

TRANSFERENCE NUMBERS IN CONCENTRATED
AQUEOUS ELECTROLYTE SOLUTIONS

by

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ABSTRACT

The upper concentration limit for the direct moving boundary method for measuring transference numbers has been considerably extended by introducing three new concepts. First, an analysis of literature density data pinpointed electrolytes whose apparent molar volumes changed relatively little with concentration: it is these salts which are most useful on the closed side of the cell. Second, a cell was devised that allowed stirring of the closed electrode chamber to avoid the build up of concentration inhomogeneities and, finally, the solution in this chamber was presaturated with the insoluble salt involved in the electrode reaction. The new technique was successfully tested with the system $\text{KCl} \leftarrow \text{LiCl}$ using 3M KCl whose transference number is known. The same method was then applied to the system $\text{HCl} \leftarrow \text{LiCl}$ for leading solute concentrations of 1, 2, and 4M. At the two highest concentrations, $T_+(\text{obs.})$ varied with current, and this current dependence has been analysed.

Transference numbers of HCl solutions in the range 0.1-7M were also measured by the e.m.f. method. Both chlorine and hydrogen electrodes were employed in the concentration cell with transference, producing potentials related to T_+ and T_- , respectively. The sum $T_+ + T_-$ was found to be unity within experimental error. In order to obtain individual ionic conductances and mobilities, conductance measurements by the a.c. method were also carried out over the same concentration range. These transference and conductance results were then combined with literature diffusion and activity coefficient data to give values for the Onsager transport coefficients, l_{ij} .

The thesis also contains a thorough review of transference numbers determined by various Soviet workers, and their published results have been critically examined. An extensive literature search for all previous transference work at high concentration was carried out and the results are listed in appendices, along with recent literature conductance, diffusion and viscosity measurements for concentrated electrolyte solutions.

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PART ONE

THEORETICAL SECTION

CHAPTER ONE

TRANSPORT PROPERTIES OF CONCENTRATED ELECTROLYTE

SOLUTIONS

I.1 Introduction

Since the 1920s most work on electrolyte solutions has been directed towards the testing of the Debye-Hückel-Onsager (D-H-O) interionic theory. Workers directed their efforts towards measuring properties in ever more dilute solutions. It was not until the 1960s that the practical and theoretical importance of concentrated solutions was realised, and attempts were then made to remedy the lack of accurate data and theory to describe these systems.

Recent models based on transition state theory have accounted very well for the temperature, pressure and concentration dependence of conductance and viscosity of concentrated electrolyte solutions.⁽¹⁻⁵⁾ To further test these models there is a great need for accurate conductance and viscosity data.

More emphasis will be put in this thesis on the representation of transport properties by the use of phenomenological coefficients. These coefficients are more fundamental than the classical transport properties and relate directly to ion-ion and ion-solvent interactions. Of the three types of phenomenological coefficient, the linear Onsager or ionic transport coefficients (l_{ij}) will be dealt with in detail and only brief mention will be made of the alternative friction coefficients (R_{ij}) and velocity correlation coefficients (f_{ij}).

First, the reasons for the breakdown of the D-H-O model and the attempts made to extend its concentration range will be described briefly.

I.2 The D-H-O Model of Electrolyte Solutions

The success of the D-H-O model for very dilute electrolyte solutions ($<0.01M$, $M \equiv \text{mol dm}^{-3}$) has made it the obvious starting point for the theoretical description of more concentrated solutions. However the various attempts at extending the concentration range of the model have not met with the same success. One of these attempts, involving the conductance, will be dealt with later. Firstly the model and the reasons for its breakdown at higher solute concentrations will be discussed.

The underlying principle behind the D-H-O model is that the structure of the solution is the result of the competition between the order-producing electrical interactions of the ions and the destructive forces of random thermal motion.⁽⁶⁾ The distribution of particles in the solution is calculated from the time-averaged distribution of electrical potential ($\bar{\Psi}$) which in turn is related to the time-averaged charge density ($\bar{\rho}$) via Poisson's equation. This is the most general expression of Coulomb's law of force between charged species. The solvent is treated as a continuum of constant dielectric constant (relative permittivity) ϵ .

The Boltzmann distribution relates $\bar{\Psi}$ (in V) and $\bar{\rho}$ (in C m^{-3})⁽⁶⁾

$$\bar{\rho}_j = \sum_i n_i z_i e \exp \left(\frac{-z_i e \bar{\Psi}_j}{kT} \right) \quad (\text{I.1})$$

where n_i is the bulk concentration of ions i per m^3 , z_i is the algebraic charge number of ion i , e is the protonic charge ($1.6021 \times 10^{-19} \text{ C}$), $T(\text{K})$ is the absolute temperature, k is Boltzmann's constant ($1.3805 \times 10^{-23} \text{ J K}^{-1}$) and the j subscript indicates that $\bar{\Psi}$ and $\bar{\rho}$ are measured relative to ion j as the origin.

However, the principle of linear superposition of fields demands a linear relationship between $\bar{\psi}$ and $\bar{\rho}$ and not, as in equation (I.1), an exponential one.⁽⁶⁾ This problem is overcome by expressing (I.1) as a series expansion of the form

$$e^{-x} = 1 - x + \frac{x^2}{2!} - \frac{x^3}{3!} + \dots \quad (\text{I.2})$$

so that

$$\bar{\rho}_j = \sum_i n_i z_i e^{-\frac{z_i e \bar{\psi}_j}{kT}} = \sum_i n_i z_i e^{-\frac{z_i e \bar{\psi}_j}{kT}} + \sum_i \frac{n_i z_i e}{2!} \left(\frac{z_i e \bar{\psi}_j}{kT} \right)^2 - \dots \quad (\text{I.3})$$

The condition of electroneutrality requires that

$$\sum_i n_i z_i = 0 \quad (\text{I.4})$$

Moreover, if the thermal energy is large in comparison to the electrical energy, then $z_i e \bar{\psi}_j \ll kT$ and (I.3) approximates to ⁽⁶⁾

$$\bar{\rho}_j = - \sum_i \left(\frac{n_i z_i^2 e^2 \bar{\psi}_j}{kT} \right) \quad (\text{I.5})$$

Equation (I.5) satisfies the theorem of linear superposition of fields with a linear relationship between $\bar{\psi}_j$ and $\bar{\rho}_j$. An expression is then obtained for $\bar{\psi}_j$ by solving a second-order differential equation. The summation of $\bar{\psi}$ over all ions in the solution gives the change in Gibbs free energy caused by the coulombic interactions. The free energy change is directly related to the ion activity and so leads to the Debye-Hückel equation⁽⁶⁾

$$\log f_j = \frac{-z_j^2 A \sqrt{I}}{1 + B a \sqrt{I}} \quad (\text{I.6})$$

where f_j is the activity coefficient of ion j , A and B are constants for a given solvent at a given temperature, a is the distance of closest approach of the ions and I is the ionic strength defined by

$$I = \frac{1}{2} \sum_i c_i z_i^2 \quad (I.7)$$

where c_i is the molar concentration of ion i .

There are three factors which limit the concentration range of the D-H-O model. Firstly, in the above derivation the ions have been treated as point charges. This is a valid assumption when the ions are far apart but becomes less satisfactory as the ionic concentration increases. Attempts to allow for the finite size of the ion do not extend the concentration range appreciably. Secondly, the solvent has been treated as a continuum of uniform dielectric constant. Finally, the truncation of the series expansion in equation (I.3) is valid only at high dilutions because the closer the ions are to one another the greater the electrical potential $\bar{\psi}_j$. Consequently as the solute concentration is increased the electrical energy becomes less and less negligible in comparison to the thermal energy.

The effect of an increase in the solute concentration on these last two factors is easily seen. For a $10^{-2}M$ aqueous solution of a uni-univalent electrolyte there are approximately 3000 water molecules per ion. However if the concentration is 5M then this figure falls to between 5 and 6. Whilst dilute solutions essentially possess the structure and properties of the bulk solvent only slightly perturbed by the presence of ions, the concentrated solutions may be better described as molten salts containing some water.

If the average volume per ion in solution is represented as a cube, then the length of one side is a measure of the interionic spacing in the solution. In

the 10^{-2}M solution each ion has an average volume of $\text{ca. } 83\text{nm}^3$ so that the interionic separation is approximately 9nm . In the concentrated solution this distance falls to 0.6nm which may be compared to the ionic crystal radii of the K^+ and Cl^- ions of 0.133nm and 0.181nm respectively.⁽⁷⁾

On average, an ion in solution will have more ions of the opposite charge surrounding it than ions of the same charge type. These oppositely charged ions constitute the so-called ionic atmosphere.

According to the D-H-O model the ionic conductance, λ_i , of an ion is reduced from its limiting value, λ_i^0 , by two effects. Firstly, the flow of solvent associated with the ions in the ionic atmosphere opposes the motion of the central ion, reducing its mobility. This is the electrophoretic effect. Secondly, when the central ion moves there is a short time delay before the ionic atmosphere moves to restore the spherical symmetry. This exerts an electrostatic drag on the central ion, again reducing its mobility. This is known as the relaxation effect. These two effects reduce λ_i according to⁽⁸⁾

$$\lambda_i = (\lambda_i^0 - \lambda_e) (1 - \Delta X/X) \quad (\text{I.8})$$

where λ_e is the electrophoretic term and $\Delta X/X$ is the fractional change in the applied field X attributable to the relaxation effect.

For more concentrated solutions the Wishaw-Stokes equation for the molar conductance Λ is⁽⁹⁾

$$\Lambda = \left(\Lambda^0 - \frac{B_2 c^{\frac{1}{2}}}{1 + B_2 a c^{\frac{1}{2}}} \right) \left(1 - \frac{B_1 c^{\frac{1}{2}}}{1 + B_2 a c^{\frac{1}{2}}} F \right) \frac{\eta^0}{\eta} \quad (\text{I.9})$$

where Λ^0 is the limiting molar conductance, B_2 and B_1 are the Onsager electrophoretic and relaxation terms respectively and F is a factor proposed by Falkenhagen. Wishaw and Stokes also included a correction term for the viscosity η , where η^0 is the viscosity of the pure solvent at the same temperature. Wishaw and Stokes found that equation (I.9) accounted for the concentration dependence of Λ for ammonium chloride up to 4M within about 1%.⁽⁹⁾

I.3 Representation by Phenomenological Coefficients

Classical thermodynamics is concerned with systems and processes at or not very far from equilibrium. Other processes, such as irreversible transport, are best dealt with using non-equilibrium thermodynamics, also known as the thermodynamics of irreversible processes (TIP). This general framework affords a description of isothermal vector transport processes in electrolyte solutions which is more fundamental than the classical description of conductance, transference, and diffusion.

I.3.1 Onsager Transport Coefficients

The Onsager transport coefficients, l_{ij} , are the most widely used and perhaps the most useful (see section I.3.4) of the various types of phenomenological coefficient.

Miller⁽¹⁰⁾ has summarised the fundamental principles of TIP. These are:

- (1) to calculate the entropy produced irreversibly inside the system,
- (2) to relate this entropy production to a set of independent flows and forces,
- (3) to write the flows as linear functions of all the independent forces, and

(4) to exploit the Onsager Reciprocal Relations (ORR).

Detailed thermodynamic considerations⁽¹¹⁾ show the isothermal rate of irreversible entropy production per unit volume, σ ($\text{J K}^{-1} \text{m}^{-3} \text{s}^{-1}$), to be given by

$$T\sigma = \sum_i J_i X_i \quad (\text{I.10})$$

where $T(\text{K})$ is the absolute temperature, J_i ($\text{mol m}^{-2} \text{s}^{-1}$) the flow of ions and solvent and X_i ($\text{J mol}^{-1} \text{m}^{-1}$) the electrochemical potential gradient (wherever the term ion appears, ion-constituent should be inferred (see section II.1)). By relating the flows to a solvent-fixed frame of reference, the solvent driving force X_0 can be eliminated (by convention the subscript 0 refers to the solvent). The set of independent flows as linear functions of the forces are then⁽¹²⁾

$$J_i = \sum_{j=1}^n l_{ij} X_j \quad i = 1, 2, \dots, n \quad (\text{I.11})$$

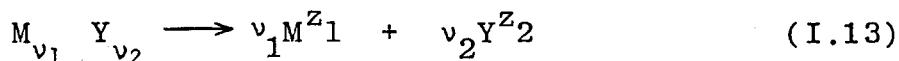
for a system of n components. The flows and driving-forces are connected by the Onsager transport coefficients l_{ij} ($\text{mol}^2 \text{J}^{-1} \text{m}^{-1} \text{s}^{-1}$).

The fourth principle, the ORR, can be written mathematically as

$$l_{ij} = l_{ji} \quad (\text{I.12})$$

The experimental verification of (I.12) has been an important feature of the application of TIP to electrolyte solutions.⁽¹³⁻¹⁶⁾

Consider an isothermal system of a binary electrolyte dissociating in a neutral solvent:



where ν is the stoichiometric coefficient, M and the subscript 1 refer to the cation and Y and subscript 2 to the anion.

The linear equations (I.11) become

$$J_1 = l_{11}X_1 + l_{12}X_2 \quad (\text{I.14})$$

$$J_2 = l_{21}X_1 + l_{22}X_2 \quad (\text{I.15})$$

From analysis of four independent experimental techniques Miller⁽¹²⁾ has derived expressions for the conductance Λ ($\text{m}^2 \Omega^{-1} \text{mol}^{-1}$), the Hittorf (or moving-boundary) and e.m.f. transference numbers (T^H and T^e respectively) and the solvent-fixed electrolyte diffusion coefficient D_0 ($\text{m}^2 \text{s}^{-1}$) in terms of the l_{ij} . On a solvent-fixed frame of reference these equations are

$$\Lambda = \frac{F^2}{c} \left[z_1^2 l_{11} + z_1 z_2 (l_{12} + l_{21}) + z_2^2 l_{22} \right] = \frac{F^2}{c} \alpha \quad (\text{I.16})$$

$$T_1^H = (z_1^2 l_{11} + z_1 z_2 l_{12}) / \alpha \quad (\text{I.17})$$

$$T_1^e = (z_1^2 l_{11} + z_1 z_2 l_{21}) / \alpha \quad (\text{I.18})$$

$$D_0 = \frac{RT\nu(1+c d \ln y / dc)}{c} \cdot \frac{|z_1 z_2|}{\nu_1 \nu_2} \cdot \frac{l_{11} l_{22} - l_{12} l_{21}}{\alpha} \quad (\text{I.19})$$

where α is defined by equation (I.16), F is Faraday's constant (96487 C mol^{-1}), c the concentration of the electrolyte (mol m^{-3}), $\nu = \nu_1 + \nu_2$, R is the gas constant ($8.314 \text{ J K}^{-1} \text{mol}^{-1}$) and y is the mean molar activity coefficient.

Equations (I.16), (I.17), (I.18) and (I.19) can be solved to yield an expression for the l_{ij} in terms of experimentally accessible quantities⁽¹²⁾_{ij}.

$$\frac{l_{ij}}{c} = \frac{T_i^H T_j^e \Lambda}{F^2 z_i z_j} + \frac{v_i v_j D_0}{RTv (1 + cd \ln y/dc)} \quad (I.20)$$

An alternative (but equivalent) equation uses the volume-fixed diffusion coefficient D_v instead of D_0 . In this case c must be replaced by the molal concentration m (mol (kg of solvent)⁻¹) and y by γ , the mean molal activity coefficient. Hence⁽¹²⁾

$$\frac{l_{ij}}{c} = \frac{T_i^H T_j^e \Lambda}{F^2 z_i z_j} + \frac{v_i v_j D_v}{RTv (1 + md \ln \gamma/dm)} \quad (I.21)$$

Equation (I.21) is usually used to calculate values of l_{11} , l_{22} , l_{12} and l_{21} as D_v is the more normal experimentally measured quantity.⁽¹²⁾

For a single binary electrolyte the ORR is

$$l_{12} = l_{21} \quad (I.22)$$

Inspection of (I.17) and (I.18) shows that the simplest test of the ORR is whether T_1^H and T_1^e are equal. It is the dearth of such data of sufficient accuracy, especially in the concentrated region where the test is particularly sensitive, that has initiated several investigations in recent years.^(13,15,17) McQuillan⁽¹⁵⁾ used a more sensitive test of equation (I.22), by dividing (I.17) by (I.18) :

$$\frac{T_1^H}{T_1^e} = \frac{z_1 l_{11} + z_2 l_{12}}{z_1 l_{11} + z_2 l_{21}} \quad (I.23)$$

The best test of equation (I.23) arises when l_{12} and l_{21} are large relative to l_{11} . An equivalent expression is⁽¹⁸⁾

$$\frac{T_1^H - T_1^e}{T_1^e} = \left(\frac{l_{12}}{l_{21}} - 1 \right) \frac{z_2 (l_{21}/c)}{z_1 (l_{11}/c) + z_2 (l_{21}/c)} \quad (I.24)$$

As the cross coefficients l_{12} and l_{21} are essentially interaction terms between the cation and anion, this condition is met in concentrated solutions of an associated electrolyte such as CdCl_2 . All investigations so far have vindicated the ORR within experimental error.

Values of l_{ij} are now usually calculated by accepting the ORR and using equation (I.20) or (I.21) with transference data obtained from one method only. Transport coefficients have now been determined in this way for several aqueous electrolyte systems. They are commonly represented by graphs of $(l_{ij}/v_i|z_i|c)$ vs. $I^{1/2}$ where the ionic strength I is given by equation (I.7). Division of the l_{ij} by $v_i|z_i|c$ reduces the concentration dependence of the transport coefficients and also means that the l_{ii} for the same ion in different valence type electrolytes have the same limiting value.⁽¹²⁾ The units of $(l_{ij}/v_i|z_i|c)$ are $\text{mol J}^{-1} \text{m}^2 \text{s}^{-1}$. Just as the ionic mobility is the speed of an ion under unit potential gradient, $(l_{ij}/v_i|z_i|c)$ is the speed under unit electrochemical potential gradient. Consequently $(l_{ii}/v_i|z_i|c)$ are known as intrinsic mobilities and the $(l_{ij}/v_i|z_i|c)$ are known as interaction mobilities.

A selection of experimental data is plotted in figures I.1-3. A recent review⁽¹⁰⁾ of TIP theory as applied to electrolyte solutions contains a comprehensive list of experimental investigations. Since then only one further study has been published, that of Miller et al.⁽¹⁶⁾ on aqueous CuSO_4 solutions up to 1.4M.

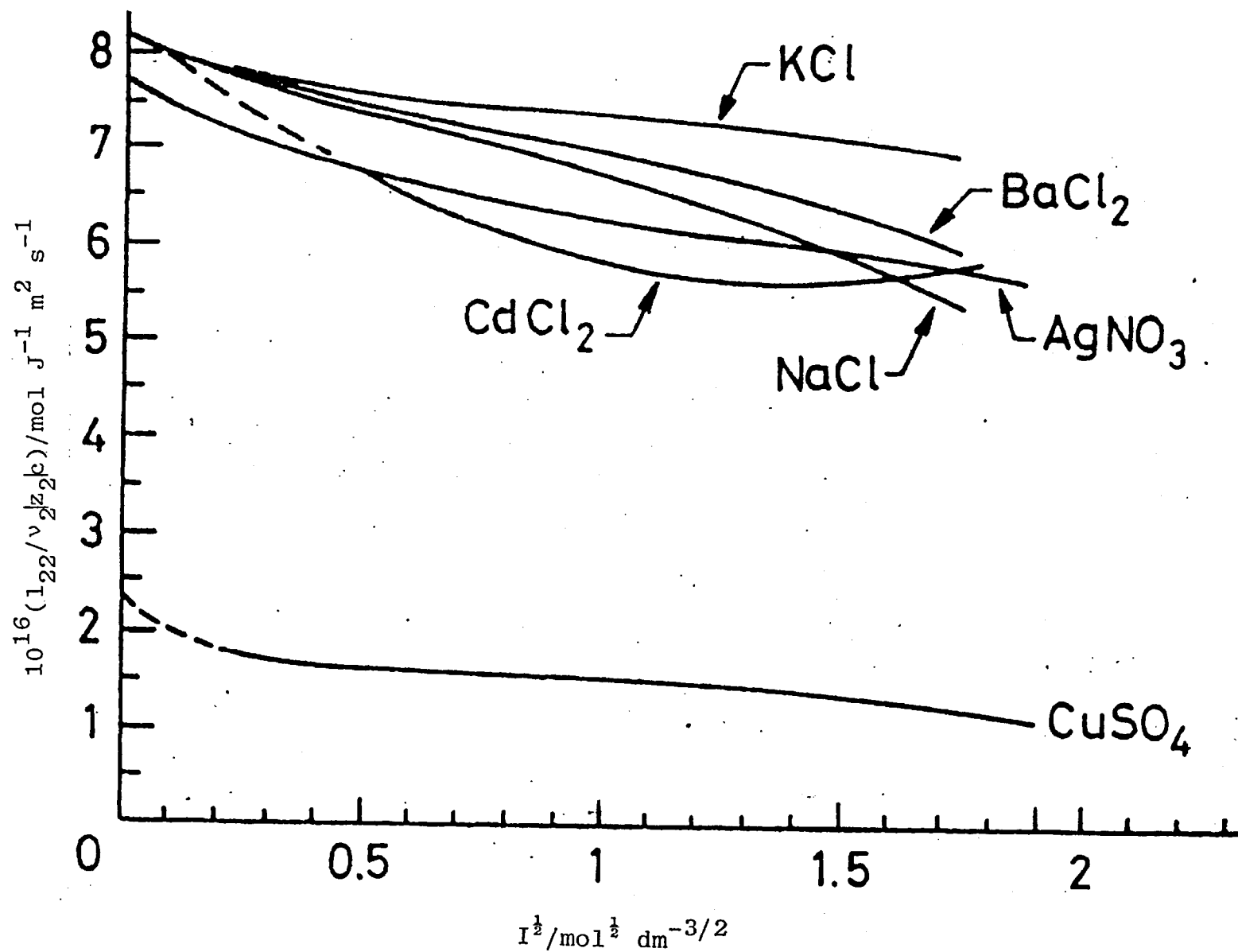
The intrinsic mobilities represent the interaction of an ion with the solvent and with similar ions. However it is now clear that the l_{ii} are also affected by the nature of the counter-ion and of the degree of ion-pairing.⁽¹⁴⁾ For instance in figure (I.1) the anion $(l_{22}/v_2|z_2|c)$ values are specific for different chloride solutions at concentrations above ca. 0.1M. If the cation had no effect on the anion intrinsic mobility the chloride

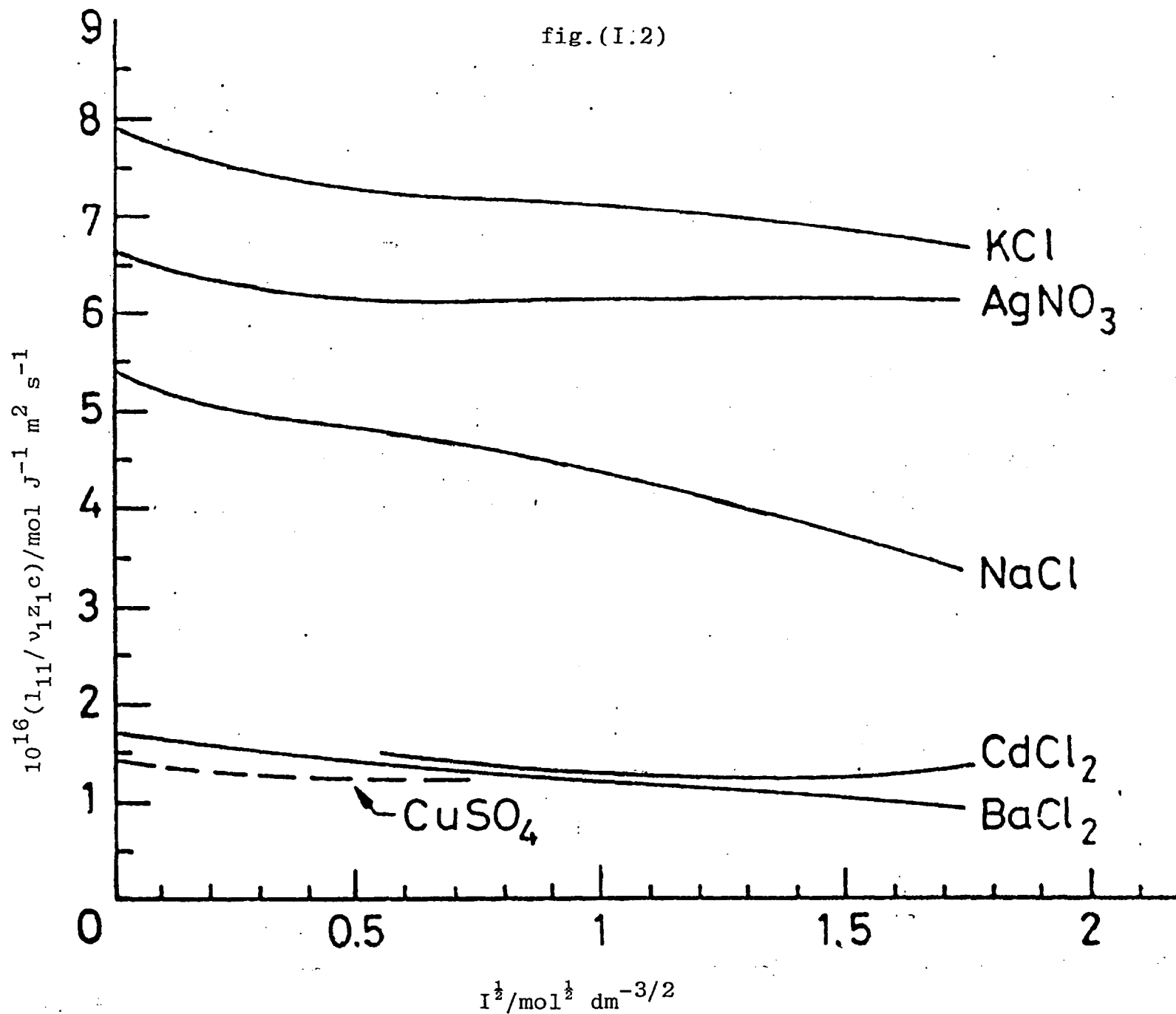
transport coefficients would have the same concentration dependence in the various chloride solutions. That they have not is due to the fact that different cations affect the solvent structure in different ways. Figure (I.1) also shows that the mobilities are relatively constant with concentration. The doubly-charged SO_4^{2-} ion has a much smaller intrinsic mobility than the singly charged anions because of its larger hydration shell. The upward curvature for chloride in CdCl_2 solutions is caused by the presence of complex anionic species in the concentrated solutions. All the anion intrinsic mobilities of chloride salts come to a common value at infinitesimal ionic strength as would be expected for salts with a common anion. The intrinsic mobilities for AgNO_3 are thought to be affected by ion-pair formation with (l_{22}/v_2z_2c) lower and (l_{11}/v_1z_1c) higher⁽¹⁴⁾ (fig.I.2) than expected at large concentrations.

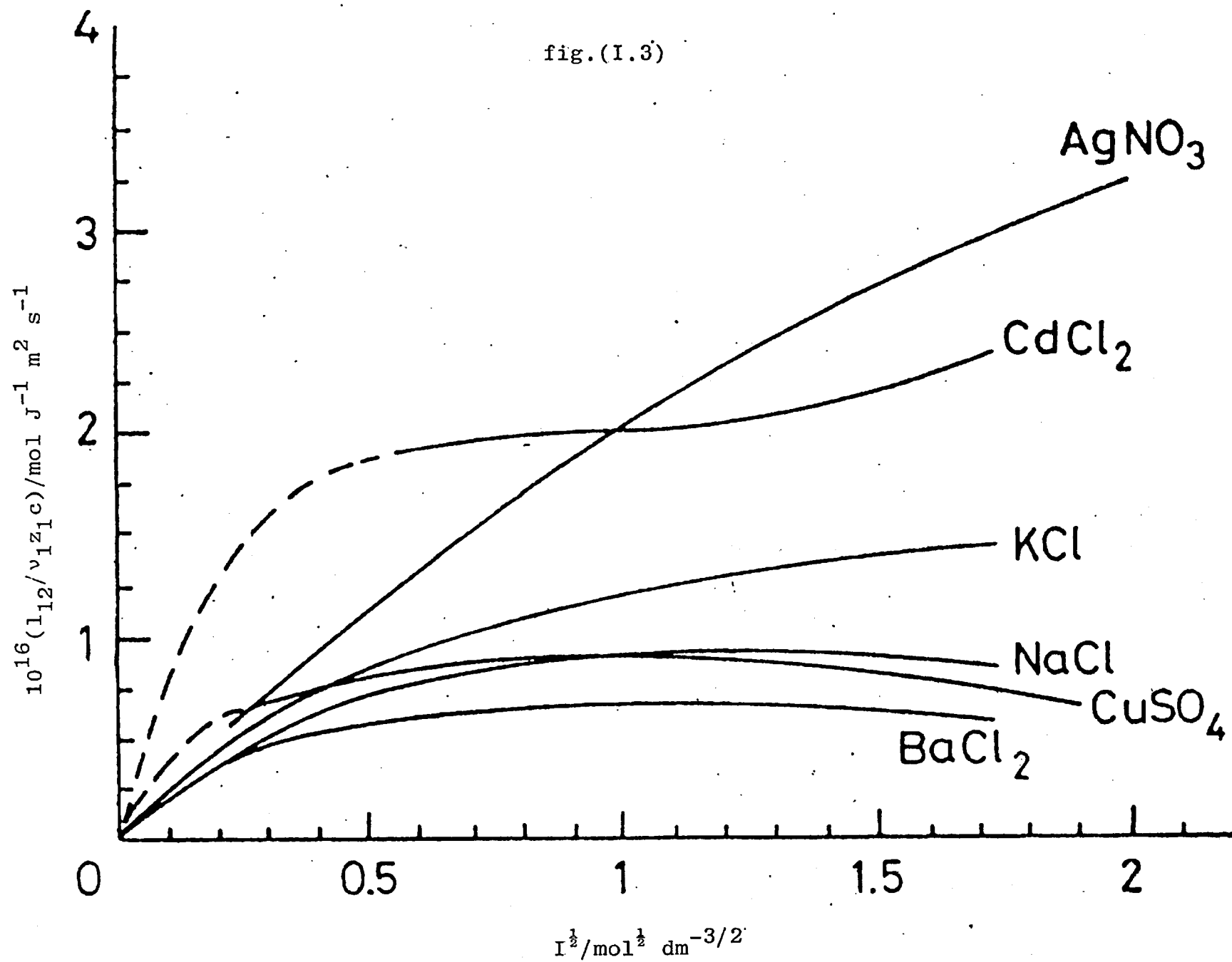
The cation intrinsic mobilities (fig.I.2) show the same slow decrease with concentration as do the anion mobilities in fig.(I.1). The rate of decrease is lower than the corresponding one for the ionic conductances and is caused by increasing i-i coulombic repulsion. The general trend of $\text{La}^{3+} < \text{Ba}^{2+} < \text{Na}^+ < \text{K}^+$ shows that highly solvated ions possess lower mobilities. The rate of decrease of (l_{11}/v_1z_1c) with increasing concentration for HCl (not shown in fig.I.2) is much greater than that for the other ions because of the breakdown in the proton-jumping mechanism at higher solute concentrations.

The interaction mobility (l_{12}/v_1z_1c) in fig.(I.3) indicates the amount of coupling between the anion and cation. Thus at infinitesimal ionic strength the mobilities are zero as the ions are infinitely far apart. With increasing ionic strength the mobilities increase as the amount of cation-anion coupling increases. This increase is specific with $l_{12}(\text{KCl}) > l_{12}(\text{NaCl}) > l_{12}(\text{LiCl})$ at all concentrations. This has been explained⁽¹²⁾ by the fact that the larger hydration shell of the Li^+ ion

fig.(I.1)







prevents the Cl^- ion approaching as closely as it does in the case of KCl . This effect is partially offset by the lower effective dielectric constant of the tightly bound Li^+ hydration shell. The increase of $(l_{12}/v_1 z_1 c)$ with concentration is the main reason for the rapid decline of conductances with increasing concentration.⁽¹²⁾

For an electrolyte of a particular valence type, ion-pair or complex ion formation leads to a higher interaction mobility. Thus for AgNO_3 $(l_{12}/v_1 z_1 c)$ is about 50% of $(l_{11}/v_1 z_1 c)$ and $(l_{22}/v_2 z_2 c)$ at 4M and for CdCl_2 $(l_{12}/v_1 z_1 c)$ is actually larger than $(l_{11}/v_1 z_1 c)$ over a wide concentration range.

The maxima in the curves for NaCl , CuSO_4 and BaCl_2 are thought to be due either to competition for the solvent or possibly arise from the choice of reference frame.⁽¹⁰⁾

I.3.2 The R_{ij} Representation

The R_{ij} representation is the inverse representation to the Onsager transport coefficients. As such they represent the "friction" between ions and solvent particles. An analogous set of independent flows and forces can be written down connected by nine reference-frame independent friction coefficients,⁽¹²⁾ namely $R_{00}, R_{01}, R_{02}, R_{10}, R_{11}, R_{12}, R_{20}, R_{21}$ and R_{22} . ORR's connect six of these. This reduces the set to six independent coefficients which represent solvent-solvent (R_{00}), cation-cation (R_{11}), anion-anion (R_{22}), cation-solvent (R_{10}), anion-solvent (R_{20}) and cation-anion (R_{12}) interactions.

The R_{ij} can be related to measurable quantities and evaluated as a function of concentration in the same way as the l_{ij} .⁽¹²⁾

I.3.3 Velocity Correlation Coefficients

As their name implies, velocity correlation coefficients (vcc) relate the velocity of one species in solution to the velocities of the other species present. The vccs (f_{ij}) are defined in terms of time integrals of ensemble average velocity correlation functions. If there is no correlation between the movement of two particular species then the relevant vcc is zero. If, however, the movement of a given ion is connected with the motion of another in the same direction then the coefficient is positive; if it is connected in the opposite direction the coefficient is negative.

Within this formalism two schools of thought exist. Hertz and his co-workers^(19,20) employ the idea of the salt self-diffusion coefficient to avoid introducing the electrochemical potential which they see as a non-physical concept. They also assume that the transference number is reference-frame independent. The ensuing coefficients represent ion-ion, salt-salt, salt-water and water-water interactions. On the other hand, Woolf⁽²¹⁾ prefers to retain the electrochemical potential and due regard is taken of the frame of reference. This leads to coefficients which depict ion-ion, ion-solvent and solvent-solvent interactions. The latter approach is preferred as transference numbers are defined relative to the solvent and the idea of a "salt" diffusion coefficient in an ionizing solvent is just as arbitrary as the electrochemical potential.

One of the underlying principles used is that of the conservation of momentum. Consequently the coefficients are related to a mass-fixed reference frame as opposed to the solvent-fixed reference frame for the l_{ij} . According to linear response theory the f_{ij} are directly related to the mass-fixed Onsager coefficients ρ_{ij} . By suitable allowance for the change of reference frame

Woolf and Harris⁽²¹⁾ have related the f_{ij} to the solvent-fixed l_{ij} . Consequently the f_{ij} can be evaluated either via the l_{ij} or directly from mass-fixed experimental quantities.

I.3.4. Choice of Representation

Although the R_{ij} are reference-frame independent this formalism has several weaknesses. Similar ion friction coefficients, R_{ii} , have positive values but the R_{ij} ($i \neq j$) are negative. The concept of negative friction is not altogether tangible. Furthermore, l_{ij} which become zero at infinitesimal ionic strength are preferable to friction coefficients which become infinite there.⁽¹²⁾ In addition the solvent-solvent friction coefficient, R_{00} , which should be independent of the solute type at $c = 0$, is found not to be.⁽¹²⁾

The choice between the l_{ij} and f_{ij} is less clear cut. As with the R_{ij} , certain f_{ij} become infinite at infinitesimal ionic strength.⁽²²⁾ The idea of a very large correlation between velocities of ions which are infinitely far apart is indeed strange. However, proponents of vcc theory argue that this formalism has a more microscopic basis than the essentially macroscopic l_{ij} quantities. Thus it gives a more direct kinetic interpretation of the motions and interactions in the electrolyte solution. On balance however, the present author prefers the l_{ij} representation for its inherent simplicity despite the fact that it does not provide a direct ion-solvent interaction parameter.

I.4 Transition State Models

In the classic transition state treatment of transport properties, a constant activation energy (E) needs to be overcome before transport can take place.

This is expressed by the Arrhenius equation

$$P = P_0 \exp(-E/RT) \quad (\text{I.25})$$

where P is a transport property and P_0 a pre-exponential factor. Plots of $\ln P$ vs. $1/T$ are straight lines of slope $(-E/R)$.

However it has been found that at low temperatures equation (I.25) is no longer valid and that E varies with T .⁽¹⁾ Much work has been done on ionic supercooled glass-forming liquids near the glass transition temperature, T_g . It was found empirically that the temperature dependence of transport properties could be described better by^(2,3,23)

$$P = P_0 \exp[-C/(T-T_0)] \quad (\text{I.26})$$

where C and T_0 are constants for a particular system.

Adam and Gibbs⁽¹⁾ have derived (I.26) using a statistical thermodynamic method. They supposed that instead of ions migrating alone, transport occurs by the simultaneous co-operative movement of a small independent microscopic region of the liquid. On this basis they derived an expression for the average probability of co-operative rearrangement of these regions, W , as a function of temperature

$$W = A \exp(-z^* \Delta\mu/kT) \quad (\text{I.27})$$

where A is a pre-exponential factor, z^* is a critical minimum number of particles per microscopic region for rearrangement to occur, and $\Delta\mu$ is the potential energy hindering co-operative rearrangement. z^* is related to s_c^* , the critical configurational entropy for rearrangement, by

$$z^*/L = s_c^*/S_c \quad (\text{I.28})$$

where L is Avogadro's number and S_c is the configurational entropy per mole of solution. S_c is given by

$$S_c = \int_{T_0}^T (\Delta C_p / T) dT \quad (I.29)$$

where T_0 is the ideal glass transition temperature. T_0 is a more fundamental temperature than T_g as the latter varies with the time-scale of the experiment. T_0 is the temperature at which there is only one possible configuration for the system, i.e. the size of the co-operative region is the size of the system, and hence the configurational entropy is zero. Typically T_0 is 10-20°C below T_g .⁽²³⁾ The difference in heat capacity ΔC_p between temperatures T_0 and T , is found to be proportional to $1/T$.⁽³⁾

Integration of (I.29) and insertion of (I.28) into (I.27) gives

$$W = A \exp[-B/(T-T_0)] \quad (I.30)$$

where B is a constant. Equation (I.30) is of the same form as (I.26).

Obviously the possibility of co-operative rearrangement is proportional to such properties as diffusion and conductance and inversely proportional to the viscosity of the solution. Many experimental investigations^(2,3) have verified the applicability of (I.30) for glass-forming ionic liquids over wide temperature and composition ranges. Such liquids tend to be solutions of a highly soluble or hygroscopic nature. Figure (I.4), taken from Angell and Bressel's⁽³⁾ work on $\text{Ca}(\text{NO}_3)_2$, shows the large variation of the molar conductance with temperature at various concentrations.

Angell and Bressel found that the values of T_0 calculated from (I.30) varied linearly with the mole fraction x of the salt,

$$T - T_0 = Q(x_0 - x) \quad (I.31)$$

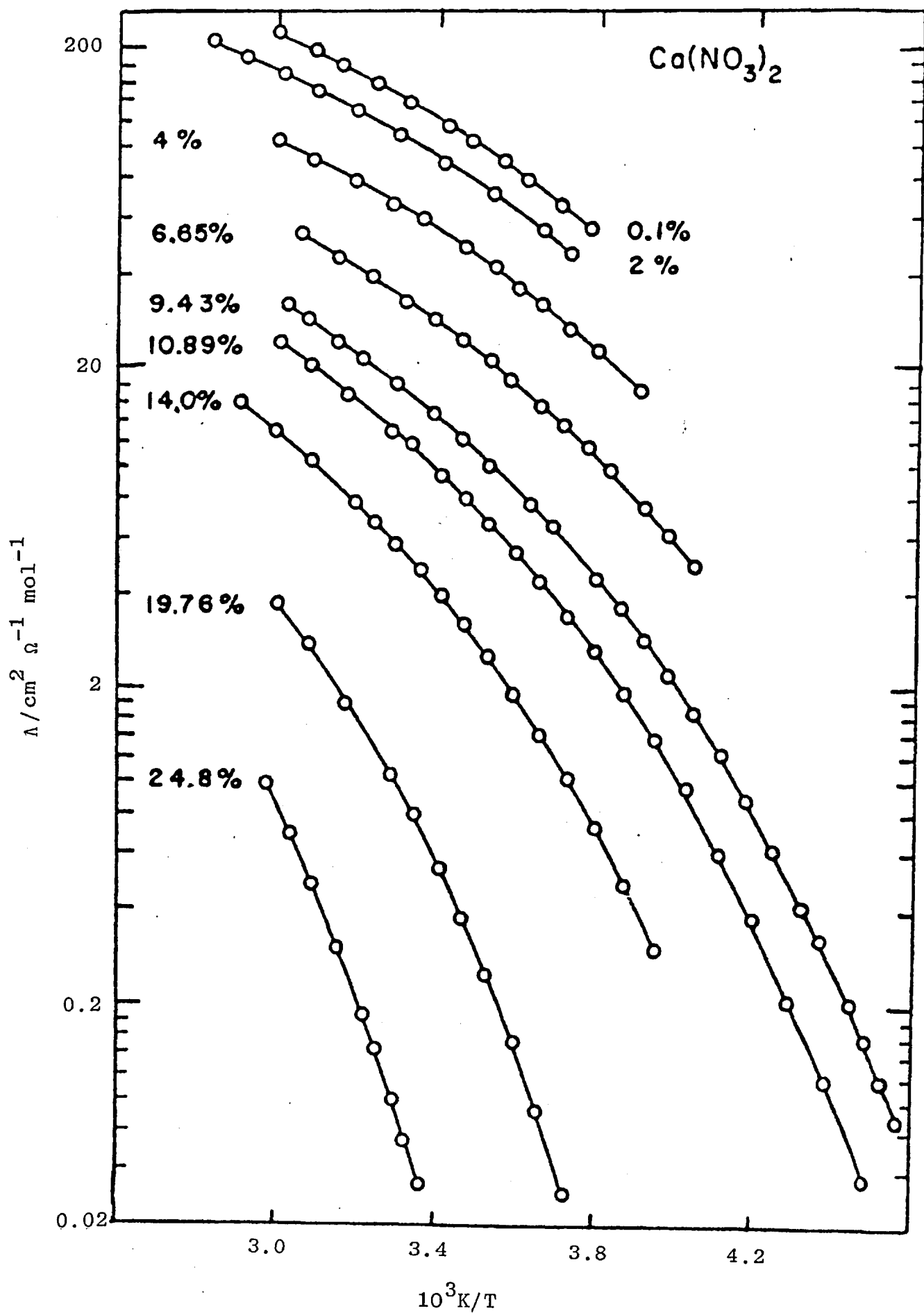


fig.(I.4)

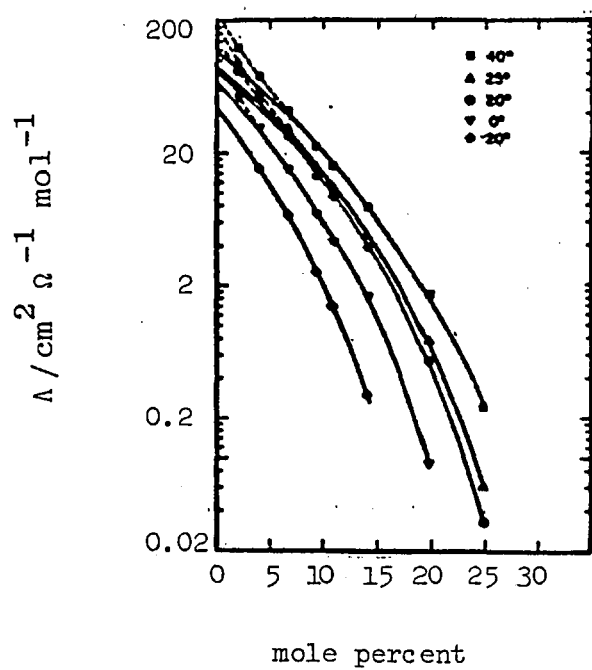


fig.(I.5)

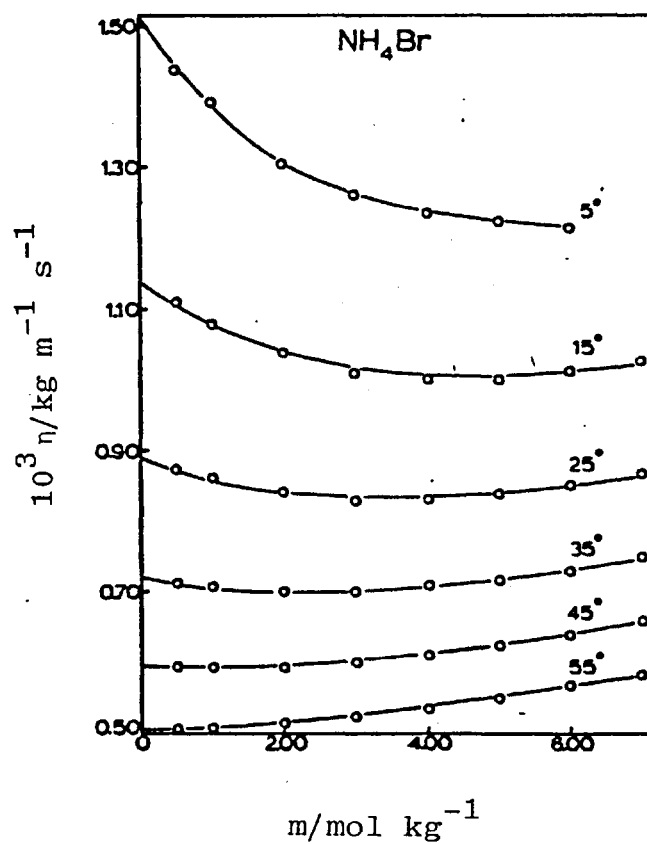


fig.(I.6)

where Q is a constant and x_0 is the mole fraction at which T_0 equals the temperature T of the solution. Substitution of (I.31) into (I.30) gives

$$W = A \exp \left[-B' / (x_0 - x) \right] \quad (\text{I.32})$$

where A and B' are constants at a given temperature. Figure (I.5) shows how well equation (I.32) accounts for the concentration dependence of the molar conductance of $\text{Ca}(\text{NO}_3)_2$ solutions at a variety of temperatures (in figs. (I.5) and (I.6) the points represent experimental values and the curves are calculated from the appropriate equation using computed least-squares best fit values of the parameters).

Some discussion has arisen in the literature⁽¹⁸⁾ as to whether a temperature factor should be included in the pre-exponential factor A . However, it is evident that⁽¹⁸⁾ most of the temperature dependence of (I.30) is due to the exponential factor. Consequently the choice of the pre-exponential temperature dependence is relatively unimportant.

The above treatment differs from those described in the previous two sections in that the solution is treated as a homogeneous liquid. No attempt has been made to distinguish between the various species present.

Another recent transition state treatment deals with the concentration and temperature dependence of the viscosity of concentrated electrolyte solutions.^(4,5) The resulting two-parameter equation for the variation of the viscosity with mole fraction of salt is

$$(\eta / \eta^0) = \exp(xE) / (1 + xv) \quad (\text{I.33})$$

where E and v are terms involving the viscous flow activation energies and molar volumes, respectively, of

the cation, anion and solvent. Although (I.33) accounts well for the concentration and temperature dependence of the viscosity for several salts (see figure I.6) this approach has recently been criticised⁽¹⁸⁾ for the lack of a physical basis for the E and v parameters required for fitting.

CHAPTER TWO

TRANSFERENCE NUMBERS AND THEIR DETERMINATION

II.1 Definition of Transference Number

When an electric current is passed through an electrolyte solution the current is carried by the motion of solvated ions. Each species of ion possesses a different mobility. Due to this fact, cations, for example, leave the region around the anode at a different rate to that at which anions arrive. As a result, and also because the electrode reaction may produce or consume solute and/or solvent molecules, there is a change in solute concentration around each electrode during electrolysis. On the other hand, in a volume element far removed from either electrode, as many ions of a given type enter one face of the volume element as leave the other. Far away from the electrode, therefore, there is no change in the concentration of the solute. The extent of the change in solute concentration around the electrode is related to a property of the ions known as the transport or transference number.

Unfortunately, due to careless usage in the literature some confusion has arisen concerning the terms transport number and transference number. The definitions given below are those now generally accepted and which have been detailed by Spiro.⁽⁸⁾ Consider an aqueous cadmium iodide solution. Among the species present in solution are the aquated Cd^{2+} and I^- ions as well as some undissociated CdI_2 molecules. In addition there are also varying amounts of the aquated complex ions CdI^+ , CdI_3^- and CdI_4^{2-} . The extent to which each of these species is present depends upon the concentration of the solution.

The transport number, t_i , of an ion is the

number of faradays of charge carried by ions of type i across a reference plane fixed with respect to the solvent when one faraday of electricity passes across that plane. In the CdI_2 solution there are transport numbers associated with the Cd^{2+} ions, the I^- ions, the CdI^+ ions and so on. Transport numbers can either be positive or zero and their sum over all ionic species present in solution is unity.

$$\sum_i t_i = 1 \quad (\text{II.1})$$

However, this is of little practical use as we have no means of measuring the actual transport of the individual ions. The only thing we can measure is the net flow of the ionic species present. Hence we have to define another sort of transport number known as the transference number. To do this we must first introduce the concept of an ion-constituent. The cadmium ion-constituent in the CdI_2 solution exists in the form of the various ions Cd^{2+} , CdI^+ , CdI_3^- etc. and also in the undissociated CdI_2 molecules. What we measure is the net flow of the cadmium ion-constituent and not the flow of Cd^{2+} ions alone. Similarly the anion-constituent, iodide, exists as I^- , CdI^+ , CdI_2 , CdI_3^- etc. The ion-constituents must be chosen so that every ion in the solution may be formed by the addition of integral numbers of the ion-constituents.

We can now formally define a transference number⁽⁸⁾ :

"The transference number, T_R , of a cation- or anion-constituent R is the net number of faradays carried by that constituent in the direction of the cathode or anode, respectively, across a reference plane fixed with respect to the solvent, when one faraday of electricity passes across the plane". As with the transport number, the sum of the transference numbers is unity.

$$\sum_R T_R = 1 \quad (\text{II.2})$$

Thus it can be seen that the transport number is only numerically equal to the transference number when the electrolyte completely dissociates into only two ionic species. In this thesis only the transference number will be referred to. It needs to be stressed that it is the transference number that is measured by experiment and not the transport number.

Not only can transference numbers be zero or positive, as with transport numbers, but they can also have negative values. For example, in aqueous cadmium iodide solutions greater than 0.28 mol dm^{-3} the cadmium ion-constituent transference number is negative.⁽²⁴⁾ In such solutions more cadmium is transported towards the anode in the form of complex anions than is transported towards the cathode as cations.

We can now derive an expression between the properties of the ions in solution and the transference number T_R of ion-constituent R.

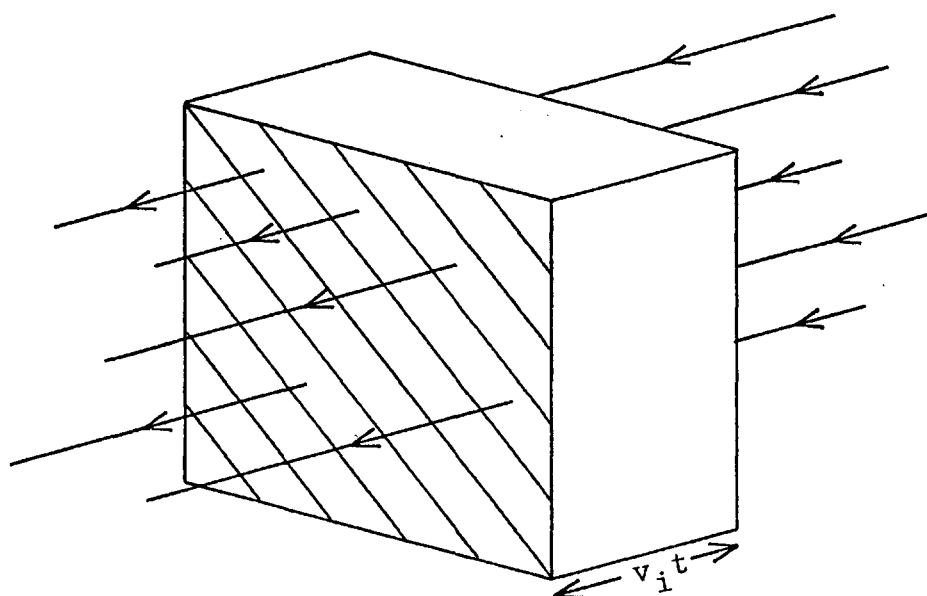


fig.(II.1)

Consider the imaginary plane (of cross-sectional area $A \text{ m}^2$) fixed with respect to the solvent shown in fig.(II.1). If v_i is the ionic speed (m s^{-1}) of ion i then all ions of this type in the volume $v_i t A \text{ m}^3$ will

cross this plane in time t seconds. This is equal to $v_i t A c_i$ moles where c_i is the concentration of ion i (mol m^{-3}). These ions carry a charge of $|z_i| v_i t A c_i$ faradays where $|z_i|$ is the arithmetic charge number of ion i . Hence the total flux of charge due to all ionic species in solution across the imaginary plane in both directions in time t seconds is $\sum_i |z_i| v_i t A c_i$ faradays. The ionic speed is used here instead of the velocity as the direction of flow of the ions is taken into account in the $(|z_i|/z_i)$ and $(z_R/|z_R|)$ terms described below.

Of this total flux the net number of faradays carried by ion-constituent R across the reference plane in time t seconds is

$$\sum_i |z_R| \left(\frac{z_R}{|z_R|} \right) \left(\frac{|z_i|}{z_i} \right) N_{R/i} v_i t A c_i \quad \text{where } z_R \text{ is the algebraic}$$

charge number of ion-constituent R and $N_{R/i}$ is the number of moles of R in each mole of ion i . The $(|z_i|/z_i)$ term arises because cations and anions carry a given ion-constituent in opposite directions across the reference plane. In addition a $(z_R/|z_R|)$ factor is required because the cation- and anion-constituent transference numbers are defined as transport in opposite directions. The transference number is then the ratio of these two summations

$$T_R = \frac{\sum_i z_R (|z_i|/z_i) N_{R/i} v_i c_i}{\sum_i |z_i| v_i c_i} \quad (\text{II.3})$$

The velocity of the ions is proportional to the electrical field strength X (V m^{-1}) and to the ionic mobility u_i ($\text{m}^2 \text{s}^{-1} \text{V}^{-1}$):

$$v_i = u_i X \quad (\text{II.4})$$

The mobility in turn is related to the ionic molar conductance λ_i ($\text{m}^2 \Omega^{-1} \text{mol}^{-1}$) by

$$\lambda_i = F u_i |z_i| \quad (\text{II.5})$$

where F is Faraday's constant ($96\,487\text{ C mol}^{-1}$). Substituting (II.4) and (II.5) into (II.3) and cancelling common terms we obtain

$$T_R = \frac{\sum_i (z_R/z_i) N_{R/i} \lambda_i c_i}{\sum_i \lambda_i c_i} \quad (\text{II.6})$$

If the solute dissociates into only two ionic species as in dilute aqueous HCl , then (II.6) reduces to

$$T_R = \frac{\lambda_R c_R}{\sum_i \lambda_i c_i} = \frac{\lambda_R c_R}{\Lambda c} = \frac{\lambda_R}{\Lambda} \quad (\text{II.7})$$

where $\Lambda (\text{m}^2 \Omega^{-1} \text{ mol}^{-1})$ is the molar conductance and $c (\text{mol m}^{-3})$ is the concentration of the electrolyte. In such cases the same expression is arrived at for the transport number t_i of ionic species i . The two terms $\sum_i \lambda_i c_i$ and Λc which appear in the denominator of equation (II.7) apply to all electrolytes, whatever the degree of dissociation, and are equal to $\kappa (\Omega^{-1} \text{ m}^{-1})$, the specific conductance of the solution

$$\sum_i \lambda_i c_i = \Lambda c = \kappa \quad (\text{II.8})$$

The mobility, $\bar{u}_R$, and molar conductance, $\bar{\lambda}_R$, of ion-constituent R (the bar denotes a property of an ion-constituent) are related to the corresponding properties of the ionic species in solution, u_i and λ_i respectively, by

$$\bar{u}_R = \sum_i N_{R/i} u_i \left(\frac{|z_i|}{z_i} \right) \left(\frac{z_R}{|z_R|} \right) \frac{c_i}{v_R c} \quad (\text{II.9})$$

$$\bar{\lambda}_R = \sum_i N_{R/i} \frac{\lambda_i}{z_i} \left(\frac{z_R}{|z_R|} \right) \frac{c_i}{c} \quad (\text{II.10})$$

where v_R is the stoichiometric number of R in the electrolyte.

The following sections will describe three of the main methods of measuring transference numbers: the Hittorf method, the moving boundary (m.b.) method, and the e.m.f. method.

II.2 The Hittorf Method

The Hittorf method is based on the analysis of the concentration change which occurs around the electrodes during the electrolysis of an electrolyte solution. The electrolysis is carried out in specially designed cells from which samples can be taken from the two electrode compartments and from a middle section. The middle section is often further subdivided into two or three smaller sections. Analysis of the solutions in the middle compartments shows if any inter-mixing has taken place. In the absence of diffusive and convective mixing the concentration of these three middle sections should remain unchanged.

Per faraday of electricity passed $T_+/|z_+|$ moles of the cation-constituent and $T_-/|z_-|$ moles of the anion-constituent migrate into the cathode and anode compartments, respectively. Assuming that the electrode reactions are known, the concentration changes occurring in the two electrode chambers can be related to T_+ and/or T_- .

Electrolysis is usually carried out until a 10-20% concentration change has occurred. Smaller changes require a high degree of accuracy in the analysis and larger changes, involving a longer period of electrolysis or a larger current, increase the possibility of diffusive or convective mixing, respectively. The change in concentration of the solute in the electrode compartments is related to the solvent-fixed frame of reference by calculating the change in concentration relative to a fixed mass of solvent.

A small part of the current is carried by the solvent, either through impurity ions or as a result of

ions formed by the self-dissociation of the solvent. To allow for this a so-called solvent correction must be applied which allows the corrected transference number, T_R (corr.) to be calculated from the observed transference number, T_R (obs.)⁽²⁵⁾:

$$T_R(\text{corr.}) = T_R(\text{obs.}) \left[1 + \left(\frac{\kappa_{\text{solvent}}}{\kappa_{\text{solute}}} \right) \right] \quad (\text{II.11})$$

Along with the e.m.f. method the Hittorf method has been the most popular method for the measurement of transference numbers in concentrated aqueous solutions. Diffusive and convective mixing can be minimised by using cells made from long lengths of tubing and by incorporating right-angled bends⁽²⁶⁾. Small electrode chambers maximise concentration changes. As long as the electrodes remain stable there is no upper concentration limit to the Hittorf method.

II.3 The Moving Boundary Method

The most accurate method for the determination of transference numbers in dilute solutions is the direct moving boundary (m.b.) method. However, due to the need to apply an ever increasing volume correction (section II.3.4) the method becomes progressively less accurate as the concentration of electrolyte increases. Here the m.b. method will be discussed with reference to dilute solutions (less than ca. 0.1M) and the modifications found necessary for more concentrated solutions will be dealt with in Chapter Four.

