expected for an electrolyte in a solvent of low dielectric constant. However the conductance behaviour of sodium solutions differs markedly from that of the other alkali metals, their equivalent conductances being much lower than for the other alkali metals and almost independent of concentration. No explanation for the abnormal behaviour of Na, which has also been observed in methylamine (49), has yet been published. However, by using a cryptand (C) to increase the solubility of the Na metal in amines, Dye (50) was recently able to crystallise the compound $NaC^{+}\ Na^{-}$. The presence of the anion Na^{-} in amine solutions was confirmed by n.m.r. studies (50). Thus the electrons in sodium-amine solutions appear to form Na^{-} ions whereas, in the case of amine solutions of the other alkali metals they are present as solvated electrons.

3.3.2 Solubilities of electrolytes in ethylenediamine

The solubilities of a large number of inorganic salts in ethylenediamine have been measured (51). Although ED is not so good a solvent as liquid ammonia, it is quantitatively similar in its solvent behaviour.

Table 3-3-2-1 gives the solubility of three of these salts in ED, which are of particular interest for this thesis.

Table 3-3-2-1

Solubilities of some electrolytes in ethylenediamine at 25° C

Salt	Solubility/mol.$(100g)^{-1}$
KI	0.451
NaI	0.231
$NaNO_3$	0.394

The alkali iodides are relatively soluble whereas the chlorides are only sparingly soluble. For the salts tested, $KClO_4$ is the only one which is more soluble in ethylenediamine than in water. As will be shown later, the present writer found that AgI is also extremely soluble in ED. Ethylenediamine forms solvates with essentially the same salts with which water forms stable hydrates, for example, $NaI.2H_2O$, $NaI.3ED$; $NaClO_4.H_2O$, $NaClO_4.3ED$; $SrCl_2.6H_2O$, $SrCl_2.6ED$.

3.3.3 Conductances of electrolytes in ethylenediamine

The conductances of a number of salts and some acids in ethylenediamine have been measured. Conductance values for some of these salts which are of particular interest for this thesis are listed in Table 3-3-3-1. Putnam and Kobe (32) have not calculated the limiting conductances, Λ^0 and Schaap et al. (25) give only the limiting values. The agreement between the values for the limiting conductances and association constants K_A, obtained by the different workers is not very good, although in their calculation all the workers have used the method of Fuoss and Kraus.(52a,b) It should be noted that the Λ^0 values obtained for $AgNO_3$ by different workers (23,24,43) are in fair agreement with each other, whereas that for AgI obtained by Hibbard and Schmidt (24) is considerably higher than that reported by the other two papers (23,43). Hibbard and Schmidt (24) attributed the difference between their results and those of Bromley and Luder (23) to the fact that their results (24) have been obtained by a concentration method rather than a dilution method (23). However, the limiting values reported for the various salts in Hibbard and Schmidt's paper (24) display such grave deviations from additivity that their results should be discarded. Also the K_A values reported for AgI (23,24,43) differ appreciably from each other, but no comments about it have been made by any of the above workers (23,24,43). Inspection of the table shows that all the electrolytes studied are highly associated. By far the largest association is shown by AgI, and this presumably is due to the partially covalent character of the silver-iodine bond.

Table 3-3-3-1

Conductivities of some salts in ethylenediamine at 25° C

Salt	Conc.rangex10^5/ mol.l^{-1}	Λ range/cm^2. Ω^{-1}.equiv^{-1}	Λ^0/cm^2. Ω^{-1}.equiv^{-1}	K_Ax10^{-3}/ dm^3.mol^{-1}	Ref.
KI			71.9	3.15	25
	4.9-460	65.6-27.8	69.2	1.66	23
	10.6-160	84.6-50.4	71.9	2.08	43
	24700-305000	16.0-10.99			32
			69.0	0.959	26
NaI			63.9	1.87	25
	29200-109000	16.4-14.2			32
	6.2-60	59.94-43.25	61.4	1.45	24
			67.6	1.00_5	26
AgI	14-660	21.95-4.79	48.8	23.2	23
	5.5-76	30.96-10.89	72.8	59.5	24
	26-350	16.8-5.54	45.5	89.3	43
$AgNO_3$	32-216	49.45-31.16	63.5	1.74	24
	8.7-330	56.0-29.7	61.4.	1.29	23
	9.3-220	57.0-30.9	65.8	2.17	43
$NaNO_3$	6.2-60	54.94-43.25	75.1	8.93	24
			66.2	7.00	25

3.3.4 Viscosities of electrolytes in ethylenediamine

Schmidt, Hoffman and Schaap (39) measured the viscosity of LiCl, $NaNO_3$, HgI_2, $AgNO_3$ and Bu_4NI at 25° C in ethylenediamine. By plotting $(\eta/\eta_o - 1)/\sqrt{m}$ against $\sqrt{m}$, where η/η_o is the relative viscosity and m the molality, they obtained a linear relationship over the concentration range studied. For $AgNO_3$, where the viscosity measurements were made up to 1.0M, this linear relationship fitted only up to ca. 0.4M. From their plots it can be seen that the coefficient B is positive for all the above electrolytes, which shows that they are "structure forming".

3.3.5 Densities and apparent molar volumes of electrolytes in ethylenediamine

Putnam and Kobe (32), Fedot'ev and Kinkul'skaya (53) and Schmidt et al. (39) have measured the densities of some salts in ethylenediamine. Schmidt et al. (39) used their density values to calculate the apparent molar volumes of various electrolytes in this solvent at 25° C. Masson's empirical rule

$$\phi = \phi^o + S\sqrt{m}$$

where ϕ is the apparent molal volume
ϕ^o the limiting apparent molal volume
S the limiting slope
m the molality

which holds well for most aqueous solutions of electrolytes, appeared also to be valid in ethylenediamine . Table 3-3-5-1 shows the limiting apparent molar volumes for the electrolytes examined.

Table 3-3-5-1

Salt	$\phi^{o}/\mathrm{cm}^3.\mathrm{mol}^{-1}$
LiCl	13.5
$NaNO_3$	35.5
HgI_2	112.0
$AgNO_3$	20.0
Bu_4NI	325

3.3.6 Heats of solution of electrolytes in ethylenediamine

Schmidt et al. (42) determined calorimetrically the heats of solution of various electrolytes and of water in anhydrous ethylenediamine at 25° C in the concentration range 1.5×10^{-3} to about 1×10^{-2} molal. They compared the heats of solution for the various electrolytes studied, such as the iodides and nitrates of the alkali metals, mercury and silver and the heat of solution of water in ED with those in other amine solvents and principally those in liquid NH_3. For the salts tested, the heats of solution in ED are all negative except that for KNO_3, which is positive as it is in water and in liquid ammonia at -33.5° C. In general, the heats of solution in ED are equal to, or more negative than those in liquid NH_3, but the order of magnitude, which ranges in ED from -2.47 kcal.mol^{-1} for CsI to -28.8 kcal.mol^{-1} for LiI, is about the same in both solvents. The heat of solution for water in anhydrous ED is -3.75 kcal.mol^{-1} and is of the same order of magnitude as it is in liquid NH_3. The salts whose cations (Ag^+, Li^+, Na^+) complex with ED show very large negative molar heat effects. No data about solvation of the cation Hg^{2+} in ED seemed to be given in the literature, but the high negative values reported (42) for the heats of solution of salts of Hg^{2+}. (-17.30 kcal.mol^{-1} for $Hg(CN)_2$ and -28.60 kcal.mol^{-1} for HgI_2) indicate that this cation is strongly solvated in ethylenediamine.

3.4 Transference numbers in liquid ammonia

No transference number measurements have previously been carried out in ethylenediamine. On the other hand, several transference studies have been made in the related solvent liquid ammonia, and a brief mention of this work is therefore relevant here. In view of the experimental difficulties involved in liquid ammonia work, it is surprising that moving boundary experiments in this solvent were attempted as early as 1904, and in 1960 a moving boundary study was published of sodium solutions. Table 3-4-1 summarizes the transference work reported for liquid ammonia.

Table 3-4-1

Temp./ ^{0}C	Solute	Conc. range/ mol.l^{-1}	Transf. No. measured	$t^0_{\pm}$	Ref.
-37	Na	0.01-0.14	t_-	0.866	54
-33	NH_4NO_3	0.01-0.2	t_+ and t_-		55
	KNO_3	0.01-0.2	t_+ and t_-		55
	$NaNO_3$	0.01-0.2	t_+ and t_-		55
	NaCl	0.01-0.2	t_+ and t_-		55
	$AgNO_3$	0.01-0.2	t_+ and t_-		55
-45	NH_4NO_3	0.01-0.16	t_+	0.413	56
-48	KNO_3	0.01-0.16	t_+	0.481	56
-65	KNO_3	0.01-0.11	t_+	0.4842	57
-55				0.4824	57
-45				0.4805	57
-65	$NaNO_3$	0.01-0.11	t_+	0.4052	57
-45				0.4170	57
-65	$LiNO_3$	0.02-0.10	t_+	0.3794	57
-45				0.3880	57
-65	NH_4NO_3	0.006-0.16	t_+	0.4040	57
-55				0.4092	57
-45				0.4140	57

CHAPTER IV

4. PURIFICATION OF ETHYLENEDIAMINE

4.1 Introduction

To choose the best source of ethylenediamine, samples from three different suppliers were analysed for their conductivity. A Pyrex conductivity cell of cell constant 0.29 cm^{-1} and a conductivity bridge, type No. E7566/3 supplied by M.E.L., were used at this stage. The measurements were made with the cell in a water bath at 18° C and the results are listed in Table 4-1-1.

Table 4-1-1

Supplier	$K \times 10^6 / \Omega^{-1}.cm^{-1}$
Union Carbide	27.3
B.D.H.	18.2
Jefferson Chemicals U.K.	12.5

ED from Jefferson Chemicals U.K. was accordingly purchased for the present work, in a 500 lb drum. The conductivity of the ED contained in this drum was found to be $17.4 \times 10^{-6} \Omega^{-1}.cm^{-1}$ at 18° C.

4.2 Methods of purification

The methods described in the literature for purifying ED are listed in Table 4-2-1. As seen from this table, two basic techniques have been used : distillation and crystallisation. The lowest conductivity was reported (25) as the result of distilling over sodium, and the lowest water content (42) by refluxing over calcium hydride. Most of the purification methods cannot be judged because of lack of information about the properties of the ED produced.

Crystallisation was not initially tried by the writer, because an insufficient quantity of solvent is obtained from it. Apparatus for refluxing and distilling under nitrogen at normal pressure was therefore set up as shown in fig. 4-2-1. Before forcing the ED from the drum into flask A by nitrogen pressure, the apparatus was evacuated and filled three times with "oxygen-free" nitrogen. This had first passed through two drying towers, one filled with molecular sieve 3A and the other with silica gel. A mercury manometer was used to regulate the pressure inside the system during these operations. The ED (4 litres) was refluxed for 2-3 hours in an atmosphere of dry nitrogen. The water supply to condenser 1 was then cut off and the water inside the condenser removed and the ED then distilled over. During the first part of the distillation, the big Teflon tap 3 was kept open and tap 4 kept closed to collect the first fraction, which was rejected. The middle portion of the purified solvent was collected in flask B. When the distillation was finished, the big Teflon taps 4 and 5 were

Table 4-2-1

Purification methods	b.p./ ^{0}C	K$\times 10^7$/ Ω^{-1}.cm^{-1}	d_4^{25}/ g.cm^{-3}	Water content/ % (w/w)	n_D^{25}	ε	η_0/cp.	Ref.
	118- 121					15.7 (18° C)		29
Zinc oxalate was mixed with ED hydrate and the compound formed dissolved in a little boiling water. After cooling, the crystals formed were filtered off, washed with alcohol, dried and heated in vacuum to 200° C. ED was liberated condensed and redistilled from Na.	116- 117		0.907 (17° C)					30
Bersworth ED was fractionated in a 6 metre column with 75% aqueous NaOH which had been shown to extract water from ED.			0.896 (20.7° C)					40
Eastman ED was thrice distilled from Na.	116.7		0.8970 (19.9° C)					31

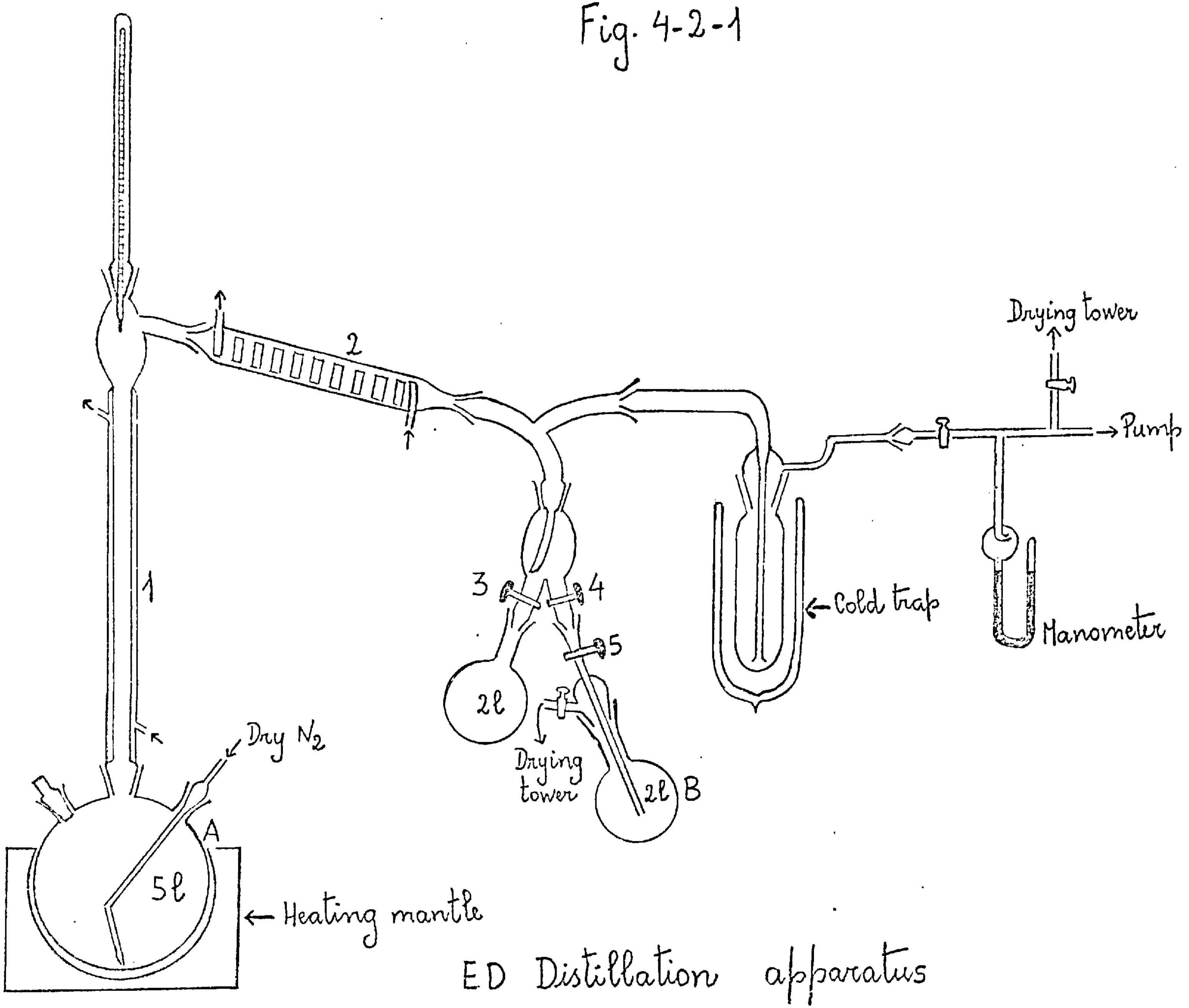
Purification methods	b.p./ °C	$K\times10^7$/ $\Omega^{-1}.cm^{-1}$	d_4^{25}/ $g.cm^{-3}$	Water content/ % (w/w)	n_D^{25}	ε	η/cp.	Ref.
ED was stored over NaOH and BaO for several days, kept over Na for a day, then fractionated off freshly activated alumina on to alumina and NaOH, and redistilled. Both distillations were carried out under dry N_2 freed from CO_2.		0.9	0.891 (32)			12.9	1.54 (25° C) (35)	23
Commercial anhydrous ED was refluxed with metallic K until the liquid turned permanently dark, then distilled and redistilled.			0.893 (20° C)				1.52 (20° C)	36
ED was refluxed for several days on metallic Li, then distilled and fractionated twice from metallic Na, all under N_2 freed from CO_2 and O_2.		2						24
ED was dried over CaH_2 and fractionated in a N_2 atmosphere until constant density was obtained.			0.8935					39

Purification methods	b.p./ °C	$K\times10^7$/ $\Omega^{-1}.cm^{-1}$	d_4^{25}/ $g.cm^{-3}$	Water content/ % (w/w)	n_D^{25}	ε	η_0/	Ref.
Anhydrous ED was placed over KOH pellets for some days, then distilled through a 1 metre packed column. The middle fraction was treated with Na wire and distilled in vacuo on to freshly distilled metal Na. A permanent blue colour was taken to indicate dryness.		5-20 (43)						58
98-100% commercial ED was distilled twice from Na at 25 cmHg. N_2 was bled into the system throughout.		0.2-0.5						25
ED was first stored for several days over KOH, refluxed for 2 days over BaO + KOH in a stream of N_2, then distilled. The same refluxing and distillation was repeated with the distillate.								48
ED was distilled with piperidine at 1 atm				<0.1				63

Purification methods	b.p./ °C	$K \times 10^7$/ Ω^{-1}.cm^{-1}	d_4^{25}/ g.cm^{-3}	Water content/ % (w/w)	n_D^{25}	ε	η/	Ref.
ED was shaken 12 hours with activated 5A molecular sieve, decanted and shaken 12 hours with CaO + KOH, and again decanted. The liquid was then fractionally distilled under N_2 over freshly activated molecular sieve. The fraction of b_{760} 117·2° C was further fractionally distilled under N_2 at least once over Na.								59
Aq. ED was distilled at 4.8 atm to remove most of the water. Then 7% aq. ED was fractionated at 5.5 atm to give 99% pure ED at the base of the column.								60
Aq. ED was cooled to 3-10.8° C and the solid separated by centrifuge. The supernatant liquid was purified continuously. Purity of ED 99.9%.								61

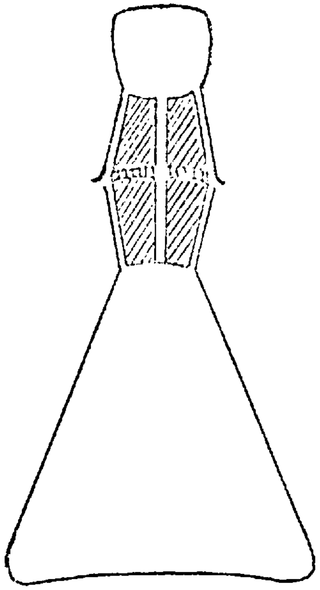
Purification methods	b.p./ °C	$K \times 10^7$/ $\Omega^{-1}.cm^{-1}$	d_4^{25}/ $g.cm^{-3}$	Water content/ % (w/w)	n_D^{25}	ε	η/	Ref.
ED (98%) was refluxed for 12 hours over CaH_2, then distilled under O_2-free N_2 on to fresh CaH_2. The ED was redistilled.		10-30		$<$ 0.02				42
Aqueous ED was distilled with hexamethylenimine to form an azeotropic mixture.				$<$ 0.3				62
ED (99%) was stood over 10% (w/w) NaOH pellets overnight. Then 2% (w/w) Na was added and the solution refluxed for 2-3 hours under dry N_2.		5-20		1.3				44

Fig. 4-2-1



ED Distillation apparatus

Fig. 4-3-1



Pycnometer

closed and flask B removed to prevent contamination of the purified solvent by moisture and carbon dioxide from the air.

To be effective, the molecular sieve employed had to be throughly dried. This was done by Notley's procedure (64). It involves a Pyrex column, 1 metre long and 5 cm in diameter, covered with a layer of asbestos and then wound with two separate nichrome coils connected in parallel. The covered column was lagged with two layers of asbestos rope. When the wire was connected to the mains, the temperature inside the column reached 360° C. The molecular sieve was washed and dried in the oven at about 110° C, before being put into the column. While the column was heated, very dry and pure nitrogen, obtained by evaporating liquid nitrogen by a method to be described later (65), was passed through the sieve. Several hours were necessary to remove all the water, after which the column was left to cool under nitrogen flow.

4.3 Results

Several drying agents were tried, either by themselves or associated with reflux for 2-3 hours and distillation. The water content of ED straight from the drum was found to be 0.57%.

Molecular sieve 3A was the first drying agent employed, after being carefully dried by the method just described (64). Different ways of using it were tried, but very little reduction in water content was observed. With B.D.H. CaH_2, an increase of water was found. This CaH_2 was contained in a closed tin, but had been kept in the laboratory for some years. One possibility was that some moisture had entered the tin, and therefore fresh B.D.H. CaH_2 (99.5%) was obtained and tried out. Even then, ED showed the same or only slightly less water after reflux and distillation (Table 4-3-1). At this stage the water content of the ED in the drum was redetermined and found to be about 1%. The possibility of leakage into the drum was investigated, but no leaks were found. Moreover, the reflux and distillation of ED over the different drying agents had been carefully carried out under dry nitrogen and the only opening to the atmosphere was through a drying tower filled with dry molecular sieve 3A. Other drying agents were tried but no improvement was obtained (see Table 4-3-1), in spite of the fact that some of them had been found efficacious in the literature.

As these results seemed unlikely, suspicion now focussed on the method of water analysis. As described in the next section, it was discovered that the glacial acetic acid used as solvent in the Karl Fischer titrations contained an appreciable amount of water, contrary to the apparent results of earlier titrations. After a bottle of acetic acid was opened, its water content was found to increase between experiments, especially as the bottle became emptier.

We concluded that the values obtained for the water content do not correspond to the water content of ED itself, but to the global water content of ED plus acetic acid. As explained in the next section, the water content of ED after reflux and distillation over B.D.H. CaH_2 was actually 0.08%(w/w).

Table 4-3-1

Drying agent	ED treatment	Water content/ % (w/w)	$K \times 10^6$/ $\Omega^{-1}.cm^{-1}$
None	ED distilled by itself	0.46	7.83
Molecular sieve 3A (B.D.H.)	1) ED left standing with molecular sieve for $1\frac{1}{2}$ hours.	0.47	
	2) ED left standing with molecular sieve for 24 hours.	0.38	
	3) ED left standing with molecular sieve for 12 days.	0.33	
	4) ED refluxed over molecular sieve for $2\frac{1}{4}$ hours under N_2.	0.33	
	5) ED was distilled over molecular sieve. Fresh molecular sieve was then added to the middle fraction which was left standing overnight (20 hours).	0.30	11.25
	6) ED was distilled by itself. Molecular sieve was added to the middle fraction and left standing overnight (20 hours)	0.31	13-15.5 after 4 days
	7) ED was distilled over molecular sieve. Fresh molecular sieve was added to the middle fraction, which was distilled again.	0.56	2.77

Drying agent	ED treatment	Water content/ % (w/w)	$Kx10^6$/ $\Omega^{-1}.cm^{-1}$
Sodium (Hopkin & Williams)	ED was distilled over sodium : 1) sodium pellets used directly from the bottle,	0.98	7.00
	2) sodium pellets were cut into thin pieces.	1	3.05
CaH_2 not fresh (B.D.H.)	ED was distilled over CaH_2.	0.87	4.35
Fresh CaH_2 (B.D.H.)	1) ED was refluxed over CaH_2 for 2½ hours and then distilled over the solid.	0.57	2.32
	2) a) ED was refluxed over CaH_2 for 12 hours and then distilled over it.	0.54	1.50
	b) CaH_2 was added to the middle fraction, which was distilled over the solid.	0.35	0.88
	c) Sodium cut into thin pieces was added to the middle fraction, which was fractionated through a column filled with Lessing rings. After fractionating it was distilled over sodium.		1.65

Drying agent	ED treatment	Water content/ % (w/w)	Kx10^6/ Ω^{-1}.cm^{-1}
	2) d) Sodium cut into thin pieces was added to the middle fraction which was fractionated through a column filled with glass balls. It was then distilled from the sodium.		1.16
Fresh CaH_2 (B.D.H.)	3) ED was refluxed over CaH_2 and distilled from the solid. The middle fraction was collected into a flask containing fresh CaH_2 and left standing overnight. It was then distilled at low pressure (4 cmHg) from the solid.		1.79
$CaSO_4$ (B.D.H.)	ED was distilled over $CaSO_4$ which had been dried in Notley's column.	1	4.35
H_2SO_4 (Hopkin & Williams)	ED was distilled after addition of 1% (w/w) conc. H_2SO_4 (98%).	0.81	5.22

Table 4-3-1 also shows values for the conductivity which seemed unlikely, because with different drying agents the results after purification are very similar as well as not being much lower than for the starting material. It was thought that these high conductivity results might be due to the alkaline products resulting from the reaction of ED with the drying agents. If this was really true, an acid such as sulphuric would destroy the alkaline product formed. It was therefore decided to add about 1% (w/w) concentrated sulphuric acid at a purity of 98% to the ED and then distil , but only a slight improvement was obtained (Table 4-3-1).

As mentioned in chapter III, ED absorbs moisture and carbon dioxide faster than it evaporates and leaves a residue of ethylenediamine carbamate, which is a white solid subliming at 170° C. Thus, a possible reason for the high conductance was slight contamination by air present in the receiving flask. The distillation was therefore repeated with special precautions. About 300 cm^3 of drum ED was then refluxed for 2-3 hours over about 12 g CaH_2 and then distilled under dry nitrogen. Before running ED into the distillation flask, the apparatus was evacuated three times and filled in turn with dry nitrogen. The middle fraction of purified ED was collected directly in the conductivity cell. The conductivity was measured and found to be about $3.2\times10^{-7}\Omega^{-1}.cm^{-1}$. A sample of B.D.H. ED purified similarly gave $3.5\times10^{-7}\Omega^{-1}.cm^{-1}$. We concluded that before starting the distillation, all the air had to be removed from the system. By flushing the apparatus with dry nitrogen, without evacuating it first, the air contained in the receiver flask (fig. 4-2-1) is not removed and sufficient carbon dioxide is absorbed to increase the conductivity of the distilled ED.

A bigger volume of ED from the drum (3500 cm^3) was further refluxed over about 50 g CaH_2 for 2-3 hours, left standing over CaH_2 for 20 hours and distilled after evacuating the system three times and filling it in turn with dry nitrogen. The reflux and distillation were carried out under dry nitrogen and the middle fraction was collected in flask B (fig. 4-2-1). The conductivity cell was filled with this purified ED by pressure with dry nitrogen and its conductivity found to be $2.4 \times 10^{-7} \Omega^{-1}.cm^{-1}$. This ED was distilled a second time over fresh CaH_2, the middle fraction collected and its conductivity found to be $2.1 \times 10^{-7} \Omega^{-1}.cm^{-1}$, which is only slightly less than the value obtained from the first distillation. There does not seem to be any significant advantage in distilling ED twice. In the present work reflux and one distillation as just described was the purification method adopted for ED.

The possibility of freezing ED as a means of removing conductivity impurities was also considered. According to Elgort (66), the system ED-H_2O shows two eutectics (m.p. -53.0° C at 16.8 mol% ; m.p. -0.8° C at 81.0 mol% ED), a transition point (m.p. -10.0° C, corresponding to a dihydrate), and a maximum (m.p. +10.0° C, corresponding to a monohydrate). It therefore seemed feasible to freeze ED a little below than 0° C and to melt the frozen ED formed. About 250 cm^3 of ED were left overnight in a water-ice bath and although after this time the solution was supercooled,

Table 4-3-2

ED treatment	Water content/ % (w/w)*	Conductivity x 10^6/ $\Omega^{-1}.cm^{-1}$
ED was frozen by adding a crystal, the liquid removed and the solid ED left to melt	0.72	4.76
ED was frozen by scratching with a glass rod, the liquid removed and the solid ED left to melt	0.59	3.84

* These results were obtained before discovering the water contribution of acetic acid in the K.F. titrations.

no solid was obtained. A crystal of solid ED was then added to the solution to act as nucleus of solidification and crystallisation occurred almost immediately. About 31% (w/w) of liquid ED was removed by pressure with dry nitrogen and the frozen ED was left to melt at room temperature. A sample of melted ED was analysed again, but the conductivity was only slightly lower (see Table 4-3-2). Some dihydrate could have been formed at the low temperature reached in this experiment and so have contaminated the ED. In the next experiment, the flask containing cooled ED was scratched with a glass rod to start the crystallisation. About 44% (w/w) liquid ED was removed and the frozen ED was melted. Even this time, only a slight improvement in conductance was obtained (Table 4-3-2). The relatively high conductivity was probably caused by contamination from the atmosphere and could only be reduced by employing a dry box throughout which would make the whole procedure experimentally cumbersome. For this reason, and because freezing produces only relatively small amounts of solvent, the distillation method of purification was preferred.

