SOME STUDIES IN THE CONDUCTIVITIES
OF RELATIVELY CONCENTRATED ELECTROLYTE SOLUTIONS

A Thesis submitted to the University of London
for the Degree of Doctor of Philosophy

By

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PREFACE

The work described in this Thesis was carried out in the Laboratories of the Chemistry Department, Battersea College of Technology, under the general supervision of the Head of the Department, the late Dr. F. R. Goss, and latterly, Dr. J. E. Salmon, and the direction of Dr. V. S. Griffiths.

The author wishes to express his most sincere appreciation of the constant help and encouragement received from Dr. Griffiths during the course of the work.

Grateful thanks are also due to Dr. D. I. Stock of the Department for valuable help and assistance and to Mr. R. Calvert of Research and Development Laboratories, Wayne-Kerr Laboratories, who designed and developed the transformer ratio-arm bridges used for the conductivity measurements.
ABSTRACT

The measurement of conductivities of relatively concentrated electrolyte solutions using an annular glass cell, without contacting or dipping electrodes, is described. An electrolyte solution in the cell serves as a conductor linking the voltage and current transformers of a transformer ratio-arm bridge operating at audio-frequencies which is also described. The use of the transformer bridge for such measurements is discussed from a theoretical standpoint.

Conductivity measurements were carried out on a series of aqueous solutions of uni-univalent salts and acids, bi-bi-, bi-unii-, uni-ter-, uni-tetra- and bi-tetravalent salts, and these are reported in terms of $\Lambda$ and $\sqrt{c}$. Where accurate data obtained using conventional apparatus are available agreement is good.

Viscosity-corrected $\Lambda$, $\sqrt{c}$ curves obtained for uni-univalent electrolytes indicate, by their general similarity of shape, that the use of the approximate viscosity correction for conductivity, $\Lambda \eta / \eta_0$, is justified.

A method for the evaluation of the mean diameter of the ions of an electrolyte using a modification of the Onsager conductivity equation is discussed and applied to the conductivity data obtained for uni-univalent electrolytes and for barium chloride for a range of concentrations. With the exception of lithium chloride, the values are nearly constant for concentrations between 0.1 and 1.0 molar and are in striking agreement with those obtained from activity coefficient data. The results for lithium chloride are greatly improved for the higher concentrations when the conductivity data used are corrected for viscosity before substitution in the modified Onsager equation.
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SECTION Ia

APPARATUS AND EXPERIMENTAL TECHNIQUE
(i) Measurement of Resistance

(a) Description of the Transformer Ratio-Arm Bridge

The conductivities of the electrolyte solutions were measured using a transformer ratio-arm bridge and the circuit is described in some detail below.

The value of an impedance $Z$ is given by the ratio $E/I$ where $E$ is the voltage across the impedance and $I$ is the current flowing through it. The most direct way of measuring impedance therefore is to measure $E$ and $I$ and compute the ratio. Unfortunately, absolute measurements of voltage or current are extremely difficult to make with any degree of accuracy. In practice it is far better to make a comparison measurement, the unknown being compared with a standard impedance by means of a bridge circuit. Thus only ratios are involved, which can be established more easily and accurately than absolute quantities.

Let the subscripts $x$ and $y$ refer to the unknown and standard, respectively. Then

$$Z_x = \frac{E_x}{I_x}$$

and

$$Z_y = \frac{E_y}{I_y}$$

or

$$Z_x = \frac{E_x}{E_y} \times \frac{I_y}{I_x} \times Z_y \quad (1)$$
Figure 1 - Transformer Ratio-Arm Bridge Basic Circuit

Figure 2 - Circuit of Bridge showing impedances divided into resistive and reactive components
This is the fundamental equation for the measurement of impedance, whatever method is employed, and it can be seen that there are two ratios, namely, \( \frac{E_x}{E_y} \) and \( \frac{I_y}{I_x} \), which govern the range of measurement with a standard \( Z_y \).

The conventional method of determining impedance is by means of a modification of the Wheatstone Bridge. This suffers from a number of disadvantages, the most important of which is that the conventional circuit cannot be achieved in practice, except over a limited range of measurement. To ensure any degree of accuracy, a Wagner earth arrangement is desirable, requiring a double balance. This method is inconvenient in practice and only "two-terminal" measurements are possible over any range; as discussed later, this is a severe restriction.

The Transformer Ratio-Arm Bridge described here offers many advantages over the conventional method. The basic circuit of such a bridge is shown in Fig.1. The subscripts \( x \) and \( y \) refer to the unknown and standards side of the bridge, respectively.

\( T_1 \) is a voltage transformer to the primary of which the source is connected. The secondary winding is tapped to give sections having \( N_x \) and \( N_y \) turns.

\( T_2 \) is a current transformer, the primary of which is tapped to give \( n_x \) and \( n_y \) turns, and the secondary winding is connected to the detector.

If we assume at this stage that the transformers are ideal and that \( Z_y \) is adjusted so as to give null indication in the detector, then under these conditions zero flux is produced in the current transformer, and
Before proceeding further, it is necessary to justify the statement that the actual transformers used in the bridge may be considered ideal.

Firstly, the transmission loss between the primary and secondary of the voltage transformer is of no consequence. The only effect of this loss is to reduce the sensitivity of the bridge, and this can be compensated for by increasing the gain of the detector. The important factor is the actual voltage ratio between the unknown and standard, both of which are tapped across the secondary windings of the voltage transformer. This voltage ratio across the bridge is based on three factors: (i) the turns ratio, (ii) the flux linkage, and (iii) the effective series resistance of the windings compared with that of the load.

The voltage induced in a coil is proportional to the number of turns multiplied by the rate of change of flux. Therefore, provided all the turns of the bridge windings embrace the same flux, the ratio of induced voltages is equal to the turns ratio. The windings are, in fact, wound with precision on a common core of high permeability material. The ratio of core flux to air flux is of the order of 1,000 : 1, and the geometrical arrangement of the two windings is such that air flux is largely common to both. Even if the windings were so badly arranged that none of the air flux was common, the error between the induced voltage ratio and the turns ratio would be only 0.01 per cent. If necessary this error can be reduced to a few parts in a million.

The remaining source of error to be considered is the voltage drop in the windings. Ignoring spurious shunt impedances for the moment, the
Figure 1 - Transformer Ratio-Arm Bridge Basic Circuit

Figure 2 - Circuit of Bridge showing impedances divided into resistive and reactive components
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If we assume at this stage that the transformers are ideal and that $Z_y$ is adjusted so as to give null indication in the detector, then under these conditions zero flux is produced in the current transformer, and
there is no voltage drop across its windings. The detector sides of both the unknown and standard impedances are therefore at neutral potential. The voltages across \( Z_x \) and \( Z_y \) are then \( E_x \) and \( E_y \) respectively.

Therefore

\[
I_x = \frac{E_x}{Z_x}
\]

and

\[
I_y = \frac{E_y}{Z_y}
\]

For conditions of zero core flux in the current transformer, the algebraic sum of the ampere-turns must be zero. Therefore

\[
I_{nx} = I_{ny}
\]

Substituting for \( I_x \) and \( I_y \) we have

\[
\frac{E_x}{Z_x} N_x = \frac{E_y}{Z_y} N_y
\]

or

\[
Z_x = \frac{E_x}{E_y} \times \frac{n_x}{n_y} \times Z_y \tag{2}
\]

For an ideal transformer the voltage ratio is equal to the turns ratio. Therefore

\[
Z_x = \left( \frac{N_x}{N_y} \times \frac{n_x}{n_y} \right) Z_y
\]

It will be seen from the above equation that, unlike the conventional bridge, two ratios are available, namely, \( \frac{N_x}{N_y} \) and \( \frac{n_x}{n_y} \). Thus, by means of a suitable combination of tappings on the two transformers, it is possible to produce a very high ratio product permitting a very high range of measurement.
Before proceeding further, it is necessary to justify the statement that the actual transformers used in the bridge may be considered ideal.

Firstly, the transmission loss between the primary and secondary of the voltage transformer is of no consequence. The only effect of this loss is to reduce the sensitivity of the bridge, and this can be compensated for by increasing the gain of the detector. The important factor is the actual voltage ratio between the unknown and standard, both of which are tapped across the secondary windings of the voltage transformer. This voltage ratio across the bridge is based on three factors: (i) the turns ratio, (ii) the flux linkage, and (iii) the effective series resistance of the windings compared with that of the load.

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The remaining source of error to be considered is the voltage drop in the windings. Ignoring spurious shunt impedances for the moment, the
Figure 3 - Bridge circuit with 10 tappings on the standards side of the voltage transformer
load current in the unknown windings is the current in the impedance being measured. In the measurement of impedances of 10 to 100 megohms, the total series impedance of both the voltage and current transformer windings is approximately 100 ohms. Even if this total series impedance was concentrated in one arm of the bridge, the worst error would only be 0.001 per cent. In practice this error is negligible.

It will be shown later that the effects of shunt loading can be effectively compensated, so that it is reasonable to assume that for all practical purposes the transformers are ideal.

The practical arrangement of the bridge is shown in Fig. 2, where the unknown and standard impedances have been divided into their resistive and reactive components, \( G_x, G_y, X_x, X_y \) respectively.

Since at balance the in-phase and quadrature ampere-turns must separately sum to zero, the conductance standard \( G_y \) and the reactance standard \( X_y \) may be connected to different tappings on the voltage transformer to balance out the currents caused by the unknown impedance.

This independence of the components of current may be put to advantage in many ways. The effect of impurities in the standards, such as dielectric loss in capacitors, can be balanced out by the insertion of compensating components across the "unknown" side of the bridge. The leakage and capacitance across the test probe can also be removed in this manner.

Fig. 3 shows a bridge arrangement in which the voltage transformer winding feeding the standards has 100 turns and is tapped at every 10 turns, the tappings being brought out to a decade switch and connected to the
Figure 4

Bridge circuit with four conductance standards connected to decade switches
standard. For convenience only the conductance standard is shown.

The equation for balance conditions may be written

\[ G_x = (G_y N_y) \frac{n_x}{N_x n_x} \quad (3) \]

It is evident that if the product term \( G_y N_y \) is taken to represent the standard, it is of no importance whether the number of turns is fixed and the conductance given ten different values (the normal procedure with a decade box), or the conductance fixed and the number of turns given ten different values. By employing the latter method only one standard per decade is necessary.

In Fig. 4 the tappings on the standard side are taken to four switches wired in parallel.

Each switch connects through a fixed standard to a common tap on the current transformer. The conductances are given the relative values 1, 10, 100, and 1,000. The effect is exactly the same as that obtained by having a transformer of fixed voltage and four-dial decade box.

Continuing with tappings to four more switches, each of which is connected through a fixed standard capacitor to the current transformer, the effect of adding a four-dial decade capacitor is produced.

So far only step-by-step adjustment of the standards has been considered. It has been shown how the decade boxes for resistance and capacitance standards normally associated with accurate bridge measurements can be replaced by a few fixed standards and banks of switches fed from taps on the voltage transformer.
Figure 5 - Circuit arrangement with a continuously variable reactance

Figure 6 - Circuit arrangement with a continuously variable conductance
Decade switching is essential when accuracies of better than 1 per cent are required. However, the provision of such switches alone makes the balancing of the bridge a slow and often laborious process, especially if the unknown is a complex impedance. Fortunately, it is possible with the transformer ratio bridge, for continuously variable controls to be added without detracting from the accuracies of the decade standards.

A continuously variable reactance is conveniently provided by an air-dielectric capacitor whose residual capacitance $C_0$ is balanced by a pre-set trimmer connected to a transformer winding of opposite sense. This arrangement is shown in Fig.5.

A continuously variable conductance control is provided by combining a potentiometer with a fixed resistor as shown in Fig.6.

The best practical compromise for accuracy and ease of operation is to use a single decade and a continuously variable control for accuracies of the order of 1 per cent. Second and third decades need only be used when it is necessary to increase the accuracy up to 0.01 per cent or when it is required to obtain very high discrimination at balance to measure small changes in impedance.

Since only one fixed standard per decade is required, it is a simple matter to make each one effectively pure. The technique adopted is illustrated in Fig.7, applied to a capacitance standard.

At a given frequency a capacitor can be represented by a pure capacitance $C_y$ shunted by a resistance $R_L$. The problem is to remove the effect of $R_L$ leaving only the pure quadrature component $C_y$. It is therefore necessary
Figure 7  -  Circuit arrangement for making a capacitance standard effectively pure
to cancel the ampere-turns produced by \( R_L \) in the current transformer. This is done by feeding the current through a fixed trimming resistor \( R_t \) into the opposite side of the transformer. The current is adjusted to give exact cancellation by adjusting the voltage at the wiper of the preset potentiometer \( P \). If the voltage applied to the capacitor is \( E \) and a fraction of this, \( kE \), is applied to the trimming resistor, the effect of \( R_L \) is removed completely when

\[
k = \frac{N_v}{N_t} \times \frac{R_t}{R_L}
\]

The adjustment is independent of the voltage, and therefore holds for all positions of the tapping switch.

The effect of a reactance term associated with the conductance standard can be removed in the same way. At a given frequency the standard can be regarded as a pure conductance shunted by a reactance. The reactance causes an unwanted quadrature current to flow in the current transformer. This can be cancelled out by a quadrature current of opposite sign, the ampere-turns being made equal. It is generally convenient to use a capacitor for the trimming control and to give it the correct sense by connecting it either to the unknown or to the standard side of the transformer, according to the sign of the spurious reactance.

To keep the number of standards to a minimum the in-phase and quadrature standards are chosen to cover approximately the same range of impedance as the operating frequency of the bridge. Occasionally, it is required to measure a complex impedance the in-phase and quadrature components of
Figure 8 - Method for shifting the effective impedance of one standard with respect to another.

Figure 9 - A "three-terminal" network.
which are of quite different orders. It is therefore convenient to be able to shift the effective impedance of one standard with respect to the other. Since the voltage transformer is tapped to provide the decade adjustment of each standard, the current transformer must be tapped to shift the relative ranges of the standards. This is shown diagrammatically in Fig. 8. A pair of taps at, say, 10 turns and 100 turns will give a 10 : 1 shift.

This facility must, however, be used with caution. If a measurement were made where the quadrature currents are in the ratio of say 1,000 : 1, perfect standards would be necessary and there would have to be no losses or stray capacitances associated with the wiring. Any small out-of-phase current introduced by the major component standard could give rise to a considerable error in the measurement of the minor component of the unknown impedance. This will be dealt with in more detail under the subject of 3-terminal measurements.

The flexibility of the bridge is improved by adding a pair of set-zero controls, taking advantage of the fact that at balance there is no interaction between the current paths leading into the current transformer.

A small variable capacitor provides a suitable set-zero for reactance and a fixed resistor, combined with a potentiometer, provides the control for conductance. They are adjusted to bring the bridge to balance with all the standards set to zero, before the unknown is applied.

As mentioned earlier, "two-terminal" measurements can impose severe restrictions and consequently it is advantageous to consider a "three-terminal" network as shown in Fig. 9.
Figure 10 - The "three-terminal" network applied to the bridge

Figure 11 - Theoretical treatment of the "three-terminal" network
The impedance to be measured is $Z_x$, but the effect of impedances $Z_{AC}$, $Z_{BC}$ must be removed before a measurement of $Z_x$ can be made. Fig. 10 shows the 3-terminal network applied to the bridge.

The arrangement can be considered as a π-network, where $Z_{EN}$ shunts the voltage transformer and $Z_{IN}$ shunts the current transformer. Once again it is assumed that the transformers are ideal.

At balance there is no voltage across the current transformer, and the only effect of $Z_{IN}$ is to reduce the input impedance to the detector, and consequently the off balance sensitivity. If necessary this can be compensated by increasing the detector gain.

$Z_{EN}$ shunts the unknown winding of the voltage transformer and has the full voltage across it at balance. It causes a voltage drop determined by the ratio of its transformed impedance at the transformer primary, to the source impedance. However, a voltage drop also occurs in the standards side of the voltage transformer in proportion to the turns ratio. The bridge is therefore unaffected and no balance error is introduced. The only effect is to again reduce the sensitivity, which can be restored either by increasing the source voltage or the detector gain.

In practice the transformers have a finite short-circuit impedance and shunt loading can cause errors. Difficulty with shunt loading is most likely to arise on the high impedance ranges. The error caused by the loading of the unknown itself is greatest at the low impedance end of each range, amounting to approximately 1 part in $10^5$ (a typical figure is
100 ohms total effective series impedance for both transformers in the measurement range 10 to 100 megohms). Shunts having a hundredth of the impedance of the unknown would therefore cause errors of 0.1 per cent, a thousandth of the impedance of the unknown 1 per cent, and so on. In the case quoted one would expect shunt impedances of 10,000 ohms to cause errors of about 1 per cent when using the bridge on the 10 to 100 megohm range.

It is only when the shunt impedances are very low compared with the impedance under measurement that errors arising from them are likely to be important, and in these circumstances they can be corrected by a simple calculation.

Since the impedance to be measured is very high compared with the shunt impedances, it can be considered as an open-circuit and the shunting effect on each side of the unknown may be considered separately.

Without any loading, the normal balance equation for the bridge applies. We have therefore

\[ Z_x = \frac{E_x}{E_y} Z_y \]  \hspace{1cm} (4)

Due to the effect of the shunt \( Z_{EN} \), the voltage applied to the unknown is reduced to \( E \) (see Fig.11).

To restore balance \( Z_y \) must be changed to, say, \( Z_m \). Therefore

\[ Z_x = \frac{E_x}{E_y} Z_m \]

But

\[ E = E_x \left( \frac{Z_{EN}}{Z_{EN} + Z_e} \right) \]
where $Z_e$ is the effective series impedance of the transformer winding.

Therefore

$$Z_x = \left( \frac{\frac{Z_{EN}}{Z_e} + \frac{Z_e}{\frac{E_x}{E_y}}} \right) Z_m \tag{5}$$

where $\left( \frac{E_x}{E_y} \right) \frac{Z_m}{Z_e}$ is the value read on the bridge.

For simplicity, consider unity ratio of the voltage transformer: then

$$Z_x = \left( \frac{1}{1 + \frac{Z_e}{\frac{E_x}{E_y}}} \right) Z_m \tag{6}$$

This may be expressed as a series as

$$Z_x = Z_m \left[ 1 - \frac{Z_e}{Z_{EN}} + \left( \frac{Z_e}{Z_{EN}} \right)^2 - \ldots \right]$$

For almost all practical cases the second and higher order terms are so small that they may be neglected. An adequate approximation is then given by

$$Z_x = \left( 1 - \frac{Z_e}{Z_{EN}} \right) Z_m$$

A similar argument applies to the error arising from loading the current side of the bridge. Under these conditions it can be shown that

$$Z_x = \left( 1 - \frac{Z_i}{Z_{IN}} \right) Z_m$$

where $Z_i$ is the effective series impedance of the current transformer winding.

Therefore the true value of the unknown impedance with both voltage
and current transformer shunting is given by

\[ Z_x = \left(1 - \frac{Z_o}{Z_{EN}}\right) \left(1 - \frac{Z_i}{Z_{IN}}\right) Z_m \]

or

\[ Z_x = \left(1 - \frac{Z_o}{Z_{EN}} - \frac{Z_i}{Z_{IN}} + \frac{Z_o Z_i}{Z_{EN} Z_{IN}}\right) \quad (7) \]

Since the short-circuit impedance of the transformers is small compared with the shunt impedances, the term \( Z_o Z_i / Z_{EN} Z_{IN} \) may be neglected, giving a final approximation

\[ Z_x = Z_m \left[1 - \left(\frac{Z_o}{Z_{EN}} + \frac{Z_i}{Z_{IN}}\right)\right] \quad (8) \]

where \( Z_x \) is the true value of the unknown impedance and \( Z_m \) the value read on the bridge.

\( Z_o \) and \( Z_i \) are constants for the bridge and can be measured quite simply on each range by measuring the apparent change in value of a 2-terminal impedance when known shunts are connected across the transformer windings.

The advantages of the transformer bridge may be summarised as follows:

(i) The measurement is dependent upon the product of the current and voltage ratios for each fixed standard used. Both of these ratios are obtained easily with great accuracy, increasing the possible range of measurement well beyond the scope of impedance arms. Voltage and current ratios each of 1,000 : 1 are possible, giving an over-all ratio of one million to one.

(ii) Since the ratios depend only upon the number of turns on the
Figure 12 - Basic circuit with unknown and standards sections electrically separate

Figure 13 - Basic circuit with unknown and standards sections electrically separate and $N_x$ and $n_x$ each reduced to a single turn
transformer windings, they are permanent and calibration is unnecessary.

(iii) Only one standard is required for each decade. Furthermore, the transformer ratios may be used to set the standard in one decade against that in another, so that only two fixed standards of known accuracy are required, one resistive and one reactive.

(iv) The standards need not be pure. The effects of a resistive term associated with a reactance standard and of a reactive term associated with a resistance standard can be entirely removed at a given frequency.

(v) The bridge will measure the impedance between any pair of terminals of a 3-terminal network.

The transformer ratio-arm bridge as described above may be used in conjunction with the normal type of dipping electrodes, but for many purposes it is advantageous to eliminate these internal electrodes. Cells with external electrodes have been described by Blake (1) and Reilly (2), but in the main, high frequencies have been employed. With the transformer bridge, however, it is possible to determine the conductance of high conductivity solutions without any metal electrodes, and using audio-frequency oscillators.

The two sections of the ratio-arm bridge can be separated electrically, as shown in Fig.12, which is in fact equivalent to Fig.1, and in practice \( N_x \) and \( n_x \) are each reduced to a single turn as indicated in Fig.13, and both transformers are wound on toroidal cores, when the balance equation becomes

\[
g_x = \frac{N_x n_y g_y}{y y y}
\]  

(9)
Figure 14

CONDUCTIVITY CELL

B 12 ground-glass joints

Voltage transformer casting

Current transformer casting

Position of Mumetal cores
Figure 15 - Transformer Ratio-Arm Bridge - model 1
Transformer windings are usually thought of in terms of metallic wire, but a piece of enamelled or plastic covered wire is equivalent to an electrolyte solution in an electrically non-conducting tube, inasmuch as both comprise a conductor in an insulating sleeve. Thus, if a closed annulus of electrolyte contained in a tube can be made to link both the voltage and current transformer cores, the circuit is complete, and nothing further in the way of connection is required. Fig.14 indicates the way in which this is done. The high permeability Mumetal toroidal cores are moulded into an inert insulating material and the cores are linked by an annular glass cell which contains the electrolyte.