II.3.1 Introduction

The direct m.b. method involves the measurement of the rate at which a boundary between two electrolytes sweeps out a known volume when an electric current is passed through the solutions. A stable boundary can only be maintained between the test electrolyte (the

leading solution) and a suitable indicator electrolyte (the following solution) if the system is gravitationally stable. This gives rise to either a falling boundary (fig. II.2a) or a rising boundary (fig. II.2b) depending upon whether the leading solution (LZ) is more dense or less dense, respectively, than the following solution (FZ). The boundary is termed a cation boundary if the non-common ion-constituents L and F are cations (as in this case) and an anion boundary if L and F are anion-constituents (in which case the electrodes would be reversed). Under proper experimental conditions the rate of movement of the boundary is solely dependent upon the properties of the leading solution and will give the transference number of the leading non-common ion-constituent.

II.3.2 The Moving Boundary Equation

Inspection of fig.(II.2a) and the definition of a transference number leads to the relation between the transference number of the leading non-common ion-constituent, T_L^{LZ} , and the boundary speed. Let the boundary move from a position x to a position x' when one faraday of electricity passes. If the volume between x and x' is $V_F \text{ m}^3$ then $c_L^{LZ} V_F$ moles of ion-constituent L, carrying a charge of $|z_L| c_L^{LZ} V_F$ faradays will cross the reference plane PQ in the leading solution which is fixed relative to the solvent. But, from section (II.1), the charge carried by this ion-constituent per faraday is equal to the transference number of the leading non-common ion-constituent L, so that:

$$T_L^{LZ} = |z_L| c_L^{LZ} V_F \quad (\text{II.12})$$

In most experiments less than one faraday will be passed. If $V(\text{m}^3)$ is the volume swept out by the boundary when It/F faradays are passed, then

$$T_L^{LZ} = \frac{|z_L| c_L^{LZ} V_F}{It} \quad (\text{II.13})$$

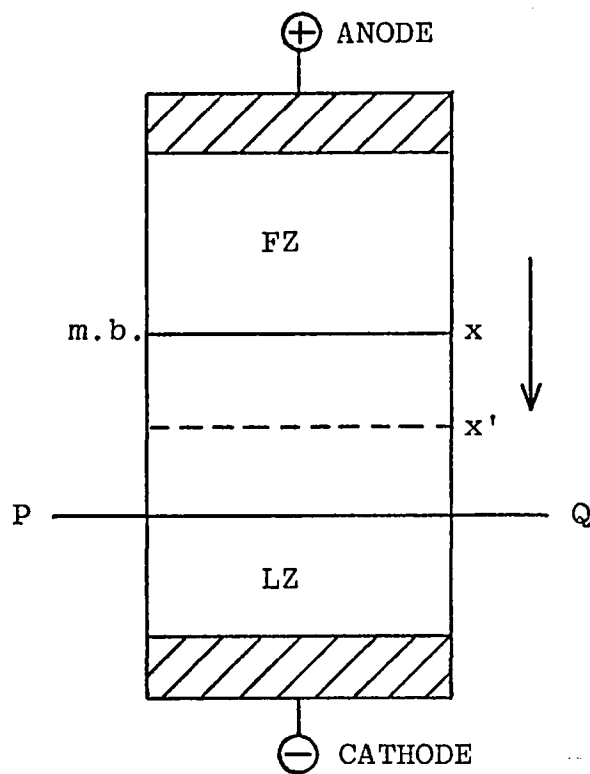


fig.(II.2a)

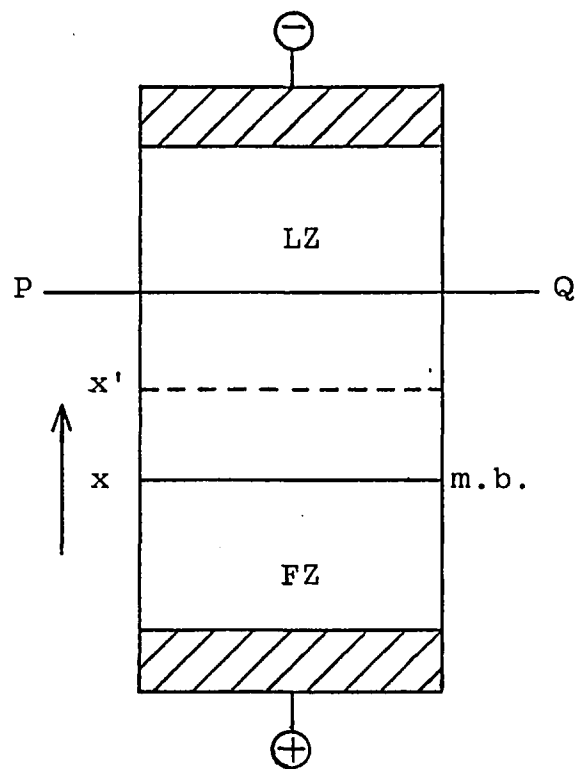


fig.(II.2b)

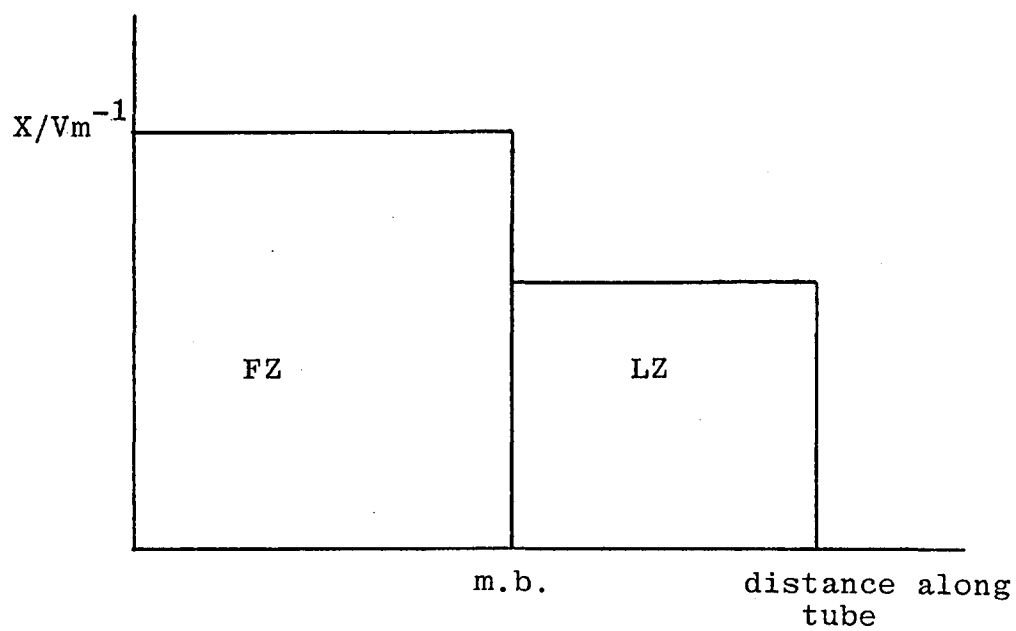


fig.(II.3)

where I is the current (A) and t is the time (s).

The above procedure can also be applied to the non-common ion-constituent F in the following solution. Hence

$$T_F^{FZ} = \frac{|z_F|c_F^{FZ}V_F}{It} \quad (\text{II.14})$$

Combination of equations (II.13) and (II.14) produces the Kohlrausch equation

$$\frac{T_L^{LZ}}{T_F^{FZ}} = \frac{|z_L|c_L^{LZ}}{|z_F|c_F^{FZ}} \quad (\text{II.15})$$

which gives the concentration c_F^{FZ} (mol m^{-3}) to which the following solution automatically adjusts itself behind the boundary. Equations (II.13), (II.14) and (II.15) must be corrected for a) the conductivity of impurity ions in the pure solvent (see section II.3.3) and b) the flow of solvent relative to the cell (see sections II.3.4 and II.3.5). The Kohlrausch equation is the basis of the indirect moving boundary method, in which a leading solution of known concentration and transference number is used. From analysis of the adjusted following solution, the transference number of the following non-common ion-constituent, T_F^{FZ} , can be calculated from equation (II.15).

It is interesting to examine the reason why diffusion does not destroy the boundary. The very existence of the boundary requires that

$$v_{m.b.} = \bar{v}_L^{LZ} = \bar{u}_L^{LZ} X_{LZ} = \bar{v}_F^{FZ} = \bar{u}_F^{FZ} X_{FZ} \quad (\text{II.16})$$

where $v_{m.b.}$ is the boundary speed (m s^{-1}). A stable boundary only exists if the mobility of the leading non-common ion-constituent is greater than that of the following non-common ion-constituent

$$\bar{u}_L^{LZ} > \bar{u}_F^{FZ} \quad (\text{II.17})$$

In such conditions

$$X_{FZ} > X_{LZ} \quad (\text{II.18})$$

as is shown in fig.(II.3). Thus when a trace of L diffuses into the following solution it finds itself in a higher potential gradient and speeds up to overtake the boundary. Alternatively if a trace of ion-constituent F diffuses into the leading solution it slows down due to the lower potential gradient and the boundary overtakes it. This phenomenon is known as the electrical restoring effect and explains why the boundary remains sharp even in the presence of diffusion. In practice a steady state is set up between these two forces and the boundary has a definite "thickness".

MacInnes and Longworth⁽²⁷⁾ defined a boundary "thickness", δ (m), in terms of $\bar{u}_L^{LZ}$, $\bar{u}_F^{FZ}$ and $v_{m.b.}$.

$$\delta = \frac{4RT}{Fv_{m.b.}} \cdot \frac{\bar{u}_L^{LZ} \bar{u}_F^{FZ}}{(\bar{u}_L^{LZ} - \bar{u}_F^{FZ})} \quad (\text{II.19})$$

Equation (II.19) explains the experimentally observed fact that the slower the boundary is the thicker it becomes.

The thickness δ for the boundary between KCl and LiCl solutions at KCl concentrations of 0.1M and 3M are about 2.3×10^{-4} m and 4.5×10^{-4} m at currents of 3.1mA and 22.3mA respectively.

Therefore for a boundary to be stable it must be both "electrically" stable ($\bar{u}_L^{LZ} > \bar{u}_F^{FZ}$) and gravitationally stable with the less dense solution uppermost.

The moving boundary method can produce results accurate to about $\pm 0.03\%$ in dilute solutions⁽⁸⁾. It is however very sensitive to good experimental technique. To ensure the validity of the results it should be shown that the boundary speed is independent of the nature of the following solution and, within a certain range its concentration. In addition, T_L^{LZ} should also be independent of the current used.

II.3.3 The Solvent Correction

The solvent correction for the direct m.b. method is the same as that for the Hittorf method. The specific conductance of the freshly prepared doubly-distilled water used was in the range $1 - 2 \times 10^{-4} \Omega^{-1} \text{ m}^{-1}$. This was mainly due to the presence of H^+ and HCO_3^- ions formed from dissolved carbon dioxide.

II.3.4 The Volume Correction

It will become apparent later that much of the effort in this project has been directed towards the accurate determination of the volume correction. It is therefore worthwhile to treat it in some detail, firstly with regards to dilute solutions and then later the refinements found necessary when dealing with higher electrolyte concentrations.

In the m.b. method the speed of the boundary is measured by recording the times at which it is coincident with marks etched on the m.b. tube. The time taken to traverse the volume between a pair of these etch marks leads directly to T_L^{LZ} in equation(II.13). This transference number, however, is defined relative to a solvent-fixed frame of reference and not an external frame of reference such as the etch marks on the m.b. tube. This would not matter if there was no movement of the frames of reference relative to each other during

an experiment. Unfortunately, due to electrode reactions and the transfer of solvated ions from one solution to another, there is a net shift of solvent relative to the cell during the run. To overcome this problem Lewis⁽²⁸⁾ proposed a quantitative correction to be applied to the observed transference number. This has subsequently become known as the volume correction.

The volume correction can only be reliably calculated if one of the electrodes is physically sealed (referred to as the closed electrode) and if the electrode reaction at this electrode does not cause gas evolution. In the direct m.b. method the relation between T_L^{LZ} (obs.) and T_L^{LZ} (corr.) is given by

$$T_L^{LZ} \text{ (corr.)} = T_L^{LZ} \text{ (obs.)} \pm |z_L^{LZ} c_L^{LZ}| \Delta V \quad (\text{II.20})$$

where ΔV is the volume gain ($\text{m}^3 \text{ mol}^{-1}$) per faraday between the air-face of the closed electrode and a point or plane in the leading homogenous solution which the boundary never passes. The plus and minus signs refer to the boundary moving towards or away from the closed electrode, respectively. The volume correction for the indirect m.b. method will be discussed in section (II.3.5). The solvent correction (see sections II.2 and II.3.3) must be applied to transference numbers measured relative to a stationary solvent frame of reference. Therefore the volume correction should be applied before the solvent correction⁽²⁵⁾.

From (II.20) it is evident that the higher the leading electrolyte concentration the greater the correction. Consider a typical volume gain of, say, $5 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$. For a uni-univalent electrolyte at 0.1M the volume correction is 0.0005. However at 4M it is 0.0200. It is because of this that the direct m.b. method has only been accurately applied to solutions up to a maximum concentration of ca. 0.2M⁽⁸⁾.

Let us now consider the volume correction for a specific system. The falling boundary system $\text{KCl} \leftarrow \text{LiCl}$ for 0.1M KCl will serve to illustrate the theoretical derivation of ΔV . This is a cationic boundary with the boundary speed giving $T_{\text{K}^+}^{\text{KCl}}$. We shall consider both a closed silver anode system and a closed silver/silver chloride cathode system.

a) Closed silver anode.

To calculate ΔV we must take into account all processes occurring between the air-face of the anode and a reference point or plane in the leading homogeneous KCl solution (fig.II.4). In this case the net volume gain can be split into contributions from three distinct sources. Firstly, the electrode reaction. For every faraday of electricity that passes, 1 mol Ag dissolves, 1 mol AgCl forms, and 1 mol Cl^- ions disappears from the LiCl solution.

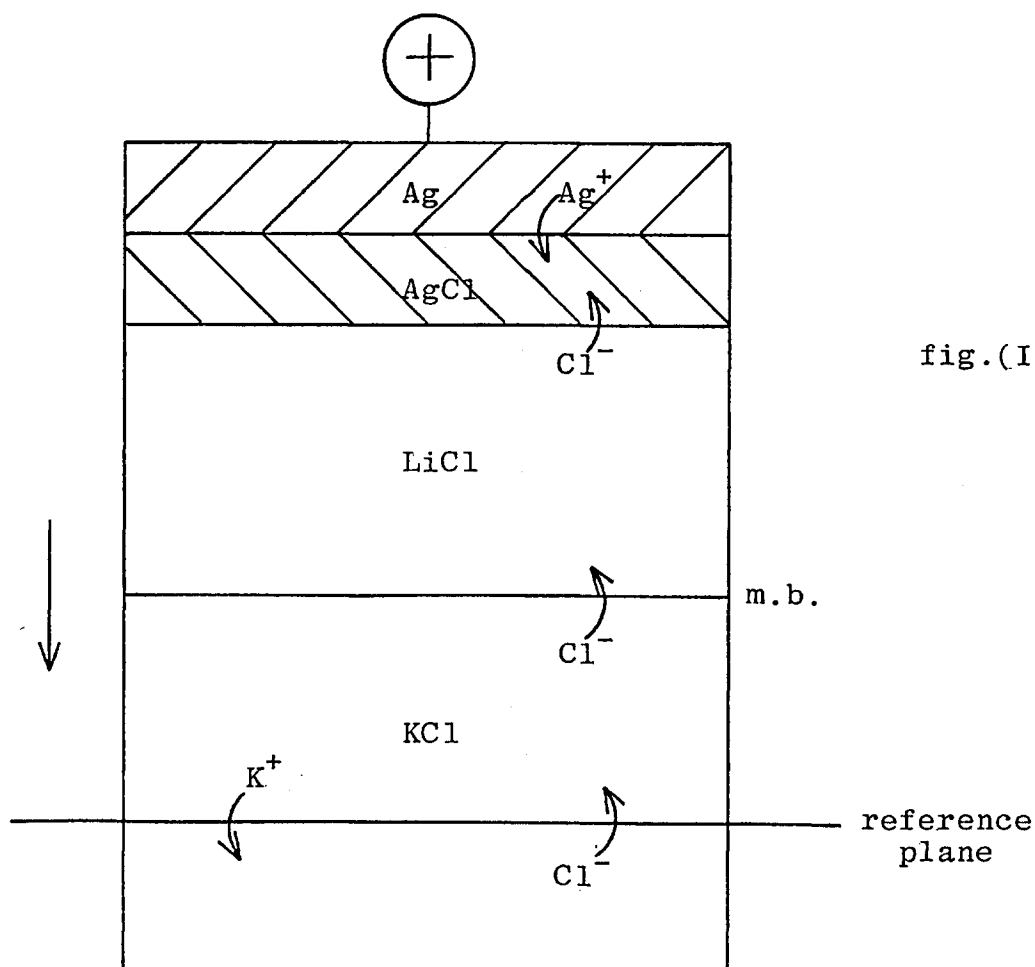


fig.(II.4)

Secondly, transfer of ions takes place across the moving boundary. Per faraday, 1 mol chloride ions is transferred from the KCl solution to the LiCl solution. (The Cl^- ions possess different apparent molar volumes ϕ ($\text{m}^3 \text{mol}^{-1}$) in the KCl and LiCl solutions). Finally, ions are transferred across the reference plane. Per faraday, $T_{\text{Cl}^-}^{\text{KCl}}$ mol chloride ions cross the reference plane and enter the volume between the reference plane and the air-face of the closed electrode. At the same time $T_{\text{K}^+}^{\text{KCl}}$ mol K^+ ions leave this volume. Summing all these contributions, the volume gain is

$$\begin{aligned} \Delta V &= -V_{\text{Ag}} + V_{\text{AgCl}} - \phi_{\text{Cl}^-}^{\text{LiCl}} + \phi_{\text{Cl}^-}^{\text{LiCl}} - \phi_{\text{Cl}^-}^{\text{KCl}} + T_{\text{Cl}^-}^{\text{KCl}} \phi_{\text{Cl}^-}^{\text{KCl}} - T_{\text{K}^+}^{\text{KCl}} \phi_{\text{K}^+}^{\text{KCl}} \\ &= -V_{\text{Ag}} + V_{\text{AgCl}} - \phi_{\text{Cl}^-}^{\text{KCl}} (1 - T_{\text{Cl}^-}^{\text{KCl}}) - T_{\text{K}^+}^{\text{KCl}} \phi_{\text{K}^+}^{\text{KCl}} \\ \text{But} \quad 1 - T_{\text{Cl}^-}^{\text{KCl}} &= T_{\text{K}^+}^{\text{KCl}} \end{aligned} \quad (\text{II.21})$$

$$\therefore \Delta V = -V_{\text{Ag}} + V_{\text{AgCl}} - T_{\text{K}^+}^{\text{KCl}} \phi_{\text{K}^+}^{\text{KCl}} \quad (\text{II.22})$$

where V is the molar volume ($\text{m}^3 \text{mol}^{-1}$) of the subscripted solid. As the boundary is moving away from the closed electrode ΔV must be subtracted from the observed transference number.

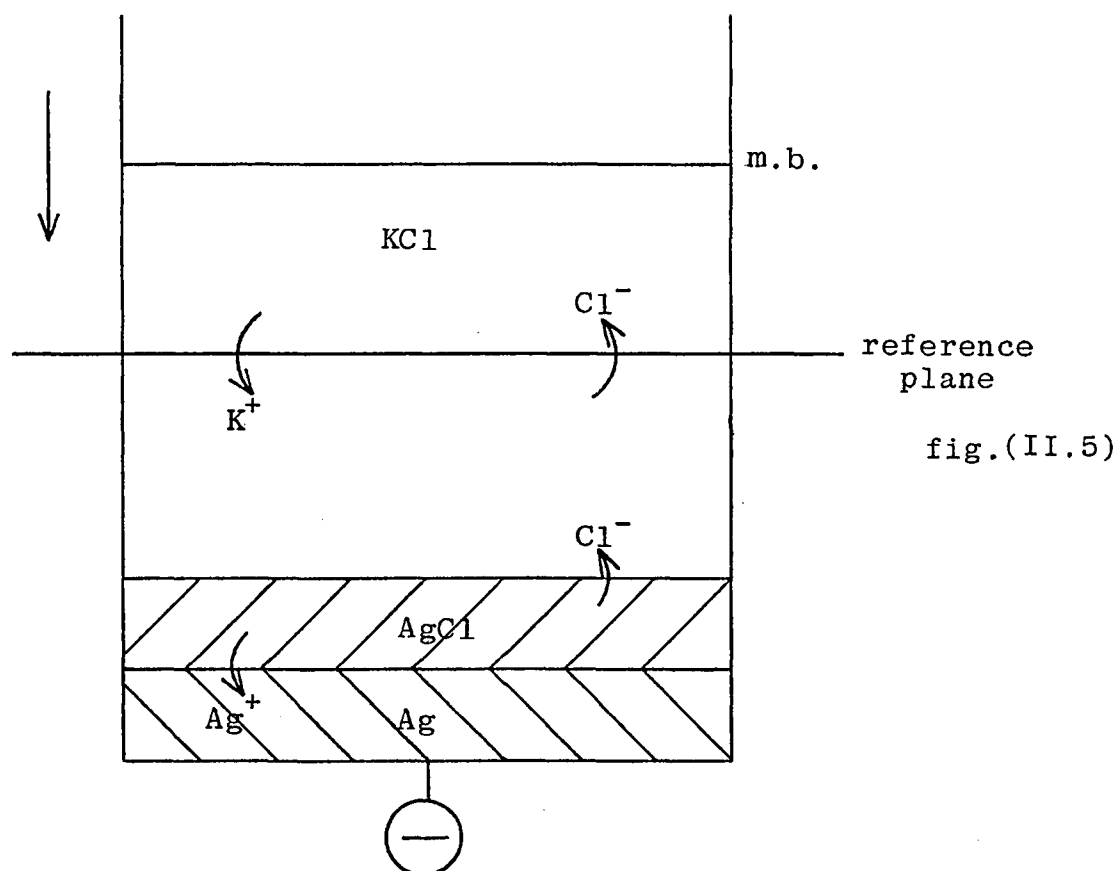
Until recently it had been usual to use the partial molar volumes, $\bar{V}$ ($\text{m}^3 \text{mol}^{-1}$), of ionic and solute species in the calculation of the volume correction and not as here, and indeed as in Lewis' original paper, the apparent molar volumes. The use of partial molar volumes however, assumes that the partial molar volume of the solvent itself remains constant. This cannot be the case as concentration changes take place around the electrode and in the following solution. The use of apparent molar volumes of the solute automatically takes into account any change in the partial molar volume of the solvent⁽²⁹⁾.

A more rigorous derivation of ΔV involves the subdivision of the volume between the reference plane and the closed electrode into many (theoretically an

infinite number of) volume elements. Transfer of ions should then be considered across the faces of all these volume elements. However the method outlined above is much simpler and, in dilute solutions, produces the same result as the more rigorous derivation.

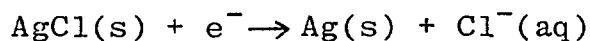
b) Closed silver/silver chloride cathode.

The system $\text{KCl} \leftarrow \text{LiCl}$ with a closed silver/silver chloride cathode is shown in fig.(II.5)



Treating this system in a similar manner to that above, the volume changes per faraday of electricity passed are:

1) Electrode reaction



- (i) loss of 1 mol AgCl(s)
- (ii) gain of 1 mol Ag(s)
- (iii) gain of 1 mol $\text{Cl}^-(\text{aq})$ in the KCl solution

$$\Delta V_1 = V_{\text{Ag}} - V_{\text{AgCl}} + \phi_{\text{Cl}^-}^{\text{KCl}}$$

2) Transfer across reference plane

- (i) loss of $T_{\text{Cl}^-}^{\text{KCl}}$ mol $\text{Cl}^-(\text{aq})$ in the KCl solution
 (ii) gain of $T_{\text{K}^+}^{\text{KCl}}$ mol $\text{K}^+(\text{aq})$ in the KCl solution

$$\Delta V_2 = -T_{\text{Cl}^-}^{\text{KCl}} \phi_{\text{Cl}^-}^{\text{KCl}} + T_{\text{K}^+}^{\text{KCl}} \phi_{\text{K}^+}^{\text{KCl}}$$

The total volume gain is therefore

$$\begin{aligned} \Delta V &= \Delta V_1 + \Delta V_2 \\ &= V_{\text{Ag}} - V_{\text{AgCl}} + \phi_{\text{Cl}^-}^{\text{KCl}} (1 - T_{\text{Cl}^-}^{\text{KCl}}) + T_{\text{K}^+}^{\text{KCl}} \phi_{\text{K}^+}^{\text{KCl}} \\ &= V_{\text{Ag}} - V_{\text{AgCl}} + T_{\text{K}^+}^{\text{KCl}} \phi_{\text{KCl}}^{\text{KCl}} \end{aligned} \quad (\text{II.23})$$

As the boundary is not in the region between the closed electrode and the reference plane ΔV is not affected by transfer of ions across the boundary. The volume gain for the closed Ag/AgCl cathode is the exact opposite of that for a closed Ag anode. Furthermore as the boundary is moving towards the closed electrode the correction must be added to the observed transference number. Therefore for this particular electrolyte/electrode assembly the observed transference number is independent of which of the electrodes is closed. However this is not usually the case.

The closed cathode system has been investigated experimentally by Smith⁽³⁰⁾ for 0.2m KCl. Using a specially designed pycnometer he was able to establish that the measured and the calculated volume changes agreed within the limits of experimental error for m.b. experiments.

II.3.5 The Kohlrausch Equation

The Kohlrausch equation

$$\frac{T_L^{\text{LZ}}}{T_F^{\text{FZ}}} = \frac{|z_L| c_L^{\text{LZ}}}{|z_F| c_F^{\text{FZ}}} \quad (\text{II.15})$$

predicts the concentration, c_F^{FZ} , to which the following solution will automatically adjust itself behind the leading solution. It was long thought that this equation, involving only ratios of concentrations and transference numbers, required no volume correction. However, in the 1960s it was realised⁽²⁹⁾ that this was not the case and that (II.15) was indeed subject to a correction.

The various attempts at deriving an expression for the correction have recently⁽²⁹⁾ been rationalised and shown to agree with an earlier expression due to Hartley.⁽³¹⁾ Corrected for volume changes the Kohlrausch equation becomes

$$\frac{t_L^{LZ}}{t_F^{FZ}} = \frac{|z_L| m_L^{LZ}}{|z_F| m_F^{FZ}} \quad (\text{II.24})$$

where m is the molality (moles of solute per kg of solvent) of the subscripted ion-constituent in the super-scripted solution.

The Kohlrausch equation is often combined with limiting transference data to give an estimate of m_F^{FZ} for direct m.b. work. This allows an experimenter to select a suitable initial concentration of the indicator electrolyte.

II.4 The E.m.f. Method

The third main method for the measurement of transference numbers is the e.m.f. method. In the two previous methods, the Hittorf and m.b. methods, an electric current is actually passed through the electrolyte solution. In this method however, one measures the electromotive force of concentration cells with liquid junctions.

The concentration cell required (called a cell with

transference) contains two solutions of the same electrolyte but at different concentrations (for an example see section II.4.2). They meet at an electrolyte/electrolyte interface to form a liquid junction. The potential across this junction, as will be shown, depends on the transference number of the electrolyte.

The e.m.f. of a cell with transference is made up of three separate potential differences. Two of these arise at the electrode/electrolyte interfaces, the third is produced at the liquid junction.

II.4.1 The Liquid Junction Potential

The liquid junction is a region in which the concentration of electrolyte varies from a constant value, c_1 , on one side of the junction to another constant concentration, c_2 , on the other side. The variation in concentration in this region is complex but we can imagine it to be made up of many thin layers involving infinitesimally small concentration differences.⁽³²⁾

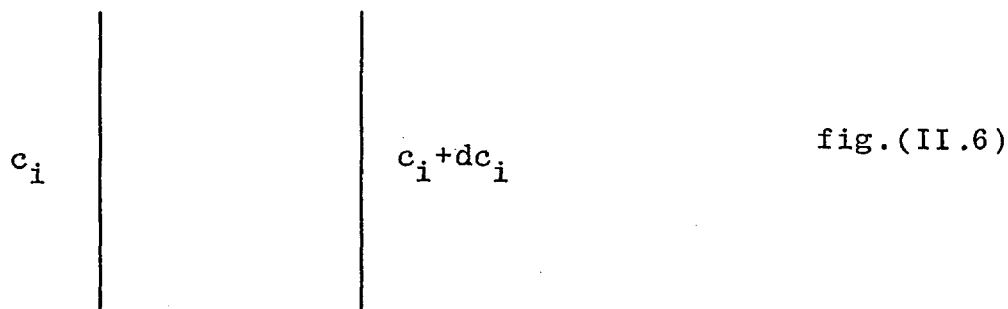


Figure (II.6) represents one such layer where c_i is the concentration of ions (or more correctly ion-constituents) of type i on one side of the layer and $c_i + dc_i$ that on the other. If one faraday of electricity is passed reversibly across this layer, T_i/z_i moles of ion-constituent i will be transferred across it. The total change in Gibbs free energy, dG , for the transference of all the ionic species in the solution is given by

$$dG = \sum (T_i/z_i) d\mu_i \quad (\text{II.25})$$

where μ_i , the chemical potential of species i , is given by

$$\mu_i = \mu_i^\ominus + RT \ln a_i \quad (\text{II.26})$$

Here $\mu_i^\ominus$ is the chemical potential under standard conditions and a_i is the activity of species i . By combining (II.25) and (II.26), and integrating over the whole liquid junction, the total change in free energy for the liquid junction between solutions 1 and 2 is given by

$$\Delta G_L = RT \int_1^2 \sum (T_i/z_i) d \ln a_i \quad (\text{II.27})$$

The free energy change is then related to the liquid junction potential E_L

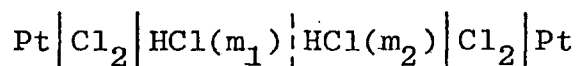
$$\Delta G_L = -FE_L \quad (\text{II.28})$$

so that

$$E_L = -\frac{RT}{F} \int_1^2 \sum (T_i/z_i) d \ln a_i \quad (\text{II.29})$$

II.4.2 The Concentration Cell with Liquid Junction

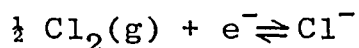
Consider the concentration cell



consisting of two chlorine electrodes and two solutions of aqueous HCl of molalities m_1 and m_2 , where $m_1 > m_2$.

The cell is "activated" by the tendency of the two HCl solutions to come to the same concentration. Thus chloride ions will have a greater tendency to give chlorine at the left hand electrode (LHE) than at the right hand electrode (RHE). The LHE is therefore the more negative one. The cell processes can be visualised best

by imagining the effect of a reversible discharge of the cell, as shown in fig.(II.7). At the two electrodes:



At the liquid junction H^+ ions will migrate towards the RHE (which now acts as the cathode) and chloride ions to the LHE. Per faraday of electricity passed $T_{\text{H}^+}^{\text{HCl}}$ mol H^+ and $T_{\text{Cl}^-}^{\text{HCl}}$ mol Cl^- ions will be so transferred.

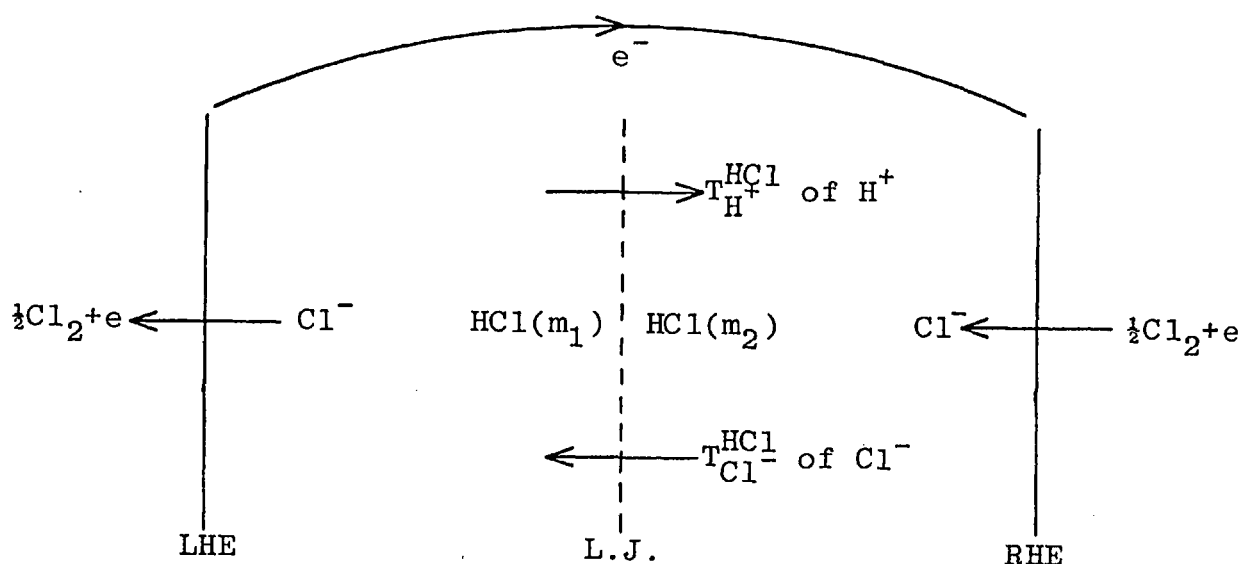


fig.(II.7)

Quantitatively, if the chlorine gas is at a pressure of p atm, the electrode potentials E_1 and E_2 for the LHE and RHE respectively are

$$E_1 = E^\ominus + \frac{RT}{F} \ln \left(\frac{p^{\frac{1}{2}}}{a_{\text{Cl}^-}(\text{m}_1)} \right) \quad (\text{II.30})$$

$$E_2 = E^\ominus + \frac{RT}{F} \ln \left(\frac{p^{\frac{1}{2}}}{a_{\text{Cl}^-}(\text{m}_2)} \right) \quad (\text{II.31})$$

where $a_{\text{Cl}^-}(\text{m}_1)$ and $a_{\text{Cl}^-}(\text{m}_2)$ are the chloride ion activities in the two HCl solutions, and $E^\ominus$ is the standard electrode potential of the $\text{Cl}_2|\text{Cl}^-$ couple. At the liquid junction, by equation (II.29):

$$E_L = -\frac{RT}{F} \int_1^2 \left[T_{H^+}^{HCl} d\ln a_{H^+} - T_{Cl^-}^{HCl} d\ln a_{Cl^-} \right] \quad (II.32)$$

Writing $T_{Cl^-}^{HCl} = 1 - T_{H^+}^{HCl}$, and combining equations (II.30), (II.31) and (II.32) with suitable rearrangement, gives for the e.m.f. of the cell, E,

$$E = E_2 - E_1 + E_L = -\frac{RT}{F} \int_1^2 T_{H^+}^{HCl} d\ln(a_{H^+} + a_{Cl^-}) \quad (II.33)$$

It is not possible to measure single ion activities but by using the mean ion activity, a_{HCl} , given by

$$a_{H^+} \cdot a_{Cl^-} = a_{HCl}^2 = m_{HCl}^2 \gamma^2 \quad (II.34)$$

where γ is the mean molal activity coefficient, equation (II.33) becomes

$$E = \frac{2RT}{F} \int_2^1 T_{H^+}^{HCl} d\ln a_{HCl} \quad (II.35)$$

Miller⁽¹²⁾ has pointed out that strictly speaking the above derivation from classical equilibrium thermodynamics is invalid as irreversible diffusion processes are taking place. However, he obtained the same equation from the theory of irreversible thermodynamics.

II.4.3 Calculation of the Transference Number

It is usual^(15,33) to calculate the transference number from the differential form of (II.35), namely

$$T_{H^+}^{HCl} = \frac{F}{2RT} \frac{dE}{d\ln(m\gamma/K)} \quad (II.36)$$

where K is the value of $m\gamma$ at some constant reference concentration. $T_{H^+}^{HCl}$ is then calculated by curve-fitting the e.m.f. and concentration data to give a polynomial expression for E in terms of $\ln(m\gamma/K)$ or $[\ln(m\gamma/K)]^{\frac{1}{2}}$. Differentiation of this expression followed by evaluation

at various values of $\ln(m\gamma/K)$ gives $T_{H^+}^{HCl}$ at the relevant value of the variable concentration.

An alternative method, devised by Pikal and Miller⁽¹³⁾, is to define an "integral transference number" $\bar{T}$ as

$$\bar{T} = \frac{F}{2RT} \cdot \frac{E}{\ln(m\gamma/K)} \quad (II.37)$$

The advantage of this method is that $\bar{T}$ is a simple and slowly varying function of $(m\gamma/K)$. It is therefore more accurate to express $\bar{T}$ rather than E as a function of $\ln(m\gamma/K)$. $\bar{T}$ is related to the actual transference number by

$$T_{H^+}^{HCl} = \bar{T} + (m\gamma/K) \ln(m\gamma/K) \cdot \left(\frac{d\bar{T}}{d(m\gamma/K)} \right) \quad (II.38)$$

The reason why the e.m.f. method is more uncertain than the other two methods is because the calculation of $T_{H^+}^{HCl}$ involves a differential expression. This produces the loss of one order of accuracy.

CHAPTER THREE

TRANSFERENCE NUMBERS IN THE SOVIET LITERATURE

III.1 Introduction

During the past twenty years much work has been done in the Soviet Union on the determination of transference numbers in concentrated aqueous electrolyte solutions. This work falls into three main categories. Firstly, the determination of transference numbers measured with respect to the solvent ("apparent" transference numbers) using the so-called simultaneous observation technique. This is based on the m.b. method in which the rate of movement of the solution is measured as well as that of the ions. Secondly, using a similar experimental technique, an attempt has been made to measure "real" or "true" transference numbers (see below). Finally, the indirect m.b. method was used to measure apparent transference numbers.

The difference between apparent and true transference numbers is an important one and it will be outlined below. The solvent in an electrolyte solution can be crudely classified into one of two groups⁽⁸⁾: that which is solvated around ions and transported along with them in an electric field, and that which is "free". In actual fact there is a rapid interchange of solvent molecules between these two groups and a dynamic equilibrium exists. Transference numbers measured by the Hittorf, m.b. and e.m.f. methods are referred to the solvent as a whole (solvated and free solvent together). "True" transference numbers, on the other hand, are defined with respect to the free part of the solvent only. All the methods so far proposed for determining them have involved basic flaws.⁽⁸⁾

Concern at certain aspects of the theoretical treatment and experimental techniques used in these Soviet papers prompted a critical survey of this work.

III.2 The Simultaneous Observation Method

The simultaneous observation (s.o.) method, so-called because it involves the simultaneous observation of the movement of the boundary and of the solution, was used by the Soviet workers for the measurement of "apparent" transference numbers in concentrated aqueous solutions of HCl (T_+),⁽³⁴⁾ LiCl (T_+),⁽³⁵⁾ CuCl₂ (T_+ and T_-),⁽³⁶⁾ LiNO₃ (T_+),⁽³⁷⁾ MgCl₂ (T_+),⁽³⁸⁾ and ZnCl₂ (T_+ and T_-).⁽³⁹⁾

In the next two sections the experimental technique and the underlying theoretical considerations will be discussed as they appear in the Soviet literature. Sections (III.2.3) and (III.2.4) will deal with the main criticisms of these aspects of the method.

III.2.1 The S.O. Method - Experimental

The s.o. cell is illustrated diagrammatically in fig.(III.1), using Kaimakov and Fiks' system⁽³⁴⁾ as an example. As in the m.b. method a boundary is formed between the two chosen solutions, in this case HCl and CdCl₂. On passing current the rates of movement of the boundary and of the solution meniscus of the following electrolyte in the anode capillary are measured to $\pm 0.05\text{mm}$ by means of cathetometers. The movement of the boundary can be controlled by means of a counter-flow device and in most experiments this was used to keep the boundary stationary. For boundaries formed from two colourless solutions a small amount of a suitable coloured electrolyte (e.g. CoCl₂, Co(NO₃)₂, CuCl₂) was placed between the leading and following solutions. Kaimakov and Sharkov⁽³⁹⁾ used a microthermistor sealed into the tube to detect the position of the boundary.

The electrodes were usually platinum wires, although dissolving cadmium anodes were also used.^(35,38) In the case of Pt cathodes a quantity of acid was placed around

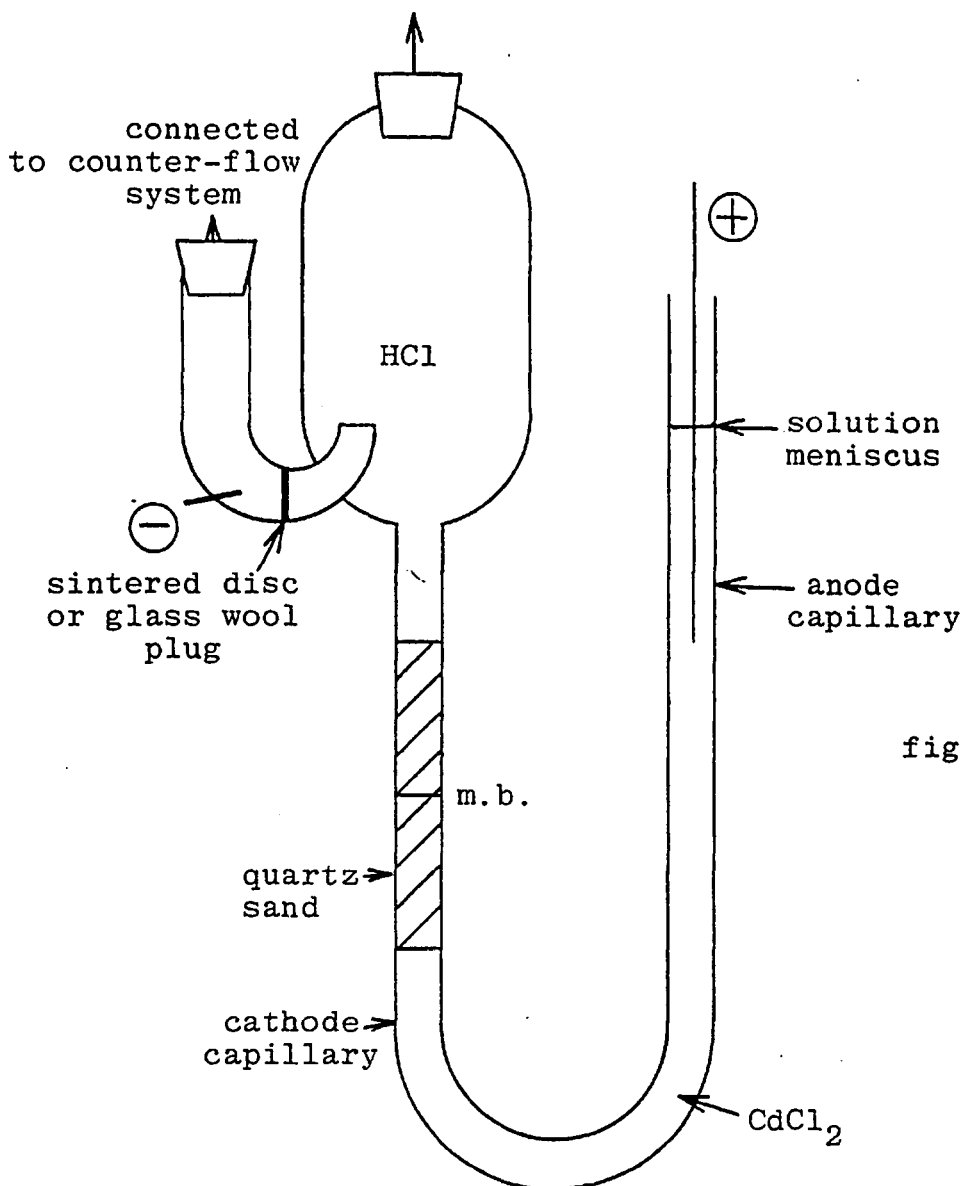


fig. (III.1)

the electrode to neutralize OH^- ions formed by the electrode reaction. The cathode compartment was separated from the rest of the cell by a sintered glass disc or glass wool plug to prevent diffusion of the acid into the m.b. tube.

Quartz sand packing was placed in the m.b. tube in order to increase the hydrodynamic resistance to flow of the solutions. The grain size of the sand (usually 20–40 μm) was chosen so as to have no effect on the transference number. As the sand packing reduces the actual cross-sectional area of the tube, experiments were carried out to find the effective area of the packed tube.

The temperature of most (but not all) of the cell was

maintained at $20 \pm 0.01^\circ\text{C}$ by means of a jacket surrounding the cell through which thermostatted liquid was passed. The currents employed varied from 5 to 15 mA. Maximum solute concentrations ranged from 4-5m for CuCl_2 and MgCl_2 , 14-15m for HCl and LiCl and as high as 23m for LiNO_3 .

III.2.2 The S.O. Method - Theoretical⁽³⁴⁾

The same notation will be employed as in section (II.3.2). In order to determine the transference number of the leading non-common ion-constituent T_L^{LZ} , it is necessary to determine its speed relative to the solvent as a whole, v_L (m s^{-1}). Then

$$T_L^{\text{LZ}} = \frac{|z_L| c_L^{\text{LZ}} v_L A F}{I} \quad (\text{III.1})$$

where A is the cross-sectional area of the cathode capillary (m^2). The ionic speed relative to the m.b. tube, $v_{L,t}$, is related to v_L by

$$v_{L,t} = v_{\text{m.b.}} = v_L - v_{0,t} \quad (\text{III.2})$$

where $v_{0,t}$ is the speed of the solvent with respect to the tube with upwards motion being defined as positive (the subscript 0 refers to the solvent and subscript t indicates a property measured with respect to the tube. If subscript t is absent then the property is measured with respect to the solvent as a whole). If the boundary is kept stationary then

$$v_{L,t} = 0 \quad (\text{III.3})$$

and

$$v_L = v_{0,t} \quad (\text{III.4})$$

To measure $v_{0,t}$ the supposition is made that the flow of solvent is uniform throughout the cell

$$c_0 v_{0,t}^A = c_0' v_{0,t}^{A'} \quad (\text{III.5})$$

where c_0 is the solvent concentration (mol dm^{-3}) and a dash superscript signifies that the property is measured in the anode capillary limb.

Rearrangement of (III.4) and (III.5) and substitution into (III.1) gives

$$T_L^{LZ} = \frac{A' F v_{0,t}^{A'} |z_L| c_L^{LZ}}{I} \cdot \frac{c_0'}{c_0} \quad (\text{III.6})$$

If, due to the electrode reaction, the concentration of solute around the anode is very small, the concentration of the solvent in this region, c_0' , can be equated to the concentration in the pure solvent. Then by saying $c_0' = 1/M_0$ where M_0 is the molar mass of the solvent (kg mol^{-1})

$$c_L^{LZ} \cdot \frac{c_0'}{c_0} = m_L^{LZ} \quad (\text{III.7})$$

so that (III.6) becomes

$$T_L^{LZ} = \frac{|z_L| m_L^{LZ} v_{0,t}^{A'} A' F}{I} \quad (\text{III.8})$$

Thus T_L^{LZ} can be determined simply by measuring the speed of the solution meniscus in the anode capillary limb, $v_{0,t}^{A'}$.

III.2.3 Criticisms of the Experimental Technique

Perhaps the most innovative aspect of the s.o. method as compared with the more conventional m.b. technique is the use of quartz sand packing in the measuring tube. Kaimakov and Fiks⁽³⁴⁾ recognised the importance of Joule heating effects in concentrated solutions when relatively high currents are being used. By solving the heat conduction

equation an expression was obtained for the mean temperature difference between the solution and the outer walls of the m.b. tube

$$\Delta\theta = \bar{\theta} - \theta_e = \frac{q R_i^2}{2 k_{\text{soln}}} \left[\frac{1}{4} + \frac{k_{\text{soln}}}{k_{\text{glass}}} \ln \left(\frac{R_e}{R_i} \right) \right] \quad (\text{III.9})$$

where $\bar{\theta}$ and θ_e are the mean temperature of the solution inside the tube and the external temperature of the tube respectively, R_e and R_i the external and internal radii of the tube, k is the thermal conductivity ($\text{J m}^{-1} \text{s}^{-1} \text{K}^{-1}$) and q the rate of heat evolution in the solution per unit volume ($\text{J s}^{-1} \text{m}^{-3}$). Equation (III.9) predicts that lower mean temperature differences are obtained by using tubes of smaller bore. Alternatively, as was done in this case, the tube can be filled with some sort of packing material.

However, closer inspection of the q term reveals an inverse fourth order dependence on R_i . The heat evolved on passing a current of I amps through a conductor of resistance R ohms is $I^2 R$. Then

$$q = \frac{I^2 R}{V} = \frac{I^2 \sigma l}{AV} = \frac{I^2}{A^2 \kappa_{\text{soln}}} = \frac{I^2}{\pi^2 R_i^4 \kappa_{\text{soln}}} \quad (\text{III.10})$$

where l , A and V are the length, cross-sectional area and volume, respectively, of the electrolyte solution in the tube, σ its specific resistance (Ωm) and κ its specific conductance ($\Omega^{-1} \text{m}^{-1}$). Insertion of (III.10) in (III.9) gives

$$\Delta\theta = \frac{I^2}{2 \pi^2 R_i^2 \kappa_{\text{soln}} k_{\text{soln}}} \left[\frac{1}{4} + \frac{k_{\text{soln}}}{k_{\text{glass}}} \ln \left(\frac{R_e}{R_i} \right) \right] \quad (\text{III.11})$$

which is the equation derived by Gwyther, Kumarasinghe and Spiro.⁽⁴⁰⁾ Equation (III.11) predicts, and common-sense

suggests, that the narrower the column of electrolyte the greater the heating effect for a given current.

The use of quartz sand has two other effects. Firstly, it introduces the possibility of electro-osmotic flow (movement of liquid relative to a stationary charged surface by an applied electric field⁽⁴¹⁾), and secondly errors are introduced when measuring the effective cross-sectional area of a packed tube.

In many of the studies⁽³⁴⁻³⁹⁾ CdCl_2 was used as the indicator electrolyte. This electrolyte occupies part of the cathode capillary as well as the whole of the anode limb (see fig.III.1). This must mean that in certain regions of the cell there is gravitational instability of the CdCl_2 solution. For instance, if a dissolving Cd anode is used the high CdCl_2 concentration around the electrode will cause the anode section of the tube to be unstable. The possibility of gravitational instability is increased when only one concentration of indicator solution is used for a wide range of leading solutions as Varshavskaya and Kaimakov⁽³⁸⁾ appear to have done. The use of CdCl_2 also causes problems in that its apparent molar volume has a relatively large concentration dependence (see section IV.2.1). Thus slight changes in concentration of the inhomogeneous CdCl_2 solution could affect the level of the anode meniscus quite considerably.

Cadmium was often used as an anode.^(35,38) In addition to certain theoretical disadvantages which will be dealt with in the next section, the use of Cd anodes also requires the calculation of a correction for the changes in volume occurring around the electrode. Kaimakov⁽³⁵⁾ appears to have used a mixture of theory and guesswork in order to estimate the size of this correction. It should be pointed out however, that where both Pt and Cd anodes have been used the agreement between the results is within the limits of the experimental error.⁽³⁸⁾

Although Kaimakov⁽³⁴⁾ applied a correction for the loss of solvent around a gassing Pt anode by the saturation of the chlorine bubbles produced with water vapour, no mention is made of the difficulties in accurately determining the position of the anode solution meniscus when gas is being evolved.

Other, smaller, criticisms include the fact that not all of the cell was thermostatted. When measuring small changes in volume, temperature control is very important. The use of coloured electrolytes to indicate the position of the boundary is not desirable. There is also a general lack of experimental details and tabulated results in the Soviet papers.

III.2.4 Theoretical Criticisms

Two major criticisms can be levelled at the theoretical background of the s.o. method. The first concerns the assumption in the derivation of equation (III.8) that the flow of solvent is uniform throughout the cell. Although the flow of solution is uniform throughout the cell, the same does not apply to the solvent.⁽⁴²⁾ For let us assume that Kaimakov and Fiks' assumption⁽³⁴⁾ is correct. Then the flow of solvent will also be constant in a more conventional moving boundary cell with one electrode closed. Consider the example of Spiro⁽⁴³⁾ (fig.III.2) with a tube of uniform cross-section. Part of the indicator NaCl solution has been irradiated to form a second m.b. ($\text{NaCl} \leftarrow \text{Na}^*\text{Cl}$) which moves with the same speed as the $\text{KCl} \leftarrow \text{NaCl}$ boundary because the intervening NaCl solution is comprised only of the homogeneous adjusted NaCl solution. If the flow of solvent is uniform throughout the cell then $c_0 dV_0/dt$ will be the same in the homogeneous KCl and adjusted NaCl solutions, where dV_0/dt is the rate of movement of the solvent. The volume changes undergone by an "average" solvent molecule⁽²⁸⁾ during the time it takes to pass one faraday of electricity in the two homogeneous solutions are given by

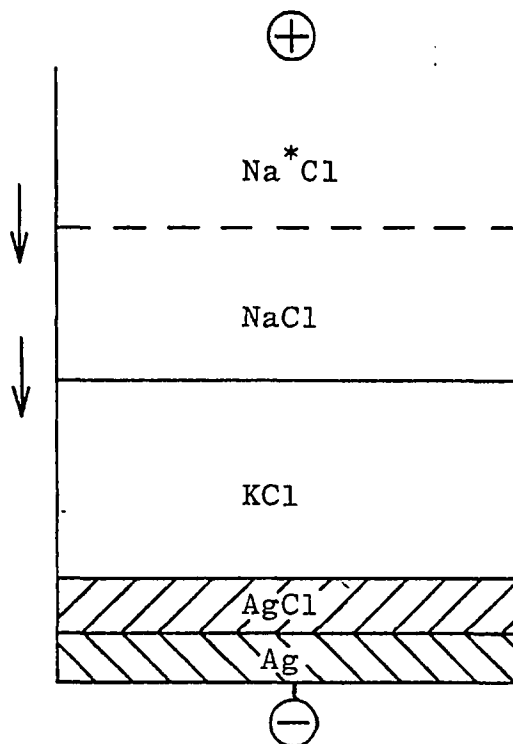


fig.(III.2)

$$\Delta V_0^{KCl} = V_{Ag} - V_{AgCl} + T_{K^+}^{KCl} \phi_{KCl} \quad (III.12)$$

$$\Delta V_0^{NaCl} = V_{Ag} - V_{AgCl} + T_{Na^+}^{NaCl} \phi_{NaCl} \quad (III.13)$$

If V_F is the volume the boundaries are observed to pass through per faraday, then the ratio of the corrected transference numbers is

$$\frac{T_{K^+}^{KCl}}{T_{Na^+}^{NaCl}} = \frac{c_{KCl} (V_F + \Delta V_0^{KCl})}{c_{NaCl} (V_F + \Delta V_0^{NaCl})} \quad (III.14)$$

Gwyther and Spiro have shown that⁽²⁹⁾

$$\frac{T_{K^+}^{KCl}}{T_{Na^+}^{NaCl}} = \frac{c_{KCl}}{c_0^{KCl}} \cdot \frac{c_0^{NaCl}}{c_{NaCl}} \quad (III.15)$$

Rearrangement of (III.14) and (III.15) gives

$$c_0^{KCl} \Delta V_0^{KCl} - c_0^{NaCl} \Delta V_0^{NaCl} = V_F (c_0^{NaCl} - c_0^{KCl}) \quad (III.16)$$

The right-hand side is not equal to zero at finite solute concentrations, and its magnitude increases as the KCl concentration rises. Thus the flow of solvent is not uniform throughout the cell and the assumption of Kaimakov and Fiks' is invalid. It may be added that in the conventional m.b. method (section II.3.4), the volume correction is calculated relative to a solvent plane in the homogeneous leading solution. The s.o. method, on the other hand, focuses entirely on the following solution, contrary to Lewis' advice.⁽²⁸⁾

The second criticism of the derivation in section (III.2.2) is that the solution in the anode limb is treated as the pure solvent. This assumption is not even true for a Pt anode where the solute concentration is partly depleted by the electrode reaction, and it is quite incorrect for a dissolving Cd anode in a chloride solution. At the relatively high current densities used large amounts of CdCl_2 would be formed around the electrode, affecting the level of the solution meniscus in the anode limb.

It must be said however, that for a technique which appears so beset by possible sources of error, any of which could have a significant effect on the measured transference numbers, reasonably good agreement is found with more conventional techniques. Recent measurements in this laboratory⁽⁴⁴⁾ support Konstantinov and Kaimakov's $T_{\text{Cu}}^{\text{CuCl}_2}$ data as opposed to the earlier Hittorf data.⁽⁴⁵⁾ For solutes where only graphical data are available there appears to be reasonable agreement between the s.o. results and Hittorf and e.m.f. values.

III.3 The Measurement of True Transference Numbers

Troshin has published a long series of papers over the past twenty years concerned with the determination of true transference numbers and the phenomena of electro-osmosis

and ionic hydration.⁽⁴⁶⁻⁶¹⁾

Knowledge of the extent (if any) of hydration of ions in solution is important in the study of electrolyte solutions. In what form do ions actually exist in solution? How many water molecules can be said to be "associated" with each ion and how does hydration effect the transport properties of ions?

Troshin's experimental procedure will be discussed below, and vagaries in the technique outlined without being dealt with in any great detail.

III.3.1 Measurement of Ionic Speeds Relative to the Solution

Troshin's experiments were carried out using the solution as a whole as the reference frame. This, it was implied,⁽⁴⁶⁾ is equivalent to taking the free part of the solvent only as immobile with respect to the ions.

The technique used was based on the s.o. method with two important differences. Firstly, instead of the molal concentration in equation (III.8) he used the molar concentration. The second difference concerns the positioning of the electrolyte boundary in the quartz sand and the processes taking place in the region of the boundary.⁽⁴⁶⁾ Figure (III.3) illustrates the boundary region for the system $M_1A \leftarrow M_2A$.

In general the volumes occupied by the M_1 and M_2 ions will be different due to differences in the ionic radii and the extent of hydration of the ions. If, for instance, the volume occupied by M_1, V_1 , is greater than that occupied by M_2, V_2 , then on passing current it is claimed⁽⁴⁶⁾ that a "pressure" difference will be set up in the region of the boundary. In this case it will cause both the M_1 and M_2 ions to be drawn towards the boundary and hence effectively decrease the observed speed of the M_1 ions and increase that of the M_2 ions. Therefore

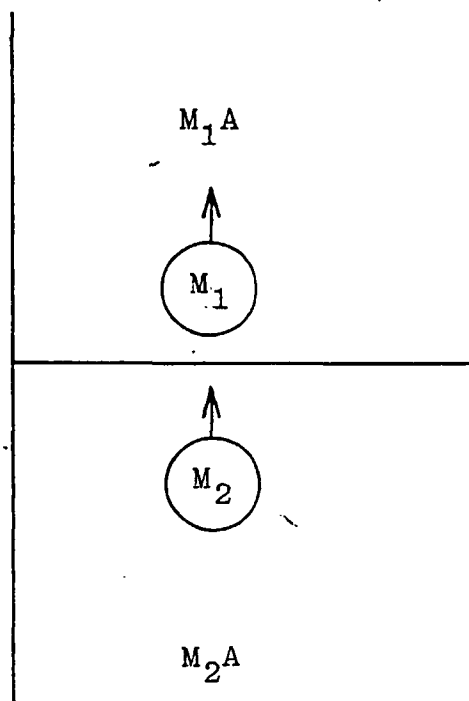


fig. (III.3)

$$v_{m.b.} = v_1 - v_1' \quad (III.17)$$

$$v_{m.b.} = v_2 + v_2' \quad (III.18)$$

where v is the speed of the ions relative to the solution and v' is the change in speed of the ions caused by the difference in the so-called "moving volumes".