The density of a sample of ED purified by this way was measured at 25° C and found to be 0.8923. The pycnometer used is shown in fig. 4-3-1 and its volume was determined, using conductivity water and applying the following equation(67)

$$V_{\text{pycn.}} = \frac{W_{H_2O}}{d_4^{25}(H_2O)}$$

The true weight of water in the pycnometer was determined from equation (4-3-1) (67)

$$W = W' + V_{pycn.}D_{air} - V_{weights}D_{air} \qquad (4\text{-}3\text{-}1)$$

where:

W = true weight

W' = apparent weight

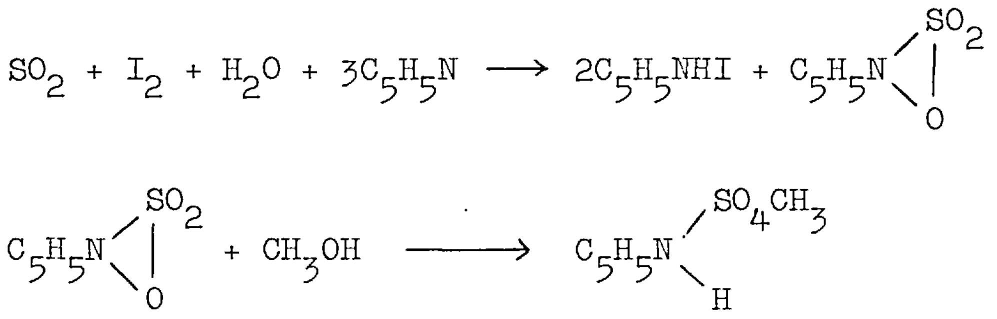
$$V_{weights} = \frac{W'}{D_{weights}} = \frac{W'}{8.5}$$

The volume of the pycnometer was found to be 24.7512 ml. The density of ED was determined, using equation (4-3-1) and the similar relation:

$$d_4^{25}(ED) = \frac{W_{ED}}{V_{pycn.}}$$

4.4 Measurement of water content

The most common chemical technique available for analysing for water is the Karl Fischer method. The non-modified K.F. reagent is a solution of iodine, sulphur dioxide and pyridine in methanol. The reactions are (68):



(4-4-1)

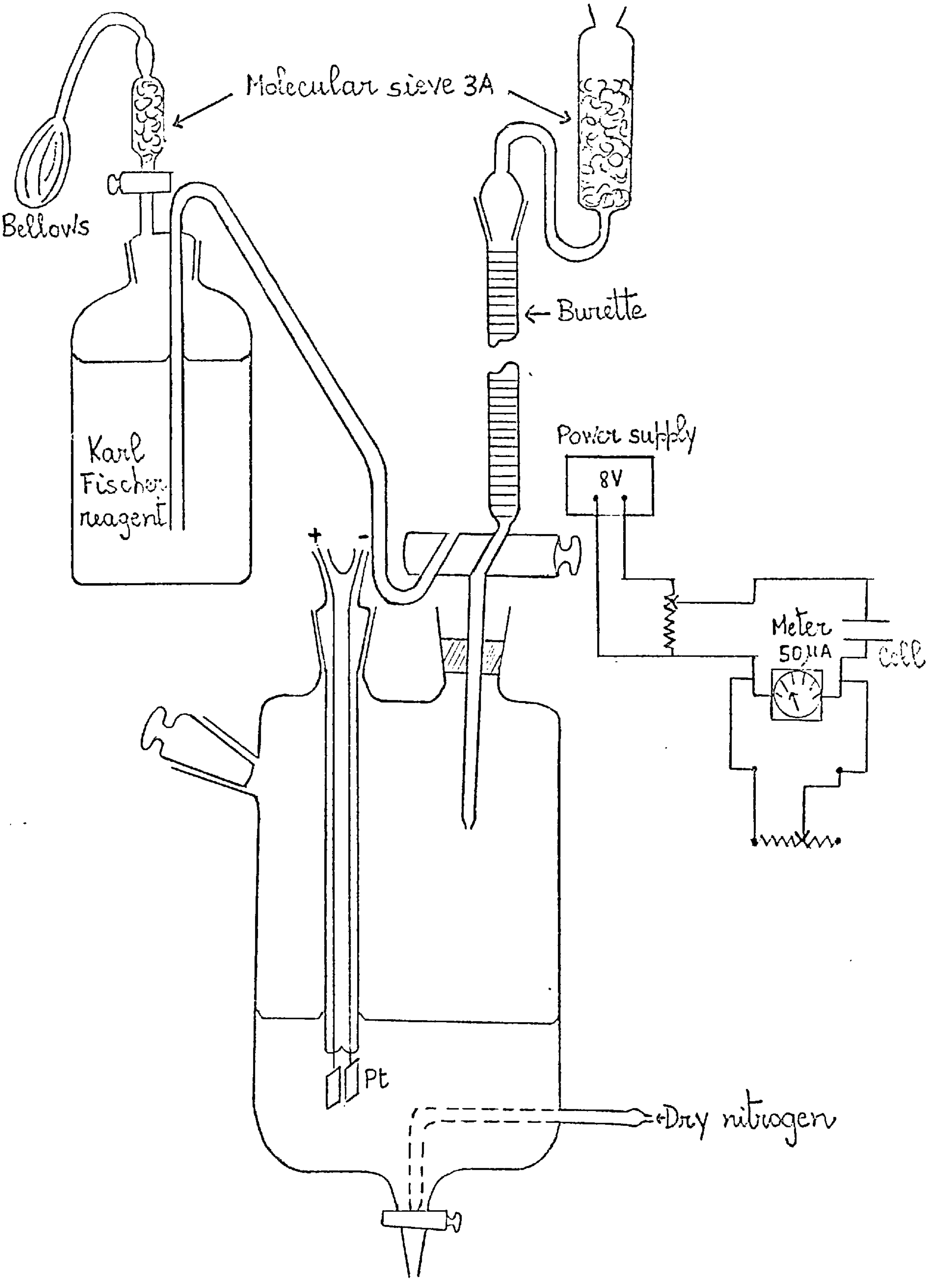
Each molecule of iodine is equivalent to one molecule of water. The end point is detected either visually, the iodine colour remaining once all the water has reacted, or electrometrically as described below.

The Karl Fischer reagent is not stable, and has to be standardised from time to time against a standard solution of water in methanol. The stability is higher in an "improved" Karl Fischer reagent in which the methanol is replaced by 2-methoxyethanol, but even this reagent requires regular standardisation (69). The Karl Fischer reagents and the standard water in methanol solution used in the present research were all supplied by B.D.H..

The apparatus and circuit to carry out the titrations are shown in fig. 4-4-1. To stir the solution and to keep moisture out, very dry nitrogen was bubbled through the titration cell. The very dry nitrogen was prepared from liquid nitrogen by the method described by Robertson (65) (see fig. 4-4-2). Liquid nitrogen was heated at a controlled rate via a 5Ω, 15 watt wire-wound resistor, whose ends were connected to a power supply. The evaporated gas was passed through a glass spiral to reach thermal equilibrium with the atmosphere. Before each analysis, dry nitrogen was allowed to pass through the apparatus for about 15 minutes.

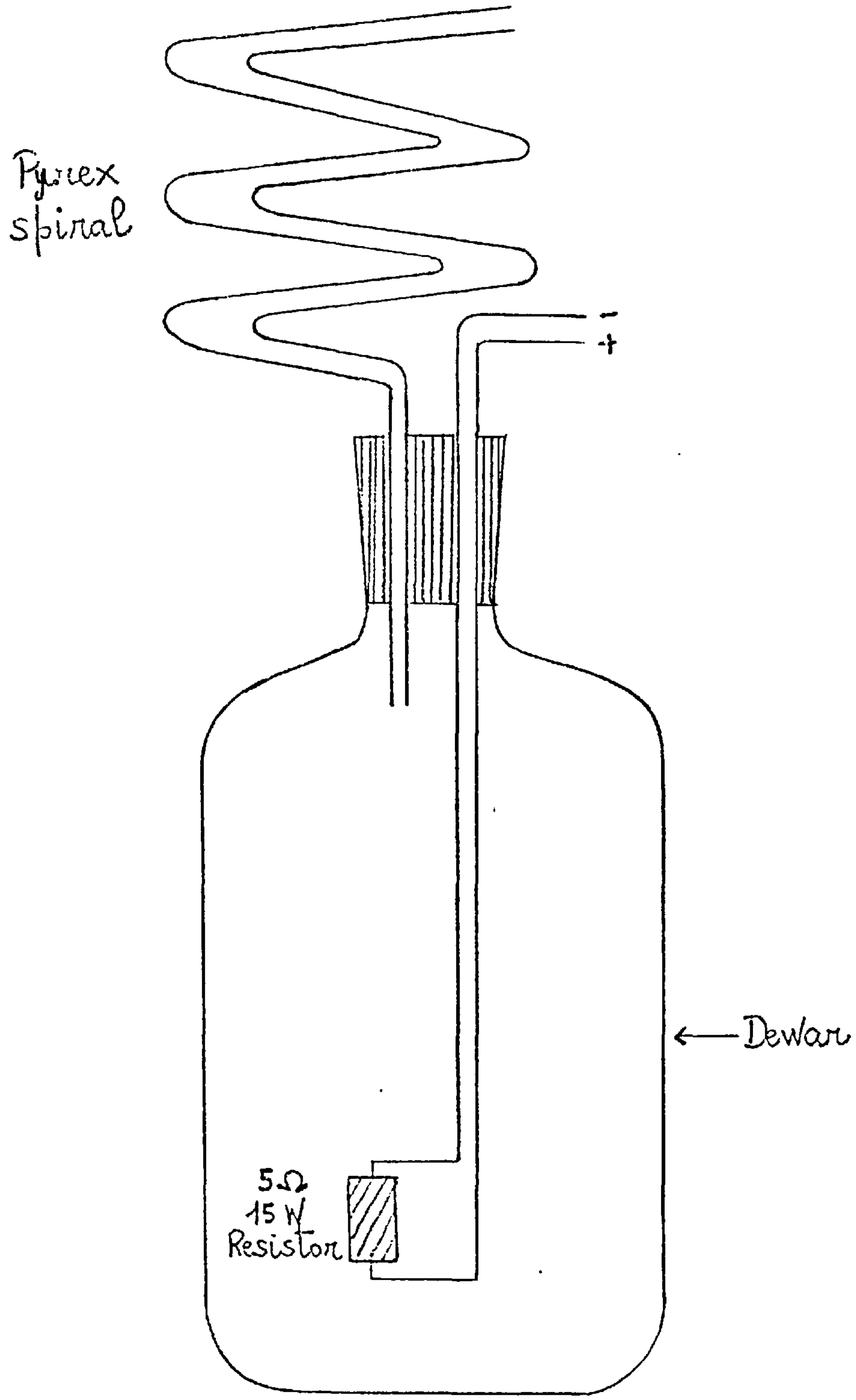
The titrations were followed electrochemically using two platinum foil electrodes 5 mm apart and 0.5 cm^2 in area (fig. 4-4-1) polarised by a power supply. At the beginning of a titration, all the iodine of the reagent reacts with the water present to give iodide. As soon as all the water has reacted, a slight excess of iodine added to the solution can be reduced at the platinum cathode:

Fig. 4-4-1



Karl Fischer apparatus

Fig. 4-4-2



Dry nitrogen apparatus

$$I_2 + 2e^- \longrightarrow 2I^-$$

while at the anode the I^- ions can be oxidised:

$$2I^- \longrightarrow I_2 + 2e^-$$

Consequently a current flows and the needle of the meter deflects. This is the dead-stop electrochemical end point. Once the end point was reached, the colour of the solution also changed from yellow to reddish brown, due to the excess of iodine staying in the solution.

Ethylenediamine, like most amines, reacts with the constituents of Karl Fischer reagent and glacial acetic acid in excess has been suggested (70) as a suitable solvent for amines. The method consists of standardisation of the Karl Fischer reagent, titration of the acetic acid and then titration of the acetic acid plus ethylenediamine. The initial experiments were carried out with B.D.H. ethylenediamine of 99% purity and non-modified Karl Fischer reagent. One cm^3 of the latter was approximately equivalent to 5 mg water. Titration of 50 cm^3 acetic acid (AnalaR, 99.7%) by itself appeared to require a zero titre with the Karl Fischer (K.F.) reagent, although there was not much sensitivity in detecting the end point. With about 1.6 V applied between the two platinum electrodes, using a shunt of 100Ω, one drop of K.F. was enough to produce a current of about 2 μA. Although small, the current remained quite stable. On addition of more acetic acid, the current kept quite constant as before this addition. However with the addition of more K.F. reagent, the current increased all the time, although very slowly. The addition of 3 drops of K.F. produced an increase of current of about 2 μA. This behaviour was confirmed on an independent K.F. set up by Clausius Lima (71). When a smaller voltage (120 mV) was applied, again with a 100 Ω shunt between the two electrodes, there was appreciable current only after adding about 0.3 cm^3 of K.F. reagent.

To increase the sensitivity of this titration, it was decided to add about 0.5 g of dried KNO_3 AnalaR, but there was no improvement except that a higher current was obtained before the addition of the Karl Fischer reagent. After its addition, the increase of current was the same as before without any salt.

In the titration of ED, 50 cm^3 of glacial acetic acid and 2 cm^3 of ED were pipetted into the titration cell. The ED was pipetted as fast as possible, to prevent or at least to reduce the moisture absorbed during the operation. The titrations were repeated until three successive titres agreed within 0.1 cm^3. Assuming no contribution from the acetic acid, 1 cm^3 of ED was found to contain 5.47 mg H_2O, which corresponds to about 0.61% (w/w) of water. To test the end point of this titration, one drop of distilled water was added by syringe to the solution of ED in acetic acid before any K.F. reagent had been added. The titre required was now greater than the previous one by the amount corresponding to the water introduced. These experiments were repeated with ED from the same source, but using the improved Karl Fischer reagent. One cm^3 of this was also approximately equivalent to 5 mg water. Similar results were obtained.

Subsequent experiments were all performed with improved K.F. and with ED from Jefferson Chemicals U.K., chosen because its conductivity was the lowest of the three sources investigated. The water content of this ED, contained in a drum, was determined as before and found to be 0.57% (w/w) water, assuming no contribution from the acetic acid. The ethylenediamine supplied was then refluxed and distilled over a variety of drying agents, some of which had been found efficacious in the literature. Surprisingly, however, very little reduction in water content was observed and in some cases even an increase, as shown in Table 4-3-1 of the previous section. As these results seemed unlikely, suspicion focussed on the method of water analysis.

One possibility was that some water had been produced by reaction of ED with acetic acid:

$$CH_3COOH + NH_2CH_2CH_2NH_2 \longrightarrow CH_3CONHCH_2CH_2NH_2 + H_2O \qquad (4\text{-}4\text{-}2)$$

Experiments were carried out using less acetic acid for the same volume of ethylenediamine. When 10 cm^3 of acetic acid plus 2 cm^3 of ED were tried, a white solid was immediately formed and the reaction became very exothermic. An attempt was made to titrate ethylenediamine directly with K.F. reagent, but although sufficient reagent was added to react with as much as 1.3% water, no current was indicated on the meter. With the addition of the K.F. reagent, a dense vapour appeared above the liquid in the titration cell and no colour change was ever observed. Mitchell and Smith in their book "Aquametry" (72a) said "Amines stronger than benzylamine (K = 2.4×10^{-5}) were preferably treated before titration with an excess of glacial acetic acid or spent Fischer reagent, ... In the absence of either of these acidic reagents, slightly high results were common with strong amines, containing small quantities of water". In an attempted titration of ED using cold methanol as solvent instead of acetic acid, although enough K.F. reagent was added to react with as much as 3.3% water, no current was indicated on the meter. During the addition of K.F., a vapour above the solution was observed. Mitchell and Smith in the same book (72a), in discussing strong amines containing small quantities of water, said "Where methanol was used as a diluent in these cases, the amine reacted vigorously with the acidic components of the reagent resulting in a dense vapour above the liquid in the flask, which tended to obscure the end point".

Theory suggested that protonated ethylenediamine, $\overset{+}{N}H_3CH_2CH_2NH_2$ or $\overset{+}{N}H_3CH_2CH_2\overset{+}{N}H_3$, would be less likely to react with acetic acid to produce water. Such protonation could be achieved by adding a stronger acid such as sulphuric. An experiment was tried with this in mind. First, to 50 cm^3 of glacial acetic acid were added 2 cm^3 of 98% AnalaR sulphuric acid, and an attempt made to titrate the water by Karl Fischer solution. Initially there was no current, but as K.F. reagent was added the pointer of the meter moved quite slowly. It was very difficult to say when the end point was reached, because a stable current was never obtained. Some charring was observed and the solution became very dark as K.F. was added. Charring has previously been observed (73) when concentrated sulphuric acid is titrated with K.F. reagent, and Mitchell, Smith and Bryant (73) therefore recommended using a dioxan solution of sulphuric acid. When ethylenediamine was added to the acetic acid-sulphuric acid mixture, a strong yellow precipitate was produced and stirring became very difficult. As K.F. reagent was added, it mixed only partially with the precipitate created.

It seemed that, even with protonated ED, methanol might still be required as a diluent. Methanol with phosphoric acid added was tried next as a solvent for ethylenediamine. Karl Fischer titration of 50 cm^3 methanol containing about 8 g of phosphoric acid gave a good end point with 4.07 cm^3 of reagent, but the addition of the ethylenediamine to this solution produced a white flocculant that stayed in suspension. Only a little of ED dissolved and so the titration could not be carried out. When 50 cm^3 methanol containing about 9 g picric acid was tried as a solvent, its titration with K.F. reagent immediately produced a precipitate which increased in extent with the addition of more reagent. The flow of dry nitrogen through the reaction vessel was obstructed and so the titration had to be stopped.

Experiments were now resumed with acetic acid. To check whether its titration with K.F. reagent had given a genuine result, a drop of distilled water was first added by syringe to 50 cm^3 acetic acid. As soon as K.F. reagent was added, the current was found to increase. A permanent current of about 14 μA and a reddish brown solution were obtained long before adding the expected volume of K.F. reagent corresponding to the amount of water introduced. Only about 1/4 of the necessary amount of reagent had been added at this stage. This seemed strange ; even stranger was the fact that addition of several more drops of water increased the current still further ! We conclude from these experiments that water and K.F. solution do not react properly in acetic acid as medium. Clearly the earlier blank titrations of acetic acid, prior to adding ED, could not be relied upon.

According to Mitchell and Smith, in their book "Aquametry" (72b), acetic acid can be titrated directly with Karl Fischer reagent. Although the acetic acid reacts slowly with the methanol of the K.F. reagent, this interference is usually limited, provided that the titration is not prolonged. In the same book (72b) they say "By direct titration is meant addition of the Fischer reagent to the sample in the presence of an inert solvent such as methanol". Further, in discussing some organic acids (72c), they state "Some acids, because of the ease with which they esterify, tended to give slightly high results when methanol was used as a diluent". According to the experiments carried out by the writer, no methanol should be present in the titration of acetic acid, because water is produced by esterification. An attempt was made to titrate 25 cm^3 of methanol with the K.F. reagent and, after reaching the end point, to add 50 cm^3 of glacial acetic acid to the titrated solution. It was observed that when the titration of the 50 cm^3 acetic acid was carried out slowly, 1-2 drops of K.F. being added some seconds apart, the current always dropped, although slowly. It was impossible to decide when a proper end point had been obtained. Levy, Murtaugh and Rosenblat (74) report the results obtained in a series of 10 determinations on glacial acetic acid samples, using a microtitration method. However, they do not say anything about using a solvent to carry out the titration.

To summarise briefly : acetic acid could not be titrated by itself with K.F. reagent (no definite end point), nor could acetic acid in methanol (esterification). Ethylenediamine could not be titrated by itself nor in methanol as solvent (no end point was reached in either case). A definite end point was attained with ED in a large excess of acetic acid, but the answer seemed too high. We therefore returned to the possibility that this was due to amide and water formation. The extent of amide formation has been measured (75) in aqueous solutions, containing various carboxylic acids and amines. The equilibrium constants for amide formation at 44.4°C between acetic acid and methylamine, and between acetic acid and isopropylamine, are 22×10^{-4} and 1.5×10^{-5}, respectively (75). The latter result is subject to a relatively large error, because the amide formation was slow (75). No equilibrium data seem to be available for ethylenediamine and acetic acid as solvent. However, dissolution of ED in glacial acetic acid is an exothermic process.

To check if a possible reaction between the acid and the amine to form water would tend to an equilibrium, it was decided to try another experiment. The usual 2 cm^3 of ethylenediamine and 50 cm^3 of acetic acid were mixed and left for about 2 1/4 hours before being titrated with K.F. reagent. The difference between the water content found in this case (about 0.80%) and that when the titration was carried out immediately after the addition of the amine (0.76%) was not significant. This suggests if there is any reaction to produce water, this reaction is fast, and equilibrium is reached. When a solution of the amine in acetic acid was titrated with K.F. reagent just up to the end point, and then left for about 1 hour, a further appreciable volume of K.F. reagent was needed to reach the end point again. The extra amount of reagent added corresponded to an increase of about 0.19% water. This could be explained by reaction of acetic acid with the alcohol of the K.F. reagent added to form the corresponding ester and water.

Until now, in the K.F. titrations, the proportion of acetic acid to ED had been 50 cm^3 of the acid to 2 cm^3 of the amine. An earlier experiment had shown that a 10:2 ratio did not work. It was therefore decided to try the same volume of acetic acid, but to add a different and smaller volume of purified ethylenediamine (refluxed and distilled over CaH_2, using nitrogen). The results, using a fresh 50 cm^3 acetic acid for each titration, were as follows (experiment A):

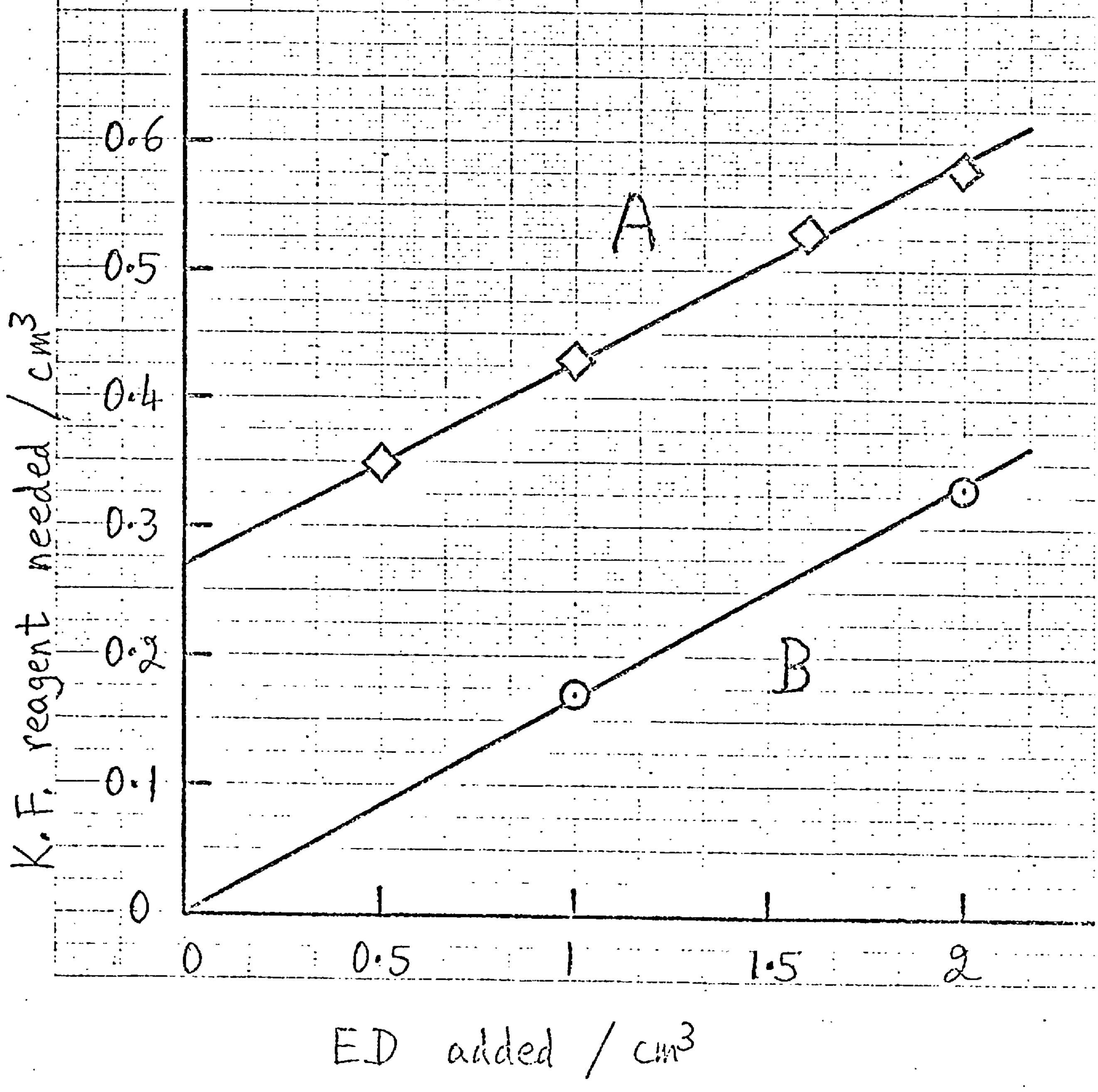
ED added/cm^3	0.5	1.0	1.6	2.0
K.F. needed/cm^3	0.35	0.43	0.53	0.58

A plot of the volumes of K.F. reagent used, against the corresponding volumes of ED, gave a straight line with a large intercept (fig. 4-4-3, line A). In another experiment (B), a titrated solution of 50 cm^3 of acetic acid and 2 cm^3 of the amine was used as solvent, and further aliquots of 1 and 2 cm^3 of ED were added to the same vessel and titrated in turn. The necessary volumes of K.F. reagent plotted against the volumes of ED added gave a straight line with the same slope as before, but this time passing through the origin (fig. 4-4-3, line B).

These results cannot be explained by the previous assumptions that the acetic acid is anhydrous, and that it reacts with ED to produce water and amide (reaction 4-4-2). For it has already been demonstrated that if such a reaction occurs it must be fast. Line A should thus have been a curve of decreasing slope passing through the origin. Line B should have been a curve also, but not parallel to curve A, because their effective starting points differ and because curve A always involves fresh samples of acetic acid. However, the results are easily explained if the acetic acid contained some water equal in amount to the intercept of line A. The fact that plots A and B are both straight lines parallel to each other suggests the absence of chemical water formation by equation (4-4-2); instead, the lines represent the straightforward titration of the water content of the ED used. The slopes of the lines give a water analysis of 0.08% (w/w) in the ED distilled over CaH_2.

When titrations of type A were carried out with an older bottle of AnalaR acetic acid, which had been opened

Fig. 4-4-3


A
B
K. F. reagent needed / cm^3
0
0·1
0·2
0·3
0·4
0·5
0·6
0
0·5
1
1·5
2
ED added / cm^3

for other experiments, a straight line was again obtained but with a much bigger intercept. This fits in with the fact that acetic acid is a hygroscopic chemical. This same bottle of acetic acid had been used earlier to analyse the water content of the drum ED and we can now understand the reason for some of the apparently high water contents obtained in Table 4-3-1.

Titrations of type A were then carried out with ED from the drum, but using rather bigger volumes of ED in the usual 50 cm^3 of acetic acid. The results were as follows:

ED added/cm^3	2	3	4	5	6
K.F. needed/cm^3	2.82	3.94	4.97	5.92	10.25

Plotting the volumes of K.F. reagent used against the corresponding volumes of ED, again yielded a straight line with a large intercept (fig. 4-4-4). The slope gave a water content of 0.54% (w/w) for the drum ED. However the 6 cm^3 ED point lies far above the line, and with 10 cm^3 of ED no end point was obtained even after adding ca. 20 cm^3 of reagent. With the addition of these large volumes of ED, the process became very exothermic and it seems likely that, at the high temperatures developed, water was beginning to be formed by reaction of ED with the acetic acid (equation 4-4-2).

The method of titrating a series of samples of ED in acetic acid thus provides a good method of obtaining the water contents both of ED and of acetic acid. It would nevertheless be useful to find an inert solvent in which

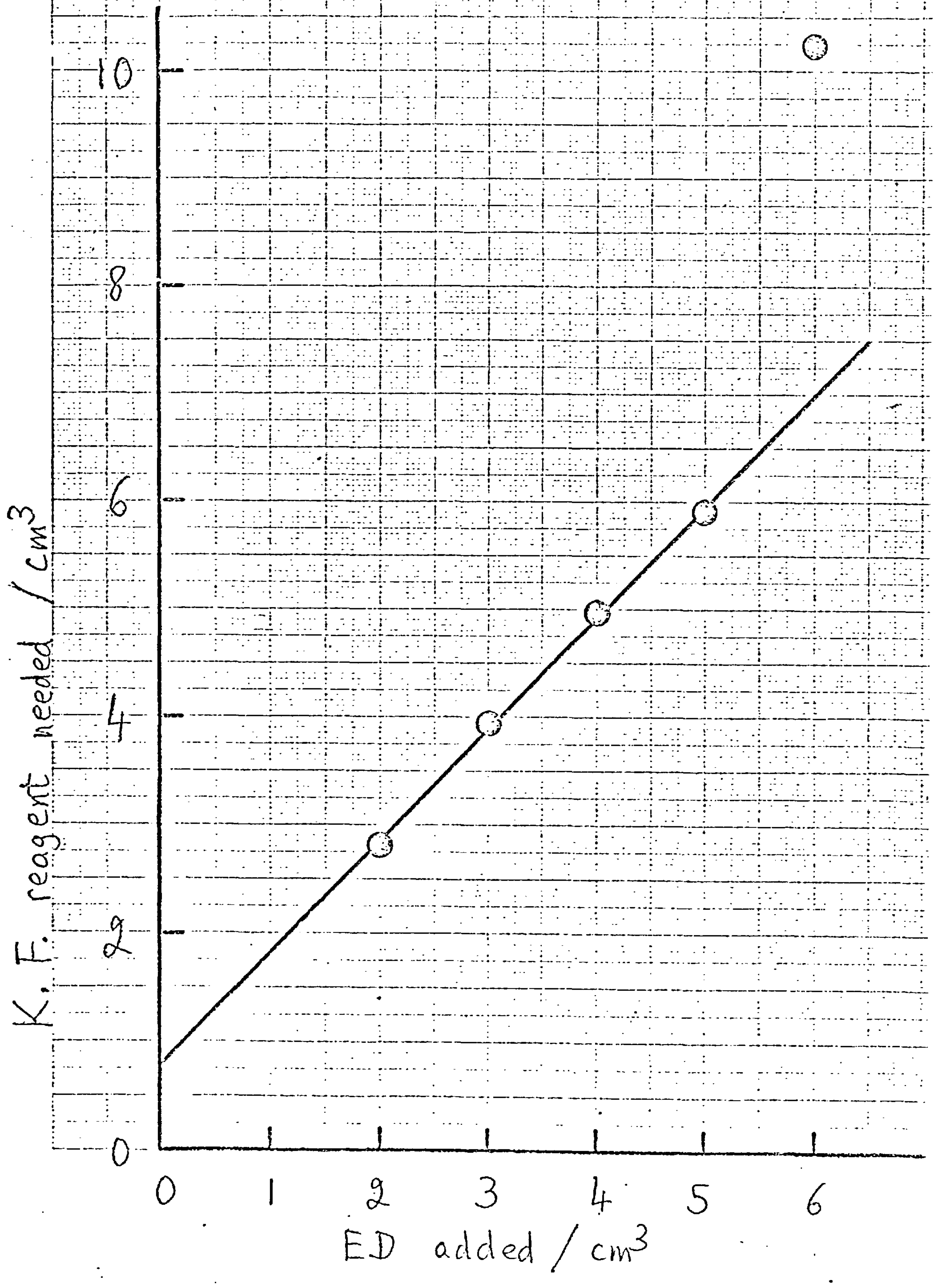


Fig. 4-4-4

acetic acid could be titrated directly. Methanol was ruled out because of esterification ; furan is ruled out as well, because when titrated with K.F. it gives a precipitate and for its titration methanol is required as solvent (71).

