THE CONDUCTANCES OF AQUEOUS SOLUTIONS OF LITHIUM

CHLORATE AT 25.00°C. AND AT 131.8°C.

A THESIS SUBMITTED TO THE COMMITTEE ON POST-GRADUATE

STUDIES AT THE UNIVERSITY OF MANITOBA IN PARTIAL

FULFILLMENT OF THE REQUIREMENTS FOR THE

DEGREE OF MASTER OF SCIENCE

by

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FEBRUARY 1957

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ACKNOWLEDGMENTS

ABSTRACT

The conductances, densities, and viscosities of aqueous solutions of lithium chlorate were determined over the complete range of concentration at 25.00°C. and at 131.8°C.

The exponential relationship between concentration and equivalent conductance discovered by Herron is not applicable to the results of this research.

The experimental results have been compared with the conductances calculated by means of the Wishaw-Stokes and the Falkenhagen-Leist equations, and good agreement has been found up to very high concentrations, in some cases up to 10 molar. A discussion of the theoretical implications is given.

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A. The Theory of Electrolytic Solutions

A very great amount of experimental research and
theoretical investigation has been expended on the
intriguing problem of the conductance of aqueous solutions
of electrolytes.

The early theory, due to Arrhenius, regarded electro-
lytes in solution as dissociated in part into mutually
independent ions which existed in equilibrium with
undissociated molecules. As applied to weak electrolytes,
this theory remains fairly satisfactory to-day. Arrhenius
assumed that dissociation into ions increased with dilution,
and he sought to express the degree of dissociation by the
Kohlrausch relation $\alpha = \Lambda / \Lambda_o$, which contains the inherent
assumption that ion velocities are constant over a range of
concentration. That is, in the expression

$$\frac{\Lambda}{\Lambda_o} = \alpha \left(\frac{u^+ + v^-}{u_o^+ + v_o^-} \right) \tag{1}$$

the ratio of the ionic velocities at a finite concentration
to those at infinite dilution remains unchanged. This
relationship could be further substituted into the Ostwald
Dilution Law, $\alpha^2 C / (1 - \alpha) = K$, to yield an equilibrium constant:

$$K = \frac{\left(\frac{\Lambda}{\Lambda_o} \right)^2 C}{1 - \frac{\Lambda}{\Lambda_o}} \tag{2}$$

The above equation failed utterly when applied to strong electrolytes. Numerous empirical modications of equation (2) were proposed, but none of them proved to be applicable over a wide range of concentration. This quandary into which electrolytic theory had stumbled indicated the need for a fresh theoretical approach.

The familiar Kohlrausch relationship

$$\Lambda = \Lambda_o - A\sqrt{c} \tag{3}$$

where A is the slope of the straight line, is strictly empirical, and is valid only for the dilute range of concentration. Any theory, however, should supply a mathematical expression that will simplify to this form for the region of high dilution.

The theory of Debye and Hückel,[1] as applied by Onsager,[2] yields an equation of this form. The basis of the theory is that strong electrolytes in solution are completely dissociated into ions. Studies in X-ray crystallography offered unequivocal endorsement to this concept of complete ionization. It was proposed that the units out of which the crystal lattice of a polar compound is formed are ions, and no entity exists which corresponds to the ordinary depiction of a molecule. Therefore, in the act of solution, the particles breaking away from the crystal are _ions_, not molecules. Until a large proportion of salt builds up in the

solution, it is logical to assume that the solute exists
as ions; in consequence of this assumption, strong electro-
lytes must be completely dissociated in dilute solution.
Hence if any neutral particles of a strong electrolyte are
to be present in concentrated solutions, they must be
thought of as resulting from association of ions. This view
is diametrically opposite to that concerning weak electro-
lytes where the ions result from dissociation of molecules.

The essential postulate of the Debye-Hückel-Onsager
theory is that every ion may be considered as being
surrounded by an ionic atmosphere of opposite sign. As long
as the ionic atmosphere is "stationary," it has spherical
symmetry. When the ion is made to move under the influence
of an external electrical field, the symmetry of the ionic
atmosphere is disturbed. As the ion moves in a given
direction, the charge density of its oppositely charged
atmosphere becomes greater behind the ion than in front. The
rate at which the atmosphere on the one side forms and that
on the other side dies away is expressed in terms of a
quantity called the time of relaxation of the ionic atmosphere.
The result is a retardation of the ionic velocity; this
influence is called the relaxation effect.

It is further proposed that each ion has associated
with it certain of the solvent molecules. An applied
potential tends to move the ionic atmosphere in a direction

opposite to that in which the central ion, with its associated solvent molecules, is moving. This viscous drag on the moving ion, an additional retarding factor, is known as the electrophoretic effect.

From a consideration of the above effects and also of the Brownian movement of the ions, Onsager developed the following equation:

$$\Lambda = \Lambda_o - \left[\frac{82.4}{(D_o T)^{1/2} \eta_o} + \frac{8.20 \times 10^5}{(D_o T)^{3/2}} \Lambda_o \right] \sqrt{C} \qquad (4)$$

For uni-univalent electrolytes in water at 25°C., equation (4) assumes the simplified form

$$\Lambda = \Lambda_o - \left(0.2273 \Lambda_o + 59.78 \right) \sqrt{C} \qquad (5)$$

which is the form of the empirical Kohlrausch law.

Due to the mathematical simplifications and the assumptions made, which are really valid only for the dilute region, the Onsager equation is not obeyed at concentrations much greater than 0.005 N. Among the several reasons which render the theory untenable in concentrated solutions are the following:

1. The Taylor expansion of e^x is employed in the development of the potential distribution functions; all terms after the second are neglected since they are quite unimportant at low concentrations.

2. The dielectric constant is considered to remain

unchanged.

3. The assumption was made that the size of the ions is negligible with respect to the distance between them. This, of course, is inadmissible in concentrated solutions.

Three distinct methods have been used to extend the range of the Onsager equation to somewhat higher concentrations. The first applies only to electrolytes for which the conductance falls below the limiting law in dilute solutions, and interprets this "conductance deficiency" in terms of finite ionization constants. An "association" term is added to the fundamental equation, such as the following modification due to Onsager himself:[3]

$$\Lambda = \Lambda_o - \left[A^* \Lambda_o + B^* \right] \sqrt{C} - \frac{C \Lambda_o}{K} \tag{6}$$

where K is the dissociation constant.