Such an "Electrodeless Cell" has the following advantages over conventional cells with internal electrodes:

(i) Conductance errors due to polarisation, adsorption or chemical attack by the electrolyte at the electrode surfaces are eliminated.

(ii) There are no errors due either to the impedance or to electro-thermal e.m.f.'s, set up in the connecting leads to be taken into account.

(iii) There is no possibility of a change in the cell constant occurring because of a shift in the relative positions of the electrodes with respect to each other.

Two different bridges were used during the course of this work. In model 1, shown in Fig.15, the complete bridge, consisting of oscillator, detector, standards, and transformers, was housed as a single unit in a metal box. The Mumetal toroidal cores of the current and voltage transformers projected outside the box to permit the attachment and manipulation of the cell.
Figure 16 - Transformer Ratio-Arm Bridge

model 2

Cell and transformer units

Standards and detector unit

Magic eye
The two transformer units were attached to a chassis separate from the unit housing the other components in the case of model 2, shown in Fig. 16. The transformers were linked to the main unit by means of screened flex. This allowed for easier manipulation of the cell than in the case of model 1.

For both models of the bridge the voltage transformer core was energized by a third winding connected to an oscillator giving a sinusoidal wave form of 1,000 c/s. The detector in each case consisted of a tuned amplifier linked to the current transformer, the null-point being detected with an integral "magic eye", or in the case of model 1, an external Cossor 1049 MkIII oscilloscope, since this gave a more precise null-point for this model.

Both models were calibrated against a standard resistance box (see Appendices IIa and IIb).

(b) Description of Conductivity Cells

The annular cells, which were all of a design similar to that shown in Fig. 14, were made of borosilicate glass and had a working capacity of between 40 and 70 ml. B 12 ground-glass joints in the loop allowed them to be dismantled and removed from the cores. To prevent leakage of solution, and to ensure that the joints did not become cemented together with solid electrolyte, it was found necessary to lubricate the joints with a small amount of vaseline, or, where the conductivity of an organic solvent such as glacial acetic acid was being determined, silicone grease.

(c) Cleaning of the Cells

Special techniques for cleaning the cells were normally found to be
unnecessary since small traces of contaminants do not have a measurable effect on conductivities of solutions of relatively high concentrations. Before a run with any particular electrolyte the cell was merely rinsed thoroughly with conductivity water, and either allowed to dry at room temperature or rinsed successively with two or three portions of ethanol and diethyl ether, traces of the latter solvent being removed by passing a current of dust-free air through the cell.

(ii) Experimental Technique

All conductivity measurements were carried out at 25°C ± 0.05°C in a thermostatically heated room. The actual temperature of the solution was recorded immediately prior to taking a balance reading using a thermometer which had been calibrated against an N.P.L. standard thermometer.

(a) The determination of Cell Constants

The cell constants were determined with the cells in the same bridge and under the same experimental conditions as for the dilution runs. 1.0 and 0.1 demal (D) potassium chloride solutions of Jones and Bradshaw (3) were used for this purpose. These solutions have weight concentrations and specific conductivities as follows:

<table>
<thead>
<tr>
<th></th>
<th>1.0 D</th>
<th>0.1 D</th>
</tr>
</thead>
<tbody>
<tr>
<td>g KCl/kg solution in vacuum</td>
<td>71.1352</td>
<td>7.41913</td>
</tr>
<tr>
<td>Specific Conductivity at 25°C, ohms⁻¹ cm⁻¹</td>
<td>0.11134₂</td>
<td>0.012856₀</td>
</tr>
</tbody>
</table>

The solutions were prepared by weight in air and the buoyancy correction...
shown in Appendix III was applied.

The standard solution was introduced into the cleaned dried cell and the bridge was balanced when the temperature of the solution was $25^\circ C \pm 0.05^\circ C$. Repeated conductivity readings were taken using fresh portions of the same standard solution. Both 1.0 D and 0.1 D solutions were used for the determination of the constant of the first cell to be used, but since the two solutions did not give significantly different results, only 1.0 D solutions were used for subsequent cells.

The cell constant ($\gamma$) is given by

$$\gamma = \frac{\text{The specific conductivity of the standard solution}}{\text{The measured conductivity of the standard solution}}$$

(b) **Technique used for Experimental Runs**

For the preparation of solutions containing solid electrolytes, sufficient of the electrolyte was weighed out to 0.1 mg in a 100 ml. volumetric flask to give a nearly saturated solution when dissolved in conductivity water and made up to 100 ml. at $25^\circ C$. This solution was used for the first conductivity reading.

Electrolytes such as hydrochloric acid and acetic acid were used in the most concentrated forms available for the first conductivity reading.

The concentrations of many of the solutions were determined analytically, either volumetrically (for the acids), or gravimetrically (for lithium chloride, nickelous chloride, nickelous sulphate, and copper sulphate).
After the first conductivity reading the solution was returned from the cell to the flask and the first dilution made by the transfer of 25, 50, or 75 ml. of solution to another 100 ml. volumetric flask by means of a pipette calibrated to deliver 25 ml. of solution at 25°C. On making up to volume at 25°C with conductivity water, a solution of $\frac{1}{4}$, $\frac{1}{2}$, or $\frac{3}{4}$ respectively of the concentration of the first solution was thus prepared for the next conductivity reading. The cell was first rinsed out at least three times with small portions of this solution before being filled for a determination. The foregoing dilution procedure was repeated for successive conductivity determinations on the same electrolyte until the solution was too dilute for accurate readings on the instrument.
SECTION Ib

PREPARATION AND PURIFICATION OF MATERIALS
Figure 17

CONDUCTIVITY WATER COLUMN
PREPARATION AND PURIFICATION OF MATERIALS

(i) Conductivity Water

Conductivity water was prepared by passing distilled water slowly through a column packed with about 150 g. of a mixture of anion and cation exchange resins, supplied by the Permutit Company Ltd. under the name of "Bio-Demineralit". The apparatus used is shown in Fig.17 and consisted of a column of glass about 20 cm long and having a coarse sintered glass disc sealed in at the lower end. Lawrence (4) showed that approximately 25 l. of ordinary distilled water could be passed through before the conductivity of the water emerging from the column rose above 0.4 gemmho and that no residue could be detected on evaporating several litres obtained from this column to dryness.

(ii) Electrolytes

(a) Ammonium chloride, $\text{NH}_4\text{Cl}$

Sodium chloride, $\text{NaCl}$

Potassium chloride, $\text{KCl}$

Potassium bromide, $\text{KBr}$

Magnesium sulphate, $\text{MgSO}_4\cdot7\text{H}_2\text{O}$

Copper sulphate, $\text{CuSO}_4\cdot5\text{H}_2\text{O}$

Nickelous sulphate, $\text{NiSO}_4\cdot(\text{hydrated})$

Barium chloride, $\text{BaCl}_2\cdot2\text{H}_2\text{O}$

Potassium ferricyanide, $\text{K}_3\text{Fe}($CN$)_6$

Potassium ferrocyanide, $\text{K}_4\text{Fe}($CN$)_6\cdot3\text{H}_2\text{O}$
All the above-mentioned electrolytes were of "AnalaR" grade and were recrystallized at least three times from conductivity water, rejecting in each case the first crystals to separate out and also the residual mother liquors. Ammonium, sodium and potassium chlorides and potassium bromide were dried for several hours in an oven at 120°C and were allowed to cool in a desiccator. The rest were dried for several days over silica gel in a desiccator at room temperature.

The concentrations of the copper and nickelous sulphate solutions used for conductivity measurements were determined gravimetrically; the former as cuprous thiocyanate and the latter as nickel dimethylglyoxime (5).

(b) Calcium ferrocyanide, Ca₂Fe(CN)₆·11H₂O.

This was a specimen of hand-picked "Kahlbaum" crystals (6). They were recrystallized three times from conductivity water.

(c) Lithium chloride, LiCl.

Nickelous chloride, NiCl₂·hydrated.

These salts were recrystallized three times from conductivity water in the same manner as described under (i) above. The concentrations in the solutions of these electrolytes used for conductivity measurements were determined by gravimetric analyses, the former as silver chloride and the latter as nickel dimethylglyoxime (5).

(d) Rubidium chloride, RbCl.

Caesium chloride, CsCl.

Only small amounts of these salts were available. The pure anhydrous commercial materials were dried for several hours in an oven at 120°C and
allowed to cool in a desiccator.

(a) Uranyl nitrate, $\mathrm{UO}_2(\mathrm{NO}_3)_2 \cdot 2\mathrm{H}_2\mathrm{O}$.
Only a small amount of this material was available. Its degree of hydration was assumed to be that indicated by the above formula.

(f) Di-sodium lead ethylenediaminetetraacetate.
$\left(\mathrm{NaO}_2\mathrm{CO.CH}_2\right)_2\mathrm{C}_2\mathrm{H}_4\mathrm{N}_2(\mathrm{CH}_2\cdot\mathrm{CO}.0)_2\mathrm{Pb}$ (hydrated).
This material was dried thermodynamically to give the di-hydrate. (See Appendix IV).

(g) Hydrochloric acid, $\mathrm{HCl}$.
"AnalaR" concentrated hydrochloric acid (sp. gr. 1.18) was used. The concentrations of solutions used for conductivity measurements were determined volumetrically by titration against borax using methyl red as the indicator (5).

(h) Acetic acid, $\mathrm{CH}_3\mathrm{CO.OH}$.
"AnalaR" glacial acetic acid was used. The concentrations of solution used for conductivity measurements were determined volumetrically by titration against a sodium hydroxide solution using phenolphthalein indicator. The sodium hydroxide solution was standardized against potassium hydrogen phthalate (5).
SECTION IIa

THE CONDUCTIVITIES OF RELATIVELY CONCENTRATED SOLUTIONS

OF UNI-UNIVALENT ELECTROLYTES IN WATER AT 25°C
The conductivities of relatively concentrated aqueous solutions of uni-univalent electrolytes have been studied by several workers in the past using conventional cells with internal electrodes together with some kind of resistance bridge for the measurement of their resistance. The present work shows good agreement with much of this previous work and provides new data for rubidium and caesium chlorides whose conductivities have not been previously reported for concentrations higher than 0.0313 molar.
(a) **Lithium chloride**

In the present work the conductivity at 25°C of aqueous solutions of this salt has been investigated within the concentration range 0.0115 to 10.844 molar. As long ago as 1908 Green (7) investigated the conductivities of aqueous solutions of lithium chloride of concentrations from 0.00625 to 12.245 molar at 25°C. He used conventional cells with internal electrodes and measured the conductivity of his solutions by means of the telephone method of Kohlrausch (8). The present results show progressively better agreement with those of Green for increasing concentration, those at 0.1 molar being about 2 per cent higher. More recently, in 1937, Nickels and Allmand (9) determined the conductivity of from 0.1 to 3.5 molar aqueous solutions in a U-shaped cell with internal platinised platinum electrodes. The effective distance between these electrodes could be adjusted to vary the cell constant by known amounts, so that a large range in concentration could be covered. A meter bridge was used in conjunction with a post office box, buzzer and head-phones for their measurement of resistance. They determined their cell constants using 0.1 normal and 1.0 normal solutions of potassium chloride, the specific conductivities of which were taken to be 0.01288 and 0.1116 ohm⁻¹ respectively.

The numerical values for A and √c found in the present work are shown in Table 1 on page 29. Those obtained by Green and by Nickels and Allmand are shown in Table 2 on page 30. The present results are shown graphically in comparison with those of Green in Fig. 18.
about \( \sqrt{c} = 0.75 \) and \( \sqrt{c} = 3.0 \) the \( \Lambda, \sqrt{c} \) plot is almost linear. The
viscosity corrected curve \( \frac{\Lambda}{\eta_0}, \sqrt{c} \) for the present data is also shown in
the figure. This curve does not fall so steeply as the \( \Lambda, \sqrt{c} \) curve and
at \( \sqrt{c} = 2, -\frac{\partial \Lambda}{\partial \sqrt{c}} \) approaches zero, after which it starts to increase
again. The viscosity data were interpolated from those given in the
International Critical Tables (10).
Figure 18

CONDUCTIVITY OF LITHIUM CHLORIDE IN WATER AT 25°C

- □ PRESENT WORK
- ○ RESULTS OF GREEN
- ■ VISCOOSITY-CORRECTED CURVE FOR THE PRESENT WORK
# Table 1

The Conductivity of Lithium Chloride in Water at 25°C

**Present work**

<table>
<thead>
<tr>
<th>( \sqrt{c} )</th>
<th>( \Lambda )</th>
<th>( \Lambda_n/\eta_0 )</th>
<th>( \sqrt{c} )</th>
<th>( \Lambda )</th>
<th>( \Lambda_n/\eta_0 )</th>
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</thead>
<tbody>
<tr>
<td>0.0945</td>
<td>113.4</td>
<td>113.5</td>
<td>1.0695</td>
<td>72.7</td>
<td>84.8</td>
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<td>0.1071</td>
<td>111.1</td>
<td>111.3</td>
<td>1.2121</td>
<td>68.6</td>
<td>83.8</td>
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<tr>
<td>0.1891</td>
<td>106.1</td>
<td>106.6</td>
<td>1.5126</td>
<td>60.2</td>
<td>82.3</td>
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<td>0.2143</td>
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<td>103.3</td>
<td>1.7142</td>
<td>53.9</td>
<td>80.9</td>
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<tr>
<td>0.2674</td>
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<td>101.7</td>
<td>1.7464</td>
<td>52.9</td>
<td>80.8</td>
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<tr>
<td>0.3030</td>
<td>98.6</td>
<td>99.8</td>
<td>1.9794</td>
<td>45.5</td>
<td>78.2</td>
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<tr>
<td>0.3761</td>
<td>95.8</td>
<td>97.7</td>
<td>2.0166</td>
<td>44.7</td>
<td>78.8</td>
</tr>
<tr>
<td>0.4285</td>
<td>93.0</td>
<td>95.4</td>
<td>2.2856</td>
<td>36.6</td>
<td>77.6</td>
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<tr>
<td>0.5348</td>
<td>89.8</td>
<td>93.4</td>
<td>2.3285</td>
<td>35.4</td>
<td>77.4</td>
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<tr>
<td>0.6061</td>
<td>86.8</td>
<td>91.2</td>
<td>2.6393</td>
<td>26.3</td>
<td>75.4</td>
</tr>
<tr>
<td>0.7562</td>
<td>82.8</td>
<td>89.5</td>
<td>3.0474</td>
<td>15.6</td>
<td>73.5</td>
</tr>
<tr>
<td>0.8571</td>
<td>78.9</td>
<td>86.9</td>
<td>3.2931</td>
<td>10.8</td>
<td>66.4</td>
</tr>
</tbody>
</table>
TABLE 2
THE CONDUCTIVITY OF LITHIUM CHLORIDE IN WATER AT 25°C

Figures of Green (7)

<table>
<thead>
<tr>
<th>$\sqrt{c}$</th>
<th>$\Lambda$</th>
<th>$\sqrt{c}$</th>
<th>$\Lambda$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0791</td>
<td>109.3</td>
<td>2.0072</td>
<td>44.60</td>
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<tr>
<td>0.1118</td>
<td>106.5</td>
<td>2.2293</td>
<td>38.03</td>
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<tr>
<td>0.1581</td>
<td>104.36</td>
<td>2.3076</td>
<td>35.76</td>
</tr>
<tr>
<td>0.2234</td>
<td>99.90</td>
<td>2.4936</td>
<td>30.32</td>
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<td>0.3162</td>
<td>96.34</td>
<td>2.6412</td>
<td>26.16</td>
</tr>
<tr>
<td>0.4472</td>
<td>91.10</td>
<td>2.9061</td>
<td>19.03</td>
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<td>0.6325</td>
<td>85.72</td>
<td>2.9672</td>
<td>17.539</td>
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<td>0.7858</td>
<td>79.71</td>
<td>3.0287</td>
<td>16.098</td>
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<td>1.0784</td>
<td>70.99</td>
<td>3.2249</td>
<td>11.997</td>
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<td>1.4145</td>
<td>61.62</td>
<td>3.3562</td>
<td>9.765</td>
</tr>
<tr>
<td>1.6912</td>
<td>53.75</td>
<td>3.5135</td>
<td>7.588</td>
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</table>

Figures of Nickels and Allmand (9)

<table>
<thead>
<tr>
<th>$\sqrt{c}$</th>
<th>$\Lambda$</th>
<th>$\sqrt{c}$</th>
<th>$\Lambda$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.316</td>
<td>96.5</td>
<td>1.414</td>
<td>61.7</td>
</tr>
<tr>
<td>0.447</td>
<td>90.3</td>
<td>1.581</td>
<td>56.9</td>
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<tr>
<td>0.707</td>
<td>81.5</td>
<td>1.732</td>
<td>52.5</td>
</tr>
<tr>
<td>1.000</td>
<td>73.0</td>
<td>1.871</td>
<td>48.4</td>
</tr>
<tr>
<td>1.225</td>
<td>67.0</td>
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</tr>
</tbody>
</table>
(b) Sodium chloride

The conductivity of sodium chloride in water at 25°C in the present work has been investigated between 0.00484 and 4.411 molar. In 1937 Nickels and Allmand (9) reported the conductivity of aqueous solutions of this salt for concentrations between 0.1 and 5.0 molar using the apparatus which they used for investigating the conductivity of lithium chloride solutions. The results of the present work and those of Nickels and Allmand in terms of $\Lambda$ and $\sqrt{c}$ are shown numerically in Table 3 on page 32 and graphically in Fig. 19. Over the common concentration range studied the agreement is good. In the region $\sqrt{c} = 1$ a point of inflection is noted in the $\Lambda, \sqrt{c}$ curve. Using viscosity data interpolated from that of Nickels and Allmand, a plot of $\Lambda \eta / \eta_0$ against $\sqrt{c}$ for the present work gives a curve which goes through a flat minimum at a concentration of about 3 molar. Over the concentration range 1.5 to 5 molar the product $\Lambda \eta / \eta_0$ varies only very slightly.
Figure 19

CONDUCTIVITY OF SODIUM CHLORIDE

IN WATER AT 25°C

- Present work
- Results of Nickels and Allmand
- Viscosity-corrected curve for the present work
### TABLE 3

**THE CONDUCTIVITY OF SODIUM CHLORIDE IN WATER AT 25°C**

**Present work**

<table>
<thead>
<tr>
<th>√c</th>
<th>Λ</th>
<th>$\Lambda \frac{\eta}{\eta_0}$</th>
<th>√c</th>
<th>Λ</th>
<th>$\Lambda \frac{\eta}{\eta_0}$</th>
</tr>
</thead>
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<tr>
<td>0.0696</td>
<td>126.2</td>
<td>126.3</td>
<td>0.7386</td>
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<td>0.0984</td>
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<td>97.4</td>
</tr>
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<td>0.1306</td>
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<td>120.1</td>
<td>1.0445</td>
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<td>93.7</td>
</tr>
<tr>
<td>0.1392</td>
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<td>1.1139</td>
<td>83.9</td>
<td>93.0</td>
</tr>
<tr>
<td>0.1969</td>
<td>115.4</td>
<td>115.8</td>
<td>1.4772</td>
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<td>90.6</td>
</tr>
<tr>
<td>0.2611</td>
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<td>99.7</td>
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</table>

**Figures of Nickels and Allmand (9)**

<table>
<thead>
<tr>
<th>√c</th>
<th>Λ</th>
<th>√c</th>
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<tr>
<td>0.316</td>
<td>107.0</td>
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<td>85.4</td>
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<tr>
<td>1.414</td>
<td>74.9</td>
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</table>
(c) **Ammonium chloride**

In the present work the conductivities of aqueous solutions of ammonium chloride at 25°C have been investigated over a concentration range of 0.1000 and 5.000 molar. Wishaw and Stokes in 1954 (11) have reported the conductivity of solutions of this salt over a similar range of concentration. Their measurements were made with a conventional a.c. bridge circuit with a Wagner earth at a frequency of about 700 c/s. The conductivity cell was tubular with electrodes which were 1 cm square and separated from one another by about 25 cm. It was calibrated using the demal solutions of Jones and Bradshaw (3). They found that the conductivity of this salt closely followed the theoretical expression

\[
\Lambda = \left( \Lambda_0 - \frac{B_2\sqrt{c}}{1 + B_2\sqrt{c}} \right) \left( 1 - \frac{B_1\sqrt{c}}{1 + B_2\sqrt{c}} \frac{P}{\eta} \right) \frac{\eta_0}{\eta}
\]

where \( P = \frac{0.2929k_A}{0.2929k_A - 1} \)

The present results in terms of \( \Lambda \) and \( \sqrt{c} \) together with those of Wishaw and Stokes are recorded numerically in Table 4 on page 34 and are shown graphically in Fig. 20. The two sets of results are in good agreement and the \( \Lambda, \sqrt{c} \) plot shows a point of inflection at about \( \sqrt{c} = 1.2 \) is present, which is more marked than that shown by the \( \Lambda, \sqrt{c} \) curve for sodium chloride. A plot of \( \Lambda \eta/\eta_0 \) against \( \sqrt{c} \) using viscosity data interpolated from the International Critical Tables (10) for the present work results in a somewhat straighter curve than that resulting from the \( \Lambda, \sqrt{c} \) plot, but a very slight inflexion is still apparent.
CONDUCTIVITY OF AMMONIUM CHLORIDE
IN WATER AT 25°C

- Present work
- Results of Wishaw and Stokes
- Viscosity-corrected curve for the present work
<table>
<thead>
<tr>
<th>$\sqrt{c}$</th>
<th>$\Lambda$</th>
<th>$\Lambda \frac{\eta}{\eta_0}$</th>
<th>$\sqrt{c}$</th>
<th>$\Lambda$</th>
<th>$\Lambda \frac{\eta}{\eta_0}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3162</td>
<td>129.0</td>
<td>128.8</td>
<td>1.6125</td>
<td>102.5</td>
<td>101.5</td>
</tr>
<tr>
<td>0.6403</td>
<td>119.0</td>
<td>118.4</td>
<td>1.7889</td>
<td>99.5</td>
<td>98.7</td>
</tr>
<tr>
<td>1.0000</td>
<td>111.0</td>
<td>110.0</td>
<td>2.0000</td>
<td>94.7</td>
<td>94.7</td>
</tr>
<tr>
<td>1.2247</td>
<td>108.5</td>
<td>107.4</td>
<td>2.2361</td>
<td>88.3</td>
<td>89.4</td>
</tr>
<tr>
<td>1.4142</td>
<td>105.0</td>
<td>103.8</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figures of Wishaw and Stokes (11)

<table>
<thead>
<tr>
<th>$\sqrt{c}$</th>
<th>$\Lambda$</th>
<th>$\sqrt{c}$</th>
<th>$\Lambda$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3192</td>
<td>128.6</td>
<td>1.4159</td>
<td>105.1</td>
</tr>
<tr>
<td>0.4489</td>
<td>123.8</td>
<td>1.7333</td>
<td>100.2</td>
</tr>
<tr>
<td>0.7084</td>
<td>116.8</td>
<td>2.0012</td>
<td>95.1</td>
</tr>
<tr>
<td>1.0055</td>
<td>111.2</td>
<td>2.2917</td>
<td>87.9</td>
</tr>
</tbody>
</table>
(d) **Potassium chloride**

The conductivity of potassium chloride in water at 25°C has been investigated in the present work between concentration ranges of 0.0072 and 3.689 molar. The results for the higher concentrations are in good agreement with those reported in 1937 by Nickels and Allmand (9) who determined the conductivity of this salt at concentrations between 0.1 and 3.5 molar using the same apparatus as used for their investigation of lithium and sodium chloride solutions (see page 27). They noted that their Λ, √c curve shows a point of inflection at about 2.2 molar and they therefore suspected that their Λ values above 3 molar were too low, perhaps through polarisation.