A possible solvent for acetic acid was suggested by Almy, Griffin and Wilcox (76). In discussing the preparation of a sample, they recommended the pyridine-methanol mixture of the K.F. reagent itself as a good solvent for most organic liquids. A diluent composed of equal parts of dry methanol and pyridine is also mentioned in Mitchell and Smith's "Aquametry" (72c) in their description of analysing the water content of adipic acid. They state that the pyridine inhibited the esterification of the acid in methanol. An experiment was therefore carried out to test whether water in acetic acid could be analysed for similarly. Equal volumes of AnalaR B.D.H. methanol and pyridine (10 cm^3 of each) were taken and the mixture titrated with K.F. reagent. After reaching the end point, 50 cm^3 of acetic acid were added to the titrated solution. Two fresh titrations of 50 cm^3 acetic acid and one of 10 cm^3 as well were performed and the titres obtained were very consistent (1.31, 1.31, and 5x0.27 cm^3 of K.F. reagent, respectively). To check, 50 cm^3 of acetic acid from the same bottle were titrated by the ED technique A, and gave an intercept of 1.29 cm^3 which agrees within experimental error. We conclude that both methods give the same result for the water content of acetic acid. However, the ED technique gives not only the water analysis for acetic acid, but also, from the slope, that for ED.

As was already shown, methanol is not a suitable solvent for acetic acid, because water is produced by esterification. To check to what extent the presence of pyridine could inhibit the esterification reaction, it was decided to titrate 20 cm^3 of methanol by itself, and to add 50 cm^3 of acetic acid to the titrated solution. The titration of acetic acid was carried out very fast. Even then, 0.35 cm^3 more K.F. reagent was needed than in titrating the same 50 cm^3 of acid in a 10 cm^3 pyridine + 10 cm^3 methanol mixture as solvent. As described earlier, a much larger excess of K.F. reagent was needed if the titration was carried out slowly, and then no definite end point appeared.

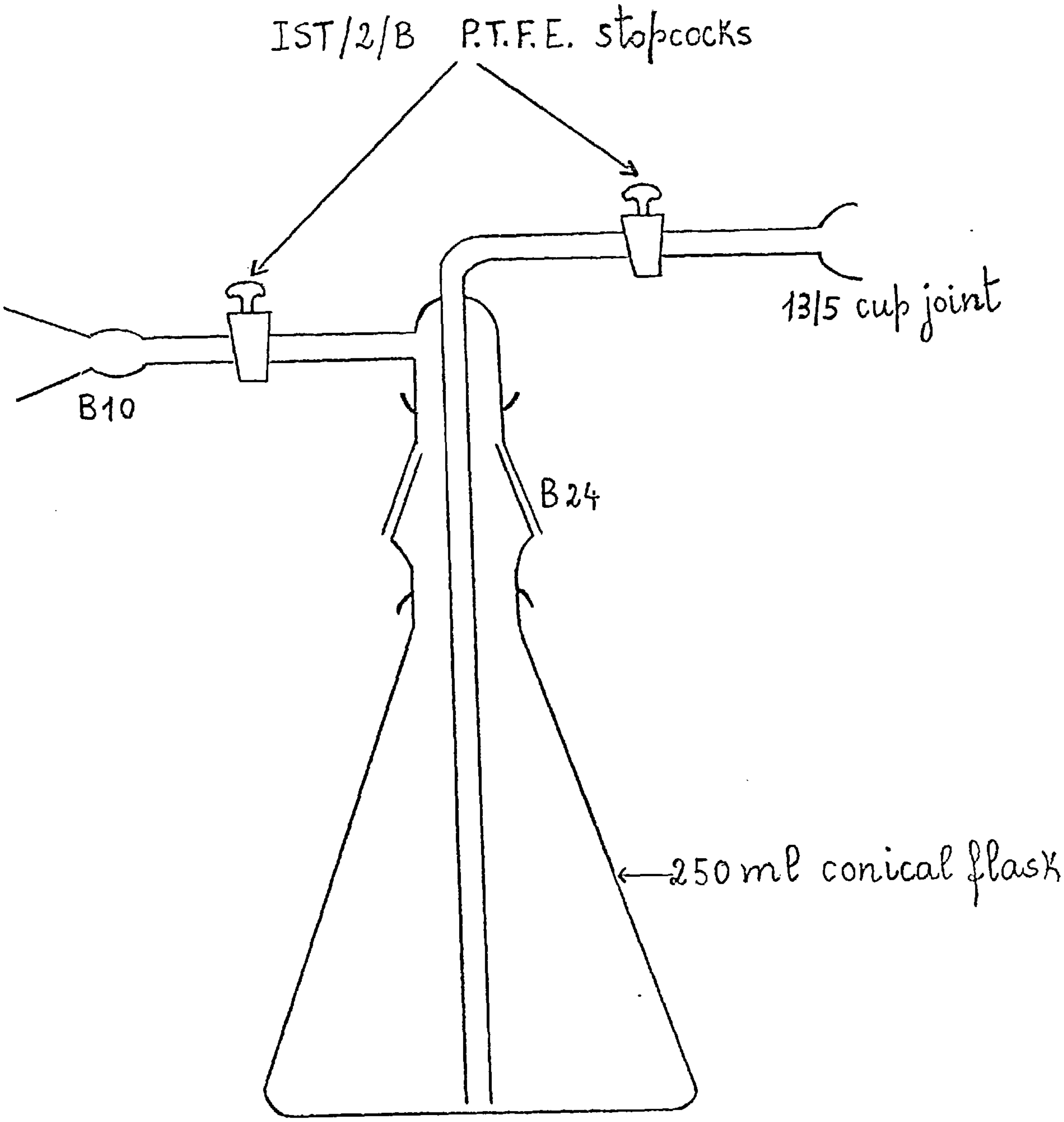
4.5 Preparation of ethylenediamine solutions

The source of the electrolytes was as follows:

Potassium iodide - AnalaR from Hopkin & Williams
Silver iodide - AnalaR from Hopkin & Williams
Silver nitrate - AnalaR from B.D.H.
Sodium nitrate - AnalaR from B.D.H.
Sodium iodide - G.P.R. from Hopkin & Williams

In the preliminary runs, the salts were used without any further purification. To prepare the solutions, specially adapted conical flasks as shown in fig. 4-5-1 were used. The flasks were cleaned with chromic-sulphuric acid solution, well rinsed with distilled water and conductivity water and dried overnight in an oven. A P.T.F.E. sleeve was fitted to

Fig. 4-5-1


IST/2/B P.T.F.E. stopcocks
13/5 cup joint
B10
B24
250 ml conical flask

the B24 cone and two springs attached to hooks on the lid and on the flask ensured an air-tight seal. The flask with its accessories was weighed empty. The solute was weighed in a weighing bottle, transferred to the flask, and the weighing bottle plus residue were reweighed. The solution flask was then attached to the flask containing purified ED and to the nitrogen line as shown in fig. 4-5-2. The procedure for transfering ED was as follows. All the taps are initially closed.

1) Taps T_4 and T_5 were opened, and T_3 was opened to the vacuum pump in order to remove all the air up to tap T_6.

2) T_3 was opened to the dry nitrogen by opening T_1, so that the volume between T_3 and T_6 was filled with dry nitrogen.

3) T_1 was closed and T_7 was opened to dry nitrogen. Taps T_6, T_5, T_4, T_3 and T_2 were opened (in that order) and ED was transferred from the storage flask to the conical flask.

4) Taps T_2, T_3, T_4, T_5, T_6 and T_7 were closed (in that order).

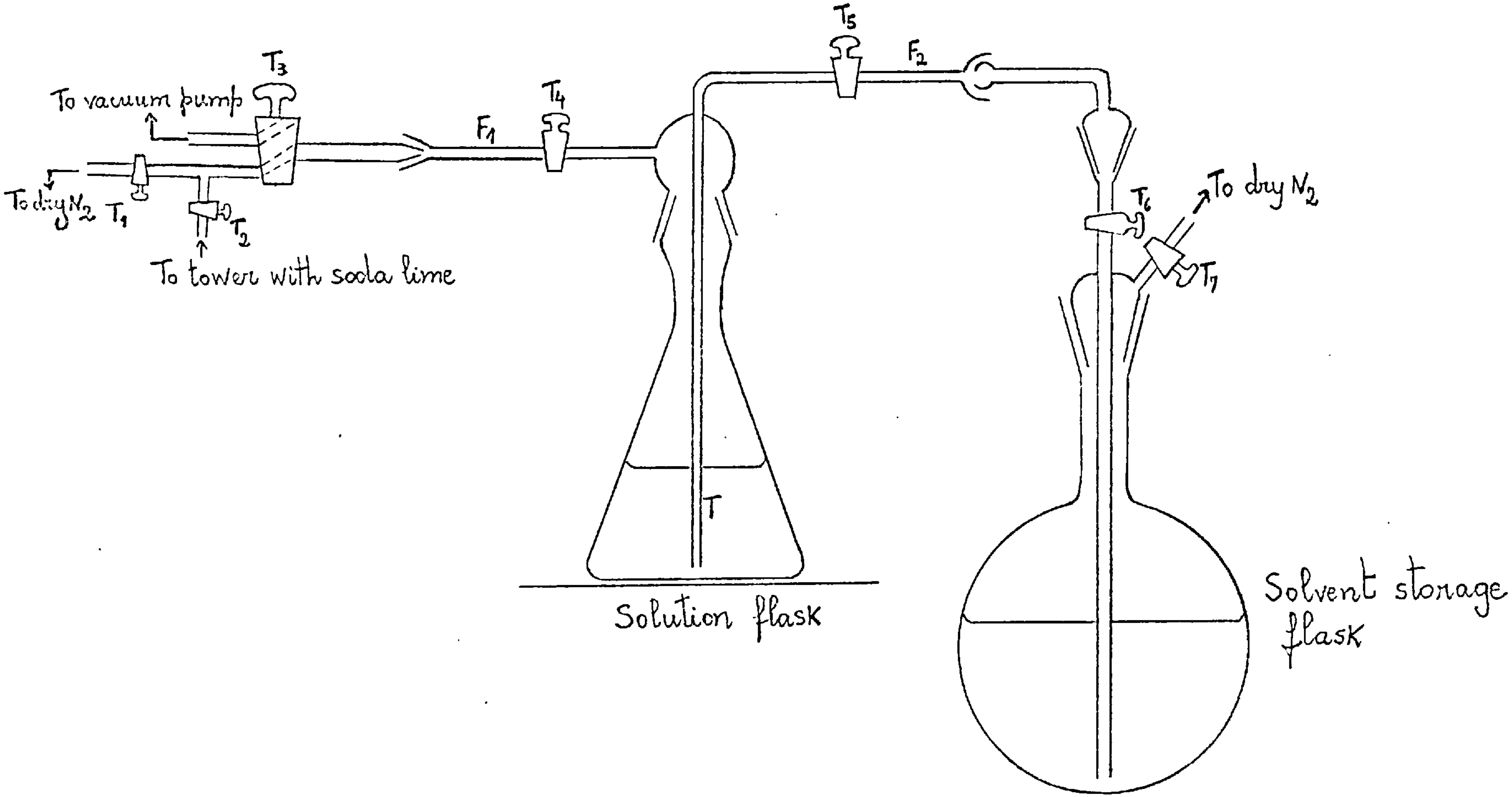
5) Tap T_3 was connected to the vacuum pump and T_4 was opened to allow the mixing of the liquid in tube T with the ED in the flask.

6) Tap T_3 was connected to the dry nitrogen after opening T_1, so that nitrogen was admitted to the flask and then T_3 and T_4 were closed.

7) The solution flask with content and accessories was disconnected from the storage flask and then shaken to dissolve the solid. The filling tubes, F_1 and F_2, were rinsed with AnalaR alcohol and dried with dry nitrogen.

8) The flask with solution and accessories was reweighed so

Fig. 4-5-2



Preparation of solutions

that the mass of the solvent and then the molality of the solution could be found.

The above method for preparing the solutions prevents their contamination with the air and carbon dioxide in the laboratory atmosphere.

The molarity was obtained by interpolating the density data of Putnam and Kobe (32), Fedot'ev and Kinkul'skaya (53) and Schmidt et al. (39). For AgI solutions no density data in ED were available and for their preparation, interpolated values for $AgNO_3$ solutions were used instead.

CHAPTER V

5. EXPLORATORY TRANSFERENCE WORK IN ETHYLENEDIAMINE

5.1 The moving boundary cells

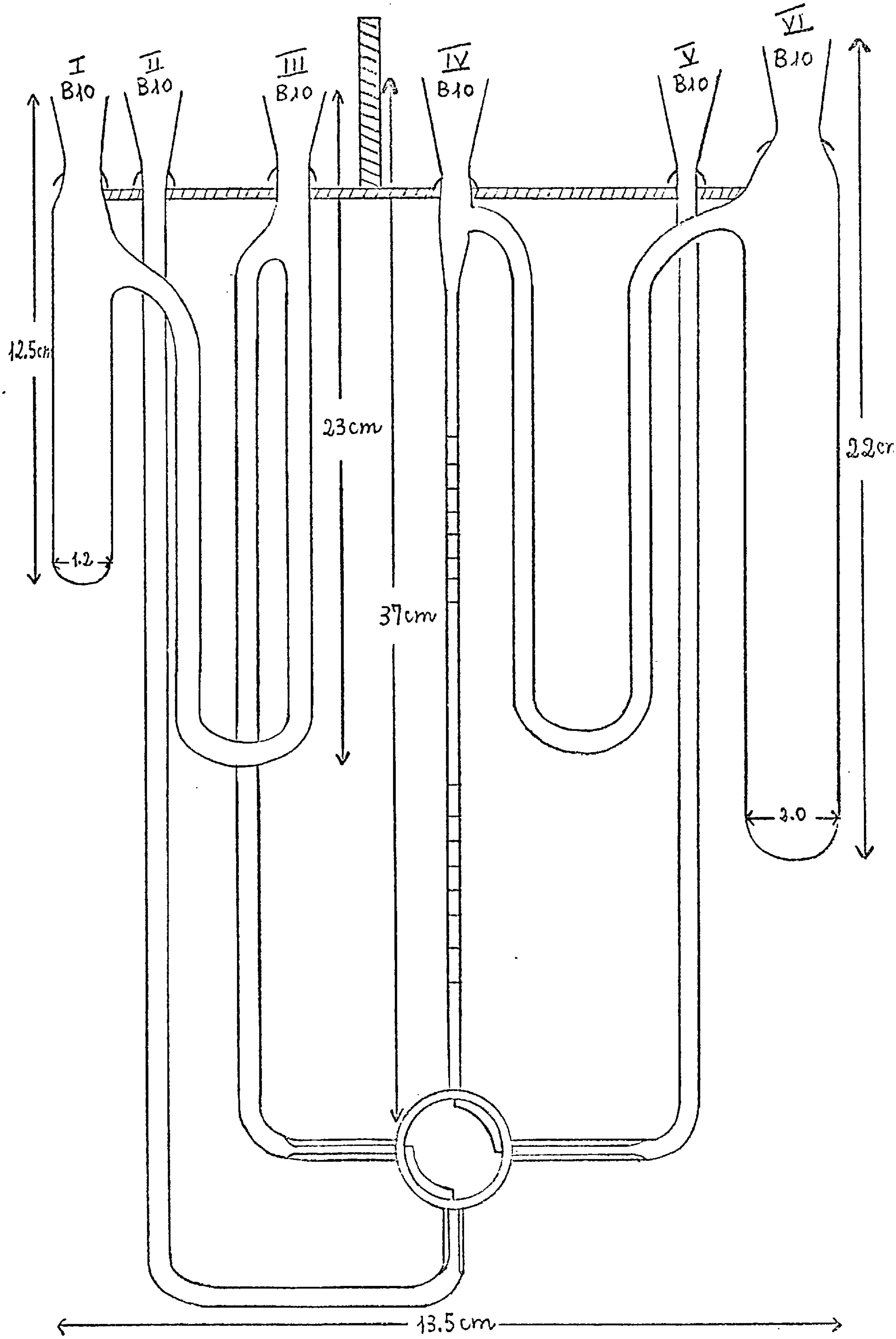
As described later, both rising and falling boundaries were observed and so two cells of different design had to be employed.

5.1.1 The rising boundary cell and its calibration

The cell was of the sheared boundary type, made entirely of Pyrex glass with a four-way P.T.F.E. stopcock. It is shown with its dimensions in fig. 5-1-1-1. The advantage of P.T.F.E. stopcocks is that they do not require any grease, although the cooling of the solution inside the tap (warmed by Joule heating) is not so efficient as with hollow glass stopcocks. The P.T.F.E. stopcocks employed had two grooves cut on the outside of the key to allow the solutions to be in direct contact with the glass barrel, where they were cooled by the thermostat liquid. The moving boundary tube was of 2 mm internal diameter and two sets of eight calibration marks were etched on it. This cell had been used by D.P. Sidebottom (21b) who had calibrated the lower set of etch marks. In this work both sets of etch marks were needed and so the whole m.b. tube had to be calibrated.

The calibration was carried out with a leading solution of 0.1N aqueous KCl followed by 0.069N aqueous KIO_3. For this system, the transport number of Cl^- is known to be

Fig. 5-1-1-1



The rising cell

0.5101 (1). This is the value obtained after solvent and volume correction : the uncorrected value of t_{Cl^-} appropriate to the speed of the boundary is 0.5098_4. This value was obtained as follows :

The volume change between one point in the leading solution and the closed silver anode is

$$\Delta V = - V_{Ag} + V_{AgCl} - t_+^{KCl} \phi_{KCl}$$

$$= - 10.3 + 25.8 - 0.490x27.4 = + 2.1 \text{ cm}^3$$

The volume correction will be :

$$C\Delta V/1000 = 0.1x2.1/1000 = 0.0002_1$$

Since the boundary moves towards the closed electrode,

$$t_-^{corr} = t_-^{obs} + C\Delta V/1000 = t_-^{obs} + 0.0002_1$$

The solvent correction will be

$$1 + K_{H_2O}/K_{solute} = 1 + 1.2x10^{-6}/1.29x10^{-2} = 1.0000_9$$

$$\therefore \; t_-^{corr} = \left[t_-^{obs} + 0.0002_1\right](1.0000_9) = t_-^{obs} + 0.0002_6$$

$$\therefore \; t_-^{obs} = 0.5101 - 0.0002_6 = 0.5098_4$$

The volumes between the etch marks were obtained by timing the boundary between them and using the equation $t_{Cl^-} = VFC_{KCl}/It$ with $t_{Cl^-} = 0.5098_4$. The two salts, KCl and KIO_3, used for the calibration were both AnalaR. KCl was recrystallised three times from conductivity water and left in the oven at 60° C for about 2 hours. The crystals were

Table 5-1-1-1

Volumes (cm^3) between the etch marks concerned

					Mean
V_{2-9}	0.5295	0.5302	0.5299	0.5292	0.5297
V_{3-10}	0.5352	0.5354	0.5352	0.5348	0.5351
V_{4-11}	0.5325	0.5331	0.5331	0.5327	0.5328
V_{5-12}	0.5348	0.5349	0.5346	0.5343	0.5346
V_{6-13}	0.5423	0.5434	0.5432	0.5429	0.5429
V_{7-14}	0.5367	0.5372	0.5370	0.5365	0.5368
V_{8-15}	0.5322	0.5327	0.5327	0.5330	0.5326
Average current used(mA)	1.5428	2.0354	2.0409_5	1.1767_5	

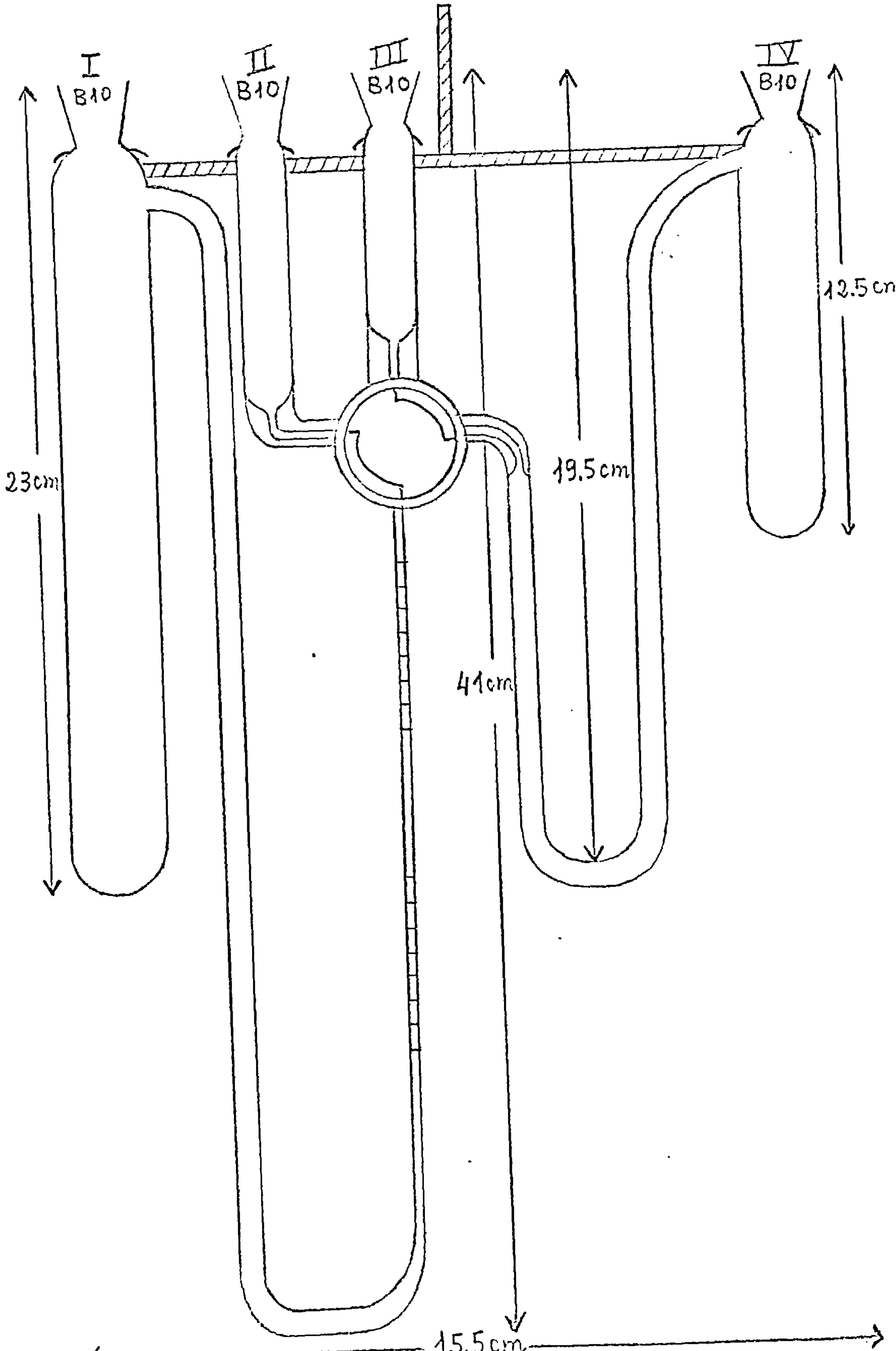
stirred with a glass rod from time to time to prevent them sticking together. The temperature was then increased to 110° C and the salt was allowed to dry at this temperature overnight. It was then left over silica gel in a desiccator attached to a vacuum pump for about 4 hours. KIO_3 was recrystallised twice from conductivity water, thoroughly dried in the oven at 110° C and stored in a desiccator over silica gel. The cathode was an open Pt wire electrode and the closed anode was a Ag electrode formed by plating silver on to a Pt spiral (see below). The use of the spiral electrode was necessary to minimize the current density, because with a wire electrode bubbles formed during the run. The silver plating was carried out with a solution 1% (w/v) in $KAg(CN)_2$ by passing 1-2 mA for 48 hours. A salt bridge of 3M KNO_3 agar gel was used and connected to a Pt foil anode in a separate beaker. After each run, the silver which had reacted with Cl^- ions to give AgCl was regenerated by making the resulting Ag/AgCl electrode a cathode in a saturated KNO_3 solution with a Pt foil as anode.

The calibration runs were performed using different currents. As the last etch mark from the tap was too faint to see properly, only two sets of seven etch marks were considered. Table 5-1-1-1 gives the results obtained, the etch marks being numbered from the tap in the order in which the boundary passed through them.

5.1.2 The falling boundary cell and its calibration

The cell is illustrated in fig. 5-1-2-1 where all the dimensions are indicated. The four-way P.T.F.E. stopcock is

Fig. 5-1-2-1



The falling cell

identical with that in the rising cell and the moving boundary tube has two sets of eight etch marks on it. The lower set of etch marks had been calibrated by D.P. Sidebottom (21b). The calibration of both sets of etch marks on the m.b. tube was carried out by Dr. M.A. Esteso (77), using the system 0.1N KCl/0.065N LiCl in aqueous solution for which $t^{corr}_{K^+} = 0.4899_1$ and $t^{uncorr}_{K^+} = 0.4900_7$. This value was obtained as follows :

The volume change between one point in the leading solution and the closed silver anode is

$$\Delta V = V_{AgCl} - V_{Ag} - t_+^{KCl} \phi_{KCl}$$

$$= 25.8 - 10.3 - 0.490 \times 27.4 = 2.1 \text{ cm}^3$$

so that the volume correction will be $0.1 \times 2.1/1000 = 0.0002_1$. Since the boundary moves away from the closed electrode,

$$t_+^{corr} = t_+^{obs} - C\Delta V/1000 \doteq t_+^{obs} - 0.0002_1$$

The solvent correction will be

$$1 + K_{H_2O}/K_{solute} = 1.0000_9$$

$$\therefore \; t_+^{corr} = \left[t_+^{obs} - 0.0002_1\right](1.0000_9) = t_+^{obs} - 0.0001_7$$

$$\therefore \; t_+^{\overset{obs}{\cancel{corr}}} = 0.4899 + 0.0001_7 = 0.4900_7$$

The B.D.H. lithium chloride was specially purified for atomic absorption spectroscopy work. The cathode was an open Pt wire electrode, and the closed anode was a Ag electrode (silver plated onto a Pt spiral). Table 5-1-2-1 shows the

Table 5-1-2-1

Volumes (cm^3) between the etch marks concerned

					Estimated mean
V_{1-9}	0.6437	0.6422	0.6438	0.6438	0.6438
V_{2-10}	0.6477	0.6482	0.6483	0.6489	0.6483
V_{3-11}	0.6522	0.6512	0.6519	0.6528	0.6521
V_{4-12}	0.6609	0.6620	0.6609	0.6613	0.6610
V_{5-13}	0.6565	*	missed	0.6575	0.6575
V_{6-14}	0.6463	*	0.6454	0.6458	0.6462
V_{7-15}	0.6570	*	0.6576	0.6575	0.6575
V_{8-16}	0.6586	*	0.6586	0.6593	0.6586
Average current used(mA)	1.3380	1.1036	2.0084	1.1038	

* The closed electrode cracked.

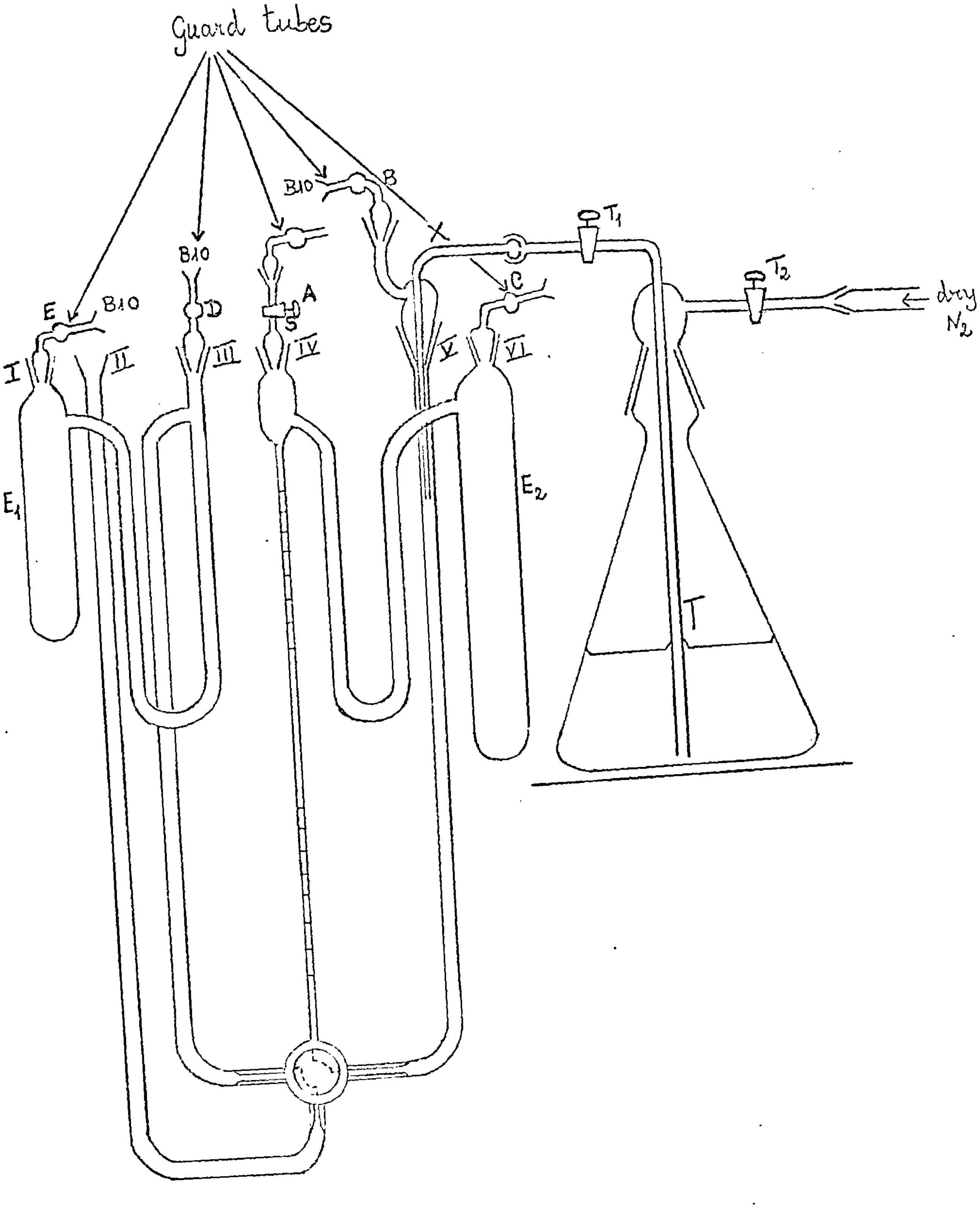
results obtained (77) with the etch marks numbered from the tap in the order in which the boundary passed through them.