Conversely, if $V_1 < V_2$ the ions have extra motion away from the boundary and

$$v_{m.b.} = v_1 + v_1' \quad (III.19)$$

$$v_{m.b.} = v_2 - v_2' \quad (III.20)$$

Unlike the s.o. method, where the quartz sand was used in an attempt to reduce the amount of Joule heating, its main purpose in this technique appears to be to increase the hydrodynamic resistance to flow of the solutions.

It is claimed⁽⁴⁶⁾ that all factors causing displacement of the solution as a whole with respect to the measuring tube, except that due to the difference in moving volumes, can be excluded by the use of the quartz sand. These factors include the difference between the densities of the leading and following solutions and the difference in solution levels in the cathode and anode limbs of the cell. The latter can be caused by changes in volume due to the electrode reactions and by preferential displacement of part of the solvent towards one of the electrodes due to hydration of the ions.

If the speed of the boundary is measured at the lower end of the sand column so that the entire column is in the leading solution then the hydrodynamic resistance of the sand will prevent the additional movement of the boundary in the M_1A solution due to the difference in the moving volumes. Therefore

$$v_{m.b.}^1 = v_1 \quad (III.21)$$

and the additional movement only effects the M_2 ions. Similarly, measurement of $v_{m.b.}$ at the upper end of the sand column causes additional movement of the M_1 ions only and

$$v_{m.b.}^u = v_2 \quad (III.22)$$

The values v_1 and v_2 are the speeds of the M_1 and M_2 ions, respectively, relative to the solution as a whole. Use of (III.1) then gives the transference numbers measured relative to the solution.

It is implicit throughout Troshin's argument that because a) the ionic speeds are measured relative to a solution reference frame and b) the additional movement

of the ions is determined by the difference in moving volumes (caused in turn largely by differences in hydration), then the measured transference numbers are somehow functions of the extent of hydration and are thus true transference numbers.

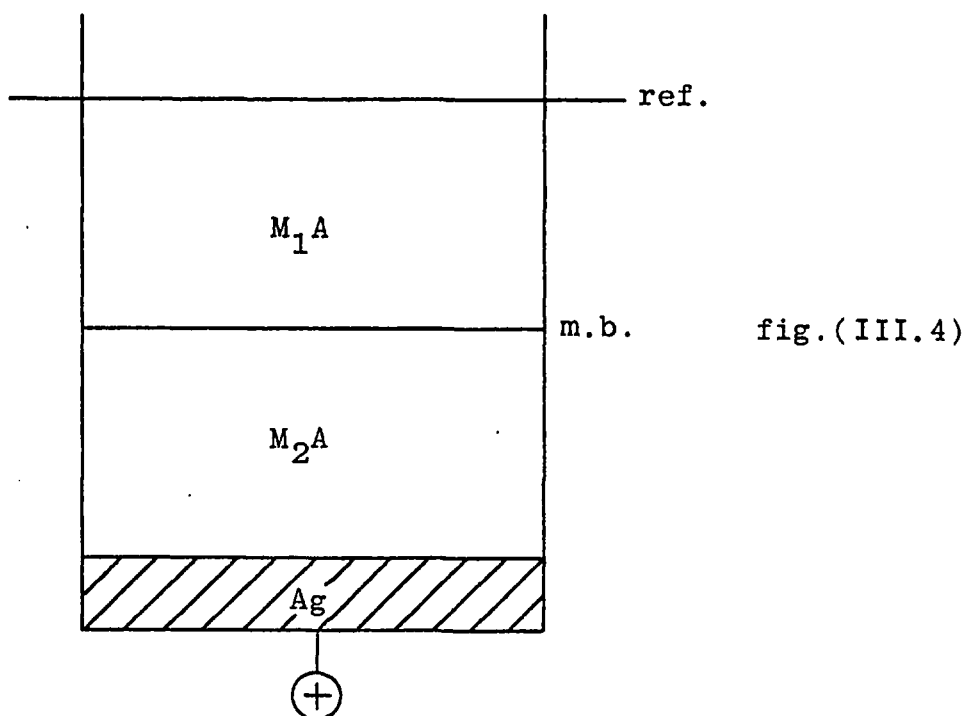
This technique has been used to measure transference numbers and the extent of hydration in concentrated aqueous solutions of HCl ^(50,51), LiCl ⁽⁴⁶⁻⁵¹⁾, NaCl ^(50,51), KCl ⁽⁴⁹⁻⁵¹⁾, LiNO_3 ⁽⁵²⁾, HNO_3 ⁽⁵³⁾, Li_2SO_4 ⁽⁵⁴⁾, NH_4Cl , NH_4NO_3 and $(\text{NH}_4)_2\text{SO}_4$ ⁽⁵⁵⁾, NiCl_2 , $\text{Ni}(\text{NO}_3)_2$ and NiSO_4 ⁽⁵⁶⁾, LiI , NaI and KI ⁽⁵⁷⁾, KOH ⁽⁵⁸⁾, LiOH ⁽⁵⁹⁾, NaOH ⁽⁶⁰⁾ and CoCl_2 ⁽⁶¹⁾.

Hydration numbers were determined by measuring the flow of the solution as a whole^(47,48). This flow was stated to be due to movement of solvent by both electro-osmotic flow and preferential transport of hydrated solvent towards one of the electrodes. The measurements were carried out for solute concentrations at which it was shown⁽⁴⁷⁾ that the electro-osmotic flow was zero. The remaining flow was then solely caused by hydration of the ions.

III.3.2 True Transference Numbers or Not?

Three major questions pertain to Troshin's technique of measuring true transference numbers. Does the frame of reference used coincide with that of the immobile free solvent? Are these moving volumes and the resultant "pressure" difference physical realities? Is the quartz sand an effective barrier to the flow of the solutions? The answers to these questions will show whether the results obtained are in fact true transference numbers or a third type of transference number measured relative to a reference frame devoid of any simple physical interpretation.

Consider the system shown in fig.(III.4)



In the direct m.b. technique the reference plane moves with respect to the cell to ensure that there is the same total amount of solvent between the reference plane and the air-face of the anode after the experiment as there was before. When measuring true transference numbers the movement of the reference plane is such that it is the total amount of free solvent which remains unchanged in this region. If the solution is crudely regarded as a mixture of free solvent molecules and solvated ions, then when using the solution as a whole as the reference frame it is the total amount of these two species which must remain constant in this region throughout the experiment. Whether this criterion is the same as that of an immobile free solvent reference frame is open to debate.

The concept of microscopic vacuous regions appearing near the boundary is indeed revolutionary in m.b. work. It is important to remember that the boundary is not a mathematical plane of infinitesimal thickness but a complex region of mixed solutions created by the effects of diffusion. If indeed "holes" are formed by

the difference in the volumes occupied by the leading and following non-common ion-constituents the holes could be filled by solvent or common ion-constituent particles with no effect on the boundary speed. That the difference in moving volumes affects the speed of the M_1 and M_2 ions only is a simplification of the situation. In addition the volumes occupied by the common A ions may also differ in the two solutions but no mention is made to this in Troshin's treatment.

It is easy to show with simple geometrical calculations, by treating the packing material as spherical particles of 20 μ m diameter, that even in a closely packed tube approximately 33% of the volume of the sand column is empty space. Consequently it is in some doubt whether the packing actually does present any substantial resistance to the flow of the solution.

From the points raised above it appears doubtful if the transference numbers measured are in fact true transference numbers. The actual physical meaning of the results is thus still unknown.

III.4 The Indirect Moving-Boundary Method

The indirect m.b. method makes use of the Kohlrausch equation (see sections II.3.2 and II.3.5) to determine the transference number of the solute in the adjusted following solution. Application of this equation

$$\frac{T_L^{LZ}}{T_F^{FZ}} = \frac{|z_L| m_L^{LZ}}{|z_F| m_F^{FZ}} \quad (\text{III.23})$$

requires no volume correction, a great advantage of the indirect method for the study of concentrated solutions.

Konstantinov, Kaimakov and Varshavskaya carried out three sets of indirect m.b. investigations⁽⁶²⁻⁶⁴⁾ with concentrated solutions of HCl, CuCl₂, CdCl₂, KCl, LiCl, ZnCl₂, CoCl₂ and NiCl₂ at 20°C. However, the results were simply quoted as steady-state concentrations of the various electrolytes involved with few tabulated transference numbers given. It was stated that by using the s.o. results of Kaimakov for HCl⁽³⁴⁾ and LiCl⁽³⁵⁾ the calculated transference numbers were in good agreement with the literature values. In sections (III.4.2) and (III.4.3) a more careful analysis of these results will be undertaken.

III.4.1 Experimental Method

The experimental technique and apparatus were very similar to those used in the s.o. method. In two of the studies,^(62,63) the steady-state concentration of the following solution, m^* , was determined from conductivity measurements with two small Pt electrodes sealed into the cell. Varshavskaya and Kaimakov⁽⁶⁴⁾ used a micro-thermistor sealed into the cell to measure m^* . In both cases calibration graphs were previously determined from solutions of known concentration.

One worrying aspect of the experimental procedure was that the initial concentration of the indicator electrolyte often differed markedly from the steady-state concentration (in some cases by as much as a factor of 2). This departs from the advice of Spiro⁽⁸⁾ whereby the difference should be limited to 10-25%; smaller differences were also found necessary in the present work (see section VI.3.3). Moreover, the adjustment to m^* was from both higher and lower values of $m_{init.}$, all for rising boundaries. This must mean that in certain experiments mixing of the following solution will have occurred due to gravitational instability.

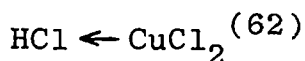
Quartz sand packing was used in an attempt to prevent

convective mixing of the following electrolyte due to Joule heating effects. However, it was shown in section (III.2.3) that this will have the opposite effect.

III.4.2 Results

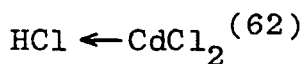
The tables below list the published results, expressed as molalities of the leading solution, m , and the adjusted following solution, m^* . The fourth columns (and in table III.7, the third column) contain the appropriate values of $T_{\text{CdCl}_2}^{\text{Cd}^{2+}}$, $T_{\text{NiCl}_2}^{\text{Ni}^{2+}}$ or $T_{\text{CuCl}_2}^{\text{Cu}^{2+}}$ interpolated by the present author from reliable literature data (see later). In the third columns (and the fourth column of table III.7) are the T values of the other electrolyte calculated from the Kohlrausch equation.

TABLE (III.1)



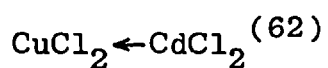
m_{HCl}	$m^*_{\text{CuCl}_2}$	$T_{\text{H}^+}^{\text{HCl}}$	$T_{\text{Cu}^{2+}}^{\text{CuCl}_2}(\text{calc})$
2.17	0.435	0.748	0.300
3.25	0.615	0.793	0.300
5.61	1.035	0.813	0.300
12.43	2.64	0.671	0.285
14.39	3.465	0.592	0.285

TABLE (III.2)



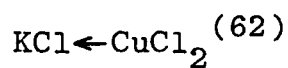
m_{HCl}	$m^*_{\text{CdCl}_2}$	$T_{\text{H}^+}^{\text{HCl}}$	$T_{\text{Cd}^{2+}}^{\text{CdCl}_2}(\text{calc})$
2.12	0.485	0.850	0.389
3.24	0.68	0.867	0.364
4.35	0.835	0.895	0.343
5.71	1.015	0.899	0.320
12.51	2.01	0.623	0.200
12.69	2.14	0.550	0.186
15.05	2.345	0.523	0.163

TABLE (III.3)



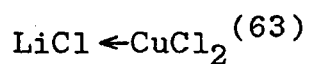
m_{CuCl_2}	$m^*_{\text{CdCl}_2}$	$T_{\text{Cu}^{2+2}}^{\text{CuCl}_2}$	$T_{\text{Cd}^{2+2}}^{\text{CdCl}_2}(\text{calc})$
0.47	0.52	0.348	0.385
0.79	0.8	0.344	0.348
2.385	1.92	0.261	0.210
3.575	2.335	0.251	0.164
4.86	2.665	0.233	0.128

TABLE (III.4)



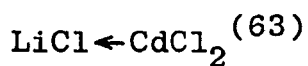
m_{KCl}	$m^*_{\text{CuCl}_2}$	$T_{\text{K}^+}^{\text{KCl}}$	$T_{\text{Cu}^{2+2}}^{\text{CuCl}_2}(\text{calc})$
0.95	0.352	0.405	0.300
1.54	0.5225	0.442	0.300
2.08	0.66	0.473	0.300
2.59	0.81	0.480	0.300
3.5	1.065	0.493	0.300

TABLE (III.5)



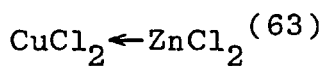
m_{LiCl}	$m^*_{\text{CuCl}_2}$	$T_{\text{Li}^+}^{\text{LiCl}}$	$T_{\text{Cu}^{2+2}}^{\text{CuCl}_2}(\text{calc})$
0.958	0.565	0.254	0.300
1.23	0.6875	0.268	0.300
1.74	0.96	0.272	0.300
2.52	1.445	0.249	0.285
5.95	3.36	0.252	0.285
6.79	3.7	0.262	0.285
7.3	4.025	0.258	0.285

TABLE (III.6)



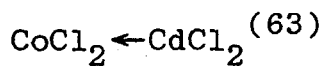
m_{LiCl}	$m_{\text{CdCl}_2}^*$	$T_{\text{Li}^+}^{\text{LiCl}}$	$T_{\text{Cd}^{2+}}^{\text{CdCl}_2(\text{calc})}$
1.695	1.09	0.241	0.310
3.89	1.81	0.239	0.223
5.78	2.225	0.229	0.176
8.05	2.58	0.214	0.137
10.58	2.75	0.227	0.118
11.18	2.835	0.215	0.109
14.31	3.01	0.212	0.089

TABLE (III.7)



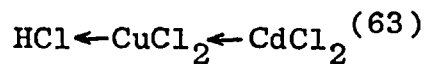
m_{CuCl_2}	$m_{\text{ZnCl}_2}^*$	$T_{\text{Cu}^{2+}}^{\text{CuCl}_2(\text{calc})}$	$T_{\text{Zn}^{2+}}^{\text{ZnCl}_2}$
0.735	0.52	0.300	0.212
1.27	0.825	0.285	0.185
2.265	1.155	0.285	0.145
3.245	1.47	0.285	0.129
5.42	1.93	0.285	0.101

TABLE (III.8)



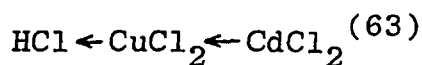
m_{CoCl_2}	$m_{\text{CdCl}_2}^*$	$T_{\text{Co}^{2+}}^{\text{CoCl}_2}$	$T_{\text{Cd}^{2+}}^{\text{CdCl}_2(\text{calc})}$
0.495	0.58	0.322	0.377
0.83	0.925	0.297	0.332
2.245	1.96	0.236	0.206
3.445	2.395	0.226	0.157
3.75	2.58	0.199	0.137

TABLE (III.9a)



m_{HCl}	$m_{\text{CuCl}_2}^*$	$T_{\text{H}^+}^{\text{HCl}} (1)$	$T_{\text{Cu}^{2+}}^{\text{CuCl}_2} (\text{calc})$
3.18	0.608	0.785	0.300
5.56	1.018	0.819	0.300
12.22	2.57	0.678	0.285
14.96	3.395	0.628	0.285

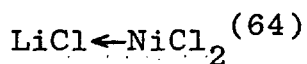
TABLE (III.9b)



m_{HCl}	$m_{\text{CdCl}_2}^*$	$T_{\text{H}^+}^{\text{HCl}} (2)$	$T_{\text{Cd}^{2+}}^{\text{CdCl}_2} (\text{calc})$
3.18	0.663	0.878	0.366
5.56	1.008	0.885	0.321
12.22	2.13	0.536	0.187
14.96	2.293	0.550	0.169

($^{\dagger}m_{\text{CuCl}_2}^*$ and $m_{\text{CdCl}_2}^*$ are the average values from two sets of experiments. $T_{\text{H}^+}^{\text{HCl}}(1)$ and $T_{\text{H}^+}^{\text{HCl}}(2)$ are calculated from the CuCl_2 and CdCl_2 data, respectively).

TABLE (III.10)



m_{LiCl}	$m_{\text{NiCl}_2}^*$	$T_{\text{Li}^+}^{\text{LiCl}}$	$T_{\text{Ni}^{2+}}^{\text{NiCl}_2} (\text{calc})$
1.88	1.165	0.220	0.273
2.57	1.42	0.239	0.264
3.18	1.663 [†]	0.245	0.256
4.42	2.075	0.260	0.244
6.31	2.64 [†]	0.276	0.231
6.61	2.885 [†]	0.259	0.226
7.36	3.25	0.247	0.218
7.54	3.298 [†]	0.249	0.217

([†]average results from two experiments)

III.4.3 Analysis of Published Results

In recent years careful transference number studies have been made on aqueous $\text{CdCl}_2^{(15)}$ and $\text{NiCl}_2^{(65)}$ solutions up to high concentrations. Work has also been done in this laboratory on concentrated CuCl_2 solutions.⁽⁴⁴⁾ It is these data that have been combined with the concentrations in the tables above to give the cation transference number of the electrolyte on the other side of the boundary. Firstly, the CdCl_2 , NiCl_2 , and CuCl_2 transference numbers employed will be specified more exactly.

McQuillan's⁽¹⁵⁾ CdCl_2 transference data were curve-fitted to various order polynomials. The most satisfactory fit was obtained with a sixth-order polynomial in m . The coefficients for the equation

$$T_{\text{Cd}^{2+}}^{\text{CdCl}_2} = a_0 + \sum_{n=1}^6 a_n m^n \quad (\text{III.24})$$

are

$$\begin{aligned} a_0 &= 0.440381 \\ a_1 &= -7.42166 \times 10^{-2} \text{ kg mol}^{-1} \\ a_2 &= -9.32241 \times 10^{-2} \text{ kg}^2 \text{ mol}^{-2} \\ a_3 &= 6.81080 \times 10^{-2} \text{ kg}^3 \text{ mol}^{-3} \\ a_4 &= -2.26752 \times 10^{-2} \text{ kg}^4 \text{ mol}^{-4} \\ a_5 &= 3.53994 \times 10^{-3} \text{ kg}^5 \text{ mol}^{-5} \\ a_6 &= -2.06699 \times 10^{-4} \text{ kg}^6 \text{ mol}^{-6} \end{aligned}$$

The error in the T values is of the order of ± 0.004 .

This process was repeated for the NiCl_2 data where a sixth-order polynomial was chosen with a fit of ± 0.004 . The coefficients are

$$\begin{aligned} a_0 &= 0.384955 \\ a_1 &= -0.219233 \text{ kg mol}^{-1} \\ a_2 &= 0.191295 \text{ kg}^2 \text{ mol}^{-2} \\ a_3 &= -0.105071 \text{ kg}^3 \text{ mol}^{-3} \end{aligned}$$

$$\begin{aligned}
 a_4 &= 3.26852 \times 10^{-2} \text{ kg}^4 \text{ mol}^{-4} \\
 a_5 &= -5.31435 \times 10^{-3} \text{ kg}^5 \text{ mol}^{-5} \\
 a_6 &= 3.50156 \times 10^{-4} \text{ kg}^6 \text{ mol}^{-6}
 \end{aligned}$$

These coefficients were then used to calculate $T_{\text{Cd}^{2+}2}^{\text{CdCl}}$ and $T_{\text{Ni}^{2+}2}^{\text{NiCl}}$ at the appropriate experimental concentrations.

The CuCl_2 data show a concentration independent transference number in the two ranges 0.35-1.1 and 1.1-6 mol kg⁻¹, with values of $T_{\text{Cu}^{2+}2}^{\text{CuCl}}$ of 0.300 and 0.285, respectively.

Combination of these results with the concentrations in tables (III.1) - (III.10) using the Kohlrausch equation gave values of $T_{\text{H}^+}^{\text{HCl}}$ (in tables III.1, III.2 and III.9), $T_{\text{Cu}^{2+}}^{\text{CuCl}_2}$ (table III.3), $T_{\text{K}^+}^{\text{KCl}}$ (table III.4), $T_{\text{Li}^+}^{\text{LiCl}}$ (tables III.5, III.6 and III.10), $T_{\text{Zn}^{2+}2}^{\text{ZnCl}_2}$ (table III.7) and $T_{\text{Co}^{2+}2}^{\text{CoCl}_2}$ (table III.8). These results are represented graphically in figs.(III.5) - (III.9) along with the corresponding literature values.

Figure (III.5) shows the concentration variation of $T_{\text{H}^+}^{\text{HCl}}$ by various methods. Although the Soviet data show maxima in the values, as do the more accepted literature values, (66,67) the Soviet peaks occur between 5 and 7m instead of 2-3m as found for the latter. There are no Soviet data for the 6-12m region but above 12m, two of the sets of data (from tables III.1 and III.9a) give reasonable agreement with the e.m.f. values. On the whole, however, the indirect m.b. (i.m.b.) data are quite widely scattered about the other literature values, with several differences of as much as 0.1.

The Soviet $T_{\text{Cu}^{2+}2}^{\text{CuCl}_2}$ values obtained from both the s.o. and i.m.b. methods (fig.III.6) show good agreement with each other and the average scatter (of about ± 0.005) is within the quoted experimental errors of $\pm 2-3\%$. However, the observed concentration dependence is far greater than that from the e.m.f. method. (44)

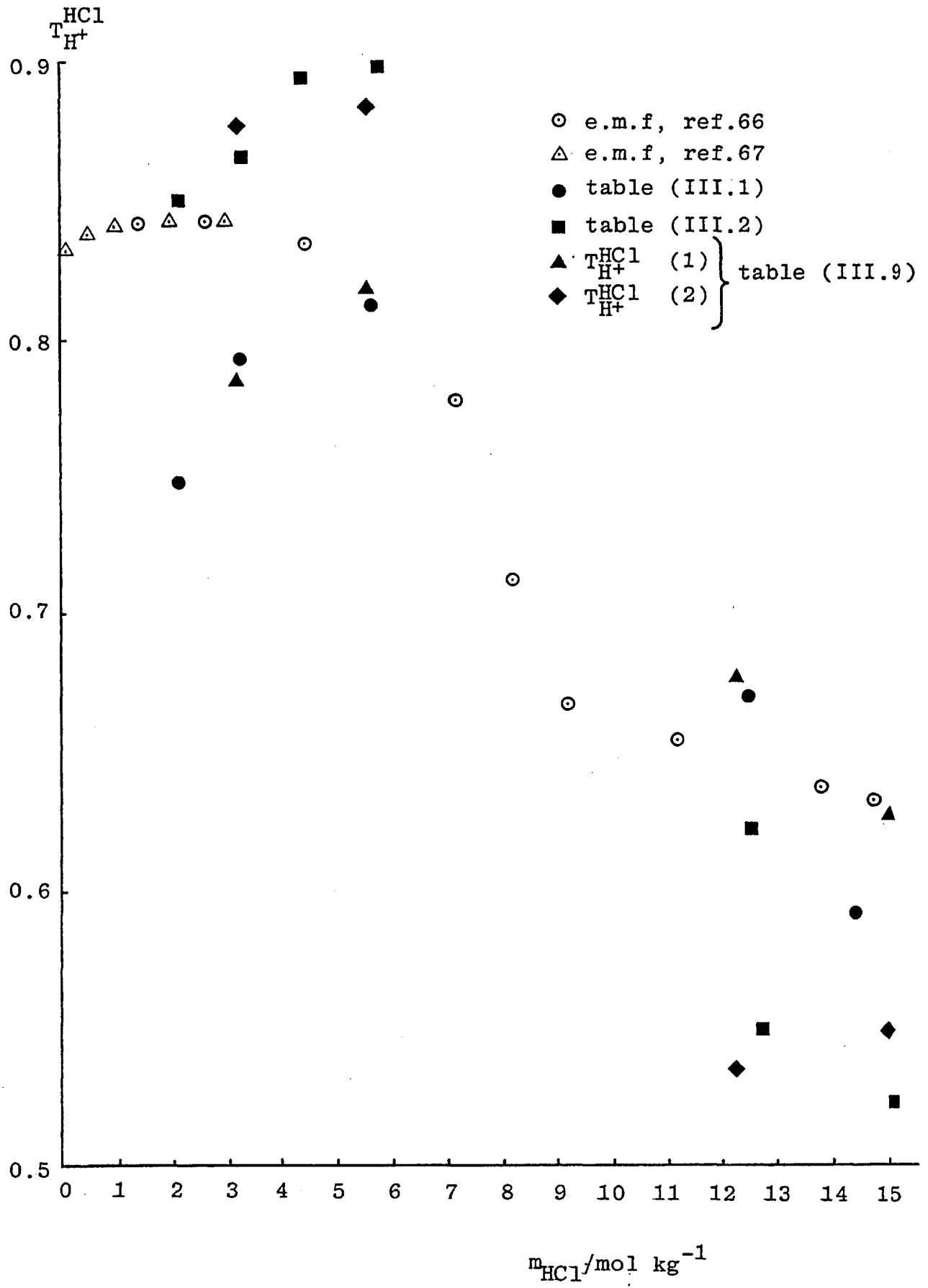
fig. (III.5) $T_{H^+}^{HCl}$ vs. m_{HCl} 

fig.(III.6) $T_{\text{Cu}^{2+2}}^{\text{CuCl}_2}$ vs. m_{CuCl_2}

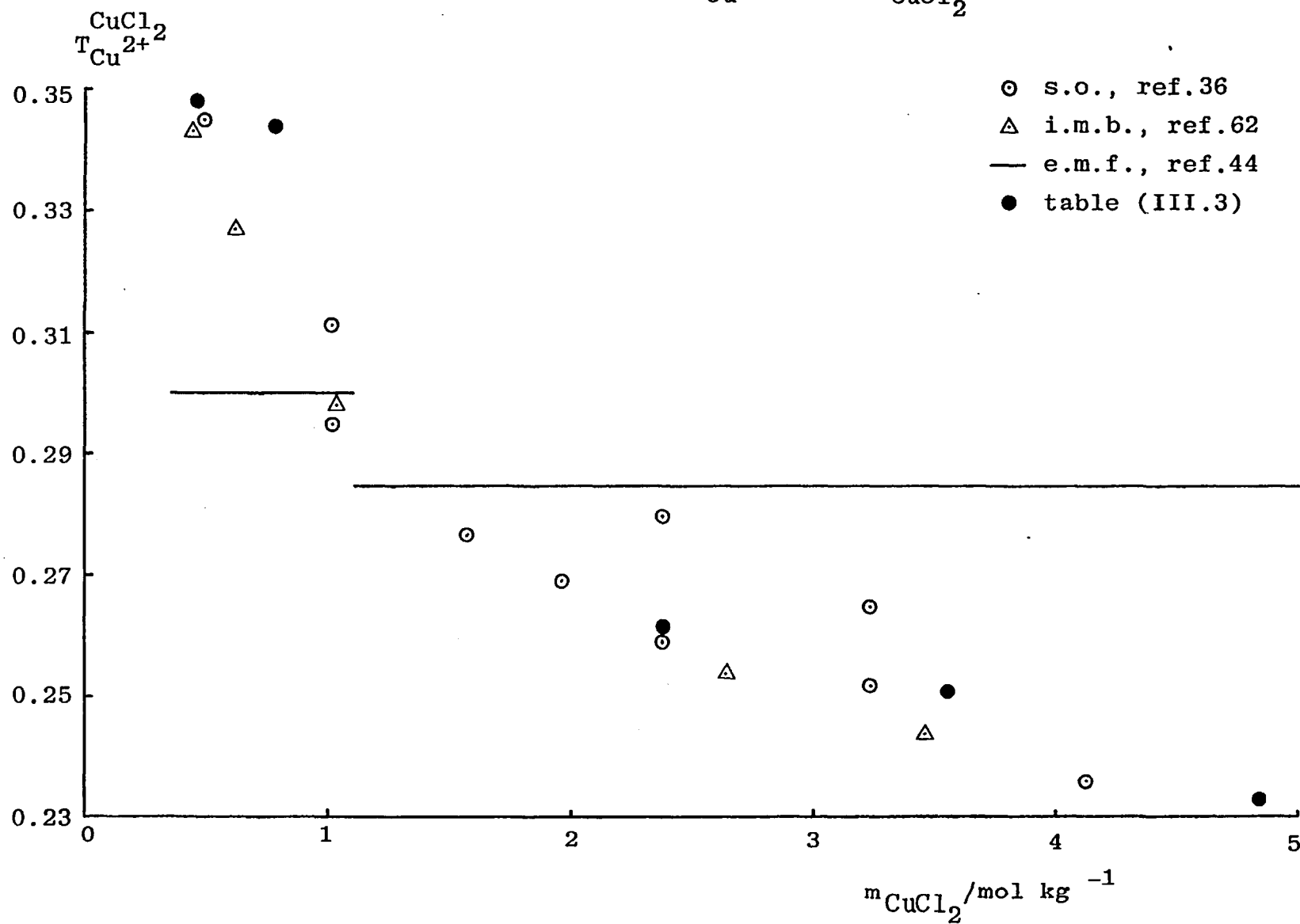


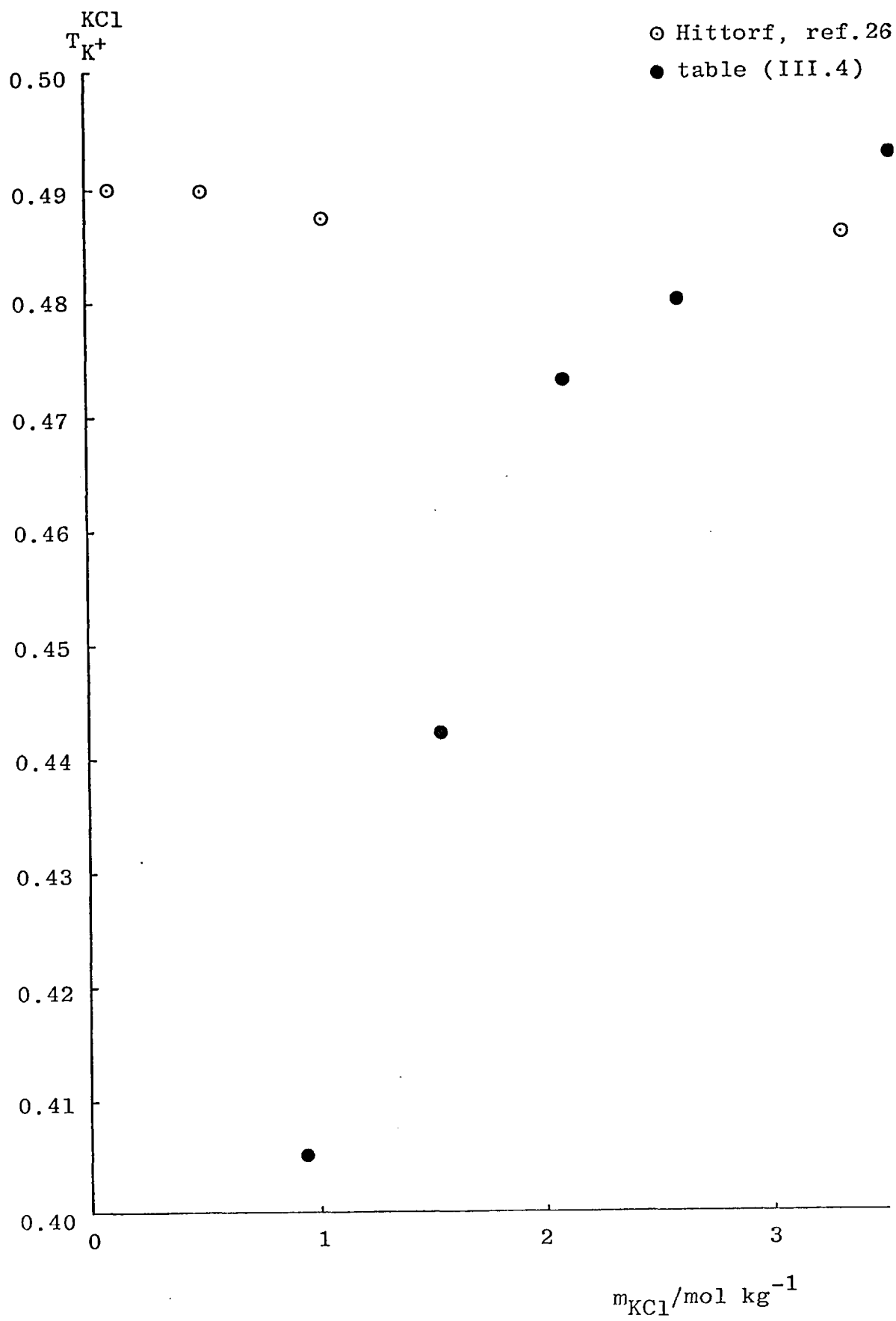
fig.(III.7) $T_{K^+}^{KCl}$ vs. m_{KCl} 

fig.(III.8) $T_{Li^+}^{LiCl}$ vs. m_{LiCl}

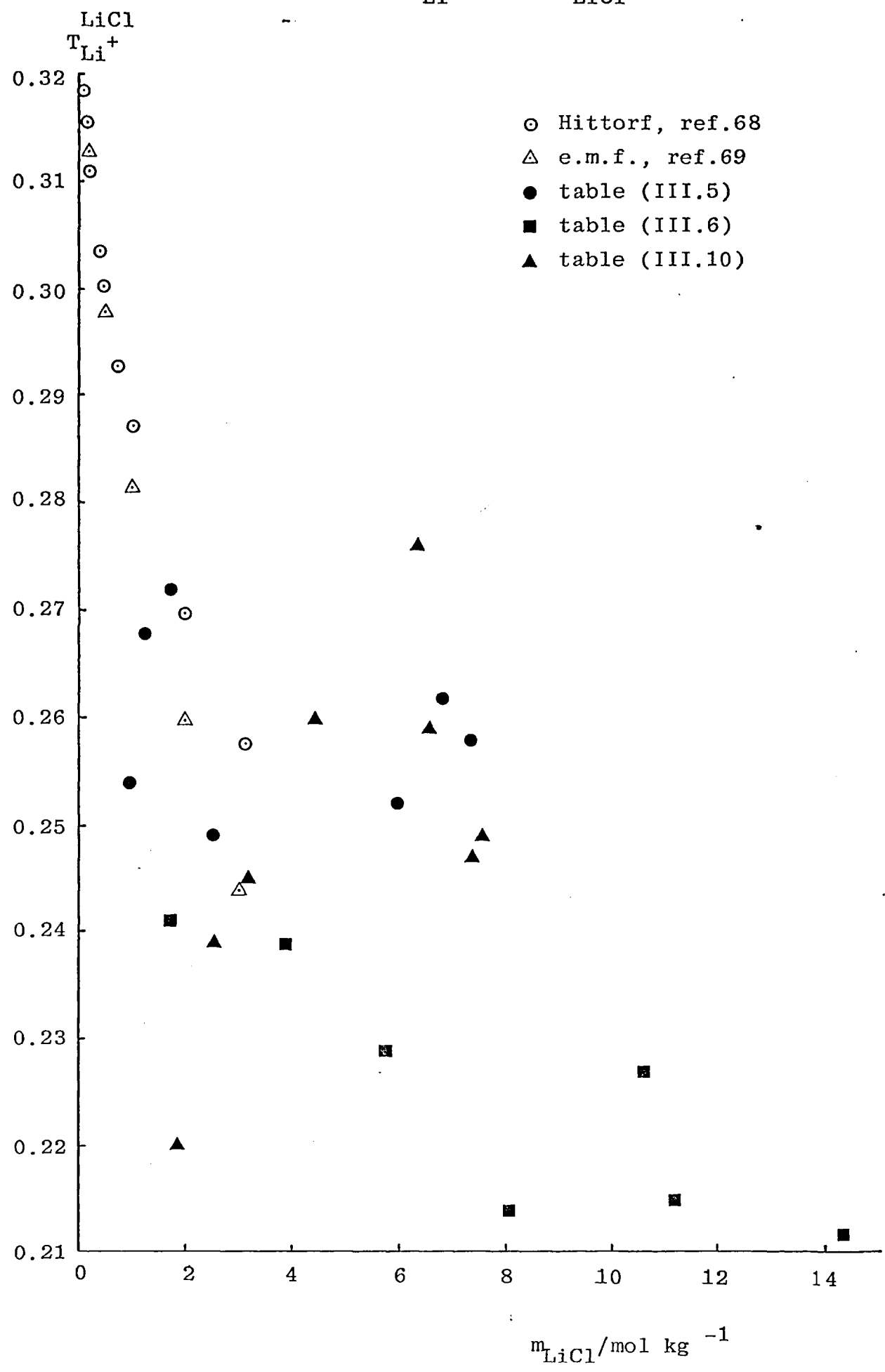
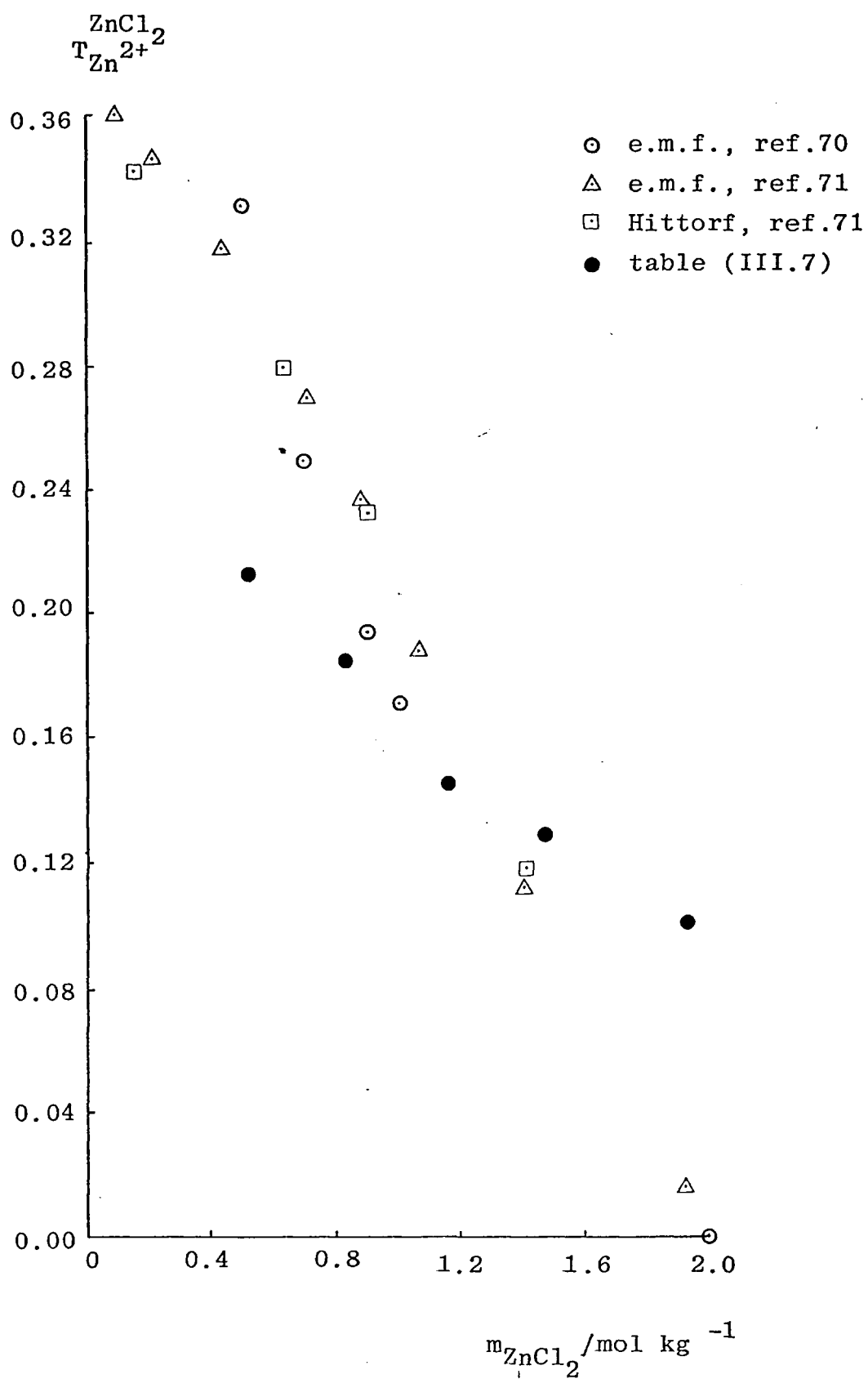


fig.(III.9) $T_{\text{Zn}^{2+}}^{\text{ZnCl}_2}$ vs. m_{ZnCl_2}



Both the magnitude and direction of the concentration dependence of $T_{K^+}^{KCl}$ in fig.(III.7) are quite unlike those of the reliable Hittorf data of MacInnes and Dole.⁽²⁶⁾ This may be explained by the lack of concentration variation in the $T_{Cu^{2+}}^{CuCl_2}$ values used in the calculation of the i.m.b. $T_{K^+}^{KCl}$ results.

There is little overlap between the calculated i.m.b. and literature^(68,69) data for $T_{Li^+}^{LiCl}$ (fig.III.8). In the 1-3 m region where comparisons can be made, the Soviet data exhibit very erratic behaviour with the values obtained via Stokes' $NiCl_2$ transference data⁽⁶⁵⁾ (table III.10) showing a curious cusp at 6.5m. However, in general the i.m.b. data are widely scattered with the values from table (III.6) derived via McQuillan's $CdCl_2$ results appearing to be the most reliable.

The i.m.b. and literature $ZnCl_2$ data in fig.(III.9) show reasonable agreement between 0.8 and 1.4m. However, the agreement in this region is probably fortuitous as the general concentration variation of the Soviet data does not tend towards the negative cation transference numbers above 2m found by other workers.^(70,71)

There are no reliable literature values for $T_{Co^{2+}}^{CoCl_2}$ at high concentration so that no comparative graphical analysis of the data in table (III.8) can be carried out.

The purpose of the analyses above was to try to calculate reliable transference numbers for the solutions used in order to supplement the meagre amount of existing data. It is unlikely that the poor correlation found can be attributed to the fact that the literature data used in the calculations were measured at 25°C while the Soviet i.m.b. experiments were performed at 20°C. A more likely explanation is that in the i.m.b. experiments some mixing occurred in the following electrolyte solutions due to gravitational instability, so that some of the adjusted Kohlrausch concentrations reported are incorrect. There

is also some doubt as to whether certain systems, especially $\text{LiCl} \leftarrow \text{NiCl}_2$ in table (III.10), are electrically stable over the whole of the concentration ranges used. A sample calculation shows that the system is electrically stable for 3.18m $\text{LiCl} \leftarrow \text{NiCl}_2$. However, the lack of accurate transference data for LiCl at higher concentrations prevents the testing of, for example, the 7.54m $\text{LiCl} \leftarrow \text{NiCl}_2$ system (table III.10).

In conclusion, the transference numbers derived in this present study from the reported concentration ratios cannot be fully relied upon.

CHAPTER FOUR

VOLUME CORRECTION IN CONCENTRATED SOLUTIONS

The discussions in the previous chapter have shown some of the many problems associated with concentrated electrolyte solutions. Much thought and ingenuity was put into the s.o. method to ensure favourable conditions for the measurement of both real and apparent transference numbers. In comparison the extension of the concentration range for the direct m.b. method centres around one problem only, accurate determination of the volume correction.

The first section of this chapter will use two illustrative m.b. systems to highlight the problems involved in working at high solute concentrations. Sections (IV.2) and (IV.3) will deal respectively with possible solutions to these problems and the final choice of experimental conditions.

In order to calculate the approximate magnitude of various effects, it is useful to define a "standard run" of 0.01F. This is equivalent to a 5M leading solution of a uni-univalent electrolyte with a non-common ion-constituent transference number of 0.5 sweeping out a volume of 1 cm^3 . For such a run, with a typical volume gain ΔV of $5 \times 10^{-8} \text{ m}^3$ during the run or $5 \times 10^{-6} \text{ m}^3$ faraday⁻¹, the volume correction is 0.0250, or 5% of the observed transference number. For a corresponding 0.1M leading solution, the volume correction would be only 0.0005, or 0.1%.

IV.1 Rigorous Derivation of the Volume Correction

The two expressions derived in section (II.3.4) for the volume changes in the $\text{KCl} \leftarrow \text{LiCl}$ system when employing either a closed Ag anode or a closed Ag/AgCl cathode are

strictly only approximations of the actual situation. In dilute solutions the error involved in using the simplified expressions is very much smaller than other experimental errors. However, when working with concentrated solutions accurate determination of the volume change is of the utmost importance.

Gwyther and Spiro⁽²⁹⁾ have rigorously derived an expression for the volume change taking as an example the anion system $\text{HOAc} \leftarrow \text{HClO}_4$ with a closed Ag anode. Their approach will now be applied to the two cases previously discussed in section (II.3.4).

IV.1.1 $\text{KCl} \leftarrow \text{LiCl}$, Closed Ag Anode

The initial conditions (at time t_0) are shown in fig.(IV.1).

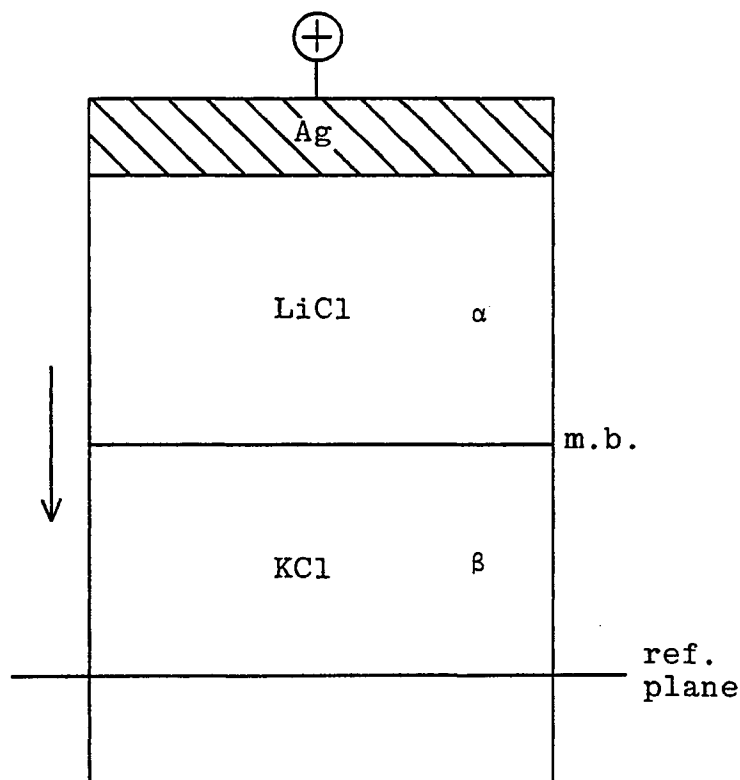


fig.(IV.1)

Before any current has been passed, let there be n_0 mol solvent between the air-face of the anode and the reference plane, n'_0 mol of which form part of the KCl solution. Thus, the volumes of the LiCl and KCl solutions at t_0 are given by⁽²⁹⁾

$$V_{\text{LiCl}}(t_0) = (n_0 - n'_0) V_0^0 + n_{\text{LiCl}} \phi_{\text{LiCl}} \quad (\text{IV.1})$$

$$V_{\text{KCl}}(t_0) = n'_0 V_0^0 + n_{\text{KCl}} \phi_{\text{KCl}} \quad (\text{IV.2})$$

where V_0^0 is the molar volume of the pure solvent and n_{LiCl} and n_{KCl} are the number of moles of LiCl and KCl in the α and β solutions, respectively. ϕ is the apparent molar volume of the subscripted electrolyte. If the electrode initially consists of n_{Ag} mol Ag (of molar volume V_{Ag}) then at time t_0 the volume between the anode air-face and the reference plane is

$$V(t_0) = n_{\text{Ag}} V_{\text{Ag}} + n_0 V_0^0 + M_0 (n_0 - n'_0) m_{\text{LiCl}} \phi_{\text{LiCl}} + M_0 n'_0 m_{\text{KCl}} \phi_{\text{KCl}} \quad (\text{IV.3})$$

where M_0 is the molar mass of the solvent.

If, by time t_f , f faradays of electricity have been passed then in the volume under consideration $f T_{\text{K}^+}^{\text{KCl}}$ mol KCl and f mol Ag have been lost and f mol AgCl have been formed. The number of moles of solvent in this region remains constant by definition. Furthermore, due to the adjustment of the LiCl concentration behind the boundary and the electrode reaction, the following solution has become inhomogeneous. The volume now becomes

$$V(t_f) = (n_{\text{Ag}} - f) V_{\text{Ag}} + f V_{\text{AgCl}} + n_0 V_0^0 + (M_0 n'_0 m_{\text{KCl}} - f T_{\text{K}^+}^{\text{KCl}}) \phi_{\text{KCl}} + \int_{\alpha} \phi_{\text{LiCl}} dn_{\text{LiCl}} \quad (\text{IV.4})$$

It may be noted that

$$\int_{\alpha} dn_{\text{LiCl}} = \text{constant} \quad (\text{IV.5})$$

because the number of moles of LiCl in solution α does not change throughout the experiment.

By sub-dividing solution α into many horizontal volume elements of volume dV , the integral term can be written as

$$\int_{\alpha} \phi_{\text{LiCl}} dn_{\text{LiCl}} = \int_{\alpha} \phi_{\text{LiCl}} c_{\text{LiCl}}(t_f) dV \quad (\text{IV.6})$$

Now let a further faraday be passed. The volume at time t_{f+1} becomes

$$\begin{aligned} V(t_{f+1}) &= \{n_{\text{Ag}}^{-(f+1)}\} V_{\text{Ag}}^{+(f+1)} V_{\text{AgCl}} + n_0^0 V_0^0 \\ &+ \{M_0^0 n_{\text{KCl}}^{-(f+1)} T_{\text{K}^+}^{\text{KCl}}\} \phi_{\text{KCl}} + \int_{\alpha} \phi_{\text{LiCl}} c_{\text{LiCl}}(t_{f+1}) dV \end{aligned} \quad (\text{IV.7})$$

The net volume gain between the air-face of the anode and the reference plane per faraday is then the difference between equations (IV.4) and (IV.7). Hence

$$\begin{aligned} \Delta V &= -V_{\text{Ag}} + V_{\text{AgCl}} - T_{\text{K}^+}^{\text{KCl}} \phi_{\text{KCl}} + \int_{\alpha} \phi_{\text{LiCl}} c_{\text{LiCl}}(t_{f+1}) dV \\ &- \int_{\alpha} \phi_{\text{LiCl}} c_{\text{LiCl}}(t_f) dV \end{aligned} \quad (\text{IV.8})$$

As Gwyther and Spiro⁽²⁹⁾ have pointed out, the effect of the volume of the m.b. itself is not only small but contributes equally to $V(t_f)$ and $V(t_{f+1})$.

If, as is the case for dilute solutions, the following LiCl solution is treated as homogeneous then the two integral terms in equation (IV.8) are equal and (IV.8) reduces to the expression previously derived (equation II.22) in section (II.3.4). As ϕ is a function of concentration, however, these integrals must be included in the rigorously derived equation (IV.8).

The two integral terms in (IV.8) can usefully be replaced by finite summations of the form

$$\int_{\alpha} \phi_{\text{LiCl}} c_{\text{LiCl}}(t_f) dV = \sum_{\alpha} \phi_{\text{LiCl}} c_{\text{LiCl}}(t_f) \delta V \quad (\text{IV.9})$$

$$\int_{\alpha} \phi_{\text{LiCl}} c_{\text{LiCl}}(t_{f+1}) dV = \sum_{\alpha} \phi_{\text{LiCl}} c_{\text{LiCl}}(t_{f+1}) \delta V \quad (\text{IV.10})$$

IV.1.2 $\text{KCl} \leftarrow \text{LiCl}$, Closed Ag/AgCl Cathode

The initial conditions are shown in fig.(IV.2).

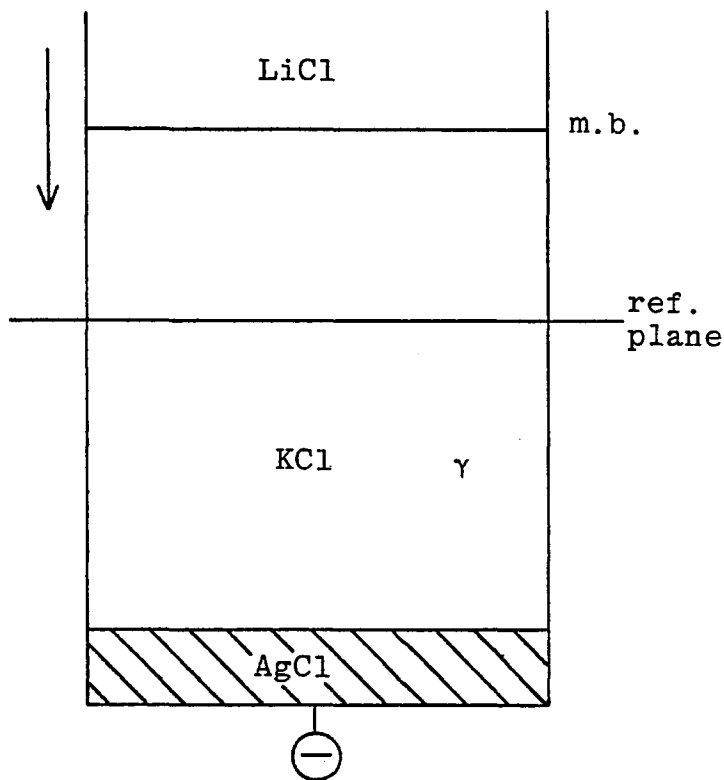


fig.(IV.2)

Hence

$$V(t_0) = n_{\text{AgCl}} V_{\text{AgCl}} + n_0^{\dagger} V_0^0 + M_0 n_0^{\dagger} \phi_{\text{KCl}} \quad (\text{IV.11})$$

where n_{AgCl} is the number of moles of AgCl in the electrode and $n_0^{\dagger}$ is the number of moles of solvent in solution γ between the air-face of the electrode and the reference plane.

In the derivation for this system in section (II.3.4) the KCl solution was treated as homogeneous throughout the cell. However, as soon as current is passed the concentration of solute around the electrode will increase. Therefore, at time t_f the volume beneath the reference plane should be written as

$$V(t_f) = (n_{AgCl} - f) V_{AgCl} + f V_{Ag} + n_0^+ V_0^0 + \int_{\gamma} \phi_{KCl} c_{KCl}(t_f) dV \quad (IV.12)$$

where

$$\int_{\gamma} c_{KCl}(t_f) dV = M_0 n_0^+ m_{KCl} + f T_{K^+}^{KCl} \quad (IV.13)$$

At time t_{f+1}

$$V(t_{f+1}) = \{n_{AgCl} - (f+1)\} V_{AgCl} + (f+1) V_{Ag} + n_0^+ V_0^0 + \int_{\gamma} \phi_{KCl} c_{KCl}(t_{f+1}) dV \quad (IV.14)$$

where

$$\int_{\gamma} c_{KCl}(t_{f+1}) dV = M_0 n_0^+ m_{KCl} + (f+1) T_{K^+}^{KCl} \quad (IV.15)$$

Thus, the volume gain is

$$\Delta V = -V_{AgCl} + V_{Ag} + \int_{\gamma} \phi_{KCl} c_{KCl}(t_{f+1}) dV - \int_{\gamma} \phi_{KCl} c_{KCl}(t_f) dV \quad (IV.16)$$

As above, the integral terms can be expressed as finite summations.

Equation (IV.16) reduces to the normal expression for the volume change (equation II.23) if solution γ is treated

as homogeneous and ϕ_{KCl} as constant. Then

$$\begin{aligned}
 & \int_Y \phi_{\text{KCl}} c_{\text{KCl}}(t_{f+1}) dV - \int_Y \phi_{\text{KCl}} c_{\text{KCl}}(t_f) dV \\
 &= \phi_{\text{KCl}} \{M_0 n_0^+ m_{\text{KCl}} + (f+1) T_{\text{K}^+}^{\text{KCl}}\} \\
 &\quad - \phi_{\text{KCl}} \{M_0 n_0^+ m_{\text{KCl}} + f T_{\text{K}^+}^{\text{KCl}}\} \\
 &= T_{\text{K}^+}^{\text{KCl}} \phi_{\text{KCl}}
 \end{aligned} \tag{IV.17}$$

IV.2 Possible Solutions to the Problems of the Volume Correction

IV.2.1 Variation of ϕ with Concentration

In the discussion above the main problem concerns the variation of the apparent molar volume with the concentration of the electrolyte. It follows that the use of solutes with small $(\Delta\phi/\Delta c)$ values would be desirable.

The apparent molar volume, ϕ ($\text{dm}^3 \text{mol}^{-1}$), of a solute at a given temperature can be written as

$$\phi = \frac{\rho_0 - \rho + cM}{c\rho_0} \tag{IV.18}$$

where ρ and ρ_0 are the density of the solution and of the pure solvent (in g dm^{-3}), respectively, c is the solute concentration (mol dm^{-3}), and M the molar mass of the solute (g mol^{-1}). This equation is a convenient one for calculating ϕ from literature density data. As an example, the variation of ϕ_{LiCl} with c_{LiCl} in aqueous solution at 25°C calculated from I.C.T.⁽⁷²⁾ densities is shown in fig.(IV.3).

In order to estimate comparative ($\Delta\phi/\Delta c$) values for various aqueous electrolytes it was assumed, to a first approximation, that in the region 1-10M ϕ varies linearly with c . For less soluble electrolytes, linearity from 1M to saturation was assumed. The results for 22 aqueous electrolytes are given in table (IV.1).