The results of the present work and also those of Nickels and Allmand, in terms of Λ and √c, are recorded numerically in Table 5, page 37 and they are shown graphically in Fig.21 which faces the numerical results. From the graph it will be seen that the present work also shows a point of inflection at about √c = 1.5 and that for concentrations higher than this the agreement with their data is particularly good. Nickels and Allmand also measured the conductivities and viscosities of lithium, sodium and potassium chlorides over a wide range of concentrations in approximately tenth normal hydrochloric acid solutions and concluded from the behaviour of the product Λτ/ν for these salts at high concentrations, together with a consideration of the factors which govern the viscosity of /ionic
solutes enumerated by Bernal and Fowler (12), suggested that their conductivity data for concentrated potassium chloride solutions in water were not after all subject to experimental error, so that the accuracy of the present data at high concentrations is confirmed.

The product \( A \eta/\eta_0 \) was calculated for the present data using viscosity data interpolated from the International Critical Tables (10) and the plot of \( A \eta/\eta_0 \) against \( \sqrt{c} \) results in a curve which closely follows the \( A, \sqrt{c} \) curve up to about \( \sqrt{c} = 1.2 \). Above this concentration the curve is practically straight, and it shows virtually no inflexion.
Figure 21

CONDUCTIVITY OF POTASSIUM CHLORIDE
IN WATER AT 25°C

- Present work
- Results of Nickels and Allmand
- Viscosity-corrected curve for the present work
### TABLE 5

**The Conductivity of Potassium Chloride in Water at 25°C**

#### Present Work

<table>
<thead>
<tr>
<th>√c</th>
<th>Λ</th>
<th>Λη/η₀</th>
<th>√c</th>
<th>Λ</th>
<th>Λη/η₀</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0849</td>
<td>147.9</td>
<td>147.9</td>
<td>0.4801</td>
<td>125.0</td>
<td>124.8</td>
</tr>
<tr>
<td>0.0999</td>
<td>145.4</td>
<td>145.4</td>
<td>0.5650</td>
<td>121.7</td>
<td>121.4</td>
</tr>
<tr>
<td>0.1201</td>
<td>144.2</td>
<td>144.2</td>
<td>0.6790</td>
<td>119.1</td>
<td>118.7</td>
</tr>
<tr>
<td>0.1412</td>
<td>141.9</td>
<td>141.9</td>
<td>0.7990</td>
<td>116.7</td>
<td>116.3</td>
</tr>
<tr>
<td>0.1698</td>
<td>140.0</td>
<td>140.0</td>
<td>0.9603</td>
<td>113.7</td>
<td>113.2</td>
</tr>
<tr>
<td>0.1998</td>
<td>137.0</td>
<td>136.9</td>
<td>1.1300</td>
<td>110.7</td>
<td>110.3</td>
</tr>
<tr>
<td>0.2401</td>
<td>134.6</td>
<td>134.5</td>
<td>1.3581</td>
<td>106.8</td>
<td>107.0</td>
</tr>
<tr>
<td>0.2825</td>
<td>132.7</td>
<td>132.6</td>
<td>1.5980</td>
<td>103.0</td>
<td>104.7</td>
</tr>
<tr>
<td>0.3395</td>
<td>129.9</td>
<td>129.8</td>
<td>1.8452</td>
<td>98.0</td>
<td>101.7</td>
</tr>
<tr>
<td>0.3995</td>
<td>127.5</td>
<td>127.3</td>
<td>1.9206</td>
<td>96.1</td>
<td>100.6</td>
</tr>
</tbody>
</table>

#### Figures of Nickels and Allmand (9)

<table>
<thead>
<tr>
<th>√c</th>
<th>Λ</th>
<th>√c</th>
<th>Λ</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.316</td>
<td>128.9</td>
<td>1.414</td>
<td>105.6</td>
</tr>
<tr>
<td>0.447</td>
<td>124.5</td>
<td>1.581</td>
<td>103.6</td>
</tr>
<tr>
<td>0.707</td>
<td>117.9</td>
<td>1.732</td>
<td>100.7</td>
</tr>
<tr>
<td>1.000</td>
<td>112.0</td>
<td>1.871</td>
<td>97.2</td>
</tr>
<tr>
<td>1.225</td>
<td>108.1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
(e) **Potassium bromide**

The conductivity of potassium bromide in water at 25°C has, in the present work, been determined between the concentrations of 0.100 and 4.000 molar. The numerical results in terms of \( A \) and \( \sqrt{c} \) are to be found in Table 6 on page 40, together with those reported in 1934 by Jones and Bickford (13). The two sets of data are shown graphically in Fig. 22. The data obtained in the present work agree well with those obtained by Jones and Bickford over the common concentration range studied, and this is particularly true for concentrations above 1 molar. They studied the conductivity of this salt between 0.00025 and 3.75 molar concentrations in a cylindrical cell containing internal platinum electrodes. At each concentration they measured the conductivity at two frequencies of about 1,090 and 2,280 cycles per second using a conventional a.c. bridge. They found that the Shedlovsky conductivity equation fitted the data for this salt for concentrations up to 0.1 molar better than any other equation. This equation for this salt may be written:

\[
A = 151.63 - 94.27\sqrt{c} + 100.96 (1 - 0.2274\sqrt{c})
\]

Jones and Bickford also found that the Jones and Dole equation fits the data up to 3.75 molar concentration better than any other equation.
This equation for potassium bromide may be written:

\[ \Lambda = 151.84 - \frac{103.77\sqrt{c}}{1 + 1.8953\sqrt{c}} \]

The Jones and Dole equation, however, gives a higher value for \( \Lambda_0 \) than does either the Onsager or the Shedlovsky extrapolation method and a greater limiting slope than is predicted by the Onsager equation.

On plotting \( \Lambda \frac{\eta}{\eta_0} \) against \( \sqrt{c} \) using viscosity data interpolated from that given by Jones and Talley (14), it is to be noted that the resulting curve is without inflexion and closely follows the \( \Lambda \frac{\eta}{\eta_0}, \sqrt{c} \) curve for potassium chloride.
Figure 22

CONDUCTIVITY OF POTASSIUM BROMIDE IN WATER AT 25°C

- Present work
- Results of Jones and Bickford
- Viscosity-corrected curve for the present work
### TABLE 6

THE CONDUCTIVITY OF POTASSIUM BROMIDE IN WATER AT 25°C

**Present work**

<table>
<thead>
<tr>
<th>√c</th>
<th>Λ</th>
<th>Λ'(n)</th>
<th>√c</th>
<th>Λ</th>
<th>Λ'(n)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3162</td>
<td>132.0</td>
<td>131.6</td>
<td>1.4142</td>
<td>109.5</td>
<td>104.8</td>
</tr>
<tr>
<td>0.6403</td>
<td>124.0</td>
<td>122.3</td>
<td>1.6127</td>
<td>105.3</td>
<td>101.2</td>
</tr>
<tr>
<td>1.0000</td>
<td>115.5</td>
<td>111.8</td>
<td>1.7888</td>
<td>102.2</td>
<td>99.5</td>
</tr>
<tr>
<td>1.1833</td>
<td>113.0</td>
<td>108.6</td>
<td>2.0000</td>
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<td>97.5</td>
</tr>
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</table>

**Figures of Jones and Bickford (13)**

<table>
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<tr>
<th>√c</th>
<th>Λ</th>
<th>√c</th>
<th>Λ</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0158</td>
<td>150.16</td>
<td>0.4472</td>
<td>126.59</td>
</tr>
<tr>
<td>0.0447</td>
<td>147.64</td>
<td>0.7071</td>
<td>120.35</td>
</tr>
<tr>
<td>0.1000</td>
<td>143.15</td>
<td>1.0000</td>
<td>115.46</td>
</tr>
<tr>
<td>0.1414</td>
<td>140.26</td>
<td>1.4142</td>
<td>109.37</td>
</tr>
<tr>
<td>0.2236</td>
<td>135.44</td>
<td>1.7321</td>
<td>103.55</td>
</tr>
<tr>
<td>0.3162</td>
<td>131.19</td>
<td>1.9365</td>
<td>98.70</td>
</tr>
</tbody>
</table>
Rubidium chloride

The conductivity of rubidium chloride in water at 25°C over the concentration range 0.00648 to 4.140 molar has been determined in the present work and the numerical results in terms of \( \Lambda \) and \( \sqrt{c} \) are shown in Table 7 (page 43) and graphically in Fig. 23. Prior to the present work, data for this salt were reported in 1897 by Boltwood (15) for concentrations up to 0.03125 molar and these are also given in Table 7 and shown on the graph. It is apparent that Boltwood's conductivities are lower than those obtained in the present work by about 8 per cent. In 1894 Bredig (16) reported conductivities over the same range of concentrations which were about 1 per cent lower than those of Boltwood. Bredig gave \( \Lambda_0 \) value for RbCl of 143.7. Figures reported by him for potassium chloride over the same concentration range include a \( \Lambda_0 \) value for KCl of 140.8 whereas more recent data, such as that of Jervis et al (17) gave \( \Lambda_0 \) for KCl as 149.85, that is, a value which is 6 per cent higher. This fact indicates that all the conductivity data reported by Bredig and Boltwood may be low. The foregoing conclusion is confirmed by the work of Voisenet (18) on the limiting conductivity of the rubidium ion which was reported in 1952 by Owen (19). Voisenet's value for \( \Lambda_0 \) for Rb\(^+\) is 77.81. Assuming \( \Lambda_0 \) for Cl\(^-\) to be 76.35 (17) this gives \( \Lambda_0 \) for RbCl to be 154.16, which is 6.8 per cent higher than Bredig's value and 6.3 per cent higher than
that given by Boltwood. From the foregoing there appears to be good reason to suppose that the data obtained in the present work are the most accurate so far reported. The graph shows a point of inflexion at about $\sqrt{c} = 1.3$.

Viscosity data are available for solutions of this salt in the International Critical Tables (10) up to a concentration of only 1 molar. Plotting $\Lambda \frac{n}{n_0}$ against $\sqrt{c}$ for the present work using interpolated viscosity data results in a curve below that for $\Lambda$, $\sqrt{c}$ as indicated in Fig.23, and, at least up to a concentration of 1 molar, the curve is similar in shape to the viscosity corrected curve for ammonium chloride.
Figure 23

CONDUCTIVITY OF RUBIDIUM CHLORIDE
IN WATER AT 25°C

Present work
Results of Boltwood
Viscosity-corrected curve for the present work
### Table 7

**The Conductivity of Rubidium Chloride in Water at 25°C**

**Present Work**

<table>
<thead>
<tr>
<th>√c</th>
<th>Λ</th>
<th>Λ/Λ₀</th>
<th>√c</th>
<th>Λ</th>
<th>Λ/Λ₀</th>
</tr>
</thead>
<tbody>
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<td>0.0805</td>
<td>151.0</td>
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<td>0.7008</td>
<td>122.8</td>
<td>121.4</td>
</tr>
<tr>
<td>0.1138</td>
<td>148.3</td>
<td>-</td>
<td>0.8093</td>
<td>120.4</td>
<td>118.6</td>
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<tr>
<td>0.1610</td>
<td>143.6</td>
<td>-</td>
<td>0.9344</td>
<td>117.7</td>
<td>115.9</td>
</tr>
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<td>0.2277</td>
<td>140.2</td>
<td>-</td>
<td>1.0790</td>
<td>115.5</td>
<td>-</td>
</tr>
<tr>
<td>0.3220</td>
<td>134.8</td>
<td>134.6</td>
<td>1.2460</td>
<td>112.9</td>
<td>-</td>
</tr>
<tr>
<td>0.4552</td>
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<td>129.0</td>
<td>1.4387</td>
<td>109.5</td>
<td>-</td>
</tr>
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<td>0.5256</td>
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<td>126.4</td>
<td>2.0346</td>
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<td>-</td>
</tr>
<tr>
<td>0.6070</td>
<td>125.0</td>
<td>123.9</td>
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</table>

**Figures of Boltwood (15)**

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<th>√c</th>
<th>Λ</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0000</td>
<td>144.5</td>
<td>0.0884</td>
<td>136.9</td>
</tr>
<tr>
<td>0.0312</td>
<td>142.0</td>
<td>0.1250</td>
<td>134.0</td>
</tr>
<tr>
<td>0.0442</td>
<td>140.0</td>
<td>0.1768</td>
<td>129.6</td>
</tr>
<tr>
<td>0.0625</td>
<td>138.6</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The conductivity of caesium chloride in water at 25°C over the concentration range 0.004124 and 2.9655 molar has been studied in the present work and the data in terms of $\Lambda$ and $\sqrt{c}$ are recorded numerically in Table 8, page 46, and are shown graphically in Fig. 24. The results up to 0.03125 molar reported by Boltwood in 1897 (15) are also given. As with rubidium chloride (see page 41), Boltwood's results are about 8 per cent low compared with the data from the present work. Bredig in 1894 (16) reported equivalent conductivities which were about 1 per cent lower than those of Boltwood for the same concentration range. Bredig reported $\Lambda_o$ as 143.8. As in the case of rubidium chloride, which is discussed on page 41, the probability that this is a low value is confirmed by the work of Voisinet (18) which was reported by Owen in 1952 (19). This gives $\lambda_o$ for Cs$^+$ as 77.26. Assuming $\lambda_o$ for Cl$^-$ to be 76.35 (17), $\Lambda_o$ for CsCl = 153.81, which is 6.4 per cent higher than Bredig's value and 5.7 per cent higher than that of Boltwood. Applying the same argument as for rubidium bromide, there seems to be good reason for supposing that the present results are the most accurate so far reported. The similarity between the $\Lambda$, $\sqrt{c}$ curves for potassium, rubidium and caesium chlorides is very close. However, unlike those for potassium and rubidium chloride, no point of inflexion is observed, but one might be revealed if data at concentrations greater than 3 molar were obtained.
Viscosity data are available for solutions of this salt in the International Critical Tables (10) up to a concentration of only 1 molar. Plotting $\frac{\Lambda}{\eta_0}$ against $\sqrt{c}$ for the present work using interpolated viscosity data results in a curve below that for $\Lambda$, $\sqrt{c}$ as indicated in Fig. 24, and the curve is similar to that for rubidium chloride, but the deviation from the $\Lambda$, $\sqrt{c}$ curve is greater as the concentration increases to 1 molar.
CONDUCTIVITY OF CAESIUM CHLORIDE
IN WATER AT 25°C

Figure 24

- Present work
- Results of Boltwood
- Viscosity-corrected curve for the present work
<table>
<thead>
<tr>
<th>$\sqrt{c}$</th>
<th>$\Lambda$</th>
<th>$\Lambda_0^{c}$</th>
<th>$\sqrt{c}$</th>
<th>$\Lambda$</th>
<th>$\Lambda_0^{c}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0642</td>
<td>152.5</td>
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<td>0.6850</td>
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<td>0.0908</td>
<td>150.4</td>
<td>-</td>
<td>0.7909</td>
<td>118.5</td>
<td>116.1</td>
</tr>
<tr>
<td>0.1316</td>
<td>143.0</td>
<td>-</td>
<td>0.9133</td>
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<td>113.4</td>
</tr>
<tr>
<td>0.2569</td>
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<td>113.9</td>
<td>111.1</td>
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<td>0.3632</td>
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<td>-</td>
<td>1.2177</td>
<td>111.1</td>
<td>-</td>
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<td>0.5137</td>
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<td>1.7222</td>
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</table>

Figures of Boltwood (15)

<table>
<thead>
<tr>
<th>$\sqrt{c}$</th>
<th>$\Lambda$</th>
<th>$\sqrt{c}$</th>
<th>$\Lambda$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0000</td>
<td>144.8</td>
<td>0.0684</td>
<td>136.8</td>
</tr>
<tr>
<td>0.0312</td>
<td>143.0</td>
<td>0.1250</td>
<td>133.9</td>
</tr>
<tr>
<td>0.0442</td>
<td>140.8</td>
<td>0.1768</td>
<td>129.9</td>
</tr>
<tr>
<td>0.0625</td>
<td>138.6</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
(h) Hydrochloric acid

The conductivity of hydrochloric acid in water at 25°C has been studied in the present work over the concentration range 0.00575 to 11.78 normal and the results agree well with those of Owen and Sweeton (20), who in 1941 reported conductivities at various temperatures, including 25°C at concentrations of from about 0.001 up to nearly 12 normal. They used tubular cells with internal electrodes of lightly platinised platinum and they measured the conductivity with a Dike Bridge with a valve oscillator operating at 500, 1,000, 2,000, and 4,000 cycles per second and the null point was detected through a tuneable amplifier. They determined the cell constant at 25°C using 0.1 demal potassium chloride according to the procedure of Jones and Bradshaw (3).

The results of the present work in terms of A and /c, together with those of Owen and Sweeton, are shown numerically in Table 9 (page 48) and graphically in Fig.25. The A, /c curve is only slightly curved throughout its length, but a very shallow point of inflexion is to be noted in the region of /c = 1.75. Any point of inflexion in the region of /c = 0.02 is unlikely, and any indication of such is probably due to experimental error at low concentrations.
Figure 25

Conductivities of hydrochloric acid in water at 25°C.

- Present work
- Results of Owen & Sweeton
### TABLE 9

**THE CONDUCTIVITY OF HYDROCHLORIC ACID IN WATER AT 25°C**

**Present work**

<table>
<thead>
<tr>
<th>√c</th>
<th>Λ</th>
<th>√c</th>
<th>Λ</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0758</td>
<td>425.3</td>
<td>0.7431</td>
<td>364.0</td>
</tr>
<tr>
<td>0.0929</td>
<td>425.2</td>
<td>1.0509</td>
<td>331.2</td>
</tr>
<tr>
<td>0.1314</td>
<td>419.1</td>
<td>1.2134</td>
<td>310.6</td>
</tr>
<tr>
<td>0.1517</td>
<td>413.1</td>
<td>1.4862</td>
<td>274.8</td>
</tr>
<tr>
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**Figures of Owen and Sweeton (20)**

<table>
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<th>√c</th>
<th>Λ</th>
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(i) \textit{Acetic Acid}

The conductivity of acetic acid in water at 25°C has been studied in the present work over the concentration range 0.02892 to 17.552 normal. In 1910 Rivett and Sidgwick (21), using cells of the normal Ostwald form, reported conductivity data over the concentration range 0.00483 to 2.9771 normal. Both sets of data are given numerically in terms of $\Lambda$ and $\sqrt{c}$ in Tables 10 and 11 (pages 50 and 51) and are shown graphically in Fig. 26. The present data agree very closely with those obtained by Rivett and Sidgwick, the $\Lambda, \sqrt{c}$ curve showing a sharp drop in conductivity with increasing concentration up to about $\sqrt{c} = 0.5$, the curve then approaching the $\sqrt{c}$ axis asymptotically as the concentration continues to rise. This indicates that there are virtually no free ions present in pure anhydrous acetic acid and that, in water, it behaves as a weak uni-univalent electrolyte.