5.1.3 Rising cell filling for ethylenediamine runs

Fig. 5-1-3-1 shows the arrangement for filling , with leading solution, the right-hand side of the rising cell when this is used as the closed compartment (e.g., in the case of the NaI ← AgI system). The four-way stopcock is in the position shown in fig. 5-1-3-1. All the guard tubes contain soda lime to trap the carbon dioxide and moisture of the laboratory atmosphere. The device fitted into socket IV has a P.T.F.E. stopcock. (Although illustrated in fig. 5-1-3-1, this device was not used in the preliminary experiments. Here a guard tube was fitted directly into the opening IV of the cell and, after filling, the guard tube was replaced by a long glass stopper so that solution spilled down the outside of the cell. However, during this replacement air can diffuse through into the m.b. tube and could disturb the speed of the boundary. To overcome this problem device A was made with a P.T.F.E. stopcock, S, to be closed after the cell filling. This device was tested, although no runs were done afterwards.)

Before the cell was filled with the solutions, it was flushed with N_2 that had passed through a tower with molecular sieve 3A, another tower with silica gel and a third one with soda lime. During the flushing, two air-steam inlet tubes were fitted into the electrode compartments I and VI, the stopcock S of element A was closed as was opening III with a stopper fitted into the guard tube D ; the N_2 passed out through II and V. The N_2 was usually passed for 1 hour. Then the air-steam inlet

Fig. 5-1-3-1

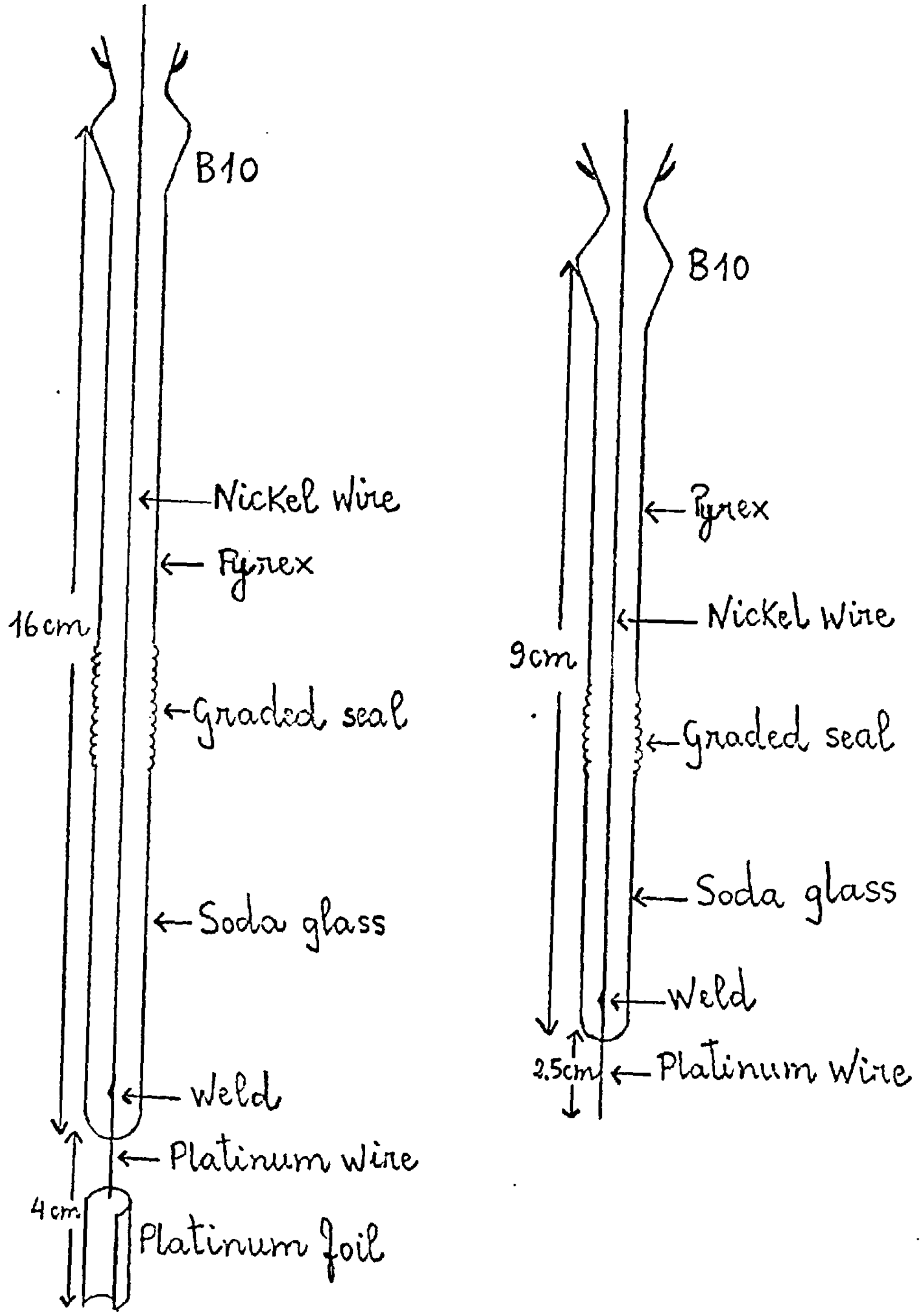


Rising cell filling

tubes were replaced by guard tubes C and E. During this replacement, N_2 was forced to pass through B and a similar device fitted into II, to prevent carbon dioxide and moisture coming into the cell.

Once the cell was filled with N_2, the solutions were transferred from the flask to the cell by N_2 under pressure, through the transfer device X. The solutions had first been degassed by attaching the flask to a vacuum pump and swirling the solution around with T_2 opened and T_1 closed. This was done to prevent dissolved gas coming out of solution during the run due to the lower solubility of gases at higher temperature. The leading solution was then admitted until the U-bend tube was full. Gas bubbles trapped in the tap were expelled by squeezing and releasing a rubber teat attached to a B10 cone fitted into the socket of the guard tube B. The soda lime contained in the guard tube prevented carbon dioxide and moisture being introduced into the solution during this operation. The openings V and VI of the cell were closed by putting stoppers into the guard tubes B and C. The solution was then forced to rise through the element A ; once the solution had risen above the tap S, the latter was closed. The guard tube fitted into A was replaced by a stopper to prevent fumes coming into the laboratory. After removing the stopper which had been placed into the guard tube C, more leading solution was admitted so that it spilled over into the electrode compartment E_2. The guard tube C was then removed and the electrode shown in fig. 5-1-3-2 (on the left) was inserted. As it was the closed electrode (in the system NaI ← AgI), its ground joint was slightly greased with

Fig. 5-1-3-2



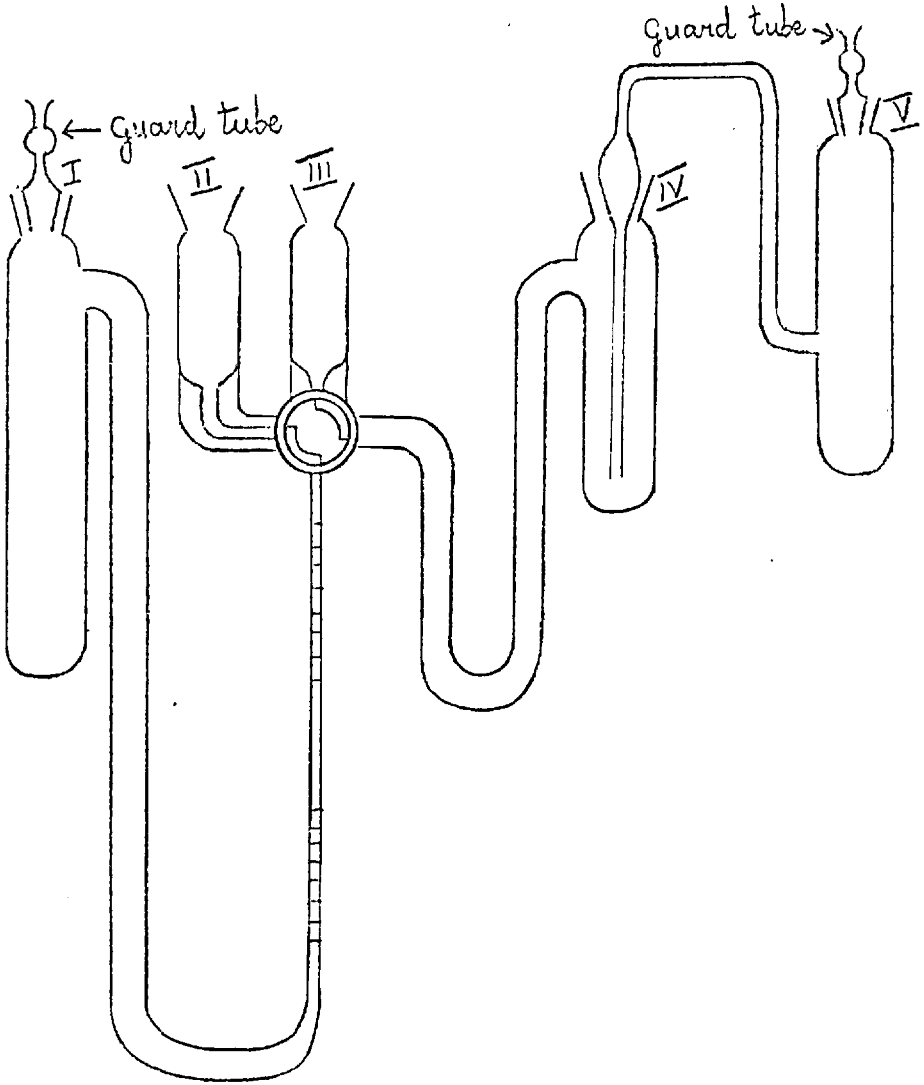
The electrodes

Silicone High Vacuum grease and it was held in place by springs. The element A had also been slightly greased and was held by springs. The left hand of the cell was filled similarly with following solution through neck II. The open electrode used in this work was that shown in fig. 5-1-3-2 (on the right). As it was the "open" side, a thin platinum wire was slipped between the cone of the electrode and the socket of the cell ; the guard tube was kept in neck III and a stopper was fitted into its socket. When the right-hand side of the cell is used as the open compartment (as in the $AgNO_3 \leftarrow AgI$ system), the cell is filled similarly, except that the element A is placed in neck III.

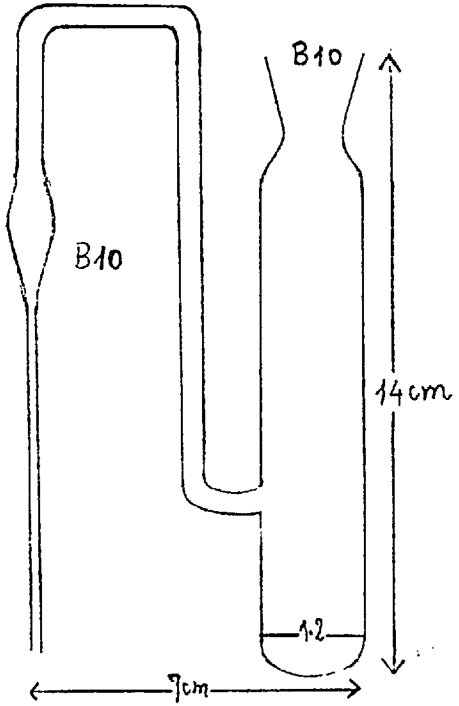
5.1.4 Falling cell filling for ethylenediamine runs

The falling cell was filled similarly to the rising cell. An extended electrode section was fitted into neck IV, as shown in fig. 5-1-4-1 to prevent electrode products reaching the boundary. Keeping the four-way P.T.F.E. stopcock in the position indicated (fig. 5-1-4-1), the cell was flushed with N_2 before being filled with the solutions. The N_2 came into the cell through V and I and out through III and II. The following solution was admitted through neck III, using a transfer device like that used in the rising cell filling. When the right-hand of the cell was full, a pumpette was attached to the guard tube fitted into neck V and the extended electrode section was filled by suction. The gas bubbles trapped in the four-way stopcock were removed, by squeezing and sucking the solution with a rubber teat attached to a cone fitted into the guard tube of the transfer device,

Fig. 5-1-4-1

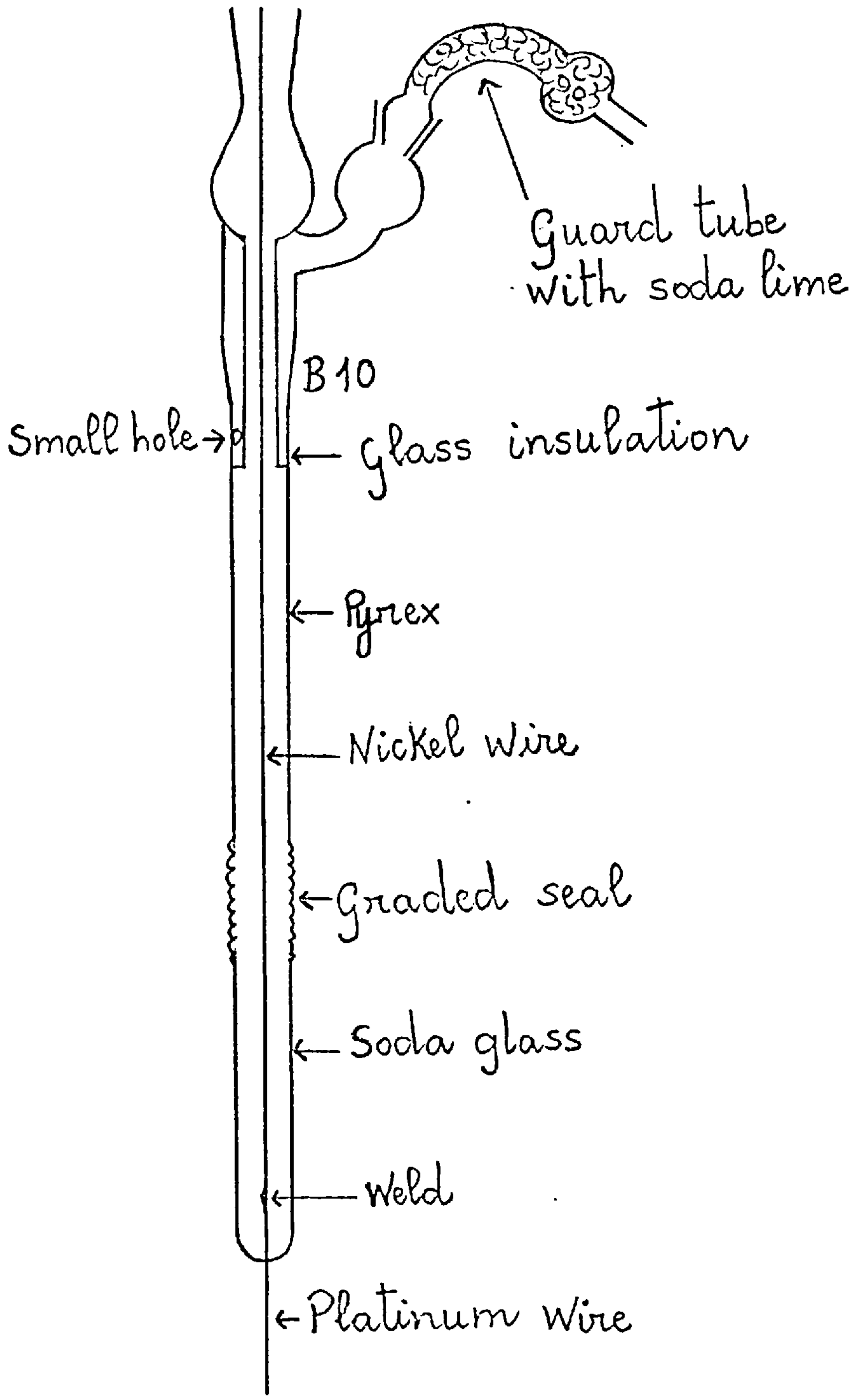


The falling cell filling



Extended section

Fig. 5-1-4-2


Guard tube with soda lime
B10
Small hole
Glass insulation
Pyrex
Nickel wire
Graded seal
Soda glass
Weld
Platinum wire

through neck III, as in the rising cell (fig. 5-1-3-1). In the preliminary experiments,the open electrode was that shown in fig 5-1-3-2 (on the right). After the removal of the transfer device, a stopper was fitted into neck III. The leading solution was admitted through II, similarly. The gas bubbles were removed, the closed electrode placed in neck I and a stopper in neck II. Although the opening to the atmosphere was quite small in the open electrode, it was thought that during a run carbon dioxide and moisture in the atmosphere could diffuse into the solution and eventually reach the boundary. With this in mind, a new design for the open electrode was then made, for more accurate runs later, and is shown in fig. 5-1-4-2. The opening to the atmosphere is through a guard tube with soda lime to trap the moisture and carbon dioxide. The nickel wire is insulated by a glass tube to prevent contact of ED with the nickel, should ED ever flow through the small hole in the side. This electrode should be slightly greased before being placed in its compartment and held in place by springs.

5.2 The thermostat

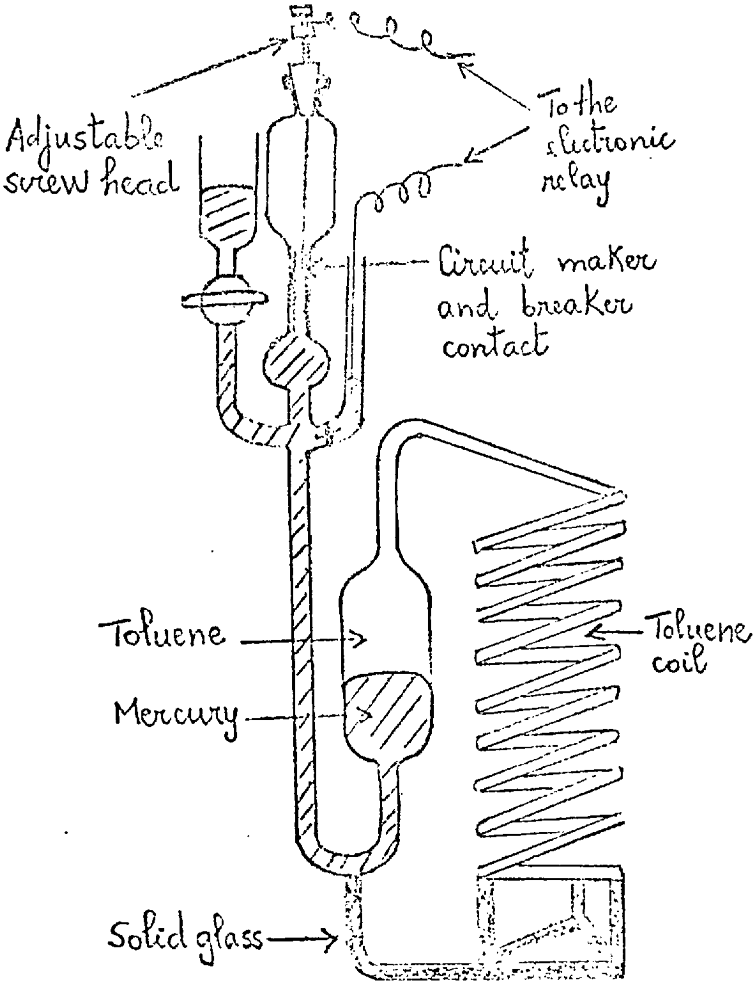
The external dimensions of the tank were length 61 cm, width 35 cm and height 58 cm. The front and back faces were made in glass, so that the cell could be seen from outside. There was a lateral small window for inspection of the cell from the side. The tank was mounted on a firm steel frame and, on a separate frame to prevent vibrations disturbing the movement of the boundary, was a 1/6 H.P. stirring motor driving a pair of paddle stirrers. The tank was filled with

Shell "Diala" oil BX, chosen for its transparency and very low conductance. A mercury-toluene thermoregulator shown in fig. 5-2-1 was used in conjuction with a 140 watt nichrome heating wire (fig. 5-2-2) wound on a frame of glass rods placed inside the coil of the thermoregulator for higher sensitivity. The current through the heating element was controlled by an electronic relay built in the electrical workshop. The temperature fluctuations were observed on a Beckmann thermometer calibrated at 25.00° C against an absolute thermometer. The temperature fluctuations were within the limits 0.005° C, but when the room temperature rose above 22° C it was necessary to cool the oil by passing cold water through a copper coil immersed in the oil bath.

5.3 The optical assembly

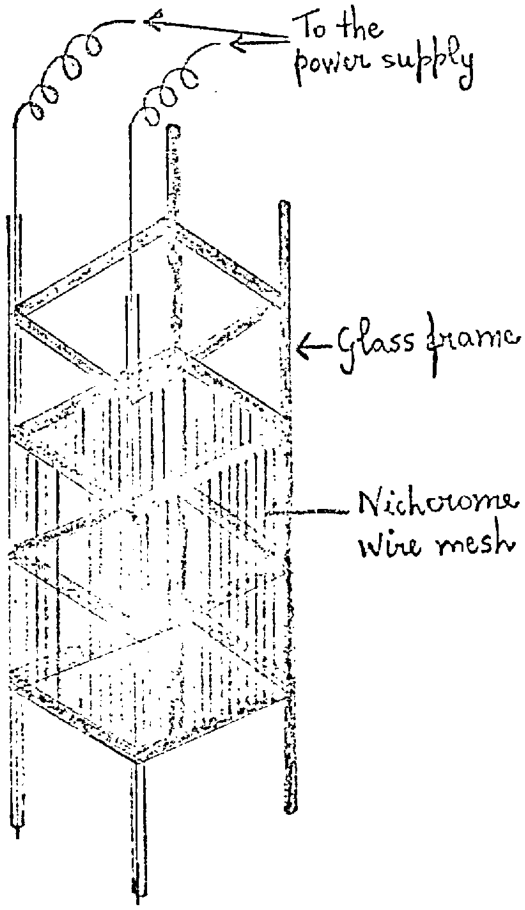
The difference in refractive index between the leading and following solutions made it possible to follow the movement of the boundary by means of the optical arrangement shown in fig. 5-3-1. The light source L was a 40 watt bulb mounted inside a black box. The light projected through a ground glass slide S to produce a rectangular light beam. Between the light source and the back face of the tank there stood a wide glass cylinder filled with water, acting as a lens. As the boundary moved along the tube it was followed by raising or lowering the light source L by means of a counterweight and a cord passing over a set of two pulleys. The boundary became visible when it was close to the upper or the lower edge of the rectangular beam. The boundary appeared as a dark line near the upper edge and white near

Fig. 5-2-1



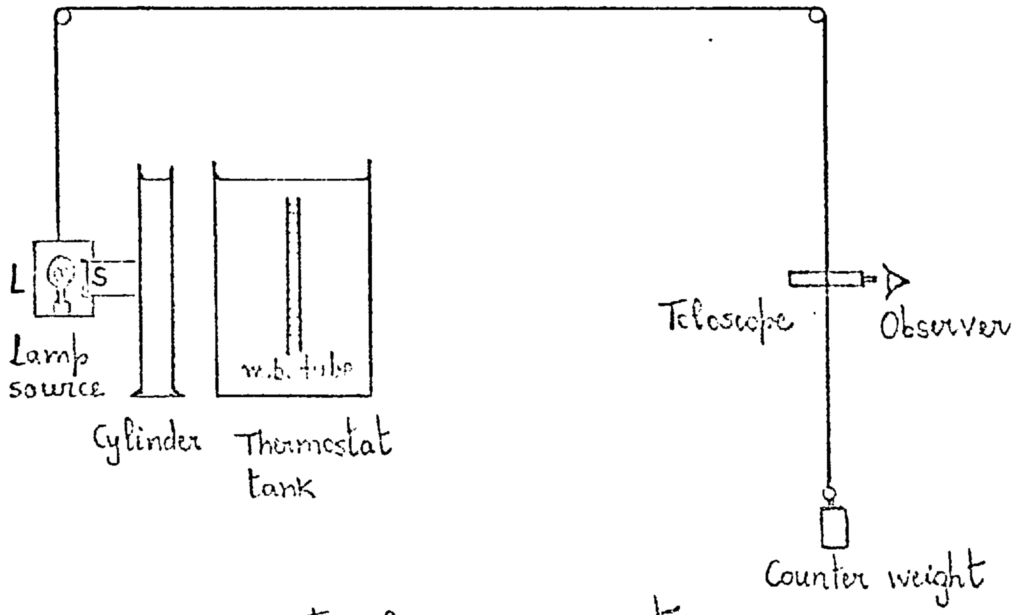
The thermoregulator

Fig. 5-2-2



The heater

Fig. 5-3-1



Optical arrangement

the lower edge, but the dark line was easier to see and so it was chosen for timing. The boundary was timed against a Zenith "Exact Time" clock using mercury batteries. The seconds were measured with a stop watch.

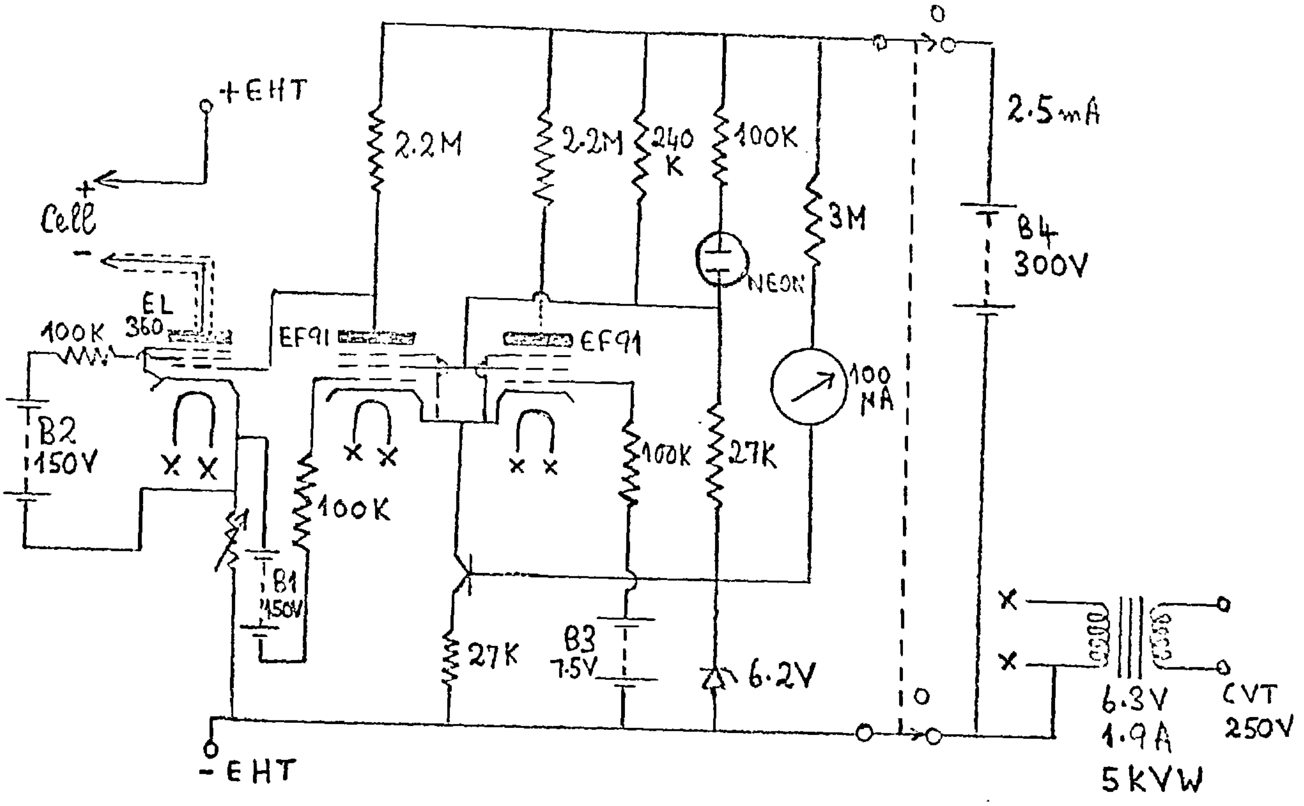
5.4 Measurement of current

The cell was in series with a 1000 Ω standard resistor, the potential difference across which was measured with a Racal 9075 digital Voltmeter. In the ED runs, the 0-0.3 V range was normally used and the instrument measured to 0.01 mV which corresponds to a precision of 0.01 μA in the current across the cell. The instrument was standardized with a Weston standard cell.

5.5 The constant current regulator

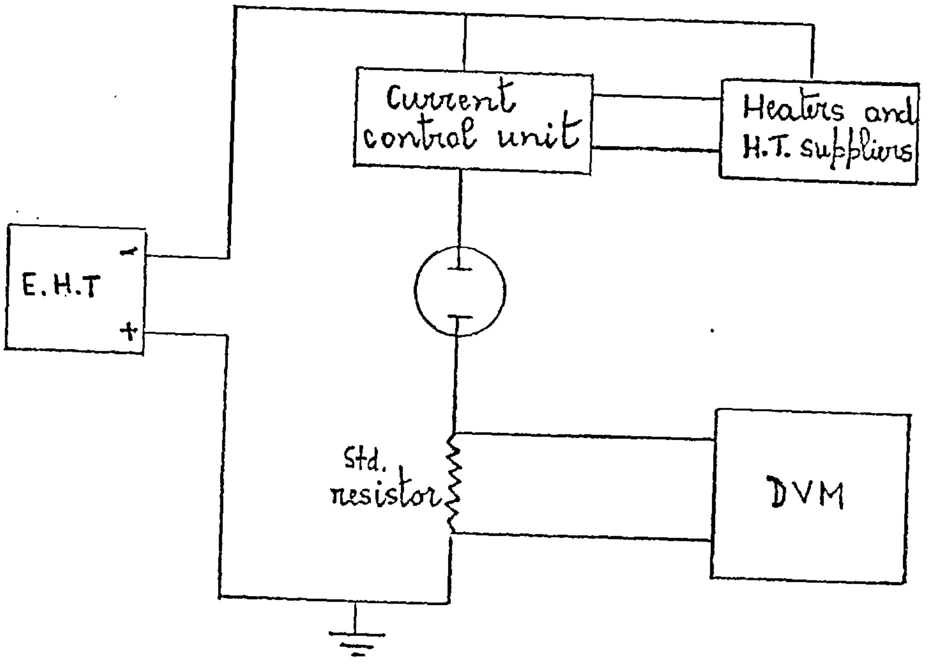
As the boundary moves along the m.b. tube, the leading solution is replaced by the following solution. Consequently, the resistance of the cell increases and the current would normally decrease. However, to measure the quantity of electricity with accuracy, it was necessary that the current be kept constant with time. In this work, a constant current source (fig. 5-5-1) designed and built by Gwyther (78) was used and is described in this thesis. It could produce a current between 0.01 mA and 5 mA in 10 μA steps. The current never changed more than 0.1% during a run. The D.C. output voltage went up to 5 kV. For the calibration work of the cell, another current unit was also used (no. 3). With this, the D.C. output voltage available went up to 2 kV and the available current range was 0-22 mA.