It is evident from the table that small ($\Delta\phi/\Delta c$) values are found for the chloride, nitrate and acetate salts of univalent cations, with the perchlorates giving larger values. Salts with doubly charged cations exhibit larger variations of ϕ with concentration. This table and the preceding theory allow one to choose suitable experimental systems for which the uncertainty in the large volume correction is minimised. For example, the $\text{KCl} \leftarrow \text{LiCl}$ system with a closed silver anode is clearly preferable to the $\text{KCl} \leftarrow \text{CdCl}_2$ system with a closed silver or cadmium anode, since ($\Delta\phi/\Delta c$) is much bigger for CdCl_2 than for LiCl . Again, since ($\Delta\phi/\Delta c$) is larger for KCl than for LiCl , there is an advantage in using the $\text{KCl} \leftarrow \text{LiCl}$ system with a closed Ag anode rather than with a closed Ag/AgCl cathode (cf. equations IV.8 and IV.16).

fig.(IV.3) Concentration Variation of ϕ_{LiCl} at 25°C

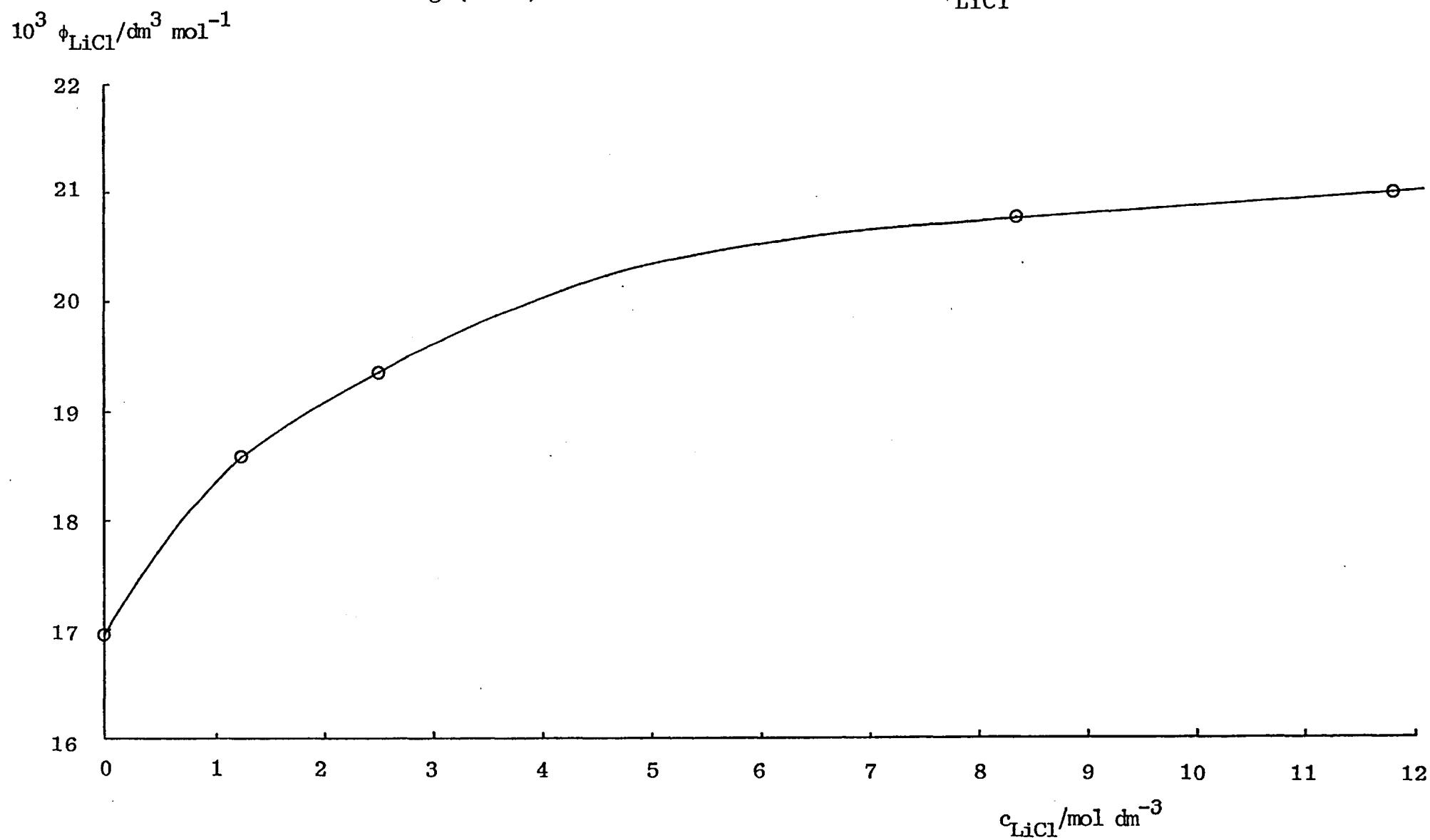


TABLE (IV.1)

Variation of ϕ with concentration

solute	$10^3(\Delta\phi/\Delta c)/\text{dm}^6 \text{mol}^{-2}$	conc.range/M	T/°C	ref.
HCl	0.214	1.1 - 9.4	25	72
HClO ₄	0.747	1.1 - 9.2	15	72
HOAc	0.256	1.2 -10.6	25	72
HIO ₃	3.32	1.2 - 3.3	18	72
LiCl	0.228	1.2 -11.8	25	72
LiNO ₃	0.168	1.0 -11.5	25	73
NaCl	0.807	0.9 - 4.8	25	72
NaClO ₄	1.25	1.1 - 4.0	18	72
NaNO ₃	0.832	1.2 - 4.8	25	74
KCl	0.841	1.0 - 3.4	25	72
KOAc	0.870	1.1 - 8.1	25	72
RbCl	0.650	1.1 - 6.3	25	72
CsCl	0.653	1.0 - 6.0	25	75
NH ₄ Cl	0.487	0.9 - 3.9	25	72
CaCl ₂	2.02	1.0 - 5.0	25	72
NiCl ₂	2.94	0.8 - 3.1	20	72
ZnCl ₂	1.72	1.2 -10.0	25	72
Zn(ClO ₄) ₂	3.04	0.9 - 3.0	25	76
AgClO ₄	0.551	0.9 - 5.6	25	77
AgNO ₃	0.544	1.1 - 8.7	25	77
CdCl ₂	1.78	1.0 - 4.6	25	72
Cd(NO ₃) ₂	3.03	1.0 - 3.5	18	72

Note (78):

$$\begin{aligned}
 \rho_0 &= 999.104 \text{ g dm}^{-3} \text{ at } 15^\circ\text{C} \\
 \rho_0 &= 998.600 \text{ g dm}^{-3} \text{ at } 18^\circ\text{C} \\
 \rho_0 &= 998.207 \text{ g dm}^{-3} \text{ at } 20^\circ\text{C} \\
 \rho_0 &= 997.045 \text{ g dm}^{-3} \text{ at } 25^\circ\text{C}
 \end{aligned}$$

IV.2.2 Removal of Metal Ions from Solution

The most commonly used dissolving metal anode is silver. For this reason much of the following discussion will deal with various methods of complexing Ag^+ ions.

The most obvious method is to place the anode in a chloride solution: on passing current an insoluble coating of AgCl forms on the electrode. However, whilst AgCl is almost insoluble in water ($0.002 \text{ g AgCl dm}^{-3}$ at 25°C)⁽⁷⁹⁾, complex formation in concentrated chloride solutions produces AgCl_2^- , AgCl_3^{2-} etc.⁽⁸⁰⁾ which increases the solubility appreciably. This in turn leads to significant but unknown volume changes. This section therefore considers alternative methods of removing Ag^+ ions from solution by complexation.

Crown ethers (CE) are cyclic organic compounds containing O, N or S donor atoms in the ring. Metal ions are complexed to varying degrees depending upon the type of donor atom and also upon the size of the central cavity of the CE.⁽⁸¹⁾ For example, the CE illustrated in fig. (IV.4), 1, 4 - diaza - 18 - crown - 6, has a stability constant for the reaction



of $\lg K = 7.8$ in water at 25°C ^(81,82), where C represents the crown ether. The $\text{C}.\text{Ag}^+$ complex must be sufficiently stable to ensure that all the dissolved cations are complexed and that none combine with the competing electrolyte anion (Cl^-). Let us take a 1M solution of 1, 4 - diaza - 18 - crown - 6 in a 1M chloride solution (aqueous solubility data for CE are sparse but a solubility of greater than 0.93M has been reported⁽⁸³⁾ for dicyclohexyl - 18 - crown - 6, fig.(IV.5), in 1M KCl at 26°C). Then the total silver ion concentration would have to be below 10^{-10}M to prevent formation of AgCl since

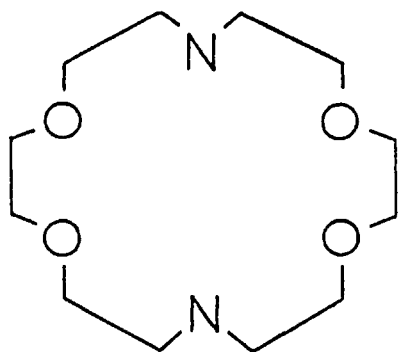


fig.(IV.4)

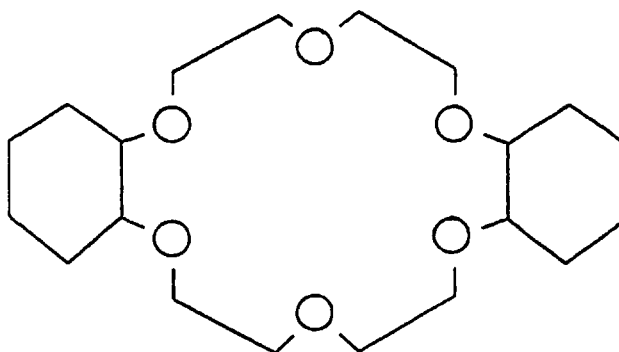


fig.(IV.5)

the solubility product, K_{sp} , is $10^{-10} \text{ mol}^2 \text{ dm}^{-6}$ (84). If

$$K = \frac{[C.Ag^+]}{[C][Ag^+]} \approx 10^8 \text{ mol}^{-1} \text{ dm}^3 \quad (\text{IV.20})$$

then $[C.Ag^+] / [C] < 10^{-2}$. Since, $[C] + [C.Ag^+] = 1 \text{ mol dm}^{-3}$ it follows that $[C.Ag^+] < 10^{-2} \text{ mol dm}^{-3}$ to prevent $AgCl$ formation. During the standard run 10^{-2} mol Ag^+ are formed so that to ensure that all the Ag^+ ions are complexed by the crown ether the volume of the electrode bulb must be at least 1 dm^3 ! This volume could probably be reduced by using an aqueous organic electrolyte (e.g. $HOAc$ or $KOAc$) in which the solubility of the CE should be greater, although no literature data could be found to support this supposition.

The important property of CE with regard to the volume correction is the volume change upon complexation. If, as is likely, the CE also complexes with the cation of the electrolyte in solution (e.g. Li^+), then as Ag^+ ions are complexed the other cation will be released producing an unknown volume change. In addition, although there is probably little difference between the volume of C and $C.Ag^+$, there may well be an appreciable volume

change for reaction (IV.19) due to the loss of 1 mol $\text{Ag}^+(\text{aq})$ per faraday passed. Høiland et al.⁽⁸⁵⁾ have studied the volume change of complex formation between 18 - crown - 6 (fig.IV.6) and NaCl, KCl and CsCl in water at 25°C.

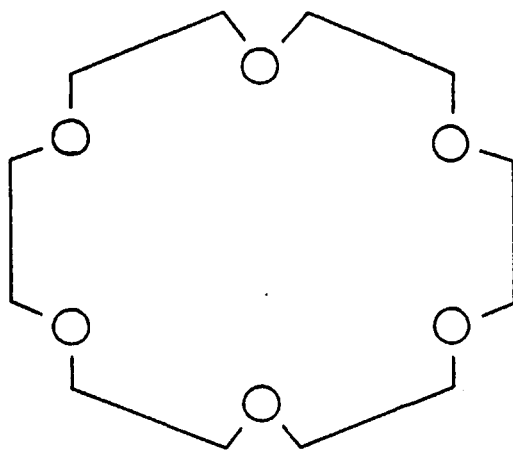
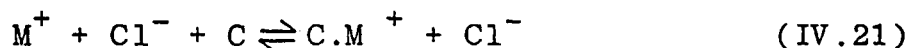


fig.(IV.6)

They report the change in apparent molar volume at infinitesimal ionic strength for the reaction



where M^+ is Na^+ , K^+ or Cs^+ , to be 11.9, 13.0 and 9.1 $\text{cm}^3 \text{mol}^{-1}$ for NaCl, KCl and CsCl, respectively.

Another, but no less serious, problem associated with the use of CE is their cost. The price of 18 - crown - 6, one of the simpler and hence cheaper CE, is £336 kg^{-1} .⁽⁸⁶⁾ Thus for the sample calculation above, where 1 mole of CE is required, the cost per run is approximately £89!

Cryptates, bicyclo crown ethers, are more selective complexing agents than CE. However, the same problems apply as with CE and they are likely to be less soluble in water than CE.

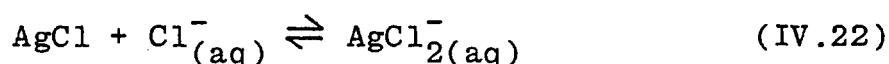
An alternative idea is to use an anion that precipitates

Ag^+ ions so thoroughly that no chloro-complexes form even in concentrated chloride solutions. The tetraphenylborate anion, BPh_4^- , known as a precipitating agent for cations, is one possibility. However, to precipitate Ag^+ ions the BPh_4^- solution must a) be in the anode compartment, and b) contain as the cation either Li^+ or Na^+ since only these salts are soluble. It should be added that the large BPh_4^- anion possesses a very low ionic conductance⁽⁸⁷⁾. It follows that the only possible single salt systems are $\text{NaBPh}_4 \leftarrow \text{LiBPh}_4$ or perhaps $\text{NaX} \rightarrow \text{NaBPh}_4$ where X is an anion even slower than BPh_4^- . Both systems would involve the determination of the transference number of a BPh_4^- salt and not of a chloride. The other possibility would be to employ a system such as $\text{KCl} \leftarrow \text{LiCl}$ with the addition of LiBPh_4 to the anode compartment. This would initially cause the precipitation of AgBPh_4 . However, after a certain time the faster moving Cl^- ions would displace the BPh_4^- ions from around the electrode surface and AgCl precipitation would occur.

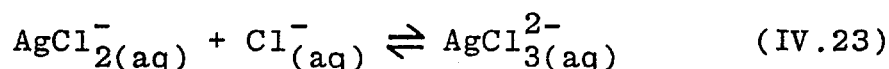
Thus there is no real alternative to the use of a dissolving Ag anode in a chloride solution.

IV.2.3 AgCl Dissolution in Concentrated Chloride Solutions

In the derivation of the volume gains in sections (II.3.4), (IV.1.1) and (IV.1.2) it was assumed that the AgCl remains in the solid state. However, as pointed out in the preceding section, in concentrated chloride solutions reactions of the type



and



solubilize part of the AgCl on the Ag/AgCl cathode or that formed on the Ag anode.

Various workers have measured the solubility of AgCl in concentrated aqueous chloride solutions at 25°C. The results for KCl, LiCl and HCl are given in table (IV.2), in which all concentrations are in mol dm⁻³. (79)

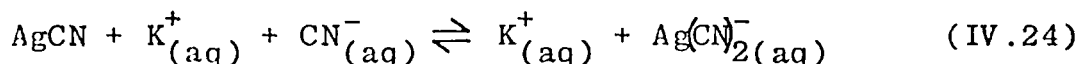
Table (IV.2)

c_{KCl}	$10^3 c_{\text{AgCl}}$	c_{LiCl}	$10^3 c_{\text{AgCl}}$	c_{HCl}	$10^3 c_{\text{AgCl}}$
1.11	0.141	0.44	0.100	4	1.1
1.425	0.235	1.24	0.180	5	3.0
1.713	0.391	1.65	0.281	6	5.1
2.022	0.616	2.10	0.605	7	7.6
2.396	1.050	2.44	1.010	8	11.2
2.628	1.390	2.74	1.480	9	15.6
2.850	1.845	3.01	2.458	10	21.5
3.081	2.435	3.30	3.278	11	26.4
3.424	3.602	3.40	3.925	12	31.2
3.843	5.725	3.60	5.084	13	35.3
		3.78	6.000	14	39.0
				15	42.4

The table shows that the AgCl solubility increases markedly with concentration. Thus, for the system $\text{KCl} \leftarrow \text{LiCl}$, as $T_{\text{K}^+}^{\text{KCl}} > T_{\text{Li}^+}^{\text{LiCl}}$, from the Kohlrausch equation (equation II.15), $c_{\text{KCl}} > c_{\text{LiCl}}$. Thus there is an advantage in using a closed Ag anode in the LiCl solution in which the chloride concentration and hence the AgCl solubility is lower. For the $\text{HCl} \leftarrow \text{LiCl}$ system the situation is more complicated as the solubility of AgCl is lower in HCl than in equimolar LiCl solutions. However, since $T_{\text{H}^+}^{\text{HCl}}$ is so much greater than $T_{\text{Li}^+}^{\text{LiCl}}$ there is probably still an advantage in using a closed anode. The lower solubility of AgCl in HCl as compared with equimolar solutions of KCl and LiCl is presumably due to the differing concentration dependences of the activity coefficients of the relevant ions in these highly concentrated solutions.

Due to the lack of literature density data for silver-chloro complexes, no estimate can be made for the volume change of reaction (IV.22). However, density data are

available for aqueous solutions of $\text{KAg}(\text{CN})_2$ and KCN at 15°C (72,88) enabling us to calculate the volume change for the analogous reaction



AgCN has many properties in common with AgCl : it is virtually insoluble in water and forms complex ions in the presence of an excess of the anion⁽⁸⁹⁾. The volume change given by

$$\Delta V = \phi_{\text{KAg}(\text{CN})_2} - \phi_{\text{KCN}} - V_{\text{AgCN}} \quad (\text{IV.25})$$

for an 0.05M solution of $\text{KAg}(\text{CN})_2$ in 3M KCN at 15°C , where V_{AgCN} is the molar volume of solid AgCN , is $4.5 \text{ cm}^3 \text{ mol}^{-1}$. If the volume change for AgCl dissolution is, say, $5 \text{ cm}^3 \text{ mol}^{-1}$, then for a closed electrode compartment of volume 65 cm^3 containing 3M KCl (in which the solubility of AgCl is approximately $2.4 \times 10^{-3} \text{ mol dm}^{-3}$) the absolute change in volume is $7.8 \times 10^{-4} \text{ cm}^3$. Although this volume change is experimentally significant, the kinetics of the dissolution process will determine whether it affects the actual result. If the dissolution is rapid and the solution is saturated with AgCl before the boundary reaches the first etch mark then no further volume changes will occur and the boundary speed will not be affected by this process. However, if the reaction is slow and the solution only gradually becomes saturated during the run then the result will be subject to an unknown correction. The latter is more likely to be the case with a closed Ag anode as there is no AgCl present on the electrode initially. The period before the boundary reaches the first mark may not be sufficient to allow the solution around the electrode to become completely saturated.

The solution to this problem is relatively simple. Any error can be obviated by saturating the solution in the closed electrode bulb with AgCl before the experiment.

This technique, henceforth called presaturation, was not applied to the solution in the rest of the electrode arm or m.b. tube so as to prevent AgCl being precipitated out in the tube itself.

IV.2.4 The Effect of Stirring in the Closed Electrode Chamber

Per faraday of electricity passed 1 mol Cl^- ions are removed from a chloride solution around a Ag anode to form 1 mol AgCl on the electrode. However, only T_- mol Cl^- are transported to the electrode by electrolytic migration. The remaining T_+ mol Cl^- must reach the electrode surface by diffusion. As soon as current is passed, these two processes produce a variation in electrolyte concentration in the electrode chamber. This change in concentration has two undesirable effects in the closed compartment. Firstly there is the actual variation in the apparent molar volume of the solute caused by the change in concentration. In the case of the closed anode, the concentration will be lowest at the electrode surface and gradually increase with increasing distance from the electrode. The situation will be reversed for a Ag/AgCl cathode, with the solute concentration being highest at the electrode surface. Secondly, if the rate of the anode electrode reaction exceeds the rate at which Cl^- ions arrive at its surface then gassing (O_2 formation) may occur producing unknown volume changes.

The solution to these problems is one of the main innovations of this project: the stirring of the solution within the closed electrode compartment. Hydrodynamic studies such as those with the rotating-disc electrode⁽⁹⁰⁾ show clearly that the so-called diffusion layer around the electrode is considerably reduced with increased rate of stirring. The thinner the (Nernst) diffusion layer, the smaller the volume of solution whose concentration is unknown and hence the smaller the uncertainty in ΔV . Virtually all the changes in concentration due to the electrolysis are then spread evenly throughout the bulk of the electrode chamber and so the average concentration

change is both less and also calculable exactly. In consequence, the ϕ value of the solute changes less and is known more accurately. Furthermore, the thinner the diffusion layer the greater the rate at which Cl^- ions will reach the anode surface and hence the smaller the risk of any secondary electrode reaction.

IV.3 Choice of System

Of the various chloride solutions listed in table (IV.1), CaCl_2 , NiCl_2 , ZnCl_2 and CdCl_2 are unsuitable for this study due to their large $(\Delta\phi/\Delta c)$ values. As a check on the results, reliable literature data for the leading electrolytes up to high concentration are required. Such data are available for HCl ^(66,67), NaCl ⁽⁹¹⁻⁹⁴⁾, KCl ⁽²⁶⁾, RbCl ⁽⁹⁵⁾ and CsCl ⁽⁹⁵⁾. For this novel study of transference numbers in concentrated solutions by the m.b. method, NaCl and KCl are to be favoured over RbCl and CsCl which have been less thoroughly studied. In addition the behaviour of $T_{\text{H}^+}^{\text{HCl}}$ at high solute concentrations is of interest because of the breakdown in the proton-jumping mechanism with increasing concentration. The obvious choice for the following electrolyte is LiCl because of its low ion-constituent mobility and its relatively small $(\Delta\phi/\Delta c)$ value.

The following systems, all using closed Ag anodes, were those finally chosen for investigation



These systems exploit the small concentration variation of ϕ_{LiCl} which was shown to be important in section (IV.1.1). There is also the possibility of using a closed Ag/AgCl cathode, although in the latter two cases, for NaCl and KCl , the rate of change of ϕ with concentration is larger

than with LiCl. Stirring will prevent large variations in solute concentration, and presaturation with AgCl should much reduce the risk of the formation of extra complex ions during a run.

Finally, it should be stressed that the absolute size of the volume correction is relatively unimportant. The essential point is that the volume change per faraday should be known as accurately as possible. If all processes taking place which cause volume changes are not taken into account in the ΔV term, then upon multiplication by the concentration of the leading electrolyte, any slight error in ΔV will become experimentally significant.

PART TWO

EXPERIMENTAL SECTION

CHAPTER FIVE

MOVING BOUNDARY EXPERIMENTAL

In order to ensure the accurate determination of the volume changes occurring in the m.b. cell, special attention was paid to the cell design and the processes taking place in and around the electrode chamber. The modifications found necessary to the experimental apparatus and technique when working with concentrated solutions are outlined in section (V.1). Section (V.2) deals with more general aspects of the method which can apply to dilute as well as to more concentrated solutions. The solvent and volume corrections are discussed quantitatively and in some detail in the final section.

V.1 Modification to M.B. Cell and Technique

V.1.1 Cell Design

The m.b. cell shown in fig.(V.1) is of the shearing boundary type. The densities of the solutions used were such that only falling boundaries were observed.

It was shown in section (IV.2) that the use of a Ag anode requires the incorporation of some form of stirring to prevent local depletions of Cl^- ion around the electrode surface. Similarly, stirring is necessary around Ag/AgCl cathodes to avoid the accumulation of high concentrations of Cl^- around the electrode as electricity is passed. Consequently both electrode compartments were widened to form a bulb at the end of the extended tubes. Stirring inside these bulbs was made possible by the use of an immersible magnetic stirrer (Rank Bros., Bottisham, Cambridgeshire). The motor could be lowered into the thermostat, and various shapes of P.T.F.E. coated stirrer bars were tested. The flow patterns produced by the various shapes were observed by

placing a crystal of potassium permanganate in the bottom of the electrode bulb. As the crystal slowly dissolved coloured "streaks" indicated the effectiveness of the stirring. One prism-shaped and two cylindrical (one with a raised central collar) stirrer bars were tested. The prism-shaped bar (Just Plastics, London) was found to be the most effective (cf. the right-hand electrode bulb in the figure). Vertical baffles (depth 4-5 mm) were glass-blown into the walls of the bulb to introduce turbulence to the flow of the solution and increase the mixing effect of the stirrer bar⁽⁹⁶⁾, as shown in the top view of fig.(V.1). The electrode compartments were extended and enlarged to prevent diffusion of electrolysis products into the m.b. tube during the long time-scale of an experiment (up to 27 hours).

V.1.2 Silver Chloride Solubility

To prevent unknown volume changes due to the dissolution of AgCl in the solution around the closed electrode the solution was saturated with J.M.C. "Specpure" AgCl prior to the run. A four-fold excess of AgCl was added to the solution, which was stirred and allowed to stand for a minimum of 24 hours before use. The presaturated solution was only placed in the electrode bulb. Unsaturated solution was used to fill the remaining part of the cell. This prevents solid AgCl precipitating out in the m.b. tube itself.

V.1.3 Electrode Design and Manufacture

The passage of large amounts of electricity requires electrodes that are large, robust, and of high surface area. Anodes formed from solid rods of the appropriate metal, a traditional form^(13,15), do not provide a sufficiently large area. Moreover, it is not possible to seal silver rods into any type of glass with a solution tight seal. The electrodes were therefore based on squares of platinum foil (2.5 x 2.5 cm) sealed via platinum wire directly into soda glass cones. The platinum foil was formed into a cylindrical shape and the

length of the glass cone was such that all of the metal was within the curved part of the electrode bulb (fig.V.2).

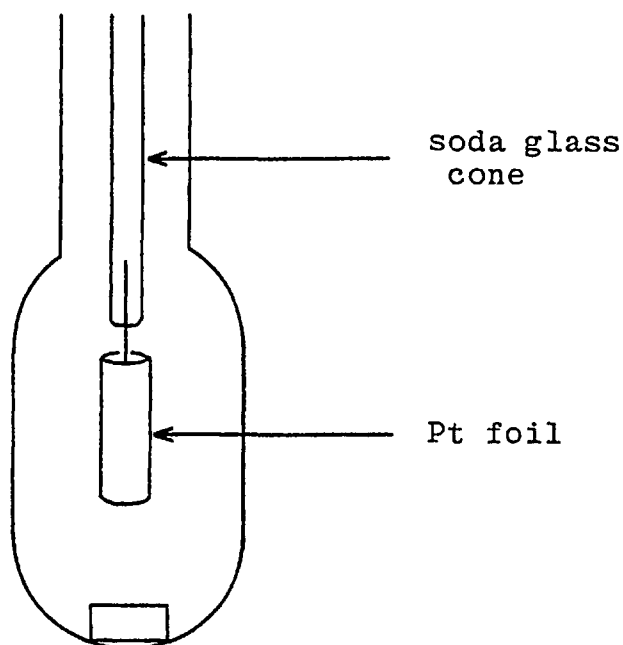


fig.(V.2)

Initially, Ag was electrolytically plated onto the de-greased Pt foil by cathodization in an aqueous solution of $\text{KAg}(\text{CN})_2^{(97)}$ (10 g dm^{-3}). A current density of 2 mA cm^{-2} was used to plate out a four-fold excess of Ag. After careful cleaning the electrode was ready for use. If it was to be employed as a Ag/AgCl cathode, approximately half the silver was first converted into AgCl by anodization in an 0.1M KCl solution. Electrolytically plated Ag has a smooth, even surface, described by Janz⁽⁹⁷⁾ as "locked".

However, when the electrode was used as the anode for the system $3\text{M KCl} \leftarrow 1.55\text{M LiCl}$ at a current of 23 mA, chlorine gas was evolved. The LiCl solution became saturated with Cl_2 and gas bubbles caused upwards progression of the results. This indicated that the current density employed was too high for this particular electrode. By estimating the amount of chlorine formed it was found that to prevent gas evolution the current would have to be reduced to such an extent that the boundary would not be visible. Thus, the effective surface area of the electrode had to be increased considerably.

This was achieved by using thermally decomposed Ag_2O paste.

High purity Ag_2O was prepared by mixing equal volumes of 0.6M AgNO_3 and 0.3M NaOH .⁽⁹⁷⁾ After the product had been thoroughly washed a paste of Ag_2O was applied to the Pt foil. The electrode was placed in a furnace and the temperature raised to just below 100°C and maintained there for $\frac{1}{2}$ -1 hour to drive off excess water. The temperature was then steadily raised to 450°C and held there for 30 minutes. The electrode was allowed to cool in the furnace to prevent thermal shock. This process was repeated five or six times with successively thinner pastes until all the Pt foil was covered. In subsequent preparations a small amount of Ag was electrolytically plated onto the foil prior to the thermal decomposition in order to aid the adhesion of the first coating of paste to the foil. Janz⁽⁹⁷⁾ describes the silver surfaces obtained by this method as "open" or "porous". The nature of the surface greatly increases the effective surface area of the electrode and in subsequent experiments no Cl_2 evolution was observed.

However, the porosity of the electrodes causes problems in that gas bubbles can be trapped in the pores. These bubbles are then subject to unknown volume changes during the course of an experiment. To preclude this possibility, the closed electrode was degassed before each run in the apparatus shown in fig.(V.3). In addition both the Ag anode and Ag/AgCl cathode were stored at all times in their respective electrolytes. Regeneration of the original electrode after each run was also carried out in either 3M KCl for the cathode or concentrated LiCl solution for the anode.

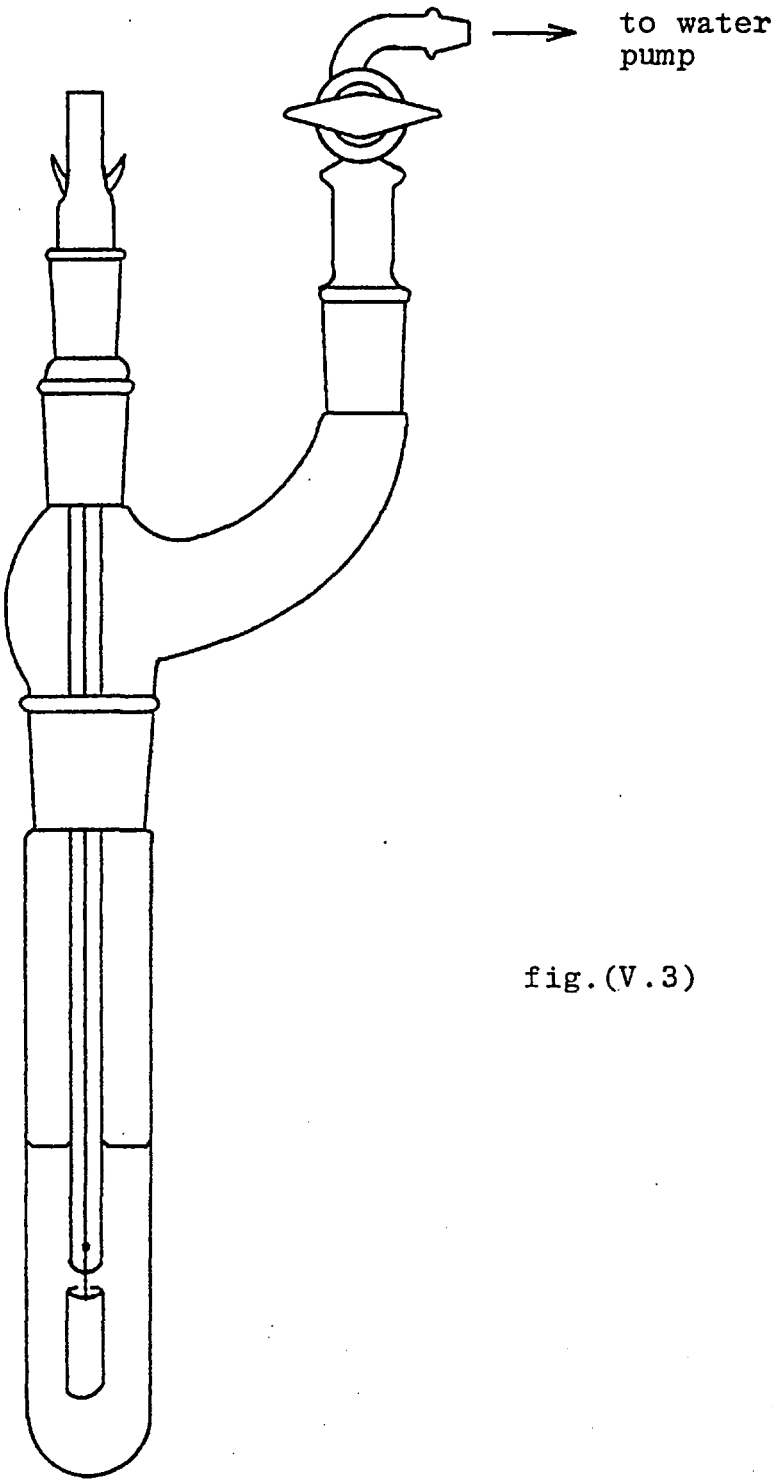


fig.(V.3)

V.2 Experimental Technique

The following section describes the general m.b. apparatus and handling techniques used in this laboratory for the measurement of transference numbers in dilute as well as in more concentrated electrolyte solutions.

V.2.1 M.B. Cell and its Calibration

The falling m.b. cell in fig.(V.1) was constructed entirely from pyrex glass except for the two side-arm taps, S_1 and S_2 , which were made from P.T.F.E. The glass tap S_3 was hollow to allow circulation of the thermostat oil to reduce Joule heating effects. The cell was mounted on a glass frame (not shown) for ease of handling. Vaseline grease was used for lubricating tap S_3 , the closed electrode joint and the stopper (not shown) in the B10 ground glass joint for the $\text{KCl} \leftarrow \text{LiCl}$ runs. Apiezon grease was used for the HCl runs as the acid reacted with vaseline forming gas bubbles in the top of the m.b. tube.

The 2.2 mm diameter m.b. tube had two sets of eight etch marks circumscribed on it, separated by a larger gap. The etch marks were numbered consecutively from 1 to 16 downwards from the tap. The tube had been aged for several years after etching to prevent volume changes occurring once the tube had been calibrated.

The volumes between marks 1 and 8, 2 and 9 etc. up to 8-16 were calibrated by means of the system $0.1\text{M } \text{KCl} \leftarrow 0.06\text{M } \text{LiCl}$, where $T_{\text{K}^+}^{\text{KCl}} = 0.4899^{(98-100)}$. The value "uncorrected" for solvent and volume corrections for a closed Ag anode is $T_{\text{K}^+}^{\text{KCl}} (\text{obs.}) = 0.4901$. The B.D.H. KCl used was of "Aristar" quality and the B.D.H. $\text{LiCl} \cdot \text{H}_2\text{O}$ was of a specially purified atomic absorption spectroscopy (AAS) grade. An electrolytically plated Ag anode was used. Runs were carried out at currents of 2 and 3 mA and the average of five runs was taken to give the volumes in table (V.1). The standard deviations of the

various volumes are also given.

Table (V.1)

mark	10^6 V/m^3	$10^6 \sigma/\text{m}^3$
9 - 1	0.6588	0.0005
10 - 2	0.6571	0.0005
11 - 3	0.6450	0.0005
12 - 4	0.6459	0.0003
13 - 5	0.6566	0.0007
14 - 6	0.6568	0.0006
15 - 7	0.6630	0.0005
16 - 8	0.6645	0.0004

V.2.2 Cell Filling

The filling procedure is described here for the system $\text{KCl} \leftarrow \text{LiCl}$ using a closed Ag anode. Analogous procedures apply for both the $\text{HCl} \leftarrow \text{LiCl}$ runs and for the cases where a closed Ag/AgCl cathode was used.

Both the KCl and LiCl solutions were degassed before filling the cell by brief (10-20s) evacuation at a water pump. This prevented dissolved gases coming out of solution in the cell at the higher thermostat temperature.

With S_1 , S_2 and S_3 open, degassed KCl solution was introduced via the LHS B14 opening until its level was just above S_3 . Tap S_3 was then closed and, with careful checks being made for air bubbles, the remainder of the leading solution was poured in. The KCl solution remaining above S_3 was removed by suction and the tube rinsed three times with doubly-distilled water and three times with the LiCl solution, the liquid being removed each time by suction.

The LiCl solution presaturated with AgCl was then poured into the RHS electrode bulb and the stirrer bar carefully

placed in the bottom of the bulb, checks again being made for adhering air bubbles. At this stage the degassed Ag electrode was loosely placed in position and unsaturated LiCl solution slowly poured in to fill the cell. After greasing the ground glass joints, the electrode and a B10 stopper were held firmly in position with small springs.

The cathode was then placed in position in the LH electrode chamber using a small piece of Pt wire to keep the electrode chamber open. For the $\text{KCl} \leftarrow \text{LiCl}$ runs a Ag/AgCl cathode was used. In the HCl runs a Pt foil cathode was acceptable as no net OH^- ions were produced that might reach the boundary during the run.

Throughout this procedure taps S_1 and S_2 were open. Tap S_2 was only closed when the solutions had reached thermal equilibrium in the thermostat tank.

V.2.3 The Thermostat and Temperature Control

Two sides of the thermostat tank used were made of glass to allow observation of the cell. A third observation window provided a side-view into the tank. Shell "Diala" BX oil was used as the thermostat liquid and the stirrer paddles were driven by a 1/6 h.p. motor, mounted on a separate frame to the tank to prevent vibrations affecting the m.b. cell.

The temperature was maintained at $25.00 \pm 0.005^\circ\text{C}$ using a mercury/toluene thermoregulator and a 150W nichrome wire heating frame (see fig.V.4). The heating frame was placed inside the toluene coil to increase the sensitivity of the temperature control. A copper coil carrying cooler tap water was used when the laboratory temperature exceeded 22°C . During a run the temperature was monitored on a Beckmann thermometer which had previously been calibrated against a standardised thermometer.

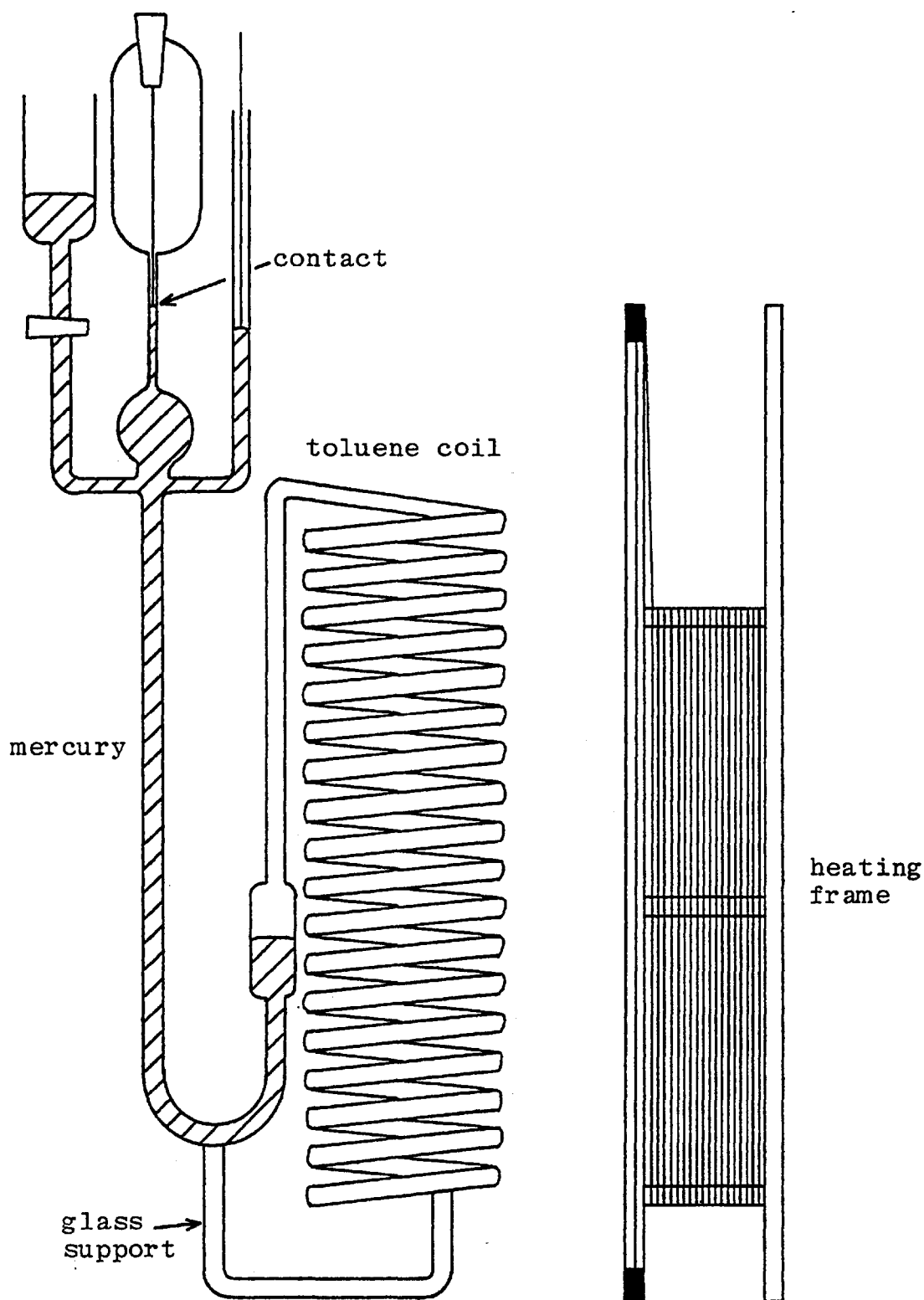


fig.(V.4)

V.2.4 Observation of the Boundary

The difference in refractive indices of the leading and following solutions was exploited to observe the boundary. A rectangular beam of light passed through a cylinder of water (acting as a lens), through the m.b. tube and was observed using a cathetometer. With this system (fig.V.5), the boundary appeared as a dark line at the top of the light beam or a light line at the bottom of the beam. Movement of the light source was via a simple pulley system.

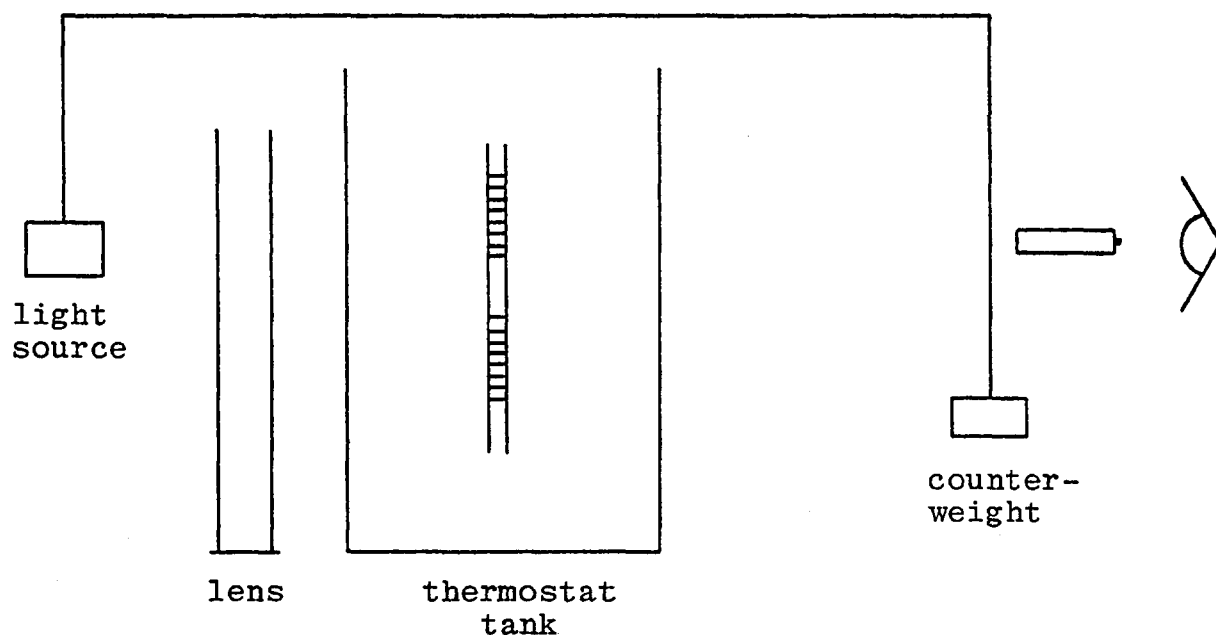


fig.(V.5)

V.2.5 Measurement of Current and Time

The current was determined by placing a Sullivan standard 1000Ω resistor in series with the cell and measuring the voltage drop across it with a Solartron 7045 digital multimeter. The voltmeter was occasionally calibrated against a standard Weston cell.

Boundary timings were made with a Zenith "Exact Time" battery clock and a metronome ticking every second. This method allows the observer to follow the progress of the boundary at all times. The seconds were counted off after the boundary was coincident with an etch mark and the time difference subtracted from the clock time at a convenient moment.

During some runs the current was not quite constant. It was then not sufficient simply to take current readings when the boundary was coincident with the etch marks, and further current readings were taken at regular intervals (every five minutes). The quantity of electricity passed between each boundary timing was calculated by integration of the current/time graph.

V.2.6 Constant Current Generator

As a run progressed the leading electrolyte was gradually displaced along the m.b. tube by the less conducting following electrolyte. The resultant increase in the cell resistance would have decreased the cell current had a constant current source not been used.

Figure (V.6) shows the circuit diagram for the control unit which was capable of sensing the change in the voltage drop across the variable resistor (current select switch) due to the change in resistance of the cell. The current could be altered by changing the value of the variable resistor. The control unit altered the output of the E.H.T. supply (fig.V.7) to maintain a constant current through the cell.

This arrangement, designated as unit 1, was capable of supplying a constant current of up to 24 mA within ± 0.05 mA for a resistance change, in the case of 3M KCl $\leftarrow$ LiCl, of 2.4 to 7.7k Ω . It was found that the current stability was improved by inserting a 50k Ω resistor in series with the cell.

V.2.7 General Procedure for a Run

After the cell had been filled, oil-insoluble ink marks were put on the tube just under each etch mark to facilitate their identification. A period of $\frac{3}{4}$ -1 hour was allowed for the cell to attain thermal equilibrium in the thermostat tank. At this stage tap S_2 was closed, effectively sealing the closed compartment, and the main stopcock S_3 opened. The current was immediately switched from the dummy load of the generator (20 mins. warm-up time was allowed) to the cell and the time noted.

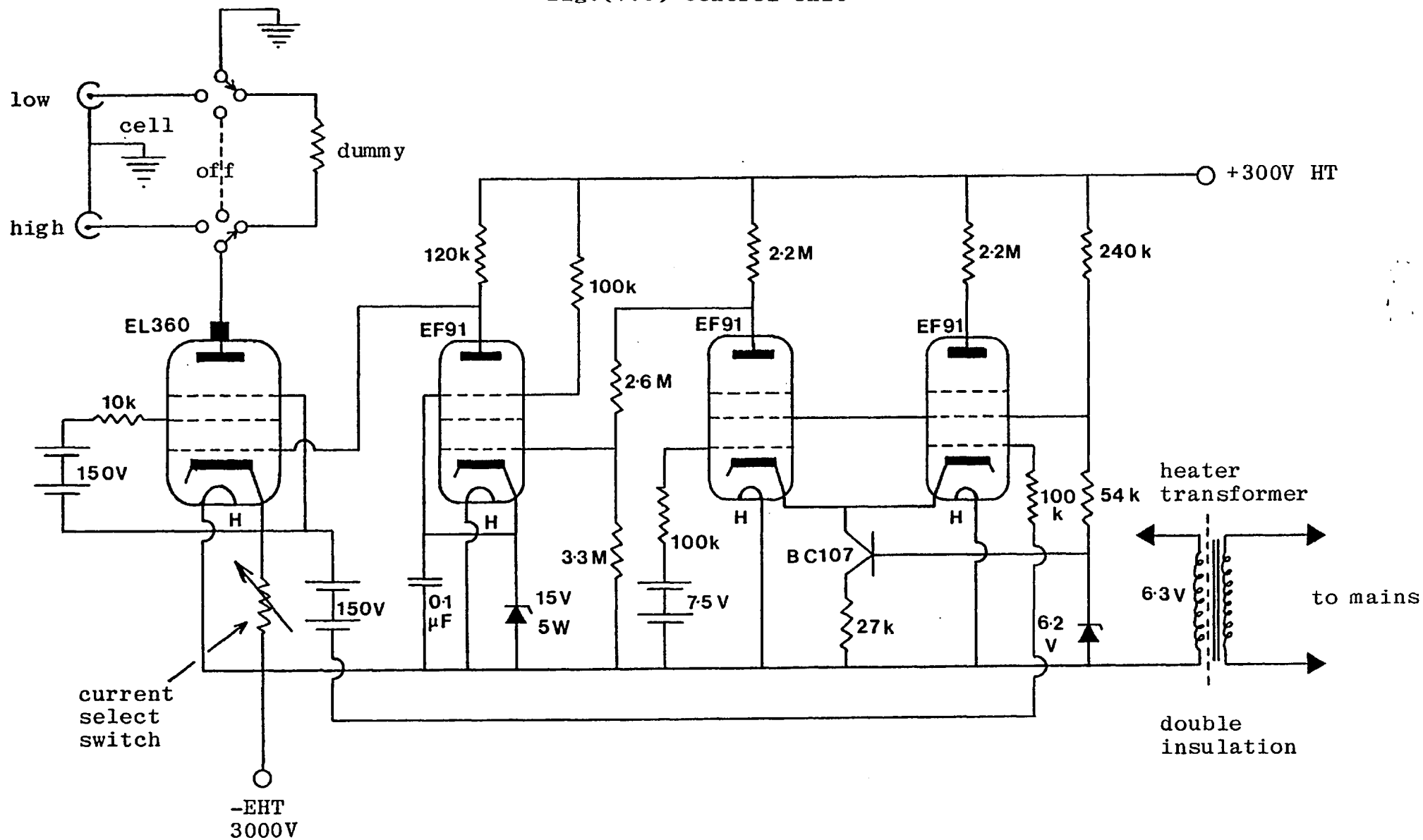
As the boundary became coincident with each etch mark the time, current and thermostat temperature were recorded. A check was made to ensure that the stirring action in the closed electrode bulb was stable. These observations were also made at various times during the long gap between the two sets of marks.

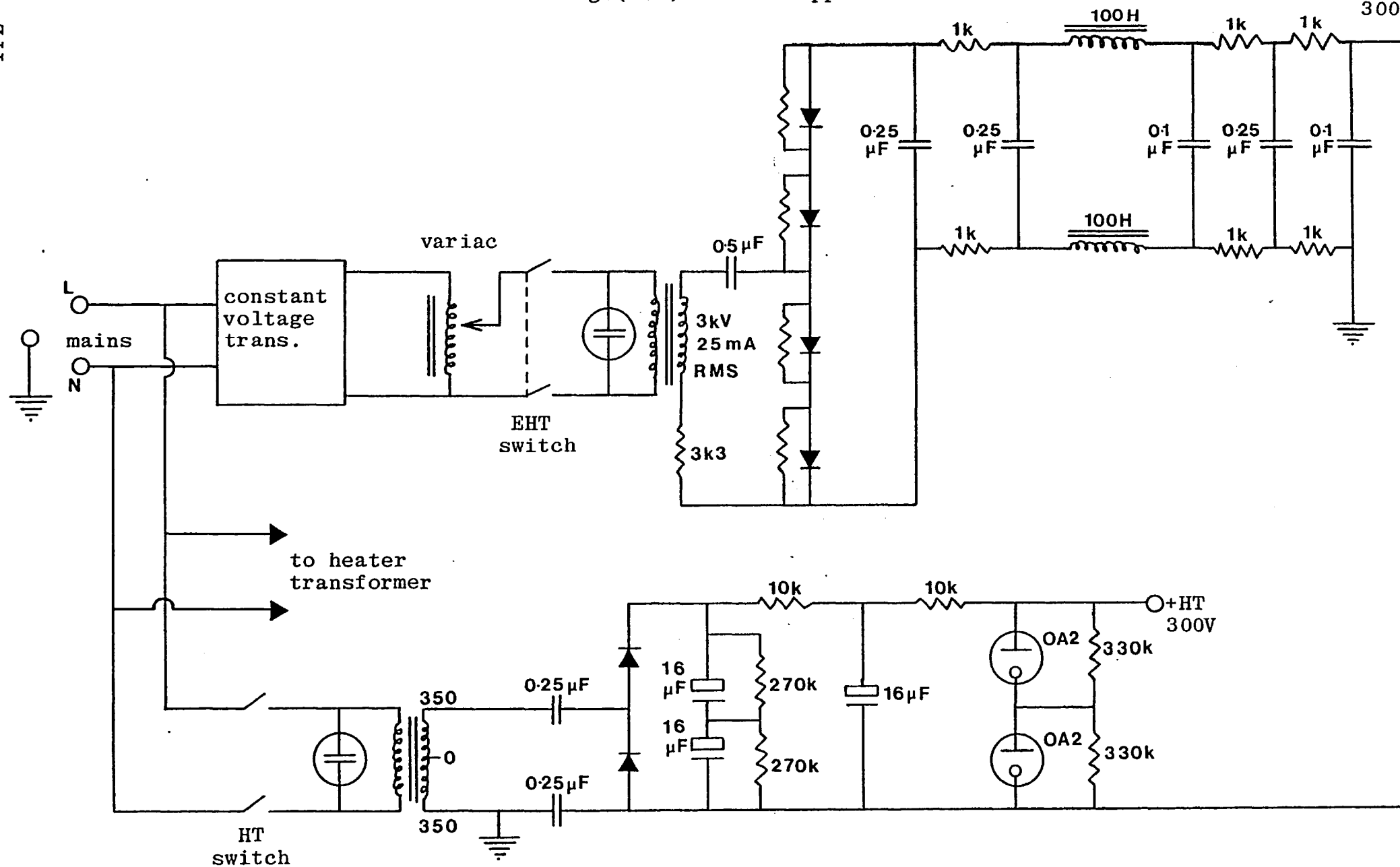
At the end of a run the cell was carefully inspected for air bubbles or other factors which might invalidate the results.

V.2.8 Cell Cleaning

Methylated spirits was used to remove oil from the outside of the cell. The electrodes, were taken out and stored in the appropriate solutions, and the cell was emptied and rinsed three or four times with distilled water. The cell was allowed to drain for several minutes before being rinsed with meths and soaked in 1,1,1-trichloroethane to

fig.(V.6) Control Unit





remove the bulk of the grease used. The lubricated ground glass surfaces were further de-greased with Kleenex tissues soaked in the chlorinated solvent. The latter was removed from the cell with meths and six further rinsings with distilled water. Concentrated chromic acid cleaning mixture (2-3 mins.) removed any remaining traces of grease. A further fifteen washings with distilled water followed by soaking overnight with water were found adequate to remove all traces of the acid. Just prior to the next experiment, the cell was rinsed three times with doubly-distilled water and dried by passing N_2 (dried via a silica gel tower) through the cell. It was found necessary to direct the N_2 flow directly into the electrode bulb as otherwise this area remained wet.

V.2.9 Materials

Doubly-distilled water of specific conductance $1 \times 10^{-6} \Omega^{-1} \text{ cm}^{-1}$ was prepared by a second distillation from alkaline permanganate solution.

B.D.H. "Aristar" KCl and NaCl and AAS grade $\text{LiCl} \cdot \text{H}_2\text{O}$ were used without further purification.

Due to the cost of the AAS grade $\text{LiCl} \cdot \text{H}_2\text{O}$ (£13-38/25g,⁽¹⁰¹⁾ i.e. £12-50 + VAT per run), a concentrated LiCl stock solution was later prepared by the addition of a slight excess of B.D.H. "AnalaR" concentrated HCl solution (diluted to 60% v/v with doubly-distilled water) to "AnalaR" Li_2CO_3 . To prevent oxidation of Cl^- to chlorine, this procedure had to be carried out in an ice-bath with an inert N_2 atmosphere. After final adjustment to pH5-6 (which corresponds to the pH of the doubly-distilled water) by the further addition of small amounts of Li_2CO_3 , the liquor was filtered and diluted to approximately 1 dm^3 . Three samples of the stock solution were analysed by potentiometric titration with AgNO_3 . The concentration of the LiCl was known to at least $\pm 0.2\%$.

Stock solutions of HCl were prepared from B.D.H. "AnalaR"

concentrated HCl and doubly-distilled water. The acid was analysed by pH titration with standardised NaOH, calibrated glassware being used throughout. B.D.H. 4M "AVS" NaOH (free from carbonate) was diluted to the approximate concentration required in an N₂ atmosphere with doubly-distilled water. Nitrogen had previously been passed through the water for $\frac{1}{2}$ hour to remove dissolved CO₂. The NaOH solution was standardised against B.D.H. "AnalaR" potassium hydrogen phthalate. The organic acid had been dried at 110°C for 2 hours and stored in a desiccator over silica gel for 24 hours before using.⁽¹⁰²⁾ The pH titrations were carried out with a Radiometer pH meter (PHM62), a glass electrode (Radiometer G202C) and a calomel reference electrode (Radiometer K401). Throughout the titrations the NaOH solution was protected with a soda-lime guard tube to prevent absorption of atmospheric CO₂. The HCl concentration was known to within $\pm 0.1\%$ at 1 and 2M and $\pm 0.03\%$ at 4M.

Sufficient LiCl solution to fill the electrode bulb (or KCl solution in the case of closed cathode runs) was saturated with a four-fold excess of J.M.C. "Specpure" AgCl. The solutions were prepared the day before use and kept in the dark overnight.

V.2.10 A Typical Run

Run 68 3M KCl ← LiCl Thursday, 11/9/80

closed Ag anode, bulb LiCl presat. with AgCl (stirring),
open Ag/AgCl cathode (no stirring)
cell in tank at 11.20 a.m., generator on dummy at 11.50 a.m.
 $c_{\text{KCl}} = 2.9999_6 \text{ mol dm}^{-3}$, $c_{\text{LiCl}} = 1.552 \text{ mol dm}^{-3}$
 $t_0 = 11.59 \text{ a.m.}$, $I_0 = 23.5 \text{ mA}$
 $T_0 = 4.261 \text{ on Beckmann } (\equiv 25.00 \pm 0.005^\circ\text{C})$

The measurements and results of run 68 are given in table (V.2).

Table (V.2)

mark	time (h-m-s)	I/mA	stirring action	T
1	2-14-58	23.06	✓	4.261
2	2-40-33	23.06	✓	4.261
3	3-06-37	23.06	✓	4.261
4	3-29-30	23.07	✓	4.261
5	3-49-16	23.07	✓	4.261
6	4-13-47	23.07	✓	4.261
7	4-36-10	23.07	✓	4.261
8	4-58-33	23.08	✓	4.261
	5-30	23.08	✓	4.261
	6-00	23.09	✓	4.261
	6-30	23.08	✓	4.261
9	6-55-43	23.09	✓	4.261
10	7-20-29	23.08	✓	4.261
11	7-41-13	23.09	✓	4.261
12	8-04-18	23.09	✓	4.261
13	8-28-00	23.09	✓	4.261
14	8-52-34	23.10	✓	4.261
15	9-17-35	23.10	✓	4.261
16	9-40-47	23.10	✓	4.261

mark	t/s	$\bar{I}/\text{mA}$	$10^6 V/\text{m}^3$	$T_{\text{K}^+}^{\text{KCl}}$ (obs.)
9-1	16845	23.07 ₄	0.6588	0.4906
10-2	16796	23.07 ₅	0.6571	0.4908
11-3	16476	23.07 ₈	0.6450	0.4910
12-4	16488	23.08 ₀	0.6459	0.4913
13-5	16724	23.08 ₂	0.6566	0.4923
14-6	16727	23.08 ₅	0.6568	0.4923
15-7	16885	23.08 ₇	0.6630	0.4923
16-8	16934	23.09 ₀	0.6645	0.4919

$$\therefore \bar{T}_{\text{K}^+}^{\text{KCl}} (\text{obs.}) = 0.4916 \pm 0.0008$$

V.3 Volume and Solvent Corrections

The expressions used to calculate the volume corrections for the system $\text{KCl} \leftarrow \text{LiCl}$ for both a closed Ag anode and a closed Ag/AgCl cathode have been derived in section (II.3.4). Quantitative values are reported below together with the corresponding closed Ag anode values for the HCl runs. In addition, semi-quantitative values are given for the rigorous derivations in section (IV.1) in order to estimate the magnitude of the errors involved in using the simplified expressions.

Finally, the magnitude of the solvent correction is shown to be experimentally insignificant.