The second assumes infinite ionization constants (complete dissociation), and attempts to account for all departures from the limiting equation by more elaborate theoretical treatments designed to include higher terms in the mathematical approximations, or to consider the "mean distance of closest approach" in the physical picture. In one of his earlier papers,[4] and later with Fuoss,[5] Onsager estimated the effect of the mathematical simplifications involved in the derivation of his limiting equation. The deviation of Λ from linearity with $\sqrt{C}$ is represented by

the addition of two terms. Thus in dilute solutions

$$\Lambda = \Lambda_o - (A^* \Lambda_o + B^*)\sqrt{C} + DC \log C + EC \qquad (7)$$

As originally proposed, this expression was semi-empirical in that the numerical values of the constants A^* and B^* had not been evaluated from theoretical considerations.

The third method is the purely empirical addition of terms in higher powers of C than the one-half. In studying the conductance of uni-univalent electrolytes, Shedlovsky[6] noted that if the limiting equation (4) is rearranged so that Λ_o may be calculated directly from individual values of Λ, the difference between the successive values of Λ_o is proportional to the difference in concentration. In mathematical formulation, Shedlovsky's observation can be written

$$\Lambda = \Lambda_o - (A^* \Lambda_o + B^*)\sqrt{C} + Bc - \alpha^* Bc^{3/2} \qquad (8)$$

The positive empirical constant B is characteristic of each electrolyte and is of the same order of magnitude as the quantity $(A^* \Lambda_o + B^*)$.

Most of the empirical extensions are such that they reduce to the Kohlrausch form. By 1934, no less than thirty different empirical and theoretical equations had been proposed.[7]

An excellent review of the interionic attraction

theory is given by Scatchard,[8] and its application to conductance by MacInnes, Shedlovsky, and Longsworth.[9, 10] For detailed discussion, the comprehensive work of Harned and Owen[11] is recommended.

Recent speculations on the conductance of strong electrolytes consist of semi-quantitative corrections to the Debye-Hückel-Onsager theory. Factors such as variation in dielectric constant, Bjerrum-type association, co-volume correction, and the structure-breaking effect of the ions are discussed by Ritson, Hasted, and Collie,[12] whose paper may be briefly summarized here.

Reference is made by these authors to the work of Hückel,[13] who considered the deviation of strong electrolytes at higher concentrations from the Debye-Hückel-Onsager theory to be due to a variation of dielectric constant with concentration:

$$D = D_o + 2\bar{\delta}C \tag{9}$$

where D_o is the dielectric constant of the solvent and

$$\bar{\delta} = \frac{\delta^+ + \delta^-}{2} \tag{10}$$

where δ^+ and δ^- are the contributions (negative) of the cation and the anion respectively.

The activity of the electrolyte obeys the relationship

$$\log_{10} f = \mathscr{D} + BC \tag{11}$$

where $\mathcal{J}$ is a complicated function from the Debye-Hückel-Onsager theory. Hückel attributes the entire value of BC to a change in the dielectric constant. Other factors, however, contribute to this term. The "co-volume" effect is a correction applied to the activity to account for the relatively large "distance of nearest approach of the ions." Another factor is the effect of the interactions of the ions with the solvent molecules. For so-called "structure-breaking" salts, the arrangement of the solvent molecules is disturbed, and it becomes increasingly random with increasing concentration.

The final effect considered by these authors is that due to ion association. Bjerrum[14] attempted to account for anomalies at high concentrations by assuming that ionic association occurs when the ions reach a certain characteristic distance from each other. The neutral unit formed was not necessarily an ordinary molecule and was termed an "ion-pair." According to Kraus,[15] there can be no ion-pairs in aqueous solution due to the high dielectric constant of water.

B. Recent Theoretical Developments

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[16] published an important extension and modification

of the theory, in which allowance was made for the finite
size of the ions. These workers adopted a slightly
different distribution function from the usual Boltzmann
one.

The theory of the electrophoretic effect in the
diffusion and conductance of strong electrolytes has been
examined critically by Stokes.[17] In a later publication,
Stokes and Robinson[18] combined the theory of the electro-
phoretic effect with Falkenhagen's modification of the
theory of the relaxation effect to yield an equation which
assumes the following form for a 1:1 electrolyte:

$$\Lambda = \Lambda_0 - \frac{(B_1 \Lambda_0 + B_2)\sqrt{C}}{1 + B \mathring{a} \sqrt{C}} \tag{12}$$

where

$$B = \frac{50.29}{(\epsilon T)^{1/2}} \tag{13}$$

$$B_1 = \frac{8.20 \times 10^5}{(\epsilon T)^{3/2}} \tag{14}$$

$$B_2 = \frac{82.5}{\eta_0 (\epsilon T)^{1/2}} \tag{15}$$

This equation was tested comprehensively in the dilute

region with accurate data of such eminent scientists as Shedlovsky, and the agreement between theory and experiment was astounding. It was found that the value of $\overset{\circ}{a}$ was constant for each solute at all temperatures from 5°C. to 65°C. This fact lends strong support to equation (12) since it indicates that $\overset{\circ}{a}$ is a real molecular parameter, and not merely a "carry-all" for all manner of deviations. The values of the ion-size parameter required for the conductivity equation are of the same order of magnitude as those used in the Debye-Hückel expression for the activity coefficient. Stokes and Robinson also present theoretical justification for the omission of a $C \log C$ term which had been introduced into many empirical modifications of the Onsager limiting formula.

A remarkably successful conductance equation was published recently by Wishaw and Stokes.[19] In an earlier paper by Stokes and Robinson, discussed briefly above, the following equation for uni-univalent electrolytes was put forward:

$$\Lambda = \left(\Lambda_0 - \frac{82.5}{(\epsilon T)^{1/2}} \frac{\sqrt{C}}{1 + K a} \right) \left(1 + \frac{\Delta X}{X} \right) \qquad (16)$$

In this expression, the term $\dfrac{82.5 \sqrt{c}}{(\epsilon T)^{1/2} (1 + K a)}$ gives the electrophoretic effect, and the term $\Delta x / x$ the relaxation effect.