Fig. 5-5-1



The constant current generator

Fig. 5-5-2



General layout of the electrical circuit

The constant current generator was in series with the cell, a milliameter and the 1000 Ω standard Sullivan resistor across which the DVM was connected. The negative cell electrode was connected to the extra high tension (E.H.T.) end of the galvanostat. The standard resistor had one of its terminals connected to the second cell electrode while the other terminal was earthed as was the low voltage side of the galvanostat. The general circuit is shown in fig. 5-5-2.

5.6 Method for carrying out a run

The cell that had been left to dry under N_2 flow overnight, was placed in its normal position. After the guard tubes had been filled with fresh soda lime, they were fitted into the cell (figs. 5-1-3-1 and 5-1-4-1). Dry N_2 was then allowed to pass for one hour, the cell was filled with the solutions, and the outside of the cell wiped with Kleenex tissues soaked in absolute alcohol. Ink marks were placed above or below the etch marks to facilitate telescopic observation. The cell was then placed in the thermostat tank, and the electrodes were connected to the current generator which was switched to the dummy load. After about ½ hour, when the cell had reached thermal equilibrium, the four-way P.T.F.E. stopcock was turned clockwise through 90^0 and the current was switched from the dummy load to the cell.

5.7 Cell cleaning and drying

After a run was finished, the current was switched off, the leads were disconnected and the cell removed from the thermostat bath. The outside of the cell was wiped with Kleenex tissues soaked in methanol to remove the oil. The electrodes, guard tubes and stoppers were removed and placed in a large beaker containing distilled water. The solutions were poured into a bucket with a large amount of water. The cell was rinsed with water, filled with triethylamine to remove the grease, well rinsed with methanol to remove the amine and then rinsed with water. After the water had been drained off, the cell was filled with chromic-sulphuric cleaning mixture for 5 minutes and then copiously rinsed with distilled water (at least twelve times). The four-way stopcock and its barrel were washed separately. Finally the cell was rinsed three times with doubly distilled water and left to drain for a while. After replacing the stopcock, dry N_2 was passed in through I and VI simultaneously and out through II and V for the rising cell. For the falling cell, the N_2 was passed in through I and V and out through II and III. The N_2 was left to flow through the cell overnight. The greased sockets and cones of the accessories used in the cell filling and cones of the electrodes were carefully cleaned with triethylamine and then with methanol. After rinsing with water, all the accessories were cleaned with chromic-sulphuric cleaning mixture, copiously rinsed with distilled water and dried in the oven at 110°C. The Pt electrodes (only Pt electrodes were used in the runs with ED) were cleaned with hot nitric acid, well rinsed with distilled water and dried with N_2.

5.8 Preliminary runs

The purpose of these experiments was to find systems which could give visible and stable boundaries in ED as solvent. In order to choose viable moving boundary systems, the ion-pair association constant and limiting conductance data. Λ^0, given by Schaap et al. (25), Hibbard and Schmidt (24), Bromley and Luder (23), Fowles and Mc Gregor (43), and Bellobono and Favini (26) were used. According to m.b. theory, the conductance of the leading non-common ion-constituent must be greater than that of the following one. Since the Λ^0 values of the various electrolytes did not differ much, it was essential to pick as leading electrolytes salts of relatively high dissociation constant : KI, NaI and $AgNO_3$ were selected mainly on these grounds. Salts with common ions and of lower dissociation constant were then chosen as following electrolytes. To decide whether to use a falling or rising cell, density data for the electrolytes were taken from the papers by Fedot'ev and Kinkul'skaya (53), Putnam with Kobe (32), and Schmidt et al. (39).

5.8.1 Results

The following table gives a summary of the preliminary runs carried out in ethylenediamine at 25 ± 0.005°C.

Table 5-8-1-1

Cation run with KI leading : rising cell

Leading solution	Following solution	Current/μA*	Result
0.0298M KI	0.024M AgI	104-329	No boundary

*Limits of the current range tried in this run.

Anode : Pt wire (open)

Cathode : Pt foil in a 0.024M AgI solution (closed). Ag plated out.

A closed silver anode would also have been suitable, but it was not used in this run. In a previous run with araldited silver rod as anode, it was observed that the araldite desintegrated in the presence of ED and a deposit dropped down in the electrode compartment.

Table 5-8-1-2

Runs with leading $AgNO_3$ solutions

Leading solution	Following solution	Current/μA*	Result
0.0287M $AgNO_3$	0.035M AgI	40-111	Good boundary (rising)
0.0316M $AgNO_3$	0.029M $NaNO_3$	200-600	Good boundary (falling)

*Limits of the current range : below the lower current limit the boundary disappeared, and at values above the upper limit the boundary became bent.

Anion run : Pt wire anode open

Pt wire cathode closed (Ag plating out)

Cation run : Pt wire anode open

Pt foil cathode closed (Ag plating out)

The transport numbers of Ag^+ and NO_3^- in the $AgNO_3$ solution were determined between two etch marks (without solvent and volume corrections) and found to be :

$t_+ = 0.28$ at 455.6μA

$t_- = 0.68$ at 107.5μA

$\therefore\ t_+ + t_- = 0.96$

Correcting the transport numbers so that they sum to unity gives :

$t_+^{corr} = 0.28/0.96 = 0.29$

Table 5-8-1-3

Runs with NaI leading

Leading solution	Following solution	Current/μA*	Result
0.0311M NaI	0.041M AgI	120-220	Good boundary (rising)
0.0311M NaI	0.023M $NaNO_3$	110-450	Good boundary (falling)

*Limits of the current range : below the lower current limit the boundary disappeared, and at values above the upper limit the boundary became bent.

<u>Anion run</u> : Pt foil anode closed (I_2 formed)
Pt wire cathode open

<u>Cation run</u> : Pt wire anode open
Pt foil in a 0.041M AgI solution as cathode (closed);
Ag plating out.

The transport numbers of Na^+ and I^- in the NaI solution were determined between two etch marks (without solvent and volume corrections) and found to be :

$t_+ = 0.35$ at 151.0μA

$t_- = 0.64$ at 108.5μA

$\therefore\ t_+ + t_- = 0.99$

Correcting these values so that they add up to the unity gives :

$t_+^{corr} = 0.35/0.99 = 0.35$

At this stage, the present worker had to stop the transference work in ethylenediamine, because she became highly sensitised to this solvent, developing an allergy to it. Schaap et al. (25) state "A small percentage of persons, after repeated exposure to its fumes, develop a physiological sensitivity to ethylenediamine and experiences asthmatic-like attacks upon subsequent exposures". The present writer suffered no adverse effects initially on exposure to ED vapour but after several months the vapour caused coughing, swelling of glands in the throat, and difficulty in breathing at night with some rattling in the throat. Any exposure of the skin to droplets of ED produced a rash, particularly after having become sensitised to the material. The writer's husband, who occasionally visited the laboratory, exhibited even stronger asthmatic-like symptoms.

5.9 Discussion of results

5.9.1 Ionic limiting conductances

From the experimental transport numbers obtained in the preliminary runs in ethylenediamine, it is possible to estimate limiting transport numbers using Stokes's equation

$$t_{\pm} = t^0_{\pm} + \frac{(t_{\pm} - 0.5)\beta\sqrt{\alpha C}}{\Lambda^0(1 + Bd\sqrt{\alpha C})} \qquad (5\text{-}9\text{-}1\text{-}1)$$

Since $\eta_0 = 0.0154$ poise and $\varepsilon = 12.7$ for this solvent,

$$\beta = \frac{82.487|Z|^3}{\eta_0(\varepsilon T)^{\frac{1}{2}}} = 87.0_7\ \Omega^{-1}.\text{cm}^2.\text{mol}^{-3/2}.\text{dm}^{3/2}$$

$$B = 50.29\text{x}10^8/(\varepsilon T)^{\frac{1}{2}} = 0.817_5\text{x}10^8\ \text{cm}^{-1}.\text{mol}^{-\frac{1}{2}}.\text{dm}^{3/2}$$

A value of 4 Å was chosen for the distance of closest approach, d. The association constants, K_A, for $AgNO_3$ was taken as 1.74×10^3 from Schmidt's review $^{(24)}$ (also cited by ref. 25) and for NaI as 1.87×10^3 from ref. 25. The degrees of dissociation α were then calculated from the equation

$$K_D' = 1/K_A = \alpha^2 C f_{\pm}^2/(1 - \alpha)$$

the activity coefficients being obtained from the Debye-Hückel equation

$$\log_{10} f_{\pm} = - \frac{A\sqrt{\alpha C}}{1 + Bd\sqrt{\alpha C}} \qquad (5\text{-}9\text{-}1\text{-}2)$$

where

$$A = \frac{1.8246\times10^6}{(\varepsilon T)^{3/2}} = 7.83_7 \ \mathrm{mol}^{-\frac{1}{2}}.\mathrm{dm}^{3/2}$$

These calculations, carried out by successive approximations, led to

α_{AgNO_3} (C = 0.0287M) = 0.45

α_{AgNO_3} (C = 0.0316M) = 0.45_5

α_{NaI} (C = 0.0311M) = 0.44

With $\Lambda^0_{AgNO_3} = 63.5$ $^{(24)}$ (also cited by ref. 25), equation (5-9-1-1) gives

$t^0_{Ag^+} = 0.32_1$

For the NaI solution, with $\Lambda^0_{NaI} = 63.9$ $^{(25)}$,

$t^0_{Na^+} = 0.36_7$

By combining these limiting transference numbers with the limiting conductances given in Schmidt's review $^{(25,24)}$, estimates of ionic conductances in ED may be obtained. Table 5-9-1-1 gives the approximate conductance values in ED for some of the most common ions. The approximate limiting conductivity of the solvated electron has been included. The figures in the table are based on the NaI results :

$$\lambda^0_{Na^+} = 0.36_7 x63.9 = 23.5 \text{ cm}^2.\Omega^{-1}.\text{mol}^{-1}$$

$$\lambda^0_{I^-} = 0.63_3 x63.9 = 40.4 \text{ cm}^2.\Omega^{-1}.\text{mol}^{-1}$$

The conductance values for the other ions were then deduced as in the following examples for Br^- and Ag^+ :

$$\lambda^0_{Br^-} - \lambda^0_{I^-} = -0.6 \text{ } (Na^+ \text{ salts}), -0.8 \text{ } (Tl^+ \text{ salts})$$
$$= -0.7 \text{ (mean)}$$

$$\therefore \lambda^0_{Br^-} = 39.7$$

Taking $\Lambda^0_{AgBr} = 62.0$ (25),

$$\lambda^0_{Ag^+} = 62.0 - 39.7 = 22.3$$

The limiting transport number for Ag^+ in $AgNO_3$ calculated from the table can now be compared with the result obtained experimentally. For the calculation, the limiting conductance of $AgNO_3$ was taken as 22.3 + 42.1 = 64.4 rather than the value of 63.5 given in the literature (24) (also cited in ref. 25). The latter figure was obtained by a different set of workers (24) whose Λ^0 values display grave deviations from additivity. Hence:

$$t^0_{Ag^+} \text{ (calc.)} = 22.3/64.4 = 0.34_6$$

This is in fair agreement with $t^0_{Ag^+} = 0.32_1$ calculated from the preliminary moving boundary runs when the various sources of uncertainty in the transference numbers and conductances are

Table 5-9-1-1

Approximate limiting ionic molar conductances in ED/cm^2. mol $^{-1}$.Ω^{-1} at 25° C

Cation	λ^0_+	Anion	λ^0_-
Li^+	19.6	Cl^-	35.4
Na^+	23.5	Br^-	39.7
K^+	31.5	I^-	40.4
Cs^+	22.6* 26.3**	SCN^-	43.5
NBu_4^+	12.7	NO_3^-	42.1
H^+	40.9	e^-(K)	107.5
Tl^+	25.7	e^-(Cs)	181.4
Ag^+	22.3		

*Obtained by using $\lambda^0_{Br^-}$ = 39.7 (calculated from data given in ref. 25) and Λ^0_{CsBr} = 62.3 (ref. 26).

**Obtained by using $\lambda^0_{I^-}$ = 40.4 (calculated from data given in ref. 25) and Λ^0_{CsI} = 66.7 (ref. 26).

borne in mind.

A method of estimating individual ionic conductances approximately is to make use of Walden's rule

$$\lambda^0 \eta_0 = \text{constant}$$

which holds reasonably well for large ions. The largest ion in the table is NBu_4^+, for which

$$\lambda^0 \eta_0 \simeq 0.22 \pm 0.07$$

by inspection of the data for a variety of solvents (18). Hence, inserting $\eta_0 = 1.54$ cp for ED, $\lambda^0_{NBu_4^+} = 14.2$. This agrees with the value in the table within the uncertainty limits of Walden's rule.

From Table 5-9-1-1, it can be seen that $\lambda^0_{Li^+} < \lambda^0_{Na^+} < \lambda^0_{K^+}$, a sequence which is also found in water and many other solvents. Thus Li^+ is the most solvated of the three alkali metal ions in ED. Surprisingly $\lambda^0_{Cs^+}$ appears to be lower than for the above alkali metals, which indicates that although it is a larger ion than K^+ it is however more solvated in ED. Variations from the usual monotone alkali ion sequence have also been observed in some other non-aqueous solvents like sulpholane and ~~cyanidric~~ hydrocyanic acid (79). Also $\lambda^0_{Cl^-} < \lambda^0_{Br^-} < \lambda^0_{I^-}$, indicating that Cl^- is the most highly solvated of the three halide ions. H^+ appears as the fastest cation, although the difference between it and, say, K^+ is not sufficiently large for us to say definitely that proton--jumping is involved.

The mobility of solvated electrons in ED can now be calculated from the ionic conductances in Table 5-9-1-1 and the limiting equivalent conductances of several alkali metals in ED determined by Dewald and Dye (48). There is a considerable difference between the values calculated for $\lambda^0_{e^-}$ from the

Table 5-9-1-2

Limiting ionic molar conductances in liquid ammonia/$cm^2.mol^{-1}.\Omega^{-1}$ at - 33.5°C

Cation	λ^0_+	Anion	λ^0_-
Li^+	112	Cl^-	179.0
Na^+	130	Br^-	172.0
K^+	168	I^-	171.0
Rb^+	176.8 (-40°C)	NO_3^-	171.0
Cs^+	168.5 (-40°C)	BrO_3^-	148.0
NH_4^+	131	NH_2^-	133.0
Ag^+	116	OH^-	451.0
Tl^+	152	e^- (Na in NH_3)	997

results in K and in Cs solutions, suggesting that other species than M^+ and e^- may be involved. This view is strengthened by data for Na solutions (48), whose limiting conductance yields $\lambda^0_{e^-} = 3.5$! It seems more than likely that the anion in this case is Na^- and not e^-, as was discussed in Chapter III.

In liquid ammonia, the same sequence as that shown in ED for the alkali metals is observed. However the halogen ions show a trend opposite to that found in ED. Table 5-9-1-2 gives the limiting ionic conductances for some common ions in liquid ammonia at -33.5°C (80) ; they are based on the transference work of Franklin and Cady (55) and Λ^0 values of Kraus and Bray (81) (except for the Rb^+ and Cs^+ values, for which the Λ^0 values of Fuoss and Kraus(52c) were employed). The conductance of the electron was obtained by the present writer from the Λ^0 value of Na in liquid ammonia (= 1127) in ref. 82. In contrast to ED, liquid ammonia dilute solutions of Na exhibit very high conductivities. It is noteworthy that the ratio of the conductance of e^- to that of other "normal" ions is significantly greater in liquid ammonia than in ED. This shows that the ability of the electron to migrate by a quantum-mechanical tunnelling mechanism is also greater in the former solvent.

5.9.2 Solvation of ions in ethylenediamine

A number of attempts to derive accurate solvation numbers has been made (83), but none is wholly satisfactory. One of them is to make use of the ionic limiting conductances and Stokes' law. This gives the velocity v of the ion, considered as a large sphere of radius r_s moving in a continuous incompressible medium of viscosity η_0, when subjected to an electric field E. It can be stated by equation (5-9-2-1)

$$v = |Z_\pm| eE/6\pi\eta_0 r_s \qquad (5\text{-}9\text{-}2\text{-}1)$$

provided that there is no slipping between the surface of the sphere and the solvent.

$$\therefore\ r_s = \frac{Z_\pm^2 F^2}{6\pi N \eta_0 \lambda_\pm^0}$$

For ions in ethylenediamine :

$$r_s/\text{Å} = 53.3/\lambda_\pm^0$$

Insertion of the molar ionic conductances in ED (Table 5-9-1-1) then gives the values of the Stokes radii of the solvated ions. Table 5-9-2-1 compares the values of the crystallographic radii (2d,2e) and the Stokes'radii of various ions in ethylenediamine and in liquid NH_3. By inspection of the table, it may be seen that apart from Bu_4N^+, the Stokes' radii, r_s, obtained for the cations in ED are greater than their crystal radii, a fact which may be taken as evidence for solvation. The opposite happens with the anions in ED, where the Stokes' radii are smaller than their crystal radii. It is important to recall that the limiting ionic conductivities have been calculated from transport numbers obtained in preliminary runs, with consequent uncertainty in their values. Nevertheless, the difference between the crystal radii and Stokes' radii for the anions is large enough to be real, though this should not be regarded as a break-down of Stokes' law which is only valid for large ions in a solvent continuum. The molecules of ED are, of course, much larger than those of water or NH_3. It is rather more surprising that for the large

Table 5-9-2-1

Stokes radii in ethylenediamine and liquid NH_3

Ions	Crystal radius, r_c/Å	Stokes radius, r_s/Å	
		ED	liq. NH_3
Li^+	0.60	2.7	2.9
Na^+	0.95	2.3	2.5
K^+	1.33	1.7	1.9
Rb^+	1.48	—	1.8
Cs^+	1.69	2.2	1.8
Bu_4N^+	4.94	4.2	—
Ag^+	1.26	2.4	2.8
Tl^+	1.44	2.1	2.1
Cl^-	1.81	1.5	1.8
Br^-	1.95	1.3	1.9
I^-	2.16	1.3	1.9
NO_3^-	—	1.3	1.9

cation Bu_4N^+ the Stokes radius is also smaller than the crystal radius, although in this case a relatively small percentage error in λ^0 could account for the difference (see also below). The most likely interpretation of these figures is that the large Bu_4N^+ cation is unsolvated and so, too, the various anions, which is consistent with the fact that the positive ends of the dipoles in ED are shielded by two amino groups.

In liquid NH_3, the Stokes radii for the cations are similar to those in ED, except that the Cs^+ cation appears to be less solvated in ammonia. For the anions, the Stokes radii in liquid NH_3 are remarkably close to the crystal radii, which suggests that the anions are unsolvated in this solvent.

Several writers (2e,83) have drawn attention to the limitations of Stokes' law, which, as already mentioned, was not derived for the motion of a spherical body in a medium consisting of entities of a size comparable to its own. Robinson and Stokes (2e) have proposed an empirical correction to Stokes' law in water, assuming that the large tetraalkylammonium ions are not solvated in water. The radii, r_c, of five of these ions were calculated from bond lengths or molar volumes of related hydrocarbons and the Stokes radii from the limiting ionic conductances by applying Walden's rule. By plotting the ratio r_c/r_s against r_s, they obtained a correction curve for intermediate values of r_s and thus were able to obtain corrected values for the radii of other solvated ions in water. Robinson and Stokes then calculated the solvation numbers of any given ion by dividing the volume of the solvated ion (less the contribution of the bare ion itself) by the molecular volume of water.

This procedure is difficult to apply for ED since Bu_4N^+ is the only tetraalkylammonium ion whose conductance is available in this solvent. In liquid NH_3, too, no conductance data appear to be available for any of these ions. Thus we must resort to the crude approximation that Walden's rule holds for water, ED and liquid NH_3. By applying it to the tetraalkylammonium ions, from Me_4N^+ to Am_4N^+, a Robinson and Stokes correction curve is obtained (fig. 5-9-2-1) and correction factors r_c/r_s can be read off. Values of r_c (= r_{eff} for the other ions) in ED and liquid NH_3 are listed in Table 5-9-2-2. So are the solvation numbers n_i in both solvents, obtained by dividing the volume of the solvation shell (equal to the volume of the solvated ion less that of the bare ion) by the average volume of a molecule of each solvent, V_s :

$$n_i = \frac{4}{3}\pi\,(r_{eff}^3 - r_c^3)/V_s$$

A value for V_s of $12.2_9 \times 10^{-23}$ cm^3 was estimated by dividing the molar volume of ED by the Avogadro number. A value for V_s of 4.15×10^{-23} cm^3 was similarly estimated for liquid NH_3, using the value 0.6814 at -33°C (8) for its density and 17.03 for its molecular weight.

Not too much significance should be attached to the results listed in the table as many assumptions and approximations have been involved in their derivation. Besides those already pointed out, the values chosen for V_s involved the neglect of electrostriction effects, which could considerably decrease their values and so increase those of n_i. Nevertheless, the solvation numbers calculated are quite reasonable. The chief conclusion to be drawn is that although the ions have similar effective radii in ED and in NH_3, the solvation numbers in liquid NH_3 are greater than in ED. This is not surprising as the ED molecule

Fig. 5-9-2-1

Corrections factors to Stokes' law for ions (based on aqueous data)

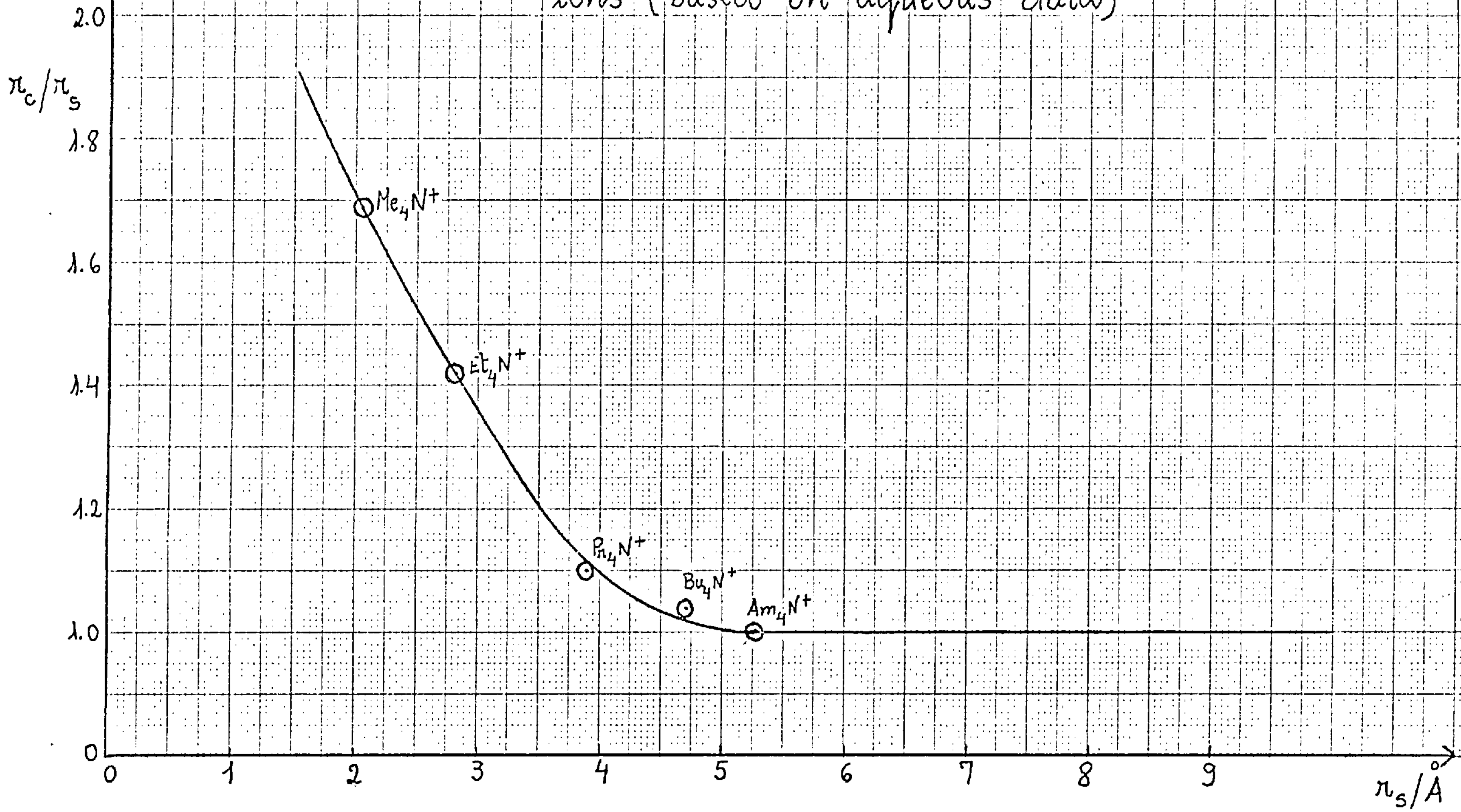


Table 5-9-2-2

A comparison of solvation numbers in ethylenediamine and liquid ammonia

	ED (25^{0}C)				Liquid NH_3 (-33^{0}C)	
Cation	r_s	r_c/r_s	r_{eff}	n_i	r_{eff}	n_i
Li^+	2.7	1.4_5	3.9	2.0	4.1	6.9
Na^+	2.3	1.6	3.7	1.7	3.7_5	5.2
K^+	1.7	1.8	3.1	0.9	3.2	3.1
Rb^+	——	——	——	——	3.2	3.0
Cs^+	2.2	1.6	3.5	1.2	3.2	2.8
Ag^+	2.4	1.5_5	3.7	1.7	3.9	5.8
Tl^+	2.1	1.7	3.6	1.5	3.6	4.4
Bu_4N^+	4.2	1.1	4.6	0(-0.79)	——	——

is approximately three times as large as the liquid NH_3 molecule. As expected, Li^+ is the most heavily solvated of the alkali metal cations. The Ag^+ and Tl^+ ions are almost as strongly solvated in both solvents, which is consistent with the strong bonds these ions form with amine ligands.

CHAPTER VI

6. MEASUREMENTS OF TRANSFERENCE NUMBERS OF MAGNESIUM SULPHATE IN WATER

6.1 Introduction

As explained in the previous chapter (section 5.8), the work with ethylenediamine as solvent was discontinued and an aqueous transference project was carried out instead. Virtually all transference numbers measurements in water have been restricted to uni-univalent electrolytes. To test further the available interionic theories,it was desirable to obtain accurate experimental data for a bi-bivalent electrolyte. Although $CuSO_4$ and $ZnSO_4$ have already been investigated (84,85), the results obtained were not very reliable as only one type of transference number (anion in the case of $CuSO_4$ and cation for $ZnSO_4$) was determined in each case. Moreover, these salts are known to hydrolyse slightly in solution and it was reported (84) that $t_{Cu^{2+}}^{CuSO_4}$ increases by about 0.001 in extrapolating to pH=7.0 from the normal pH of the solution. There is however a 2:2 electrolyte that hardly hydrolyses at all in aqueous solution, namely magnesium sulphate.

$$Mg^{2+} + H_2O \rightleftharpoons MgOH^+ + H^+ \qquad K = 3.8\text{x}10^{-12}\ \text{mol.dm}^{-3} \qquad (86)$$

$$Cu^{2+} + H_2O \rightleftharpoons CuOH^+ + H^+ \qquad K = 2.9\text{x}10^{-8}\ \text{mol.dm}^{-3} \qquad (87)$$

$$Zn^{2+} + H_2O \rightleftharpoons ZnOH^+ + H^+ \qquad K = 2.6_5\text{x}10^{-10}\ \text{mol.dm}^{-3} \qquad (88)$$

$$SO_4{}^{2-} + H_2O \rightleftharpoons HSO_4{}^- + OH^- \qquad K = 8.3\text{x}10^{-13}\ \text{mol.dm}^{-3} \qquad (89)$$

The hydrolysis constant for Mg^{2+} is much smaller than those of Cu^{2+} and Zn^{2+} and is, moreover, comparable in magnitude with that of SO_4^{2-}. Solutions of $MgSO_4$ are therefore expected to be very close to neutrality. This was confirmed by measuring the pH of the solution made from the recrystallised salt, the value being 6.0.

A preliminary transference number study of magnesium sulphate in water has already been carried out by Kumarasinghe (22). His results suffered not only from poor reproducibility but more seriously, the sum of cation and anion transference numbers (after all corrections had been applied) differed appreciably from unity, by up to 0.017. His solutions had been prepared from AnalaR $MgSO_4.7H_2O$ without further purification and it was later discovered that the real $MgSO_4$ concentrations were not the same as those weighed out. A more accurate study of $MgSO_4$ was therefore undertaken.

In the present work, the $MgSO_4.7H_2O$ was first recrystallised from doubly distilled water and dried to constant weight at 350° C to produce the anhydrous salt. The solutions were then made up by weight.

6.2 Materials

(a) Magnesium sulphate

$MgSO_4.7H_2O$ from Hopkin & Williams was recrystallised twice from doubly distilled water. It was then dried first as the heptahydrate at 150° C overnight in a Petri dish in a Gallenkamp oven type OV-060 and then put into a large porcelain crucible and heated at 350° C in a Gallenkamp oven type FR-550 or FR-570, to constant weight to obtain the anhydrous salt.

It has been reported (90) that decomposition of $MgSO_4$ occurs only at temperatures around 500° C. For a batch of ca. 10 g of $MgSO_4$, about five days were necessary to attain constant weight at the higher temperature.