The viscosities of aqueous acetic acid mixtures are only slightly greater than for water over the whole range of concentrations and, consequently, the $\Lambda \frac{n}{n_0}, \sqrt{c}$ curve for the present work, from viscosity data interpolated from that given in the International Critical Tables (10), differs but slightly from the $\Lambda, \sqrt{c}$ curve.
Figure 26

CONDUCTIVITY OF ACETIC ACID
IN WATER AT 25°C

- Present work
- Results of Rivett and Sidgwick
- Viscosity-corrected curve for the present work
TABLE 10
THE CONDUCTIVITY OF ACETIC ACID IN WATER AT 25°C

Present work

<table>
<thead>
<tr>
<th>( \sqrt{c} )</th>
<th>( \Lambda )</th>
<th>( \Lambda \frac{\eta}{\eta_0} )</th>
<th>( \sqrt{c} )</th>
<th>( \Lambda )</th>
<th>( \Lambda \frac{\eta}{\eta_0} )</th>
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<td>0.72</td>
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<td>3.29</td>
<td>3.1422</td>
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<td>0.16</td>
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<td>0.6803</td>
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<td>2.46</td>
<td>3.6281</td>
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<td>0.04</td>
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<td>1.73</td>
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<td>0.00</td>
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<td>1.61</td>
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TABLE 11

THE CONDUCTIVITY OF ACETIC ACID IN WATER AT 25°C

Figures of Rivett and Sidgwick (21)

<table>
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<th>( \sqrt{c} )</th>
<th>( \Lambda )</th>
<th>( \sqrt{c} )</th>
<th>( \Lambda )</th>
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<td>8.39</td>
<td>0.6677</td>
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<td>0.8177</td>
<td>1.89</td>
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<td>0.3473</td>
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<td>0.4314</td>
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<td>1.2202</td>
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<td>0.4452</td>
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<td>1.4163</td>
<td>0.89</td>
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<tr>
<td>0.5453</td>
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</table>
SECTION IIb

THE CONDUCTIVITIES OF RELATIVELY CONCENTRATED SOLUTIONS
OF BI-BIVALENT ELECTROLYTES IN WATER AT 25°C
THE CONDUCTIVITIES OF RELATIVELY CONCENTRATED SOLUTIONS
OF BI-BIVALENT ELECTROLYTES IN WATER AT 25°C

(a) Magnesium sulphate
(b) Nickelous sulphate
(c) Copper sulphate

Bi-bivalent electrolytes in water give rise to two ionic species
at any given concentration in the same manner as do uni-univalent
electrolytes, namely:

\[ MA \rightleftharpoons M^{++} + A^{-} \]

In the more dilute solutions, however, both cation and anion are liable
to hydrolysis, which takes place in the following ways:

(i) For the cation:

\[ M^{++} + H_2O \rightleftharpoons M(OH)^+ + H^+ \]

and

\[ M(OH)^+ + H_2O \rightleftharpoons M(OH)_2 + H^+ \]

(ii) For the anion:

\[ A^- + H_2O \rightleftharpoons HA^- + OH^- \]

and

\[ HA^- + H_2O \rightleftharpoons H_2A + OH^- \]

Accordingly, as the solution becomes more dilute an increasing proportion
of the conductivity will be due to ions other than those of the bi-
bivalent electrolyte.
Conductivity data for concentrated solutions of bi-bivalent electrolytes are not numerous. The existing data for magnesium and nickelous sulphates, which are not recent, have, in the present work, been extended to much higher concentrations and the data for copper sulphate have also been extended to some extent.

(a) Magnesium sulphate

The conductivity of magnesium sulphate in water at 25°C has been investigated in the present work over the concentration range 0.002806 to 2.8738 molar. In 1919, Harkins and Paine (22) reported data between 0.0002532 and 0.50335 molar and it is clear from other data given in their paper that these determinations were carried out at 25°C and not at 18°C which is erroneously indicated in their table. They used a roller bridge with conventional cells of the Washburn type (23). The conductivities recorded in their paper are rather lower than those shown by the present data for the lower concentrations but are in fairly close agreement at high concentrations.

Both sets of results, in terms of $\Lambda$ and $\sqrt{c}$, are shown numerically in Table 12 (page 55) and graphically in Fig. 27.

Viscosity data up to $\sqrt{c} = 1.6$ were interpolated from the International Critical Tables (10) and a plot of $\frac{\Lambda}{\eta} \sqrt{c}$ against $\sqrt{c}$ for the present work shows a relatively sharp minimum at about $\sqrt{c} = 0.8$. Above this concentration, up to $\sqrt{c} = 1.56$ (above which published viscosity data were not available), the product $\frac{\Lambda}{\eta} \sqrt{c}$ rises fairly steeply as shown in Fig. 27.
Figure 27

CONDUCTIVITY OF MAGNESIUM SULPHATE IN WATER AT 25°C

Present work

Results of Harkins and Paine

Viscosity-corrected curve for the present work
### TABLE 12

**THE CONDUCTIVITY OF MAGNESIUM SULPHATE IN WATER AT 25°C**

**Present work**

<table>
<thead>
<tr>
<th>$\sqrt{c}$</th>
<th>$\Lambda$</th>
<th>$\frac{\Lambda}{\eta_0}$</th>
<th>$\sqrt{c}$</th>
<th>$\Lambda$</th>
<th>$\frac{\Lambda}{\eta_0}$</th>
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<td>131.9</td>
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<td>106.5</td>
<td>1.0131</td>
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</tr>
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<td>0.1498</td>
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<td>64.3</td>
<td>1.3509</td>
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<tr>
<td>0.3582</td>
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<td>59.7</td>
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**Figures of Harkins and Paine (22)**

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<th>$\frac{\Lambda}{\eta_0}$</th>
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<td>78.98</td>
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<td>0.0225</td>
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<td>0.1002</td>
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(b) Nickelous sulphate

The conductivity of nickelous sulphate in water at 25°C has been investigated in the present work over the concentration range 0.0005347 to 1.2979 molar. In 1928, Murata (24) reported equivalent conductivities at 25°C for concentrations of between 0.00005 and 0.5 molar. He used the ordinary Kohlrausch bridge (8) with cells of the Washburn type (25). The cell constants were determined using 0.1 molar potassium chloride.

The equivalent conductivities reported by Murata are somewhat lower than those of the present data throughout the concentration range. Both sets of data, in terms of $A$ and $\sqrt{c}$, are recorded numerically in Tables 13 and 14 (pages 57 and 58) and graphically in Fig. 28.
CONDUCTIVITY OF NICKEL SULPHATE (NiSO₄) IN WATER AT 25°C

Figure 28

Present work
Results of Murata
**TABLE 13**

THE CONDUCTIVITY OF NICKELOUS SULPHATE IN WATER AT 25°C

**Present work**

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<td>0.0573</td>
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<td>39.0</td>
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<td>0.0654</td>
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<td>Λ</td>
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<td>-----</td>
<td>-----</td>
</tr>
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</table>

TABLE 14

THE CONDUCTIVITY OF NICKELOUS SULPHATE IN WATER AT 25°C

Figures of Murata (24)
(c) Copper sulphate

The conductivity of copper sulphate in water at 25°C has been investigated in the present work over the concentration range 0.0006444 to 1.3198 molar. In 1919 Harkins and Paine (22) reported the conductivity of this salt between 0.012578 and 0.96675 molar using a roller bridge and conventional cells of the Washburn type and in 1938 Owen and Gurry (26) reported the conductivity of this salt between 0.0004945 and 0.115265 molar using a Dike bridge (27) operating at 1,000 cycles per second and cells with lightly platinised internal electrodes. The cell constants were determined by Owen and Gurry using 0.1 molar potassium chloride solution according to Jones and Bradshaw (3). Owen and Gurry also determined the pH values of their solutions at the same temperature and "corrected" their results for conductivities to those which would be given by the unhydrolysed salt. Using the corrected values of $\Lambda$, by means of a Shedlovsky plot (28), they obtained a value for $\Lambda_0$ for copper sulphate in water at 25°C of 133.6.

The present results, in terms of $\Lambda$ and $\sqrt{c}$, together with those of Harkins and Paine, and Owen and Gurry (uncorrected for hydrolysis), are given numerically in Tables 15 and 16 (pages 60 and 61) and graphically in Fig.29. It will be seen that the present results are in close agreement with those of the previous workers for concentrations of over 0.02 molar.
Figure 29

CONDUCTIVITY OF COPPER SULPHATE IN WATER AT 25°C

- Present work
- Results of Owen and Gurry
- Results of Harkins and Paine
TABLE 15

THE CONDUCTIVITY OF COPPER SULPHATE IN WATER AT 25°C

<table>
<thead>
<tr>
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<th>√c</th>
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<td>45.6</td>
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<td>0.0508</td>
<td>120.2</td>
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<td>43.8</td>
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<td>0.0552</td>
<td>105.0</td>
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<td>41.0</td>
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<td>0.0718</td>
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<td>0.0780</td>
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</tr>
<tr>
<td>0.1016</td>
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</tr>
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<td>60.0</td>
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<td>23.7</td>
</tr>
<tr>
<td>0.2872</td>
<td>53.7</td>
<td>1.6120</td>
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## TABLE 16

THE CONDUCTIVITY OF COPPER SULPHATE IN WATER AT 25°C

**Figures of Harkins and Paine (22)**

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<td>0.31635</td>
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</table>

**Figures of Owen and Gurry (26)**

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<td>0.0000</td>
<td>133.6</td>
<td>0.2516</td>
<td>55.97</td>
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<td>0.03145</td>
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<td>97.50</td>
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<td>51.17</td>
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<td>83.19</td>
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<td>49.31</td>
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<td>0.1330</td>
<td>74.18</td>
<td>0.3649</td>
<td>47.39</td>
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<td>0.1613</td>
<td>68.28</td>
<td>0.3935</td>
<td>45.84</td>
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<td>63.69</td>
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<td>42.01</td>
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<td>0.2199</td>
<td>59.47</td>
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SECTION IIc

THE CONDUCTIVITIES OF RELATIVELY CONCENTRATED SOLUTIONS
OF BI-UNIVALENT ELECTROLYTES IN WATER AT 25°C
THE CONDUCTIVITIES OF RELATIVELY CONCENTRATED SOLUTIONS
OF BI-UNIVALENT ELECTROLYTES IN WATER AT 25°C

(a) Barium chloride

(b) Nickelous chloride

At any given concentration a solution of a bi-univalent or a uni-
bivalent electrolyte will contain four distinct ionic species since such
electrolytes dissociate in two steps:

(i) \[ M_2^* \rightleftharpoons MA^+ + A^- \]

(ii) \[ MA^+ \rightleftharpoons M^{++} + A^- \]

\( M_2^* \) is the undissociated portion of the electrolyte, including both non-
ionized molecules and ion pairs.

To determine the composition of such a solution, a knowledge is required
for two dissociation constants

\[ \frac{[MA^+][A^-]}{[M_2^*]} = K_1 \]

and

\[ \frac{[M^{++}][A^-]}{[MA^+]} = K_2 \]

where \([MA^+]\) etc. represent the activities of the various species.

In concentrated solutions, \( K_2 \) is small and the formation of triple,
quaduple and higher aggregates will occur, i.e. :

\[ MA_2^+ + MA^+ \rightleftharpoons MA_2 MA^+ \]

\[ MA_2^+ + A^- \rightleftharpoons MA_2^- \]

\[ MA_2^+ + 2A^- \rightleftharpoons MA_4^- \]

In dilute aqueous solutions hydrolysis of the bivalent ion is likely
to occur, leading to high conductivities :

\[ M^{++} + H_2O \rightleftharpoons MOH^+ + H^+ \]

and

\[ MOH^+ + H_2O \rightleftharpoons M(OH)_2 + H^+ \]
(a) Barium chloride

The conductivity of barium chloride in water at 25°C has been studied in the present work over the concentration range 0.0794 to 1.4276 molar. The conductivity of this salt has been previously investigated at 25°C in 1930 by Jones and Dole (29) for the concentration range 0.001 to 1.00 molar and in 1934 by Shedlovsky and Brown (30) for solutions of up to 0.05175 molar concentration. The results from the present work agree closely with those obtained by the above-mentioned workers over the common concentration range studied and they are given numerically in terms of \( \Lambda \) and \( \sqrt{c} \), together with those of Jones and Dole, in Table 17 (page 66). These data are shown graphically in Fig. 30. It will be seen that the curve shows no point of inflection and for concentrations above \( \sqrt{c} = 0.5 \) the curve is almost linear.

Jones and Dole used for their conductivity determinations a conventional bridge circuit which is described by Jones and Josephs (31) with Washburn pipette type cells. They showed that the conductivity equations of Kohlrausch (32), Debye-Hückel (33), Onsager (34), (35), and Walden (36) differed widely from the experimental data at high concentrations and they derived an empirical equation, based on that suggested by Lettewy (37), which fitted the data within 0.06 mho at all points from 0.001 to 0.1 molar. The equation they derived is:

\[
\Lambda = 141.065 - \frac{224.98\sqrt{c}}{1 + 3.2725\sqrt{c}} - 15.56c
\]
Shedlovsky and Brown used an a.c. bridge and a flask cell with internal electrodes in a side tube.

For strong uni-univalent electrolytes Shedlovsky (38) obtained an equation derived from the Onsager equation having the form:

\[ \Lambda_0 = \frac{A + 2\sqrt{c}}{1 - a\sqrt{c}} - Bc \]

which holds up to 0.1 molar. This equation also applies to bi-univalent electrolytes when the concentration is expressed in "ionic strengths", when, for solutes in water at 25°C

\[ \beta = 109.80 \text{ and } a = 1.267/(1 + t_2^0 + 0.816\sqrt{1 + t_2^0}) \]

With this equation they obtained results for \( \Lambda_0 \) which agree with those obtained by linear extrapolation from plotting \( \Lambda \) against \( \sqrt{c} \) for measurements of very dilute solutions and for barium chloride, \( \Lambda_0 = 139.98 \).

Using viscosity data interpolated from the International Critical Tables (10), the product \( \frac{\Lambda}{\eta} \) was calculated for the present data up to \( \sqrt{c} = 1.114 \). The plot of \( \frac{\Lambda}{\eta} \) against \( \sqrt{c} \) results in a smooth uninflected curve which is indicated in Fig. 30. The numerical data are given in Table 17 (page 66).
Figure 30

CONDUCTIVITY OF BARIUM CHLORIDE
IN WATER AT 25°C

- Present work
- Results of Jones and Dole
- Viscosity-corrected curve for the present work
### TABLE 17

**THE CONDUCTIVITY OF BARIUM CHLORIDE IN WATER AT 25°C**

<table>
<thead>
<tr>
<th>$\sqrt{c}$</th>
<th>$\Lambda$</th>
<th>$\Lambda \frac{\eta}{\eta_0}$</th>
<th>$\sqrt{c}$</th>
<th>$\Lambda$</th>
<th>$\Lambda \frac{\eta}{\eta_0}$</th>
</tr>
</thead>
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<tr>
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<td>123.0</td>
<td>0.7317</td>
<td>87.8</td>
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</tr>
<tr>
<td>0.1782</td>
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<td>116.7</td>
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</tr>
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<td>0.2520</td>
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<td>0.3564</td>
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<td>103.6</td>
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<td>0.4116</td>
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<td>0.4752</td>
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<td>-</td>
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<td>0.5488</td>
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<td>1.6898</td>
<td>59.8</td>
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<td>0.6337</td>
<td>91.0</td>
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*Figures of Jones and Dole (29)*

<table>
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<tr>
<th>$\sqrt{c}$</th>
<th>$\Lambda$</th>
<th>$\sqrt{c}$</th>
<th>$\Lambda$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.045</td>
<td>132.26</td>
<td>0.316</td>
<td>105.32</td>
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<tr>
<td>0.071</td>
<td>128.12</td>
<td>0.447</td>
<td>98.68</td>
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<tr>
<td>0.100</td>
<td>124.06</td>
<td>0.707</td>
<td>89.20</td>
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<tr>
<td>0.141</td>
<td>119.14</td>
<td>1.000</td>
<td>80.60</td>
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<tr>
<td>0.224</td>
<td>111.62</td>
<td>1.414</td>
<td>68.98</td>
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</tbody>
</table>
(b) Nickelous chloride

The conductivity of nickelous chloride in water at 25°C has been studied in the present work over the concentration range 0.016225 to 4.1534 molar. The conductivity of this salt has been previously reported only up to 0.0021125 molar. This was in 1949 by Jones et al. (39) who used a resistance bridge operating at either 1,000 or 3,150 cycles per second and a telephone detector. The cells had lightly blackened internal platinum electrodes. Both sets of data are given numerically, in terms of $A$ and $\sqrt{c}$, in Table 18 (page 68) and are shown graphically in Fig. 31.

The data of the present work and those of Jones et al. lie on a smooth curve of similar shape to the $A, \sqrt{c}$ curve for barium chloride. It has no inflexions, and above $\sqrt{c} = 0.8$ it is almost linear.
CONDUCTIVITY OF NICKEL CHLORIDE (NiCl₂)
IN WATER AT 25°C

Figure 31

Present work

Results of Jones, Monk and Davies
TABLE 18

THE CONDUCTIVITY OF NICKELOUS CHLORIDE IN WATER AT 25°C

<table>
<thead>
<tr>
<th>(c/\text{c})</th>
<th>(\Lambda)</th>
<th>(\sqrt{c}/\text{c})</th>
<th>(\Lambda)</th>
</tr>
</thead>
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<td>0.1801</td>
<td>110.3</td>
<td>1.5629</td>
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<td>0.3603</td>
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<td>1.8048</td>
<td>44.4</td>
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<td>0.7206</td>
<td>80.8</td>
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<td>36.7</td>
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<td>0.7815</td>
<td>77.9</td>
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<td>35.3</td>
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<td>1.1051</td>
<td>67.3</td>
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<td>1.4410</td>
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Figures of Jones, Monk and Davis (39)

<table>
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<th>(c/\text{c})</th>
<th>(\Lambda)</th>
<th>(\sqrt{c}/\text{c})</th>
<th>(\Lambda)</th>
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</thead>
<tbody>
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<td>0.0000</td>
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<tr>
<td>0.0415</td>
<td>122.96</td>
<td>0.0650</td>
<td>119.62</td>
</tr>
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</table>
SECTION IIa

THE CONDUCTIVITIES OF RELATIVELY CONCENTRATED SOLUTIONS
OF MULTIVALENT ELECTROLYTES IN WATER AT 25°C
THE CONDUCTIVITIES OF RELATIVELY CONCENTRATED SOLUTIONS
OF MULTIVALENT ELECTROLYTES IN WATER AT 25°C

(a) Potassium Ferricyanide
(b) Potassium Ferrocyanide
(c) Calcium Ferrocyanide

These salts were chosen as examples of uni-trivalent, uni-quadrivalent and bi-quadrivalent electrolytes respectively because they could be purified easily and are only slightly hydrolysed by water.

In 1916 Schoch and Felsing (40) reported the conductivities of potassium ferricyanide and calcium ferrocyanide at equivalent concentrations ranging from 0.0005 up to 1.000 and of potassium ferrocyanide at equivalent concentrations between 0.002 and 1.000. They used a Nernst conductivity vessel whose cell constant was determined using 0.1 normal potassium chloride, the specific conductivity of which was taken as 0.01289 at 25°C.
(a) Potassium ferricyanide

The conductivity of potassium ferricyanide in water at 25°C has been studied in the present work over the concentration range 0.011743 to 0.9989 molar. As noted in the preceding paragraph, in 1916 Schoch and Felsing (40) reported the conductivity of aqueous solutions of this salt over the concentration range 0.0001667 to 0.333 molar. In 1937 Hartley and Donaldson (41) reported conductivity data for aqueous solutions in the concentration range 0.000011801 to 0.0008333 molar using a conventional cell with internal platinum electrodes and a resistance bridge operating at 1,000, 1,000√2 and 2,000 cycles per second. The cell was calibrated using potassium chloride and the data and extrapolation of Shedlovsky (38). They obtained Λ₀ for potassium ferricyanide by graphical extrapolation.

Hartley and Donaldson considered the possibility of part of the conductivity of the ferricyanide ion being due to hydrolysis taking place according to either of two equations:

\[ \text{[Fe(CN)₆]}^{3-} + 2\text{H}_2\text{O} \rightleftharpoons \text{[Fe(CN)₅(H₂O)]}^{2-} + \text{HCN} + \text{OH}^- \]

or \[ \text{[Fe(CN)₆]}^{3-} + \text{H}_2\text{O} \rightleftharpoons \text{[Fe(CN)₅OH]}^{2-} + \text{HCN} \]

or some combination of these.

Since both processes give rise to almost completely undissociated hydrocyanic acid, by addition of this substance to the water used in the conductivity measurements, the hydrolysis would be suppressed without seriously affecting the residual conductivity of the solvent. They found
that when the water was made approximately $2 \times 10^{-4}$ normal in HCN the conductivity of the salt at even the lowest concentrations was not changed by more than that due to experimental error. There was, however, a considerable time effect on the solution in immediate contact with the electrodes. After the temperature of the conductivity vessel had accommodated to that of the thermostat, a steady fall of conductivity persisted when no hydrogen cyanide had been added to the solution, whilst in the solution to which hydrogen cyanide had been added, there was a steady rise of conductivity. After stirring the contents of the vessel so that the solution in contact with the electrodes was changed, the behaviour was repeated. Extrapolating the resistance against time back to the time of stirring (taking into consideration only the readings in the period of steady change after thermal equilibrium had been established) concordant values were obtained. There was, therefore, no appreciable effect in the bulk of the solution and they concluded that some reaction takes place on the surface of the platinum electrodes.

The findings of the above workers therefore suggest that no part of the conductivity measurements in the present work are due to hydrolysis of the ferricyanide ion, and they will be free from any errors due to reactions at the electrode surface. The ionic species making up the recorded conductivities therefore are:
The results of the present work in terms of \( \Lambda \) and \( \sqrt{c} \) together with those of Schoch and Felsing are shown numerically in Table 19 (page 74) and graphically in Fig. 32. These results show quite good agreement over the concentration range studied.

The product \( \Lambda \frac{\eta}{\eta_0} \) was calculated for the present data up to \( \sqrt{c} = 1.1244 \) using viscosity data interpolated from the International Critical Tables (10) and is recorded in Table 19. The plot of \( \Lambda \frac{\eta}{\eta_0} \) against \( \sqrt{c} \) results in a smooth curve which in the region of \( \sqrt{c} = 1.0 \) is almost parallel with the \( \sqrt{c} \) axis. Above this concentration the curve turns downwards slightly and this may be because the published viscosity data for this salt are not accurate above \( \sqrt{c} = 1.0 \). The curve is indicated in Fig. 32.
Figure 32

CONDUCTIVITY OF
POTASSIUM FERRICYANIDE
IN WATER AT 25°C

- Present work
- Results of Schoch and Felsing
- Viscosity-corrected curve for the present work
<table>
<thead>
<tr>
<th>√c</th>
<th>Λ</th>
<th>Λη/η₀</th>
<th>√c</th>
<th>Λ</th>
<th>Λη/η₀</th>
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</thead>
<tbody>
<tr>
<td>0.1877</td>
<td>128.4</td>
<td>128.6</td>
<td>0.8432</td>
<td>96.1</td>
<td>100.4</td>
</tr>
<tr>
<td>0.2167</td>
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<td>124.0</td>
<td>0.8929</td>
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<td>101.4</td>
</tr>
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<td>121.0</td>
<td>0.9738</td>
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<td>99.7</td>
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<tr>
<td>0.2890</td>
<td>118.0</td>
<td>118.0</td>
<td>1.0311</td>
<td>93.4</td>
<td>100.1</td>
</tr>
<tr>
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Figures of Schoch and Felsing (40)

<table>
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<th>Λ</th>
<th>√c</th>
<th>Λ</th>
</tr>
</thead>
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<td>0.1000</td>
<td>141.7</td>
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<td>93.6</td>
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</table>
(b) **Potassium ferrocyanide**

The conductivity of potassium ferrocyanide in water at 25°C has been studied in the present work over the concentration range 0.009938 to 0.670075 molar. In 1916 Schoch and Felsing (40) reported the conductivity at 25°C up to 0.25 molar and in 1936 Jones and Jelen (42) reported the conductivity at 25°C over the concentration range 0.00025 to 0.5 molar. The method used by Jones and Jelen for determining the conductivity was that previously used by Jones and Bickford (13) for potassium bromide and the details of their method are described under that salt on page 38. Jones and Jelen used their data to test the various conductivity equations that have been proposed to express the conductance as a function of the concentration and they showed that the Jones and Dole equation was the best formula known to them for the more concentrated solutions. The coefficients of this equation were determined by the method of least squares using all the experimental points including 0.5 molar, giving the equation:

\[ \Lambda_m = 785.16 - \frac{9171.38}{1 + 17.106\Lambda_m} - 12.84\Lambda_m \]

They further found that when the conductivities were corrected for viscosity, the deviations between the curve from the Jones and Dole equation and the experimental curve were substantially reduced for the more concentrated solutions and gave a \( \Lambda \frac{\eta}{\eta_o} \sqrt{c} \) curve with a flat minimum at 0.2 molar.