V.3.1 Volume Correction

The volume changes for the system $\text{KCl} \leftarrow \text{LiCl}$ with a closed Ag anode and a closed Ag/AgCl cathode are, respectively

$$\Delta V = -V_{\text{Ag}} + V_{\text{AgCl}} - T_{\text{K}^+}^{\text{KCl}} \phi_{\text{KCl}}^{\text{KCl}} \quad (\text{V.1})$$

$$\Delta V = V_{\text{Ag}} - V_{\text{AgCl}} + T_{\text{K}^+}^{\text{KCl}} \phi_{\text{KCl}}^{\text{KCl}} \quad (\text{V.2})$$

The molar volume of Ag is $10.28_2 \text{ cm}^3 \text{ mol}^{-1}$, calculated from the density of electrolytically produced Ag at 25°C ($10.491_4 \text{ g cm}^{-3}$),⁽⁷²⁾ and that of AgCl $25.77_7 \text{ cm}^3 \text{ mol}^{-1}$ (from the value given by Mellor⁽⁸⁴⁾ of $\rho_{\text{AgCl}} = 5.5671 \text{ g cm}^{-3}$). MacInnes and Dole's⁽²⁶⁾ value of $T_{\text{K}^+}^{\text{KCl}} = 0.4857$ at 3M was used throughout the calculations. Aqueous KCl density data⁽⁷²⁾ at 25°C were curve-fitted to a sixth-order polynomial in c_{KCl} with a fit of $9 \times 10^{-2} \text{ g dm}^{-3}$. The coefficients are

$$\begin{array}{lll}
a_0 & = & 997.320 \quad \text{g dm}^{-3} \\
a_1 & = & 45.5267 \quad \text{g mol}^{-1} \\
a_2 & = & 1.07321 \quad \text{g mol}^{-2} \text{ dm}^3 \\
a_3 & = & -1.58920 \quad \text{g mol}^{-3} \text{ dm}^6 \\
a_4 & = & 0.613021 \quad \text{g mol}^{-4} \text{ dm}^9 \\
a_5 & = & -0.108429 \quad \text{g mol}^{-5} \text{ dm}^{12} \\
a_6 & = & 7.35954 \times 10^{-3} \quad \text{g mol}^{-6} \text{ dm}^{15}
\end{array}$$

These coefficients were then used to calculate ϕ_{KCl} from equation (IV.18). For 3M KCl, $\phi_{\text{KCl}} = 3.055_3 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1}$ ($30.55_3 \text{ cm}^3 \text{ mol}^{-1}$). Thus the values of ΔV in (V.1) and (V.2) are 0.65_5 and $-0.65_5 \text{ cm}^3 \text{ mol}^{-1}$, respectively. The volume correction is therefore ± 0.0020 .

The volume change for the system $\text{HCl} \leftarrow \text{LiCl}$ with a closed Ag anode is

$$\Delta V = -V_{\text{Ag}} + V_{\text{AgCl}} - T_{\text{H}^+}^{\text{HCl}} \phi_{\text{HCl}}^{\text{HCl}} \quad (\text{V.3})$$

The experiments were carried out for leading HCl concentrations of 0.9996, 2.0088 and $4.181 \text{ mol dm}^{-3}$. Literature HCl density data^(72,103) were fitted to a sixth-order polynomial with a fit of $7 \times 10^{-2} \text{ g dm}^{-3}$. The coefficients are

$$\begin{array}{lll}
a_0 & = & 997.043 \quad \text{g dm}^{-3} \\
a_1 & = & 18.4593 \quad \text{g mol}^{-1} \\
a_2 & = & -0.900599 \quad \text{g mol}^{-2} \text{ dm}^3 \\
a_3 & = & -0.193423 \quad \text{g mol}^{-3} \text{ dm}^6 \\
a_4 & = & -2.39397 \times 10^{-2} \quad \text{g mol}^{-4} \text{ dm}^9 \\
a_5 & = & 1.41407 \times 10^{-3} \quad \text{g mol}^{-5} \text{ dm}^{12} \\
a_6 & = & -3.24960 \times 10^{-5} \quad \text{g mol}^{-6} \text{ dm}^{15}
\end{array}$$

The $T_{\text{H}^+}^{\text{HCl}}$ data of Lengyel⁽⁶⁶⁾ and Harned and Dreby⁽⁶⁷⁾ were fitted to a sixth-order polynomial in m_{HCl} with a fit of 0.007. The corresponding coefficients are

$$\begin{aligned}
a_0 &= 0.828536 \\
a_1 &= 1.21013 \times 10^{-2} \text{ kg mol}^{-1} \\
a_2 &= -2.85393 \times 10^{-3} \text{ kg}^2 \text{ mol}^{-2} \\
a_3 &= 8.40279 \times 10^{-4} \text{ kg}^3 \text{ mol}^{-3} \\
a_4 &= -2.68301 \times 10^{-4} \text{ kg}^4 \text{ mol}^{-4} \\
a_5 &= 2.62149 \times 10^{-5} \text{ kg}^5 \text{ mol}^{-5} \\
a_6 &= -7.82474 \times 10^{-7} \text{ kg}^6 \text{ mol}^{-6}
\end{aligned}$$

In table (V.3) are given the relevant molar and molal concentrations (c/m conversion via the curve-fitted density data) and the appropriate values of ϕ_{HCl} and $T_{\text{H}^+}^{\text{HCl}}$ at 25°C.

Table (V.3)

$c_{\text{HCl}}/\text{mol dm}^{-3}$	$m_{\text{HCl}}/\text{mol kg}^{-1}$	$\phi_{\text{HCl}}/\text{cm}^3 \text{ mol}^{-1}$	$T_{\text{H}^+}^{\text{HCl}}$
0.9996	1.0217	18.78 ₉	0.839
2.0088	2.0958	19.26 ₀	0.845
4.181	4.572	19.80 ₄	0.833

From these values, $c\Delta V$ is -0.0003 at 0.9996M, -0.0016 at 2.0088M and -0.0042 at 4.181M HCl. These values have been calculated on the assumption that the literature $T_{\text{H}^+}^{\text{HCl}}$ are correct. If they are found not to be then these values will have to be recalculated.

The rigorous volume change expression derived in section (IV.1.1) differs from equation (V.1) by a term (S)

$$S = \int_{\alpha} \phi_{\text{LiCl}} c_{\text{LiCl}}(t_{f+1}) \delta V - \int_{\alpha} \phi_{\text{LiCl}} c_{\text{LiCl}}(t_f) \delta V \quad (\text{V.4})$$

This is the change in volume of the LiCl solute caused by the passage of one faraday of electricity. During the typical run in table (V.2) only 8.4×10^{-3} F were passed. In order to estimate the magnitude of S the change in volume during this run will be calculated, with time t_f being taken as the start of the run (time t_0) and t_{f+1} the time after

passing 8.4×10^{-3} F (time t_e). Although t_0 and t_e do not strictly correspond to t_f and t_{f+1} , respectively, they will serve for this approximate calculation. The value obtained (S') will then be "scaled-up" by a factor of $(1/8.4 \times 10^{-3})$ to give an estimate for S .

In order to simplify the calculation, three assumptions will be made:

- 1) due to the stirring action and the shape of the electrode bulb, all concentration changes caused by the electrode reaction are confined to the electrode bulb in which the electrolyte concentration is uniform,
- 2) there is no net diffusion of solute species into or out of the bulb, and ionic transport is by electrolytic transference only and,
- 3) the solution in the bulb has been presaturated with AgCl and no further volume change takes place due to AgCl dissolution.

As for the KCl and HCl solutions, literature LiCl density data^(68,72) at 25°C were fitted to various order polynomials in c . A seventh-order polynomial was chosen with a fit of 5×10^{-2} g dm⁻³, for which the coefficients are

$a_0 =$	997.054	g dm ⁻³
$a_1 =$	26.2811	g mol ⁻¹
$a_2 =$	-7.97892	g mol ⁻² dm ³
$a_3 =$	18.5716	g mol ⁻³ dm ⁶
$a_4 =$	-23.8935	g mol ⁻⁴ dm ⁹
$a_5 =$	15.2396	g mol ⁻⁵ dm ¹²
$a_6 =$	-4.60367	g mol ⁻⁶ dm ¹⁵
$a_7 =$	0.525414	g mol ⁻⁷ dm ¹⁸

These coefficients were then used to calculate ϕ_{LiCl} from equation (IV.18).

The volume of the cell, illustrated in fig.(V.1), above and to the right of the main tap, S_3 , is approximately 106 cm^3 , of which 63 cm^3 is in the electrode bulb. This was initially filled with homogeneous LiCl solution with a concentration of 1.55 mol dm^{-3} . Thus

$$\begin{aligned} \int_a \phi_{\text{LiCl}} c_{\text{LiCl}}(t_0) \delta V &= 18.823 \times 1.55 \times 0.106 \text{ cm}^3 \\ &= 3.0926 \text{ cm}^3 \end{aligned} \quad (\text{V.5})$$

At the end of the run, time t_e , $8.4 \times 10^{-3} \text{ F}$ have been passed and LiCl solution now fills tap S_3 and the whole m.b. tube, an additional volume of approximately 1.5 cm^3 . The concentration of the solution in this volume is the adjusted Kohlrausch concentration which by successive approximation was found to be 1.72 mol dm^{-3} . Initially the solution in the electrode bulb contained $0.063 \times 1.55 = 0.09765 \text{ mol LiCl}$. At time t_e this has been depleted by an amount $0.0084 \times T_{\text{Li}^+}^{\text{LiCl}} \text{ mol}$. If $T_{\text{Li}^+}^{\text{LiCl}}$ is taken as 0.264 for 1.53M LiCl,^(68,69) the concentration of solute in the bulb at time t_e is 1.51 mol dm^{-3} . The concentration of the remainder of the LiCl solution between tap S_3 and the bulb (volume 43 cm^3) will also have changed due to the adjustment to the Kohlrausch concentration of the solution in the m.b. tube. As the total number of moles of LiCl remains constant throughout the experiment (cf. equation IV.5) the concentration of solution in this region is easily calculated. At time t_0 there was a total of $1.55 \times 0.106 = 0.1643 \text{ mol LiCl}$ in the cell. At time t_e there are $1.72 \times 0.0015 = 0.00258 \text{ mol LiCl}$ in the m.b. tube and $1.51 \times 0.063 = 0.09513 \text{ mol LiCl}$ in the bulb. Thus the remaining 43 cm^3 of the cell contain 0.06659 mol LiCl at a concentration of $1.549 \text{ mol dm}^{-3}$.

These, then, are the three volume elements into which the following solution can be divided to enable us to estimate the solute volume at time t_e .

$$\sum_{\alpha} \phi_{\text{LiCl}} c_{\text{LiCl}} (t_e) \delta V = 18.844 \times 1.72 \times 0.0015 + \\ 18.812 \times 1.51 \times 0.063 + \\ 18.823 \times 1.549 \times 0.043 \text{ cm}^3 \\ = 3.0919 \text{ cm}^3 \quad (\text{V.6})$$

Therefore

$$S' = -0.0007 \text{ cm}^3 \quad (\text{V.7})$$

and

$$S = \frac{-7 \times 10^{-4}}{8.4 \times 10^{-3}} = -0.083 \text{ cm}^3 \text{ mol}^{-1} \quad (\text{V.8})$$

This analysis suggests that ΔV , instead of being taken as $0.655 \text{ cm}^3 \text{ mol}^{-1}$ (p.117) should really be $0.572 \text{ cm}^3 \text{ mol}^{-1}$. However, the error incurred by using the former value in the volume correction is approximately 0.0002, which in concentrated solutions is less than other experimental errors. Although this sub-division of the LiCl solution into only three volume elements is crude, it shows that the error in ignoring the S term in the volume change is small.

The situation for the closed cathode case is somewhat different as fig.(V.8) shows. Let us arbitrarily position the reference plane in the homogeneous KCl solution at time t_0 so that the volume below it is 100 cm^3 , of which 63 cm^3 constitutes the electrode bulb. Using similar principles to those introduced above and the same notation as in section (IV.1), then

$$\sum_Y \phi_{\text{KCl}} c_{\text{KCl}} (t_0) \delta V = 30.553 \times 3.000 \times 0.100 \text{ cm}^3 \\ = 9.166 \text{ cm}^3 \quad (\text{V.9})$$

At time t_e , the number of moles of KCl in the electrode bulb will have increased by $0.0084 \times T_{\text{K}^+}^{\text{KCl}} = 4.08 \times 10^{-3} \text{ mol}$, and the KCl concentration in the electrode bulb will now be $3.065 \text{ mol dm}^{-3}$. The concentration of the remaining KCl

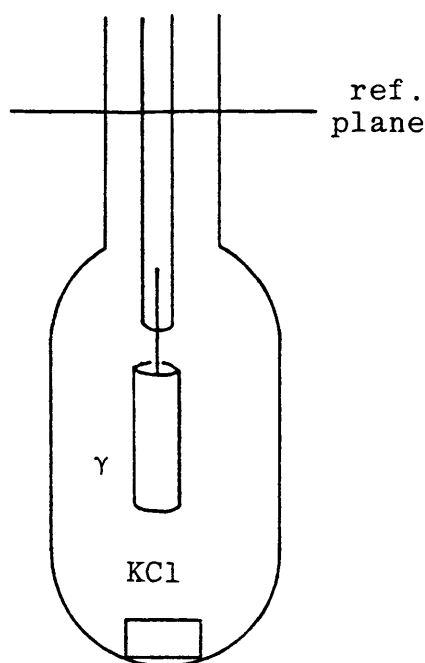


fig.(V.8)

solution below the reference plane will still be $3.000 \text{ mol dm}^{-3}$. Thus

$$\begin{aligned} \int_{\gamma} \phi_{\text{KCl}} c_{\text{KCl}} (t_e) \delta V &= 30.596 \times 3.065 \times 0.063 + \\ &\quad 30.553 \times 3.000 \times 0.037 \text{ cm}^3 \\ &= 9.299 \text{ cm}^3 \end{aligned} \quad (\text{V.10})$$

The difference per faraday is then

$$\frac{(9.299 - 9.166)}{0.0084} = 15.833 \text{ cm}^3 \text{ mol}^{-1} \quad (\text{V.11})$$

This may be compared with $T_{\text{K}^+}^{\text{KCl}} \phi_{\text{KCl}}$ for 3M KCl by the normal expression (IV.17) of $0.4857 \times 30.553 = 14.840 \text{ cm}^3 \text{ mol}^{-1}$.

Hence the volume change is given by (see section IV.1.2)

$$\begin{aligned} \Delta V &= V_{\text{Ag}} - V_{\text{AgCl}} + 15.833 \text{ cm}^3 \text{ mol}^{-1} \\ &= 0.338 \text{ cm}^3 \text{ mol}^{-1} \end{aligned} \quad (\text{V.12})$$

The difference between (V.12) and the value of $-0.655 \text{ cm}^3 \text{ mol}^{-1}$ is quite significant. The volume corrections, $c\Delta V$, are 0.0010 and -0.0020 , respectively. This is a much greater difference than was found for the closed anode case and can be attributed to the greater variation of ϕ_{KCl} with concentration as compared with ϕ_{LiCl} and the approximations necessarily made in the calculations. This analysis indicates that more importance should be attached to the closed anode runs for which $(\Delta\phi_{\text{LiCl}}/\Delta c)$ is smaller than to the corresponding results from runs employing closed cathodes.

V.3.2. Solvent Correction

The solvent correction is given by⁽²⁵⁾

$$T (\text{corr.}) = T \left[1 + \left(\frac{\kappa_{\text{solvent}}}{\kappa_{\text{solute}}} \right) \right] \quad (\text{V.13})$$

where T is the observed transference number corrected for volume changes. The specific conductance of the solute is

$$\kappa_{\text{solute}} = \kappa_{\text{solution}} - \kappa_{\text{solvent}} \quad (\text{V.14})$$

Postler⁽¹⁰⁴⁾ has reported the molar conductance of 3M KCl at 25°C to be $9.946 \times 10^{-3} \Omega^{-1} \text{ m}^2 \text{ mol}^{-1}$ and hence

$$\kappa_{\text{solution}} = 29.84 \Omega^{-1} \text{ m}^{-1} \quad (\text{V.15})$$

The specific conductance of the solvent is $10^{-6} \Omega^{-1} \text{ cm}^{-1}$ or $10^{-4} \Omega^{-1} \text{ m}^{-1}$. Thus

$$\kappa_{\text{solvent}}/\kappa_{\text{solute}} = 3.4 \times 10^{-6} \quad (\text{V.16})$$

According to the data of Owen and Sweeton,⁽¹⁰⁵⁾ the corresponding ratios for 1.1, 2.0 and 4.1M HCl are 2.9×10^{-6} , 1.8×10^{-6} and 1.2×10^{-6} , respectively. Obviously

in such highly concentrated solutions the contribution to the solution conductance by the solvent is negligible and no solvent correction was necessary.

CHAPTER SIX

MOVING BOUNDARY RESULTS AND DISCUSSION

VI.1 Exploratory Work

Very little m.b. work has been carried out at solute concentrations greater than 0.2M. In their 1932 review, MacInnes and Longworth⁽²⁷⁾ reported previously unpublished values for $T_{K^+}^{KCl}$ up to 1M. Fritz and Fuget⁽¹⁰⁶⁾ carried out anion runs for $CuSO_4$ up to a concentration of 0.5M. The only other study in the literature is that of Haase et al.⁽¹⁰⁷⁾ who measured T_+ for $AgNO_3$ up to 2M, $HClO_4$ up to 5M and HNO_3 up to 9.4M. The $HClO_4$ data in the region 0.1 - 0.3M have been shown to be incorrect⁽⁴⁰⁾ and it seems likely that the experiments were affected by Joule heating caused by the high currents used (10-100 mA) and poor temperature control. Consequently the validity of the $AgNO_3$ and HNO_3 results is also in doubt.

Of these three studies only the first two employed the direct optical observation method used in this project. Haase's results were obtained using the optical schlieren technique. Thus it seemed advisable to carry out some preliminary experiments to ensure that stable boundaries were actually visible at concentrations of 1M and above. The range of currents over which measurements could be made was also studied. Table (VI.1) gives the results of six preliminary experiments.

The $KCl \leftarrow LiCl$ system was visible over a wide concentration and current range and was thus suitable for investigation. However, the $NaCl \leftarrow LiCl$ system required higher currents than for equimolar KCl solutions to allow measurements to be made. As the constant current generator available produced a maximum current of 25 mA, no further $NaCl$ runs were attempted.

Table (VI.1)

system	current range/mA	boundary appearance
0.5M KCl ← 0.25M LiCl	5 - 20	sharp but thick at 8 mA
1.0M KCl ← 0.50M LiCl	7 - 25	sharp but thick at 16 mA
2.0M KCl ← 1.0M LiCl	7 - 24	sharp but thick at 17 mA
3.5M KCl ← 1.7M LiCl	23	thick
1.0M NaCl ← 0.81M LiCl	20	very faint and diffuse
2.0M NaCl ← 1.4M LiCl	24	not visible

Whether a boundary appears or not is determined by the difference in refractive indices of the solutions on either side of the boundary. The boundary visibility is also affected by the thickness of the boundary layer: thin boundaries lead to sharp, easily measurable images whilst thicker ones produce a more diffuse image. Longsworth's⁽²⁷⁾ equation for the boundary "thickness" δ (eqn.II.19) can be usefully rearranged by using the moving boundary equation (II.14) and

$$\bar{\lambda}_{\pm} = F\bar{u}_{\pm} |z_{\pm}| \quad (\text{VI.1})$$

to give

$$\delta = \frac{4RTcA}{FIT_{\pm}} \frac{\bar{\lambda}_L \cdot \bar{\lambda}_F}{(\bar{\lambda}_L - \bar{\lambda}_F)} \quad (\text{VI.2})$$

where the symbols are those introduced in chapter II. It may be noted that $T_{\pm}$ in (VI.2) is the observed transference number as it is related to v , the boundary speed, in Longsworth's original equation. The difference between $T_{\pm}(\text{obs.})$ and $T_{\pm}(\text{corr.})$ will usually be insignificant but it may become important at very high concentrations for systems with large ΔV terms. Table (VI.2) gives the "thickness" of some of the boundary systems studied in the preliminary work, with LiCl always the following electrolyte.

Limiting ionic conductances⁽¹⁰⁸⁾ have been used in the calculations along with literature $T_{K^+}^{KCl}$ (26) and $T_{Na^+}^{NaCl}$ (91-94) data "uncorrected" for a closed Ag anode. The cross-sectional area of the m.b. tube was $3.80 \times 10^{-6} \text{ m}^2$.

Table (VI.2)

leading solute	c/mol dm ⁻³	T ₊ (obs.)	I/mA	δ/mm
KCl	1.0	0.488	20	0.33
KCl	2.0	0.488	20	0.65
KCl	3.5	0.488	20	1.1
NaCl	1.0	0.378	20	0.88
NaCl	2.0	0.379	20	1.7
NaCl	2.0	0.379	23	1.5
KCl	3.0	0.488	12	1.6
KCl	0.1	0.4901	3	0.22

The first five entries in the table show that the boundary is almost three times thicker for the NaCl←LiCl system than for KCl←LiCl at the same current. This is due to $(\lambda_{K^+}^0 - \lambda_{Li^+}^0)$ being greater than $(\lambda_{Na^+}^0 - \lambda_{Li^+}^0)$, and to the KCl boundary being faster. The table also shows that the 2M NaCl←LiCl system which was not visible at 23 mA ($\delta = 1.5 \text{ mm}$) was actually thinner than the 3M KCl←LiCl boundary at 12 mA ($\delta = 1.6 \text{ mm}$) whose progress has been successfully followed (section VI.2.1). That the NaCl boundary was not seen could be due to a greater difference in refractive indices for the KCl and LiCl solutions at the concentrations used, although no literature data are available to verify this.

For comparison, the last line of table (VI.2) gives the thickness of the boundary for the 0.1M KCl←LiCl system which is sharp and easily measurable to $\pm 1 \text{ s}$.

VI.2 KCl ← LiCl Experiments

All new experimental techniques or extensions of existing techniques must first be thoroughly tested with a system of known properties. There are very few concentrated electrolyte solutions whose transference numbers are sufficiently well known: one of the few is 3M KCl where $T_{K^+}^{KCl}$ (corr.) = 0.4857⁽²⁶⁾. Accordingly, the test system chosen for this project was 3M KCl ← LiCl, with either a closed Ag anode or a closed Ag/AgCl cathode. It might be argued that, since $T_{K^+}^{KCl}$ is relatively independent of concentration, KCl does not provide a sufficiently sensitive test. However, as stated before, it is the volume change that we are concerned with and any error in ΔV would cause the same absolute error in $T_{K^+}^{KCl}$ as it would in $T_{Na^+}^{NaCl}$ or $T_{H^+}^{HCl}$ at equal concentrations.

VI.2.1 Compilation of Results

The complete set of m.b. experiments with 3M KCl at 25°C is presented in table (VI.3). The runs are in chronological order so that the progress of the research, including the effects of stirring, presaturation and current variation, can be assessed. At this stage only the observed $T_{K^+}^{KCl}$ values are given as it is obviously meaningless to apply the theoretical volume correction to run 43 where other, unknown, processes are clearly taking place. No solvent correction was needed (section V.3.2). Column 8 gives the standard deviation of the separate sets of etch-mark readings (usually 8) in a run about the average $T_{K^+}^{KCl}$ (obs.) value.

In the majority of runs a closed anode was used as a theoretical analysis of the volume correction (section V.3.1) indicated that more reliance could be placed on these results. Also, as the chloride concentration is lower than in the cathode compartment, the AgCl solubility (and the resultant unknown volume change) is smaller.

Table (VI.3)

run	$c_{\text{LiCl}}/\text{mol dm}^{-3}$	closed electrode	I/mA	stirring	presat.	$T_{\text{K}^+}^{\text{KCl}}(\text{obs.})$	$10^4 \sigma$	comments
38	1.55	cathode	22.5	✓	×	-		gassing
39	1.55	anode	23.0	✓	×	-		gassing
40	1.55	anode	22.9	✓	×	0.4923	1	
42	1.55	cathode	22.5	✓	×	0.4879	4	
43	1.55	cathode	22.4	×	×	0.4701	10	
44	1.55	anode	22.3	✓	×	0.4895	6	
45	1.55	anode	22.2	×	×	0.4903	5	
46	1.57	anode	22.2	✓	✓	0.4889	4	
47	1.57	anode	16.0	✓	✓	0.4901	4	
48	1.57	anode	12.6	✓	✓	0.4901	11	
50	1.57	anode	10.9	✓	✓	-		low, progression up
51	1.53	anode	22.7	✓	✓	-		low, progression up
53	1.53	cathode	22.4	✓	✓	-		high, progression down
54	1.53	anode	23.1	✓	✓	-		low, slight progression up
60	1.58	anode	22.6	✓	✓	0.4920	10	
61	1.58	anode	23.4	✓	✓	0.4926	6	
64	1.58	anode	22.9	×	✓	0.4930	10	
65	1.58	anode	22.9	✓	✓	0.4920	4	
66	1.58	cathode	24.3	✓	✓	0.4906	3	
68	1.55	anode	23.1	✓	✓	0.4917	8	
69a	1.55	anode	12.5	✓	✓	0.4890	3	
69b	1.55	anode	12.5	×	✓	0.4881	28	

Runs 38 and 39 were performed with electrolytically produced electrodes and gassing occurred. Subsequent runs were all carried out with electrodes based on thermally decomposed Ag_2O paste. The progression observed in runs 50-54 caused problems for some time. Four possible causes were suspected: impurities in the LiCl stock solution, a cracked stirrer bar which would absorb electrolyte during the run, a leaky main stopcock or current leakage. No definite conclusion was reached as to which one (or more) of these possible sources of error was responsible. In run 69 the immersible stirrer stopped halfway through the run. The run was continued enabling a stirred and non-stirred result to be obtained from the one experiment.

The Kohlrausch concentration of the LiCl solution was estimated from a graph of $T_{\text{LiCl}}^{\text{Li}^+}/m_{\text{LiCl}}$ vs. m_{LiCl} and also by successive approximation and found to be 1.78 mol kg^{-1} or 1.72 mol dm^{-3} . Thus the values of c_{LiCl} used, 1.53, 1.55, 1.57 and 1.58 mol dm^{-3} , are 11%, 10%, 9% and 8% below the Kohlrausch value, respectively. No effect due to the change in $c_{\text{LiCl}}^{\text{init.}}$ was observed.

Figures (VI.1) and (VI.2) show the appearance of the boundary through the cathetometer at currents of 22 and 12 mA, respectively.

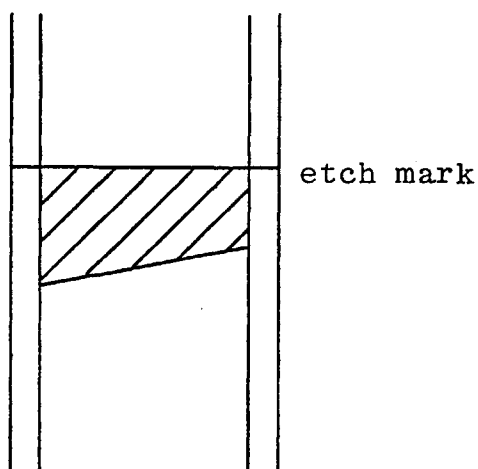


fig.(VI.1)

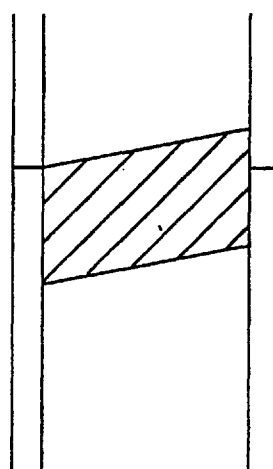


fig.(VI.2)

The bottom of the boundary was diffuse and attempts to measure the time to better than ± 10 s were unsuccessful. The top of the image was much sharper and readings to within ± 4 s were made when the boundaries were in the positions shown. Although for dilute solutions the boundary can be timed to ± 1 s or better, this produces the same percentage error in the time intervals as the boundary speed is that much faster. With the naked eye the boundaries in figs.(VI.1) and (VI.2) appeared sharp and horizontal.

VI.2.2 The Effect of Stirring

The most striking feature in table (VI.3) is the large difference between the results for the unstirred closed cathode compartment ($T_{K^+}^{KCl}(\text{obs.}) = 0.4701$) and for the stirred runs ($T_{K^+}^{KCl}(\text{obs.}) = 0.4879$ and 0.4906). In comparison the difference between the stirred and unstirred closed anode results is small.

During a run the KCl concentration increases in the cathode bulb and in an unstirred compartment this increase will tend to be localised around the electrode. Although diffusion processes will partially equalise the concentration there will be no gravitational mixing of the bulb solution with that in the electrode arm as the system is stable, with the densest solution at the bottom. As a consequence, not only will the apparent molar volume of the solute increase but so too will the AgCl solubility.

Let us assume that the increase in solute concentration is limited to a volume in which c_{KCl} is, say, 4M. On the passage of 0.0084F the amount of solute around the electrode increases by $T_{K^+}^{KCl} \times 8.4 \times 10^{-3} = 0.0041$ mol. Therefore the volume of this region is 4.1 cm^3 . Now, by treating the solute volume as in section (V.3.1) we can calculate the increase in volume due to this increase in concentration. At time t_0 (see p.121-123) the volume of the solute in 100 cm^3 of 3M KCl solution is

$$\int \phi_{\text{KCl}} c_{\text{KCl}} (t_0) \delta V = 9.166 \text{ cm}^3 \quad (\text{V.9})$$

At time t_e , after the passage of $8.4 \times 10^{-3} \text{ F}$

$$\begin{aligned} \int \phi_{\text{KCl}} c_{\text{KCl}} (t_e) \delta V &= 30.553 \times 3.000 \times 0.0959 + \\ &\quad 31.174 \times 4.0 \times 0.0041 \text{ cm}^3 \\ &= 9.301 \text{ cm}^3 \end{aligned} \quad (\text{VI.3})$$

The difference per faraday is $(9.301 - 9.166)/0.0084 = 16.071 \text{ cm}^3 \text{ mol}^{-1}$ and the volume change is (cf. equation V.12)

$$\begin{aligned} \Delta V &= V_{\text{Ag}} - V_{\text{AgCl}} + 16.071 \text{ cm}^3 \text{ mol}^{-1} \\ &= 0.576 \text{ cm}^3 \text{ mol}^{-1} \end{aligned} \quad (\text{VI.4})$$

This leads to a volume correction of 0.0017, which must be added to $T_{\text{K}^+}^{\text{KCl}}(\text{obs.})$ as the boundary is moving towards the electrode.

In addition, as the KCl solution was not presaturated with AgCl we must take into account the volume increase due to AgCl dissolution. In section (IV.2.3) it was estimated that the absolute volume change due to AgCl dissolution in the cathode bulb is approximately $8 \times 10^{-4} \text{ cm}^3$. Let us accept this figure. If the AgCl dissolves steadily during the run then between each pair of etch marks like 8-1 (which each constitute approximately 45% of the time of a run) the absolute volume change is about $3.6 \times 10^{-4} \text{ cm}^3$. During this time the boundary is observed to move through approximately 0.65 cm^3 . Thus, $T_{\text{K}^+}^{\text{KCl}}(\text{obs.})$ must be multiplied by a factor of $(1 + 3.6 \times 10^{-4}/0.65)$ to account for AgCl dissolution and hence $T_{\text{K}^+}^{\text{KCl}}$ becomes 0.4704 instead of 0.4701. Adding the volume

correction calculated above gives $T_{K^+}^{KCl}(\text{corr.}) = 0.4721$.

Although these calculations qualitatively explain why the result for run 43 is low they do not quantitatively account for a value as low as that observed. However, the calculations for the volume of the solute are very sensitive to small errors in either (V.9) or (VI.3). If, instead of a value of 9.30 cm^3 , (VI.3) is actually 9.35 cm^3 then the volume correction would be 0.0192 and hence $T_{K^+}^{KCl}(\text{corr.}) = 0.4893$.

Three runs (45, 64 and 69b) were carried out with an unstirred Ag anode. The observed values were 0.4903, 0.4930 (both at 22-23 mA) and 0.4881 (at 12.5 mA), respectively. These results compare favourably with the stirred results and it appears that stirring or not stirring makes little (or no) difference to runs with a closed anode chamber. In the latter the amount of LiCl is gradually depleted during a run and hence the solute concentration falls. Unlike the closed cathode case, gravitational instability occurs and mixing of the solution will take place even in the absence of stirring. This may well explain the above findings.

The difference between the results at the two currents is probably due to heating effects which were also found for the stirred runs (section VI.2.4). There may also be a small contribution due to the longer time intervals in the run with the lower current, thus making it more likely that the solution concentration became equalised by diffusion and gravitational mixing.

VI.2.3 Effect of Presaturation

Presaturation with AgCl produced no significant effect on the closed anode runs. Considering only stirred runs with currents in the range 22.2 to 23.4 mA, $T_{K^+}^{KCl}(\text{obs.})$ is 0.4923 (run 40) and 0.4895 (run 44) for non-presaturated

solutions and 0.4889 (run 46), 0.4920 (run 60), 0.4926 (run 61), 0.4920 (run 65) and 0.4917 (run 68) for the presaturated solutions. Thus the results for the non-presaturated runs lie between the extreme values of the presaturated runs, the average values being 0.4909 (non-presaturated) and 0.4914 (presaturated).

A greater difference was found for the stirred closed cathode runs with $T_{K^+}^{KCl}$ (obs.) values of 0.4879 (non-presaturated, run 42) and 0.4906 (presaturated, run 66). In a non-presaturated solution more AgCl will have dissolved during a run, so producing a volume increase (section IV.2.3) which would have slowed the boundary down. The lower result is therefore understandable although it is difficult to reach a significant conclusion from only two runs.

Although the closed anode results suggest that the error due to AgCl dissolution is small, a conclusion supported by calculations based on AgCN data (section IV.2.3), presaturation seems a worthwhile precaution. It must become increasingly worthwhile as the solute concentration is increased.

VI.2.4 The Dependence of $T_{K^+}^{KCl}$ (obs.) on Current

The basic cause of variation of the observed transference number with current is Joule heating. Spiro et al.⁽⁴⁰⁾ have given an equation enabling the mean temperature of the solution inside a m.b. tube to be calculated as a function of the current. Hence

$$\Delta\theta = \bar{\theta} - \theta_e = \frac{I^2}{2\pi R_i^2 \kappa_{soln} k_{soln}} \left[\frac{1}{4} + \frac{k_{soln}}{k_{glass}} \ln\left(\frac{R_e}{R_i}\right) \right] \quad (VI.5)$$

where the symbols have been defined on p.53. The thermal conductivity of Pyrex glass is $1.1 \text{ J m}^{-1} \text{ s}^{-1} \text{ K}^{-1}$ (40) and those of the solutions can be approximated⁽⁴⁰⁾ to that of water ($0.60 \text{ J m}^{-1} \text{ s}^{-1} \text{ K}^{-1}$). The dimensions of the tube used were $R_e = 2.1 \times 10^{-3} \text{ m}$ and $R_i = 1.1 \times 10^{-3} \text{ m}$. The mean temperature increases over the temperature of the thermostat, $\Delta\theta$, calculated from literature conductance data for 3M KCl⁽¹⁰⁴⁾ and the adjusted LiCl solution^(104,109) ($c_{\text{LiCl}}^* = 1.72 \text{ M}$) are given in table (VI.4).

Table (VI.4)

I/ma	$\Delta\theta_{\text{KCl}}/\text{K}$	$\Delta\theta_{\text{LiCl}}/\text{K}$
12.5	0.22	0.60
16	0.36	0.99
23	0.75	2.05

These temperature increases can affect the boundary speed in four ways⁽⁴⁰⁾:

1) The concentration of the leading solution decreases by a factor $\rho_{\text{hot}}/\rho_{25}$ and the volume it sweeps out per faraday increases by a factor $\rho_{25}/\rho_{\text{hot}}$. Although one measures the volume of the hot solution, the concentration of the solution at 25°C is used in the calculation of the results. The temperature variation of the density of 3M KCl is approximately $-0.00034 \text{ g cm}^{-3} \text{ K}^{-1}$ (72) in the region of 25°C and as the observed transference number is too high by a factor of $\rho_{25}/\rho_{\text{hot}}$ it must be multiplied by $(1 + 0.00034 \Delta\theta)$. Hence⁽⁴⁰⁾, $dT_{\text{K}^+}^{\text{KCl}}/d\theta = 0.00034 T_{\text{K}^+}^{\text{KCl}}$ $= 0.00017 \text{ K}^{-1}$.

2) $T_{\text{K}^+}^{\text{KCl}}$ is itself temperature dependent (0.00017 K^{-1} for 0.1M KCl⁽⁹⁹⁾). Thus the total theoretical temperature dependence of 1) and 2) is $dT_{\text{K}^+}^{\text{KCl}}/d\theta = 0.00034 \text{ K}^{-1}$.

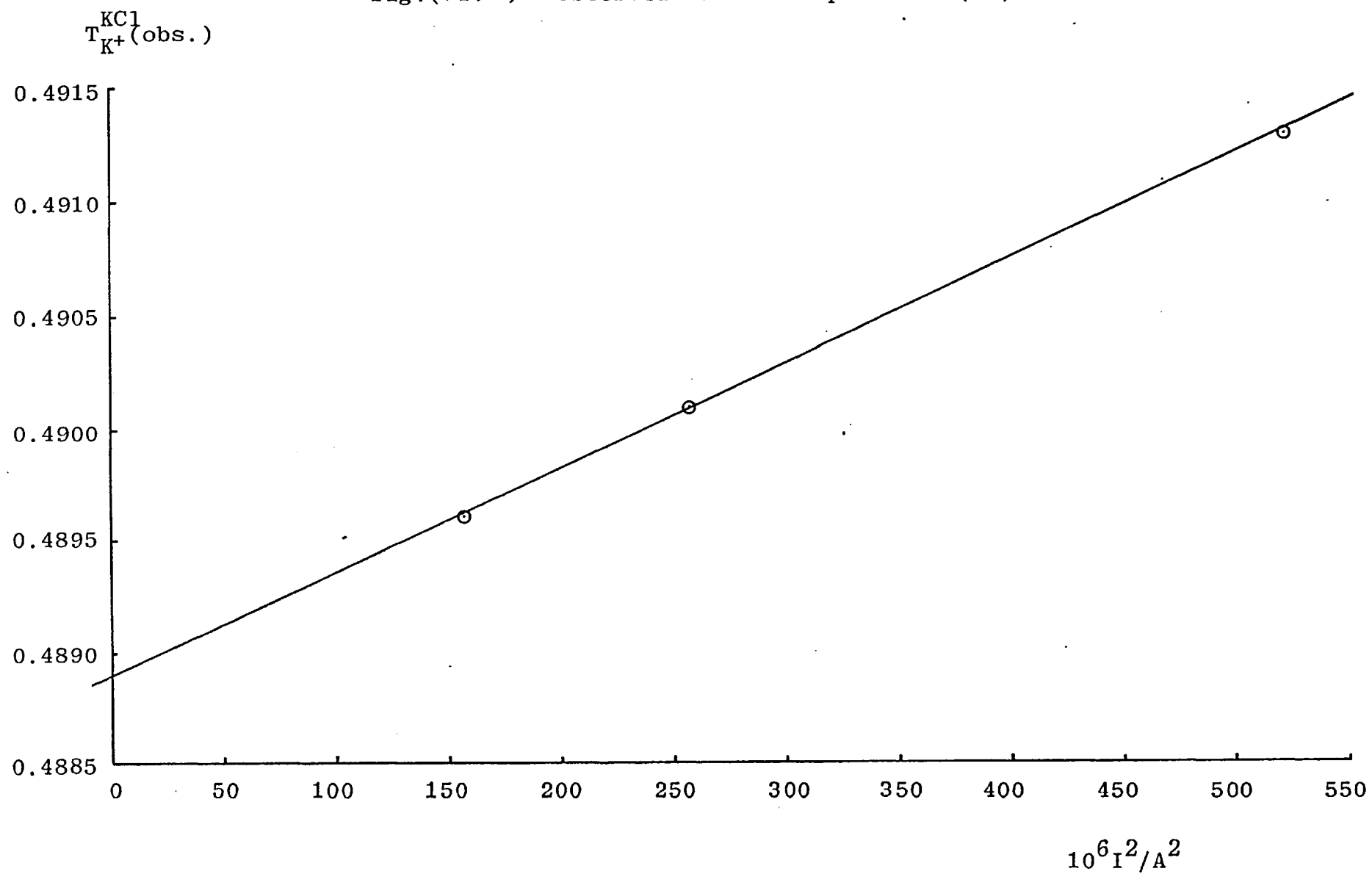
3) Heat flows across the boundary from the hotter LiCl solution. It is difficult to quantify this process but it will exacerbate the effects of the first two processes.

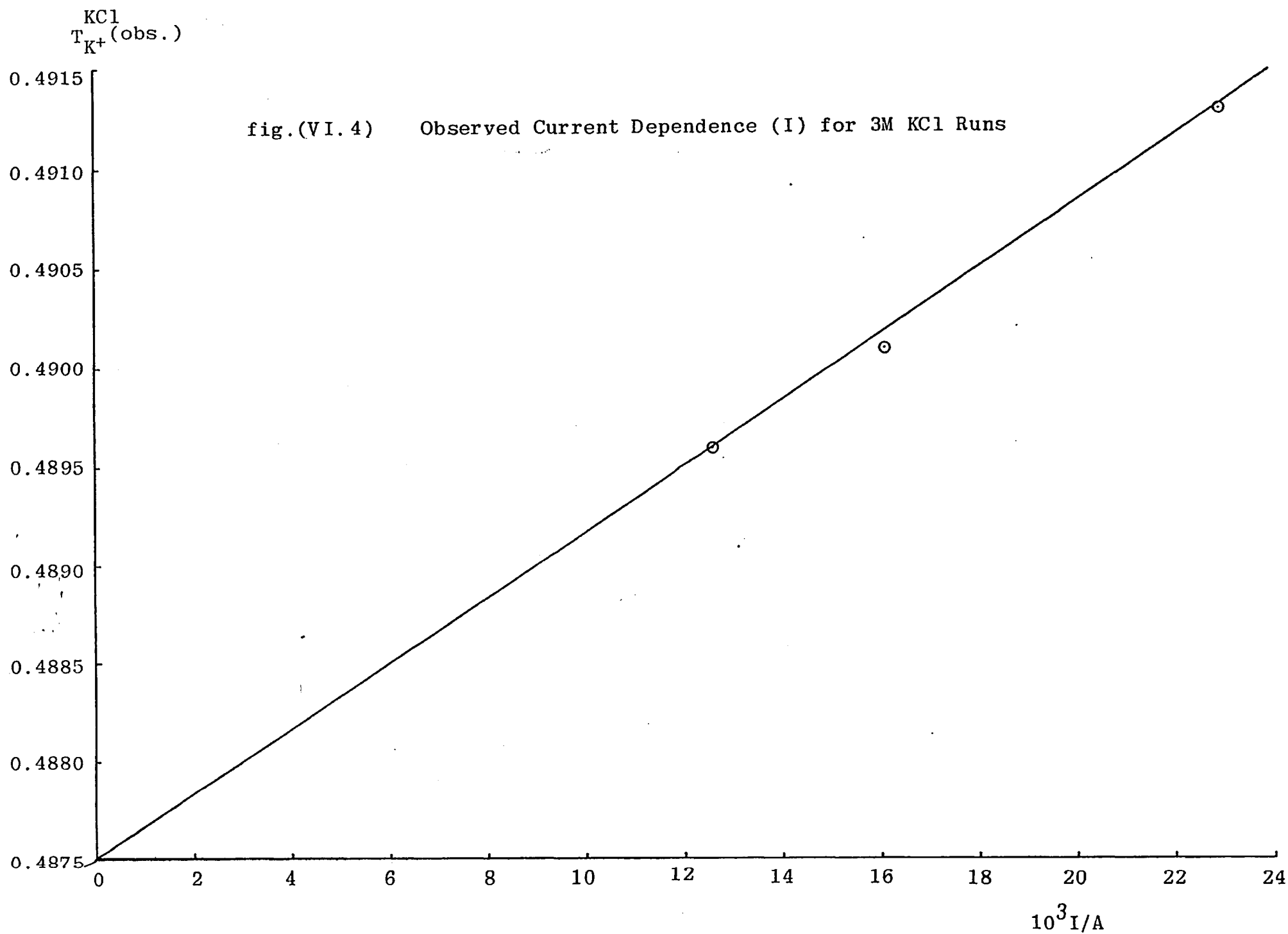
4) The decrease in LiCl concentration around the closed Ag anode will result in a gradual increase in the temperature of the solution. Although the increase is small due to the relatively large radius of the tubing, the volume of solution involved is large so the effect may be significant. The expansion of the solution in the closed electrode compartment will increase the observed speed of the boundary.

A fifth process is related to the volume correction. With lower currents, the longer time-scale of the experiment allows greater time for equalisation by diffusion of the concentration of solute around the closed electrode. However, as the solution was stirred in the majority of runs this effect should be negligible in this work.

The $T_{K^+}^{KCl}(\text{obs.})$ values for the stirred closed anode runs at high currents (22-24 mA) were 0.4923 (run 40), 0.4895 (run 44), 0.4889 (run 46), 0.4920 (run 60), 0.4926 (run 61), 0.4920 (run 65) and 0.4917 (run 68). The average of these values is 0.4913 (with a standard deviation of 0.0015) at an average current of 22.8 mA. Two runs (48 and 69a) were carried out at 12.5 mA with an average result of 0.4896. The result from the single 16.0 mA run was $T_{K^+}^{KCl}(\text{obs.}) = 0.4901$. Although equation (VI.5) predicts an I^2 dependence for the temperature increase, and hence for the transference number, an I dependence has also been observed⁽⁴⁰⁾. Figures (VI.3) and (VI.4) show the extrapolation of $T_{K^+}^{KCl}(\text{obs.})$ to zero current against I^2 and I , respectively. Both graphs exhibit straight line dependences with fits of better than 0.0001. The values extrapolated to zero current are $T_{K^+}^{KCl}(\text{obs.}) = 0.4889$ ($I^2 \rightarrow 0$) and 0.4875 ($I \rightarrow 0$).

fig.(VI.3) Observed Current Dependence (I^2) for 3M KCl Runs





If the theoretically predicted I^2 dependence were correct, the experimentally determined slope $dT_{K^+}^{KCl}/dI^2$ should agree with that calculated from the theory. From fig.(VI.3), the experimental value of $dT_{K^+}^{KCl}/dI^2$ is $4.69 A^{-2}$. Now, from the discussion on p.135,136 the theoretical value of $dT_{K^+}^{KCl}/d(\Delta\theta)$ due to the factors discussed there is $0.00034 K^{-1}$. Also, by differentiating eqn.(VI.5) with respect to I^2 and evaluation of the expression for 3M KCl at $25^\circ C$, the theoretical value of $d(\Delta\theta)/dI^2$ is $1409 K A^{-2}$. Hence

$$\frac{dT_{K^+}^{KCl}}{d(\Delta\theta)} \cdot \frac{d(\Delta\theta)}{dI^2} = \frac{dT_{K^+}^{KCl}}{dI^2} = 0.479 A^{-2} \quad (VI.6)$$

The observed current dependence is, therefore, ten times that which we have predicted theoretically. Part of this discrepancy may be due to heat flow across the boundary from the hotter LiCl solution. Thus the value of $d(\Delta\theta)/dI^2 = 1409 K A^{-2}$ in eqn.(VI.6) is too low. However, the figures in table (VI.4) show that the temperature of the KCl solution, and hence the value of $dT_{K^+}^{KCl}/dI^2$, would only increase by a factor of 3 at the most because of this process.

That the $T_{K^+}^{KCl}$ versus I^2 slope was found to be so much greater than the predicted value suggests that another unknown factor might be operative (cf. HCl results later). We shall therefore adopt as the experimental result the mean of the two extrapolated values of 0.4889 ($I^2 \rightarrow 0$) and 0.4875 ($I \rightarrow 0$), i.e. $T_{K^+}^{KCl}(\text{obs.}) = 0.4882$.

This zero-current value is subject to a volume correction of -0.0019 as the boundary is moving away from the closed electrode. Thus $T_{K^+}^{KCl}(\text{corr.}) = 0.4863$. In fact it was necessary to use successive approximations to obtain this volume correction because the latter involves $T_{K^+}^{KCl}$ (eqn.II.22). This problem is avoided by rearranging the equation in the form

$$T_{K^+}^{KCl}(\text{corr.}) = \frac{T_{K^+}^{KCl}(\text{obs.}) - c_{KCl} (V_{AgCl} - V_{Ag})}{(1 - c_{KCl} \phi_{KCl})} \quad (\text{VI.7})$$

This modification of the volume correction equation will be used in subsequent sections (VI.3.4).

The two observed closed cathode values for stirred runs are: 0.4879 (run 42, not-presaturated) and 0.4906 (run 66, presaturated), the average being 0.4893. The corrected value is then $T_{K^+}^{KCl}(\text{corr.}) = 0.4875$. However, this result is less reliable than the closed anode value because of the greater uncertainty in the volume correction. This may also explain the large difference between the two cathode results.

VI.2.5 Comparison with Literature Values

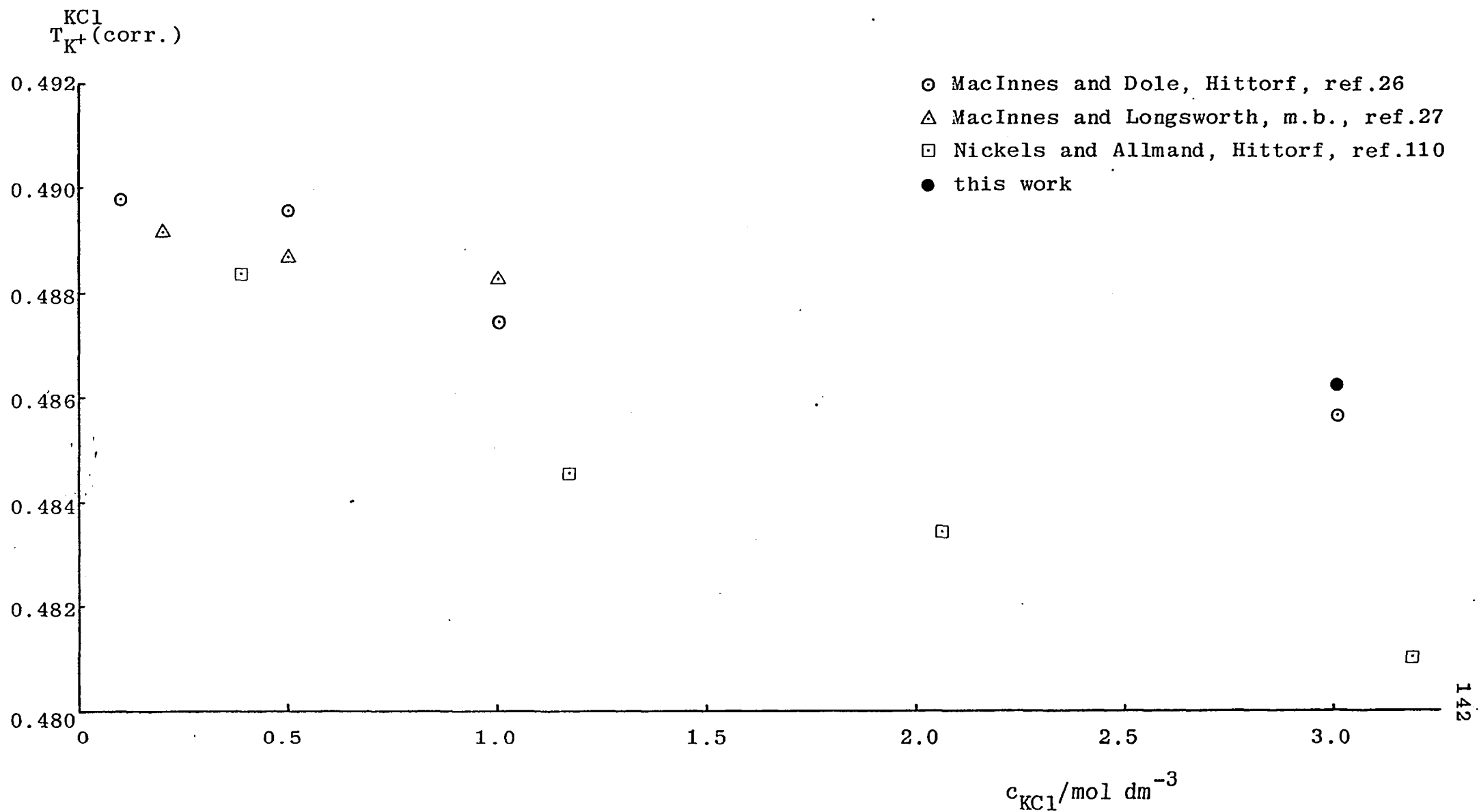
Figure (VI.5) summarises the published values of $T_{K^+}^{KCl}(\text{corr.})$ at concentrations greater than 0.1M. All measurements were made at 25°C except for the Hittorf data of Nickels and Allmand⁽¹¹⁰⁾ whose cell was not thermostatted. The reported (room) temperatures of their various experiments ranged from 15–20°C, with no temperature quoted for the 3.2M result. That their results are lower than those of the other workers cannot be explained by this temperature variation because $dT_{K^+}^{KCl}/dT$ is very small, being 0.00017 K⁻¹ for 0.1M KCl (section VI.2.4). There appears to be a systematic experimental error involved in their work, possibly due to increasing dissolution of their Ag/AgCl cathode and Cd anode with increasing Cl⁻ concentration. For the latter electrode dissolved oxygen in the solution might have acted as the oxidising agent.

The other two sets of literature data appear more reliable. Although no experimental details are available

for the m.b. work up to 1M⁽²⁷⁾, the Hittorf work was particularly meticulous. Thus, MacInnes and Dole⁽²⁶⁾ minimised convective and diffusive mixing by careful cell design. A correction was also made for AgCl dissolution. For 3M KCl, results were reported from two different experiments, for one of which both cathode and anode analyses were carried out. The average of the three values is 0.4859 with a maximum scatter in the results of 0.0006. The final value reported of 0.4857 has presumably been corrected for the AgCl dissolution. Bearing the various uncertainties in mind, this Hittorf value is in very satisfactory agreement with our "best" corrected value of 0.4863.

In conclusion, it has been shown that the m.b. method can be successfully extended to high solute concentrations. Precautions such as stirring the solution in the closed electrode bulb and, with Ag or AgCl electrodes in chloride solutions, presaturation of the solution around the electrode with AgCl have been applied to prevent errors in the volume correction. The experimental technique has been tested for the system 3M KCl ← LiCl for which $T_{K^+}^{KCl}$ (corr.) was found to be 0.4863. The error in this value is better than 0.001 and possibly as little as 0.0005. Within experimental error, this value agrees well with the only other reliable literature value at this concentration, 0.4857⁽²⁶⁾.

fig.(VI.5) Concentration Variation of $T_{K^+}^{KCl}$ at High Concentrations



VI.3 HCl←LiCl Experiments

VI.3.1 Compilation of Results

Tables (VI.5)-(VI.7) report the results of the HCl←LiCl runs for HCl concentrations of 0.9996, 2.009 and 4.181 mol dm⁻³, respectively (except in runs 73 and 74 where $c_{\text{HCl}} = 4.171\text{M}$). All runs were performed with a closed Ag anode with the precautions of stirring and presaturation of the bulb LiCl solution. A gassing Pt cathode was used in all the runs.

Many problems were encountered in maintaining a constant current through the cell. Current regulation is most efficient for high cell resistances ($> 10\text{ k}\Omega$). Initially, when the m.b. tube was totally filled with HCl solution, the cell resistances were approximately 2 k Ω at 1M and 800 Ω at 4M. The current stability was improved in later experiments by reducing the input voltage to the generator and by placing a 50 k Ω resistor in series with the cell. In runs where current variation occurred the current was read at 5 min. intervals.

The amended cell cleaning procedure noted in table (VI.6) is discussed in section (VI.3.2).

The boundary appearance and timing were similar to those discussed in section (VI.2.1).

Table (VI.5)

1M HCl Results

run	c_{LiCl}/M	I/mA	$T_{\text{H}^+}^{\text{HCl}}(\text{obs.})$	$10^4 \sigma$	comments
88	0.348	6.4	0.8424	6	4% upwards drift in I
89	0.348	10.3	0.8417	10	0.5% fluctuation in I
90	0.348	15.3	0.8424	7	
91	0.331	10.4	0.8417	14	

Table (VI.6)

2M HCl Results

run	c_{LiCl}/M	I/mA	$T_{\text{H}^+}^{\text{HCl}}(\text{obs.})$	$10^4 \sigma$	comments
92	0.673	11.0	0.8295	5	5% downwards drift in I
93	0.673	19.4	0.8383	9	
94	0.639	19.6	0.8325	11	
95	0.639	10.9	0.8292	10	
96	0.673	19.5	0.8359	5	
97	0.673	19.6	0.8379	9	
98	0.673	11.0	0.8103	13	amended cell cleaning procedure
99	0.673	10.9	0.8296	13	amended cell cleaning procedure

Table (VI.7)

4M HCl Results

run	c_{LiCl}/M	I/mA	$T_{\text{H}^+}^{\text{HCl}}(\text{obs.})$	$10^4 \sigma$	comments
73	1.17	24.7	0.7119	11	$c_{\text{LiCl}}^{\text{init.}}$ too low
74	1.47	23.1	0.7524	16	
75	1.47	23.2	0.7542	19	
76	1.55	23.2	-		progression down
77	1.55	23.4	-		progression down
78	1.50	24.0	0.7360		6% upwards drift in I
79	1.50	23.2	0.7495	10	
80	1.49	11.2	0.7328	25	3% fluctuation in I
81	1.49	7.76	0.7243	80	
83	1.49	17.1	0.7412	10	

VI.3.2 Variation with Current

The variation of $T_{H^+}^{HCl}(\text{obs.})$ with current was tested at all three concentrations. Although at 1M the results were independent of current, the 2M and especially the 4M results showed a rise of $T_{H^+}^{HCl}(\text{obs.})$ with increasing I .

Consider first the 2M experiments. Four runs (93, 94, 96 and 97) were carried out at 19 mA, with the result from run 94 much lower than the others. There is no apparent reason for this except that a lower initial $c_{LiCl}^{init.}$ was not found for the 11 mA runs (92 and 95), although the longer time-scale of these runs may have allowed better adjustment to the Kohlrausch value (see section VI.3.3). If run 94 is rejected the average value of $T_{H^+}^{HCl}(\text{obs.})$ at 19 mA is 0.8374. At a current of 11 mA the average value of $T_{H^+}^{HCl}(\text{obs.})$ is 0.8294 for runs 92, 95 and 99. For run 98 a different cell cleaning procedure had been used which produced the lower result (see later). The extrapolations of these two values, 0.8374 at 19.5 mA and 0.8294 at 11.0 mA, to zero current against I^2 and I leads to 0.8257 and 0.8190, respectively.

The 4M HCl experiments also include one apparently spurious $T_{H^+}^{HCl}(\text{obs.})$ value at high current. The result of 0.7360 for run 78 is substantially lower than 0.7524 (run 74), 0.7542 (run 75) and 0.7495 (run 79). The average of the last three values is 0.7520 at an average current of 23.2 mA. Figures (VI.6) and (VI.7) show the current dependence of this result and the results of runs 80 (0.7328 at 11.2 mA), 81 (0.7243, 7.76 mA) and 83 (0.7412, 17.1 mA). The zero current values are 0.7233 ($I^2 \rightarrow 0$) and 0.7118 ($I \rightarrow 0$).