Each time a solution of the salt was made up, the sample weighed in a weighing bottle was again heated to 350° C to constant weight. This was done to remove any water absorbed by the $MgSO_4$ during the weighing. These weight changes were generally about 0.7%. The salt contained in the weighing bottle with a cap loosely held was left cooling in a desiccator over fresh silica gel. Dry N_2 was then introduced into the desiccator, the cap of the weighing bottle was put into its place, and the weighing bottle with cap and salt were weighed. The salt was transferred into the solution flask, which had been weighed when empty, and the weighing bottle with cap and residue were reweighed. Doubly distilled water was then added to the flask, and this with solution was reweighed, to find the molality of the solution. The molarity was obtained by interpolating the density data for $MgSO_4$ solutions at 25° C taken from Int. Crit. Tables (91a). The buoyancy correction was applied for all the $MgSO_4$ solutions.

(b) Magnesium iodate

The first lot of magnesium iodate was prepared by adding B.D.H. (G.P.R.) magnesium carbonate little by little to a warm solution of B.D.H. (AnalaR) iodic acid as had been done in the previous work (22). The slight excess of magnesium carbonate added was separated from the neutral solution by filtration through a sintered glass funnel, the solution was concentrated on a hot plate and the product recrystallised from doubly distilled water. Later on, a second lot of G.P.R. magnesium iodate tetrahydrate from Hopkin & Williams was purified by recrystallising from conductivity water. The concentration of the solutions was estimated by titration against a standard solution of AnalaR sodium thiosulphate.

(c) Sodium benzenesulphonate

Some preliminary runs were done with a non-purified sodium benzenesulphonate from B.D.H.. For accurate work, the salt was recrystallised from conductivity water and dried at 65° C under vacuum. The results obtained with the purified and non-purified salt agreed within experimental error. It was not possible to prepare magnesium benzenesulphonate salt from the pure acid and the hydroxide or carbonate of the base, as had been done by Dunn and Phylip (92) as no benzenesulphonic acid was available at the time.

(d) Tetra-n-butylammonium chloride

Tetra-*n*-butylammonium chloride was prepared by the method described in the previous work (22). A slight excess of a 40% solution of tetra-n-butylammonium hydroxide from B.D.H. was added to B.D.H. AnalaR hydrochloric acid in an atmosphere of nitrogen to prevent absorption of carbon dioxide. A neutral solution was obtained by careful addition of diluted hydrochloric acid, using a pH meter to indicate neutrality. The solution was concentrated on a hot plate with gentle heat and then dried in a desiccator in vacuo. The viscous solid mass obtained was recrystallised from EtOAc and Et_2O, both AnalaR from B.D.H.. EtOAc was added in the first place and to the viscous solution thus obtained, Et_2O was then added and the crystals appeared in the separation between the solution and the ether. The solutions of required concentration were obtained by dilution of a ca. 0.2M stock solution and its strength was determined by titrating against a standard $AgNO_3$ solution.

(e) Tetra-n-butylammonium sulphate

An attempt to prepare tetra-n-butylammonium sulphate by addition of the hydroxide to sulphuric acid had already been made (22) but the crystallisation of the substance failed although several solvents (water, methanol, ethanol, benzene and diethyl ether) had been tried.

In the present work another attempt was made to obtain the salt, using acetone as solvent for crystallising, which had not been tried in the previous work (22). The salt was prepared by adding a slight excess of a 40% n-Bu_4NOH solution to sulphuric acid in an atmosphere of nitrogen, a neutral solution being obtained by careful addition of diluted sulphuric acid as in the case of the chloride. During this addition, some crystals appeared around the calomel reference electrode, probably due to the reaction between K^+ with SO_4^{2-}. Acetone was then added to the concentrated solution which was left to stand overnight, but no crystals were obtained. This solution was then placed in an acetone + dry ice bath for some time ; this produced a large crop of crystals, which, however, started to dissolve when the solution was left at room temperature. The acetone was then removed immediately by filtration through a sintered glass funnel, but the crystals started dissolving. They also dissolved quickly in ether, petrol ether and ethyl acetate.

(f) Oxalic acid

AnalaR oxalic acid ($H_2C_2O_4.2H_2O$) from B.D.H. was used without further purification.

6.3 Direct moving boundary runs with magnesium sulphate

The moving boundary cells, both rising and falling, for this work were the same as those used in the runs done with ED as solvent, and they have already been described.

The electrical equipment, the controlled heating system and the optical assembly used for transport numbers measurements of magnesium sulphate have also already been outlined.

6.4 Electrodes

As mentioned earlier, a non-gassing electrode with specific characteristics is required for the closed section of the moving boundary cell.

In the previous work (22), cadmium and copper rods sealed into Quickfit cones with "Araldite" were used as closed electrodes for the anion runs. In this work a cadmium electrode was also employed for these runs, but as no volume changes should occur in the closed section, "Araldite" was not used. Instead, cadmium was plated on a Pt coil, 18 cm long and 0.05 cm in diameter, sealed into a soda glass cone of the required size. The cadmium plating bath was made by dissolving about 12.5 g CdO and 45 g AnalaR NaCN in 500 ml solution (93a). Several attempts were made to get a smooth cadmium surface on the Pt coil. In a first trial, the anode was a Pt foil in a 0.05M KNO_3 solution connected by a salt bridge of the same solution, and a current of 2 mA was passed, but the cadmium did not plate smoothly on the Pt surface and did not cover all its surface. Smaller currents and stirring of the plating solution were tried, but no improvement was obtained. It was then decided to use a cadmium rod as anode, this and the Pt coil used as cathode being dipped into the same plating bath. This time, although the cadmium did not plate very smoothly, the cadmium crystals were regularly plated on to the Pt coil, covering all its surface. To begin with, a current of 1 mA was used and this was successively increased up to 3 mA. The same attempts made to plate copper on a Pt coil, from a solution containing 7.5 g of CuCN, 11.5 g of NaCN and 7.5 g of Na_2CO_3 in a volume of 500 ml (93b), failed. The copper crystals did not stick to the platinum and fell down into the solution.

Platinum electrodes were used as open electrodes in the anion runs ; they were made by sealing a 2 cm Pt wire into graded (Pyrex-soda glass) seals. For the cation runs Ag and Ag/AgCl electrodes were first used as closed and open electrodes respectively, as had been done in the previous work (22). For reasons discussed later (see section 7.1), it was decided to use Ag as open and Ag/AgCl as closed electrode. The latter was always kept in distilled water to prevent it drying, because the porous AgCl trapped air inside it and in the runs,bubbles appeared around the electrode. Before being introduced into the cell compartment, the electrode was washed several times with the respective solution. Both Ag and Ag/AgCl electrodes were made in soda glass and the silver was plated on a Pt coil from a 1% (w/v) $KAg(CN)_2$ solution, using a current of 1-2 mA (see section 5.1). Ag/AgCl electrodes were obtained by anodising part of the silver into AgCl, by electrolysing in a 0.05N KCl solution. The cathode here was a platinum wire.

6.5 Preparation of solutions

All solutions were prepared with conductivity water obtained by redistilling distilled water with alkaline $KMnO_4$. Redistillation was carried out in a Pyrex glass still and only the middle fraction, which had a conductivity of $0.98_4 \times 10^{-6}$ $\Omega^{-1}.cm^{-1}$, was collected.

6.6 Rising and falling cells filling

In the $MgSO_4$ runs, the cell fillings did not need as much special care as in the case of ED as solvent, as here there was not the problem of moisture and carbon dioxide from the air being absorbed by the solvent. After being degassed, the leading and following solutions were poured into the respective compartments through the openings I and II and V and VI in the rising cell (see fig. 5-1-1-1) and I and II and III and IV in the falling cell (see fig. 5-1-2-1). In the falling runs when the cathode extension was used (see section 7.1), once the right-hand side of the cell was full, a pumpette was attached to the neck of the extended electrode section (whose cone had been slightly greased) and this was filled by suction. The gas bubbles trapped in the four-way stopcock were removed by squeezing and releasing a rubber teat attached to a cone fitted into the sockets II and V in the rising and II and III in the falling cell. The closed compartment was completely filled with the corresponding solution and the respective electrode was greased and held in place by springs. In the rising anion runs, the right-hand side was always used as closed compartment, and the stopper fitted into the socket of the m.b. tube was also slightly greased and held in place by springs.

6.7 Cell cleaning and drying

The cells were cleaned the same way as that already described for ED runs. After being left to drain for a while, they were dried for about two hours with nitrogen dried by passing through towers of silica gel, calcium chloride and charcoal in that order. If this was done on the day before the run, the cell filling was only started after further passing nitrogen through the cell for about twenty minutes to remove any moisture which could have been adsorbed during the night on the walls of the m.b. tube.

6.8 A typical direct moving boundary run

27th January 1976

C_{MgSO_4} = 0.050214_5M, Cx2F = 9690.0929 coulomb.dm^{-3}
(F = 96487 coulomb.equiv^{-1})

C_{Bu_4NCl} = 0.0468M

Ag anode closed (boundary moving away from it)
Ag/AgCl cathode open

Grease: Edwards Silicone

Table 6-8-1

Etch		Time		Current/mA	Temperature
mark	hr	min	sec		(Beckmann)
1	12	14	13.2	1.0319_5	4.68_0
2	12	37	8	1.0319_5	4.68_0
3	12	56	54	1.0320_5	4.68_0
4	1	18	41.4	1.0321_5	4.68_0
5	1	38	40.6	1.0321_5	4.68_0
6	2	5	51.8	1.0322_5	4.68_0
7	7	25	20.3	1.0322_5	4.68_0
8	2	49	31.8	1.0322_5	4.68_0
9	4	46	54.5	1.0324_5	4.68_0
10	5	11	52.8	1.0324_5	4.68_0
11	5	33	11	1.0324_5	4.68_0
12	5	58	36.3	1.0324_5	4.68_0
13*					
14	6	39	40	1.0324_5	4.68_0
15	7	3	58.3	1.0324_5	4.68_0
16	7	28	21.7	1.0324_5	4.68_0

* Etch mark not visible

Table 6-8-1

(Calculations)

Etch marks interval	Δt/sec	$I\Delta t$/mA.sec	Volume/cm^3	t_+^{obs} = $VC2F/I\Delta t$
1-9	16361.3	16888.14	0.6438	0.3694
2-10	16484.8	17015.61	0.6438	0.3692
3-11	16577.0	17111.60	0.6521	0.3693
4-12	16794.9	17337.37$_5$	0.6610	0.3694
6-14	16428.2	16959.65	0.6462	0.3692
7-15	16718.0	17258.83	0.6575	0.3692
8-16	16729.9	17271.11	0.6586	0.3695

Mean t_+^{obs} = 0.3693

Note: The reproducibility (due mainly to time errors) was generally ca ± 0.0002.

6.9 Volume corrections

In order to apply the correction for the volume change that occurs in the closed compartment during the m.b. runs, the molar volumes of the solids Ag, Cd and AgCl and also the apparent molar volumes of aqueous $MgSO_4$, $CdSO_4$, $MgCl_2$, Bu_4NCl and $(Bu_4N)_2SO_4$ were required at 25° C. The values used for the molar volumes of the solids were:

Table 6-9-1

$$V_{Ag} = 10.30 \text{ cm}^3$$

$$V_{Cd} = 13.01 \text{ cm}^3$$

$$V_{AgCl} = 25.78 \text{ cm}^3$$

In the previous work (22) it was reported that the apparent molar volumes of $MgSO_4$ had been calculated from :

$$\phi/\text{cm}^3.\text{mol}^{-1} = 7.19 + 9.5C^{\frac{1}{2}} \qquad (6\text{-}9\text{-}1)$$

However the ϕ values given (22) for the series of concentrations used are all negative, which means that either the equation or the calculations are wrong. Even assuming an omission in typing of the minus sign before the given limiting apparent molar volume value (7.19), the ϕ values obtained are not the same as those presented. Millero and Masterton (94) gave the equation

$$\phi_V = \phi_V^0 + Am^{\frac{1}{2}} + Bm + Cm^{3/2} + Dm^2 + Em^{5/2} \qquad (6\text{-}9\text{-}2)$$

for the calculation of the ϕ values for NaCl, KCl, $MgCl_2$, Na_2SO_4, K_2SO_4 and $MgSO_4$ and also a table with the values of the constants A,B, etc. for each salt at 0, 25 and 50° C. The ϕ values for $MgSO_4$ and $MgCl_2$ were then calculated from equation (6-9-2) and they are given in the following table at the appropriate concentration values.

Table 6-9-2

C_{MgSO_4}/M	$\phi/cm^3.mol^{-1}$	$C^K_{MgCl_2}/M$	$\phi/cm^3.mol^{-1}$
0.005	-5.01 (-5.65*)	0.0049	15.04
0.01	-4.27 (-5.21*)	0.0098	15.23_5
0.025	-3.06 (-4.11*)	0.024_5	15.51
0.05	-1.96 (-2.90*)	0.049	15.93

*Values given in the previous work (22).

The values given for the apparent molar volumes of $CdSO_4$ in the previous work(22) are based in the assumption that the variation of $\phi(CdSO_4)$ with concentration is the mean of those of $MgSO_4$ and $CuSO_4$. However, this assumption was not confirmed by $\phi(CdSO_4)$ values calculated by the present writer from density data of 0.2-1.0% (w/w) $CdSO_4$ solutions at 18° C listed in Int. Crit. Tables (91b), no other values being found in the literature. A small correction to obtain the corresponding values at 25° C was applied by using the equation

$$d^{25} = d^{18} - d_0^{18} + d_0^{25}$$

where d and d_0 are the densities of $CdSO_4$ solution and of water respectively at the temperatures indicated. The ϕ values were then calculated and plotted against concentration being read off from the plot (Table 6-9-3). The ϕ versus C behaviour of $CdSO_4$ appeared to be very different from that of $MgSO_4$ and $CuSO_4$.

Table 6-9-3

$C^K_{CdSO_4}$/M (approx.)	0.005	0.01	0.025	0.05
$\phi_V/cm^3.mol^{-1}$	-6.4_0	-4.5_0	$+3.0_0$	$+1.7_5$

The ϕ values for $CuSO_4$ were calculated at Kohlrausch concentrations using equation (6-9-3) given by Pearce and Pumplin (95)

$$\phi/cm^3.mol^{-1} = -5.594 + 9.6841C^{\frac{1}{2}} + 0.87224C \qquad (6\text{-}9\text{-}3)$$

and their variation with concentration is similar to that of $MgSO_4$, but quite different from that of $CdSO_4$.

For Bu_4NCl and $(Bu_4N)_2SO_4$, as only m.b. runs at 0.05M were carried out with Ag as closed electrode, only one ϕ value at the appropriate Kohlrausch concentration was required. The ϕ value for Bu_4NCl was calculated from equation (6-9-4)

$$\phi/cm^3.mol^{-1} = 294.3 + 1.868C^{\frac{1}{2}} - 35.5C \qquad (6\text{-}9\text{-}4)$$

given by Conway et al.(96) which had already been used in the previous work (22).

As no density data for $(Bu_4N)_2SO_4$ have been reported in the literature, its apparent molar volume at the appropriate

Kohlrausch concentration was estimated from the additivity relationship

$$\phi((Bu_4N)_2SO_4) = 2\phi(Bu_4NBr) - 2\phi(KBr) + \phi(K_2SO_4) \qquad (6\text{-}9\text{-}5)$$

as had been done in the previous work (22), the data for $\phi(Bu_4NBr)$ (97,98), ϕ (KBr) (98,99) and $\phi(K_2SO_4)$ (100) being taken from the references cited. Table 6-9-4 gives the apparent molar volumes of Bu_4NCl and $(Bu_4N)_2SO_4$ at the appropriate Kohlrausch concentration.

Table 6-9-4

c_{MgSO_4}/M	$\phi(MgSO_4)/cm^{+3}.mol^{-1}$
0.05	- 1.96
$c^K_{Bu_4NCl}$/M	$\phi(Bu_4NCl)/cm^{+3}.mol^{-1}$
0.049	292.9_7
$c^K_{(Bu_4N)_2SO_4}$/M	$\phi((Bu_4N)_2SO_4)/cm^{+3}.mol^{-1}$
0.025	567.5_0

For the cation runs, with Ag/AgCl as closed electrode, the volume change was estimated by substituting the ϕ values given in Table 6-9-2 and the volumes of the solids Ag and AgCl given in Table 6-9-1 into equation (1-4-2). Table 6-9-5 shows the volume corrections for $MgSO_4$ cation runs with Ag/AgCl as closed electrode.

Table 6-9-5

$MgSO_4$ cation runs volume corrections
(Ag/AgCl closed electrode)

C_{MgSO_4}/M	$\Delta V/cm^3.faraday^{-1}$	Vol. corrn = $2C\Delta V/1000$
0.005	- 6.43	- 0.00006_4
0.01	- 6.55	- 0.0001_3
0.025	- 6.74	- 0.0003_4
0.05	- 6.90	- 0.0006_6

The boundary moved towards the closed Ag/AgCl cathode, therefore $t_+^{corr} = t_+^{obs}$ + (vol. corrn). The volume correction for the cation runs done at 0.05M with Ag as closed electrode was obtained by substituting the ϕ values given in Table 6-9-4 and the molar volumes of the solids Ag and AgCl given in Table 6-9-1 into equation (1-4-3). Table 6-9-6 shows the volume correction for the cation runs at 0.05M with a closed silver anode.

Table 6-9-6

$MgSO_4$ cation runs volume correction
(Ag closed electrode)

C_{MgSO_4}/M	$\Delta V/cm^3.faraday^{-1}$	Vol. corrn = $2C\Delta V/1000$
0.05	6.62	0.0006_6

The boundary here moved away from the closed silver anode, hence $t_+^{corr} = t_+^{obs}$ - (vol. corrn).

In all anion runs the boundary moved towards a closed Cd anode giving rise to the same type of volume change. The volume change was estimated by substituting the ϕ values given in tables 6-9-2 and 6-9-3 and the molar volume of solid Cd in Table 6-9-1 into equation (1-4-4). Table 6-9-7 shows the volume corrections for $MgSO_4$ anion runs.

Table 6-9-7

$MgSO_4$ anion runs volume corrections

C_{MgSO_4}/M	ΔV/cm^3.faraday^{-1}	Vol. corrn = $2C\Delta V/1000$
0.005	- 8.73	-0.00008_7
0.01	- 7.93	-0.0001_6
0.025	- 4.43	-0.0002_2
0.05	- 5.27	-0.0005_3

The boundary here moved towards the closed Cd anode, and therefore $t_-^{corr} = t_-^{obs}$ + (vol. corrn).

The $CdSO_4$ concentrations were taken as the Kohlrausch values, but near the Cd anode they will have been greater. The volume correction should therefore really be $\int_\gamma \phi_{AX}\, c_{AX}\, dV$ where γ =const. In order to estimate the value of ϕ_{CdSO_4}, a calculation was carried out in which it was assumed that the profile of $CdSO_4$ concentration versus distance from the Cd anode was the same as that determined by Gwyther (4) for a

$AgClO_4$ solution formed at a Ag anode. As in the $AgClO_4$ case, the region of high concentration was divided into slices, the solute contribution to the volume of each slice being obtained by multiplying the apparent molar volume in the slice by the number of moles of solute in it (dn = CdV). The dimensions of the diameters and lengths of the relevant tubing in the m.b. falling cell were taken, and the maximum concentration was assumed to be equal to 2.5M, the solubility of $CdSO_4$ solution being approximately 3.4M. The apparent molar volume at the concentration of each slice was calculated from density data given in Int. Crit. Tables $^{(91b)}$. The value obtained for the average apparent molar volume was almost eight times higher, 13.12 $cm^3.mol^{-1}$, than that obtained for the Kohlrausch concentration. Insertion of this bigger value found for the ϕ_{CdSO_4} in the volume correction for the most concentrated $MgSO_4$ solution used, gave a corrected anion transport number about 0.0005 higher than that initially calculated. This makes the sum of the corrected cation and anion transport numbers differ more from unity. In view of these results, it may well be that the profile of $CdSO_4$ concentration versus distance from the Cd anode is not the same as that obtained for $AgClO_4$ with a Ag anode.

6.10 Solvent corrections

In order to apply the solvent correction due to the current carried by the solvent and its impurities, the specific conductivities of $MgSO_4$ at the appropriate concentrations were required. Some conductivity measurements were therefore carried out at 25°C in a Pyrex conductivity cell of cell constant

0.203 cm^{-1} and with a M.E.L. conductivity bridge type no. E 7566/3. As little accuracy was required in these measurements, the $MgSO_4$ solutions were prepared by dilution from the most concentrated solution. The specific conductivity of the water employed was $0.98_4 \times 10^{-6} \Omega^{-1}.cm^{-1}$. Given in Table 6-10-1 are the solvent corrections at appropriate concentrations.

Table 6-10-1

C_{MgSO_4}/M	$K \times 10^4 / \Omega^{-1}.cm^{-1}$	Solvent corrn $1 + K_{solvent}/K_{solute}$
0.005	8.68	1.001_1
0.01	15.3_9	1.000_6
0.025	31.2_7	1.000_3
0.05	52.0_6	1.000_2

CHAPTER VII

7. RESULTS AND DISCUSSION OF $MgSO_4$ TRANSFERENCE NUMBERS

7.1 Direct moving boundary results

Both anion and cation transference numbers were measured at 0.05, 0.025. 0.01 and 0.005M concentrations of $MgSO_4$.

In the previous work (22) several indicators had been tried and with some of them, good and stable boundaries were observed. Magnesium iodate gave a good rising boundary and oxalic acid and tetra-n-butylammonium chloride both gave easily visible falling boundaries.

In the present work the same indicators were employed and their concentrations estimated from the Kohlrausch equation by using limiting conductivities.

(a) Results in 0.05M solutions

Anion runs

Results obtained for the anion transport numbers at 0.05M $MgSO_4$ concentration with $Mg(IO_3)_2$ as indicator are summarized in Table 7-1-1. At currents less than 2 mA the boundary, although visible, was too faint to take accurate measurements. At 4 mA the results were lower by 0.0020 than those tabulated and some progression up was observed in certain runs. This could be attributed to mixing of the solutions due to Joule heating. In the small current range used, change in the concentration of the

Table 7-1-1

ANION RUNS

$C_{MgSO_4} = 0.05M$

$Mg(IO_3)_2$ following
Rising boundary

Cd plated on Pt coil anode closed
Pt wire gassing ($HIO_3(s)$) cathode open

C_{MgSO_4}/M	$C_{Mg(IO_3)_2}/M$	Current/mA	t_-^{obs}
0.050214_5	0.0358	2.00	0.6321
0.050190_3	0.0388	2.04	0.6325
0.050190_3	0.0388	2.08	0.6325
0.050190_3	0.0388	2.99	0.6323

t_- does not depend on current or C_{foll}.
Mean $t_-^{obs} = 0.6323_5$

Vol. corrn = -0.0005_3 (Table 6-9-7)
Solv. corrn = 1.000_2 (Table 6-10-1)

$\therefore t_-^{corr} = 0.6319$

Taking $t_+^{corr} = 0.3687$ (Table 7-1-4)

$$t_+^{corr} + t_-^{corr} = 1.0006$$

$\therefore t_+ = 0.3685$ (when corrected to give $t_+ + t_- = 1.0000$)

following solution had no significant effect on the transference values.

Oxalic acid (H_2Ox) as indicator always gave low results compared with those obtained with magnesium iodate, results which did not add up to the unity with the cation transference number. Some progression up was also observed. The possibility of the initial concentration used for oxalic acid being very different from the Kohlrausch value was considered. When the current flows, two boundaries are formed, one between oxalic acid and magnesium oxalate and the other between the latter and magnesium sulphate. One can assume either that all the H^+ ions from oxalic acid move away and MgC_2O_4 is formed or that $Mg(HC_2O_4)_2$ is formed instead. As explained in section 1.2, the appropriate initial concentration of the following solution for both cases is calculated by combining two Kohlrausch relationships

$$C^{H_2Ox}_{H^+} = \frac{2C^{MgSO_4}_{SO_4{}^{2-}}\, t^{MgOx}_{Ox^{2-}}\, t^{H_2Ox}_{H^+}}{t^{MgSO_4}_{SO_4{}^{2-}}\, t^{MgOx}_{Mg^{2+}}} \qquad (7\text{-}1\text{-}1)$$

if MgOx is formed, and

$$C^{H_2Ox}_{H^+} = \frac{2C^{MgSO_4}_{SO_4{}^{2-}}\, t^{Mg(HOx)_2}_{HOx^-}\, t^{H_2Ox}_{H^+}}{t^{MgSO_4}_{SO_4{}^{2-}}\, t^{Mg(HOx)_2}_{Mg^{2+}}} \qquad (7\text{-}1\text{-}2)$$

if $Mg(HOx)_2$ is formed. In both equations, limiting transference numbers obtained from limiting conductivities (2a) were used as described in section 1.2. Two very different Kohlrausch concentrations for oxalic acid are calculated according to which assumption is used (0.095_9M from equation (7-1-1) and 0.056_5M from equation (7-1-2) for a leading 0.05M $MgSO_4$ solution). Both initial concentrations of $H_2C_2O_4$ were tried and the results are shown in Table 7-1-2. Kumarasinghe (22) obtained anion transport numbers at 0.025M $MgSO_4$ concentration with oxalic acid as indicator that were 0.0007 lower than those with magnesium iodate following. No progression had been reported.

To check the anion transference numbers obtained with magnesium iodate as indicator, another independent following solution was required. To avoid the oxalate quandary,the acid of the anion chosen should be strong and the anion itself sufficiently slow. The picrate ion meets these requirements but unfortunately the acid is not sufficiently soluble in water. The benzenesulphonate anion looked more promising. It is large and therefore likely to be slow, and the acid itself is very soluble and completely dissociated so that there should be no trouble about hydrolysis products. As the acid was not available at the time, its sodium salt was considered. No data for the conductivity of benzenesulphonate anion are given in the literature and so its value was calculated from Jeffery and Vogel's (102) published molar conductances,Λ,of sodium benzenesulphonate solutions. For each point,the extrapolation function $\Lambda^{0\prime}$ defined by Shedlovsky (8) by

$$\Lambda^{0\prime} = (\Lambda + B_2\sqrt{C})\Big/(1 - B_1\sqrt{C})$$

Table 7-1-2

Transference numbers in 0.05M $MgSO_4$

$H_2C_2O_4$ following
Falling boundary

Cd plated on Pt coil anode closed
Pt wire gassing cathode open

C_{MgSO_4}/M	$C_{H_2C_2O_4}$/M	Current/mA	t_-^{obs}
0.049989_6	0.0500	1.21	0.6277
0.050214_5	0.0500	2.50	0.6308
0.049989_6	0.0850	1.21	0.6278
0.049989_6	0.0850	1.21	0.6279

Note: Some progression up was observed in these runs.

was calculated and plotted against C. For the concentrations between 10.0×10^{-4} and 60.0×10^{-4}N, a straight line was obtained which extrapolated to $\Lambda^0 = 87.3\ \mathrm{cm}^2.\Omega^{-1}.\mathrm{equiv}^{-1}$. However, the points in the concentration range between 60.0×10^{-4} and 100.0×10^{-4}N appeared to lie on a different straight line which extrapolated to $\Lambda^0 = 86.3\ \mathrm{cm}^2.\Omega^{-1}.\mathrm{equiv}^{-1}$. Taking $\lambda^0_{Na^+} = 50.1$, the corresponding values of $\lambda^0_{PhSO_3^-}$ obtained were 37.2 and 36.2 respectively. From the Kohlrausch equation and these values for $\lambda^0_{PhSO_3^-}$, the initial concentration of $NaPhSO_3$ solution was then calculated based on the formation of the system $MgSO_4 \longleftarrow Mg(PhSO_3)_2 \longleftarrow NaPhSO_3$, by combining two Kohlrausch relationships

$$C^{NaPhSO_3}_{Na^+} = \frac{2C^{Mg(PhSO_3)_2}_{Mg^{2+}}\ t^{NaPhSO_3}_{Na^+}}{t^{Mg(PhSO_3)_2}_{Mg^{2+}}} = \frac{2C^{MgSO_4}_{SO_4^{2-}}\ t^{Mg(PhSO_3)_2}_{PhSO_3^-}\ t^{NaPhSO_3}_{Na^+}}{t^{MgSO_4}_{SO_4^{2-}}\ t^{Mg(PhSO_3)_2}_{Mg^{2+}}}$$

The anion boundaries obtained with $NaPhSO_3$ solution were falling and sharp. The average anion transport number was only 0.0002 lower than that obtained with $Mg(IO_3)_2$ as indicator (Table 7-1-3) and so agreed well within experimental error. No current or concentration dependence was observed. A cathode extension, which was already described for the ED moving boundary runs, was used to prevent hydroxide ions generated at the cathode from reaching the boundary. In a preliminary run in which no cathode extension was used, a white precipitate was formed in the bottom of the U-bend tube of the falling cell (fig. 5-1-2-1) - probably $Mg(OH)_2$.

Table 7-1-3

ANION RUNS

$C_{MgSO_4} = 0.05M$

$PhSO_3Na$ following
Falling boundary

Cd plated on Pt coil anode closed
Pt wire gassing cathode open

C_{MgSO_4}/M	C_{PhSO_3Na}/M	Current/mA	t_-^{obs}
0.050190_3	0.0669	3.38	0.6320
0.050113_5	0.0622	1.65	0.6321
0.050113_5	0.0669	3.38	0.6321
0.050113_5	0.0622	3.38	0.6323

t_- does not depend on current or C_{foll}
Mean $t_-^{obs} = 0.6321$

Vol. corrn = -0.0005_3 (Table 6-9-7)
Solv. corrn = 1.000_2 (Table 6-10-1)

$\therefore t_-^{corr} = 0.6317$

Taking $t_+^{corr} = 0.3687$ (Table 7-1-4)

$t_+^{corr} + t_-^{corr} = 1.0004$

$\therefore t_+ = 0.3687$ (when corrected to give $t_+ + t_- = 1.0000$)

Note: A cathode extension was used in all these runs.

Cation runs

The results obtained for the cation transference numbers by using tetra-butylammonium chloride as following solution are collected in Table 7-1-4. Changes in current and concentration of the indicator produced no effect on the transference numbers. The initial concentration of tetra-n-butylammonium chloride was calculated on the basis that two boundaries are formed, one between $MgSO_4$ and $n(Bu_4N)_2SO_4$ solution and the other between the latter and $n\text{-}Bu_4NCl$ solution. Later runs with more dilute $MgSO_4$ solutions indicated that an addition compound, probably $AgCl.n\text{-}Bu_4NCl$, was formed at the closed silver anode, and led to high results (see later). Although at 0.05M $MgSO_4$ visual inspection had not shown this addition compound, it was decided as a check to carry out a run with Ag/AgCl as the closed electrode. The result obtained, after application of all corrections, was only 0.0001 lower than the average of the tabulated values in Table 7-1-4. This strengthens the belief that the addition compound was not formed at the high $MgSO_4$ concentration, perhaps because the main electrode reaction was too rapid.