The viscosity corrected equation obtained by them was:

\[ \Lambda_m \frac{\eta}{\eta_o} = 783.75 - \frac{9.000.35\Lambda_m}{1 + 16.8424\Lambda_m} + 133.9\Lambda_m \]
James (43) noted that for equivalent concentrations of below 0.002, an apparent steady decrease in conductivity occurred during measurements but that gentle shaking of the cell caused the conductivity to rise again. This effect was also noted by Hartley and Donaldson (41) for potassium ferricyanide. James attributed this behaviour to adsorption or decomposition of the electrolyte on the surface of the electrodes with a consequent decrease in conductivity in the immediate vicinity. This kind of effect is eliminated when cells such as those used in the present work are employed.

James found that his conductivity data showed marked deviations from the limiting Onsager equation even in very dilute solutions. He considered that this could be ascribed to the occurrence of first-stage association:

\[ K^+ + \text{Fe(CN)}_6^{4-} \rightleftharpoons K\text{Fe(CN)}_6^{4-} \]

The results of the present work in terms of \( \Lambda \), \( \frac{n}{\eta_0} \), and \( \sqrt{c} \), together with those of Jones and Jelen, are given numerically in Table 20 (page 77) and they are shown graphically in Fig. 33.

The present data for \( \Lambda \) and \( \sqrt{c} \) are in good agreement with those of Jones and Jelen over the common concentration range studied. The viscosity data used for calculating \( \Lambda \frac{n}{\eta_0} \) were interpolated from those reported by Jones and Stauffer (44). As reported by Jones and Jelen, the present data give a \( \Lambda \frac{n}{\eta_0} \sqrt{c} \) curve with a flat minimum at about \( \sqrt{c} = 0.9 \) or approximately 0.2 molar.
Figure 33

CONDUCTIVITY OF POTASSIUM FERROCYANIDE IN WATER AT 25°C

- Present work
- Results of Jones and Jelen
- Viscosity-corrected curve for the present work
### Table 20

The Conductivity of Potassium Ferrocyanide in Water at 25°C

<table>
<thead>
<tr>
<th>( \sqrt{c} )</th>
<th>( \Lambda )</th>
<th>( \Lambda \frac{\eta}{\eta_0} )</th>
<th>( \sqrt{c} )</th>
<th>( \Lambda )</th>
<th>( \Lambda \frac{\eta}{\eta_0} )</th>
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<td>0.8528</td>
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<td>86.1</td>
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<td>1.3172</td>
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<td>86.8</td>
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Figures of Jones and Jelen (42)

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<td>0.0632</td>
<td>149.58</td>
<td>0.8944</td>
<td>77.72</td>
</tr>
<tr>
<td>0.0894</td>
<td>138.54</td>
<td>1.4142</td>
<td>70.66</td>
</tr>
<tr>
<td>0.1414</td>
<td>122.82</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
(c) Calcium ferrocyanide

The conductivity of calcium ferrocyanide in water at 25°C has been studied in the present work over the concentration range 0.0036 to 1.69 molar. In 1916, Schoch and Felsing (40) reported data for this salt over the concentration range 0.000125 to 0.25 molar, so that in the present work the data have been extended to considerably higher concentrations.

In 1949, James (43) reported conductivity data for this salt up to 0.000304 molar and he concluded that, since large deviations from the limiting Onsager equation occur, the dissociation is far from complete even in dilute solutions. Calcium ferrocyanide will dissociate in two stages:

\[
\text{Ca}_2\text{Fe(CN)}_6 \rightleftharpoons \text{Ca}^{++} + \text{CaFe(CN)}_6
\]

and

\[
\text{CaFe(CN)}_6 \rightleftharpoons \text{Ca}^{++} + \text{Fe(CN)}_6
\]

James found that approximate calculation indicated that even at an equivalent concentration of 0.0002 the second-stage dissociation is only about 75 per cent complete. Using an empirical extension of the Debye-Hückel equation, he calculated for the first-stage dissociation, \( K_1 = 3.7 \times 10^{-2} \text{ moles/l.} \) and for the second-stage dissociation, \( K_2 = 1.69 \times 10^{-4} \text{ moles/l.} \) for concentrations between 0.000151 and 0.000304 molar.

The results of the present work, in terms of \( \Lambda \) and \( \sqrt{c} \) together with those of Schoch and Felsing, are given numerically in Table 21 (page 79) and are shown graphically in Fig. 34. Above \( \sqrt{c} = 1 \) the equivalent conductivity decreases rapidly. This is attributed not only to the occurrence of extensive association but also to the high viscosity which is shown by concentrated solutions of this salt. There are no viscosity data published for high concentrations except for that reported in 1937 by Jones and Stauffer (44). At a concentration of 1.43 molar they found that at 25°C \( \frac{\eta}{\eta_0} = 15.1 \) which is exceptionally high.
Figure 34

CONDUCTIVITY OF
CALCIUM FERROCYANIDE
IN WATER AT 25°C

- Present work
- Results of Schoch and Felsing
### TABLE 21

THE CONDUCTIVITY OF CALCIUM FERROCYANIDE IN WATER AT 25°C

**Present work**

<table>
<thead>
<tr>
<th>√c</th>
<th>Λ</th>
<th>√c</th>
<th>Λ</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.12</td>
<td>54.0</td>
<td>0.87</td>
<td>33.5</td>
</tr>
<tr>
<td>0.14</td>
<td>48.5</td>
<td>0.98</td>
<td>33.5</td>
</tr>
<tr>
<td>0.16</td>
<td>47.5</td>
<td>1.35</td>
<td>31.0</td>
</tr>
<tr>
<td>0.33</td>
<td>38.0</td>
<td>1.82</td>
<td>24.5</td>
</tr>
<tr>
<td>0.52</td>
<td>35.5</td>
<td>2.47</td>
<td>10.0</td>
</tr>
<tr>
<td>0.71</td>
<td>34.5</td>
<td>2.60</td>
<td>6.5</td>
</tr>
</tbody>
</table>

**Figures of Schoch and Felsing (40)**

<table>
<thead>
<tr>
<th>√c</th>
<th>Λ</th>
<th>√c</th>
<th>Λ</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>171.0</td>
<td>0.141</td>
<td>49.30</td>
</tr>
<tr>
<td>0.022</td>
<td>112.3</td>
<td>0.224</td>
<td>41.85</td>
</tr>
<tr>
<td>0.032</td>
<td>105.1</td>
<td>0.316</td>
<td>37.61</td>
</tr>
<tr>
<td>0.045</td>
<td>89.40</td>
<td>0.447</td>
<td>35.63</td>
</tr>
<tr>
<td>0.071</td>
<td>67.10</td>
<td>0.707</td>
<td>34.70</td>
</tr>
<tr>
<td>0.100</td>
<td>57.70</td>
<td>1.000</td>
<td>33.86</td>
</tr>
</tbody>
</table>
SECTION IIe

THE CONDUCTIVITIES OF RELATIVELY CONCENTRATED SOLUTIONS

OF URANYL NITRATE AND DI-SODIUM LEAD

ETHYLENEDIAMINETETRAACETATE IN WATER AT 25°C
Conductivity data were required in connection with other work being carried out on these two salts. This conductivity work is placed in a separate section because these salts were not provided in amounts which were large enough to permit their purification by re-crystallisation. However, the di-sodium lead ethylenediaminetetraacetate was dried thermodynamically to give the dihydrate as described in Appendix IV.
(a) Uranyl nitrate

The conductivity of uranyl nitrate in water at 25°C has been studied in the present work over the concentration range 0.0027085 to 0.6931 molar. The conductivity of aqueous solutions of this salt were reported as long ago as 1899 by Dittrich(45). His data, which cover the concentration range 0.00012168 to 0.125 molar, show conductivities which are some 10 per cent lower than the present data at the same concentrations. In 1911, Winston and Jones (46) reported conductivity data up to 0.25 molar and their conductivities are slightly nearer to those obtained in the present work and are those most recently published.

The conductivity curve from the data of Dittrich does not approach a constant value with increasing dilution although Gomez (47) showed that by taking the differences between each value of $\Lambda$ and the next succeeding one at double the dilution, the difference decreases down to a concentration of 0.0156 molar. Below this concentration the difference increases progressively. This was attributed by Gomez to the progressive ionization of the salt in the following manner:

$$UO_2(NO_3)_2 \rightleftharpoons UO_2(NO_3)^+ + NO_3^-$$

followed by

$$UO_2(NO_3)^+ \rightleftharpoons UO_2^{++} + NO_3^-$$

with hydrolysis below a concentration of 0.0156 molar.

$$UO_2^{++} + H_2O \rightleftharpoons UO_3^- + 2H^+$$
Gomez also measured the transport numbers of the anions at concentrations between 0.0024 and 0.074 molar and obtained a curve which is typical of that of a ternary electrolyte, and shows a minimum at a concentration of 0.015 molar, from which he concluded that a maximum concentration of the \([\text{UO}_2(\text{NO}_3)]^+\) ion occurred at this concentration. At concentrations above 0.07 molar the transport number approaches unity, and this indicates that the metallic radical now forms part of the anion.

The results of the present work, in terms of \(\Lambda\) and \(\sqrt{c}\), together with those of Dittrich and of Winston and Jones, are given numerically in Tables 22 and 23 (pages 84 and 85) and are shown graphically in Fig. 35. It will be noted that the curve is a smooth one which becomes practically linear for concentrations above \(\sqrt{c} = 0.5\).
Figure 35

CONDUCTIVITY OF URANYL NITRATE IN WATER AT 25°C

- ○ Present work
- ○ Results of Dittrich
- ● Results of Winston and Jones
### TABLE 22

**THE CONDUCTIVITY OF URANYL NITRATE IN WATER AT 25°C**

**Present work**

<table>
<thead>
<tr>
<th>√c</th>
<th>Λ</th>
<th>√c</th>
<th>Λ</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0736</td>
<td>121.3</td>
<td>0.3744</td>
<td>88.8</td>
</tr>
<tr>
<td>0.0936</td>
<td>126.5</td>
<td>0.4163</td>
<td>85.8</td>
</tr>
<tr>
<td>0.1041</td>
<td>117.5</td>
<td>0.5294</td>
<td>79.7</td>
</tr>
<tr>
<td>0.1324</td>
<td>114.8</td>
<td>0.5887</td>
<td>77.4</td>
</tr>
<tr>
<td>0.1472</td>
<td>109.0</td>
<td>0.7487</td>
<td>69.8</td>
</tr>
<tr>
<td>0.1872</td>
<td>105.4</td>
<td>0.8325</td>
<td>66.3</td>
</tr>
<tr>
<td>0.2081</td>
<td>101.4</td>
<td>1.0589</td>
<td>57.0</td>
</tr>
<tr>
<td>0.2647</td>
<td>97.2</td>
<td>1.1774</td>
<td>52.1</td>
</tr>
<tr>
<td>0.2944</td>
<td>93.6</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
TABLE 23

THE CONDUCTIVITY OF URANYL NITRATE IN WATER AT 25°C

Figures of Dittrich (45)

<table>
<thead>
<tr>
<th>√c</th>
<th>Λ</th>
<th>√c</th>
<th>Λ</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0156</td>
<td>151.8</td>
<td>0.1250</td>
<td>100.8</td>
</tr>
<tr>
<td>0.0221</td>
<td>140.7</td>
<td>0.1768</td>
<td>94.34</td>
</tr>
<tr>
<td>0.0312</td>
<td>131.5</td>
<td>0.2500</td>
<td>88.23</td>
</tr>
<tr>
<td>0.0442</td>
<td>122.7</td>
<td>0.3536</td>
<td>81.42</td>
</tr>
<tr>
<td>0.0625</td>
<td>115.0</td>
<td>0.5000</td>
<td>74.09</td>
</tr>
<tr>
<td>0.0884</td>
<td>107.6</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figures of Winston and Jones (46)

<table>
<thead>
<tr>
<th>√c</th>
<th>Λ</th>
<th>√c</th>
<th>Λ</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0625</td>
<td>137.25</td>
<td>0.2500</td>
<td>103.945</td>
</tr>
<tr>
<td>0.0884</td>
<td>127.69</td>
<td>0.3535</td>
<td>90.32</td>
</tr>
<tr>
<td>0.1250</td>
<td>120.735</td>
<td>0.5000</td>
<td>75.285</td>
</tr>
<tr>
<td>0.1768</td>
<td>112.475</td>
<td>0.7071</td>
<td>66.455</td>
</tr>
</tbody>
</table>
(b) Di-sodium lead ethylenediaminetetraacetate

The conductivity of aqueous solutions of this salt have not been previously reported and in the present work data for the concentration range 0.000982 to 1.333 molar have been obtained. The numerical results, in terms of Λ and \( \sqrt{c} \), are given in Table 24 (page 87) and are shown graphically in Fig. 36. The Λ, \( \sqrt{c} \) curve is a smooth one approaching linearity for concentrations of between \( \sqrt{c} = 0.5 \) and \( \sqrt{c} = 1.4 \).

Ethylenediaminetetraacetic acid has the following structural formula

![Structural formula of ethylenediaminetetraacetic acid](image)

According to Chapman (48), the structure for the di-sodium salt is

![Structural formula of di-sodium lead ethylenediaminetetraacetate](image)

This salt forms a complex with bivalent ions such as Pb\(^{++} \) to give a complex which carries two negative charges which has been assigned the following structure by Schwarzenbach (49)

![Structure of complex with Pb](image)

The three-dimensional structure is probably octahedral.
CONDUCTIVITY OF DISODIUM LEAD ETHERENEDIAMINOTETRAACETATE IN WATER AT 25°C
Table 24

The Conductivity of Di-sodium Lead Ethylenediaminetetraacetate in Water at 25°C

<table>
<thead>
<tr>
<th>( \sqrt{c} )</th>
<th>( \Lambda )</th>
<th>( \sqrt{c} )</th>
<th>( \Lambda )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0443</td>
<td>80.6</td>
<td>0.3536</td>
<td>57.9</td>
</tr>
<tr>
<td>0.0625</td>
<td>77.1</td>
<td>0.5000</td>
<td>52.0</td>
</tr>
<tr>
<td>0.0884</td>
<td>74.6</td>
<td>0.7071</td>
<td>44.4</td>
</tr>
<tr>
<td>0.1250</td>
<td>71.6</td>
<td>1.0000</td>
<td>34.5</td>
</tr>
<tr>
<td>0.1768</td>
<td>67.9</td>
<td>1.4142</td>
<td>20.4</td>
</tr>
<tr>
<td>0.2500</td>
<td>62.5</td>
<td>1.6328</td>
<td>14.4</td>
</tr>
</tbody>
</table>
SECTION III

THE DETERMINATION OF THE MEAN IONIC RADIUS OF ELECTROLYTES FROM CONDUCTIVITY DATA
THE DETERMINATION OF THE MEAN IONIC RADIIS
OF ELECTROLYTES FROM CONDUCTIVITY DATA

With the exception of acetic acid, the conductivity data, obtained in the present work and described in Section II, for all the uni-univalent electrolytes and also for barium chloride, were treated by the method of Robinson and Stokes (50) to obtain an "a" parameter, which is the mean distance of "closest approach" of the ions. This method is based upon the Onsager equation (35) modified for higher concentrations by the introduction of a factor \( (1 + K_a) \) into the denominator of the \( \sqrt{I} \) term (37)(51). The equation may be written:

\[
\Lambda = \Lambda_0 - \frac{41.25 (|Z_1| + |Z_2|) \sqrt{I}}{\eta (\varepsilon \tau)^{1/2} (1 + K_a)} \left[ 1 - \frac{2.801 \times 10^6 |Z_1 Z_2| q \sqrt{I}}{(\varepsilon \tau)^{3/2} (1 + q)(1 + K_a)} \right] (10)
\]

where

\[
K_a = \left( \frac{8\pi N_a^2}{1000 \varepsilon \tau} \right)^{1/2} a \sqrt{I}
\]

In the most complete form, Falkenhagen's equation for the relaxation effect (22)(page 107) may be introduced into equation (10) to give:

\[
\Lambda = \Lambda_0 - \frac{41.25 (|Z_1| + |Z_2|) \sqrt{I}}{\eta (\varepsilon \tau)^{1/2} (1 + K_a)} \left[ 1 - \frac{2.801 \times 10^6 |Z_1 Z_2| q \sqrt{I}}{(\varepsilon \tau)^{3/2} (1 + q)(1 + K_a)} \right] (11)
\]

where

\[
F = \frac{e K_a (1 - \sqrt{q}) - 1}{K_a (1 - \sqrt{q})}
\]

which for a uni-univalent electrolyte with "a" in ångströms reduces to:
\[ \Lambda = \left[ \Lambda_0 - \frac{B_2 \sqrt{m}}{1 + B_0 \sqrt{m}} \right] \left[ 1 - \frac{B_1 \sqrt{m}}{1 + B_0 \sqrt{m}} P \right] \]

\[ P = \frac{0.2929B_0 \sqrt{m}}{0.02929B_0 \sqrt{m}} - 1 \]

where \( B, B_1 \) and \( B_2 \) are constants for a given solvent and temperature, and for water at 25°C are 0.3286, 0.2289 and 60.32, respectively.

The values for "a" obtained by applying equation (10) are given in Tables 25 to 33. The viscosities used in calculating these values were interpolated from those recorded in the International Critical Tables (10). The mean ionic radii for these electrolytes given by Stokes and Robinson (52), who obtained them from activity coefficient data, with the exception of those for ammonium and caesium chlorides, are also given in the tables. The mean ionic radius shown in Table 27 for ammonium chloride is that given by Robinson and Stokes (50). A value for caesium has not been previously reported. By applying equation (11) to the values for two or three concentrations for each electrolyte, it was shown that the extra factor made no significant difference to the "a" values except in the cases of lithium chloride and rubidium chloride. The differing values are noted in brackets in Tables 25 and 30. For lithium chloride (Table 25) a series of "a" values have also been obtained by using viscosity-corrected equivalent conductivities (\( \Lambda \eta/\eta_0 \)) in equation (11).
TABLE 25

THE "a" PARAMETER FOR LITHIUM CHLORIDE AT 25°C

<table>
<thead>
<tr>
<th>Present work</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sqrt{c}$</td>
</tr>
<tr>
<td>0.27</td>
</tr>
<tr>
<td>0.30</td>
</tr>
<tr>
<td>0.38</td>
</tr>
<tr>
<td>0.43</td>
</tr>
<tr>
<td>0.53</td>
</tr>
<tr>
<td>0.61</td>
</tr>
<tr>
<td>0.77</td>
</tr>
<tr>
<td>0.86</td>
</tr>
<tr>
<td>1.07</td>
</tr>
<tr>
<td>1.21</td>
</tr>
</tbody>
</table>

+ Values calculated from viscosity-corrected equivalent conductivities.