The latter was evaluated by Falkenhagen[16] as

$$\frac{\Delta X}{X} = -\frac{e^2}{3\epsilon kT} \cdot \frac{0.2929\, K}{1+Ka} \cdot \frac{e^{0.2929\, Ka}-1}{e^{0.2929\, Ka}} \tag{17}$$

where

$$K = \left(\frac{8\pi N e^2}{1000\,\epsilon\, kT}\right)^{1/2} \sqrt{C} \tag{18}$$

With reference to equation (16), the concentrations there considered were such that the final factor $\dfrac{e^{0.2929\, Ka}-1}{e^{0.2929\, Ka}}$, which will now be denoted by F, approximated closely to unity. For higher concentrations, this approximation is inadmissible.

Combination of equations (16), (17), and (18) leads to the result

$$\Lambda = \left(\Lambda_0 - \frac{B_2\sqrt{C}}{1+B\mathring{a}\sqrt{C}}\right)\left(1 - \frac{B_1\sqrt{C}}{1+B\mathring{a}\sqrt{C}}\cdot F\right) \tag{19}$$

where the coefficients B_1 and B_2 are those expressed by equations (14) and (15), and

$$B\mathring{a}\sqrt{C} = \frac{50.29\,\mathring{a}\sqrt{C}}{(\epsilon T)^{1/2}} = Ka \tag{20}$$

The only adjustable parameter in equation (19) is the effective ionic diameter $\mathring{a}$ if one assumes that Λ_0 is already known from suitable measurements.

There remains the perplexing problem of the probable necessity for a viscosity correction. As measured in an ordinary viscometer, the viscosity is a measure of the

shearing force required to move one layer of solution with respect to its neighbour. The shearing force encounters resistance in the form of intermolecular attractions of two types: firstly, the short range solvent-solvent and ion-solvent forces, and secondly, the long range Coulomb forces between ions. The effects are quite specific for different ions of the same valence; lithium salts, for example, cause a much greater increase in viscosity than that caused by potassium salts. This effect is no doubt due to the interference of the ions with the loosely coordinated water structure.

Considering now the "viscosity" of an ion in motion as in conductance experiments, the interionic contribution to the bulk viscosity may be neglected since the forces causing it have been considered in the theory that culminates in equation (19). The specific short range contributions completely overwhelm the small interionic contribution at concentrations above a few tenths molar. Hence there is reason to believe that the relative bulk viscosity could be justifiably introduced into the theoretical equations. Equation (19) was modified accordingly by Wishaw and Stokes:

$$\Lambda = \left(\Lambda_0 - \frac{B_2\sqrt{c}}{1+B\mathring{a}\sqrt{c}}\right)\left(1 - \frac{B_1\sqrt{c}}{1+B\mathring{a}\sqrt{c}}\cdot F\right)\frac{\eta_0}{\eta} \qquad (21)$$

This equation agrees with experimental NH_4Cl data within

one unit in equivalent conductance up to a concentration of 5 molar. The agreement with data for LiCl is excellent up to 10 molar.

Stokes has written a timely review[20] of the phenomena encountered in concentrated solutions. For further discussion, Stokes' and Robinson's recently published "Electrolyte Solutions"[21] should be consulted.

Within a few months of the appearance of the paper by Wishaw and Stokes,[19] an equation of comparable validity was published by Falkenhagen and Leist.[22] For uni-univalent electrolytes, their equation assumes the following form:

$$\Lambda = \Lambda_0 \frac{\eta_0}{\eta} - \frac{e^2}{3\epsilon kT} \cdot \frac{\kappa \Lambda_0 \eta_0/\eta}{1+\kappa a} \cdot \frac{q}{(1+\sqrt{q})(1+\kappa a \sqrt{q})}$$
$$- \frac{ne^2}{3\pi\eta_0} \cdot \frac{1000}{C \times 9 \times 10^{11}} \cdot \frac{\kappa}{1+\kappa a} \cdot \frac{\eta_0}{\eta} \tag{22}$$

A new distribution function due to Eigen and Wicke[23] is employed by these authors. Whereas the Boltzmann distribution function is based on the assumption that ions may be regarded as point charges, the theory of Eigen and Wicke considers the proper volume of the ions and their hydration shells in the solution; this leads to a finite number of locations for the ions. This latter consequence necessitates the result that the new distribution function be different from that of Boltzmann. Wishaw and Stokes[19]

consider the theory of Eigen and Wicke to be of questionable validity.

Falkenhagen tests his equation with data for LiCl at 18°C., which he has extracted from the International Critical Tables. Using a value of $\overset{\circ}{a} = 4.8A$., the agreement with experimental data is remarkable; at a concentration of 10 molar, the experimental and calculated equivalent conductances differ by less than one mho. Similarly good agreement is claimed for the other alkali halides. The treatment of Falkenhagen and Leist yields results which are slightly better than those obtained from calculations with the equation of Wishaw and Stokes.

It should be further emphasized here that the choice of the value of $\overset{\circ}{a}$ seems to be quite arbitrary. In calculations with LiCl, for example, Falkenhagen and Leist use a value of 4.8 A; the calculations of Wishaw and Stokes[19] are based on the selection of 5.2 A. as the distance of closest approach; Fuoss and Onsager[24] use 4.31 A in calculations with their equation for the dilute region.

C. The Solvation of Ions

The phenomenon of solvation of ions in solution is now generally accepted. The mechanism of solvation appears to be one of ion-dipole attraction; a solvent such as water has a large dipole moment and the dissolved ions have either

positive or negative charges. There is a well-defined force of attraction between such physical entities.

The speed of an ion, and consequently its conductance, will depend on its size, and this will obviously vary with the degree of solvation. The latter is closely associated with the charge on the ion, for the higher the electric field surrounding the ion, the greater will be its power of combination with a solvent dipole. Further, for ions of equal charge, solvation will be greater the smaller the atomic volume of the ion. These effects may combine in such a way that the effective ionic volumes in solution are quite out of line with the crystallographic data on atomic volumes.

The ions of the alkali metals have their conductances in aqueous solution in the order $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$. Their crystallographic radii are in the same order.[25] In the anhydrous melts,[26] however, the above order is reversed. Since the size of the ions is the most important factor influencing the conductance of such a series, one is led to the conclusion that the lithium ion has the largest and the cesium ion the smallest effective radius in aqueous solution. The only reasonable explanation of such facts is hydration.