(b) Results in 0.005M solutions

Anion runs

Anion transference numbers in 0.005M $MgSO_4$ solutions obtained with $Mg(IO_3)_2$ as indicator do not show any dependence with current or concentration of the following solution, and are summarized in Table 7-1-5.

Table 7-1-4

CATION RUNS

$C_{MgSO_4} = 0.05M$

Bu_4NCl following
Falling boundary

Ag anode closed
Ag/AgCl cathode open

C_{MgSO_4}/M	C_{Bu_4NCl}/M	Current/mA	t_+^{obs}
0.049989_6	0.0468	1.64	0.3694_5
0.049989_6	0.0468	1.75	0.3693
0.050214_5	0.0468	2.04	0.3691_5
0.050214_5	0.0468	1.03	0.3693
0.050214_5	0.0480	2.05	0.3692
0.050190_3	0.0435	2.04	0.3695

t_+ does not depend on current or C_{foll}
Mean $t_+^{obs} = 0.3693$

Vol. corrn = 0.0006_6 (Table 6-9-6)
Solv. corrn = 1.000_2 (Table 6-10-1)

$\therefore t_+^{corr} = 0.3687$

Table 7-1-5

ANION RUNS

$C_{MgSO_4} = 0.005M$

Details as in Table 7-1-1

C_{MgSO_4}/M	$C_{Mg(IO_3)_2}/M$	Current/mA	t_-^{obs}
0.004968_8	0.00387	0.61	0.6118
0.004968_8	0.00387	0.31	0.6119_5
0.004968_8	0.00361	0.61	0.6120

t_- does not depend on current or C_{foll}

Mean $t_-^{obs} = 0.6119$

Vol. corrn = -0.00008_7 (Table 6-9-7)

Solv. corrn = 1.001_1 (Table 6-10-1)

$\therefore t_-^{corr} = 0.6125$

Taking $t_+^{corr} = 0.3880$ (Table 7-1-8)

$t_+^{corr} + t_-^{corr} = 1.0005$

$\therefore t_+ = 0.3878$ (when corrected to give $t_+ + t_- = 1.0000$)

Note: $HIO_3(s)$ was introduced into the bottom of the open compartment through a funnel and $Mg(IO_3)_2$ solution then carefully added.

Table 7-1-6

c_{MgSO_4} = 0.005M

Details as in Table 7-1-3

c_{MgSO_4}/M	c_{PhSO_3Na}/M	Current/mA	t_-^{obs}
0.004994_5	0.00669	0.61	0.6112
0.004994_5	0.00669	0.30	0.6086
0.004994_5	0.00669	0.61	0.6097
0.004994_5	0.00662	0.30	0.6109
0.004994_5	0.00662	0.30	0.6103
0.004993_1	0.00669	0.30	0.6124
0.004993_1	0.00669	0.61	0.6105
0.004993_1	0.00622	0.61	0.6125*
0.004993_1	0.00622	0.61	0.6101*
0.004993_1	0.00622	0.61	0.6096*
0.004968_8	0.00622	0.61	0.6101*

* HIO_3(s) was added to the cathode compartment to prevent hydroxide ions reaching the boundary, although a cathode extension was used in all these runs.

Sodium benzenesulphonate as indicator gave very low results for the transference numbers of the sulphate anion, except for two runs in which the observed values differed less than 0.1% from those obtained with $Mg(IO_3)_2$ as indicator (Table 7-1-5). Table 7-1-6 gives the results at 0.005M with $PhSO_3Na$. The possibility of hydroxide ions reaching the boundary and disturbing its speed was considered, although progression never had been observed. The cathode extension used in all the runs with $PhSO_3Na$ as indicator was modified by increasing its volume and in some cases $HIO_3(s)$ was added to it, but no improvement was obtained. The pH of $Mg(PhSO_3)_2$ solution formed in the m.b. cell when the current flows was calculated and found to be about 6.5 ; it therefore seems unlikely that hydroxide ions had reached the boundary. The calculation of pH took into account the hydrolysis of the cation Mg^{2+}

$$Mg^{2+} + H_2O \rightleftharpoons MgOH^{+} + H^{+} . \qquad K = 3.8\times10^{-12}\ \text{mole.dm}^{-3}\,(86)$$

and in the absence of any data, neglected association between $PhSO_3^-$ ions and any cation.

Cation runs

The cation boundary was followed by n-Bu_4NCl solution. In a first set of three runs, a Ag anode was employed as closed electrode as has been done at 0.05M $MgSO_4$. The results are shown in Table 7-1-7. In runs 1 and 3, the values found for the cation transference numbers were much higher than that obtained in run 2. Taking the average of the results in runs 1 and 3, the sum of the anion and cation transference numbers

Table 7-1-7

CATION RUNS

$C_{MgSO_4} = 0.005M$

Details as in Table 7-1-4

Run No.	C_{MgSO_4}/M	C_{Bu_4NCl}/M	Current/mA	t_+^{obs}
1	0.004994_5	0.00467	0.40	0.3932(a)
2	0.004994_5	0.00467	0.20	0.3882(b)
3	0.004994_5	0.00435	0.20	0.3936_5(a)

(a) A greyish-white mass was visible around the closed Ag anode.

(b) No such mass was observed in this run.

differed appreciably from unity by up to 0.0063, after all the corrections have been applied. However, t_+ from run 2 gave $t_+^{corr} + t_-^{corr} = 1.0011$ (In these calculations, the corrected anion transference number was taken as 0.6125.)

After each run, the cell was always checked for the presence of gas bubbles and after runs 1 and 3, the appearance of a white-greyish mass on the top of the Ag electrode and a white precipitate in the bottom of its compartment was noticed. The mass which had not been deposited smoothly around the electrode was easily removed with a spatula. In run 2, which gave a better transference result, no such mass was observed. Furthermore, it was the usual practice (e.g., for the 0.05M $MgSO_4$ runs) to regenerate the silver spent in each run by cathodising the AgCl formed in a saturated KNO_3 solution. In the runs above this could only be done if the deposit around the Ag electrode was first removed and extra silver also had to be plated from time to time to assure that enough silver was present on the top of the electrode for the next run. These observations suggested that silver was removed by the formation of some addition compound during runs 1 and 3 at 0.005M $MgSO_4$. It seems likely that this compound was of the type $AgCl.n\text{-}Bu_4NCl$, since Fernandez-Prini and Prue (103) had published evidence that the compound $2AgI.NR_4I$ was formed on AgI electrodes immersed in aqueous R_4NI solutions. Whatever the exact formula of the substance in our case, it is clear that its formation had a large effect on the transference number. The changed volume correction alone, however, seems unlikely to explain the results.

It was then decided to repeat the above runs using Ag/AgCl as closed electrode in $MgSO_4$ solution and to make the

Table 7-1-8

CATION RUNS

$C_{MgSO_4} = 0.005M$

Bu_4NCl following
Falling boundary

Ag anode open
Ag/AgCl cathode closed

C_{MgSO_4}/M	C_{Bu_4NCl}/M	Current/mA	t_+^{obs}
0.004993_1	0.00467	0.40	0.3873
0.004993_1	0.00467	0.20	0.3876
0.004993_1	0.00435	0.40	0.3878

t_+ does not depend on current or C_{foll}

Mean $t_+^{obs} = 0.3876$

Vol. corrn = -0.00006_4 (Table 6-9-5)
Solv. corrn = 1.001_1 (Table 6-10-1)

$\therefore t_+^{corr} = 0.3880$

Ag anode in the n-Bu_4NCl solution the open electrode. This time, the results obtained were much lower than those in Table 7-1-7 and fairly reproducible. They are summarized in Table 7-1-8 and do not show any significant variation with current or concentration of the following solution.

(c) Results in 0.025M and 0.01M $MgSO_4$ solutions

Results obtained at 0.025M and 0.01M $MgSO_4$ concentrations are summarized in Tables 7-1-9, 7-1-10, 7-1-11 and 7-1-12, respectively.

The cation runs at the above concentrations were also carried out with Ag/AgCl as closed electrode to prevent the possible appearance of the supposed addition compound. Both anion and cation transference numbers at these concentrations show no any significant variation with current or concentration of the following solution.

Table 7-1-9

ANION RUNS

C_{MgSO_4} = 0.025M

Details as in Table 7-1-1

C_{MgSO_4}/M	$C_{Mg(IO_3)_2}$/M	Current/mA	t_-^{obs}
0.02500_8	0.0193	2.01	0.6230
0.02500_8	0.0193	1.00	0.6230
0.02500_8	0.0180	2.01	0.6231_5

t_- does not depend on current or C_{foll}

Mean $t_-^{obs} = 0.6230_5$

Vol. corrn = -0.0002_2 (Table 6-9-7)

Solv. corrn = 1.000_3 (Table 6-10-1)

$\therefore t_-^{corr} = 0.6230$

Taking $t_+^{corr} = 0.3768$ (Table 7-1-10)

$t_+^{corr} + t_-^{corr} = 0.9998$

$\therefore t_+ = 0.3769$ (when corrected to give $t_+ + t_- = 1.0000$)

Table 7-1-10

CATION RUNS

C_{MgSO_4} = 0.025M

Details as in Table 7-1-8

C_{Bu_4NCl}/M	Current/mA	t_+^{obs}
0.0240	2.01	0.3770
0.0240	1.01	0.3770
0.0223	2.01	0.3771

t_+ does not depend on current or C_{foll}

Mean t_+^{obs} = 0.3770

Vol. corrn = -0.0003_4 (Table 6-9-5)
Solv. corrn = 1.000_3 (Table 6-10-1)

$\therefore$ t_+^{corr} = 0.3768

Table 7-1-11

ANION RUNS

$C_{MgSO_4} = 0.01M$

Details as in Table 7-1-1

C_{MgSO_4}/M	$C_{Mg(IO_3)_2}$/M	Current/mA	t_-^{obs}
0.0099891_8	0.00767	0.799	0.6156
0.0099891_8	0.00767	0.393	0.6155
0.0099891_8	0.00713	0.799	0.6152

t_- does not depend on current or C_{foll}

Mean $t_-^{obs} = 0.6154$

Vol. corrn = -0.0001_6 (Table 6-9-7)
Solv. corrn = 1.000_6 (Table 6-10-1)

$\therefore t_-^{corr} = 0.6156$

Taking $t_+^{corr} = 0.3842$ (Table 7-1-12)

$t_+^{corr} + t_-^{corr} = 0.9998$

$\therefore t_+ = 0.3843$ (when corrected to give $t_+ + t_- = 1.0000$)

Table 7-1-12

CATION RUNS

C_{MgSO_4} = 0.01M

Details as in Table 7-1-8

C_{Bu_4NCl}/M	Current/mA	t_+^{obs}
0.00946	1.02	0.3843
0.00946	0.498	0.3840
0.0088_0	1.01	0.3841

t_+ does not depend on current or C_{foll}

Mean t_+^{obs} = 0.3841

Vol. corrn = -0.0001_3 (Table 6-9-7)

Solv. corrn = 1.000_6 (Table 6-10-1)

$\therefore\ t_+^{corr}$ = 0.3842

7.2 Discussion

7.2.1 Comparison with previous results

Table 7-2-1 compares the cation transference numbers obtained in the present work with those of Kumarasinghe (22).

Table 7-2-1

C/M	t_+ (present work)	t_+ (ref. 22)
0.005	0.3878	0.388_7
0.01	0.3843	0.385_0
0.025	0.3769	0.376_9
0.05	0.3685	0.368_1

As mentioned in Chapter VI, the cation and anion transference numbers obtained in the previous work (22) did not add up to unity and their reproducibility was very poor. This was mainly due to the fact that the concentrations used for the $MgSO_4$ solutions were not the real ones. Kumarasinghe's results as listed in Table 7-2-1 were corrected to make the sum of the anion and cation transference numbers equal to unity. Nevertheless, Kumarasinghe (22) did not believe them to be accurate beyond 0.001.

In the present work, the reproducibility of the results was good and the sums of the anion and cation transference numbers were always close to unity, as can be seen by inspection of the tables in section 7.1. It is interesting to see that the cation transference numbers agree well with those of the previous work at 0.025M and 0.05M $MgSO_4$. However, at the two lower concentrations, the results obtained in the previous work are about 0.0008 higher. As mentioned in section 7.1, the formation of a suspected addition compound of the type $AgCl.n\text{-}Bu_4NCl$ during the cation runs at low $MgSO_4$ concentrations, when Ag was used as closed electrode, led to high values for the cation transference numbers. Kumarasinghe used a closed Ag anode in all the $MgSO_4$ cation runs, whereas in the present work, a closed Ag/AgCl cathode was employed instead to overcome this problem. This is the most likely explanation for the relatively high t_+ values reported earlier (22).

Another difference between the two researches is that the apparent molar volumes of $MgSO_4$ and $CdSO_4$, used for the volume corrections in the anion runs, were based on different calculations (cf. Chapter VI). However, this seems unlikely to explain the disagreement of the results at the two lower concentrations where the volume corrections are small. They become more important at the two higher concentrations where the results agree well. At the highest concentration of 0.05M, Kumarasinghe used $\Delta V = -0.0007_4$ $cm^3.faraday^{-1}$, while $\Delta V = -0.0005_3$ $cm^3.faraday^{-1}$ was used in the present work. The effect of this is to make the value of the transference number obtained here larger by 0.0002 than that obtained by Kumarasinghe (22).

7.2.2 Choice of an association constant for $MgSO_4$

Several values for the association constant, K_A, of $MgSO_4$ have been quoted in the literature and they are listed in Table 7-2-2-1. The agreement between them is clearly very poor. One

Table 7-2-2-1

Association constants for $MgSO_4$ at 25°C

$K_A/dm^3.mol^{-1}$	d/Å	Method	Ref.
238.1	14.3	Osmotic coeffs	104
179	4.3	E.m.f.s	105
135.0	6.18	Conductances using the (F-O) theory (106)	107
161	5.06	Conductances using the limiting Onsager equation $\Lambda/\alpha = \Lambda^0 - S(\alpha C)^{\frac{1}{2}}$	108
185	5.06	Cond. data recalcd from ref. 108 allowing for a drift in K with concentration	109
201.6	14.3	Cond data recalcd from ref. 108 using Bjerrum dist = 14.3 Å in act. coeffs	2f
227	——	E.m.f.s	109
110	5.4_6	Osmotic coeffs	110
111	5.4_4	Cond. data recalcd from ref. 108 using the Fuoss-Hsia equation (12)	110
106	5.5_8	Cond. data recalcd from ref. 107 using the Fuoss-Hsia equation (12)	110
173	10.7	Cond. data recalcd from ref. 108 using the Fuoss-Hsia equation (12)	111

reason for such a situation was pointed out by Guggenheim (112) on the basis of the Bjerrum theory of ion association. Each value of K_A in the table corresponds to a different value of the distance of closest approach of the free ions d, and thus the definition of what is meant by an ion-pair varies from case to case.

In more detail, according to the Bjerrum theory of ion association,

$$K_A = 4\pi N \left(\frac{|Z_+Z_-| e^2}{4\pi\varepsilon KT} \right)^3 Q(b)$$

where

$$Q(b) = \int_2^b e^x x^{-4} dx$$

$$b = \frac{|Z_+Z_-| e^2}{4\pi\varepsilon KTa}, \quad 2 = \frac{|Z_+Z_-| e^2}{4\pi\varepsilon KTq}$$

Here a is the distance of closest approach of the bound ions and q that of the free ions. The value of a, and hence of b, is fixed by the sizes of the (partially hydrated) ions, but q is to some extent a matter of choice. Bjerrum himself chose $q = |Z_+Z_-| e^2/8\pi\varepsilon KT$ from a simplified model, but other choices are possible. In general we will call this distance d, with $d = q$ as Bjerrum's choice. Since the fraction of ion-pairs is the fraction of ions that finds itself between a distance a and a distance d from a given central ion of opposite charge, K_A will increase as d increases. Thus, if one worker uses as the distance of closest approach of the free ions a value of d Å and obtains K_A, and another uses d′ Å and obtains K'_A, then we would expect

Table 7-2-2-2

Association constants, K'_A for $MgSO_4$ at the Bjerrum distance 14.3 Å

$K_A/mol^{-1}.dm^3$	$K'_A/mol^{-1}.dm^3$
238.1 (d = 14.3)	238
179 (d = 4.3)	404
135 (d = 6.18)	258^*
161 (d = 5.06)	327
185 (d = 5.06)	351
201.6 (d = 14.3)	202
227	——
110 (d = 5.4_6)	259^*
111 (d = 5.4_4)	257^*
106 (d = 5.5_8)	249^*
173 (d = 10.7)	217

that

$$K_A' - K_A = 4\pi N\left(\frac{|Z_+Z_-|e^2}{4\pi\varepsilon KT}\right)^3\left\{\int_{\frac{|Z_+Z_-|e^2}{4\pi\varepsilon KTd'}}^{b} e^x x^{-4}dx - \int_{\frac{|Z_+Z_-|e^2}{4\pi\varepsilon KTd}}^{b} e^x x^{-4}dx\right\}$$

$$= 4\pi N\left(\frac{|Z_+Z_-|e^2}{4\pi\varepsilon KT}\right)^3\left\{Q\left(\frac{|Z_+Z_-|e^2}{4\pi\varepsilon KTd}\right) - Q\left(\frac{|Z_+Z_-|e^2}{4\pi\varepsilon KTd'}\right)\right\} \qquad (7\text{-}2\text{-}2\text{-}1)$$

The distance d' was taken as the Bjerrum distance for $MgSO_4$ ($q = 14.3$ Å), so that the second Q term becomes zero. The K_A' values each author would have found if he had used the Bjerrum distance as the distance of closest approach of the free ions instead of d Å are shown in Table 7-2-2-2. The values indicated by an asterisk agree fairly well and their average, 256 $mol^{-1}.dm^3$, was taken as the best value of K_A at 14.3 Å. Another reason for choosing this set is that there are as many values of K_A' above it as there are below.

7.2.3 Results of computer calculations

As mentioned in Chapter II, the fit of the experimentally obtained cation transference numbers to the $(F\text{-}O)_1$, $(F\text{-}O)_2$ and P_A theories has been carried out by computer calculations. Because $MgSO_4$ is incompletely dissociated, ionic concentrations (αC) need to be substituted in the corresponding theoretical equations and the degree of dissociation, α, calculated from the equation

$$K_A = (1 - \alpha)/C\gamma_\pm^2 \qquad (7\text{-}2\text{-}3\text{-}1)$$

where $\gamma_\pm$ is the mean stoichiometric activity coefficient at the molarity C. Values of $\gamma_\pm$ were taken from Pitzer $^{(104)}$ obtained from theoretical considerations and are shown in Table 7-2-3-1.

Table 7-2-3-1

Activity coefficients for $MgSO_4$ at 25° C

$C/mol.dm^{-3}$	$\gamma_\pm$
0.005	0.493
0.01	0.398
0.025	0.291
0.05	0.218

The $\gamma_\pm$ values obtained by Pitzer (104) at 0° C agree well with those of Gardner and Glueckauf (113), based on a similar treatment. More recent $\gamma_\pm$ values for $MgSO_4$ at 0, 25 and 50° C have been reported by Millero and Masterton (94) from osmotic and thermal data. However, these are given for the concentration range 0.03-1.00m and therefore they were not used in the present work, where lower $MgSO_4$ concentrations were employed. A comparison between Pitzer's (104) $\gamma_\pm$ values for 0.05M $MgSO_4$ at 25° C and the corresponding values obtained by Millero and Masterton (94) gives agreement to 0.001.

Preliminary computer calculations were carried out using three different values of K_A (135, 173 and 179 $dm^3.mol^{-1}$) and the corresponding best-fit values of d (based on the minimum standard deviation) were found to decrease with increasing K_A. These d values, it must be emphasized, correspond to the distance of closest approach of the free ions, since ion-pairs do not conduct. Now the Bjerrum model, and equation (7-2-2-1), show that K_A increases with increasing d. Thus for each transference theory ($(F-0)_1$, $(F-0)_2$ and P_A), there must be a unique value of K_A at which the d value of best-fit is the same as the Bjerrum d value consistent with this K_A figure. To find it, computer calculations were carried out with a range of K_A values, and the best-fit d and Bjerrum d values (from equation (7-2-2-1)) were compared each time (using $K_A = 256\ dm^3.mol^{-1}$ at d = 14.3 Å as the reference point). The results are listed in Table 7-2-3-2.

Inspection of the figures shows that self-consistent results were obtained for the $(F-0)_1$, $(F-0)_2$ and P_A theories at $K_A/dm^3.mol^{-1} = 70$, 145 and 240, respectively. The details are given in Table 7-2-3-3.

Inspection of this table and the figures shows that of the three theories, P_A gives the poorest fit of the experimental results over both the concentration ranges.

For all three theories, a decrease is found in the standard deviations as the higher concentration is excluded, the least decrease being observed for the $(F-0)_1$ theory and the largest for the P_A theory (Table 7-2-3-3). The variation of $t_+^0(C)$ with C appears to be of the same type for all three theories, as can be observed in the figures.

P_A theory gives a value for the mean $t_+^0(C)$ about 0.006-0.007 higher than those obtained with $(F-0)_1$ and $(F-0)_2$. The limiting values all decrease as the higher concentration is excluded, the least decrease being found in the $(F-0)_1$ and the largest in the P_A theory. The Longsworth plot (114) in fig. 7-2-3-4 leads to $t_+^0\ (C=0) = 0.3987_5$, which is in agreement with that (0.3987) obtained from literature ionic limiting conductivities (115,116). The λ^0 value for Mg^{2+} was obtained from conductance measurements of aqueous $MgCl_2$ solutions (115) and

Table 7-2-3-2

K_A/ $mol^{-1}.dm^3$	d/Å (Bjerrum)	$Cx10^3$/ $mol.dm^{-3}$	d/Å (computer)		
			$(F-O)_1$	$(F-O)_2$	P_A
256	14.3	5-50	0.9	5.4	12.0
		5-25	0.9	5.4	13.4
179	8.2_8	5-50	2.8	6.3	—
		5-25	3.1	6.4	—
250	13.7	5-50	—	—	12.1
		5-25	—	—	13.5
245	13.4	5-50	—	—	12.2
		5-25	—	—	13.7
173	7.9_5	5-50	2.9	6.3	—
		5-25	3.2	6.5	—
145	6.6_1	5-50	—	6.4	—
		5-25	—	6.7	—
240	13.0	5-50	—	—	12.3
		5-25	—	—	13.8

Table 7-2-3-2 (cont.)

K_A/ $mol^{-1}.dm^3$	d/Å (Bjerrum)	$Cx10^3$/ $mol.dm^{-3}$	d/Å (computer)		
			$(F\text{-}O)_1$	$(F\text{-}O)_2$	P_A
135	6.1_2	5-50	3.5	6.5	——
		5-25	3.9	6.7	——
110	5.5_1	5-50	3.8	6.5	13.8
		5-25	4.3	6.9	15.7
70	4.7_4	5-50	4.3	6.6	——
		5-25	4.8	7.0	——

Table 7-2-3-3

Computer calculations of $MgSO_4$ data

Theory	K_A/ mol^{-1}.dm^3	$C\times10^3$/ mol.dm^{-3}	Best d/ Å	$\sigma_{min}\times10^4$	Mean t^0_+	Trend in t^0_+
$(F-O)_1$	70	5-50	4.3	2.90	0.3997_5	Fig. 7-2-3-1
		5-25	4.8	1.79	0.3994	Fig. 7-2-3-1
$(F-O)_2$	145	5-50	6.4	3.46	0.4002	Fig. 7-2-3-2
		5-25	6.7	2.14	0.3996	Fig. 7-2-3-2
P_A	240	5-50	12.3	7.06	0.4077_5	Fig. 7-2-3-3
		5-25	13.8	4.20	0.4063	Fig. 7-2-3-3

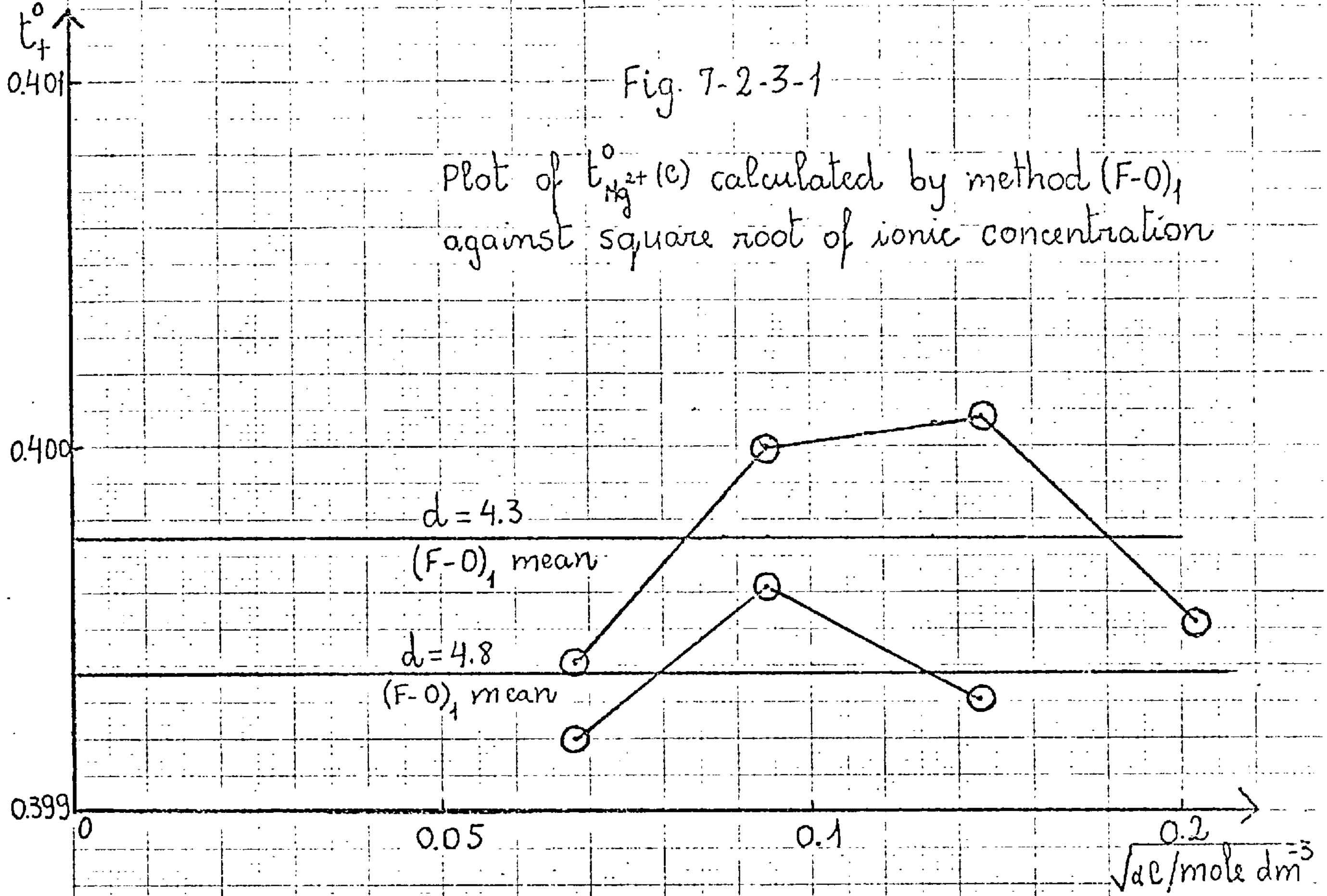


Fig. 7-2-3-1

Plot of $t^{o}_{Mg^{2+}}(c)$ calculated by method $(F-O)_1$ against square root of ionic concentration