Figure of Stokes and Robinson (52)

$a \times 10^8 = 4.32$ cm
TABLE 26

THE "a" PARAMETER FOR SODIUM CHLORIDE AT 25°C

Present work

<table>
<thead>
<tr>
<th>√c</th>
<th>a x 10^8 cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.39</td>
<td>4.6</td>
</tr>
<tr>
<td>0.52</td>
<td>4.0</td>
</tr>
<tr>
<td>0.56</td>
<td>3.8</td>
</tr>
<tr>
<td>0.74</td>
<td>3.4</td>
</tr>
<tr>
<td>0.79</td>
<td>3.4</td>
</tr>
<tr>
<td>1.04</td>
<td>2.8</td>
</tr>
<tr>
<td>1.11</td>
<td>2.7</td>
</tr>
<tr>
<td>1.48</td>
<td>2.6</td>
</tr>
</tbody>
</table>

Figure of Stokes and Robinson (52)

a x 10^8 = 3.97 cm
## Table 27

The "a" Parameter for Ammonium Chloride at 25°C

**Present Work**

<table>
<thead>
<tr>
<th>√c</th>
<th>a x 10^8 cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.32</td>
<td>3.8</td>
</tr>
<tr>
<td>0.64</td>
<td>4.2</td>
</tr>
<tr>
<td>1.00</td>
<td>4.0</td>
</tr>
<tr>
<td>1.18</td>
<td>4.0</td>
</tr>
<tr>
<td>1.41</td>
<td>3.9</td>
</tr>
<tr>
<td>1.79</td>
<td>3.6</td>
</tr>
</tbody>
</table>

*Figure of Robinson and Stokes (50)*

\[ a \times 10^8 = 3.75 \text{ cm} \]
TABLE 28

THE "a" PARAMETER FOR POTASSIUM CHLORIDE AT 25°C

<table>
<thead>
<tr>
<th>√c</th>
<th>a x 10^8 cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.34</td>
<td>5.0</td>
</tr>
<tr>
<td>0.40</td>
<td>4.8</td>
</tr>
<tr>
<td>0.48</td>
<td>4.8</td>
</tr>
<tr>
<td>0.56</td>
<td>4.4</td>
</tr>
<tr>
<td>0.68</td>
<td>4.5</td>
</tr>
<tr>
<td>0.80</td>
<td>4.4</td>
</tr>
<tr>
<td>0.96</td>
<td>4.3</td>
</tr>
<tr>
<td>1.13</td>
<td>4.2</td>
</tr>
<tr>
<td>1.36</td>
<td>4.0</td>
</tr>
<tr>
<td>1.60</td>
<td>3.7</td>
</tr>
</tbody>
</table>

Figure of Stokes and Robinson (52)

a x 10^8 = 3.63 cm
## TABLE 29

**THE "a" PARAMETER FOR POTASSIUM BROMIDE AT 25°C**

<table>
<thead>
<tr>
<th>(c)</th>
<th>(a \times 10^8) cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.32</td>
<td>4.6</td>
</tr>
<tr>
<td>0.60</td>
<td>4.9</td>
</tr>
<tr>
<td>1.00</td>
<td>4.6</td>
</tr>
<tr>
<td>1.18</td>
<td>4.6</td>
</tr>
<tr>
<td>1.41</td>
<td>4.4</td>
</tr>
<tr>
<td>1.61</td>
<td>4.0</td>
</tr>
</tbody>
</table>

**Present work**

**Figure of Stokes and Robinson (52)**

\[ a \times 10^8 = 3.85\text{ cm} \]
### TABLE 30

**THE "a" PARAMETER FOR RUBIDIUM CHLORIDE AT 25°C**

**Present work**

<table>
<thead>
<tr>
<th>( \sqrt{c} )</th>
<th>( a \times 10^8 ) cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.32</td>
<td>5.1 (5.3)</td>
</tr>
<tr>
<td>0.46</td>
<td>4.8</td>
</tr>
<tr>
<td>0.53</td>
<td>4.6</td>
</tr>
<tr>
<td>0.61</td>
<td>4.5 (4.9)</td>
</tr>
<tr>
<td>0.70</td>
<td>4.5</td>
</tr>
<tr>
<td>0.81</td>
<td>4.4</td>
</tr>
<tr>
<td>0.93</td>
<td>4.2 (4.3)</td>
</tr>
</tbody>
</table>

**Figure of Stokes and Robinson (52)**

\[
a \times 10^8 = 3.49 \text{ cm}
\]
**TABLE 31**

THE "a" PARAMETER FOR CAESIUM CHLORIDE AT 25°C

Present work

<table>
<thead>
<tr>
<th>√c</th>
<th>a x 10^8 cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.51</td>
<td>4.0</td>
</tr>
<tr>
<td>0.59</td>
<td>4.2</td>
</tr>
<tr>
<td>0.68</td>
<td>4.0</td>
</tr>
<tr>
<td>0.79</td>
<td>4.1</td>
</tr>
<tr>
<td>0.91</td>
<td>4.1</td>
</tr>
<tr>
<td>1.06</td>
<td>4.1</td>
</tr>
</tbody>
</table>
## Table 32
THE "a" PARAMETER FOR HYDROCHLORIC ACID AT 25°C

<table>
<thead>
<tr>
<th>$\sqrt{c}$</th>
<th>$a \times 10^8$ cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.30</td>
<td>6.9</td>
</tr>
<tr>
<td>0.37</td>
<td>7.4</td>
</tr>
<tr>
<td>0.53</td>
<td>5.5</td>
</tr>
<tr>
<td>0.61</td>
<td>4.3</td>
</tr>
<tr>
<td>0.74</td>
<td>3.3</td>
</tr>
<tr>
<td>1.05</td>
<td>1.8</td>
</tr>
<tr>
<td>1.21</td>
<td>1.2</td>
</tr>
<tr>
<td>1.49</td>
<td>0.7</td>
</tr>
<tr>
<td>1.72</td>
<td>0.4</td>
</tr>
<tr>
<td>2.10</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Figure of Stokes and Robinson (52)

\[ a \times 10^8 = 4.47 \text{ cm} \]
### TABLE 33

**THE "a" PARAMETER FOR BARIUM CHLORIDE AT 25°C**

<table>
<thead>
<tr>
<th>$\sqrt{c}$</th>
<th>$a \times 10^8$ cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.18</td>
<td>4.2</td>
</tr>
<tr>
<td>0.25</td>
<td>4.2</td>
</tr>
<tr>
<td>0.36</td>
<td>4.0</td>
</tr>
<tr>
<td>0.41</td>
<td>4.0</td>
</tr>
<tr>
<td>0.48</td>
<td>4.0</td>
</tr>
<tr>
<td>0.62</td>
<td>4.2</td>
</tr>
<tr>
<td>0.73</td>
<td>4.5</td>
</tr>
<tr>
<td>0.79</td>
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</tr>
<tr>
<td>0.84</td>
<td>4.2</td>
</tr>
<tr>
<td>0.95</td>
<td>3.9</td>
</tr>
<tr>
<td>1.11</td>
<td>3.7</td>
</tr>
<tr>
<td>1.27</td>
<td>3.3</td>
</tr>
</tbody>
</table>

**Figure of Stokes and Robinson (52)**

$$a \times 10^8 = 4.45 \text{ cm}$$
SECTION IV

DISCUSSION
DISCUSSION

(i) The Theory of Conductivity

The passage of electricity through electrolytes is characterised by the movement of ions, the dimensions and masses of which are much larger than electrons which alone are responsible for metallic electrical conduction. The ions of course share in the general Brownian motion of the liquid, and may therefore be expected to have randomly-directed instantaneous velocities of the order of $10^{-4}$ cm sec$^{-1}$, but with an extremely short mean free path as is characteristic of the liquid state. In the absence of an external field or a concentration-gradient, the Brownian movement is entirely random, and does not lead to a drift of ions in any one direction. The presence of an electric field, as in conductance, or of a concentration-gradient, as in diffusion, has the effect of biasing the Brownian movement in a particular direction. In a field of 1 volt/cm the average velocity of the ions in the direction of the field is of the order of $10^{-3}$ to $10^{-4}$ cm sec$^{-1}$, and hence represents only a very small perturbation of the random ionic motions. The actual path of an ion under an electric field of ordinary intensity is thus extremely erratic, bearing very little resemblance to that of a billiard ball sinking in water. Nevertheless, the drastic simplification of substituting for the actual chaotic motion a steady progress of all the ions of one kind with equal velocities in one direction of the field is extraordinarily successful: the Brownian motion needs to be considered only in regard to its effect on the interionic forces.
When solutions are considered, as opposed to fused salts, at low concentrations, the equivalent conductivity of strong electrolytes is found to be accurately a linear function of the square root of concentration, decreasing as the concentration increases. Extrapolation to zero concentration yields the limiting equivalent conductivity $\Lambda_0$, and Kohlrausch (32) observed that the equivalent conductivity $\Lambda$ at very low concentrations can be represented by the equation:

$$\Lambda = \Lambda_0 - \Lambda_0 \cdot c$$  \hspace{1cm} (12)

A complete theory of electrolytic conduction should therefore be capable of predicting the value of $\Lambda_0$ from the dimensions, but this is so far some way from solution. Secondly, it should be capable of predicting the value of the constant $\Lambda$ in the above equation, and this problem has been solved. Thirdly, a complete theory should be able to account quantitatively for deviations from the equation at higher concentrations, and the position with regard to this third problem has recently been greatly improved as a result of the development of the interionic attraction theory.

At very low concentrations the ions are far enough apart to be without influence upon one another. At higher concentrations the interaction between the electric charges of the ions come into play and give rise to two main effects. These are the relaxation effect and the electrophoretic effect.

(a) The Relaxation Effect in Conductivity

The fundamental idea underlying the interionic attraction theory is that in electrolyte solutions, as a consequence of electrical attractions
between anions and cations there are, on the average, more ions of unlike than of like sign in the neighbourhood of any ion. Every ion may, therefore, be regarded as being surrounded by an ionic atmosphere of opposite charge. As long as the system is not exposed to an applied field or to a shearing force which tends to cause the liquid to flow, the ionic atmosphere has central symmetry. The central ion may then be pictured as moving to an off-centre position when an external force is applied, and experiencing a restoring force, which, however, rapidly dies away as the 'atmosphere' is rearranged by the thermal motions of its constituent ions. The molecular picture thus involves the concept of the 'relaxation' of the ion atmosphere and the average restoring force experienced by the ion is called the relaxation effect, the overall result of this effect being to decrease the velocity of the ions.

The external force acting on the ion may, in the conductivity problem, be taken as a field of intensity \( \mathbf{X} \) (c.g.s. units) acting in the \( x \)-direction; the 'relaxation field' will clearly act in the same direction but in the opposite sense, and will be denoted by \( \Delta \mathbf{X} \). The computation of \( \Delta \mathbf{X} \) involves a combination of the ideas of the interionic attraction theory with the equation of continuity of hydrodynamics, and is mathematically the most difficult part of the electrolyte theory.

The first attack on the problem of the relaxation effect was made by Debye and Hückel (53); a more successful approach, however, was that of Onsager (35), who obtained the following limiting law for the relaxation effect on the conductivity of an extremely dilute solution of a
single electrolyte dissociating into ions 1 and 2:

\[
\frac{\Delta X}{X} = \frac{z_1 z_2 e^2}{3kT} \cdot \frac{qK}{1 + \sqrt{q}} \tag{13}
\]

Here the quantity \( q \) is defined by:

\[
q = \left| \frac{z_1 z_2}{|z_1| + |z_2|} \right| \cdot \frac{\lambda_1 + \lambda_2}{|z_1| \lambda_1 + |z_2| \lambda_2} = \frac{|z_1 z_2|}{(|z_1| + |z_2|)(\mu_1 t_1 + \mu_2 t_2)} \tag{14}
\]

equals one half for symmetrical electrolytes where \( |z_1| = |z_2| \).

The total electric force acting on an ion \( j \) is thus given by:

\[
X z_j e (1 + \frac{\Delta X}{X}) \tag{15}
\]

and produces a velocity (relative to the solvent) of:

\[
v_j' = X z_j e u_j^o (1 + \frac{\Delta X}{X}) \tag{16}
\]

where \( u_j^o \) is the absolute mobility of the ion in c.g.s. units. At infinite dilution the velocity produced by the field \( X \) is:

\[
v_j^o = X z_j e u_j^o \tag{17}
\]

Hence introducing (13) we have:

\[
v_j' = v_j^o \left( 1 + \frac{z_1 z_2 e^2}{3kT} \cdot \frac{qK}{1 + \sqrt{q}} \right)
\]

as Onsager's expression for the velocity of the ion, corrected for the relaxation effect. Before calculating the further correction required to take the electrophoretic effect into account, later developments in the theory of the relaxation effect will be considered. In Onsager's treatment, several approximations are made: the factor \( e^{\kappa a}/(1 + \kappa a) \) is
omitted from Debye and Hückel's fundamental expression for the potential \( \nu_j \) at a distance \( r \) from an ion of valency \( z_j \):

\[
\nu_j = \frac{z_j e}{\varepsilon} \cdot \frac{\kappa a}{(1 + \kappa a)} \cdot e^{-\kappa r}
\]

(18)

This means that the resulting expression is valid only at great dilutions where \( \kappa a \) is small compared with unity.

Various other approximations involving the relation \( \Delta X \ll X \) are made; these also will be admissible at great dilutions where the relaxation effect is small.

For some twenty-five years after the appearance of Onsager's theory no further major progress was made with the relaxation effect. In 1952, however, Falkenhagen, Leist and Kelbg (54) published an important extension and modification of the theory, in which allowance was made for the finite size of the ions. These workers adopt a slightly different distribution function from the usual Boltzmann one, viz., that of Eigen and Wicke (55). The major advance made in this recent work of Falkenhagen is the introduction of the effect of finite ion size into the relaxation term. This is accomplished by using the complete expression for the potential in addition to the new distribution function.

In Falkenhagen's theory \( \kappa \) is defined as:

\[
\kappa^2 = \frac{4\pi e^2}{\varepsilon kT} \left[ n_1 z_1^2 \left( 1 - \frac{n_1}{N_1} \right) + n_2 z_2^2 \left( 1 - \frac{n_2}{N_2} \right) \right]
\]
and Falkenhagen's complete expression for the relaxation effect on the conductivity in a single electrolyte may be written:

$$\frac{\Delta X}{X} = \frac{z_1 z_2 e^2}{3 e k T} \cdot \frac{q}{1 - q} \cdot \frac{\kappa}{(1 + ka) N} \left[ e^{\kappa a (1 - \sqrt{q})} - 1 \right] \left( 1 - \frac{n_1}{N_1} \right) \left( 1 - \frac{n_2}{N_2} \right)$$  (19)

The last two factors make only a minor difference, and for simplification may be omitted. Expanding the exponential in the square bracket:

$$e^{\kappa a (1 - \sqrt{q})} - 1 = \kappa a (1 - \sqrt{q}) + \frac{(\kappa a)^2 (1 - \sqrt{q})^2}{2!} + \ldots \quad (20)$$

For low concentrations only the first term of this expression need be employed when equation (19) becomes:

$$\frac{\Delta X}{X} = \frac{z_1 z_2 e^2}{3 e k T} \cdot \frac{q}{1 + \sqrt{q}} \cdot \frac{\kappa}{1 + \kappa a}$$  (21)

This equation differs from equation (13) only by the presence of $1 + \kappa a$ in the denominator. However, the higher terms of expansion (20) will be appreciable at moderate concentrations and whereas for a hundredth molar solution of a uni-univalent electrolyte the second term is about 1.5 per cent of the first, for a molar solution it is 15 per cent, so for such concentrations the full exponential expression should be used.

The ion size parameter "a" is essentially arbitrarily chosen to suit the experimental facts, and by varying it slightly it is probable that any differences introduced by the use of the modified distribution function could be compensated for; therefore, in the remainder of the
discussion the expression (21) will be used for the relaxation effect for dilute solutions and:

$$\Delta X = \frac{z_1 z_2 e^2}{3\varepsilon k T} \cdot \frac{q}{1 - q} \cdot \frac{\kappa}{\kappa_0(1 - q) - 1}$$ (22)

for more concentrated solutions, giving \( \kappa \) the definition:

$$\kappa^2 = \frac{4\pi e^2 \sum n_i z_i^2}{\varepsilon k T}$$ (23)

The relaxation-field given by these equations is the same for both anion and cation.

(b) **The Electrophoretic Effect in Conductivity**

The tendency of an applied field to move the ionic atmosphere with its associated molecules of solvent in a direction opposite to that in which the ion, accompanied by solvent molecules, is itself moving accounts for the other factor retarding the velocities of the ions, which is known as the electrophoretic effect. This effect is clearly dependent upon concentration, falling to zero at infinite dilution.

The treatment of electrophoresis which follows is confined to the case of a single electrolyte and is essentially that of Onsager and Fuoss (56) but employing the general term of the Boltzmann distribution law.

In the cases considered here, bulk motion of the solution as a whole is irrelevant; it follows that the forces \( k_1 \) and \( k_2 \) acting on the ions must be balanced by other forces \( k_A \) acting on the solvent molecules; and
denoting the respective bulk concentrations by $n_1$, $n_2$ and $n_A$, we have:

$$n_A^k = -n_1^k - n_2^k$$  \hspace{1cm} (24)

at a distance $r$ from the chosen cation the local concentrations of ions are given by the Boltzmann expressions:

$$n_1' = n_1 \exp \left(-\frac{z_1 e \psi}{kT} \right)$$

$$n_2' = n_2 \exp \left(-\frac{z_2 e \psi}{kT} \right)$$  \hspace{1cm} (25)

A spherical shell of radius $r$ and thickness $dr$ is therefore subject to a resultant force given by:

$$(n_1' k_1 + n_2' k_2 + n_A^k) 4\pi r^2 dr$$

Provided that any variation in $n_A$ at this point from its bulk value is neglected (a course which is safe for dilute solutions), $n_A^k$ can be eliminated by means of equation (24) obtaining for the resultant force on the shell:

$$[ (n_1' - n_1) k_1 + (n_2' - n_2) k_2 ] 4\pi r^2 dr$$

This force is assumed to cause the shell and all points within it to move with a velocity obtained, according to Stokes's law, by dividing the force by $6\pi \eta r$ where $\eta$ is the viscosity. Each shell thus contributes to an electrophoretic increment, to the velocity of the central ion, and the whole increment, $\Delta v_1$, is obtained by integrating over all the shells, beginning at $r = a$ (the distance between which no other ions can penetrate and within which the electrophoretic velocity remains constant).

This gives:
\[
\Delta V_1 = \frac{2}{3\pi} \int_0^\infty [(n_1' = n_1)k_1 + (n_2' - n_2)k_2] r dr \quad (26)
\]

If \(n_1\) and \(n_2\) are taken to be given by the Boltzmann distribution (25) this gives on expanding the exponentials:

\[
n_1' - n_1 = n_1 \sum_{n=1}^{\infty} \frac{(-1)^n}{n!} \left( \frac{z_1 e^\psi}{kT} \right)^n
\]

\[
n_2' - n_2 = n_2 \sum_{n=1}^{\infty} \frac{(-1)^n}{n!} \left( \frac{z_2 e^\psi}{kT} \right)^n
\]

(27)

It will prove convenient to express the concentrations \(n_1\) and \(n_2\) in these formulae in terms of the quantity \((\kappa a)\). From equation (23) we have, using the electrical neutrality condition, \(n_1 z_1 + n_2 z_2 = 0\),

\[
n_1 = \frac{(\kappa a)^2}{4\pi a^2} \left( \frac{e^2}{\varepsilon kT} \right)^{-1} \frac{1}{z_1(z_1 - z_2)}
\]

\[
n_2 = \frac{(\kappa a)^2}{4\pi a^2} \left( \frac{e^2}{\varepsilon kT} \right)^{-1} \frac{1}{z_2(z_2 - z_1)}
\]

Using these values in (27) and taking the potential \(\psi\) to be given by the equation (18), we obtain from equation (26):

\[
\Delta V_1 = \frac{1}{6\pi} \frac{(\kappa a)^2}{a^2} \left( \frac{e^2}{\varepsilon kT} \right)^{-1} \sum_{n=1}^{\infty} n \frac{z_1^{n-1}k_1 - z_2^{n-1}k_2}{z_1 - z_2} \cdot \frac{(-1)^n}{n!} \\
\cdot \left( \frac{e^2}{\varepsilon kT} \right)^n \left( \frac{\kappa a}{1 + \kappa a} \right)^n \int_0^r \frac{e^{-nkr}}{r^{n-1}} dr
\]

(28)
The integral occurring with (28) can always be evaluated as:

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

(29)

Where $S_n(\kappa a)$ is a function of $(\kappa a)$ only. Equation (28) may therefore be more briefly expressed as:

$$\Delta v_1 = \sum_{n=1}^{\infty} (-1)^n \frac{n! \, \delta n}{\xi m n!} \left( \frac{\varepsilon^2}{\kappa a} \right)^{n-1} \frac{s_n}{a^n} \cdot \frac{z_1^{n-1} k_1 - z_2^{n-1} k_2}{z_1 - z_2} \, \phi_n(\kappa a)$$

(30)

Where the function $\phi_n(\kappa a)$ is a function of $(\kappa a)$ only, and is defined by

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

in equation (30) the ion size parameter "a" has been written "a" = $a \times 10^{-9}$. so that $a$ is the 'ionic diameter' in Ångströms. The corresponding equation for the electrolytic increment to the velocity of an anion, $\Delta v_2$, is obtained by merely interchanging the subscripts 1 and 2 throughout equation (30).

The further abbreviation:

$$\Delta v_1 = \sum_{n=1}^{\infty} A_n \cdot \frac{s_n^{n-1} k_1 - s_n^{n-1} k_2}{a(z_1 - z_2)}$$

(31)

is useful where $A_n$ depends only on $(\kappa a)$, temperature, and solvent properties and is given by:

$$A_n = \frac{(-1)^n \delta n}{n! \xi m n} \left( \frac{\varepsilon^2}{\kappa a} \right)^{n-1} \phi_n(\kappa a)$$

(32)

In conductance, the forces $k_1$ and $k_2$ are given by the product of
the field intensity and the ionic charge, the field being the sum of
the external field \( X \) and the relaxation field \( \Delta X \) (see page 103) giving:

\[
\begin{align*}
    k_1 &= (X + \Delta X) z_1 e, \\
    k_2 &= (X + \Delta X) z_2 e
\end{align*}
\]

Equation (31) then becomes:

\[
\begin{align*}
    \Delta v_1 &= (X + \Delta X) e \left( \sum_{n=1}^{\infty} \frac{A_n}{n!} \left( \frac{z_1^{2n} - z_2^{2n}}{\delta_n(z_1 - z_2)} \right) \right) \\
    \Delta v_2 &= (X + \Delta X) e \left( \sum_{n=1}^{\infty} \frac{A_n}{n!} \left( \frac{z_1^{2n} - z_2^{2n}}{\delta_n(z_1 - z_2)} \right) \right)
\end{align*}
\]

(33)

Hence the final velocity of the ions, corrected both for electrophoretic
and relaxation effects, is given by combining the equations (16) and (33):

\[
\begin{align*}
    v_1 &= v_1' + \Delta v_1 \\
    &= (X + \Delta X) z_1 e u_1^0 + (X + \Delta X) e \left( \sum_{n=1}^{\infty} \frac{A_n}{n!} \left( \frac{z_1^{2n} - z_2^{2n}}{\delta_n(z_1 - z_2)} \right) \right)
\end{align*}
\]

(34)

But the absolute c.g.s. mobility \( u_1^0 \) is also given by equation (17) in
terms of the velocity \( v_1^0 \) produced by the field \( X \) at infinite dilution.

\[
v_1^0 = X z_1 e u_1^0
\]

(35)

Dividing equation (34) by (35) gives:

\[
\frac{v_1}{v_1^0} = \left( 1 + \frac{\Delta X}{X} \right) \left( 1 + \frac{1}{z_1 e u_1^0} \sum_{n=1}^{\infty} A_n \left( \frac{z_1^{2n} - z_2^{2n}}{\delta_n(z_1 - z_2)} \right) \right)
\]

(36)

Since the velocities \( v_1 \) and \( v_1^0 \) are those obtained under the same external
field \( X \) in the actual solution and in the infinitely dilute solution.
respectively, the ratio $v_1/v_1^0$ may be replaced by the ratio of the equivalent ionic conductivities $\lambda_1/\lambda_1^0$; and the factor $1/z_1u_1^0$ preceding the summation on the right may be put in terms of $\lambda_1^0$, by the relation:

$$u_1^0 = 6.469 \times 10^6 \frac{\lambda_1^0}{|z_1|}$$

so that (36) becomes:

$$\lambda_1 = \left(\lambda_1^0 + 1.546 \times 10^{-7} \sum_n \frac{z_1^{2n} - z_1^n z_2^n}{a^n (|z_1| + |z_2|)}\right) \left(1 + \frac{\Delta X}{X}\right)$$

(37)

the relaxation terms $\Delta X/X$ being given by equations (13), (21) or (22) according to the degree of approximation desired. The corresponding expression for the anion is:

$$\lambda_2 = \left(\lambda_2^0 + 1.546 \times 10^{-7} \sum_n \frac{z_2^{2n} - z_2^n z_1^n}{a^n (|z_1| + |z_2|)}\right) \left(1 + \frac{\Delta X}{X}\right)$$

(38)

The equivalent conductivity of the electrolyte $\Lambda = \lambda_1 + \lambda_2$, is therefore:

$$\Lambda = \left(\Lambda_0 + 1.546 \times 10^{-7} \sum_n \frac{z_1^n - z_2^n}{a^n (|z_1| + |z_2|)}\right) \left(1 + \frac{\Delta X}{X}\right)$$

(39)

Though the general expression for the electrophoretic terms have been retained in developing these expressions, the Boltzmann distribution on which these expressions are based is not mathematically consistent with the Poisson equation, and, for consistency, the series can be taken only as far as the first term for unsymmetrical valency types, and the second for symmetrical types. Furthermore, it is obvious from equations (37), (38) and (39) that in the case of symmetrical electrolytes, $(z_1 = -z_2)$, the second-order electrophoretic term $(n = 2)$ vanishes identically.
Hence, in all cases, the first-order term alone need really be considered, although examination of the convergence of higher-order terms may throw useful light on the validity of the approximation made to the Boltzmann distribution.