There is some confusion in the literature as to the actual meaning of the terms "degree of hydration" and "hydration number." The latter are reported in a varying manner, depending on the method of determination. Some

workers consider only a tightly held unimolecular layer analogous to ionic coordination complexes. Another value considerably larger in magnitude is reported by those who consider all the water molecules which are subject to the "influence" of a given ion.

In an important paper on the structure of water, Bernal and Fowler[27] suggest a coordination model. On this basis, they deduce the hydration number to be four for all monovalent ions in dilute solution.

Recently, Hasted, Ritson, and Collie[12] undertook an evaluation of hydration numbers through a consideration of the depression in dielectric constant of water produced by the addition of ions. Their assumption is that the first layer is tightly held, and that other layers may be present. Their published values include the following: $H^+(10)$, $Li^+(6)$, $Na^+(4)$, $K^+(4)$, $Rb^+(4)$, $Mg^{++}(14)$, $La^{+++}(22)$. These values are in agreement with the extent of hydration obtained from conductance data.

Obviously these ideas are not applicable to concentrated solutions, where, in many instances, the number of ions may exceed the number of water molecules. A discussion of hydration throughout the range of concentration is given by Stokes and Robinson.[28] In their opinion, ion-ion forces are dominant in dilute solutions, and the simple Debye-Hückel treatment may be used. At more moderate

concentrations, the ion-ion and the ion-solvent forces become of comparable importance. A two parameter equation is developed for activity coefficients which reproduces experimental data up to a concentration of 5 normal. These authors assume that hydration renders the effective ionic radius in solution considerably greater than the crystallographic value.

At high concentrations, they contend that the ion-solvent forces are the dominant factor, and as a first approximation, a theory is presented which assumes that ion-ion forces are little affected by concentration in the range to be discussed.

These investigators, working with concentrated solutions of $Ca(NO_3)_2$, found that by isothermal evaporation at $25^{\circ}C$., the solutions pass into semi-solid gels without a discontinuity in vapour pressure. The possibility was considered that at high concentrations, the system could be treated as an adsorbent (calcium nitrate) - adsorbate (water) system. The ions are depicted as being in varying stages of hydration and in constant equilibrium with one another. This model bears a striking resemblance to that from which the adsorption isotherm of Brunauer, Emmett, and Teller[29] was derived. Equations were developed by Stokes and Robinson and applied to nine electrolytes for which data at high concentrations were available. The accuracy of their results

is astounding. The parameters of the equations are listed and their physical significance is discussed. Their hydration numbers are entirely self-consistent, and in all cases are considerably larger in the more dilute region of concentration.

D. Conclusion

No adequate theory of concentrated solutions of strong electrolytes exists at the present time. A vigorous attack on the theoretical and experimental aspects of the subject is needed. It is encouraging to note that several important papers have recently been published on this important problem.

NATURE OF THE PROBLEM

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A survey of the literature of conductance investigations indicates at once that the region of moderate and high concentration has been neglected until recently.

In the face of this paucity of data, an extensive study of the conductance and viscosity of appropriate electrolytic solutions was undertaken several years ago in this laboratory. Salts were chosen such that a wide range of concentration could be studied. Experimental research has been carried out on the following salts: ammonium nitrate at 25°C.,[30] 35°C.,[31] 95°C.,[32] and 180.0°C.,[33] silver nitrate at 25°C.,[30] 35°C.,[31] 95°C.,[32] and 221.7°C.,[33] and lithium nitrate at 25°C.,[34, 35] and 110°C.[34]

It is of further interest to compare experimental data with theoretical calculations based on the recent equations of Wishaw and Stokes[19] and of Falkenhagen and Leist.[22] This has been done with the first of these two theories.[36] The present research on lithium chlorate over the complete range of concentration provides data for a comprehensive test of these two theoretical equations.

SURVEY OF THE LITERATURE

SURVEY OF THE LITERATURE

The conductances of aqueous solutions of lithium chlorate over a wide range of concentration and at several temperatures are reported in the literature, but for various reasons, the work appears to be either inadequate or erroneous.

Kraus and Burgess[37] give data on conductances at a series of temperatures. Certain of their experimental methods are now considered obsolete. A water thermostat was used for the measurements at 25°C.; such a polar thermostatic liquid leads to considerable error.[38] The cell constant standards were those of Parker and Parker,[39] whereas the accepted modern standards are those put forward by Jones and Bradshaw.[40] It should be pointed out that these investigators were primarily interested in the conductance of lithium chlorate on the addition of small amounts of water, and hence their data are somewhat incomplete at 25°C.

Accurate measurements were made by Scatchard[41] and his co-workers in the dilute range at 10°C.

The investigations of Klotschko and Grigorjew[42] cover a wide range of concentration at six different temperatures, one of which is 25°C. These authors prefer the specific to the equivalent conductance as a basis of theoretical interpretation. When the results of their research are plotted against concentration, it is immediately evident that there

is a considerable scattering of the points on the graph.
It is my contention that these results are too inaccurate
to be of great value. For example, the specific conductance
of their weakest solution at 25°C. yields a value of the
equivalent conductance greatly in excess of the limiting
value as calculated from the sum of the individual limit-
ing ionic conductances. Further, when the curves of density
and viscosity vs. concentration are extrapolated to zero
concentration, the values of density and viscosity for pure
water so obtained are considerably different from the
accepted values.

EXPERIMENTAL PROCEDURE

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A. Preparation of Lithium Chlorate

The method used was essentially that of Potilitzin[43] and Kraus,[37] as modified by Griffiths,[44] which utilizes the metathetical reaction between barium chlorate and lithium sulphate. A good grade of lithium sulphate was obtained from the Fisher Scientific Company and was used without further purification. The barium chlorate was procured from the British Drug Houses Limited and was also used without further purification. An aqueous solution of the latter gave no evidence of the presence of chloride ion when tested with a solution of silver nitrate.

A one molar solution of barium chlorate was heated to approximately 80°C., and a solution of lithium sulphate was added dropwise until equivalence was reached. The resultant precipitate of barium sulphate was allowed to digest for at least twenty-four hours, and was subsequently removed by repeated filtration. To be certain that the equivalence point had been reached, the filtrate was titrated with dilute solutions of barium chlorate and lithium sulphate.