The observed effect of current probably arose from Joule heating. Table (VI.8) gives the increase in

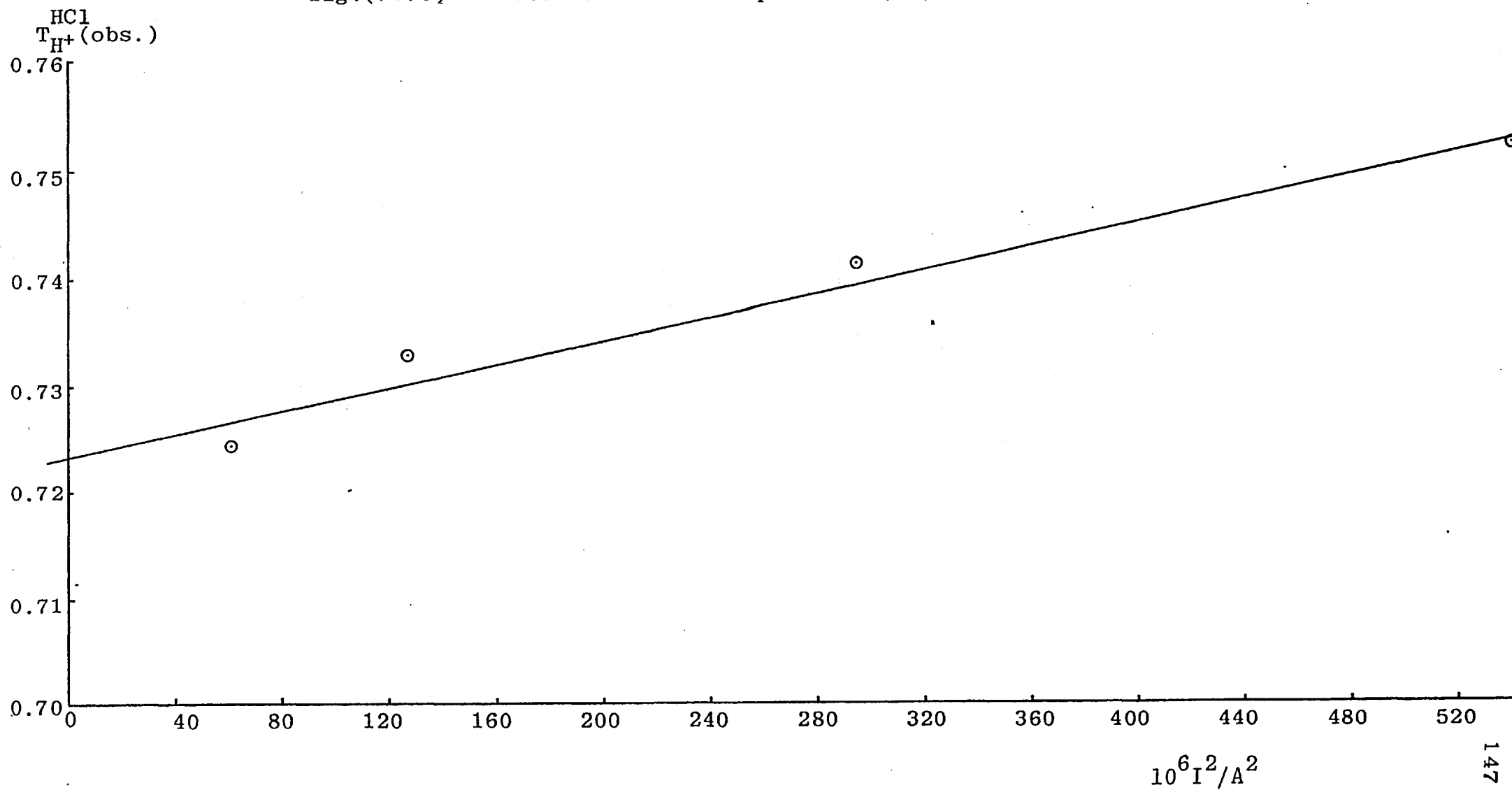
temperature of the HCl and adjusted LiCl solutions as a function of concentration and current as calculated from equation (VI.5). These figures, which are quoted as the difference in temperature (K) between the solutions and 25°C, were calculated using the conductance data of Owen and Sweeton⁽¹⁰⁵⁾ for HCl and of Postler⁽¹⁰⁴⁾ and Nickels and Allmand⁽¹⁰⁹⁾ for LiCl.

Table (VI.8)

I/mA	4M HCl	1.54M LiCl	I/mA	2M HCl	0.72M LiCl
8	0.03	0.27	11	0.09	0.92
11	0.06	0.51	20	0.30	3.06
17	0.15	1.21			
23	0.28	2.22			

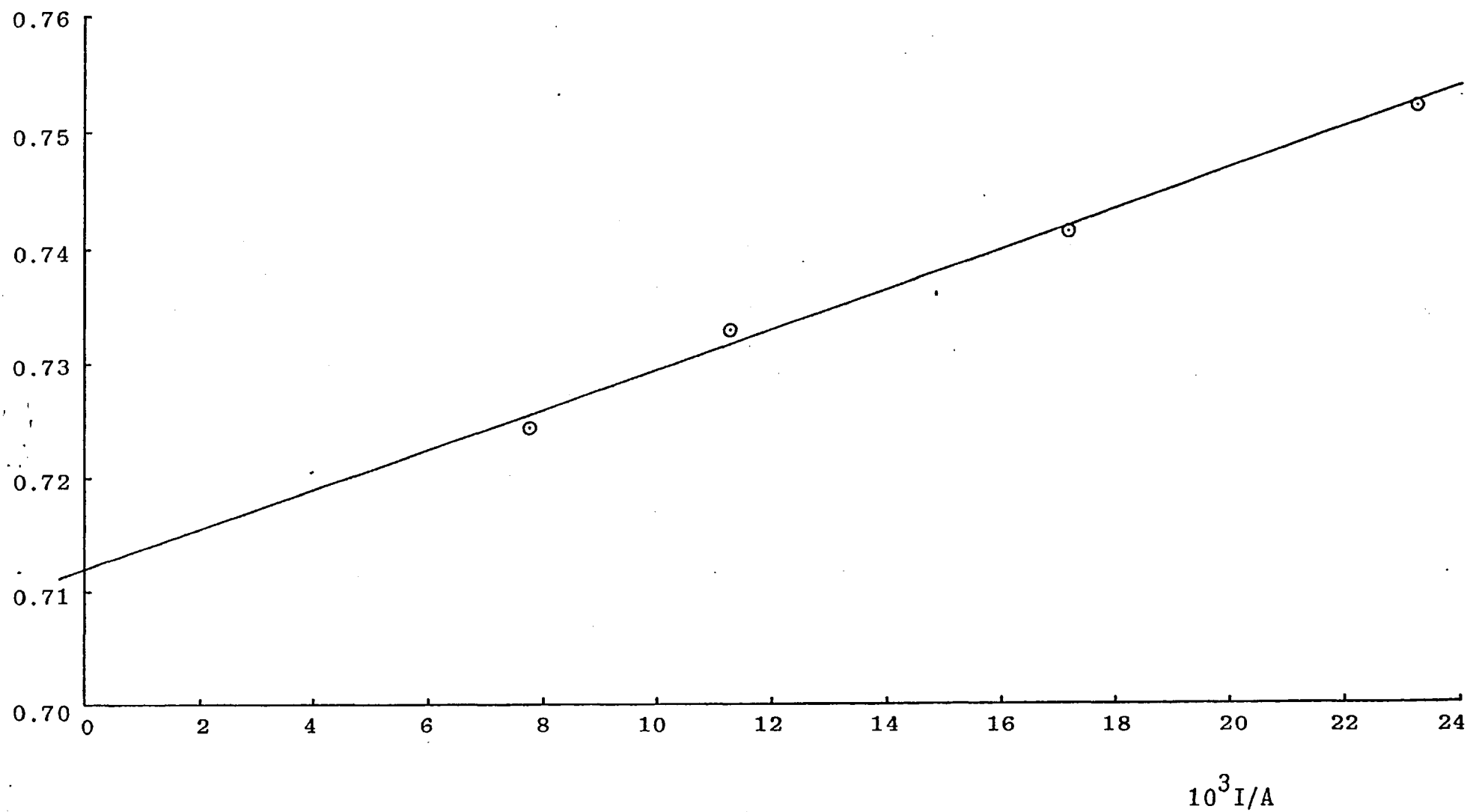
As with the KCl results, the observed current dependence of $T_{H^+}^{HCl}(\text{obs.})$ can be compared with a theoretically derived value of $dT_{H^+}^{HCl}/dI^2$. Thus, the experimental current (I^2) dependences for the 2M and 4M runs are 30.86 A^{-2} and 53.92 A^{-2} , respectively. As in section (VI.2.4), we can also calculate the theoretical temperature dependence of the transference number, $dT_{H^+}^{HCl}/d(\Delta\theta)$, due to the expansion of the HCl solution and the temperature coefficient of $T_{H^+}^{HCl}$ (effects 1) and 2)) from I.C.T. density data⁽⁷²⁾ and the $T_{H^+}^{HCl}$ data of Harned and Dreby⁽⁶⁷⁾. Due to the negative temperature coefficient for $T_{H^+}^{HCl}$ we find that the theoretical values are approximately -0.0005 K^{-1} and -0.0002 K^{-1} at 2M and 4 M, respectively. By differentiation of eqn.(VI.5) with respect to I^2 and evaluation of the expression for 2M and 4M HCl at 25°C the theoretical values of $d(\Delta\theta)/dI^2$ are 748 and 522 K A^{-2} , respectively. Thus the theoretical current dependences of $T_{H^+}^{HCl}(\text{obs.})$ are -0.37 A^{-2} and -0.10 A^{-2} for 2M and 4M HCl, respectively, i.e. in the opposite direction to the observed trend. Furthermore, heat flow across the boundary from the hotter LiCl solution will increase the negative dependence of

fig.(VI.6) Observed Current Dependence (I^2) for 4M HCl Runs



$T_{H^+}^{HCl}$ (obs.)

fig.(VI.7) Observed Current Dependence (I) for 4M HCl Runs



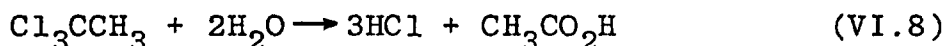
$T_{H^+}^{HCl}$ with increasing current. The fourth temperature related effect discussed in section (VI.2.4), the expansion of the following LiCl solution, would tend to increase $T_{H^+}^{HCl}$ (obs.) with increasing current. However, this cannot explain the observed trend because the Kohlrausch LiCl concentration behind the 4M HCl solution (1.55M) was approximately the same as that in the 3M KCl runs, yet the observed current dependence in the HCl case is 12 times greater than that in the KCl experiments.

There is of course the possibility that instead of the results being current dependent, they are in fact time dependent. The higher the current, the shorter the time of the experiment. Thus one might postulate an ion exchange reaction between the HCl solution and Na^+ ions in the glass, the latter being introduced during the cleaning of the cell with the chromic acid mixture (conc. $H_2SO_4/Na_2Cr_2O_7$). The ion exchange would result in a) a decrease of the leading HCl concentration and b) the setting up of an interstitial $HCl \leftarrow NaCl \leftarrow LiCl$ boundary. A decrease in $[HCl]$ would speed the boundary up (increase $T_{H^+}^{HCl}$) but the percentage decrease in $[HCl]$ should be higher at lower concentrations and hence one would expect a greater effect at low concentrations, which was not found. Furthermore, at a given HCl concentration, the smaller the current (longer time) the greater should be the decrease in $[HCl]$ and hence the faster the boundary. Again, this was not found. The addition of Na^+ ion impurities to the HCl solution would decrease the boundary speed, and for longer runs $T_{H^+}^{HCl}$ (obs.) would, as was observed, be lower.

If $T_{H^+}^{HCl}$ (obs.) is time dependent the results must be extrapolated to zero time or infinite current ($1/I^2$ or $1/I \rightarrow 0$). When this is done the extrapolated values are found to be 0.8411 ($1/I^2 \rightarrow 0$) and 0.8478 ($1/I \rightarrow 0$) for 2M HCl and 0.7500 ($1/I^2 \rightarrow 0$) and 0.7618 ($1/I \rightarrow 0$) for 4M HCl.

Several other hypotheses were put forward to explain the observed results:

1) If traces of 1,1,1-trichloroethane, which was used for removing grease, were absorbed into the glass then during the run hydrolysis of the organic solvent might occur. Hence



This would increase $[\text{HCl}]$ and so decrease $T_{\text{H}^+}^{\text{HCl}}$ (obs.). This was tested in run 98 (table VI.6). Here the cell was rinsed with 1,1,1-trichloroethane and with water as usual but cleaning with chromic acid was omitted. The result is very low compared to other runs at 11 mA, an effect consistent with the hydrolysis reaction (VI.8). However, no such effect was observed in the next run (99) for which the cell had been soaked with meths to remove all traces of the organic solvent. Again chromic acid was not used. This appears to vindicate the use of the acid cleaning mixture for removing all traces of solvent and grease from the cell, and shows also that Na^+ ions introduced by chromic acid caused no harm.

2) Current leakage from the cell would result in the observed transference number being too low. However, the current leakage should increase with increasing current and so $T_{\text{H}^+}^{\text{HCl}}$ should decrease. This was not found. Furthermore, from direct measurements, the currents in and out of the cell were found to differ by only 8-9 μA for a current of 20 mA (one part in 2400) which is experimentally insignificant.

3) $T_{\text{H}^+}^{\text{HCl}}$ is very dependent upon the solvent structure due to its proton-jumping mode of conduction. For instance, $T_{\text{H}^+}^{\text{HCl}}$ increases with increasing pressure⁽⁸⁾ due to increased ordering of the solvent structure but decreases with increasing temperature and concentration⁽⁶⁷⁾ because of the breakdown in the structure. The application of an electric field might also introduce extra order into the

solvent structure. Consequently, $T_{H^+}^{HCl}(\text{obs.})$ would increase with increasing applied electric field (increasing current), as observed. However, the applied fields were small (in the range 24-3000 V m⁻¹) and it is unclear as to why the effect would be smaller for 1M and 2M HCl than for 4M HCl.

VI.3.3 The Choice of $c_{LiCl}^{init.}$

A problem encountered in this work but not in the KCl experiments was the calculation of the LiCl Kohlrausch concentration, c_{LiCl}^* , and hence $c_{LiCl}^{init.}$. For the KCl work an accurate value of $T_{K^+}^{KCl}$ at 3M KCl was available to calculate c_{LiCl}^* . For 4M HCl it was predicted from the literature⁽⁶⁶⁾ ($T_{H^+}^{HCl} = 0.837$) that c_{LiCl}^* would be 1.32M. A value of $c_{LiCl}^{init.} = 1.17M$ (11% below c_{LiCl}^*) was accordingly used in run 73 but the $T_{H^+}^{HCl}(\text{obs.})$ value obtained was much lower than expected (0.7119). This result corresponds to a LiCl Kohlrausch concentration of 1.69M. In run 74, therefore, an initial LiCl concentration of 1.47M (13% below c_{LiCl}^*) was employed and this led to a value of $T_{H^+}^{HCl}(\text{obs.}) = 0.7524$. Further recalculation on the basis of this result suggested a value of $c_{LiCl}^* = 1.58M$. Subsequent runs with $c_{LiCl}^{init.}$ of 1.47M (run 75), 1.50M (runs 78 and 79) and 1.49M (runs 80, 81 and 83) proved successful. These $c_{LiCl}^{init.}$ values were 7%, 5% and 6%, respectively, below $c_{LiCl}^* = 1.58M$. However, runs 76 and 77, employing $c_{LiCl}^{init.} = 1.55M$ (2% below 1.58M) gave progression downwards, which suggests that the Kohlrausch LiCl concentration might in fact be lower (perhaps 1.50 - 1.54M). If so, there would have been density instability in the following solution in runs 76 and 77.

The literature data are more reliable for 1M HCl as no variation in $T_{H^+}^{HCl}(\text{obs.})$ was observed for $c_{LiCl}^{init.}$ values of 4% below (0.348M) and 9% below (0.331M) the calculated Kohlrausch concentration of 0.364M.

For the 2M runs the two $c_{LiCl}^{init.}$ values used were

0.673M and 0.639M, 5% and 10%, respectively, below the calculated c_{LiCl}^* value of 0.718M. In the two runs (94 and 95) for which $c_{\text{LiCl}}^{\text{init.}} = 0.639\text{M}$ the result of the low current run (run 95) agreed well with the two other reliable low current runs (92 and 99). However, the high current run 94 gave a lower result than the high current runs in which $c_{\text{LiCl}}^{\text{init.}} = 0.673\text{M}$ (runs 93, 96 and 97). It may be that at high solute concentrations it takes longer for the concentration of the following solution to adjust to the Kohlrausch value. The longer time-scale of the low current run enables this adjustment to take place before the boundary reaches the first etch mark. If this is so then for concentrated solutions the initial concentration of the following solution should not differ by more than 5-6% from the Kohlrausch value. Furthermore, the difference should be less as the concentration is increased. However, for the KCl runs no effect was observed for $c_{\text{LiCl}}^{\text{init.}}$ values 8-11% below c_{LiCl}^* .

VI.3.4 Final Results and Comparison with Literature Values

Table (VI.9) summarises the cation-constituent transference numbers obtained from the analysis of the current dependence. The second column shows the average observed values obtained for the 1M runs and the extrapolated values and mode of extrapolation for the 2M and 4M results. Column 3 lists the corrected values calculated from equation (VI.7).

The result for 1M HCl agrees within 0.001 with Harned and Dreby's⁽⁶⁷⁾ e.m.f. value of 0.841, although it is higher than the value of 0.836 found in the present e.m.f. work (chapter VIII).

Harned and Dreby report a value of $T_{\text{H}^+}^{\text{HCl}} = 0.843$ at 2M. The value of $T_{\text{H}^+}^{\text{HCl}}(\text{corr.}) = 0.8426$, obtained from extrapolation of $1/I^2 \rightarrow 0$, is in excellent agreement but the actual process of extrapolation to zero time must be treated with scepticism. An average value of 0.823 ± 0.003

Table (VI.9)

$c_{\text{HCl}}/\text{mol dm}^{-3}$	$T_{\text{H}^+}^{\text{HCl}}(\text{obs.})$	$T_{\text{H}^+}^{\text{HCl}}(\text{corr.})$
1	0.8421	0.8424
2	0.8257 ($I^2 \rightarrow 0$)	0.8266
	0.8190 ($I \rightarrow 0$)	0.8196
	0.8411 ($1/I^2 \rightarrow 0$)	0.8426
	0.8478 ($1/I \rightarrow 0$)	0.8495
4	0.7233 ($I^2 \rightarrow 0$)	0.7180
	0.7118 ($I \rightarrow 0$)	0.7054
	0.7500 ($1/I^2 \rightarrow 0$)	0.7471
	0.7618 ($1/I \rightarrow 0$)	0.7599

is found for the zero current values at 2M. This is 0.020 lower than the literature result but agrees better with the result from the present e.m.f. work of approximately 0.831 (chapter VIII).

At 4M, the values extrapolated to zero current give an average of $T_{\text{H}^+}^{\text{HCl}} = 0.712 \pm 0.007$. The interpolated literature^(66,67) value is 0.837 and that from the author's own e.m.f. work approximately 0.806. Even the values extrapolated to zero time are considerably lower than these results and the 4M HCl m.b. work must be considered to be totally unreliable. The cause of these anomalous values remains unknown.

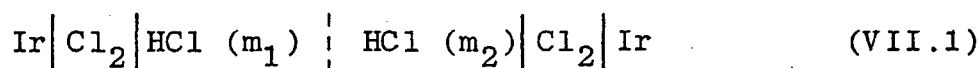
Despite the reasonable agreement between the 1M and 2M HCl results with those from other studies, it must be stated that great difficulties were encountered with the HCl m.b. work. In particular, it is quite clear from the foregoing discussion that the results for the 2M and 4M runs exhibit a degree of current dependence never before observed in m.b. work. It is interesting to note that other workers have also found problems when measuring $T_{\text{H}^+}^{\text{HCl}}$ by the m.b. method. Both

Longsworth⁽⁹⁸⁾ and Samis⁽¹¹¹⁾ observed current dependence at concentrations of 0.1M and 0.05-0.15M, respectively. Although no details of the currents used are given, Samis⁽¹¹¹⁾ reports that in order to remove any current dependence he had to reduce the current to such an extent that the boundary was invisible unless methyl orange indicator was added to the solution. At these low solute concentrations current dependence is usually found only for weak electrolytes (e.g. succinic and acetic acids⁽⁴⁰⁾). In this respect HCl, a strong electrolyte, appears to be an exception. Kell⁽¹¹²⁾ obtained different transference numbers for 0.01M HCl when using KCl and BaCl₂ as the indicator solutions.

CHAPTER SEVEN

E.M.F. EXPERIMENTAL

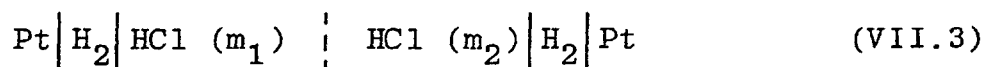
The transference numbers of concentrated aqueous HCl solutions were also measured by the e.m.f. method. This was done partly because of the breakdown in the m.b. work for concentrated HCl solutions and partly through a desire to check the literature HCl data^(66,67). These had been determined by the e.m.f. method but with the use of AgCl electrodes. As has been shown in section (IV.2.3) AgCl dissolves in concentrated chloride solutions. This changes the chloride activity in the solution and so seriously affects the e.m.f. readings. In the present work, hydrogen and chlorine electrodes were used instead. The problem of the solubility of chlorine was much reduced by diluting the gas with nitrogen. The cell with chlorine electrodes



produces e.m.f.s related to $T_{\text{H}^+}^{\text{HCl}}$ by

$$E = \frac{2RT}{F} \int_2^1 T_{\text{H}^+}^{\text{HCl}} d \ln a_{\text{HCl}} \quad (\text{VII.2})$$

where $m_1 > m_2$, and that with hydrogen electrodes



e.m.f.s related to $T_{\text{Cl}^-}^{\text{HCl}}$ by

$$E = -\frac{2RT}{F} \int_2^1 T_{\text{Cl}^-}^{\text{HCl}} d \ln a_{\text{HCl}} \quad (\text{VII.4})$$

again with $m_1 > m_2$. The two independent e.m.f. determinations could thus be checked by the ultimate test for

transference work: $T_+ + T_- = 1$.

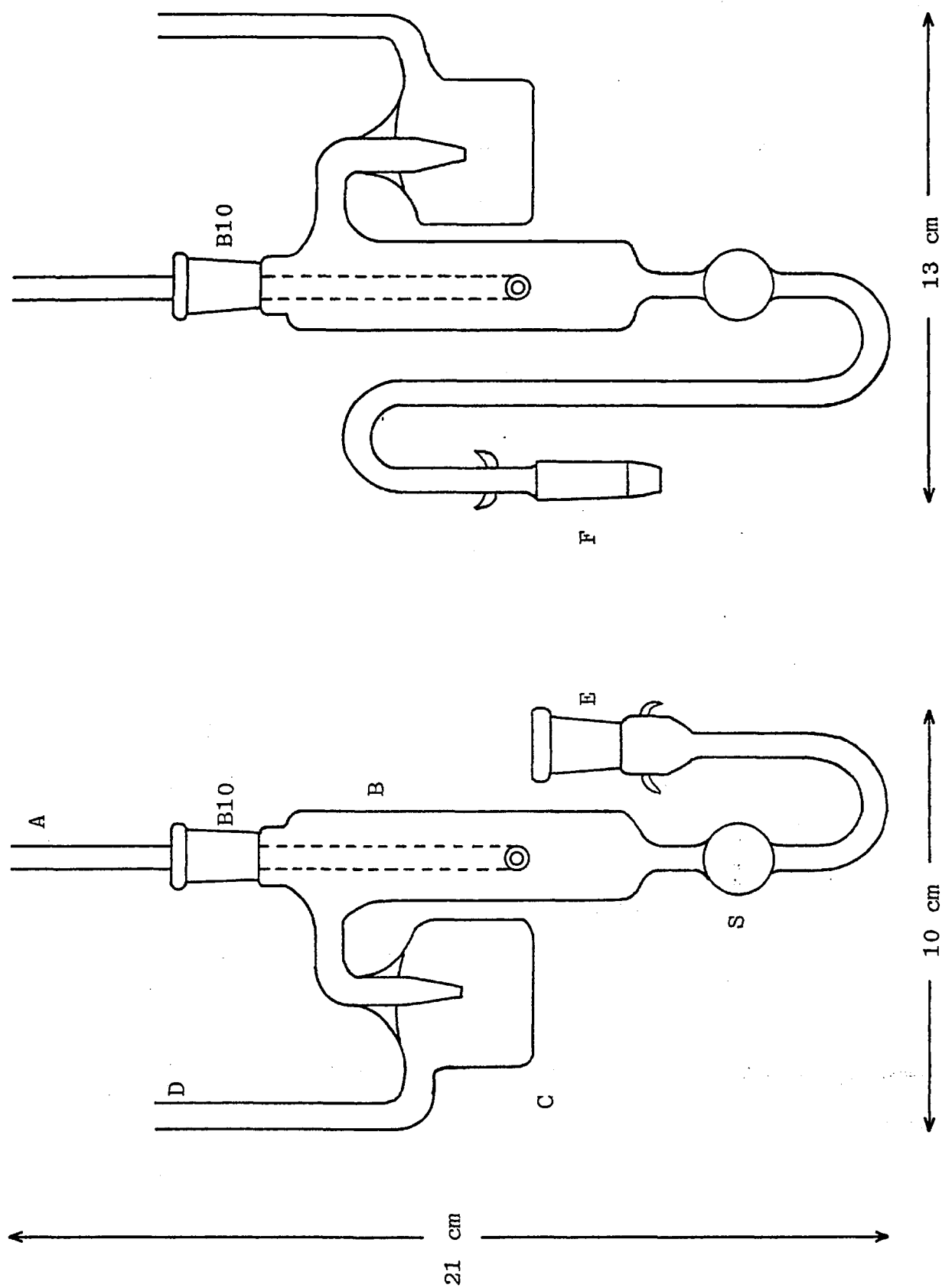
The description of most of the experimental technique and apparatus is given in section (VII.1) for the chlorine electrode experiments. Aspects of the work which differed for the hydrogen electrodes will be given in section (VII.2).

VII.1 Chlorine Electrode Experiments

VII.1.1 The E.m.f. Cell

The cell illustrated in fig.(VII.1) was based on the design of Stokes and Levien.⁽⁷⁶⁾ Their basic design was modified according to Faita, Longhi and Mussini's⁽¹¹³⁾ chlorine half-cell to permit the entry and exit of the gas. The entire apparatus was made from pyrex glass except for the two 1.2 mm bore P.T.F.E. taps (S). The gas (mixture) entered each half-cell via the inlet tubes (A). After bubbling through the solution in the main body of the cell (B), the gas left the cell via the bubble chambers (C) and exit tubes (D). The main body of the cell was made from 1.8 cm (inside) diameter glass tubing and the inlet and outlet tubes from 4 mm i.d. tubing. Five mm i.d. tube was used for the sections of the cell between the two taps which terminated in a B10 socket (E, LH half-cell) and a corresponding B10 cone (F, RH half-cell). Liquid junction formation was accomplished by simply joining the two half-cells via the "Quickfit" joint. For gravitational stability at the junction the LH half-cell was filled with the more concentrated solution. Figure (VII.2) shows the position of the electrode when in place in relation to the main body of the cell (B) and the gas inlet tube (A).

fig.(VII.1) E.m.f. Cell



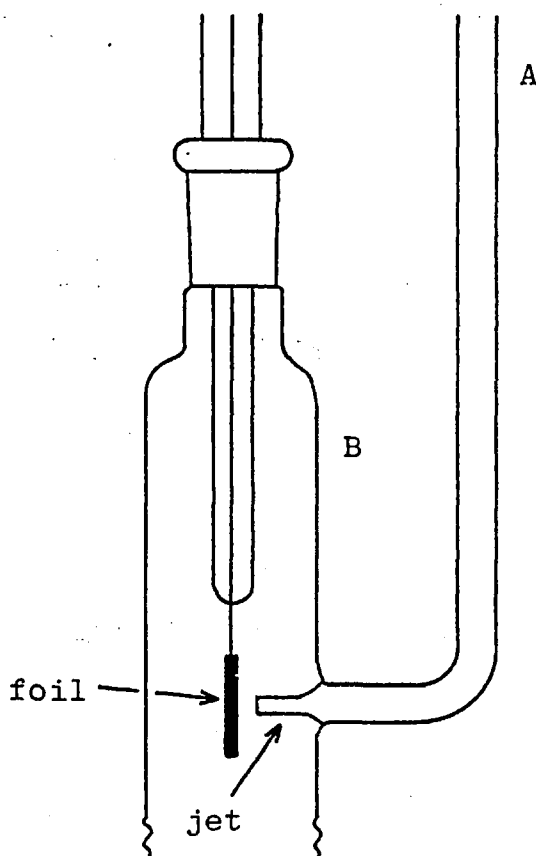


fig.(VII.2)

VII.1.2 Electrodes

Faita et al.⁽¹¹³⁾ report that Pt is not a suitable electrode material for the Cl_2 electrode as it is corroded by chloride solutions containing dissolved Cl_2 . Instead these workers used a Pt/Ir (45%) alloy on a Ta base which was found to be totally resistant to corrosive attack. To avoid such a complex system the present work was begun with electrodes made of a piece of Ir foil (1 x 0.5 cm, 0.6 mm thick) spot-welded to a length of Pt wire which was sealed directly into a soda glass cone. The length of the cone was such that, when the electrode was in position, the foil was adjacent to the jet of the gas inlet tube (fig.VII.2).

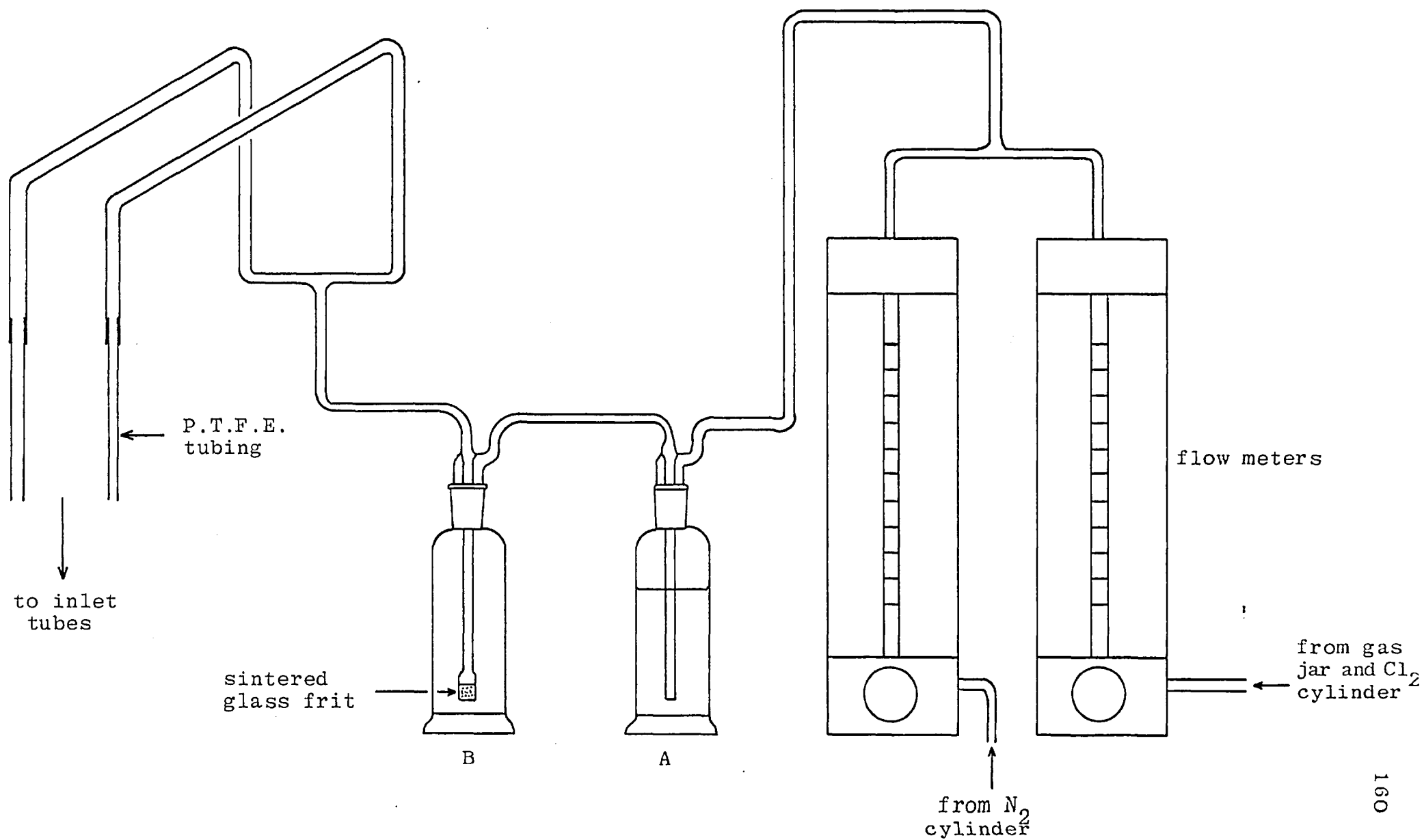
Both half-cells were first filled with the same HCl solution to obtain the bias potential (E_b) for these electrodes. With 2m HCl E_b was found to be 0.08 mV.

Although this is higher than the 0.01 mV reported by Faita et al.⁽¹¹³⁾, the potential differences of the cell with transference were large (22-167 mV for 1m vs. 1.5-8.0 m HCl) and the percentage errors were thus 0.3-0.05%, respectively. After the completion of the 1-8m HCl concentration region, work was started for the 0.1-2m HCl range. However, the bias potentials increased to approx. 2.8 mV for 0.1m HCl and 3.5 mV for 0.05m HCl. Thus it appeared that the bias potential was either a function of the solute concentration or that the electrodes had become corroded during the previous set of experiments. To avoid the use of a Pt/Ir junction, which might have caused these high bias potentials, Pt electrodes (Pt wire and Pt foil) and Ir electrodes (Ir wire and Ir foil) were tested. Bias potentials of 1.3, 0.8 and 0.2 mV were observed for the purely Pt electrodes for 7m HCl but for 12m HCl they were in the region of 3-4 mV. The purely Ir electrodes produced a bias potential of 0.9 mV at 7.5m HCl and after pretreatment (cathodisation followed by anodisation in dil. aq. HNO₃) 1.2 mV at 8m HCl and 2.6 mV for conc. HCl (14-15m). Such large bias potentials were considered too high for further work to continue.

VII.1.3 Chlorine Gas Line

The Cl₂ gas line is shown diagrammatically in fig.(VII.3). The apparatus was constructed from glass and P.T.F.E. as only these two materials are resistant to corrosive attack by Cl₂⁽¹¹³⁾. Most of the gas line was made from glass with connections between the sections made gas tight with P.T.F.E. sleeves wrapped in P.T.F.E. tape. Connection to the gas inlet tubes of the cell was via two lengths of P.T.F.E. tubing. Chlorine/nitrogen gas mixtures were used in this work as pure Cl₂ would have introduced errors in the chloride activity due to Cl₃⁻ ion formation⁽¹¹³⁾. The proportion of chlorine in the mixture was varied from 3-6% with no effect on the observed e.m.f.s. Most experiments were carried out with a 5-6% Cl₂/N₂ mixture.

fig.(VII.3) Chlorine Gas Line



The chlorine was admitted via an empty Dreschel bottle (to prevent a sudden build-up of Cl_2 pressure when the cylinder was opened) to an 1100 series flow meter calibrated from $20\text{--}250\text{ cm}^3\text{ min}^{-1}$ (Fisher Controls Ltd., Croydon). Nitrogen was fed directly to another flow meter of capacity $100\text{--}1200\text{ cm}^3\text{ min}^{-1}$. The flow rates were adjusted with stainless steel needle valves to give rates of approximately $50\text{--}60\text{ cm}^3\text{ min}^{-1}$ for Cl_2 and $1000\text{ cm}^3\text{ min}^{-1}$ for N_2 . Every 20-30 runs the Cl_2 flow meter was dismantled and cleaned to remove contamination from the float and needle valve. From the flow meters the gases were fed into a Dreschel bottle containing HCl solution (A) at a concentration corresponding to the middle of the range being studied. This served to mix the gases and saturate the bubbles with HCl solution. Excess vapour was removed in a second gas bottle (B) containing a sintered glass frit. The whole apparatus was supported by a frame and mounted in a fume cupboard.

VII.1.4 Thermostat and Temperature Control

The thermostat tank measured $30 \times 19 \times 19\text{ cm}$ and was filled with Shell "Diala" BX oil. The temperature was regulated at $25.00 \pm 0.05^\circ\text{C}$ by a proportional temperature controller and sensing thermistor (Radio Spares Components Ltd., London). Tap water was run through a copper cooling coil when the laboratory temperature exceeded 23°C . Stirring was provided by a "Mini Stirrer" (Electrothermal Engineering Ltd., London). In later experiments a more powerful motor was used (J.W.Towers and Co.Ltd., Widnes).

In the Cl_2 experiments the level of the oil was just below the ground glass joint of the liquid junction. For the H_2 work, the cell was more deeply immersed so that the complete cell was thermostatted. The hydrogen bias potentials then fell by 0.01 mV . Thus, although better temperature control for the Cl_2 work would have

been desirable, the error incurred by not doing so was small and, compared to the observed bias potentials, insignificant.

VII.1.5 Filling Procedure

The RH half-cell in fig.(VII.1) was filled with the less concentrated reference solution. With the tap closed, solution was poured in through the top B10 joint to a level just below that of the arm connecting the bubble chamber to the main body of the cell. The tap was opened and solution filled the tube leading to the cone (F). Air bubbles trapped in the bore of the tap were removed with a disposable Pasteur pipette and, after closing the tap, the solution was removed from the electrode chamber by turning the cell upside down. With the cell still inverted, extra solution was added with a disposable pipette into cone F until a drop of liquid projected from the end of the cone. The cell compartment was turned the right way up, and re-filled so that the level of the solution was approximately half-way between the jet and the B10 joint. A total of about 30 cm³ of solution was required altogether.

With the tap closed, about 5 cm³ of the more concentrated HCl solution was poured into the LH half-cell. The tap was opened and solution allowed to flow through the tubing towards socket E. Air bubbles were again removed from the tap using a pipette. The level of the solution was adjusted so that it corresponded to that of the glass hooks just below the socket. This ensured that when the liquid junction was formed an air pocket was trapped between the cone and socket so that no solution came into contact with the ground glass surfaces (greased in the H₂ experiments). After closing the tap the rest of the cell compartment was filled to the same level as in the RH half-cell (total volume of HCl solution required approx. 25 cm³). The electrodes were then placed in position with careful note being taken of which electrode

was in each side of the cell. For the H_2 work socket F was lightly lubricated with Apiezon grease and the cell held together with small springs attached to the glass hooks shown.

Once the cell had been filled it was placed in the thermostat tank and the electrode leads and gas inlet pipes connected. The gas flows were adjusted to the required levels and the taps immediately opened. Readings were then taken as outlined in the next section.

VII.1.6 Measurement of the E.m.f.

The measurements were made using a Solartron 7045 digital multimeter with an input resistance of $10.1\text{ M}\Omega$. Readings were taken every minute after the taps had been opened. It was found that a period of approximately five minutes was required for thermal equilibration of the cell and the saturation of the solutions around the electrodes with gas. After this period, the e.m.f.s remained stable (over a range of $\pm 0.1\text{ mV}$ or better) for a period of ten minutes or more. The length of this stable period was found to decrease as the difference in HCl concentrations in the half-cells increased. Consequently, readings were taken every 30 s for runs involving the more concentrated solutions in the 1-8m HCl concentration range. For the Cl_2 work from 1.5-8m HCl the measured e.m.f.s ranged from 22-167 mV, and for the same solute concentrations with hydrogen electrodes the e.m.f.s spanned 4 to 41 mV. This difference arises from the fact that these e.m.f.s are related to $T_{H^+}^{HCl}$ and $T_{Cl^-}^{HCl}$, respectively.

VII.1.7 Cell Cleaning

At the end of the run the electrodes were first removed from the cell, thoroughly washed with doubly-distilled water and dried in a vacuum oven (room temperature). The outside of the cell was washed with methylated spirits

to remove the oil and, after the two halves were emptied and separated, the inside of each half-cell was cleaned with distilled water (to remove the remaining solution), meths and a further six times with distilled water. Finally, the half-cells were rinsed three times with doubly-distilled water and dried in an oven at 120°C. The taps were cleaned in the same fashion and dried in the vacuum oven.

VII.1.8 Materials

A concentrated HCl stock solution (approx. 11M or 14m) was prepared from B.D.H. "AnalaR" HCl and doubly-distilled water. The acid was analysed by pH titration as in section (V.2.9). Conversion of the molarity to molality was via the curve-fitted literature density data (section V.3.1). The weight % of solute in the solution was calculated from the molality. About 100 g of each of the solutions was prepared in 100 cm³ pyrex volumetric flasks by adding a given amount of the HCl stock solution to a known weight of doubly-distilled water.

Initially, B.D.H. 5.4 cu. ft. Cl₂ cylinders were used (purity > 99.9%, impurities : 0.002% H₂O, < 10 ppm nitrogen trichloride). In later experiments B.O.C. 4CH cylinders were employed (purity 99.8%, impurities : 1600 ppm Br₂, 60 ppm nitrogen trichloride, 50 ppm moisture, 150 ppm non-volatile matter). The oxygen-free nitrogen was supplied by B.O.C. No further purification of any of the gases was attempted.

VII.1.9 A Typical Run

Run E7 6m HCl vs. 1m HCl, Cl₂ electrodes Wednesday, 18/3/81

H electrode (red), $m_{\text{HCl}} = 5.9901 \text{ mol kg}^{-1}$

L electrode (black), $m_{\text{HCl}} = 1.0097 \text{ mol kg}^{-1}$

$J_{\text{N}_2} \approx 1000 \text{ cm}^3 \text{ min}^{-1}$

$J_{\text{Cl}_2} \approx 60 \text{ cm}^3 \text{ min}^{-1}$

$T = 25.00 \pm 0.05^\circ\text{C}$

The electrodes were of the first type described in section (VII.1.2), i.e. Pt wire/Ir foil. H and L refer to the heavy (more concentrated) side and light (less concentrated) side of the cell, respectively, and red and black to the terminals of the multimeter. The readings taken are given in table (VII.1).

Table (VII.1)

time (h-min.)	-E/mV	time (h-min.)	-E/mV
12-32	junction	12-45	90.74
12-33	90.72	12-46	90.73
12-34	90.52	12-47	90.73
12-35	90.57	12-48	90.70
12-36	90.54	12-49	90.67
12-37	90.62	12-50	90.65
12-38	90.64	12-51	90.62
12-39	90.69	12-52	90.61
12-40	90.72	12-53	90.58
12-41	90.75	12-54	90.56
12-42	90.75	12-55	90.50
12-43	90.76	12-56	90.47
12-44	90.75		

The stable period was taken between times 12-39 and 12-49 inclusive, giving an average observed e.m.f. of

$$\bar{E}_{\text{obs.}} = -90.73 \pm 0.06 \text{ mV}$$

VII.2 Hydrogen Electrode Experiments

The cell, thermostat, method of e.m.f. measurement and the cell filling and cleaning procedures were exactly the same as those discussed in the previous section.

VII.2.1 Electrodes

Platinised Pt electrodes were used as the metallic base for the H_2 electrodes. Six electrodes, of the same basic construction as the electrodes for the Cl_2 work, were prepared by the following procedure^(114,115). The Pt foils were first degreased by brief immersion in triethylamine followed by washing in meths, distilled water and doubly-distilled water. They were then dipped in dilute aqua regia and conc. nitric acid and finally well washed with distilled and doubly-distilled water. Immediately before electrolysis, the electrodes were cathodised in 0.1M H_2SO_4 at a current density of 30 mA cm^{-2} for 10 mins. to remove surface oxides.

The plating solution and procedure were those recommended by Feltham⁽¹¹⁵⁾ : 3.5% (w/v) chloroplatinic acid (Johnson Matthey Ltd.) and 0.005% lead acetate (B.D.H. "AnalaR") prepared in 2M HCl. Electrolysis was carried out for 5 mins. at 30 mA cm^{-2} using two Ag/AgCl anodes. Stirring was provided in the container to prevent gassing at the Pt electrode. The electrodes, which were sooty black and evenly coated, were thoroughly washed with doubly-distilled water and dried in vacuo. Feltham and Spiro⁽¹¹⁶⁾ recommend this short electrolysis period for e.m.f. electrodes in order to produce a lighter deposit which when used shortens the equilibration time and reduces the extent of adsorption of the electrolyte.

Each of the set of six electrodes were tested against the others in bias potential experiments. Two pairs of electrodes were identified which produced bias potentials of 0.01 mV at HCl concentrations up to 3 mol kg^{-1} . The bias potential was found to be a linear function of the concentration up to 8m, at which the value was 0.15 mV. The corresponding corrections were calculated for intermediate values of m_{HCl} . At least one bias potential run was performed each day as a check on the reproducibility of the electrodes.

When the electrodes were placed in the cell care was taken to avoid adhering air (O_2) bubbles which might have caused false e.m.f.s to be produced (section VII.2.3).

VII.2.2 Hydrogen Gas Line

The apparatus was basically the same as that used for the chlorine work. Hydrogen was used at a pressure of 1 atmosphere with no nitrogen mixing and at a flow rate of $800 \text{ cm}^3 \text{ min}^{-1}$. As hydrogen slowly permeates through P.V.C. tubing⁽¹¹⁴⁾, 1/8" o.d. copper tubing connected the cylinder to the flow meter. Gas tight seals were made using "swagelock" fittings.

VII.2.3 Materials

HCl solutions were prepared as in section (VII.1.8).

Oxygen must be removed from the hydrogen (B.O.C.) to prevent a shift of the e.m.f. to a more positive potential⁽¹¹⁴⁾. This was achieved by placing a B.O.C. "Deoxo" catalytic purifier between the cylinder regulator and needle valve. This device uses a platinum catalyst to reduce O_2 to water. Less than 1 ppm of oxygen remained in the H_2 stream.

VII.2.4 A Typical Run

Run E128 4m HCl vs. 1m HCl, H_2 electrodes Friday, 7/8/81

3 electrode (red) heavy-side, $m_{HCl} = 3.9703 \text{ mol kg}^{-1}$
 1 electrode (black) light-side, $m_{HCl} = 1.0060 \text{ mol kg}^{-1}$
 $J_{H_2} = 800 \text{ cm}^3 \text{ min}^{-1}$
 $T = 25.00 \pm 0.05^\circ\text{C}$

3 and 1 identify the electrodes used from the set of six prepared (section VII.2.1). Heavy and light indicate the half-cells into which each electrode was placed and red

and black refer to the terminals of the multimeter.
The readings taken are given in table (VII.2).

Table (VII.2)

time (h-min.)	E/mV	time (h-min.)	E/mV
1-25	junction	1-33	18.801
1-26	17.822	1-34	18.802
1-27	18.677	1-35	18.797
1-28	18.739	1-36	18.791
1-29	18.772	1-37	18.792
1-30	18.797	1-38	18.788
1-31	18.802	1-39	18.778
1-32	18.796		

The stable period was taken between times 1-30 and 1-38 inclusive, giving an average observed e.m.f. of

$$\bar{E}_{\text{obs.}} = 18.79_6 \pm 0.00_8 \text{ mV}$$

CHAPTER EIGHT

E.M.F. RESULTS

The e.m.f.s of the concentration cells with transference were measured for aqueous HCl solutions at 25°C between 0.1 and 8.0 mol kg⁻¹. This concentration range was divided into two parts : a "dilute" region (0.1-2.0m) and a "concentrated" region (1.0-8.0m). Both chlorine and hydrogen electrodes were used, producing potentials related to $T_{H^+}^{HCl}$ and $T_{Cl^-}^{HCl}$, respectively. For both of these ranges the lower limit was used as the constant reference concentration (in the concentrated range, two sets of runs were performed with the Cl₂ electrodes, the second set using 2m HCl as the reference concentration). Fourteen runs were performed in each range (except for the 2m HCl reference Cl₂ runs in which only eleven results were taken) to increase the accuracy of the curve-fitting. The concentrations of the dilute and concentrated ranges overlapped to provide a check between the two sets of results.

VIII.1 Calculation of Results

VIII.1.1 Methods of Calculation

All three of the methods outlined in section (II.4.3) were used to calculate the transference data from the e.m.f. readings. Of these, the curve-fitting of $\ln(m\gamma/K)$ against E and Pikal's method have been sufficiently discussed in that section. The third method, that of fitting E data to $[\ln(m\gamma/K)]^{\frac{1}{2}}$ values, deserves a little more explanation.

In the differential form of the e.m.f. of the cell (equation II.36), namely

$$T_{\pm} = \frac{F}{2RT} \cdot \frac{dE}{d \ln(m\gamma/K)} \quad (\text{VIII.1})$$

let $x = \ln(m\gamma/K)$. For the first method of calculating $T_{\pm}$ we simply calculate dE/dx . When fitting E against $[\ln(m\gamma/K)]^{\frac{1}{2}}$, which corresponds to $x^{\frac{1}{2}}$, we require

$$\frac{dE}{dx} = \frac{dE}{dx^{\frac{1}{2}}} \cdot \frac{dx^{\frac{1}{2}}}{dx} = \frac{dE}{dx^{\frac{1}{2}}} \cdot \frac{1}{2}x^{-\frac{1}{2}} \quad (\text{VIII.2})$$

Thus, in order to calculate $T_{\pm}$ from the slope, $dE/d[\ln(m\gamma/K)]^{\frac{1}{2}}$, the required expression is

$$T_{\pm} = \frac{F}{4RT [\ln(m\gamma/K)]^{\frac{1}{2}}} \cdot \frac{dE}{d[\ln(m\gamma/K)]^{\frac{1}{2}}} \quad (\text{VIII.3})$$

The computer programme used to calculate the derivatives $dE/d \ln(m\gamma/K)$, $dE/d[\ln(m\gamma/K)]^{\frac{1}{2}}$ and $d\bar{T}/d(m\gamma/K)$ (the latter for Pikal's method) is given in appendix 1. This is the same programme as used extensively throughout this thesis for the curve-fitting of density and transference data and activity coefficients (see next section). For the present purpose the programme was amended according to appendices (1a-1c) to produce $T_{\pm}$ values directly from the raw E (or $\bar{T}$) vs. activity data. The programme, written in BASIC, calculates the fit of each polynomial equation (of orders 1-9 inclusive) by a least mean squares method. The polynomial coefficients are calculated from the resultant set of simultaneous equations by matrix inversion.

The transference numbers derived from the fitting process were found to vary with the degree of fitting. In general, polynomials of order 5 or greater gave "anomalous" fitting with irregular trends in $T_{\pm}$ with concentration, often combined with certain spurious values (sometimes with $T_{H^+}^{HCl}$ greater than unity), and were thus

discarded. Previous workers^(15,33,117,118) who have employed curve-fitting procedures have used third- or fourth-order polynomials. In the concentrated region fits of order 2, 3 and 4 were often found to give similar $T_{\pm}$ data. For the dilute region, where $T_{\pm}$ was found to be constant with concentration, first-order polynomials (straight line fits) were also used. The final choice for the degree of fitting was partly objective, based on the size of the standard deviation as compared with the accuracy of the results, and partly subjective, based on the general trend in the $T_{\pm}$ values and the number of anomalous results.

Of the three fits, E vs. $\ln(m\gamma/K)$ was found to be the most useful. Pikal's method required particularly accurate e.m.f. measurements and was thus more successfully applied to the H_2 work where the bias potentials were lower.

VIII.1.2 Activity Coefficient Data

Values for the activity coefficient given by Robinson and Stokes⁽¹¹⁹⁾ were employed to calculate the activities of the various solutions used. In the dilute region 20 values for m_{HCl} between 0.01 and 3.0m HCl were curve-fitted to a sixth-order polynomial in $m^{\frac{1}{2}}$ with a fit of 0.0004. The coefficients were

$$\begin{aligned}
 a_0 &= 0.997707 \\
 a_1 &= -1.11445 \quad \text{kg}^{\frac{1}{2}} \text{mol}^{-\frac{1}{2}} \\
 a_2 &= 2.07940 \quad \text{kg} \text{mol}^{-1} \\
 a_3 &= -2.29346 \quad \text{kg}^{\frac{3}{2}} \text{mol}^{-\frac{3}{2}} \\
 a_4 &= 1.68146 \quad \text{kg}^2 \text{mol}^{-2} \\
 a_5 &= -0.651056 \quad \text{kg}^{\frac{5}{2}} \text{mol}^{-\frac{5}{2}} \\
 a_6 &= 0.109012 \quad \text{kg}^3 \text{mol}^{-3}
 \end{aligned}$$

These coefficients were then used to calculate the activity coefficients at the relevant concentrations.

For the concentrated region (1.0-8.0m), 33 values between 0.1 and 16m were curve-fitted to various order polynomials. A sixth-order fit (± 0.01) was chosen because of its better fitting in the 1-8m region. The polynomial coefficients were

$$\begin{aligned}
 a_0 &= 0.778114 \\
 a_1 &= -8.95602 \times 10^{-2} \text{ kg mol}^{-1} \\
 a_2 &= 0.146361 \text{ kg}^2 \text{ mol}^{-2} \\
 a_3 &= -3.11474 \times 10^{-2} \text{ kg}^3 \text{ mol}^{-3} \\
 a_4 &= 4.92035 \times 10^{-3} \text{ kg}^4 \text{ mol}^{-4} \\
 a_5 &= -2.89934 \times 10^{-4} \text{ kg}^5 \text{ mol}^{-5} \\
 a_6 &= 6.83873 \times 10^{-6} \text{ kg}^6 \text{ mol}^{-6}
 \end{aligned}$$

VIII.2 Chlorine Electrode Experiments

VIII.2.1 Dilute Region, 0.1-2.0m HCl

These experiments were performed after those for the concentrated region and the bias potential for the Pt/Ir electrodes was found to have increased to approximately +2.8 mV in 0.1m HCl solution. Although this is too high for much confidence to be placed in the $T_{\text{H}^+}^{\text{HCl}}$ values, some of the results were later found to correspond closely with those derived from the H_2 work. Consequently, it is worthwhile to give the calculated results. The observed e.m.f.s of the cells were negative. Thus to calculate the corrected e.m.f.s, 2.8 mV was added to each of the $|E_{\text{obs.}}|$ values. The values of $E_{\text{corr.}}$ are given in table (VIII.1) along with the variable concentration to which they apply, $m(\text{mol kg}^{-1})$, and the other functions required for curve-fitting. The reference concentration was 0.1m HCl for which the molal activity coefficient, γ , is 0.796.

Table (VIII.1)

m_{HCl}	$m\gamma/K$	$\ln(m\gamma/K)$	$[\ln(m\gamma/K)]^{\frac{1}{2}}$	E/mV	$\bar{T}$
0.2149	1.9121	0.6482	0.8051	23.43	0.70349
0.3036	2.6730	0.9832	0.9916	38.49	0.76190
0.4019	3.5306	1.2615	1.1232	50.40	0.77757
0.5055	4.4285	1.4881	1.2199	60.14	0.78655
0.5955	5.2548	1.6591	1.2881	67.00	0.78595
0.6902	6.1535	1.8170	1.3480	74.15	0.79424
0.8020	7.5658	2.0236	1.4225	82.69	0.79528
0.8896	8.5059	2.1408	1.4631	88.46	0.80420
1.0113	9.8742	2.2899	1.5132	94.08	0.79960
1.2128	11.902	2.4767	1.5738	100.94	0.79320
1.4072	14.461	2.6715	1.6345	110.22	0.80297
1.5998	17.168	2.8430	1.6861	118.14	0.80875
1.7845	20.000	2.9958	1.7308	125.08	0.81259
1.9826	23.381	3.1519	1.7754	131.50	0.81198

Throughout the calculations more figures were retained than were significant to prevent accumulative errors. The results of the curve-fittings are given below.

A) E vs. $\ln(m\gamma/K)$

For fits of $n = 3$ and 4 , curious minima were observed in the $T_{\text{H}^+}^{\text{HCl}}$ values with results of 0.89 or 0.90 for the concentrations at the extreme ends of the range. The standard deviation for the E values was ± 0.41 mV. A slightly larger error of 0.49 mV was obtained for the $n = 1$ and 2 fits. The latter produced a slow increase in $T_{\text{H}^+}^{\text{HCl}}$ from 0.831 at $0.2m$ to 0.839 at $2.0m$. A value of 0.835 was obtained from the straight line plot.

B) E vs. $[\ln(m\gamma/K)]^{\frac{1}{2}}$

Again, $n = 3, 4$ and 5 gave minima in $T_{\text{H}^+}^{\text{HCl}}$ at about 0.8 - $0.9m$. The second-order polynomial produced a constant

$T_{H^+}^{HCl}$ value of 0.835 ± 0.001 over the whole concentration range.

C) Pikal's Method

As can be seen from the last column in table (VIII.1), the $\bar{T}$ values were not a smooth function of $(m\gamma/K)$ and this method produced totally unreliable results.

The coefficients for the various reliable fits are given in table (VIII.2).

Table (VIII.2)

method	a_0/mV	a_1/mV	a_2/mV
A, $n = 1$	-3.99511	42.9047	
A, $n = 2$	-3.73466	42.5918	0.080323
B, $n = 2$	-4.18921	0.300777	42.7929

It would appear, therefore, that within the experimental error of $\pm 0.002-0.003$, $T_{H^+}^{HCl}$ is constant at 0.835 over the concentration range from 0.2-2.0m HCl.

VIII.2.2 Concentrated Range, 1.0-8.0m HCl

For this range two sets of experiments were performed, with constant reference concentrations of 1.0 and 2.0m HCl. The bias potentials were 0.17 and 0.08 mV for 1m and 2m HCl solutions, respectively. These values were added to $|E_{\text{obs.}}|$ to give the corrected e.m.f.s in tables (VIII.3) and (VIII.7). Table (VIII.3) and the following discussion refer to the results for the 1.0m HCl runs ($\gamma = 0.809$).

Table (VIII.3)

m_{HCl}	$m\gamma/K$	$\ln(m\gamma/K)$	$[\ln(m\gamma/K)]^{\frac{1}{2}}$	E/mV	$\bar{T}$
1.5111	1.6787	0.5180	0.7197	22.30	0.83786
2.0084	2.4745	0.9061	0.9519	38.49	0.82673
2.5029	3.5770	1.2745	1.1289	54.40	0.83072
3.0004	4.8403	1.5770	1.2558	67.49	0.83292
3.4976	6.6124	1.8889	1.3744	80.00	0.82428
4.0000	8.6057	2.1524	1.4671	90.90	0.82193
4.5107	11.484	2.4410	1.5624	103.10	0.82202
5.0072	14.559	2.6782	1.6365	113.14	0.82218
5.4918	18.508	2.9182	1.7083	122.61	0.81772
5.9901	23.544	3.1589	1.7773	132.32	0.81524
6.5132	30.070	3.4035	1.8449	141.87	0.81126
6.9217	36.244	3.5903	1.8948	149.67	0.81133
7.4852	46.504	3.8395	1.9595	158.60	0.80394
8.0059	58.121	4.0625	2.0156	167.35	0.80173

A) E vs. $\ln(m\gamma/K)$

The results from the third- and fourth-order polynomials agreed with each other to ± 0.002 (except for the 1.5 and 8.0m points). The fourth-order polynomial (fit ± 0.2 mV) was considered to be the most reliable as the value at 2m (0.830) was in the closest agreement with the dilute region results.

B) E vs. $[\ln(m\gamma/K)]^{\frac{1}{2}}$

A fourth-order polynomial was again chosen (fit ± 0.2 mV). Agreement with the $\ln(m\gamma/K)$ fitting was ± 0.003 over the whole concentration range except for $m_{\text{HCl}} = 7.5$ and 8.0 mol kg^{-1} where the differences were 0.004 and 0.009, respectively.