Taking only the term for \( n = 1 \) and using the definitions of \( A_n, \phi_n \text{ and } S_n \), given on page 110, gives:

\[
A_1 = -\frac{10^8}{6\pi} \cdot \frac{\kappa a}{1 + \kappa a}
\]

Equation (39) therefore becomes:

\[
\Lambda = \left(\Lambda_0 - \frac{1.546 \times 10^{-7}}{6\pi} (|z_1| + |z_2|) \frac{\kappa}{1 + \kappa a}\right) \left(1 + \frac{\Delta X}{X}\right) (40)
\]

(c) The Onsager Limiting Law for the Conductivity

In Onsager's treatment, the further approximation of writing \((1 + \kappa a) \approx 1\) in the denominator of the first-order electrophoretic correction is made, and the relaxation term \(\Delta X/X\) is expressed by the limiting equation (13). Further, in evaluating the electrophoretic effect forces \(k_1\) and \(k_2\) are taken as \(Xz_1e\) and \(Xz_2e\) rather than as \((X + \Delta X)z_1e\) and \((X + \Delta X)z_2e\); this is equivalent to neglecting the cross-product of the electrophoretic and relaxation terms in equation (40).

All these approximations are of course quite justified for the purpose of finding the limiting law, but it is clear that the resulting expression will apply only at extreme dilutions, since \((\kappa a)\) is far from negligible compared with unity at ordinary concentrations, and diminishes
only as $\sqrt{c}$. The Onsager limiting law is thus:

$$
\Lambda = \Lambda_0 - \frac{|z_1 z_2|^2}{3\xi_k T} \cdot \frac{\Lambda_0 qK}{1 + \sqrt{q}} - \frac{1.566 \times 10^{-7}}{6\pi} \left(|z_1| + |z_2|\right)K \tag{41}
$$

Since $K$ is given by equation (23) it may be written as:

$$
K = \left(\frac{8\eta e^2}{1000 \xi_k T}\right)^\frac{1}{3} \sqrt{I}
$$

where $I$ is the 'ionic strength' defined by:

$$
I = \frac{1}{2\xi_k}(\nu_1^2 + \nu_2^2)
$$

Equation (41) then becomes, on inserting the values of the physical constants:

$$
\Lambda = \Lambda_0 - \left[\frac{2.801 \times 10^6 |z_1 z_2|^2 q\Lambda_0}{(\xi_k T)^{1.5}(1 + \sqrt{q})} + \frac{41.25\left(|z_1| + |z_2|\right)}{\eta(\xi_k T)^{1.5}}\right] \sqrt{I} \tag{42}
$$

This limiting law is of the form:

$$
\Lambda = \Lambda_0 - \Delta/c \tag{43}
$$

which was found by Kohlrausch to describe the variation of equivalent conductivity with concentration in dilute solutions. For aqueous solutions at 25°C it reduces on putting $\xi_k = 78.54$, $T = 298.16$ and $\eta = 0.008937$ poise to:

$$
\Lambda = \Lambda_0 - \left[0.7816 |z_1 z_2|^2 \frac{q\Lambda_0}{1 + \sqrt{q}} + 30.16\left(|z_1| + |z_2|\right)\right] \sqrt{I} \tag{44}
$$

For many years equation (42) was employed with added empirical terms in $c$, $c^{3/2}$, $c \log c$, etc., to represent the data at higher concentrations, no more complete theory being available. In 1927 Lattey (37) and in 1933 Kaneko (51) pointed out that the introduction of a factor of the form $(1 + \Delta K)$ into the denominator of the $\sqrt{I}$ term would greatly
improve agreement with the experimental data at higher concentrations, but this proposal was not taken sufficiently seriously. The suggestion was revived in 1948 by Ritson and Hasted (57), again on the basis of the excellent agreement with experiment resulting from the use of reasonable values of the parameter "a".

That this correction was justified for the electrophoretic term was in fact implied by Onsager's treatment, where the factor (1 + \(K_a\)) was dropped for the purpose of obtaining a limiting law; its essential theoretical correctness in the case of the relaxation term was, however, not demonstrated until the appearance of the theory of Falkenhagen, Leist and Kelbg. It follows that the equation

\[
\Lambda = \Lambda_0 - \left( \frac{2.801 \times 10^6 \left| z_1 z_2 \right| q \Lambda_0}{(\varepsilon T)^{1.5} (1 + \sqrt{q})} + \frac{41.25 (\left| z_1 \right| + \left| z_2 \right|)}{\eta (\varepsilon T)^{1.5}} \right) \sqrt{I} (1 + \frac{1}{1 + K_a})
\]

with

\[K_a = \left( \frac{8 \pi N e^2}{1000 \varepsilon k T} \right)^{1/2} a \sqrt{I}\]

gives the simplest form of the theory for higher concentrations, the cross-product of the relaxation term and the electrophoretic term in equation (40) being omitted. There is, however, little to choose in convenience of form between equation (45) and the slightly more correct expression obtained by using equation (40) with \(\Delta X/X\) given by equation (21) viz.:

\[
\Lambda = \left( \Lambda_0 - \frac{41.25 (\left| z_1 \right| + \left| z_2 \right|) \sqrt{I}}{\eta (\varepsilon T)^{1.5}} \right) \left( 1 - \frac{2.801 \times 10^6 \left| z_1 z_2 \right| q \sqrt{I}}{(\varepsilon T)^{1.5} (1 + \sqrt{q})(1 + K_a)} \right)
\]

Falkenhagen's equation for the relaxation effect given in expression
(22) may be inserted into the above equation to give the most complete form for the theory at higher concentrations as is shown on page 89.

Using equation (45) it has been shown by Robinson and Stokes (58) that for aqueous uni-univalent electrolytes which are completely dissociated, when a value of the parameter "a" is determined by trial to give constant values of \( \Lambda_o \) throughout the concentration range studied up to 0.1 molar, that with aqueous hydrochloric acid and alkali halides at temperatures from 5°C to 65°C, the average and maximum deviations of the values from the mean for each series of measurements were 0.02 per cent and 0.09 per cent respectively. The fact that the parameter "a" is the same for the whole temperature range studied seems to imply that it is a real molecular dimension and not merely an arbitrary way of representing the deviations from the limiting law. Agreement is almost within experimental error up to 0.05 molar concentration for sodium chloride at 25°C and even for a concentration of 0.1 molar the discrepancy is only 0.2 in \( \Lambda \).

At higher concentrations Robinson and Stokes found that the more exact form of the equation, i.e., equation (11) gave better agreement, and using values for "a" \( \times 10^8 \) of 4.35 cm for ammonium chloride and potassium bromide, they obtained moderate agreement with published conductivity data even up to concentrations of several molar. For lithium chloride, however, using a value of 5.2 for "a" \( \times 10^8 \) cm, although there is satisfactory agreement up to 0.1 molar, the agreement progressively deteriorates at higher concentrations, and at 4 molar, using this value
for "a", the value of A calculated from equation (11) is 72.1, whereas the observed value is 44.7 and it may be that the explanation of this failure lies in the fact that whereas for ammonium chloride and potassium bromide the viscosities of the solutions do not change much with concentration, the viscosity of aqueous lithium chloride increases by more than six-fold over its concentration range up to saturation. When the conductivity is corrected for relative viscosity to give, for a uni-univalent electrolyte, the equation:

\[
\frac{A}{n} = \left( A - \frac{B_2 \sqrt{m}}{1 + B_0 \sqrt{m}} \right) \left( 1 - \frac{B_1 \sqrt{mF}}{1 + B_0 \sqrt{m}} \right)
\]  

(47)

this has been shown to be more successful than equation (11) for concentrated lithium chloride solutions.

As described in Section III, equations (10) and (11) have been used in the present work to calculate a value for the parameter "a" at various concentrations and with the exception of lithium chloride, for the fully dissociated solutions of alkali halides, an approximately constant range of values for "a" have been obtained for concentrations higher than 0.1 molar up to concentrations as high as 1.0 molar. These results for "a" are in striking agreement with those obtained from activity coefficient data and reported by Robinson and Stokes. The results for lithium chloride, however, are much lower, falling to "a" x 10^8 = 2.0 cm for a concentration of 1.469 molar. When the viscosity-corrected conductivities of this salt are used for the calculation of "a" the results are greatly
improved as indicated in Table 25. The results for "a" for hydrochloric acid also fall steeply with rise in concentration, being only about $2.0 \times 10^{-8}$ cm for a concentration of 1.0 molar. Barium chloride, on the other hand, gave constant values for "a" of about $4.1 \times 10^{-8}$ cm over a relatively wide range of concentrations although, being an unsymmetrical electrolyte, even though it be fully ionized it is not to be expected that equation (11) would be so successful with it as for fully ionized univalent electrolytes. Equation (11) contains all the terms that can be logically justified for unsymmetrical electrolytes but the higher order electrophoretic terms, which have been omitted from the expression on the grounds of self-consistency, are far from negligible.

(ii) The Influence of Viscosity

The bulk viscosity of an electrolyte solution is a measure of the force required to move one layer of the solution with respect to another. The forces opposing such shearing are partly the long-range coulomb forces between ions, and partly the short-range forces between ions and water molecules, and between one water molecule and another. The former result in a dependence of the relative viscosity on the square root of the concentration at great dilutions, and on the quantity $\kappa/(1 + \kappa a)$ at higher concentrations; while the short-range forces give rise to an approximately linear dependence of the relative viscosity on the concentration. This may be attributed to the direct effect of ion-solvent interactions as well as to their influence in modifying the normal water
structure. The relative viscosity of an electrolyte solution is usually represented by equations of the form:

\[ \frac{\eta}{\eta_0} = 1 + A\sqrt{m} + Bm \]

The constant \( A \) relating to the interionic effects has been evaluated theoretically, but the constant \( B \) is a highly specific property of the individual ions, and is furthermore strongly temperature-dependent. As a general rule, strongly hydrated ions such as \( Li^+ \) cause a large increase in viscosity (i.e., \( B \) is large and positive) while relatively unhydrated ions have only a small effect. Now, when the motion of an ion through its surrounding solution is considered, it is reasonable to suppose that the relevant viscosity is essentially that due to the short-range forces only, for the coulomb forces have already been dealt with in computing the electrophoretic and relaxation effects. The viscosity appearing in equation (47) should therefore be, not the relative bulk viscosity, but only that part of it attributable to the short-range forces. The only justification for using the observed bulk viscosity is that, above a few tenths molar, the coulomb contribution is usually smaller than that of the short-range forces. In solutions of below 0.1 molar concentration it seems legitimate to omit the relative viscosity altogether, as in fact is done in equation (10).

The use of viscosity-corrected conductivities in the \( A, \sqrt{c} \) plots of uni-univalent electrolytes results in curves which by their general similarity of shape, indicate that the use of the approximate viscosity correction, \( \frac{A}{\eta_0} \), is justified.
(iii) The Conductivity of Higher Valency Electrolytes

For higher valency electrolytes the theory is inadequate. We have already seen that the higher order electrophoretic terms omitted from expression (11) are far from negligible in the case of unsymmetrical electrolytes. Also, in most cases these electrolytes are not completely dissociated, even in aqueous solutions. The theory should be applicable for bi-bivalent electrolytes but here a large proportion of the ions are present as closely associated ion-pairs and give results for "a" which are too low.
APPENDICES
APPENDIX I

PRINCIPAL SYMBOLS AND CONSTANTS USED

a  Mean diameter of ions (in cm).

b  Mean diameter of ions (in Å).

C  Capacitance.

c  Equivalent concentration (gram-equivalents per litre).

D  Decimal concentration.

E  Potential difference.

e  Electronic charge (4.8022 \times 10^{-10} \text{ e.s.u.}).

\text{e}  Base of natural logarithms (2.7183).

F  Function in Falkenhagen's formula for relaxation effect (pages 89 and 90).

G  Resistive component of an impedance.

I  Current (Section I).

I  Ionic strength \left[ \frac{1}{2} \left( \frac{1}{z_1} + \frac{1}{z_2} \right) \right] (Section IV).

K  Dissociation constant.

k  Boltzmann's constant (1.380257 \times 10^{-16} \text{ erg degree}^{-1} \text{ molecule}^{-1}).

m  Molar concentration (gram-molecules per litre).

N  Avagadro's number (6.0238 \times 10^{23}) (Sections III and IV).

N  Number of turns of secondary winding of voltage transformer (Section I).
$N_i$ Reciprocal of the effective volume of ionic species $i$. (Section IV).

$n$ Number of turns of primary winding of current transformer (Section I).

$n_i$ Number of particles of ionic species $i$ per c.c. (Section IV).

$q$ Mobility function in theory of relaxation effect

$$\begin{align*}
= \frac{|z_1 z_2| (\lambda_1^0 + \lambda_2^0)}{(|z_1| + |z_2|) (|z_2| \lambda_1^0 + |z_1| \lambda_2^0)}
\end{align*}$$

$R$ Resistance.

$T$ Absolute temperature ($298.16^\circ$ at $25^\circ$C).

$t_1^0, t_2^0$ Transport numbers of cation and anion respectively.

$u_i$ Absolute c.g.s. mobility of particles of ionic species $i$.

$v_i$ Velocity of particles of ionic species $i$ (cm/sec).

$X$ Reactive component of an impedance (Section I).

$X$ Field intensity (in e.s.u.). (Section IV).

Subscript $x$ Unknown side of bridge (Section I).

$y$ Standards side of bridge (Section I).

$Z$ Impedance.

$z_1, z_2$ Algebraic valency of cations and anions respectively.
α  Degree of electrolytic dissociation.
γ  Cell constant.
ɛ  Dielectric constant.
η  Viscosity (in centipoises).
\frac{η}{η_0}  Viscosity of solution relative to viscosity of solvent.
\kappa  \left( \frac{8\pi Ne^2}{1000\varepsilon kT} \right)^{1/2} \sqrt{I}.
Λ  Equivalent conductivity of electrolyte.
Λ_0  Equivalent conductivity of electrolyte at infinite dilution.
Λ_m  Molar conductivity of electrolyte.
\lambda_0^1, \lambda_0^2  Ionic equivalent conductivities at infinite dilution.
\nu_1, \nu_2  Number of moles of ions formed from 1 mole of electrolyte by cations and anions respectively.
π  3.1416.
\sum \text{Sum of}.
\psi  Potential (in e.s.u.).
### APPENDIX IIa

**CALIBRATION OF THE TRANSFORMER RATIO-ARM BRIDGE (MODEL 1) AGAINST A STANDARD RESISTANCE BOX**

<table>
<thead>
<tr>
<th>Conductance of box (m mho)</th>
<th>Bridge reading (m mho)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1000</td>
<td>0.100</td>
</tr>
<tr>
<td>0.2000</td>
<td>0.200</td>
</tr>
<tr>
<td>1.0000</td>
<td>1.000</td>
</tr>
<tr>
<td>2.0000</td>
<td>2.000</td>
</tr>
<tr>
<td>2.5000</td>
<td>2.500</td>
</tr>
<tr>
<td>3.3333</td>
<td>3.330</td>
</tr>
<tr>
<td>5.0000</td>
<td>4.996</td>
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<tr>
<td>10.000</td>
<td>9.990</td>
</tr>
<tr>
<td>12.500</td>
<td>11.840</td>
</tr>
<tr>
<td>20.000</td>
<td>16.827</td>
</tr>
</tbody>
</table>
CALIBRATION OF THE TRANSFORMER RATIO-ARM BRIDGE (MODEL 2) AGAINST A STANDARD RESISTANCE BOX

<table>
<thead>
<tr>
<th>Conductance of box</th>
<th>Bridge reading</th>
</tr>
</thead>
<tbody>
<tr>
<td>m mho</td>
<td>m mho</td>
</tr>
<tr>
<td>0.1000</td>
<td>0.1000</td>
</tr>
<tr>
<td>0.2000</td>
<td>0.2005</td>
</tr>
<tr>
<td>1.0000</td>
<td>1.0010</td>
</tr>
<tr>
<td>2.0000</td>
<td>1.9948</td>
</tr>
<tr>
<td>2.5000</td>
<td>2.4785</td>
</tr>
<tr>
<td>3.3333</td>
<td>3.326</td>
</tr>
<tr>
<td>5.0000</td>
<td>4.981</td>
</tr>
<tr>
<td>10.000</td>
<td>9.917</td>
</tr>
<tr>
<td>12.500</td>
<td>12.633</td>
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<tr>
<td>20.000</td>
<td>19.444</td>
</tr>
<tr>
<td>40.000</td>
<td>38.556</td>
</tr>
</tbody>
</table>

Bridge readings of over 12 m mho were not encountered in the present work except for measurements for aqueous hydrochloric acid solutions of 1.472 molar and above.
APPENDIX III

CORRECTION FOR BUOYANCY IN THE PREPARATION OF DEMAL POTASSIUM CHLORIDE SOLUTIONS

Correction for buoyancy in air was required for preparing the demal potassium chloride solutions which were used for the determination of cell constants. The correction was applied according to the formula:

\[ W_0 = W \left(1 + \frac{d_1 - d_2}{d_j} \right) \]

where

- \( W_0 \) = Weight of body in vacuo
- \( W \) = Weight of body in air
- \( d_1 \) = Density of air (= 0.0012 g/ml.)
- \( d_2 \) = Density of material of weights (= 8.5 g/ml.)
- \( d_j \) = Density of body

(potassium chloride = 1.984 g/ml.)
(water at 25°C = 0.997044 g/ml.)

Hence, for potassium chloride:

\[ W_0 = 1.00046W \]

and for water at 25°C:

\[ W_0 = 1.00106W \]
APPENDIX IV

THERMODYNAMIC DRYING OF

DI-SODIUM LEAD ETHYLENEDIAMINETETRAACETATE

The principle of this method of drying a sample of a salt containing water in excess of that required for its highest hydrate is based on the application of the Phase Rule which was originally deduced by Gibbs in 1876. This rule relates the number of degrees of freedom (F) of any system to the number of components (C) and phases (P) in it provided that the equilibrium between any number of phases is only influenced by temperature, pressure and concentration. Then, for any system at equilibrium at a definite temperature and pressure:

\[ P + F = C + 2 \]

Consider a sample of the dihydrate of di-sodium lead ethylenediaminetetraacetate (\( \text{Na}_2\text{PbEDTA.2H}_2\text{O} \)). On partial dehydration the salt-hydrate system:

\[ \text{Na}_2\text{PbEDTA.2H}_2\text{O} \xrightarrow{\text{dehydrate}} \text{Na}_2\text{PbEDTA + 2H}_2\text{O} \]

will contain water vapour and two solid phases; i.e., \( P = 3 \). It will contain two components, i.e., \( \text{Na}_2\text{PbEDTA} \) and \( \text{H}_2\text{O} \); i.e., \( C = 2 \). Therefore, \( F = 2 + 2 - 3 = 1 \). Hence, at a particular temperature the system will have a definite vapour pressure which is independent of the amounts of the components so long as they are actually present in the system.

A wet sample of the dihydrate will possess a vapour pressure at a
Figure 37

Loss of weight on drying
Hydrated disodium lead
Ethylenediaminetetraacetate
particular temperature which is greater than that of the dihydrate-anhydrous system. Therefore, if a sample of the partially dried salt is placed in a closed vessel together with a sample of the wet salt, owing to the difference in vapour pressure the former will have a desiccating action on the latter until either the partially dried sample is completely converted to the dihydrate or the wet sample is dried to give the pure dihydrate.

A small portion of the salt was placed in a vacuum desiccator over sulphuric acid and weighed at intervals until the weight became nearly constant. It was found that the salt lost nearly 3 per cent of its original weight in 100 days. On plotting a graph (Fig. 37) it was seen that approximately a half of this loss of weight occurred in 25 days. A further sample was dried under the same conditions for 25 days and this sample was used as a desiccant for drying the sample which was used for obtaining the conductivity data reported in Section IIe.
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(37) Lattey, R.T., Phil.Mag., 1927, 4, (7), 631.
(53) Debye, P. and Hückel, E., Phys.Z., 1923, 24, 305.
The determination of the electrical conductivities of some concentrated electrolyte solutions using a transformer bridge

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A method for the determination of the conductivities of solution without the use of contacting or dipping electrodes is described. This involves the use of a transformer ratio-arm bridge operating at audio-frequencies, and this is described in detail. Results obtained for concentrated solutions of barium chloride, magnesium sulfate and potassium ferro- and ferrocyanides are given.