The solution was evaporated slowly at a temperature of 70°C. to 80°C., to an approximate concentration of sixty per cent by weight of lithium chlorate. The last traces of dust and barium sulphate were removed by filtration through

a sintered glass filter funnel of medium porosity. The
filtered concentrate was transferred to a 1000 mls. Claissen
flask, and dehydration was effected under a reduced pressure
of less than ten mms. mercury. The distillate was taken up
in concentrated sulphuric acid. The temperature was
maintained below 90°C. since decomposition is incipient at
this temperature when the solution becomes very concentrated.
The dehydration was terminated at a point such that, on
cooling, a mother liquor would remain after crystallization
had taken place, and it was anticipated that any remaining
soluble impurities would stay in solution. The mother liquor
was removed by suction and discarded.

The moist salt was stored in desiccators over
concentrated sulphuric acid until required for use. To
prepare anhydrous lithium chlorate, the wet material was
placed under a vacuum over phosphorus pentoxide. At the end
of five or six weeks, the water content had been reduced to
roughly one-half per cent. The last traces of water were
removed by a different technique. After the initial drying,
the salt was crushed to a fine powder in a "dry box," inside
of which was maintained an atmosphere of dried nitrogen gas
at a pressure greater than atmospheric. While still in the
"dry box," the salt was transferred to a special apparatus
constructed for the specific purpose of removing the last

vestiges of water. It consisted of two cylindrical glass
tubes, each being twenty-five cms. in length and each
having a diameter of four cms., jointed by a stopcock. Each
could be opened by means of a ground glass joint located
near the end of the tube. The tube containing the lithium
chlorate was sealed at one end and enclosed in an
electrically heated asbestos jacket, the temperature of which
was maintained near $80^\circ C$. The tube containing the phosphorus
pentoxide had small tubular apertures at both ends. The
entire system was evacuated. After six to eight weeks, the
final traces of water had disappeared from the salt.

B. Analysis of Lithium Chlorate

No satisfactory method for the accurate analysis of
lithium in large quantities exists to-day.[45] Most methods
of chlorate analysis give non-reproducible results.[46] The
analytical scheme employed in this research was quite simple:
A sample of solution to be analyzed was weighed out, an
excess of concentrated sulphuric acid was added, and gradual
evaporation to dryness was effected in Vycor dishes. The
resultant lithium sulphate was ignited to constant weight.
The procedure was standardized using sodium chlorate of high
quality; the method is capable of an accuracy of 0.01 per
cent. A graph of weight per cent vs. density of solution
was plotted on a large scale. Interpolation from this

graph was the analytical method used for the remainder of the research; thus the necessity for recurrent gravimetric analyses was obviated.

C. Conductance Measurements

1. The Bridge

The bridge employed was a Campbell - Shackleton Bridge obtained from the Leeds and Northrup Company. The manufacturers claimed an accuracy of 0.05 per cent. Further details are given in the Leeds and Northrup pamphlet, "Directions for Capacitance and Conductance Bridge using # 1553 Shielded Ratio Box."

The signal was amplified by a simple triode-type amplifier and detected by means of a telephone headpiece. The amplifier is essential in order that the very faint signal be heard. It is necessary that the voltage output of the audio-oscillator be kept at a low value to avoid heating the solution in the conductance cell.[38]

2. The Conductance Cells

Three types of conductance cell were used in the experimental investigations. For the work at room temperature, a cell of the type recommended by Jones and Bollinger[47] was used. This type of cell has the filling tubes and the electrical leads of opposite polarity widely

separated. Such a cell does not exhibit the Parker effect,[48]
i.e., errors in measurement due to a parallel capacitive
shunt.

For use in the bomb, the compact vertical cell of
Figure 1 was used. This cell gives a pronounced Parker effect,
and consequently the measurements at the higher temperature
are less accurate than those at 25.00°C.

Use was made of a third type of cell at 131.8°C. in
determining the conductances of solutions containing less than
ten per cent by weight of water and also the anhydrous melt.
This instrument is shown in Figure 2, page 32; its filling
apparatus is similar to that in Figure 5, page 43. The tubes
leading to the atmosphere were fitted with stopcocks. A
charge of lithium chlorate was placed in the filling bottle
in the "dry box" previously described, and the apparatus was
connected through its ground glass joints. The entire
apparatus was immersed in the oil bath; when the salt had
melted, it was forced into the cell by the alternate applica-
tion of suction and compression until the electrodes were
completely covered.

The cells were not platinized; the sharp minimum in
the detector indicated that this procedure was unnecessary.
After use, they were flushed several times with water, then
washed five times with acetone, and finally dried in an oven
at 80°C.
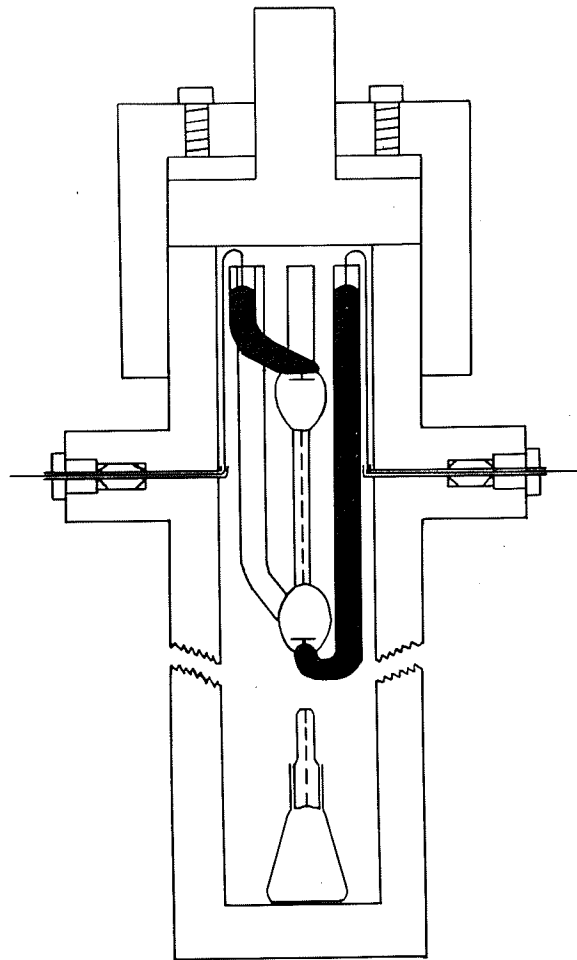
BOMB, CONDUCTANCE CELL,
AND PYKNOMETER.
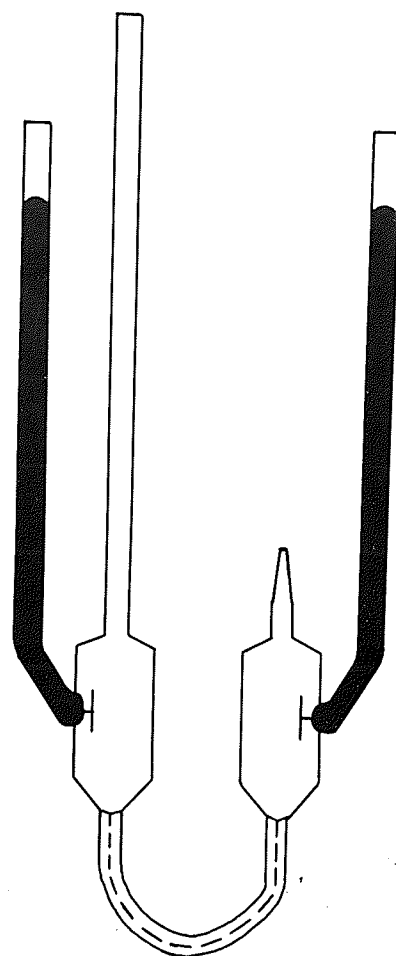
FIGURE 1