C) Pikal's Method

As with the dilute range the $\bar{T}$ values were not a smooth function of (mV/K) and thus the derived $T_{H^+}^{HCl}$ values were unreliable. The $\bar{T}$ values were then smoothed by means of polynomials in (mV/K) , and $T_{H^+}^{HCl}$ calculated from these $\bar{T}$ (smooth) figures. These transference numbers varied monotonely with concentration and they were in reasonable agreement with the results from the first two analyses. An $n = 3$ polynomial of fit ± 0.003 , using the $\bar{T}$ (smooth) data was selected.

The coefficients of the various polynomials for the 1.0 vs. 1.5-8.0m HCl results are given in table (VIII.4), in which the a values have the units of mV, except for those for Pikal's method (C, $n = 3$) which are dimensionless. Table (VIII.5) gives the $T_{H^+}^{HCl}$ values derived from these coefficients. Table (VIII.6) presents the average $T_{H^+}^{HCl}$ data in the 1.5-8.0m region. These values have been derived from the 1m results given in table (VIII.5). In the averaging, all of the data were given the same weighting except for those marked * which were excluded. The maximum uncertainty in these results is estimated to be ± 0.003 with many of the results more accurate than this limit would suggest.

Table (VIII.4)

method	a_0	a_1	a_2	a_3	a_4
A, n=4	6.27336×10^{-2}	42.9645	-0.39496	0.113371	-3.09654×10^{-2}
B, n=4	-4.75030	20.0202	12.9130	19.2562	-4.75237
C, n=3	0.835125	-1.37144×10^{-3}	2.65013×10^{-5}	-2.23715×10^{-7}	

Table (VIII.5)

m_{HCl}	$T_{\text{H}^+}^{\text{HCl}} \text{ (A)}^\dagger$	$T_{\text{H}^+}^{\text{HCl}} \text{ (B)}^\dagger$	$T_{\text{H}^+}^{\text{HCl}} \text{ (C)}^\dagger$
1.5111	0.830	0.831	0.832
2.0084	0.826	0.823	0.829
2.5029	0.822	0.823	0.825
3.0004	0.819	0.821	0.820
3.4976	0.815	0.816	0.814
4.0000	0.810	0.811	0.807
4.5107	0.803	0.803	0.799
5.0072	0.796	0.795	0.791
5.4918	0.788	0.786	0.784
5.9901	0.778	0.776	0.778
6.5132	0.766	0.764	0.772*
6.9217	0.755	0.755	0.766*
7.4852	0.738	0.742	0.742*
8.0059	0.721	0.730	0.669*

$^\dagger T_{\text{H}^+}^{\text{HCl}} \text{ (A)}$, $T_{\text{H}^+}^{\text{HCl}} \text{ (B)}$ and $T_{\text{H}^+}^{\text{HCl}} \text{ (C)}$ are derived from the $\ln(m\gamma/K)$ and $[\ln(m\gamma/K)]^{\frac{1}{2}}$ curve-fits and Pical's method, respectively.

* Values not used in averaging (see text).

Table (VIII.6)

$m_{\text{HCl}}/\text{mol kg}^{-1}$	$T_{\text{H}^+}^{\text{HCl}}$	$m_{\text{HCl}}/\text{mol kg}^{-1}$	$T_{\text{H}^+}^{\text{HCl}}$
1.5111	0.831	5.0072	0.794
2.0084	0.826	5.4918	0.786
2.5029	0.823	5.9901	0.777
3.0004	0.820	6.5132	0.765
3.4976	0.815	6.9217	0.755
4.0000	0.809	7.4852	0.740
4.5107	0.802	8.0059	0.726

Table (VIII.7) gives the results for the 2.0m HCl reference runs ($\gamma = 1.006$).

Table (VIII.7)

m_{HCl}	$m\gamma/K$	$\ln(m\gamma/K)$	$[\ln(m\gamma/K)]^{\frac{1}{2}}$	E/mV	$\bar{T}$
2.5029	1.4213	0.3516	0.5929	14.64	0.81038
2.9991	1.9480	0.6668	0.8166	28.10	0.82017
3.4976	2.6185	0.9626	0.9811	40.02	0.80914
4.0000	3.4660	1.2430	1.1149	50.75	0.79462
4.5107	4.5709	1.5197	1.2328	62.23	0.79696
5.0072	5.8934	1.7738	1.3319	72.91	0.79998
5.4696	7.4025	2.0018	1.4149	83.20	0.80890
5.9687	9.4193	2.2428	1.4976	92.85	0.80572
6.9217	14.644	2.6840	1.6383	109.07	0.79089
7.4852	18.735	2.9304	1.7118	116.81	0.77580
8.0059	23.415	3.1534	1.7758	126.39	0.78006

There was little correlation between the results obtained by the three methods of analysis. In addition, although there was agreement in the middle of the concentration range (4-6m) for some of the fits with the results in table (VIII.5); the correlation between the 1m and 2m results was generally poor. This may be due to the fact that only 11 data points were available for the fitting of the 2m results.

For comparison with the 1m results, table (VIII.8) gives the polynomial coefficients for the $n = 3$ polynomials for the 2m results. Methods A, B and C refer to the $\ln(m\gamma/K)$ and $[\ln(m\gamma/K)]^{\frac{1}{2}}$ curve-fits and Pikal's method, respectively. Table (VIII.9) lists the transference numbers derived from these coefficients, namely $T_{\text{H}^+}^{\text{HCl}}$ (A), $T_{\text{H}^+}^{\text{HCl}}$ (B) and $T_{\text{H}^+}^{\text{HCl}}$ (C), respectively.

Table (VIII.8)

method	a_0	a_1	a_2	a_3
A	1.31699	37.7524	2.91847	-0.755039
B	11.9835	-37.8408	79.6103	-12.4727
C	0.810694	-7.32905×10^{-4}	-8.61118×10^{-5}	2.42967×10^{-6}

Table (VIII.9)

$m_{\text{HCl}}/\text{mol kg}^{-1}$	$T_{\text{H}^+}^{\text{HCl}} \text{ (A)}$	$T_{\text{H}^+}^{\text{HCl}} \text{ (B)}$	$T_{\text{H}^+}^{\text{HCl}} \text{ (C)}$
2.5029	0.769	0.712	0.810
2.9991	0.791	0.801	0.819
3.4976	0.803	0.817	0.806
4.0000	0.808	0.813	0.789
4.5107	0.806	0.802	0.787
5.0072	0.798	0.788	0.784
5.4696	0.785	0.774	0.785
5.9687	0.768	0.758	0.770
6.9217	0.722	0.728	0.724
7.4852	0.689	0.711	0.699
8.0059	0.655	0.695	0.723

VIII.3 Hydrogen Electrode ExperimentsVIII.3.1 Dilute Region, 0.1-2.0m HCl

For the 0.2m-1.0m HCl experiments the bias potential was -0.001 ± 0.023 mV. No correction was made to the observed e.m.f.s for these runs. A different pair of electrodes were used for the 1.2, 1.4 and 1.6m runs, the bias potential being -0.012 mV. The electrodes for the 1.8 and 2.0m HCl experiments gave a bias potential of -0.017 mV. All the transference cell e.m.f.s were positive.

Thus, where appropriate, 0.01₂ or 0.01₇ mV were added to $E_{\text{obs.}}$ to give the corrected e.m.f.s. The e.m.f.s. are quoted to three decimal places as in many of the experiments the e.m.f. was sufficiently stable for the last figure to be significant. Table (VIII.10) gives the data required for the curve-fitting procedures for the 0.1m HCl ($\gamma = 0.796$) reference runs using H₂ electrodes.

Table (VIII.10)

m_{HCl}	$m\gamma/K$	$\ln(m\gamma/K)$	$[\ln(m\gamma/K)]^{\frac{1}{2}}$	E/mV	$\bar{T}$
0.2043	1.8124	0.5947	0.7712	5.03 ₀	0.16461
0.2872	2.5077	0.9194	0.9589	7.66 ₈	0.16232
0.3915	3.4325	1.2333	1.1105	10.32 ₀	0.16286
0.5055	4.4310	1.4886	1.2201	12.54 ₅	0.16402
0.6057	5.3526	1.6776	1.2952	14.07 ₈	0.16332
0.7087	6.3196	1.8437	1.3578	15.48 ₇	0.16348
0.8115	7.3397	1.9933	1.4118	16.73 ₉	0.16344
0.9007	8.2616	2.1116	1.4531	17.75 ₉	0.16368
1.0018	9.3639	2.2369	1.4956	18.84 ₅	0.16396
1.2170	11.880	2.4748	1.5731	20.79 ₈	0.16356
1.4163	14.421	2.6687	1.6336	22.43 ₇	0.16363
1.5933	16.880	2.8261	1.6811	23.95 ₄	0.16496
1.7963	19.932	2.9923	1.7298	25.09 ₅	0.16322
1.9910	23.153	3.1421	1.7726	26.41 ₃	0.16360

A) E vs. $\ln(m\gamma/K)$

The fits for the polynomials of order $n = 1, 2, 3$ and 4 were all ± 0.06 mV. Thus the straight line plot fitted the data as well as the more powerful polynomials. For $n = 1$ and 2, $T_{\text{Cl}^-}^{\text{HCl}}$ was 0.164 for the complete concentration range. For $n = 3$ and 4 the average value of $T_{\text{Cl}^-}^{\text{HCl}}$ over this range was 0.163 with a maximum scatter of 0.002 for all the points except those for 0.2m and 2.0m (the end values). This indicated that the transference number was constant from 0.2-2.0m HCl with $T_{\text{Cl}^-}^{\text{HCl}} = 0.164$.

B) E vs. $[\ln(m\gamma/K)]^{\frac{1}{2}}$

Again, excluding the results for 0.2 and 2.0m HCl, fits of $n = 2, 3$ and 4 gave a constant value for T_{Cl}^{HCl} of 0.164 with a maximum scatter in the results of 0.002 .

C) Pikal's Method

Using the same criteria as in B) the average values of T_{Cl}^{HCl} and the maximum scatter in the results for $n = 1, 2, 3$ and 4 were $0.164 (\pm 0.002)$, $0.164 (\pm 0.002)$, $0.164 (\pm 0.007)$ and $0.164 (\pm 0.007)$, respectively.

The polynomial coefficients for methods A), B) and C) for $n = 2$ and 3 are given in table (VIII.11). The units of the coefficients are mV for methods A) and B) and for method C) the coefficients are dimensionless.

Table (VIII.11)

method	a_0	a_1	a_2	a_3
A), $n=2$	-1.83607×10^{-2}	8.40509	5.80645×10^{-3}	
A), $n=3$	0.250114	7.83577	0.345060	-6.01221×10^{-2}
B), $n=2$	0.100217	-0.218412	8.51047	
B), $n=3$	1.85552	-4.67190	12.1082	-0.933038
C), $n=2$	0.163147	9.01153×10^{-5}	-2.95376×10^{-6}	
C), $n=3$	0.163751	-1.61601×10^{-4}	2.25286×10^{-5}	-7.00790×10^{-7}

These results show conclusively that in the dilute region $T_{Cl}^{HCl} = 0.164$. The maximum error in this result is ± 0.002 .

VIII.3.2 Concentrated Region, 1.0-8.0m HCl

The bias potential, E_b in mV, was found to vary with m_{HCl} for the 1m vs. 1.5-8.0m HCl experiments according to the equation

$$E_b = 0.044 - 2.455 \times 10^{-2} m_{\text{HCl}} \quad (\text{VIII.4})$$

This equation was used to calculate the bias potentials at the relevant variable concentrations, which have been incorporated in the corrected e.m.f.s given in table (VIII.12). The constant reference concentration was 1.0 mol kg^{-1} ($\gamma = 0.809$).

Table (VIII.12)

m_{HCl}	$m\gamma/K$	$\ln(m\gamma/K)$	$[\ln(m\gamma/K)]^{\frac{1}{2}}$	E/mV	$\bar{T}$
1.4956	1.6378	0.4933	0.7024	4.07 ₃	0.16069
1.9896	2.4544	0.8979	0.9476	6.99 ₁	0.15153
2.4836	3.4923	1.2506	1.1183	10.55 ₅	0.16426
3.0028	4.8683	1.5828	1.2581	13.53 ₀	0.16637
3.4779	6.4559	1.8650	1.3657	16.14 ₂	0.16845
3.9703	8.5044	2.1406	1.4631	18.84 ₉	0.17138
4.5785	11.509	2.4431	1.5630	21.81 ₉	0.17382
4.9930	14.673	2.6860	1.6389	24.43 ₇	0.17707
5.4940	18.815	2.9347	1.7131	27.13 ₄	0.17995
6.0289	23.929	3.1751	1.7819	29.90 ₄	0.18330
6.4899	29.694	3.3909	1.8414	32.47 ₁	0.18637
6.9851	37.210	3.6166	1.9017	35.21 ₇	0.18952
7.4837	47.067	3.8516	1.9625	38.14 ₈	0.19276
7.9785	58.187	4.0637	2.0159	41.01 ₀	0.19641

A) E vs. $\ln(m\gamma/K)$

The fits for both $n = 3$ and 4 were $\pm 0.1 \text{ mV}$. A fourth-order polynomial was selected as it gave a smoother trend in $T_{\text{Cl}^-}^{\text{HCl}}$.

B) E vs. $[\ln(m\gamma/K)]^{\frac{1}{2}}$

The results were very similar to those for the $\ln(m\gamma/K)$ analysis and hence a fourth-order polynomial (of fit $\pm 0.09 \text{ mV}$) was again preferred.

C) Pikal's Method

This method produced more reliable results than for the corresponding concentration range for the Cl_2 work. As with the previous two methods, a fourth-order polynomial, with a fit of ± 0.003 , was chosen.

The polynomial coefficients for these three fourth-order fits are given in table (VIII.13)

Table (VIII.13)

method	a_0	a_1	a_2	a_3	a_4
A	0.393777	6.65783	1.37096	-0.299133	4.03968×10^{-2}
B	13.8943	-47.0590	65.1580	-30.3101	6.39025
C	0.152879	2.88320×10^{-3}	-1.08527×10^{-4}	2.06702×10^{-6}	-1.43206×10^{-8}

The results from these analyses are given in table (VIII.14), along with the average $T_{\text{Cl}^-}^{\text{HCl}}$ values. The data not used for averaging are indicated by *.

Table (VIII.14)

$m_{\text{HCl}}/\text{mol kg}^{-1}$	$T_{\text{Cl}^-}^{\text{HCl}}$ (A)	$T_{\text{Cl}^-}^{\text{HCl}}$ (B)	$T_{\text{Cl}^-}^{\text{HCl}}$ (C)	$\bar{T}_{\text{Cl}^-}^{\text{HCl}}$
1.4956	0.152	0.117*	0.163	0.158
1.9896	0.166	0.170	0.165	0.167
2.4836	0.175	0.180	0.174	0.176
3.0028	0.183	0.185	0.182	0.183
3.4779	0.189	0.188	0.189	0.189
3.9703	0.195	0.193	0.198	0.195
4.5185	0.202	0.200	0.205	0.202
4.9930	0.208	0.207	0.211	0.209
5.4940	0.215	0.215	0.214	0.215
6.0289	0.224	0.224	0.218	0.222
6.4899	0.232	0.233	0.227	0.231
6.9851	0.243	0.244	0.249	0.245
7.4837	0.256	0.256	0.271*	0.256
7.9785	0.269	0.268	0.188*	0.269

VIII.4 Discussion of E.m.f. Results

VIII.4.1 Calculation of "Best" Transference Numbers

The two dilute region studies gave values of $T_{H^+}^{HCl} = 0.835$ and $T_{Cl^-}^{HCl} = 0.164$ for $m_{HCl} = 0.2-1.8 \text{ mol kg}^{-1}$. Although the curve-fitting also gave these values for 2m HCl, this point was at the extreme end of the concentration range studied and was thus less reliable than the other results.

For the concentrated range (1.5-8.0m HCl) the $T_{H^+}^{HCl}$ and $T_{Cl^-}^{HCl}$ values were measured at slightly different concentrations. To enable accurate comparisons to be made between these values, the averaged data in tables (VIII.6) and (VIII.14) were curve-fitted to fourth-order polynomials with fits in $T_{\pm}$ of 5×10^{-4} and 9×10^{-4} , respectively. The coefficients for the $T_{H^+}^{HCl}$ data were

$$\begin{aligned} a_0 &= 0.844003 \\ a_1 &= -1.19017 \times 10^{-2} \text{ kg mol}^{-1} \\ a_2 &= 2.85040 \times 10^{-3} \text{ kg}^2 \text{ mol}^{-2} \\ a_3 &= -6.32182 \times 10^{-4} \text{ kg}^3 \text{ mol}^{-3} \\ a_4 &= 2.89369 \times 10^{-5} \text{ kg}^4 \text{ mol}^{-4} \end{aligned}$$

and for the $T_{Cl^-}^{HCl}$ data

$$\begin{aligned} a_0 &= 0.112845 \\ a_1 &= 3.97586 \times 10^{-2} \text{ kg mol}^{-1} \\ a_2 &= -7.70140 \times 10^{-3} \text{ kg}^2 \text{ mol}^{-2} \\ a_3 &= 8.12819 \times 10^{-4} \text{ kg}^3 \text{ mol}^{-3} \\ a_4 &= -2.04849 \times 10^{-5} \text{ kg}^4 \text{ mol}^{-4} \end{aligned}$$

These coefficients were then used to calculate values of $T_{H^+}^{HCl}$ and $T_{Cl^-}^{HCl}$ at rounded concentrations of m_{HCl} (mol kg^{-1}). The results are given in table (VIII.15) along with the sum ($T_{H^+}^{HCl} + T_{Cl^-}^{HCl}$) and the values for the "best" transference

numbers calculated from the equation

$$T_{\pm} \text{ (best)} = \frac{T_{\pm}}{T_{\pm} + T_{\mp}} \quad (\text{VIII.5})$$

Also given in table (VIII.15) are the best values for the dilute region at concentrations of 0.5, 1.0 and 1.5m.

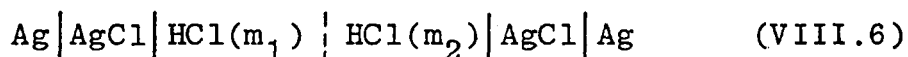
Table (VIII.15)

m_{HCl}	$T_{\text{H}^+}^{\text{HCl}}$	$T_{\text{Cl}^-}^{\text{HCl}}$	$T_{\text{H}^+}^{\text{HCl}} + T_{\text{Cl}^-}^{\text{HCl}}$	$T_{\text{H}^+}^{\text{HCl}} \text{ (best)}$	$T_{\text{Cl}^-}^{\text{HCl}} \text{ (best)}$
0.5	0.835	0.164	0.999	0.836	0.164
1.0	0.835	0.164	0.999	0.836	0.164
1.5	0.835	0.164	0.999	0.836	0.164
2.0	0.827	0.168	0.995	0.831	0.169
2.5	0.823	0.176	0.999	0.824	0.176
3.0	0.819	0.183	1.002	0.817	0.183
3.5	0.815	0.189	1.004	0.812	0.188
4.0	0.809	0.195	1.004	0.806	0.194
4.5	0.802	0.201	1.003	0.800	0.200
5.0	0.795	0.208	1.003	0.793	0.207
5.5	0.786	0.215	1.001	0.785	0.215
6.0	0.776	0.223	0.999	0.777	0.223
6.5	0.765	0.233	0.998	0.767	0.233
7.0	0.753	0.243	0.996	0.756	0.244
7.5	0.740	0.256	0.996	0.743	0.257
8.0	0.726	0.270	0.996	0.729	0.271

An indication of the overall accuracy of the results is that the average value for the sum is 0.999_6 . The maximum error in any individual value is estimated to be ± 0.003 with some of the results accurate to within ± 0.001 .

VIII.4.2 Comparison with Literature Results

Plotted in fig.(VIII.1) are the $T_{H^+}^{HCl}$ results at 25°C from the two previous HCl transference studies^(66,67) and the figures from the fifth column of table (VIII.15) as functions of m_{HCl} . Both Lengyel⁽⁶⁶⁾ and Harned and Dreby⁽⁶⁷⁾ measured the e.m.f.s of cells of the type

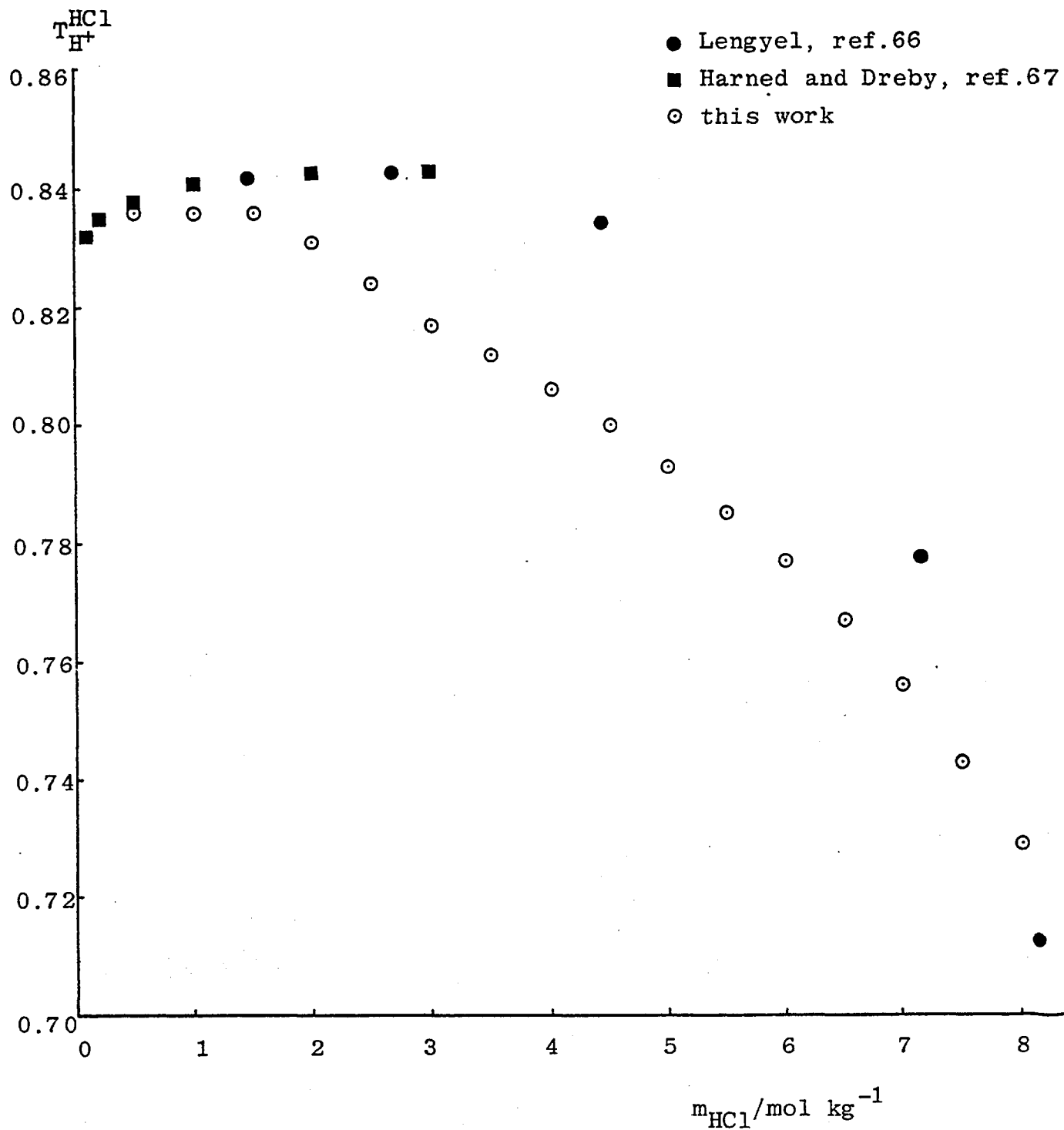


Lengyel reports the results up to a concentration of 14.7m at 25°C and the latter studied concentrations up to 3m at 5-50°C. As can be seen, the two sets of data diverge with increasing concentration up to about 4-5m. At higher concentrations the data of Lengyel⁽⁶⁶⁾ and those from the present work converge and meet at approximately 8m. Both Lengyel's and Harned and Dreby's studies show that $T_{H^+}^{HCl}$ increases slowly with concentration to a value of 0.843 at 2-3m. A gradual decrease with increasing concentration is observed up to about 5m. At higher solute concentrations Lengyel's $T_{H^+}^{HCl}$ data decrease rapidly with increasing m_{HCl} . However, the results from the present study indicate that $T_{H^+}^{HCl}$ is constant at 0.836 for $m_{HCl} = 0.2-1.8 \text{ mol kg}^{-1}$ and decreases steadily with increasing concentration. The difference between the two sets of results may be due to errors in the literature data caused by the dissolution of the AgCl electrodes in the concentrated chloride solutions.

The graph of the data from the present work exhibits a small point of inflection at about 3m HCl (fig.VIII.1). This region of the graph was further investigated by the following procedure. The best $T_{H^+}^{HCl}$ values from table (VIII.15) for $m_{HCl} = 1.5-8.0 \text{ mol kg}^{-1}$ were curve-fitted to a fourth-order polynomial with a fit of 4×10^{-4} . The coefficients were

fig.(VIII.1)

Comparison of Literature $T_{H^+}^{HCl}$ Data at 25°C with
the Present Work



$$\begin{aligned}
 a_0 &= 0.859991 \\
 a_1 &= -1.81835 \times 10^{-2} \text{ kg mol}^{-1} \\
 a_2 &= 1.96779 \times 10^{-3} \text{ kg}^2 \text{ mol}^{-2} \\
 a_3 &= -1.79144 \times 10^{-4} \text{ kg}^3 \text{ mol}^{-3} \\
 a_4 &= -4.86768 \times 10^{-6} \text{ kg}^4 \text{ mol}^{-4}
 \end{aligned}$$

Using these coefficients, $T_{H^+}^{HCl}$ was then calculated at 0.1m intervals for $m_{HCl} = 1.5\text{--}4.9 \text{ mol kg}^{-1}$. These 35 results were then further fitted to a fourth-order polynomial. The derivative of the polynomial was observed to decrease (in a negative sense) for concentrations up to 3.1m. At higher concentrations the gradient increased (again in a negative sense) up to 4.9m HCl. Below are given the coefficients for this last curve-fit and in table (VIII.16) the values of $T_{H^+}^{HCl}$ and $dT_{H^+}^{HCl}/dm$ at concentrations between 1.5 and 4.9m. This set of coefficients differs slightly from the previous set as here the curve-fitting was over a smaller concentration range.

$$\begin{aligned}
 a_0 &= 0.859987 \\
 a_1 &= -1.81791 \times 10^{-2} \text{ kg mol}^{-1} \\
 a_2 &= 1.96576 \times 10^{-3} \text{ kg}^2 \text{ mol}^{-2} \\
 a_3 &= -1.78725 \times 10^{-4} \text{ kg}^3 \text{ mol}^{-3} \\
 a_4 &= -4.90045 \times 10^{-6} \text{ kg}^4 \text{ mol}^{-4}
 \end{aligned}$$

Owen and Sweeton⁽¹⁰⁵⁾ reported two points of inflection in their HCl conductance results at concentrations of 0.25 and 3.5M (at 25°C these molarities correspond to 0.25 and 3.8 mol kg⁻¹, respectively). A more detailed discussion of these points of inflection will be given in section (IX.2.2). The point of inflection in this work might indicate that between 3.1 and 3.2m there is a sudden breakdown in the solution structure which reduces the number of H⁺ ions taking part in the proton-jumping conduction mechanism.

Table (VIII.16)

$m_{\text{HCl}}^{\dagger}$	$T_{\text{H}^+}^{\text{HCl}}$	$-10^2 dT_{\text{H}^+}^{\text{HCl}}/dm^{\dagger\dagger}$	m_{HCl}	$T_{\text{H}^+}^{\text{HCl}}$	$-10^2 dT_{\text{H}^+}^{\text{HCl}}/dm$
1.5	0.8365	1.355	3.3	0.8144	1.175
1.6	0.8352	1.334	3.4	0.8132	1.178
1.7	0.8338	1.314	3.5	0.8120	1.183
1.8	0.8325	1.295	3.6	0.8109	1.189
1.9	0.8313	1.278	3.7	0.8097	1.197
2.0	0.8300	1.262	3.8	0.8085	1.206
2.1	0.8287	1.247	3.9	0.8073	1.216
2.2	0.8275	1.233	4.0	0.8060	1.229
2.3	0.8263	1.221	4.1	0.8048	1.242
2.4	0.8250	1.210	4.2	0.8035	1.258
2.5	0.8238	1.201	4.3	0.8023	1.275
2.6	0.8226	1.193	4.4	0.8010	1.293
2.7	0.8215	1.186	4.5	0.7997	1.313
2.8	0.8203	1.181	4.6	0.7984	1.335
2.9	0.8191	1.177	4.7	0.7970	1.358
3.0	0.8179	1.174	4.8	0.7957	1.383
3.1	0.8167	1.173	4.9	0.7943	1.409
3.2	0.8156	1.173			

$\dagger$ Units of m_{HCl} are mol kg^{-1}

$\dagger\dagger$ Units of $dT_{\text{H}^+}^{\text{HCl}}/dm$ are kg mol^{-1}

CHAPTER NINE

THE CONDUCTANCE OF AQUEOUS HCl SOLUTIONS

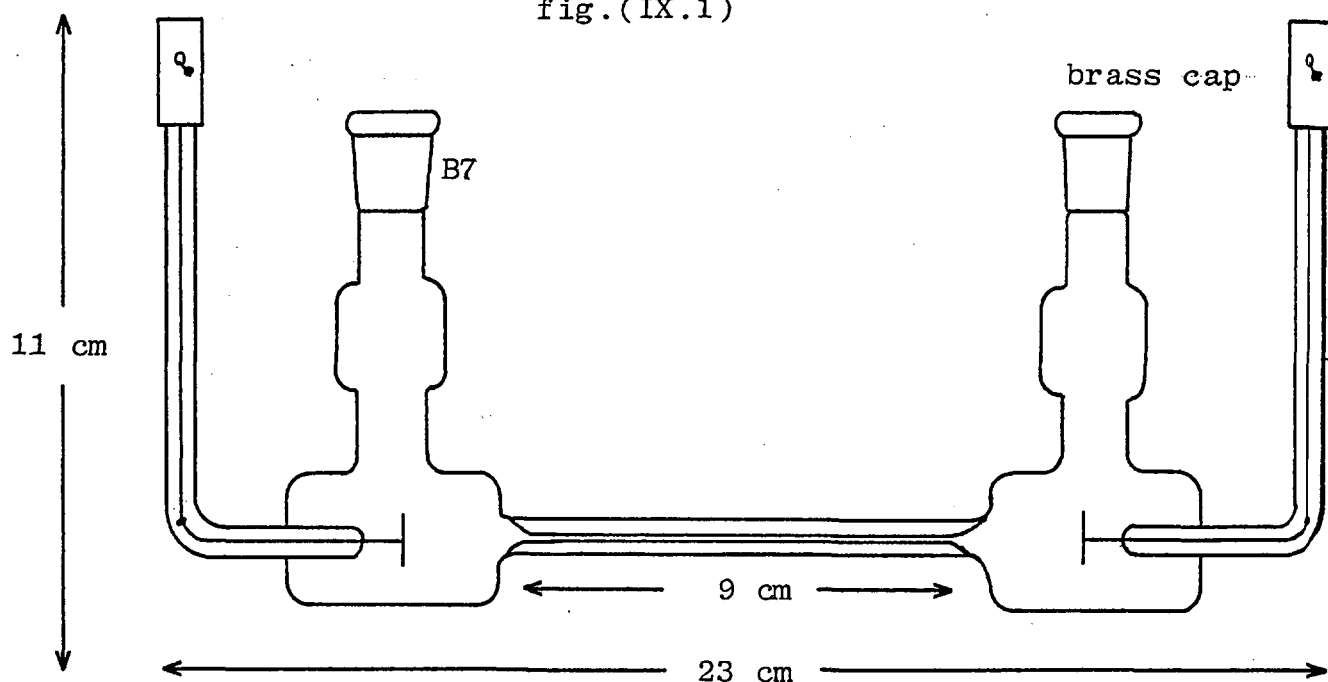
IX.1 Experimental Procedure

IX.1.1 Conductance Cell and its Calibration

The cell used for the a.c. measurement of the conductances of aqueous HCl solutions from 0.1-7M at 25°C is shown in fig.(IX.1). The central section of the cell consisted of a 9 cm length of 0.1 cm diameter capillary tube; at each end of which there was a larger chamber containing a circular (1 cm diameter) Pt electrode firmly sealed into the glass. The small bore of the tubing ensured that the measured resistances were between 2 and 39 k Ω . Pyrex glass only was used to make the cell. The Pt electrodes were each soldered to lengths of silver wire which in turn were soldered to the brass caps shown to provide good electrical contact.

The KCl conductance standards of Jones and Bradshaw⁽¹²⁰⁾ were used to calibrate the cell. Initially, the cell was

fig.(IX.1)



calibrated with bright Pt electrodes with both 0.1D (D $\equiv$ demal) and 1D solutions. The solutions were prepared from B.D.H. "Aristar" KCl and doubly distilled water of specific conductance $1 \times 10^{-6} \text{ S cm}^{-1}$. All weights were converted to the corresponding weights in vacuo and the units of resistance changed from the original international ohms to absolute ohms ($1 \text{ int. ohm} = 1.000495 \text{ abs. ohm}^{(121)}$). In this chapter all resistances referred to are quoted in absolute ohms. The errors in the preparation of the 0.1 and 1D solutions were 0.01% and 0.0007%, respectively. Both the resistance (R) and conductance (G) were measured at frequencies of 100, 1000 and 10000 Hz with a Wayne Kerr B905 Automatic Precision Bridge (for experimental details see sections IX.1.2 and IX.1.3). The cell constant, $1/A$, is related to the specific conductance of the solutions, κ , by

$$1/A = R\kappa = \kappa/G \quad (\text{IX.1})$$

where $\kappa = 0.012849_6 \text{ S cm}^{-1}$ and $0.11128_7 \text{ S cm}^{-1}$ for the 0.1D and 1D KCl solutions, respectively. The measured values of G, R and C_p (the equivalent parallel capacitance) are presented in tables (IX.1a) and (IX.1b) as functions of the measuring frequency (ν) for the 0.1D and 1D solutions, respectively. Also given in the tables are the values for the cell constant derived from equation (IX.1).

Table (IX.1a)

ν/Hz	$G/\mu\text{S}$	$R/\text{k}\Omega$	C_p/pF	$(1/A)/\text{cm}^{-1}$
100	7.836	127.63	6.0	1639.9
1000	7.835	127.63	0.31	1640.0
10000	7.852	127.54	0.160	1637.7

Table (IX.1b)

1D solution

ν/Hz	$G/\mu\text{S}$	$R/\text{k}\Omega$	C_p/pF	$(1/A)/\text{cm}^{-1}$
100	67.78	14.754	210	1641.9
1000	67.79	14.753	4.0	1641.7
10000	67.82	14.745	1.40	1640.9

Thus, although the values measured at 100 and 1000 Hz were in good agreement for each solution, not only were the $(1/A)$ values derived from the measurements at 10 kHz approximately 0.1% lower but the values at the two different concentrations also differed by 0.1%. As this may have been caused by polarisation effects at the electrodes they were platinised according to the procedure used for the H_2 electrodes in section (VII.2.1). Platinisation of the electrodes vastly increases the surface area and hence greatly reduces the current density⁽¹¹⁶⁾.

The corresponding results for the platinised electrodes are given in tables (IX.2a) and (IX.2b). It should be added that two cracks had been repaired after the bright-platinum calibration experiments which might have slightly changed the cell constant.

Table (IX.2a)

0.1D solution

ν/Hz	$G/\mu\text{S}$	$R/\text{k}\Omega$	C_p/pF	$(1/A)/\text{cm}^{-1}$
100	7.825	127.80	0.5	1642.2
1000	7.824	127.81	0.23	1642.3
10000	7.826	127.78	0.14	1641.9

Table (IX.2b)

1D solution

ν/Hz	$G/\mu\text{S}$	$R/\text{k}\Omega$	C_p/pF	$(1/A)/\text{cm}^{-1}$
100	67.78	14.754	10	1641.9
1000	67.79	14.752	2	1641.7
10000	67.89	14.730	0.6	1639.3

Apart from the result for the 1D solution at 10 kHz, the results from both solutions agreed to within 0.02%. Hence, the cell constant was taken to be

$$1/A = 1642.0 \pm 0.3 \text{ cm}^{-1} \quad (\text{IX.2})$$

IX.1.2 Thermostat and Temperature Control

The thermostat tank measured 27 x 27 x 39 cm and was filled with Shell "Diala" BX oil to prevent electrical leakage. The current to a 75W immersion heater (Singleton Bros., Penryn) was regulated by a relay box (Gallenkamp) and a mercury contact thermometer (Electrical Thermometer Co.Ltd.). A single paddle stirrer (J.W.Towers Co.Ltd., Widnes) provided sufficient agitation of the thermostat liquid. When the laboratory temperature exceeded 23°C a copper coil carrying cooler tap water was inserted into the tank.

IX.1.3 General Procedure for a Run

The solutions that had been prepared for the hydrogen electrode e.m.f. work were also employed for the present measurements (section VIII.3). Any solution whose conductance was to be measured was allowed to attain thermal equilibrium in the tank for 20 mins. This prevented errors due to the Soret effect whereby thermal equilibration of the solution in the cell is accompanied by the formation of a concentration gradient⁽¹²²⁾. A.c. conductance and

resistance measurements were made with a Wayne Kerr B905 Automatic Precision Bridge. Before filling the cell, the resistance of the leads was "trimmed out" using the "trim open circuit" feature of the bridge. The cell was then filled and, after ensuring that no air bubbles had become trapped, allowed to equilibrate thermally for a further 20 mins.

Although the apparatus described in the previous section was only capable of controlling the temperature of the bath to $\pm 0.05^{\circ}\text{C}$, the measurements were taken at $25.000 \pm 0.005^{\circ}\text{C}$ by using the following technique. It was observed that during the heating/cooling cycle the rate of cooling was approximately $0.01^{\circ}\text{C min}^{-1}$. Thus by using a thermometer graduated in 1/100 ths of a degree a period of about 30 s was identified in which both conductance and resistance measurements could be taken at $25.000 \pm 0.005^{\circ}\text{C}$. An estimate of the error in each reading was also made. For any given temperature the G and R values could be determined to $\pm 0.1\mu\text{S}$ and $\pm 0.0001\text{ k}\Omega$, respectively.

After the measurements had been taken, the cell was removed from the oil bath and the outside washed with acetone. The cell was then emptied and rinsed twelve times with distilled water. During each rinsing it was checked that water flowed through the capillary section of the cell. After a further four rinsings with doubly-distilled water the cell was dried in a vacuum oven (room temperature) prior to the next experiment. When not in use the cell was filled with doubly-distilled water.

IX.2 Results and Discussion

IX.2.1 Results

All the quoted measurements were carried out at a frequency of 1000 Hz. No variability of the results with the measuring frequency was observed. The values of the R and G parameters are given in table (IX.3) at the appropriate

Table (IX.3)

$m_{\text{HCl}}/\text{mol kg}^{-1}$	$G/\mu\text{S}$	$R/\text{k}\Omega$	C_p/pF
0.1093	25.850	38.673	0.8
0.2043	47.074	21.243	1.0
0.2872	64.97	15.392	1.2
0.3915	86.77	11.525	2
0.5055	109.65	9.120	2
0.6057	129.30	7.733	0
0.7087	148.54	6.732	0
0.8115	166.98	5.989	0
0.9007	182.46	5.481	2
1.0079	200.13	4.9967	2
1.2170	233.16	4.2887	2
1.4163	262.11	3.8152	2
1.5933	285.88	3.4980	0
1.7958	311.07	3.2147	2
1.9910	333.38	2.9996	0
2.4836	381.29	2.6226	2
3.0028	420.76	2.3767	4
3.4779	450.63	2.2191	3
3.9703	473.63	2.1113	2
4.5185	491.62	2.0341	5
4.9930	503.0	1.9880	5
5.4940	510.4	1.9590	6
6.0289	514.4	1.9440	5
6.4899	515.2	1.9410	2
6.9851	513.7	1.9466	3
7.4837	510.3	1.9595	4
7.9785	505.4	1.9786	3

molalities. If the first digit of either the R or G display was between 5 and 10 only four significant figures were shown for that quantity. Thus, by taking both R and G measurements it was ensured that at least one of the quantities was known to five figures.

For the 0.1m - 2.0m solutions the corresponding molarity at 25°C was calculated from the equation given by Harned and Owen⁽¹²³⁾, namely

$$c/m = 0.9970 - 0.0182m \quad (\text{IX.3})$$

This equation is accurate to $\pm 0.05\%$ up to 4M. For solution concentrations between 2.5 and 8.0m, the literature^(72,103) density data used in section (V.3.1) were curve-fitted to a sixth-order polynomial in m (fit $\pm 5 \times 10^{-5} \text{ kg dm}^{-3}$). The coefficients were

$$\begin{aligned} a_0 &= 0.996897 && \text{kg} && \text{dm}^{-3} \\ a_1 &= 1.88843 \times 10^{-2} && \text{kg}^2 && \text{dm}^{-3} \text{ mol}^{-1} \\ a_2 &= -1.66718 \times 10^{-3} && \text{kg}^3 && \text{dm}^{-3} \text{ mol}^{-2} \\ a_3 &= 3.74514 \times 10^{-4} && \text{kg}^4 && \text{dm}^{-3} \text{ mol}^{-3} \\ a_4 &= -5.59532 \times 10^{-5} && \text{kg}^5 && \text{dm}^{-3} \text{ mol}^{-4} \\ a_5 &= 4.18115 \times 10^{-6} && \text{kg}^6 && \text{dm}^{-3} \text{ mol}^{-5} \\ a_6 &= -1.21994 \times 10^{-7} && \text{kg}^7 && \text{dm}^{-3} \text{ mol}^{-6} \end{aligned}$$

These coefficients were then used to calculate the densities of the solutions at the relevant molalities, enabling the molarities to be calculated.

Table (IX.4) gives the specific conductances, κ , and molar conductances, Λ , of the HCl solutions studied at 25°C. The values are the average of the results derived from the G and R measurements. The specific conductances, which were calculated directly from equation (IX.1), have a maximum estimated error of $\pm 1 \times 10^{-4} \text{ S cm}^{-1}$. Values for the molar conductance (maximum estimated error $\pm 0.1 \text{ cm}^2 \text{ S mol}^{-1}$) were calculated from

Table (IX.4)

$m_{\text{HCl}}/\text{mol kg}^{-1}$	$c_{\text{HCl}}/\text{mol dm}^{-3}$	$\kappa/\text{S cm}^{-1}$	$\Lambda/\text{cm}^2 \text{ S mol}^{-1}$
0.1093	0.1088	0.04245 ₉	390.3 ₅
0.2043	0.2030	0.07729 ₆	380.8 ₆
0.2872	0.2849	0.1066 ₈	374.4 ₄
0.3915	0.3876	0.1424 ₈	367.5 ₈
0.5055	0.4995	0.1800 ₅	360.4 ₈
0.6057	0.5974	0.2123 ₃	355.4 ₄
0.7087	0.6976	0.2439 ₁	349.6 ₅
0.8115	0.7972	0.2741 ₈	343.9 ₂
0.9007	0.8835	0.2995 ₉	339.1 ₁
1.0079	0.9866	0.3286 ₂	333.0 ₈
1.2170	1.1867	0.3828 ₆	322.6 ₃
1.4163	1.3759	0.4303 ₈	312.8 ₀
1.5933	1.5427	0.4694 ₁	304.2 ₈
1.7958	1.7322	0.5107 ₈	294.8 ₇
1.9910	1.9134	0.5474 ₁	286.0 ₉
2.4836	2.3628	0.6260 ₉	264.9 ₈
3.0028	2.8285	0.6908 ₈	244.2 ₆
3.4779	3.2467	0.7399 ₄	227.9 ₁
3.9703	3.6722	0.7777 ₁	211.7 ₉
4.5185	4.1366	0.8072 ₄	195.1 ₅
4.9930	4.5307	0.8259 ₅	182.3 ₀
5.4940	4.9387	0.8381 ₃	169.7 ₁
6.0289	5.3660	0.8446 ₅	157.4 ₁
6.4899	5.7277	0.8459 ₆	147.7 ₀
6.9851	6.1089	0.8435 ₁	138.0 ₈
7.4837	6.4850	0.8379 ₄	129.2 ₂
7.9785	6.8518	0.8298 ₈	121.1 ₂

$$\Lambda = \frac{1000 (1/A)}{Rc} \quad (\text{IX.4})$$

and

$$\Lambda = \frac{1000 (1/A)G}{c} \quad (\text{IX.5})$$

where the molar concentration, c , is in mol dm^{-3} .

IX.2.2 Comparison with Literature Values

Hamer and DeWane⁽¹²¹⁾ have published a comprehensive review and analysis of the conductances of aqueous solutions of HF, HCl, HBr and HI. They have, where necessary, corrected the literature data to the Jones and Bradshaw conductance standards⁽¹²⁰⁾ and have also converted the conductances from international to absolute ohms. They gave four fitting equations for the molar (or equivalent) conductance of HCl solutions at 25°C for the concentration ranges 0-0.01M, 0.01-0.1M, 0.1-3.0M and 3.0-11.6M, with fits of 0.05, 0.14, 0.10 and 0.15 $\text{cm}^2 \text{ S mol}^{-1}$, respectively. The equations pertaining to the two highest concentration regions are, respectively

$$\begin{aligned} \Lambda = & 426.06 - 158.63c^{\frac{1}{2}} + 221.501c - 252.771c^{3/2} \\ & + 115.606c^2 - 19.5824c^{5/2} \text{ cm}^2 \text{ S mol}^{-1} \end{aligned} \quad (\text{IX.6})$$

and

$$\begin{aligned} \Lambda = & 426.06 - 158.63c^{\frac{1}{2}} + 143.554c - 116.628c^{3/2} \\ & + 35.2535c^2 - 3.56231c^{5/2} \text{ cm}^2 \text{ S mol}^{-1} \end{aligned} \quad (\text{IX.7})$$

They obtained these equations by curve-fitting literature conductance data, which for equation (IX.6), the 0.1-3.0M range, were those of Owen and Sweeton⁽¹⁰⁵⁾, Klochko and Kurbanov⁽¹²⁴⁾ and Stokes⁽¹²⁵⁾. For the concentration range

3.0-11.6M the data of Hlasko⁽¹²⁶⁾ and Howell⁽¹²⁷⁾ were employed in addition to those from the first two references mentioned above for the 0.1-3.0M range.

The first term in each equation ($426.06 \text{ cm}^2 \text{ S mol}^{-1}$) is the limiting value, Λ^0 , calculated by Hamer and DeWane from various literature sources and the coefficient of the second term ($158.63 \text{ cm}^2 \text{ dm}^{3/2} \text{ S mol}^{-3/2}$) involves the D-H-O electrophoretic and relaxation terms.

Table (IX.5) gives the observed and calculated (from eqns. IX.6 and IX.7) values for Λ at the experimental concentrations used in the present work. Equation (IX.6) was used to determine $\Lambda(\text{calc.})$ for HCl concentrations from 0.1-2.8M inclusive and equation (IX.7) for c_{HCl} from 3.2-6.9M. The last two columns of table (IX.5) give the difference, δ , between $\Lambda(\text{obs.})$ and $\Lambda(\text{calc.})$ and the percentage difference, Δ , given by the expression

$$\Delta = \frac{\Lambda(\text{obs.}) - \Lambda(\text{calc.})}{\Lambda(\text{obs.})} \times 100\% \quad (\text{IX.8})$$

The average value of Δ for $c_{\text{HCl}} = 0.1-4.5\text{M}$ is +0.04%, but due to the greater differences for the higher concentrations, the overall average value is 0.20%. Such a large difference is difficult to explain. Although for the majority of solutions $\Lambda(\text{obs.}) > \Lambda(\text{calc.})$ there are a sufficient number of negative δ values to suggest that no systematic error was involved in the present work (at least up to 4.5M). At higher concentrations, 4.9-6.9M, there may either be an error in the present work or in the literature data used to determine the coefficients of equation (IX.7). Two of the sets of literature data^(126,127) are over fifty years old. Hlasko⁽¹²⁶⁾ went up to a concentration of 7.3M whilst Howell⁽¹²⁷⁾ studied only the one concentration (4M). Klochko and Kurbanov⁽¹²⁴⁾ measured Λ up to 28.7 mol % ($\approx 16\text{M}$). Alternatively, equation (IX.7) may be inaccurate at higher solute concentrations.

Table (IX.5)

$c/\text{mol dm}^{-3}$	$\Lambda(\text{obs.})^\dagger$	$\Lambda(\text{calc.})^\dagger$	$\delta^\dagger$	Δ
0.1088	390.3 ₅	390.0 ₆	0.2 ₉	0.07
0.2030	380.8 ₆	380.8 ₃	0.0 ₃	0.01
0.2849	374.4 ₄	374.5 ₉	-0.1 ₅	-0.04
0.3876	367.5 ₈	367.7 ₀	-0.1 ₂	-0.03
0.4995	360.4 ₈	360.7 ₄	-0.2 ₆	-0.07
0.5974	355.4 ₄	354.9 ₂	0.5 ₂	0.15
0.6976	349.6 ₅	349.1 ₁	0.5 ₄	0.15
0.7972	343.9 ₂	343.4 ₅	0.4 ₇	0.14
0.8835	339.1 ₁	338.6 ₁	0.5 ₀	0.15
0.9866	333.0 ₈	332.9 ₂	0.1 ₆	0.05
1.1867	322.6 ₃	322.1 ₁	0.5 ₂	0.16
1.3759	312.8 ₀	312.1 ₇	0.6 ₃	0.20
1.5427	304.2 ₈	303.6 ₅	0.6 ₃	0.21
1.7322	294.8 ₇	294.2 ₄	0.6 ₃	0.21
1.9134	286.0 ₉	285.5 ₁	0.5 ₈	0.20
2.3628	264.9 ₈	264.8 ₉	0.0 ₉	0.03
2.8285	244.2 ₆	244.7 ₇	-0.5 ₁	-0.21
3.2467	227.9 ₁	227.9 ₇	-0.0 ₆	-0.03
3.6722	211.7 ₉	211.8 ₆	-0.0 ₇	-0.03
4.1366	195.1 ₅	195.2 ₉	-0.1 ₄	-0.07
4.5307	182.3 ₀	182.0 ₈	0.2 ₂	0.12
4.9387	169.7 ₁	169.2 ₄	0.4 ₇	0.28
5.3660	157.4 ₁	156.6 ₉	0.7 ₂	0.46
5.7277	147.7 ₀	146.7 ₈	0.9 ₂	0.62
6.1089	138.0 ₈	137.0 ₃	1.0 ₅	0.76
6.4850	129.2 ₂	128.0 ₈	1.1 ₄	0.88
6.8518	121.1 ₂	119.9 ₇	1.1 ₅	0.95

† units of $\text{cm}^2 \text{ S mol}^{-1}$

In order to test this last possibility, Owen and Sweeton's⁽¹⁰⁵⁾ data (corrected to abs. ohms) were treated in the same fashion as the present results were in table (IX.5). Their results and the calculated values (0.1-2.5M via equation IX.6 and 3.0-9.8M via equation IX.7) are given in table (IX.6), along with the δ and percentage deviation Δ values. Λ and δ have units of $\text{cm}^2 \text{ S mol}^{-1}$.

Table (IX.6)

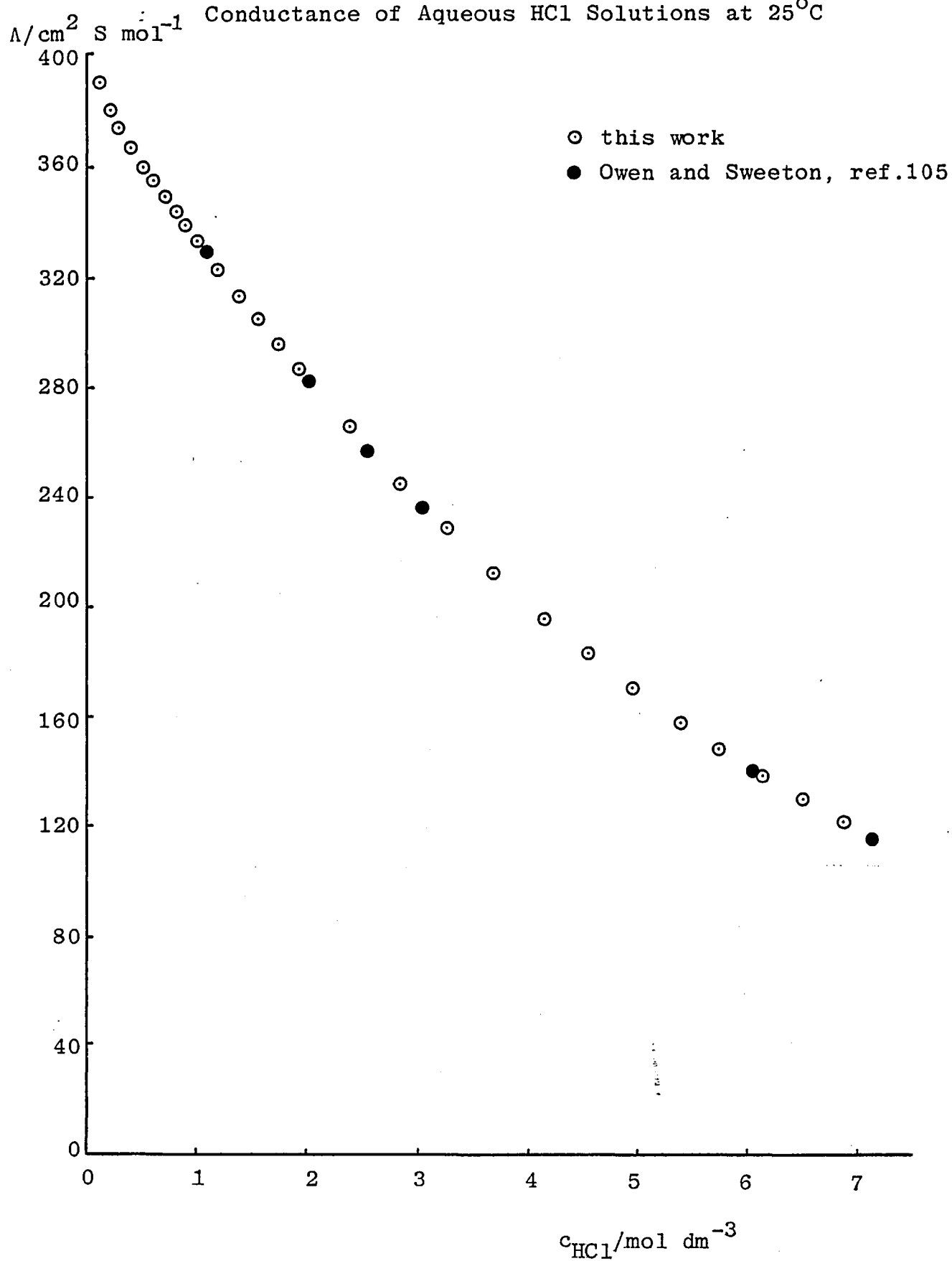
$c/\text{mol dm}^{-3}$	$\Lambda(\text{obs.})$	$\Lambda(\text{calc.})$	δ	Δ
0.1235	388.40	388.36	0.04	0.01
0.4356	364.64	364.66	-0.02	-0.01
0.7979	343.27	343.41	-0.14	-0.04
1.0646	328.67	328.67	0	0
1.4213	309.97	309.83	0.14	0.05
1.9471	284.06	283.92	0.14	0.05
2.0099	281.00	280.97	0.03	0.01
2.5326	257.33	257.43	-0.10	-0.04
3.0370	236.10	236.22	-0.12	-0.05
4.0663	197.75	197.73	0.02	0.01
4.0852	196.99	197.07	-0.08	-0.04
6.0408	139.71	138.72	0.99	0.71
7.1193	115.46	114.42	1.04	0.90
8.5732	89.71	89.16	0.55	0.61
9.7988	72.94	73.03	-0.09	-0.12

It is evident from table (IX.6) that the quoted standard deviation of $0.15 \text{ cm}^2 \text{ S mol}^{-1}$ for equation (IX.7) is overly optimistic. Both Owen and Sweeton's data and the present results indicate that in the region 5-9M the difference between the calculated and observed values is as large as $1 \text{ cm}^2 \text{ S mol}^{-1}$. These sets of results give higher molar conductances than the values calculated from this equation. Between 0.1 and 3M, the observed and calculated (eqn. IX.6) results in table (IX.6) are in better agreement than those for the present work (table IX.5).

In conclusion, it has been found that the accuracy of two fitting equations⁽¹²¹⁾ for the conductance of HCl solutions at 25°C is less than is claimed. The results from this present study are presented in fig.(IX.2). On this scale, Owen and Sweeton's data⁽¹⁰⁵⁾ are indistinguishable from those of the present author.

As mentioned in section (VIII.4.2), Owen and Sweeton reported two points of inflection in their HCl conductance results at concentrations of 0.25 and 3.5M. It was stated that both of these points shifted to lower concentrations as the temperature was decreased. However, they failed to report to which temperature the quoted concentrations referred. Their experiments were performed at 10°C intervals between 5°C and 65°C. Thus, as 25°C was the third lowest temperature they studied, it is not unreasonable to assume that these points of inflection were at somewhat lower concentrations at 25°C than the two values reported. Although this is in agreement with the point of inflection found for the present transference work (VIII.4.2) at 3.2m, no such points are apparent in fig.(IX.2).

fig.(IX.2) Concentration Variation of the
Conductance of Aqueous HCl Solutions at 25°C



PART THREE

GENERAL DISCUSSION

CHAPTER TEN

GENERAL DISCUSSION

In this chapter the various experimental data determined for concentrated aqueous HCl solutions will be discussed and used to calculate ion-constituent conductances and the Onsager transport coefficients introduced in chapter I. Section (X.4) deals with the proton-jumping mechanism which accounts for the anomalous transference numbers and conductances found for HCl. Finally, a brief overview of the project and ideas for future work are given.

X.1 Ion-Constituent Conductances

The molar conductance of a singly-charged ion-constituent R is given by⁽⁸⁾

$$\bar{\lambda}_R = T_R \Lambda \quad (\text{X.1})$$

Since both the transference numbers and conductances of HCl solutions have been measured up to 7M at 25°C we can now calculate $\bar{\lambda}_{\text{H}^+}^{\text{HCl}}$ and $\bar{\lambda}_{\text{Cl}^-}^{\text{HCl}}$.

All the Λ values given in table (IX.4) were fitted to a sixth-order polynomial in c ($\pm 0.6 \text{ cm}^2 \text{ S mol}^{-1}$) with the following coefficients

a_0	=	397.231	$\text{cm}^2 \text{ S mol}^{-1}$
a_1	=	-82.5246	$\text{cm}^2 \text{ S mol}^{-2} \text{ dm}^3$
a_2	=	25.9642	$\text{cm}^2 \text{ S mol}^{-3} \text{ dm}^6$
a_3	=	-10.7800	$\text{cm}^2 \text{ S mol}^{-4} \text{ dm}^9$
a_4	=	2.57182	$\text{cm}^2 \text{ S mol}^{-5} \text{ dm}^{12}$
a_5	=	-0.29930	$\text{cm}^2 \text{ S mol}^{-6} \text{ dm}^{15}$
a_6	=	1.34313×10^{-2}	$\text{cm}^2 \text{ S mol}^{-7} \text{ dm}^{18}$

These were then used to give the molar conductances at rounded concentrations shown in the second column of table (X.1). The best $T_{H^+}^{HCl}$ results presented in table (VIII.15) between 2.0 and 8.0m were fitted to a fourth-order polynomial in c (± 0.0003). Molal concentrations were converted to molarities as in section (IX.2.1). The coefficients of the fourth-order polynomial were

$$\begin{aligned} a_0 &= 0.881529 \\ a_1 &= -3.92071 \times 10^{-2} \text{ mol}^{-1} \text{ dm}^3 \\ a_2 &= 8.64028 \times 10^{-3} \text{ mol}^{-2} \text{ dm}^6 \\ a_3 &= -1.04343 \times 10^{-3} \text{ mol}^{-3} \text{ dm}^9 \\ a_4 &= 2.12142 \times 10^{-5} \text{ mol}^{-4} \text{ dm}^{12} \end{aligned}$$

Values of $T_{H^+}^{HCl}$ at rounded concentrations between 2.0 and 7.0M were then derived from these coefficients. For $c = 0.1-1.8 \text{ mol dm}^{-3}$, $T_{H^+}^{HCl}$ was taken as 0.836.