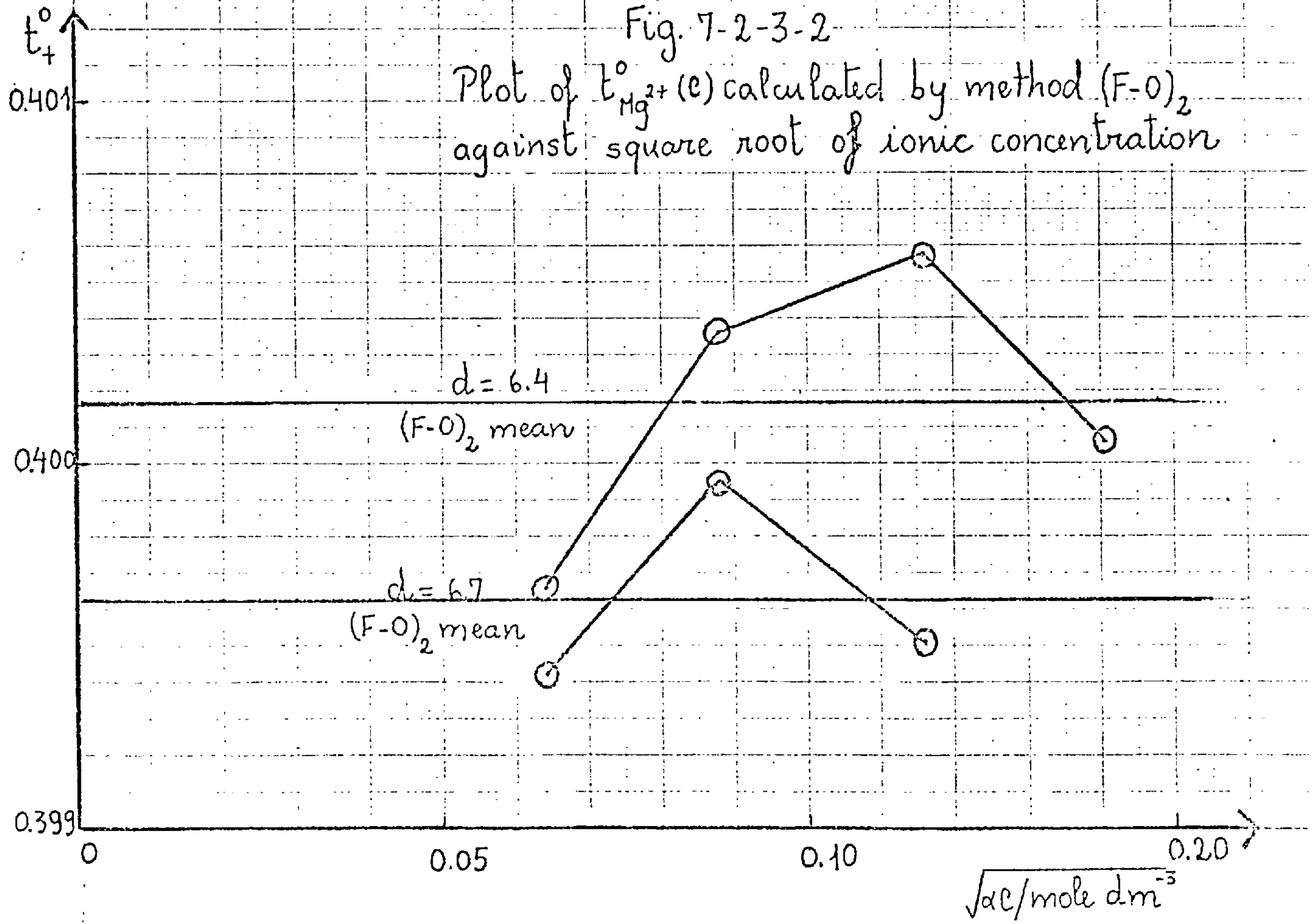
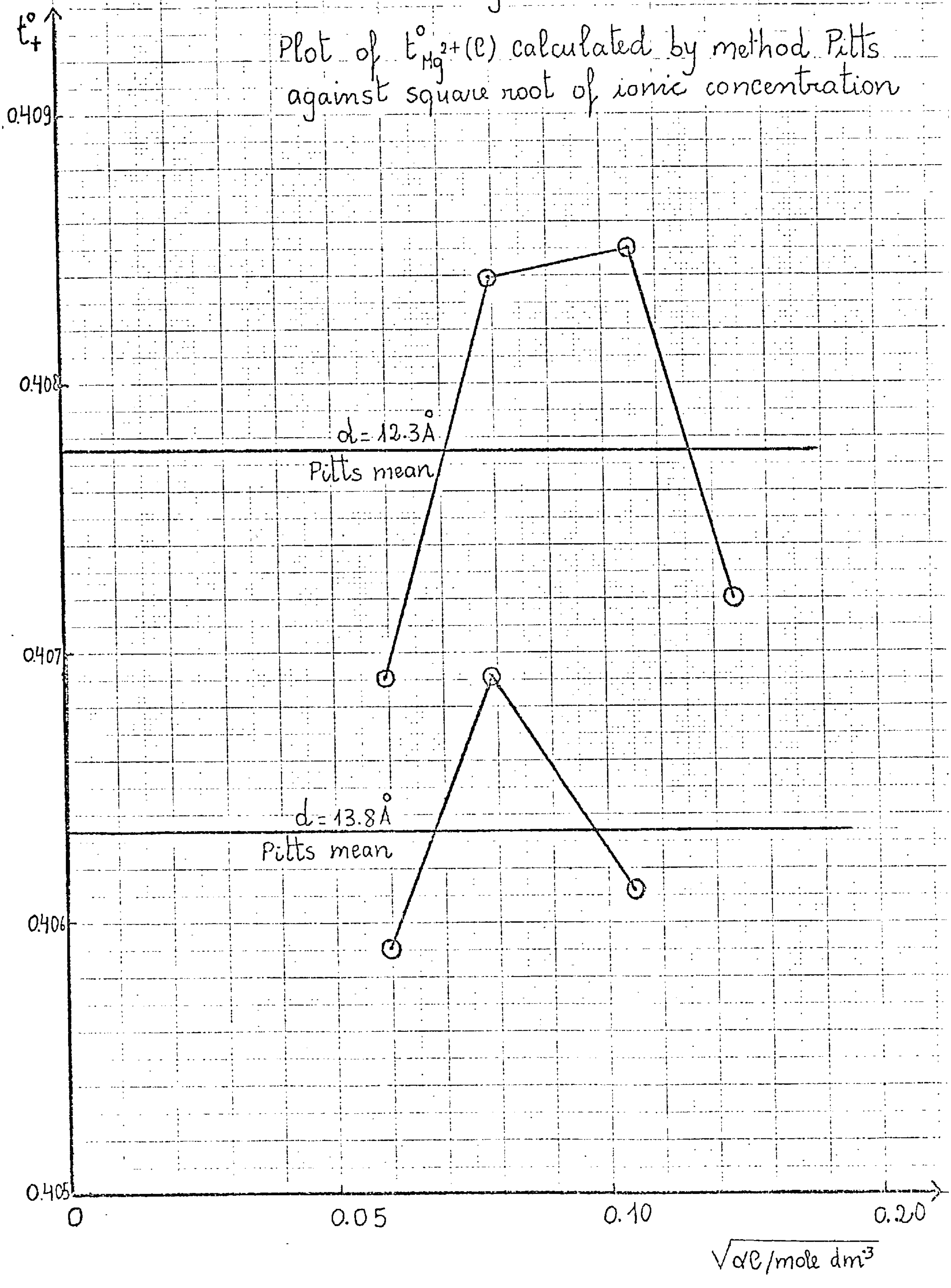


Fig. 7-2-3-2

Plot of $t^{o}_{Mg^{2+}}(c)$ calculated by method $(F-O)_2$ against square root of ionic concentration

Fig. 7-2-3-3

Plot of $t^{\circ}_{Mg^{2+}}(c)$ calculated by method Pitts against square root of ionic concentration



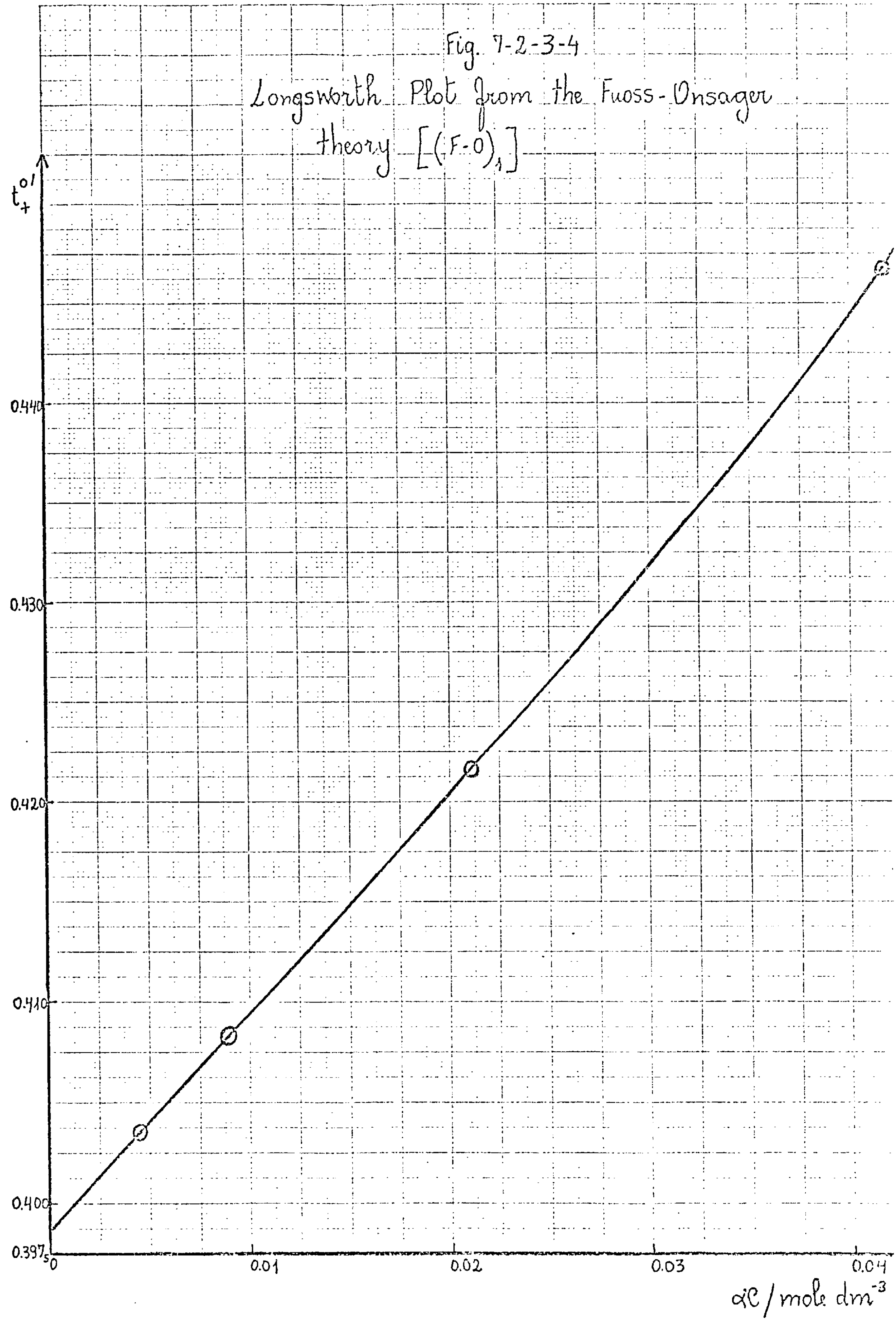


Fig. 7-2-3-4
Longsworth Plot from the Fuoss-Onsager theory $[(F\text{-}O)_1]$

that of SO_4^{2-} from conductance measurements of aqueous Na_2SO_4 and K_2SO_4 solutions (116). However, these conductance extrapolations were based on older conductance theories. All three transference theories give t_+^0 values higher than these, the P_A theory producing the highest value as mentioned above.

Fig. 7-2-3-5 shows the variation of the experimental values for the cation transference numbers with square root of ionic molarity, corresponding to the K_A value for each theory. The limiting values t_+^0 shown are the mean t_+^0 values obtained by the computer calculations. The limiting Onsager slope has been drawn through the intercept ($t_+^0 = 0.3987$) (115,116). The experimental points lie above this line for the $(F-O)_1$ and $(F-O)_2$ theories, which is in agreement with a positive value for the distance of closest approach, d. The experimental limiting slope for the above theories is about the same as the theoretical one. For the P_A theory the experimental limiting slope is much higher than the limiting Onsager slope, the experimental points lying below it, which compares curiously with the positive value of d given as the "best" for this theory.

Conductance measurements have recently been carried out by S. Taba and A. D. Pethybridge (117) on aqueous anhydrous $MgSO_4$ solutions at 25°C over the concentration range 2.46×10^{-4} – 38.5×10^{-4}M. The fit of the experimental values to the P_A theory was then tested by computer calculations (117). The best Λ^0 value found using the criterion of the minimum standard deviation was 132.507 corresponding to a d value of 6.650 Å for which the mean K_A obtained equals 144.43. They obtained Λ^0 = 131.899 if d was taken as the Bjerrum distance q. Assuming a linear relationship between these two Λ^0 values, the Λ^0 value corresponding to the best d value obtained in the present work

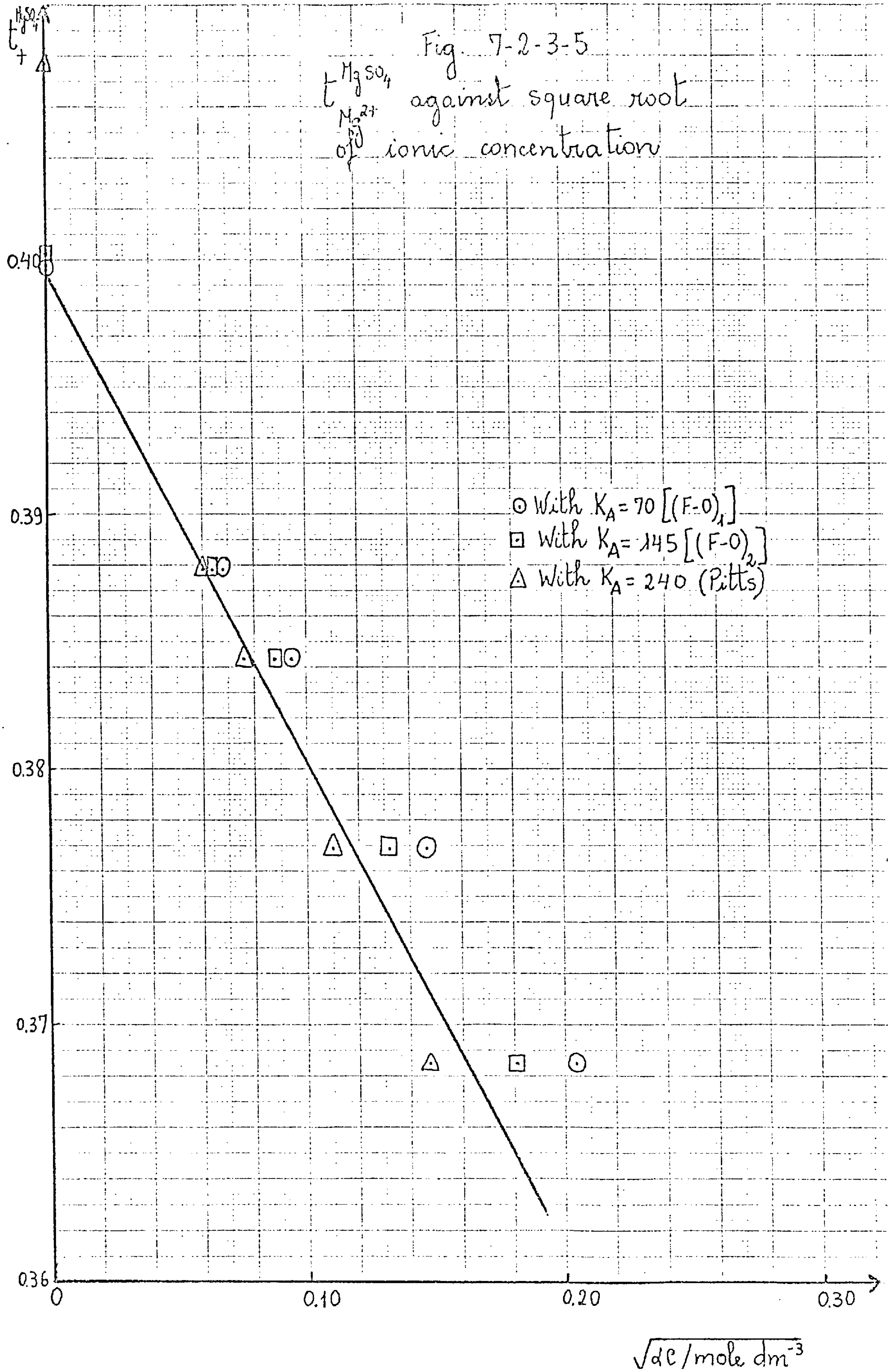


Fig. 7-2-3-5

$t^{MgSO_4}_{Mg^{2+}}$ against square root of ionic concentration

(13.8 Å, when the higher concentration is excluded) is then 131.9_4 (P_A theory). From this value and the mean $t_+^0 = 0.4063$ appropriate to that d value, the limiting ionic equivalent conductance found for Mg^{2+} is 53.6_1, which is about 0.6 higher than the literature figure (115). Similarly the λ^0 value obtained for SO_4^{2-} is 78.3_3, which is about 1.7 lower than that in the literature (116). These differences seem rather large and suggest strongly that the Pitts limiting transference value is too high.

S. Taba and A. D. Pethybridge (117) have also tested the fit of the experimental conductances to the 1975 Fuoss equation (13) by computer calculations and found that the best Λ^0 value was 131.679 corresponding to a d value of 5.44 Å. If d was taken as the Bjerrum distance q, the Λ^0 value obtained was 133.737. Assuming a linear relationship between these two Λ^0 values, the Λ^0 value corresponding to the best d value obtained in the present work for the $(F-O)_2$ theory (6.7 Å, when the higher concentration is excluded) is 131.6_8. If this Λ^0 value is combined with the mean $t_+^0 = 0.3996$ appropriate to that d value, the λ^0 value found for Mg^{2+} is 52.6_2, which is about 0.4 lower than the literature figure (115). The λ^0 value obtained for SO_4^{2-} is 79.0_6 which is about 1.0 lower than that in the literature (116). Similar λ^0 values are found by combining the Λ^0 value corresponding to the best d value obtained in the present work for the $(F-O)_1$ theory (4.8 Å, when the higher concentration is excluded) with the corresponding mean $t_+^0 =$ 0.3994. These results look quite reasonable, especially bearing in mind that the 1975 Fuoss conductance formula differs slightly from the Fuoss-Onsager equations on which the $(F-O)_1$ and $(F-O)_2$ transference formulae are based.

The best transference d values obtained from the $(F-O)_1$ equation seem very reasonable when compared with that (3.46 Å) given by crystallographic evidence (118) for the metal-sulphur distance of anhydrous $CuSO_4$ and $ZnSO_4$. The best transference d value given by the P_A theory is much higher than that obtained from conductance measurements and those produced by the $(F-O)_1$ and the $(F-O)_2$ theories. The d value given by the P_A theory obtained in the present work is of course based on a value of $K_A = 240$, whereas the best value of d found from conductance measurements (117) is consistent with $K_A = 144.43$.

In conclusion, the computer calculations indicate a better fit of the experimental transference data to the two Fuoss-Onsager theories than to the Pitts equation, the $(F-O)_1$ theory being the most satisfactory.

The computer programmes applying method A to the $(F-O)_1$, $(F-O)_2$ and Pitts equations are given in Appendixes I, II and III, respectively.

APPENDIX I

This is the programme appropriate to the application of method A to the Fuoss-Onsager equation with the old electrophoretic term $(F\text{-}O)_1$. In addition to the main programme SUBROUTINE ATLFO1 computes the average limiting transference number, and SUBROUTINE STDFO1 computes the standard deviation of the calculated limiting transference numbers from their average value.

```
C APPLICATION OF FUCSS ONSAGER CONDUCTANCE EQUATION
C OLD ELECTROPHORETIC TERM
      DIMENSION T(20),C(20),ALPHA(20),TLIM(20),Y(20),GAMMA(20)
      COMMON Y,B,I,L,TLIM,TAVG,SIGMA,NC,SIGMN,B,A,J,C,U,CONLIM,ALPHA,
     1DC,VIS,TEM,T,Z,NB,M,GAMMA
 706  I = 0
      Z = 2.0
      WRITE (6,50) Z
 50   FORMAT (12X, F5.2)
      READ (5,1000) DC,VIS,TEM
 1000 FORMAT (10X, F10.4, F10.7, F10.4)
      WRITE (6,500) DC,VIS,TEM
 500  FORMAT (10X, F10.4, F10.7, F10.4)
      READ (5,1001) CONLIM
 1001 FORMAT (10X, F10.4)
      WRITE (6,501) CONLIM
 501  FORMAT (10X, F10.4)
 10   I = I + 1
      READ (5,1002) T(I),C(I),GAMMA(I)
 1002 FORMAT (10X,F10.6,F10.7,F10.4)
      WRITE (6,502) T(I),C(I),GAMMA(I)
 502  FORMAT(10X,F10.6,F10.7,F10.4)
      IF (C(I).NE.0.0) GO TO 10

      M = I
 254  READ(5,252)ASSCON,AA
 252  FORMAT(10X,,F10.5,F10.5)
      IF(ASSCON.EQ.0.0)GO TO 253

      WRITE(6,255)ASSCON

 255  FORMAT(/////10X,3HKA=,F10.5)
      DO 256 K=1,4
      ALPHA(K)=(1.0-ASSCON*(GAMMA(K)**2.0)*C(K))
 256  CONTINUE

 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',7X,'ALPHA',8X,'C'
     1,10X,'Y',11X,'TAVG')
      CALL ATLF01
 104  A = B - 1.0
      U = 0.1
      CALL ATLF01
      IF (L.GT.3) GO TO 100
      GO TO 254
  253 STOP
      END
```

```
      SUBROUTINE ATLF01
      DIMENSION T(20),C(20),ALPHA(20),TLIM(20),Y(20),GAMMA(20)
      COMMON Y,R,I,L,TLIM,TAVG,SIGMA,NC,SIGMN,B,A,J,C,U,CONLIM,ALPHA,
     1DC,VIS,TEM,T,Z,NB,M,GAMMA
      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*((ALPHA(I)*C(I)*(Z**2)/(DC*TEM))**0.5)
      Y(I) = CAPA*A
      NC = NC+1
      B2 = 82.5*(Z**2)/(VIS*((DC*TEM)**0.5))
      R = 1.0 + Y(I)
      TLIM(I) = T(I)-((T(I)-0.5)*B2*((ALPHA(I)*C(I))**0.5)/(CONLIM*R))
      TSUM = TSUM + TLIM(I)
      TAVG = TSUM/NC

13    CONTINUE
      CALL STDF01
      GO TO 12
      END
```

```
      SUBROUTINE STDF01
      DIMENSION T(20),C(20),ALPHA(20),TLIM(20),Y(20),GAMMA(20)
      COMMON Y,R,I,L,TLIM,TAVG,SIGMA,NC,SIGMN,B,A,J,C,U,CONLIM,ALPHA,
     1DC,VIS,TEM,T,Z,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,F10.8,50X,F8.5)
141   WRITE (6,1006) (TLIM(I),ALPHA(I),C(I),Y(I), I=1,L)
1006  FORMAT (40X,F8.5,4X,F7.5,4X,F8.6,4X,F6.4)
      RETURN
      END
```

APPENDIX II

This is the programme appropriate to the application of method A to the Fuoss-Onsager transference equation with the new electrophoretic term $(F\text{-}O)_2$. In addition to the main programme SUBROUTINE ATLFO2 computes the average limiting transference number and SUBROUTINE STDFO2 computes the standard deviation of the calculated limiting transference numbers from their average value. The calculation of the new electrophoretic term requires the addition of SUBROUTINE FUNCB (EPS, ETA, THETA, DIS, FB), SUBROUTINE SUBEN (X, EN) and SUBROUTINE SUBEP (BX, EP).

```
C THE CONCENTRATION DEPENDENCE OF TRANSFERENCE NUMBERS
C APPLICATION OF FUCSS ONSAGER CONDUCTANCE EQUATION
C NEW ELECTROPHORETIC TERM
      DIMENSION T(20),C(20),ALPHA(20),TLIM(20),Y(20),GAMMA(20)
      COMMON Y,R,I,L,TLIM,TAVG,SIGMA,NC,SIGMN,B,A,J,C,U,CONLIM,ALPHA,
     1DC,VIS,TEM,T,Z,NB,M,GAMMA
 706  I = 0
      Z = 2.0
      WRITE (6,50) Z
 50   FORMAT (12X, F5.2)
      READ (5,1000) DC,VIS,TEM
 1000 FORMAT (10X, F10.4, F10.7, F10.4)
      WRITE (6,500) DC,VIS,TEM
 500  FORMAT (10X, F10.4, F10.7, F10.4)
      READ (5,1001) CONLIM
 1001 FORMAT (10X, F10.4)
      WRITE (6,501) CONLIM
 501  FORMAT (10X, F10.4)
 10   I = I + 1
      READ (5,1002) T(I),C(I),GAMMA(I)
 1002 FORMAT (10X,F10.6,F10.7,F10.4)
      WRITE (6,502) T(I),C(I),GAMMA(I)
 502  FORMAT(10X,F10.6,F10.7,F10.4)
      IF (C(I).NE.0.0) GO TO 10

      M = I
 254  READ(5,252)ASSCON,AA
 252  FORMAT(10X,,F10.5,F10.5)
      IF(ASSCON.EQ.0.0)GO TO 253
      WRITE(5,255)ASSCON
 255  FORMAT(/////10X,3HKA=,F10.5)
      DO 256 K=1,4
      ALPHA(K)=(1.0-ASSCON*(GAMMA(K)**2.0)*C(K))
 256  CONTINUE

 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',11X,'SIGMA',9X,'TLIM',7X,'ALPHA',8X,'C'
     1,10X,'Y',11X,'TAVG')
      CALL ATLFO2
 104  A = B - 1.0
      U = 0.1
      CALL ATLFO2
      IF (L.GT.3) GO TO 100
      GO TO 254
  253 STOP
      END
```

```
      SUBROUTINE ATLF02
      DIMENSION T(20),C(20),ALPHA(20),TLIM(20),Y(20),GAMMA(20)
      COMMON Y,R,I,L,TLIM,TAVG,SIGMA,NC,SIGMN,B,A,J,C,U,CONLIM,ALPHA,
     1DC,VIS,TEM,T,Z,NB,N,GAMMA
      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,Z)
      DO 13 I=1,L
      CAPA = 50.291*((ALPHA(I)*C(I)*(Z**2)/(DC*TEM))**0.5)
      Y(I) = CAPA*A
      NC = NC+1
      B2 = 82.48*(Z**2)/(VIS*((DC*TEM)**0.5))
       B31 = 17329.0*ALPHA(I)*C(I)*(Z**5)/(VIS*((DC*TEM)**2))
      B3=1000.0*B31*FBB
      TLIM(I)=T(I)-(T(I)-0.5)*(B2*((ALPHA(I)*C(I))**0.5)-B3)/CONLIM
      TSUM = TSUM + TLIM(I)
      TAVG = TSUM/NC

13    CONTINUE
      CALL STDF02
      GO TO 12
      END
      SUBROUTINE STDF02


      DIMENSION T(20),C(20),ALPHA(20),TLIM(20),Y(20),GAMMA(20)
      COMMON Y,R,I,L,TLIM,TAVG,SIGMA,NC,SIGMN,B,A,J,C,U,CONLIM,ALPHA,
     1DC,VIS,TEM,T,Z,NB,N,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,F10.8,50X,F8.5)
141   WRITE (6,1006) (TLIM(I),ALPHA(I),C(I),Y(I), I=1,L)
1006  FORMAT (40X,F8.5,4X,F7.5,4X,F8.6,4X,F6.4)
      RETURN
      END

      SUBROUTINE FUNCB (EPS,ETA,THETA,DIS,FB,Z)
      BE = 167098.5*(Z**2)/(DIS*EPS*THETA)


C THIS PROGRAMME CALCULATES F(B) - THE ELECTROPHORETIC CORRECTION TERM
 2007 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
      TIB = (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 = -TIB/(1.0 - TIB)
      FIB = (EM*FNB) + (EMA*FPB)
      FX = (1.0/(1.0 - TIB)) - (1.0/(T2B - 1.0))
      FB = (2.0/BE) + ((BE*FX)/4.0) - FIB
      RETURN
      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 III

This is the computer programme appropriate to the application of method A to the Pitts transference equation. In addition to the main programme SUBROUTINE AVTLIM computes the average limiting transference number, and SUBROUTINE STDEV computes the standard deviation of the calculated transference numbers from their average values. SUBROUTINE PITTS calculates S_1 and T_1 from the interpolation polynomials.

```
C THE CONCENTRATION DEPENDENCE OF TRANCFEFENCE NUMBERS
C APPLICATION OF THE PITTS CONDUCTANCE EQUATION TO TRANSFERENCE
C       MAIN PROGRAM 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,
       1CONLIM,Z,DC,VIS,TEM,T,ALPHA,NB,M,GAMMA
        KI=0
 708    I=0
        Z = 2.0
        WRITE (6,50) Z
 50     FORMAT (12X, F5.2)
        READ (5,1000) DC,VIS,TEM
 1000   FORMAT (10X, F10.4, F10.7, F10.4)
        WRITE (6,500) DC,VIS,TEM
 500    FORMAT (10X, F10.4, F10.7, F10.4)
        READ (5,1001) CONLIM
 1001   FORMAT (10X, F10.4)
        WRITE (6,501) CONLIM
 501    FORMAT (10X, F10.4)
 10     I = I + 1
        READ (5,1002) T(I),C(I),GAMMA(I)
 1002   FORMAT (10X,F10.6,F10.7,F10.4)
        WRITE (6,502) T(I),C(I),GAMMA(I)
 502    FORMAT(10X,F10.6,F10.7,F10.4)
        IF (C(I).NE.0.0) GO TO 10

        M = I
 254    READ(5,252)ASSCON,AA
 252    FORMAT(10X,,F10.5,F10.5)
       IF(ASSCON.EQ.0.0)GO TO 253

       WRITE(6,255)ASSCON
 255   FORMAT(/////10X,3HKA=,F10.5)
       DO 256 K=1,4
       ALPHA(K)=(1.0-ASSCON*(GAMMA(K)**2.0)*C(K))
 256   CONTINJE

 102   L = M
 100   L = L-1
       A = 0.0
       SIGMN = 1.0
 105   U = 1.0
       WRITE (6,3000)
 3000  FORMAT (8X,'J',8X,'A',10X,'SIGMA',9X,'TLIM',9X,'ALPHA',6X,'G',
      110X,'LAMDA')
       WRITE (6,4000)
 4000  FORMAT (90X,'Y',11X,'S1',8X,'T1',15X,'TAVG')
       CALL AVTLIM
       A = B-1.0
       IF (A.NE.0.0) GOTO 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
       GO TO 254
  253  STOP
       END
```

```
      SUBROUTINE AVTLIM
      DIMENSION T(20),ALPHA(20),C(20),TLIM(20),COND(20),Y(20),S1(20),
     1T1(20)
      COMMON Y,S1,T1,R,Q,I,L,TLIM,TAVG,SIGMA,NC,SIGMN,B,A,J,C,COND,U,
     1CONLIM,Z,DC,VIS,TEM,T,ALPHA,NB,M,GAMA
      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*((ALPHA(I)*C(I)*(Z**2)/(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))*(Z**2)+ 104672.0*(Z**2)*S1(I)*((CAPA
     6/DC)**2))*(Z**2)
      Y2 = ((((CAPA/R)**2)*126.713)/(DC*VIS*Q))*(Z**4)
      Y3 = (1.0 - ((186.791*CAPA*T1(I))/DC) *(Z**2))*1.6398*(CAPA*(Z**2))
     1/(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
      END
      SUBROUTINE STDEV
      DIMENSION T(20),C(20),ALPHA(20),TLIM(20),COND(20),Y(20),S1(20),
     1T1(20)
      COMMON Y,S1,T1,R,Q,I,L,TLIM,TAVG,SIGMA,NC,SIGMN,B,A,J,C,COND,U,
     1CONLIM,Z,DC,VIS,TEM,T,ALPHA,NB,M,GAMA
      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,F10.8,95X,F8.5)
141   WRITE (6,1006) (TLIM(I),ALPHA(I),C(I),COND(I),Y(I),S1(I),T1(I),
     1I = 1,L)
1006  FORMAT (40X,F8.5,4X,F6.4,4X,F8.6,4X,F8.3,4X,F6.4,6X,F6.4,6X,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,
     1CONLIM,Z,DC,VIS,TEM,T,ALPHA,NB,M,GAMA
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 = 37.54*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 = 5.7148*Y(I) + 2.0455*(Y(I)**0.5) + 0.4311
336   T1(I) = R/T2
      RETURN
      END
```

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