CONDUCTANCE CELL
FOR MOLTEN SALTS.

FIGURE 2

3. The Conductance Water

A commercial water distillation unit was employed to prepare conductance water. This apparatus was lined with tinned copper. The water so collected had a specific conductance of less than 5×10^{-6} mhos, which was more than sufficiently pure for the purpose of the measurements at hand.

4. The Cell Constants

Potassium chloride was used as a standard for the determination of the cell constant. The maximum impurities in this material were 0.02 per cent solid matter and 0.3 per cent water. The salt was fused in a platinum dish and stored over sulphuric acid in a desiccator until required.

The solutions were made up according to the specifications of Jones and Bradshaw.[40] The salt was weighed to 0.005 per cent and the solution to 0.003 per cent. The weights used were calibrated by direct comparison with a set standardized by the National Research Council at Ottawa. Each cell constant was determined several times and a mean taken; the precision was never less than 0.02 per cent.

Due to the obvious fact that no standard is available for the determination of cell constants at high temperatures, it was necessary to apply an appropriate correction. The difference in cell constant is due to geometry changes in

the cell; these changes and their corrections are discussed by Washburn.[49] In the instance at hand, the required modification reduces to a simple linear expansion correction.

Consider the effect of temperature on the cell constant K. By definition, the latter is the ratio of the distance ℓ between the electrodes to the effective area a of the solution between the electrodes, i.e.,

$$K = \frac{\ell}{a} \tag{23}$$

Differentiation with respect to temperature yields

$$\frac{dK}{dt} = \frac{1}{a}\frac{d\ell}{dt} - \frac{\ell}{a^2}\frac{da}{dt} \tag{24}$$

However,

$$\frac{d\ell}{dt} = \beta(\ell + s) - \beta's \tag{25}$$

where β = coefficient of linear expansion of Pyrex glass,

s = length of electrode posts,

β' = coefficient of linear expansion of platinum.

For cells whose electrodes are separated by a long capillary, equation (25) becomes

$$\frac{d\ell}{dt} = \beta\ell \tag{26}$$

Also, we have that

$$\frac{da}{dt} = 2\beta a \tag{27}$$

Therefore

$$\frac{dK}{dt} = \frac{1}{a}\beta l - \frac{l}{a^2} \cdot 2\beta a = -\beta K \qquad (28)$$

Thus

$$\Delta K = -\beta K \Delta t$$

$$(29)$$

the resultant correction was of the order of 0.03 per cent
and was applied in each instance.

D. The Thermostats

The thermostat employed at room temperature consisted
of a thick-walled Pyrex cylinder of approximately four
gallons capacity. It was insulated with a half inch layer
of felt. The thermostat fluid was Marcol bleached oil
supplied by the Imperial Oil Company; oil is used in
preference to water to eliminate errors due to a capacity
effect.[38] Temperature control was maintained through the use
of a mercury thermoregulator. To record the temperature, a
Beckmann thermometer was used which had been calibrated
several times against a standard platinum resistance
thermometer by means of a Mueller Bridge. The temperature
of the thermostat was $25.00 \pm 0.01^{\circ}C$.

The thermostat used for conductance measurements at
high temperatures was designed by M. E. Bednas of this
laboratory.[33] It is shown in Figure 3. An inner