The determination of the equivalent conductivities of concentrated solutions of barium chloride, potassium ferri- and ferrocyanides, and magnesium sulfate using electrodeless cells in a transformer bridge is described. The “a” parameter of Robin-son and Stokes for potassium bromide, ammonium chloride and barium chloride has been calculated.

The use of transformer bridges and electrodeless cells has already been briefly reported and will

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(2) R. Calvert, J. A. Cornelius, V. S. Griffiths and D. I. Stock, Research Correspondence, Suppl. to Research (London), 9, 114 (1956).


The value of an impedance $Z$ is given by the ratio $E/I$ where $E$ is the voltage across the impedance and $I$ the current flowing through it. The most direct way of measuring impedance is therefore to measure $E$ and $I$ and compute the ratio. Unfortunately, it is extremely difficult to make absolute measurements of voltage or current with any degree of accuracy. In practice it is far easier to make a comparison measurement, the unknown being compared with a standard impedance by means of a bridge circuit. Thus only ratios are involved, which can be established more easily and accurately than absolute quantities.

Let the subscripts $u$ and $s$ refer to the unknown and standard, respectively. Then

$$Z_u = \frac{E_u}{I_u}$$

and

$$Z_s = \frac{E_s}{I_s}$$

or

$$Z_u = \frac{E_u}{E_s} \times \frac{I_s}{I_u} \times Z_s$$  \hspace{1cm} (1)$$

This is the fundamental equation for the measurement of impedance, whatever method is employed, and it is seen that there are two ratios $E_u/E_s$ and $I_u/I_s$ which govern the range of measurement with a standard $Z_a$.

The conventional method of determining the impedance is by means of a modified Wheatstone bridge. This suffers from a number of disadvantages, the most important of which is that the theoretical conventional circuit cannot be achieved in practice, except over a limited range of measurement. To ensure any degree of accuracy, a Wagner earth arrangement is desirable, requiring a double balance. This method is inconvenient in practice and only “two-terminal” measurements are possible over any range; as discussed later this is a severe restriction.

The Transformer Ratio-Arm Bridge described here offers many advantages. The basic circuit of the transformer bridge is shown in Fig. 1. The subscripts $u$ and $s$ refer to the unknown and standard sides of the bridge, respectively.

$T_1$ is a voltage transformer to the primary of which the source is connected. The secondary winding is tapped to give sections having $N_u$ and $N_s$ turns.

$T_2$ is a current transformer, the primary of which is tapped to give $n_u$ and $n_s$ turns, and the secondary winding is connected to the detector.

Assume at this stage that the transformers are ideal and that $Z_a$ is adjusted to give null indication in the detector. Under these conditions zero flux is produced in the current transformer, and there is therefore no voltage drop across its windings. The detector sides of both the unknown and standard impedances are therefore at neutral potential. The voltages across the unknown and standard are then $E_u$ and $E_s$, respectively.

Therefore

$$I_u = \frac{E_u}{Z_u}$$  \hspace{1cm} (2)$$

and

$$I_s = \frac{E_s}{Z_s}$$

For conditions of zero core flux in the current transformer, the algebraic sum of the ampere-turns must be zero. Therefore

$$I_u n_u = I_s n_s$$

Substituting for $I_u$ and $I_s$ we have

$$\frac{E_u}{Z_u} n_u = \frac{E_s}{Z_s} n_s$$

or

$$Z_u = \frac{E_u}{E_s} \times \frac{n_u}{n_s} \times Z_s$$  \hspace{1cm} (3)$$

For an ideal transformer the voltage ratio is equal to the turns ratio, therefore

$$Z_u = \left( \frac{N_u}{N_s} \times \frac{n_u}{n_s} \right) Z_a$$  \hspace{1cm} (4)$$

It will be seen from equation 4 that unlike the conventional bridge, two ratios $N_u/N_s$ and $n_u/n_s$ are available. Thus it is possible, by means of a suitable combination of tappings on the two transformers, to produce a very high ratio product permitting a very wide range of measurement.

Before proceeding further, it is necessary to justify the statement that the actual transformers used in the bridge may be considered ideal.

Firstly, the transmission loss between the primary and secondary of the voltage transformers is of no consequence. The only effect of this loss is to reduce the sensitivity of the bridge, and this can be compensated by increasing the gain of the detector. The important factor is the actual voltage ratio between the unknown and standard, both of which are tapped across the secondary windings of the voltage transformer. This voltage ratio...
across the bridge windings is dependent upon three factors: (a) the turns ratio, (b) the flux linkage, (c) the effective series impedance of the windings compared with that of the load.

The voltage induced in a coil is proportional to the number of turns multiplied by the rate of change of flux. Therefore, provided all the turns of the bridge windings embrace the same flux, the ratio of induced voltages is equal to the turns ratio. The windings are, in fact, wound with precision on a common core of high permeability material. The ratio of core flux to air flux is of the order of 1000:1, and the geometrical arrangement of the windings is such that the air flux is largely common to the two windings. Even if the windings were so badly arranged that none of the air flux was common, the error between the induced voltage ratio and the turns ratio would be only 0.01%. If necessary this error can be reduced to a few parts in a million.

The only error which need be considered is that caused by the voltage drop in the windings. Ignoring spurious shunt impedances for the moment, the load current in the unknown windings is the current in the impedance being measured. In the measurement of impedances of 10 to 100 megohms, the total series impedance of both the voltage and current transformer windings is approximately 100 ohms. Even if all this impedance were concentrated in one arm of the bridge the worst error would only be 0.001%. In practice this error is negligible.

It will be shown later that the effects of shunt loading can be effectively compensated, so that it is reasonable to presume that for all practical purposes the transformers are ideal.

The practical arrangement of the bridge is shown in Fig. 2, where the unknown and standard impedances have been divided into their resistive and reactive components.

Since at balance the in-phase and quadrature ampere-turns must separately sum to zero, the conductance standard $G_s$ and the reactance standard $X_B$ may be connected to different tappings on the voltage transformer to balance out the currents caused by the unknown impedance.

This independence of the components of current may be put to advantage in many ways. The effect of impurities in the standards (for example, dielectric loss in capacitors) can be balanced out by the insertion of compensating components across the "unknown" side of the bridge. The leakage and capacitance across the test probe also can be removed in this manner.

Figure 3 shows a bridge arrangement in which the voltage transformer winding feeding the standards has one hundred turns and is tapped at every ten turns, the tappings being brought out to a switch and connected to the standard. For convenience only the conductance standard is shown.

The equation for balance conditions may be written

$$G_u = (G_N_s) \frac{N_s}{N_u}$$

If the product term inside the parenthesis is taken to represent the standard, it is of no importance whether the number of turns is fixed and the conductance given ten different values (the normal procedure with a decade box), or the conductance fixed and the number of turns given ten different values. By employing the latter method only one standard per decade is necessary.

In Fig. 4 the tappings on the standard side are taken to four switches wired in parallel.

Each switch connects through a fixed standard to a common tap on the current transformer. The
conductances are given the relative value 1, 10, 100 and 1,000. The effect is exactly the same as that obtained by having a transformer of fixed voltage and a four-dial decade box.

Continuing with tapings to four more switches, each of which is connected through a fixed standard capacitor to the current transformer, the effect of adding a four-dial decade capacitor is produced.

So far only the step-by-step adjustment of the standards has been considered. It has been shown how the decade boxes for resistance and capacitance standards normally associated with accurate bridge measurements can be replaced by a few fixed standards and banks of switches fed from taps on the voltage transformer.

Decade switching is essential when accuracies of better than 1% are required. However the provision of such switches alone makes the balancing of the bridge a slow and often laborious process, especially if the unknown is a complex impedance. The provision of a pair of continuously-variable direct-reading controls makes the bridge quick and easy to handle, but calibration difficulties would limit the accuracy of such an arrangement to 1-2%. Fortunately, it is possible with the transformer ratio bridge for continuously variable reactance standards normally associated with accurate bridge measurements can be replaced by a few fixed standards and banks of switches fed from taps on the voltage transformer.

Decade switching is essential when accuracies of better than 1% are required. However the provision of such switches alone makes the balancing of the bridge a slow and often laborious process, especially if the unknown is a complex impedance. The provision of a pair of continuously-variable direct-reading controls makes the bridge quick and easy to handle, but calibration difficulties would limit the accuracy of such an arrangement to 1-2%. Fortunately, it is possible with the transformer ratio bridge for continuously variable reactance standards normally associated with accurate bridge measurements can be replaced by a few fixed standards and banks of switches fed from taps on the voltage transformer.

A continuously variable reactance is conveniently provided by an air-dielectric capacitor whose residual capacitance \( C_0 \) is balanced by a pre-set trimmer connected to a transformer winding of opposite sign. This arrangement is shown in Fig. 5.

A continuously variable conductance control is provided by combining a potentiometer with a fixed resistor as shown in Fig. 6.

The best practical compromise for accuracy and ease of operation is to use a single decade and a continuously variable conductance. They are adjusted to bring the bridge into balance, where

\[
\frac{k}{E} = \frac{N_a/N_c \times R_a/R_c}{kE}\]

The adjustment is independent of the voltage, and therefore holds for all positions of the tapping switch.

The effect of a reactance term associated with the conductance standard can be removed in the same way. At a given frequency the standard can be regarded as a pure conductance shunted by a reactance. The reactance causes an unwanted quadrature current to flow in the current transformer. This can be cancelled by a quadrature current of opposite sign, the ampere-turns being made equal. It is generally convenient to use a capacitor for the trimming control and to give it the correct sense by connecting it either to the unknown or standard site of the transformer, according to the sign of the spurious reactance.

To keep the number of standards to a minimum the in-phase and quadrature standards are chosen to cover approximately the same range of impedances at the operating frequency of the bridge. Occasionally, it is required to measure a complex impedance the in-phase and quadrature components of which are of quite different orders. It is therefore convenient to be able to shift the effective impedance of one standard with respect to the other. Since the voltage transformer is tapped to provide the decade adjustment of each standard the current transformer must be tapped to shift the relative ranges of the standards. This is shown diagrammatically in Fig. 8. A pair of taps at, say, 10 turns and 100 turns will give a 10:1 shift.

This facility must, however, be used with caution. If a measurement were made where the quadrature currents are in the ratio of say 1000:1 perfect standards would be necessary and there would have to be no losses or stray capacitances associated with the wiring. Any small out-of-phase current introduced by the major component standard could give rise to a considerable error in the measurement of the minor component of the unknown impedance. This will be dealt with in more detail under the subject of 3-terminal measurements.

The flexibility of the bridge is improved by adding a pair of set-zero controls, taking advantage of the fact that at balance there is no interaction between the current paths leading into the current transformer.

A small variable capacitor provides a suitable set-zero for reactance and a fixed resistor, combined with a potentiometer, provides the control for conductance. They are adjusted to bring the bridge to balance with all the standards set to zero, before the unknown is applied.

As mentioned earlier “two-terminal” measurements can impose severe restrictions and consequently it is advantageous to consider a “three-terminal” network as shown in Fig. 9.

The impedance to be measured is \( \text{Z}_0 \), but the effect of impedances \( \text{Z}_{AC} \), \( \text{Z}_{BC} \) must be removed before a measurement of \( \text{Z}_0 \) can be made. Figure 10 shows the 3-terminal network applied to the bridge.

The arrangement can be considered as a \( \pi \)-network, where \( \text{Z}_{\text{EN}} \) shunts the voltage transformer and \( \text{Z}_{\text{IN}} \) shunts the current transformer. Once again it is assumed that the transformers are ideal.

At balance there is no voltage across the current transformer, and therefore the only effect of \( \text{Z}_{\text{IN}} \) is
to reduce the input impedance to the detector, and consequently the off balance sensitivity. If necessary this can be compensated by increasing the detector gain.

$Z_{EN}$ shunts the unknown winding of the voltage transformer and has the full voltage across it at balance. It causes a voltage drop determined by the ratio of its transformed impedance at the transformer primary to the source impedance. However, a voltage drop also occurs in the standards side of the voltage transformer in proportion to the turns ratio. The bridge is therefore unaffected and no balance error is introduced. The only effect is again to reduce the sensitivity, which can be restored either by increasing the source voltage or the detector gain.

In practice the transformers have a finite short-circuit impedance and shunt loading can cause errors. Difficulty with shunt loading is most likely to arise on the high impedance ranges. The error caused by the loading of the unknown itself is greatest at the low impedance end of each range, amounting to approximately 1 part in $10^6$ (a typical figure is 100 ohms total effective series impedance for both transformers in the measurement range 10 to 100 megohms). Shunts having a hundredth of the impedance of the unknown would cause errors of 0.1%, a thousandth of the impedance of the unknown 1%, and so on. In the case quoted one would expect shunt impedances of 10,000 ohms to cause errors of about 1% when using the bridge on the 10 to 100 megohm range.

It is only when the shunt impedances are very low compared with the impedance under measurement that errors arising from them are likely to be important, and in these circumstances they can be corrected by a simple calculation. Since the unknown has an insignificant loading effect, it can be neglected and the arrangement of Fig. 11 used for computation.

$R_a$ represents the effective series resistance of the voltage transformer winding and $L_a$ the leakage inductance. Let $Z_a = R_a + j \omega L_a$.

$Z_i$, $R_i$ and $L_i$ are the equivalent components of the current transformer winding.

Since the impedance to be measured is very high compared with the shunt impedances, it can be considered as an open-circuit and the shunting effect on each side of the unknown may be considered separately.

Without any loading, the normal balance equation for the bridge applies. We have therefore

$$Z_u = \frac{E_u}{E_a} Z_m$$

(7)

Due to the effect of the shunt $Z_{EN}$, the voltage applied to the unknown is reduced to $E$. To restore balance $Z_u$ must be changed to, say, $Z_m$. Therefore

$$Z_u = \frac{E_u}{E_a} Z_m$$

(8)

But

$$E = E_a \left( \frac{Z_{EN}}{Z_{EN} + Z_a} \right)$$

(9)

Therefore

$$Z_u = \frac{Z_{EN}}{Z_{EN} + Z_a} Z_m$$

(10)

where $\left[ (E_u/E_a) Z_m \right]$ is the value read on the bridge.

For simplicity, consider unity ratio of the voltage transformer; Then

$$Z_u = \frac{1}{1 + \frac{Z_a}{Z_{EN}}} Z_m$$

(11)

This may be expressed as a series as

$$Z_u = Z_m \left[ 1 - \frac{Z_a}{Z_{EN}} + \left( \frac{Z_a}{Z_{EN}} \right)^2 - \ldots \right]$$

(12)

For almost all practical cases the second and higher order terms are so small that they may be neglected. An adequate approximation is then given by

$$Z_u = \left( 1 - \frac{Z_a}{Z_{EN}} \right) Z_m$$

(13)

A similar argument applies to the error arising from loading the current side of the bridge. Under these conditions it can be shown that

$$Z_u = \left( 1 - \frac{Z_i}{Z_{IN}} \right) Z_m$$

(14)

Therefore the true value of the unknown impedance with both voltage and current transformer shunting is given by

$$Z_u = \left( 1 - \frac{Z_u}{Z_{EN}} \right) \left( 1 - \frac{Z_i}{Z_{IN}} \right) Z_m$$

(15)

or

$$Z_u = \left[ 1 - \left( \frac{Z_u}{Z_{EN}} + \frac{Z_i}{Z_{IN}} + \frac{Z_u Z_i}{Z_{EN} Z_{IN}} \right) \right]$$

(16)

Since the short circuit impedance of the transformers is small compared with the shunt impedances, the term $Z_u Z_i / Z_{EN} Z_{IN}$ may be neglected, giving a final approximation

$$Z_u = Z_m \left[ 1 - \left( \frac{Z_u}{Z_{EN}} + \frac{Z_i}{Z_{IN}} \right) \right]$$

(17)

where $Z_u$ is the true value of the unknown impedance and $Z_m$ the value read on the bridge.

$Z_u$ and $Z_i$ are constants for the bridge and can be measured quite simply on each range by measuring the apparent change in value of a 2-terminal impedance when known shunts are connected across the transformer windings.

It has been shown that the attributes of the transformer ratio-arm bridge are such that complicated measurements can be made quite simply which would be very difficult, if not impossible, with a conventional bridge arrangement.

The advantages of the transformer bridge may be summarized as follows.

1. The measurement is dependent upon the
product of the current and voltage ratios for each fixed standard used. Both of these ratios are obtained easily with great accuracy, increasing the possible range of measurement to a figure well beyond the scope of impedance arms. Voltage and current ratios each of 1000:1 are possible, giving an over-all ratio of one million to one.

2. Since the ratios depend only upon the number of turns on the transformer windings, they are permanent and calibration is unnecessary.

3. Only one standard is required for each decade. Furthermore, the transformer ratios may be used to set the standard in one decade against that in another, so that only two fixed standards of known accuracy are required, one resistive and one reactive.

4. The standards need not be pure. The effects of a resistive term associated with a reactance standard and of a reactive term associated with a resistive standard can be removed entirely at a given frequency.

5. The bridge will measure the impedance between any pair of terminals of a 3-terminal network. In situ measurements are possible on impedances remote from the bridge and on components wired into a circuit. The capacitance of long connecting leads and spurious impedances connected to the unknown terminals are completely counteracted by the appropriate use of the third terminal of the bridge.

The type of bridge described above may be used in conjunction with the normal type of dipping electrodes, but for certain purposes it is advantageous to eliminate these internal electrodes. Cells with external electrodes have been described, but in the main high frequencies have been employed. With the transformer bridge, however, it is possible to determine the conductance of high conductivity solutions without any metal electrodes, and using audio-frequency oscillators.

In practice $N_a$ and $n_a$ are each reduced to a single turn and both transformers are wound on toroidal cores, when the balance equation becomes

$$G_a = N_a n_a G_a$$  \hspace{1cm} (18)

It is customary to think of transformer windings in terms of metallic wire, but flux linkages are a matter of geometry, not of materials. Thus electronic and electrolytic conductors can be regarded as equivalent from the point of view of circuitry. Indeed a piece of enamelled or plastic covered wire may be compared directly with an electrolyte solution in an electrically non-conducting tube, in as much as both comprise a conductor in an insulating sleeve. Thus if a closed annulus of liquid contained within a tube of glass or other non-conducting material can be made to link both the voltage and current transformer cores, the circuit is complete and nothing further in the way of connections is required. Some methods of doing this are shown in Fig. 12. The high permeability Mumetal toroidal cores are moulded into an inert insulating material and the cores linked by a glass tube. Several designs of loop were used in this work, that most frequently used being one which could be dismantled by means of ground-glass joints in the loop. For certain purposes flow-through cells of glass or polythene were found to be useful, whilst in the case of the cell 12b the unit can be immersed directly in the vessel containing the test solution. Part of the loop is formed by the column of liquid which fills the cylinder linking the cores, and the return path is through the body of liquid in the container. The geometry of the current flow lines outside the cylinder is indefinite, but if the container is large compared with the transformer assembly the effective cross-sectional area of the return path is so great as to constitute almost a short-circuit across the ends of the cylinder. The small "end-effect" in any case can be found by calibration in a liquid of known conductivity.

In the work described here, the voltage transformer core was energized by a third winding connected to a 1000 c.p.s. oscillator. The oscillator frequency determines the minimum size of the toroidal cores and a bridge to operate at 50 Kc.p.s. is being designed in order to reduce the size of the test probe and thus to economize in test solution. The detector consisted of a tuned amplifier linked to the current transformer, the null-point being


Electrical Conductivities of Concentrated Electrolyte Solutions

Jan., 1958

detected with a Cossor 1049 MkIII oscilloscope, or for certain purposes an integral "magic eye."

In the form described the bridge is best suited to the measurement of the conductivities of concentrated solutions, and to this end solutions of barium chloride, potassium ferri- and ferro-cyanides, and magnesium sulfate have been studied.

Experimental

The cell constants were determined with the Jones and Bradshaw\(^7\) demal potassium chloride solutions. Since nearly all the literature data of the past twenty years are based on these standards, which are given in the terms of the old International Ohm unit of resistance, the conductances reported here have not been converted to the new absolute ohm basis. All the salts used were of the analytical reagent grade, and were recrystallized at least three times from good quality conductivity water, and their conductances over the common concentration range studied.

Results and Discussion

These are given in Table I and shown graphically in Fig. 13, and the data so obtained are in agreement with those obtained by conventional methods. The equation may be written

\[
\Lambda = \frac{4.25 \times 10^{-10} \, |z| \sqrt{T}}{\pi (T)^{1/2} (1 + a) \sqrt{I}}
\]

where

\[
F = \frac{e \omega (1 - \sqrt{q})}{a \omega (1 - \sqrt{q})} - 1
\]

which for a 1:1 electrolyte with \(a\) in ångströms reduces to

\[
\Lambda = \left[ \frac{A_0 - B_{\text{cv}} \sqrt{\varepsilon}}{1 + B_{\text{cv}} \sqrt{\varepsilon}} \right] \left[ 1 - \frac{B_{\text{cv}} \sqrt{\varepsilon}}{1 + B_{\text{cv}} \sqrt{\varepsilon}} \right] F
\]

where \(B_1, B_2, B_3\) are constants for a given solvent and temperature, and for water at 25°C are 0.3286, 0.2289 and 60.32, respectively.

<table>
<thead>
<tr>
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<tr>
<td>(\text{BaCl}_2)</td>
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<tr>
<td>116.3</td>
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<tr>
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The values obtained are shown in Table II.

<table>
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<tbody>
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<td>(\text{KBr})</td>
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<tr>
<td>(\sqrt{m})</td>
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</tbody>
</table>

(The viscosities used in calculating these values were interpolated from those recorded in the International Critical Tables.)

The mean ionic radii given by Stokes and Robinson\(^11\) are: KBr, 3.85; NHCl, 3.75; BaCl\(_2\), 4.45 (all \(\times 10^{-8}\) cm.), and it can be seen that the values of \(\alpha\) reported here show reasonable agreement in view of the differing concentrations. Attempts to treat mathematically the experimental results obtained for the weak electrolytes potassium ferri- and ferro-cyanides\(^14-16\) have as yet met with little success.

(14) C. W. Davies, ibid., 59, 1760 (1937).
(15) J. C. James, ibid., 55, 457 (1953).