Table (X.1) presents the individual ion-constituent conductances calculated from eqn. (X.1) and (for $\bar{\lambda}_{Cl^-}^{HCl}$) from

$$\bar{\lambda}_{Cl^-}^{HCl} = \Lambda^{HCl} - \bar{\lambda}_{H^+}^{HCl} \quad (X.2)$$

Table (X.1)

$c/\text{mol dm}^{-3}$	$\Lambda^{\text{HCl}^\dagger}$	$\bar{\lambda}_{\text{H}^+}^{\text{HCl}^\dagger}$	$\bar{\lambda}_{\text{Cl}^-}^{\text{HCl}^\dagger}$
0.1	389.2	325.4	63.8
0.2	381.7	319.1	62.6
0.3	374.5	313.1	61.4
0.4	367.7	307.4	60.3
0.5	361.3	302.0	59.3
0.6	355.0	296.8	58.2
0.7	349.1	291.8	57.3
0.8	343.3	287.0	56.3
0.9	337.6	282.2	55.4
1.0	332.2	277.7	54.5
1.2	321.6	268.9	52.7
1.4	311.4	260.3	51.1
1.6	301.4	252.0	49.4
1.8	291.7	243.9	47.8
2.0	282.2	234.1	48.1
2.5	259.3	213.2	46.1
3.0	237.7	193.8	43.9
3.5	217.7	176.0	41.7
4.0	199.6	160.0	39.6
4.5	183.2	145.4	37.8
5.0	168.2	131.9	36.3
5.5	154.1	119.1	35.0
6.0	140.7	106.9	33.8
6.5	128.4	95.4	33.0
7.0	119.0	86.1	32.9

† units of $\text{cm}^2 \text{ S mol}^{-1}$

X.2 Testing of the Wishaw-Stokes Equation

In the discussion in chapter I on the applicability of the D-H-O model at higher solute concentrations, one of the more successful extensions of the theory, the Wishaw-Stokes (W-S) conductance equation⁽⁹⁾, was briefly mentioned. The D-H-O model accounts well for the concentration dependence of Λ_{HCl} in dilute solutions (0-0.09M)⁽¹²⁸⁾, and we shall now test how well the W-S equation applies at higher concentrations of HCl.

This equation is

$$\Lambda = \left(\Lambda^{\circ} - \frac{B_2 c^{\frac{1}{2}}}{1 + B a c^{\frac{1}{2}}} \right) \left(1 - \frac{B_1 c^{\frac{1}{2}}}{1 + B a c^{\frac{1}{2}}} \cdot F \right) \frac{\eta^{\circ}}{\eta} \quad (\text{X.3})$$

where the symbols are those introduced in section (I.2). In water at 25°C the limiting molar conductance $\Lambda_{\text{HCl}}^{\circ}$ is 426.06 cm² S mol⁻¹ (121), the electrophoretic term, B_2 , is 60.65 cm² S dm^{3/2} mol^{-3/2}, the relaxation term, B_1 , 0.2299 dm^{3/2} mol^{-1/2} and B is 0.3291×10^8 cm⁻¹ mol^{-1/2} dm^{3/2}. F is an extra factor for the relaxation effect due to Falkenhagen, given by

$$F = \frac{\exp(0.2929 \kappa a') - 1}{0.2929 \kappa a'} \quad (\text{X.4})$$

and $\kappa a'$ is defined by

$$\kappa a' = B a c^{\frac{1}{2}} \quad (\text{X.5})$$

where a , the distance of closest approach of cations and anions, is in cm. Robinson and Harned⁽¹²⁹⁾ have given values for a calculated from activity coefficient data by various authors. Thus, in the region 0.1-3M, a value of

3.6×10^{-8} cm has been found whilst for 0.1-4M, $a = 4.3 \times 10^{-8}$ cm has also been reported. Stokes⁽¹³⁰⁾ used a value of 4.4×10^{-8} cm to calculate $T_{H^+}^{HCl}$ for $c_{HCl} = 0.01-3.0M$.

Wishaw and Stokes also applied the viscosity correction (η^0/η) although this is now believed⁽¹³¹⁾ to over-compensate for the viscosity effect and that perhaps a correction of $(\eta^0/\eta)^{0.7}$ would be more appropriate. Wishaw and Stokes argued that the $c^{\frac{1}{2}}$ term of the Jones-Dole viscosity equation should be excluded as its affect had already been included in the derivation of (X.3). Since this term is swamped by the larger B' coefficient in concentrated solutions, it will be left out of this treatment. Consequently, I.C.T.⁽⁷²⁾ viscosity data at 25°C for $m_{HCl} = 0.1-8$ mol kg⁻¹ were fitted to a straight line plot of $(\eta/\eta^0 - 1)$ vs. c to yield the B' coefficient given by

$$\eta/\eta^0 = 1 + B'c \quad (X.6)$$

Conversion from m to c was performed as in section (IX.2.1). The slope of this plot, B' , was 0.06893 mol⁻¹ dm³.

The computer programme given in appendix 2 calculates Λ_{HCl} values from the W-S equation as a function of a , the only variable factor in equation (X.3). This programme can be amended for other uni-univalent electrolytes in water at 25°C by simply changing the Λ^0 value (line 00240) and the viscosity correction factor (E , line 00230).

Table (X.2) gives the observed (section IX.2.1) and calculated molar conductances (as a function of a) at some of the concentrations used in chapter IX. Λ has units of cm² S mol⁻¹. It is obvious from the table that equation (X.3) does not represent the concentration variation of the molar conductance for HCl as successfully as for NH₄Cl (for which the agreement was within $\frac{1}{2}\%$ up to 4M⁽⁹⁾). The equation is even less successful when a viscosity correction of $(\eta^0/\eta)^{0.7}$ is applied, e.g. at 6.9M for $a = 4.4 \times 10^{-8}$ cm, $\Lambda(\text{calc.}) = 230.7$ cm² S mol⁻¹. Thus the W-S equation fails

Table (X.2)

$c/\text{mol dm}^{-3}$	$\Lambda(\text{obs.})$	$\Lambda(\text{calc.})^\dagger$	$\Lambda(\text{calc.})^{\dagger\dagger}$	$\Lambda(\text{calc.})^{\dagger\dagger\dagger}$
0.1088	390.4	385.0	386.7	386.9
0.4995	360.5	350.3	354.2	354.8
0.9866	333.1	326.3	331.4	332.0
1.9134	286.1	294.4	300.3	301.1
2.8285	244.3	270.5	276.5	277.2
4.1366	195.2	242.9	248.7	249.4
4.9387	169.7	228.7	234.2	234.8
6.1089	138.1	210.5	215.5	216.1
6.8518	121.1	200.2	204.9	205.4

$^\dagger \quad a = 3.6 \times 10^{-8} \text{ cm}$
 $^{\dagger\dagger} \quad a = 4.3 \times 10^{-8} \text{ cm}$
 $^{\dagger\dagger\dagger} \quad a = 4.4 \times 10^{-8} \text{ cm}$

to account for the conductance of these solutions in which "abnormal" transport processes are taking place. It is apparent that at concentrations greater than 1M, the solution structure becomes increasingly disrupted and hence reduces the number of H^+ (or H_3O^+) ions participating in the proton-jump mechanism.

X.3 The Onsager Transport Coefficients for Aqueous HCl Solutions

The Onsager transport coefficients, l_{ij} , of HCl solutions up to 4M can now be calculated since the transference numbers and conductances have been measured and diffusion coefficient and activity data exist in the literature. Section (X.3.1) will present the interpolation of the required parameters at even concentrations between 0.1 and 4.0M and the calculation of l_{11}/c , l_{12}/c and l_{22}/c . These results will be compared with other literature l_{ij} coefficients in section (X.3.2).

X.3.1 Calculation of the l_{ij}

The equation given in section (I.3.1) for the calculation of the l_{ij} from experimental quantities was

$$\frac{l_{ij}}{c} = \frac{T_i^H T_j^e \Lambda}{F^2 z_i z_j} + \frac{v_i v_j D_v}{RTv(1 + m \ln \gamma / dm)} \quad (X.7)$$

where the symbols have been defined in that section. For this present treatment the ORR will be assumed so that

$$T_i^H = T_i^e \quad (X.8)$$

If subscripts 1 and 2 represent the cation and anion, respectively, then for HCl, $v_1 = v_2 = 1$, $v = 2$, $z_1 = 1$ and $z_2 = -1$.

Stokes⁽¹³²⁾ has determined diffusion coefficients for HCl up to 4M by the diaphragm cell method. As there are no other studies in the literature at higher concentrations, this is the upper limit for the present calculations. These data are presented in the fifth column of table (X.3).

In section (VIII.1.2) molal activity coefficient data from 0.01-3.0m were fitted to a polynomial in $m^{1/2}$. To calculate the parameter $(1 + m \ln \gamma / dm)$ these data were supplemented with γ values for 3.5-6.0m and refitted to a sixth-order polynomial in $m^{1/2}$. The fit was 0.001 and the coefficients were

a_0	=	0.988269	
a_1	=	-0.983649	$\text{mol}^{-1/2} \text{ kg}^{1/2}$
a_2	=	1.51293	$\text{mol}^{-1} \text{ kg}$
a_3	=	-1.21680	$\text{mol}^{-3/2} \text{ kg}^{3/2}$
a_4	=	0.678690	$\text{mol}^{-2} \text{ kg}^2$
a_5	=	-0.201424	$\text{mol}^{-5/2} \text{ kg}^{5/2}$
a_6	=	3.13743×10^{-2}	$\text{mol}^{-3} \text{ kg}^3$

Now

$$\begin{aligned}
 1 + m \ln \gamma / dm &= 1 + (m/\gamma)(d\gamma/dm) \\
 &= 1 + (m/\gamma)(1/2m^{1/2})(d\gamma/dm^{1/2}) \\
 &= 1 + (m^{1/2}/2\gamma)(d\gamma/dm^{1/2}) \quad (X.9)
 \end{aligned}$$

The computer programme also calculated values of $d\gamma/dm^{1/2}$, so that expression (X.9) can be determined as a function of concentration. Molal concentrations were converted to molarities as in section (IX.2.1) and the function $(1 + m \ln \gamma / dm)$ smoothed by fitting it to a sixth-order polynomial in c (fit ± 0.006). Values of $(1 + m \ln \gamma / dm)$ were then determined at rounded molarities via the coefficients

$$\begin{array}{llll}
 a_0 & = & 0.941614 & \\
 a_1 & = & 6.89024 \times 10^{-2} & dm^3 \text{ mol}^{-1} \\
 a_2 & = & 0.297939 & dm^6 \text{ mol}^{-2} \\
 a_3 & = & -0.172204 & dm^9 \text{ mol}^{-3} \\
 a_4 & = & 5.47234 \times 10^{-2} & dm^{12} \text{ mol}^{-4} \\
 a_5 & = & -8.54225 \times 10^{-3} & dm^{15} \text{ mol}^{-5} \\
 a_6 & = & 5.09959 \times 10^{-4} & dm^{18} \text{ mol}^{-6}
 \end{array}$$

These values appear in column six of table (X.3) except for the results at 0.1, 0.2 and 0.3M. In this concentration range the fitting was found to be less accurate and since in dilute solutions molalities and molarities are almost equal, the unsmoothed values at 0.1, 0.2 and 0.3m were used instead.

The best $T_{H^+}^{HCl}$ data have been fitted to a fourth-order polynomial in c in section (X.1). Using the coefficients reported there, values of $T_{H^+}^{HCl}$ were calculated at rounded values of c (column 3, table X.3).

Since we are only interested in concentrations up to 4M, the curve-fitting of the conductance data was carried out over a narrower concentration range (0.1-4.9M) than in section (X.1). The coefficients of the sixth-order polynomial (fit $\pm 0.5 \text{ cm}^2 \text{ S mol}^{-1}$) are

$$\begin{aligned}
a_0 &= 399.168 \text{ cm}^2 \text{ S mol}^{-1} \\
a_1 &= -96.5950 \text{ cm}^2 \text{ S dm}^3 \text{ mol}^{-2} \\
a_2 &= 53.6604 \text{ cm}^2 \text{ S dm}^6 \text{ mol}^{-3} \\
a_3 &= -32.8850 \text{ cm}^2 \text{ S dm}^9 \text{ mol}^{-4} \\
a_4 &= 10.7882 \text{ cm}^2 \text{ S dm}^{12} \text{ mol}^{-5} \\
a_5 &= -1.72199 \text{ cm}^2 \text{ S dm}^{15} \text{ mol}^{-6} \\
a_6 &= 0.106239 \text{ cm}^2 \text{ S dm}^{18} \text{ mol}^{-7}
\end{aligned}$$

The values derived from these coefficients at rounded c appear in column 4 of table (X.3).

Also given in the table are the $c = 0$ l_{ij} values calculated from literature limiting $T_{\text{HCl}}^{\text{H}^+}$ (8), $\Lambda_{\text{HCl}}^{\text{H}^+}$ (121) and D_v (132) data. If c is defined in mol dm^{-3} (as here) then the l_{ij}/c are most usefully expressed in units of $10^{13} \text{ mol J}^{-1} \text{ m}^2 \text{ s}^{-1}$. However, if as in chapter I, the units of c are mol m^{-3} then the order of magnitude is 10^{16} and not 10^{13} .

X.3.2 Discussion of the l_{ij} Values

Figure (X.1) shows the variation of the l_{ij}/c with $I^{1/2}$, where I is the ionic strength (mol dm^{-3}). For ease of representation, a factor of $15 \times 10^{-13} \text{ mol J}^{-1} \text{ m}^2 \text{ s}^{-1}$ has been subtracted from the l_{11}/c values. The solid lines are the results calculated from the present work and the individual points are those values given by Miller (12). Although at low concentrations the l_{11}/c and l_{12}/c from both studies are in good agreement, at higher concentrations the l_{11}/c values in particular diverge with the present values lower than those given by Miller. His l_{12}/c data show a much greater concentration dependence than do those from table (X.3). The magnitudes of the l_{12}/c values in comparison to those of l_{11}/c and l_{22}/c , are typical of a fully dissociated electrolyte.

Even more interesting are figs. (X.2) and (X.3) which show the variation of $l_{22}/v_2|z_2|c$ and l_{12}/v_1z_1c with

Table (X.3)

c_{HCl}	m_{HCl}	$T_{\text{H}^+}^{\text{HCl}}$	Λ^+	D_v^{++}	$(1+m \ln \gamma / dm)$	$10^{13} l_{11}^{+++}/c$	$10^{13} l_{12}^{+++}/c$	$10^{13} l_{22}^{+++}/c$
0	0	0.8209	426.06	3.336	1	37.6	0	8.20
0.1	0.1005	0.836	390.0	3.050	0.937 ₃	35.8	0.820	7.69
0.2	0.2013	0.836	381.8	3.064	0.954 ₉	35.1	0.849	7.58
0.3	0.3026	0.836	374.2	3.093	0.979 ₄	34.5	0.859	7.45
0.5	0.5062	0.836	360.8	3.184	1.032	33.3	0.910	7.27
0.7	0.7113	0.836	348.9	3.286	1.089	32.3	0.948	7.09
1.0	1.0221	0.836	332.5	3.436	1.183	30.8	0.962	6.82
1.5	1.5483	0.836	306.8	3.743	1.352	28.6	1.066	6.47
2.0	2.0854	0.830	281.9	4.046	1.528	26.2	1.068	6.22
2.5	2.6342	0.822	258.4	4.337	1.713	23.9	1.046	5.99
3.0	3.1954	0.815	237.3	4.658	1.909	21.9	1.078	5.79
3.5	3.7700	0.809	218.3	4.920	2.112	20.0	1.075	5.55
4.0	4.3589	0.802	200.3	5.17	2.314	18.3	1.090	5.35

⁺ units of $\text{cm}^2 \text{S mol}^{-1}$

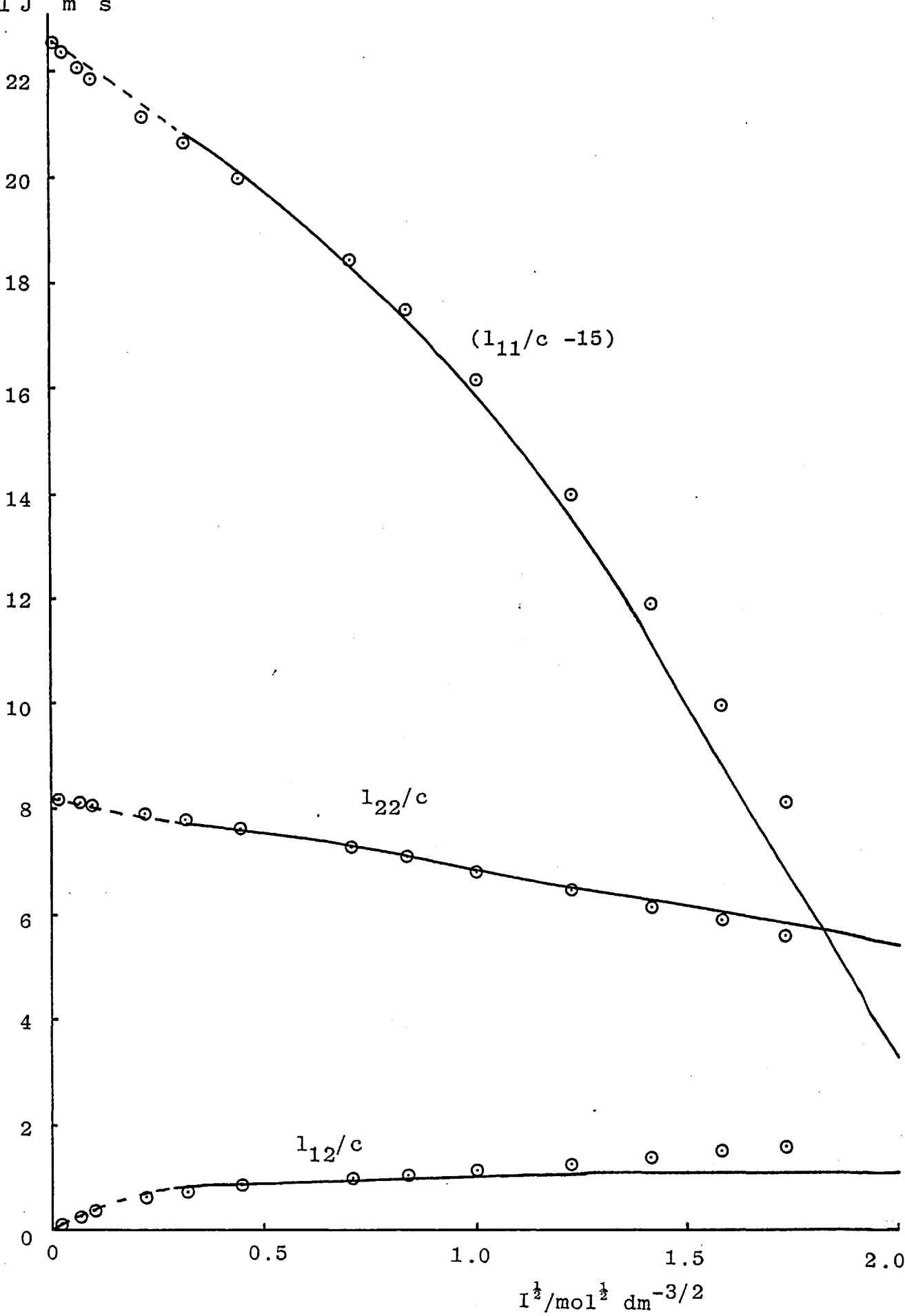
⁺⁺ units of $10^{-5} \text{cm}^2 \text{s}^{-1}$

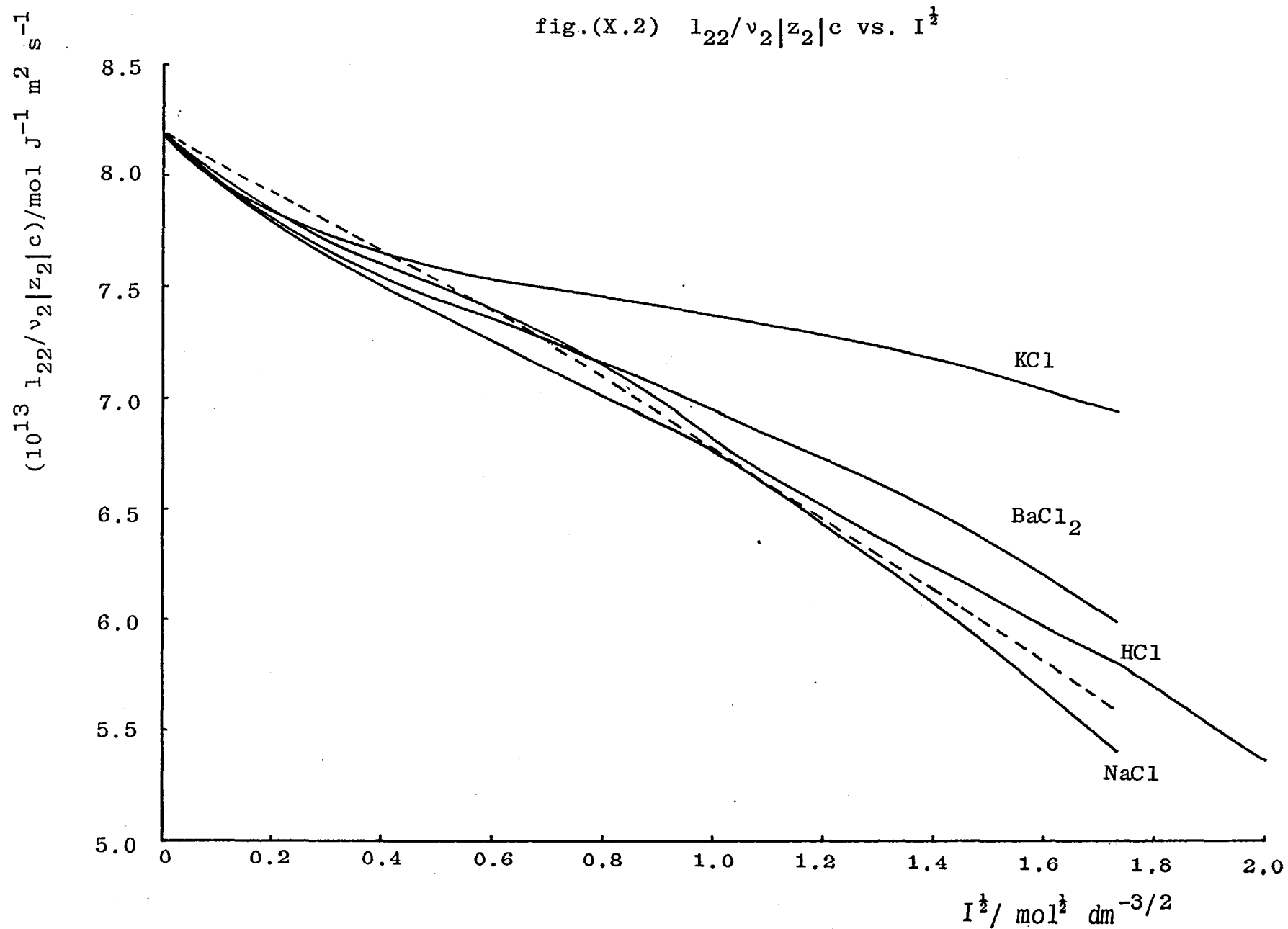
⁺⁺⁺ units of $\text{mol J}^{-1} \text{m}^2 \text{s}^{-1}$

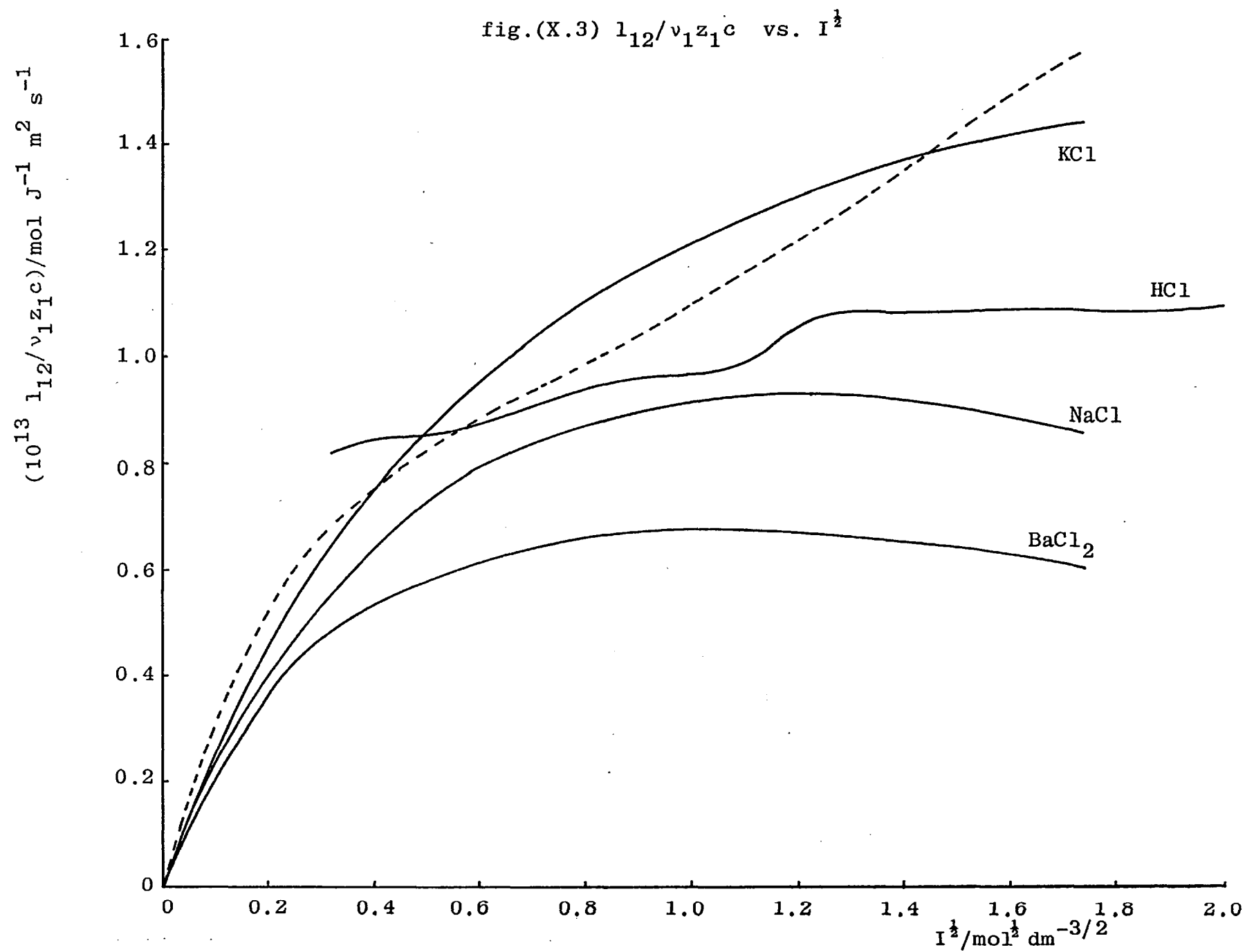
concentration. The solid lines represent Miller's⁽¹²⁾²¹⁵ results for NaCl, KCl and BaCl₂ and the present HCl work, the broken lines being Miller's HCl data. In fig.(X.2), the two sets of HCl $l_{22}/\nu_2|z_2|c$ are in good agreement, with those from the present work slightly larger than Miller's values above $I^{\frac{1}{2}} = 0.55 \text{ mol}^{\frac{1}{2}} \text{ dm}^{-3/2}$. In fig.(X.3) the present $l_{12}/z_1\nu_1c$ for HCl have a much smaller concentration dependence than the results from the previous study. Although the crossover between the HCl and KCl curves at $0.45 \text{ mol}^{\frac{1}{2}} \text{ dm}^{-3/2}$, which Miller⁽¹²⁾ considered to be anomalous behaviour, still exists with the present results, the crossover at $1.45 \text{ mol}^{\frac{1}{2}} \text{ dm}^{-3/2}$ is absent. This is a consequence of the transference number data used in the calculations. As there is no apparent reason why l_{12}/ν_1z_1c for HCl should increase sharply above 1M this indicates that the present e.m.f. transference results are more reliable than those of Harned and Dreby⁽⁶⁷⁾. However, the "bumps" in the new HCl curve do suggest some imperfections in the experimental data. It is interesting to note that a change of only ± 0.002 in the transference numbers would result in a smoother curve.

$(10^{13} l_{ij}/c)/$
 $\text{mol J}^{-1} \text{m}^2 \text{s}^{-1}$

fig.(X.1) l_{ij} vs. $I^{1/2}$ for HCl





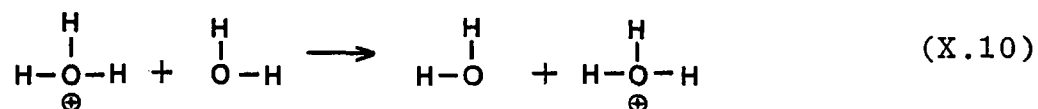


X.4 Proton Transfer in Solution

Ions formed by the self-dissociation of the solvent are often found to have abnormally high mobilities⁽¹³³⁾. Thus, not only do the H^+ and OH^- ions have high observed conductances in aqueous solutions, but so too do acetate ions in acetic acid, CH_3O^- ions in methanol and pyridinium ions ($\text{C}_5\text{H}_5\text{NH}^+$) in pyridine⁽¹³³⁾. In these systems the ions possess an extra transport mechanism in addition to the usual hydrodynamic migration ("bodily transport") mode common to other ions. This mechanism is referred to as proton transfer or proton-jumping. Taking $(\lambda_{\text{H}^+}^{\text{O}} - \lambda_{\text{K}^+}^{\text{O}})/\lambda_{\text{K}^+}^{\text{O}}$ as a measure of this extra motion, at infinitesimal ionic strength this ratio is 3.76 in water at 25°C ⁽¹⁰⁸⁾.

Many theories have been put forward to account for the proton transfer reaction, all of which assume some form of hydrogen-bonding in the solution. These have been extensively reviewed by Conway⁽¹³⁴⁾ and Erdey-Grúz and Lengyel⁽¹³³⁾. Four of these theories will be discussed here with the emphasis being placed on the reactions in aqueous solutions.

Glasstone, Laidler and Eyring's⁽¹³⁵⁾ rate process theory envisaged an energy barrier which had to be overcome for the reaction



to occur. In the absence of an applied electric field the activation energies (E) for the forward and backward reactions are equal and no net proton transfer occurs. However, when a field is applied, E for the forward reaction is decreased and the reaction in (X.10) proceeds favourably. Two steps are involved in (X.10) : the relative orientation

of the reactants into positions favourable for the second step, proton transfer, to take place. From the right-hand side of (X.10) it is apparent that the H_2O molecule is now in the wrong position to accept a further proton and hence the reaction stops here. At any one time only a small proportion of the H_3O^+ ions in the solution are involved in this process. Glasstone et al.⁽¹³⁵⁾ believed proton transfer to be the rate-determining step.

Bernal and Fowler⁽¹³⁶⁾ proposed a quantum-mechanical theory in which the proton "tunnelled" through an energy barrier once the species were in a favourable orientation. By considering the relative rates of this process and that of the rotation of the water molecule, they suggested that the proton tunnelling process was the rate-determining step. However, Glasstone et al.⁽¹³⁵⁾ have criticised this approach on the basis that the deuteron (D^+) would not be expected to exhibit abnormal conductance due to its larger mass which would greatly diminish the extent of the tunnelling. In fact the mobility of D_3O^+ is also abnormally high, although not as much as that of H_3O^+ .

Other theories⁽¹³³⁾ regard the proton in solution not as the H_3O^+ ion as above but as part of larger aggregates or clusters of water molecules. Proton transfer in such species as H_5O_2^+ , H_9O_4^+ etc. then occurs within the cluster. The size of the aggregates, and hence the extent of the abnormal conductance, would decrease with increasing temperature and increase with increasing pressure, in accordance with experimental findings.⁽⁸⁾

Conway, Bockris and Linton⁽¹³⁷⁾ rejected the concept of rotation of the H_3O^+ ion due to the equivalence of the three protons and the flatness of the molecule. Their calculations also showed that the rate of proton transfer for reaction (X.10) could not quantitatively account for the size of the experimentally observed abnormal conductance. In addition, the proton tunnelling mechanism of Bernal and Fowler⁽¹³⁶⁾ leads to a figure of twice the observed quantity.

Instead they obtained better agreement with experiment by assuming that the rate-determining step was the rotation of one water molecule in a H_9O_4^+ cluster followed by fast proton transfer.

Recently, Hertz et al.^(138,139) have applied linear response theory to this problem. They attribute the high conductance of aqueous HCl solutions to the breakdown in velocity correlations between the H^+ and OH^- ions of the solvent when the acid is added.

Whatever the actual processes taking place it is evident that proton transfer depends to a large degree upon hydrogen-bonding and the structure of the solution. Thus, the addition of a non-electrolyte (e.g. alcohols) to aqueous acid solutions decreases the mobility of the proton for mixtures up to ~ 90% of non-electrolyte⁽¹³³⁾. In pure methanol the molar conductance of HCl is very similar to that of NaCl indicating that proton transfer involving the CH_3OH_2^+ ion is less efficient than via the H_3O^+ ion.⁽¹⁴⁰⁾ The same effects have been observed in this work for increasing solute concentration, with $T_{\text{H}^+}^{\text{HCl}}$ decreasing with increasing m_{HCl} above ~ 1 mol kg⁻¹. This is also shown strikingly by the rapid decrease of $\bar{\lambda}_{\text{H}^+}$ and l_{11}/c with increasing concentration. Erdey-Grúz and Lengyel⁽¹³³⁾ report that the ratio $\bar{\lambda}_{\text{H}^+}/\bar{\lambda}_{\text{Cl}^-}$ has a value of 5.4 at 1m and 1.8 at 12m in HCl solutions at 25°C. From table (X.1), the corresponding ratios from the present work at 1M and 7M are 5.1 and 2.6, respectively.

X.5 Concluding Remarks

The most interesting aspect of this research has been the attempt to extend the concentration range of the direct m.b. technique. As has been shown, much thought concerning the volume correction has been required to produce reliable results for the system 3M KCl ← LiCl. Although this is the first such study, the author is confident that the technique can now be applied to many halide salts up to

relatively high concentrations. In the case of HCl solutions, however, it is clear that a more thorough study is necessary. The best approach may be to increase the experimental concentrations steadily from 0.2M to 0.4M to 0.6M etc., at each stage carefully examining the results for evidence of current dependence and abnormal behaviour. For solutes other than halides, the use of crown ethers as proposed in section (IV.2.2) may allow the volume correction to be determined accurately.

The work with gaseous electrodes described in the later sections of this thesis represents the most thorough determination yet of transference numbers of HCl solutions at 25°C. The use of such electrodes avoids errors due to dissolution of metal halide electrodes in concentrated solutions. As with the m.b. work, it is now possible to measure T_+ for a wide range of chloride salts and T_- for acids up to high concentrations with more certainty than has previously been possible.

APPENDIX ONEProgramme FITTER

Programme FITTER curve-fits data to polynomials of order 1 to 9 inclusive by a least mean squares method. The programme employs matrix inversion to obtain the polynomial coefficients. I am grateful to Mr. D.C. Kuo for the loan of the original programme.

PROGRAM FITTER

```

00100  FILE%2="TAPE5"
00110  DIMX(50),Y(50),Z(50),Z1(50),U(50),V(50)
00120  DIMA(10,10),B(10,10),C(10,1),D(10,1),E(10,10)
00130  PRINT"DEGREE OF FITTING REQUIRED"
00140  PRINT"PROGRAMME EXECUTION FOR UP TO 9TH POWER OF X"
00150  INPUTP
00160  MAT B=ZER(P+1,P+1)
00170  MAT C=ZER(P+1,1)
00180  MAT A=ZER(P+1,P+1)
00190  MAT D=ZER(P+1,1)
00200  MAT E=ZER(P+1,P+1)
00210  GOSUB 01030
00220  INPUT%2,N
00230  IFP=0THEN 00250
00240  GOSUB 01120
00250  INPUT%2,A$
00260  FORI=1TON
00270  INPUT%2,X(I),Y(I)
00280  NEXTI
00290  REM SORTS DATA INTO ASCENDING ORDER OF X
00300  FORI=1TON-1
00310  FORJ=I+1TON
00320  IFX(J)>X(I)THEN 00390
00330  X1=X(I)
00340  Y1=Y(I)
00350  X(I)=X(J)
00360  Y(I)=Y(J)
00370  X(J)=X1
00380  Y(J)=Y1
00390  NEXTJ
00400  NEXTI
00410  IFP=0THEN 00730
00420  REM STATISTICAL CALCULATIONS
00430  FORT=1TO(P+P)
00440  FORI=1TON
00450  U(T)=U(T)+X(I)**T
00460  V(T)=V(T)+Y(I)*X(I)**(T-1)
00470  NEXTI
00480  NEXTT
00490  REM ASSIGNS ELEMENTS OF MATRIX B

```

```

00500 FORI=1TOP+1
00510 FORJ=1TOP+1
00520 IFI+J><2THEN 00550
00530 B(I,J)=N
00540 GOTO 00570
00550 D=I+J-2
00560 B(I,J)=U(D)
00570 NEXTJ
00580 NEXTI
00590 REM ASSIGNS ELEMENTS TO VECTOR C
00600 FORI=1TOP+1
00610 C(I,1)=V(I)
00620 NEXTI
00630 MARGIN160
00640 MAT A=INV(B)
00650 MAT E=A*B
00660 MAT D=A*C
00670 FORJ=1TON
00680 FORI=1TOP+1
00690 Z(J)=Z(J)+D(I,1)*X(J)**(I-1)
00700 Z1(J)=Z1(J)+(I-1)*D(I,1)*(X(J)**(I-2))
00710 NEXTI
00720 NEXTJ
00730 PRINT
00740 PRINT
00750 PRINTTAB(20);"*";A$"*"
00760 PRINT
00770 PRINT
00780 PRINT,"X","Y(EXPT)","Y(CALC)","DERIV"
00790 PRINT,;
00800 FORI=1TO37
00810 PRINT"-";
00820 NEXTI
00830 PRINT
00840 FORI=1TON
00850 PRINT,X(I),Y(I),Z(I),Z1(I)
00860 NEXTI
00870 PRINT
00880 PRINT,;
00890 FORI=1TO37
00900 PRINT"-";
00910 NEXTI
00920 GOSUB 01190
00930 PRINT
00940 PRINT,"SIGMA    ",, "...";S2
00950 FORK=1TOP+1
00960 PRINT,"A";K-1,, "....";D(K,1)
00970 NEXTK
00980 STOP
00990 REM SUBROUTINE TEST
01000 REM TESTS FOR VALIDITY OF X INDEX
01010 REM NON-INTEGRAL X ARE ILLEGAL
01020 REM X VALUES > 9 AND < 0 ARE ILLEGAL
01030 IFP<0THEN 01060
01040 IFP>9THEN 01060
01050 IFP-INT(P)=0THEN 01110
01060 PRINT"DEFAULT DUE TO INCORRECT ENTRY"
01070 PRINT"DEGREE OF FITTING MUST BE INTEGRAL VALUE BETWEEN
      0 AND 9"
01080 PRINT

```

```

01090 PRINT
01100 GOTO 00130
01110 RETURN
01120 REM SUBROUTINE TEST2
01130 REM TEST FOR VALIDITY OF FIT REQUIRED
01140 IF N>P-1 GOTO 01180
01150 PRINT"ATTEMPT TO FIT ";N;"DATA POINTS TO POLYNOMIAL
      OF INDEX";P
01160 PRINT"FITTING ABORTED"
01170 STOP
01180 RETURN
01190 REM SUBROUTINE STANDARD DEVIATION
01200 REM DETERMINES ROOT MEAN SQUARE DEVIATION
01210 S1=0
01220 FOR I=1TON
01230 S1=S1+(Y(I)-Z(I))**2
01240 NEXTI
01250 S2=(S1/(I-1))*0.5
01260 RETURN

```

Appendix 1a.

In order to calculate the transference numbers directly from the E vs. $\ln(m\gamma/K)$ data the following amendments and additions were made to programme FITTER. The data are entered as $X(I) = \ln(m\gamma/K)$ and $Y(I) = E$ (in mV).

Amendments:

```

00110 DIMX(50),Y(50),Z(50),Z1(50),Z2(50),U(50),V(50)
00780 PRINT,"X","Y(EXPT)","Y(CALC)","DERIV","T"
00850 PRINT,X(I),Y(I),Z(I),Z1(I),Z2(I)

```

Addition:

```

00705 Z2(J)=1.946229E-2*Z1(J)

```

Line 705 multiplies the derivative $dE/d\ln(m\gamma/K)$ by a factor of $10^{-3} F/2RT$, where the factor of 10^{-3} converts mV to V.

Appendix 1b.

These changes apply to the calculation of transference numbers from the derivative $dE/d [\ln(m\gamma/K)]^{\frac{1}{2}}$ (section V111.1.1).

The data are entered as $X(I) = [\ln(m\gamma/K)]^{\frac{1}{2}}$ and $Y(I) = E$ (in mV).

Amendments:

```
00110 DIMX(50),Y(50),Z(50),Z1(50),Z2(50),U(50),V(50)
00780 PRINT,"X","Y(EXPT)","Y(CALC)","DERIV","T"
00850 PRINT,X(I),Y(I),Z(I),Z1(I),Z2(I)
```

Addition:

```
00705 Z2(J)=(9.731146E-3*Z1(J))/X(J)
```

where $9.731146E-3$ is the factor $10^{-3}F/4RT$.

Appendix 1c.

The changes to programme FITTER necessary to calculate transference numbers by Pikal's method allowed T to be determined from both experimental (TEX) and calculated (TCALC) values of $\bar{T}$. The data are entered as $X(I) = m\gamma/K$ and $Y(I) = \bar{T}$.

Amendments:

```
00110 DIMX(50),Y(50),Z(50),Z1(50),Z2(50),Z3(50),U(50),V(50)
00780 PRINT,"X","Y(EXPT)","Y(CALC)","DERIV","TEX","TCALC"
00850 PRINT,X(I),Y(I),Z(I),Z1(I),Z2(I),Z3(I)
```

Additions:

```
00703 Z2(J)=Y(J)+X(J)*LOG(X(J))*Z1(J)
00706 Z3(J)=Z2(J)-Y(J)+Z(J)
```

Line 00703 calculates the quantity $\bar{T} + (m\gamma/K) \ln(m\gamma/K) [d\bar{T}/d(m\gamma/K)]$.

APPENDIX TWO

This BASIC programme calculates Λ_{HCl} from the Wishaw-Stokes equation as a function of a , the distance of closest approach. For other uni-univalent electrolytes in water at 25°C the limiting value in line 00240 ($\Lambda_{\text{HCl}}^{\circ} = 426.06 \text{ cm}^2 \text{ S mol}^{-1}$) and the viscosity correction, $E(I)$, in line 00230 should be amended.

PROGRAM WS

```

00100 DIMC(30),C1(30),K(30),F(30),E(30),L1(30),L2(30),L(30)
00110 PRINT"ENTER DIST. CLOSEST APP.,A (IN ANGSTROMS)"
00120 INPUTA
00130 PRINT"ENTER NO. OF CONCS."
00140 INPUTN
00150 PRINT"ENTER MOLARITIES"
00160 FORI=1TON
00170 INPUTC(I)
00180 C1(I)=SQR(C(I))
00190 NEXTI
00200 FORI=1TON
00210 K(I)=0.3291*A*C1(I)
00220 F(I)=(EXP(0.2929*K(I))-1)/(0.2929*K(I))
00230 E(I)=1/(1+0.06893*C(I))
00240 L1(I)=426.06-((60.65*C1(I))/(1+0.3291*A*C1(I)))
00250 L2(I)=1-((0.2299*C1(I)*F(I))/(1+0.3291*A*C1(I)))
00260 L(I)=L1(I)*L2(I)*E(I)
00270 NEXTI
00280 PRINT"DIST. CLOSEST APP."
00290 PRINTA
00300 PRINT"CONC.", "LAMBDA", "F", "KA", "INV.VISC."
00310 FORI=1TON
00320 PRINTC(I),L(I),F(I),K(I),E(I)
00330 NEXTI
00340 STOP

```

APPENDIX THREE

An extensive literature search has been carried out for the transport properties of concentrated aqueous electrolyte solutions. The properties concerned were transference numbers, conductance, diffusion coefficients and viscosity. Several criteria were applied to the selection of the data which appear in appendices 3-6. Only studies *with* tabulated data at concentrations significantly above 1M have been included. Excluded have been references to solutes which are likely to hydrolyse or decompose in water and also all non-binary electrolytes. In some cases data of questionable accuracy have not been considered. Thus, in this appendix, the Soviet transference work discussed in Chapter III has been left out. Also, in this appendix all references prior to 1918 have been left out.

Despite the restrictions that these criteria impose there are still many studies which could be included in these appendices. Consequently, only transference numbers (the main subject of this thesis) have been tabulated in full (see below). For the conductance (app.4), diffusion coefficients (app.5) and viscosity (app.6) the tables have further been restricted to include only those references which have appeared since the publication of the last previous reliable compilation for each property. References to these collections are made at the beginning of each appendix.

Transference Number Measurements in Concentrated Aqueous
Solutions

Solute	Method	Max.conc.†	T/°C	Ref.
HCl	e.m.f.	3.0m	5-50	67
HCl	e.m.f.	14.7m	25	66
HBr	e.m.f.	5.5m	20-40	141
HClO ₄	m.b.	6.5m	25	107
HNO ₃	m.b.	13.6m	25	107
H ₂ SO ₄	e.m.f.	17m	0-60	142
LiCl	Hittorf	4.8M	15-25	110
LiCl	e.m.f.	3m	25	69
LiCl	Hittorf	3.0M	25	68
NaCl	Hittorf	2.9M	16-23	110
NaCl	i.m.b.	2.3M	25	91
NaCl	e.m.f.	6.1m	25	93
NaCl	e.m.f.	5.0m	25-70	92
NaCl	e.m.f.	5m	0-50	143
NaCl	Hittorf	5.0M	25	94
NaClO ₄	e.m.f.	10m	25	144
NaOH	e.m.f.	17.0m	20	145
KCl	Hittorf	3.2M	15-20	110
KCl	Hittorf	3.0M	25	26
KCl	m.b.	1.0M	25	27
KOH	e.m.f.	3m	25	146
KOH	e.m.f.	17.0m	20	145
RbCl	i.m.b.	4.7m	25	95
CsCl	i.m.b.	3.5m	25	95
MgCl ₂	e.m.f.	4.5M	25	147
MgCl ₂	e.m.f.	5.7m	25	33
CaCl ₂	e.m.f.	2.6m	25	148
CaCl ₂	tracer migration	5.3M	25	149
SrCl ₂	e.m.f.	3.0m	25	148
BaCl ₂	e.m.f.	1.7m	25	148
BaCl ₂	Hittorf, e.m.f.	1.0m	25	150
MnCl ₂	e.m.f.	5.5m	25	117
CoCl ₂	e.m.f.	4.0m	25	118
NiCl ₂	m.b., i.m.b., Hittorf	3.9M	25	65
NiCl ₂	e.m.f.	4M	25	151

Solute	Method	Max.conc. [†]	T/°C	Ref.
CuCl ₂	Hittorf	4M	35,45	45
CuBr ₂	Hittorf	3.6M	35,45	45
CuSO ₄	Hittorf	1.4m	25	17
ZnCl ₂	e.m.f.	12m	25,35	70
ZnCl ₂	Hittorf,e.m.f.	4.4M	25	71
ZnBr ₂	e.m.f.	16m	25	152
ZnI ₂	e.m.f.	10m	25	153
Zn(ClO ₄) ₂	e.m.f.	4.0m	25	76
Zn(ClO ₄) ₂	Hittorf	2.4M	25	154
ZnSO ₄	e.m.f.	2.2m	25	155
ZnSO ₄	e.m.f.	2m	25	156
AgClO ₄	Hittorf	4.2M	25	77
AgClO ₄	Hittorf	20%	25	157
AgNO ₃	Hittorf	7.6M	25	77
AgNO ₃	Hittorf	14m	25	158
AgNO ₃	Hittorf,e.m.f.	14m	25	13
AgNO ₃	m.b.	2.1m	25	107
CdCl ₂	e.m.f.	6.1m	25	159
CdCl ₂	Hittorf,e.m.f.	6m	25	15
CdBr ₂	e.m.f.	3.1m	25	159
CdSO ₄	e.m.f.	2.4m	25	155
CdSO ₄	e.m.f.	2.1m	25	160

[†] M = mol dm⁻³, m = mol kg⁻¹, % = wt.%.

APPENDIX FOURRecent Conductance Measurements in Concentrated Aqueous
Solutions

For earlier data see the compilations of Landolt-Börnstein⁽¹⁶¹⁾
and of Robinson and Stokes.⁽¹⁶²⁾

Solute	Max. conc.	T/°C	Ref.
LiCl	12M	25	163
LiCl	6.0M	25	104
LiCl	12M	-122-(-102)	164
LiBr	9.0m	23-60	165
LiI	7.6M	25	163
LiI	6.0M	25	104
LiClO ₃	100%	131.8	166, 167
LiClO ₄	4.0M	25	104
LiNO ₃	6.0M	25	104
Li ₂ SO ₄	2.9M	25-75	168
Li ₂ SO ₄	2.5M	25	169
NaCl	5.0M	25	170
NaCl	5.0M	25	104
NaCl	5.0M	25	165
NaBr	6.2M	25	163
NaBr	4.0M	25	104
NaBr	8.0m	0-55	165
NaI	7.6M	25	163
NaI	4.0M	25	104
NaClO ₄	9.0m	25	170
NaClO ₄	6.0M	25	104
NaNO ₃	7.0M	25	170
NaNO ₃	7.8M	25	171
NaNO ₃	6.0M	25	104
NaSCN	9.0M	25	170
Na ₂ SO ₄	3.1M	25-75	168
Na ₂ S ₂ O ₈	2.4M	15-25	172

Solute	Max. conc.	T/°C	Ref.
KF	5.0M	25	104
KCl	4.0M	25	104
KCl	4.0M	25	165
KBr	4.3M	25	163
KBr	4.0M	25	104
KBr	5.0m	0-55	165
KI	5.9M	25	163
KI	4.0M	25	104
KI	3.0m	0-45	165
K ₂ SO ₄	1.1M	25-75	168
RbCl	5.6M	25	163
RbCl	3.0M	25	173
RbCl	8.0m	23-60	165
RbBr	5.0M	25	163
RbI	4.9M	25	163
Rb ₂ SO ₄	2.4M	25-75	168
CsCl	7.1M	25	163
CsCl	9.0m	23-60	165
CsBr	4.1M	4-60	163
CsI	2.5M	25	163
Cs ₂ SO ₄	3.9M	25-75	168
NH ₄ Cl	5.3M	25	163
NH ₄ Cl	4.0M	25	104
NH ₄ Cl	5.0M	25	165
NH ₄ Cl	9.0m	23-60	165
NH ₄ Br	5.5M	25	163
NH ₄ Br	7.0m	0-45	165
NH ₄ I	6.9M	25	163
(NH ₄) ₂ S ₂ O ₈	2.6M	15-25	172
CH ₃ NH ₃ Cl	7.8M	25	163
(CH ₃) ₂ NH ₂ Cl	8.8M	25	163
(CH ₃) ₃ NHCl	7.4M	25	163
(CH ₃) ₄ NCl	5.6M	25	163
MgCl ₂	2.5M	25	169
MgCl ₂	5.7m	25	33
Mg(ClO ₄) ₂	3.0M	25	169
Mg(NO ₃) ₂	3.0M	25	169

Solute	Max.conc.	T/°C	Ref.
CaCl ₂	4.0M	25	169
Ca(NO ₃) ₂	4.0M	25	169
Ca(NO ₃) ₂	7.5M	0.35, 18.1	174
Ca(NO ₃) ₂	20.3 mol %	6-96	174
Ca(NO ₃) ₂	19.8%	17-107	175
BaCl ₂	1.3M	25	169
NiCl ₂	3.9M	25	65
CuSO ₄	1.3m	25	16
CuSO ₄	1.3m	20-70	176
ZnCl ₂	3.5M	25	71
Zn(ClO ₄) ₂	3.0M	25	154
AgClO ₄	5.6M	25	77
AgNO ₃	8.7M	25	77
CdCl ₂	6.0m	25	15
AlBr ₃	1.9M	25	177
Al(NO ₃) ₃	1.3M	25	169
InBr ₃	1.6M	25	177
In(NO ₃) ₃	2.6M	25	177
LaCl ₃	1.0M	25	169
MCl ₃ (M=La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu)	~4m	25	178
M(ClO ₄) ₃ (as for MCl ₃ but not Eu, Yb)	~4.6m	25	179
M(NO ₃) ₃ (as for MCl ₃ but not Eu, Tm)	4.3-6.8m	25	180

APPENDIX FIVERecent Diffusion Coefficient Measurements in Concentrated
Aqueous Solutions

Earlier data may be found in the compilation of Landolt-Börnstein.⁽¹⁸¹⁾

Solute	D of species [†]	Max.conc.	T/°C	Ref.
HNO ₃	Salt	9.2M	25	182
LiCl	Li ⁺	7.0M	-	183
LiCl	Cl ⁻	2.0M	-	183
LiCl	H ₂ O	2.5M	25	184
LiClO ₃	Salt	14.6M	25	185
NaCl	Salt	5.3M	25	186
NaCl	Salt	4.0M	25	170
NaCl	Na ⁺ , H ₂ O	2.2, 2.9M	25	184
NaCl	Na ⁺ , Cl ⁻	5.0M	10	187
NaClO ₃	Salt	6.3M	25	185
NaClO ₄	Salt	9.0M	25	170
NaNO ₃	Salt	7.0M	25	170
NaSCN	Salt	9.0M	25	170
Na ₂ SO ₄	Salt	1.5M	25	188
KCl	Salt	4.0M	25	189
KCl	K ⁺	4.0M	25	190
KCl	Cl ⁻	4.0M	25	183
KCl	Cl ⁻	4.0M	25	191
KCl	H ₂ O	3.0M	25	184
KCl	H ₂ O	4.0M	25	191
KCl	H ₂ O	4.0M	25	192
KCl	K ⁺ , Cl ⁻ , H ₂ O	3.0M	10	191
KBr	H ₂ O	3.5M	25	192
KI	K ⁺ , I ⁻	6.0M	25	190
KI	H ₂ O	6.0M	25	191
KI	H ₂ O	4.7M	25	192

Solute	D of species	Max.conc.	T/°C	Ref.
KI	K^+, I^-	5.0M	10	190
KI	H_2O	5.0M	10	191
RbCl	Salt	3.0M	25	173
RbCl	Cl^-, H_2O	2.7M	25	184
RbCl	H_2O	5.7M	25	192
RbBr	H_2O	3.8M	25	192
RbI	H_2O	4.6M	25	192
CsCl	Cs^+, Cl^-, H_2O	2.4-2.8M	25	184
CsCl	Cs^+, Cl^-, H_2O	4.0M	25	191
CsCl	Cs^+, Cl^-, H_2O	4.0M	10	191
CsCl	H_2O	5.2M	25	192
CsBr	H_2O	3.8M	25	192
CsI	H_2O	1.7M	25	192
$MgCl_2$	Mg^+, Cl^-	3.9M	25	187
$MgCl_2$	Mg^+, Cl^-	3.9M	10	187
$MgSO_4$	Salt	2.8M	25	188
$CaCl_2$	Salt	5.6M	25	186
$CaCl_2$	Ca^{2+}, Cl^-	4.0M	25	193
$BaCl_2$	Salt	1.6M	25	189
$BaCl_2$	Ba^{2+}, Cl^-, H_2O	1.5M	25	193
$NiCl_2$	Ni^{2+}, Cl^-, H_2O	4.0M	25	65
$CuSO_4$	Salt	1.3M	25	16
$CuSO_4$	Salt	1.4M	25	194
$ZnCl_2$	Salt	3.9M	25	71
$Zn(ClO_4)_2$	Salt	3.2M	25	154
$ZnSO_4$	Salt	3.2M	25	195
CdI_2	I^-	1.0M	25	196

† Salt refers to the mutual diffusion coefficient. Otherwise D is the tracer (self) diffusion coefficient.

APPENDIX SIXRecent Viscosity Measurements in Concentrated Aqueous
Solutions

See also the earlier collections of Landolt-Börnstein⁽¹⁹⁷⁾
and Stokes and Mills.⁽¹³¹⁾

Solute	Max.conc.	T/°C	Ref.
HCl	8.5m	25	198
LiCl	1.2m	5-95	199
LiBr	8.2M	25	200
LiI	2.0M	25	200
LiClO ₃	100%	25,131.8	166,167
NaCl	1.2m	5-95	199
NaCl	5.8m	25-50	201
NaCl	5.0M	25	170
NaBr	7.0m	25	4
NaBr	7.0m	5-55	5
NaI	3.0m	25	4
NaI	3.0m	5-45	5
NaI	4.0M	25	200
NaClO ₄	9.0M	25	170
NaNO ₃	7.0M	25	170
NaNO ₃	7.8M	25	171
NaNO ₃	7.3M	25	200
NaSCN	9.0M	25	170
KF	7.0m	25	4
KF	7.0m	5-55	5
KCl	4.6m	20-50	201
KCl	1.0m	5-95	199
KBr	5.0m	25	4
KBr	5.0m	5-55	5
KBr	1.2m	5-95	199
KI	3.0m	25	4
KI	3.0m	5-45	5

Solute	Max. conc.	T/°C	Ref.
KI	1.0m	5-95	199
KNO ₃	3.0M	25	200
NH ₄ Cl	7.0m	10-60	5
NH ₄ Cl	5.0M	25	200
NH ₄ Br	7.0m	25	4
NH ₄ Br	7.0m	5-55	5
NH ₄ Br	3.4M	25	200
NH ₄ I	4.8M	25	200
(NH ₄) ₂ SO ₄	4.0m	25	198
Me ₄ NBr	4m	15-35	202
Et ₄ NBr	4m	15-35	202
Pr ₄ NBr	4m	15-35	202
Bu ₄ NBr	4m	15-36	202
MgCl ₂	5.7m	25	33
MnCl ₂	5.8m	25	117
CoCl ₂	4.0m	25	118
NiCl ₂	4.3M	25	151
NiSO ₄ ·6H ₂ O	50-60%	20-60	203
CuSO ₄	1.4M	25	194
CuSO ₄	1.3m	20-70	176
AgClO ₄	5.6M	25	77
AlBr ₃	1.3M	25	177
InBr ₃	1.6M	25	177
In(NO ₃) ₃	2.6M	25	177
MCl ₃ (M=Pr, Eu, Gd, Tm, Yb, Lu)	~4m	25	204
M(ClO ₄) ₃ (M=La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu)	~4.6m	25	205
M(NO ₃) ₃ (as for M(ClO ₄) ₃ but not Eu, Tm)	4.3-6.8m	25	206

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