36

HIGH TEMPERATURE THERMOSTAT
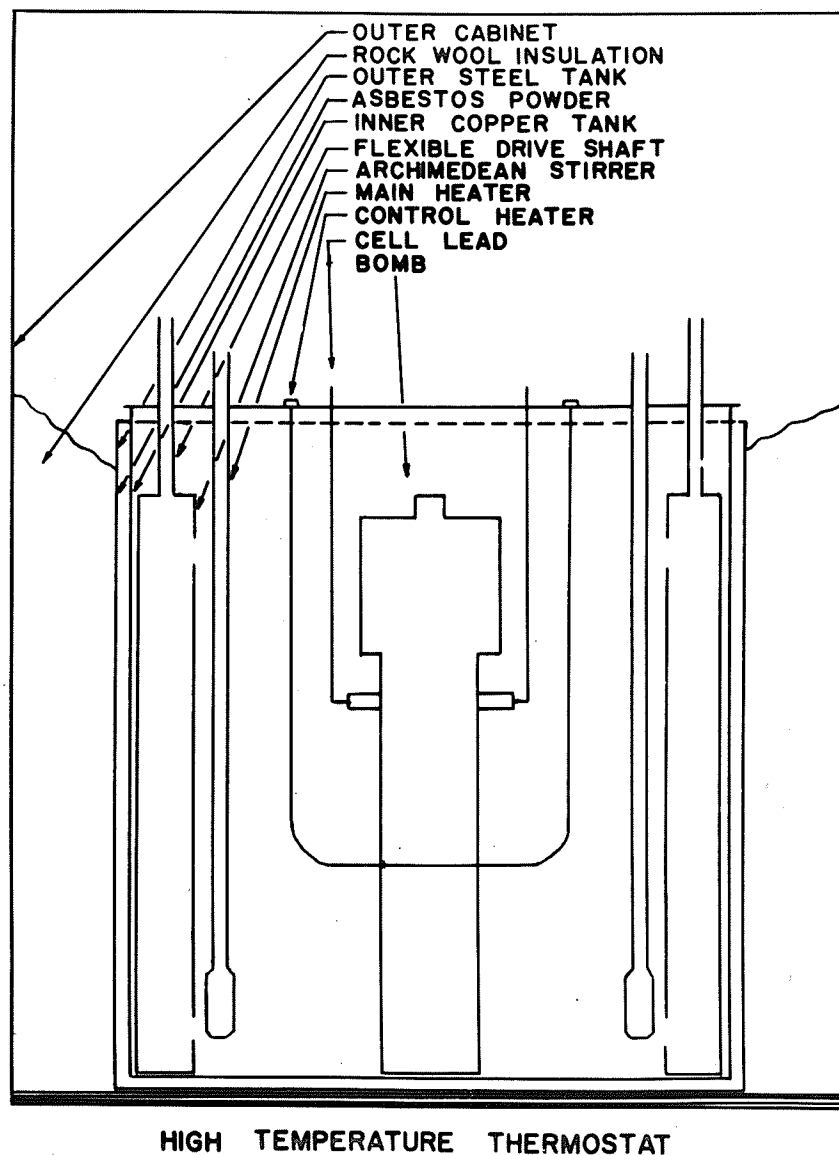
FIGURE 3

rectangular copper tank of eight gallons capacity was set in
an outer steel tank insulated with one inch of powdered
asbestos. In turn, this outer tank was enclosed in a large
wooden box with hinged doors and a hinged top. The bottom
of the box was lined with several layers of asbestos paper,
and rock wool insulation was packed between the box and the
steel tank. The thermostat fluid was Teresso # 85 obtained
from the Imperial Oil Company. The principal heating source
was a parallel connection of two immersion type engine block
heaters which maintained a temperature just below $130^{\circ}C$.
A smaller copper tube heater acted as a control through a
Swedish "Labora" thermoregulator connected to a standard
electronic relay. Very efficient stirring was realized
through the use of two large Archimedean stirrers. Again the
temperature was recorded on a Beckmann thermometer, which
had been calibrated against a standard platinum resistance
thermometer. It was found possible to maintain the temperature
within $0.05^{\circ}C$. Since the steel bomb used in the measurements
had walls of considerable thickness, the actual temperature
fluctuations in the solutions themselves would be significant-
ly less than this.

Finally, the thermostat used for viscosity measure-
ments at high temperatures consisted of a tall Pyrex cylinder
of three gallons capacity. The thermostat fluid in this case

was Stanolax (mineral oil), a product of the Imperial Oil
Company. Two copper tube heaters were used, one to maintain
a temperature just below $130^{\circ}C.$, and the other to serve as
a control heater via a Swedish "Labora" thermregulator,
connected, as before, to a standard electronic relay. The
glass cylinder was insulated with several layers of asbestos
paper and an inch thickness of felt. Stirring was
accomplished by means of an Archimedean stirrer.
Temperature was maintained constant within $0.1^{\circ}C.$, which was
sufficient for the purpose of the viscosity measurements.

E. The Bomb

Due to the fact that the solutions used were above
their normal boiling points at $131.8^{\circ}C.$, the conductance cell
and the density bottle were enclosed in a bomb. For this
purpose a standard steel bomb was obtained from the American
Instrument Company. The electrical leads were enclosed in
teflon tubing to prevent short circuits, and the bomb was
rendered airtight by crushing soapstone cones together under
considerable pressure. The position of the conductance cell
and the density bottle in the bomb is shown in Figure 1, page
31. The density bottle was placed in a pool of the solution
at the bottom of the bomb to eliminate distillation effects
in the density bottle and in the conductance cell.

F. The Viscometers

Two capillary viscometers of the design of Cannon and Fenske[50] were used for the viscosity measurements at $25.00^{\circ}C$. The drainage and kinetic energy corrections were assumed to be negligible by virtue of the rather narrow capillary diameter. The surface tension correction was not allowed for in such a viscometer because the change in surface tension between the calibrating liquid, water, and an aqueous salt solution, does not cause a large error. The method of filling the instrument rendered the working volume correction negligible. The viscometer was inverted and the capillary arm placed in the solution. Suction was subsequently applied to the wide-bore arm and the liquid was drawn to a suitable reference mark. This method is very convenient and reproducible results are possible within a precision of 0.1 per cent. The efflux times of the viscometers were of the order of two and five minutes respectively. The instrument with the shorter efflux time was used for the very viscous solutions. Measurements were repeated until consecutive readings differed by less than 0.1 per cent.

At the higher temperature, the viscometer of Figure 4 was employed. This apparatus was sealed after it had been filled to prevent boiling and evaporation of the liquid; it was calibrated with water. Obviously the total volume

VISCOSITY APPARATUS FOR HIGH TEMPERATURES
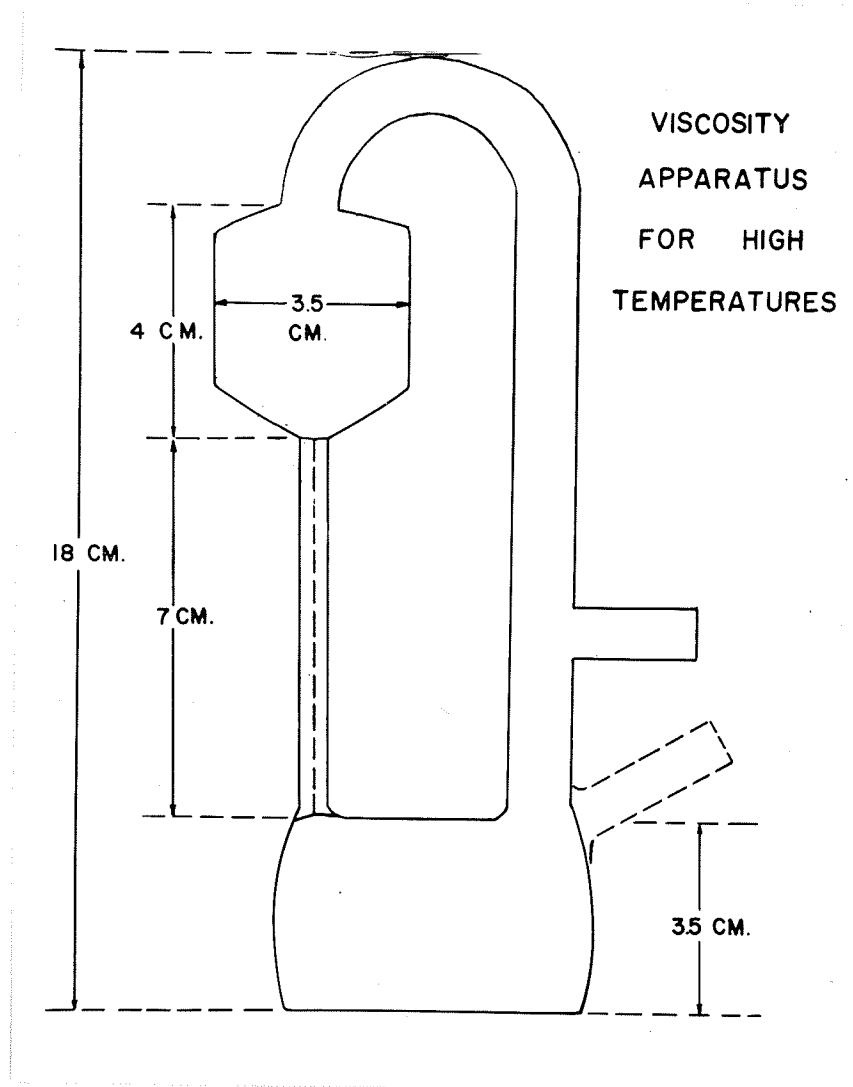
FIGURE 4

of solution in the viscometer is not critical as long as
there is sufficient to fill the calibrated bulb and not an
excess so that a back pressure is initiated when drainage
nears completion. The efflux time of the viscometer was
approximately fifty seconds; it was determined many times
and an average taken. Thus, the time was determined to
within one-tenth of a second. This permitted a precision
of 0.2 per cent in the measurement of efflux time. The
viscometer could be rotated through 180 degrees while still
in the thermostat by means of a rack and pinion, and it was
thereby automatically set in the same vertical position.

G. Preparation of Solutions

Lithium chlorate is a salt of such notorious
hygroscopicity that preparation of solutions by direct
weighing is exceedingly difficult. The fresh concentrate,
which was stored in desiccators, was diluted with water to
the approximate concentration required. In each case,
roughly one hundred mls. of solution were prepared. The
accurate concentration was obtained by interpolation from
the density graph as previously described.

H. Density Determinations

A Weld pyknometer of twenty-five mls. capacity was
used to measure densities at 25.00°C.; the instrument was
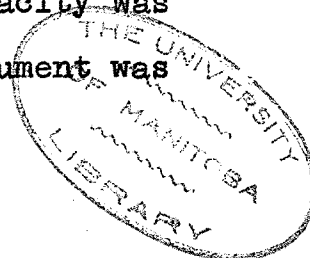
calibrated with water. Reproducibility to 0.005 per cent was attained.

At the higher temperature, two pyknometers were employed, one for use in the steel bomb with the aqueous solutions, and another (Figure 5) for the anhydrous melt. The apparatus used in the bomb was also a Weld type of ten mls. capacity; it was calibrated several times with water at $131.8^{\circ}C$.

The technique of filling the instrument of Figure 5 is identical to that described for the conductance cell of Figure 2, page 32. After the melt had been forced into the pyknometer, the apparatus was partially removed from the hot oil, the instrument was rapidly disconnected from the filling tubes, the excess oil was quickly wiped off, and the apparatus was allowed to cool in a desiccator over phosphorus pentoxide prior to weighing. This particular instrument was calibrated with mercury at $25.00^{\circ}C.$ and its volume at the higher temperature was calculated through the use of the formula

$$V_t = V_{25}\left(1 + \gamma(t-25)\right) \tag{30}$$

where t is the temperature in question, and γ the coefficient of cubical expansion of Pyrex glass.
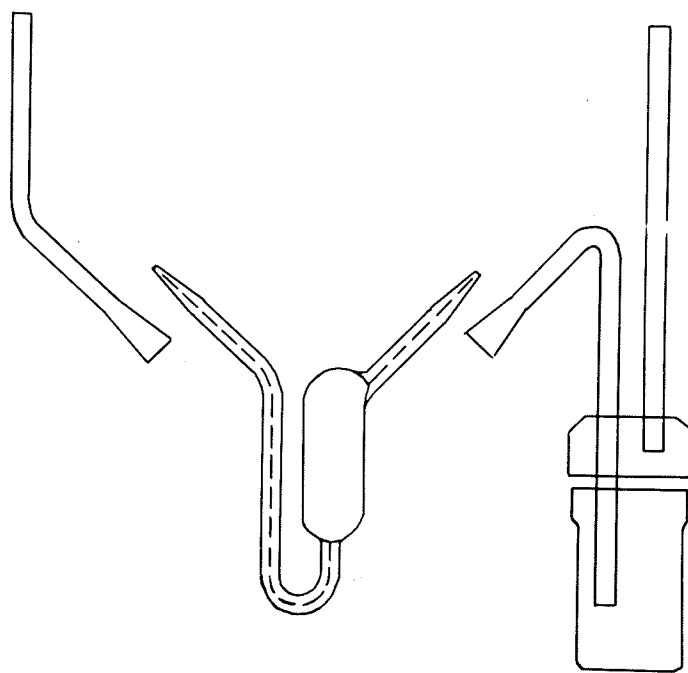
DENSITY APPARATUS

FOR HIGH TEMPERATURES

FIGURE 5

EXPERIMENTAL RESULTS

EXPERIMENTAL RESULTS

The design of the bridge circuit was such that K , the specific conductance, was calculated from the formula

$$K = \frac{K\,(10,000.0 - R)}{R \times 10^4} \tag{31}$$

where K is the cell constant and R the reading of the resistance box in ohms at the balance point.

The relative viscosity of each solution was calculated from the relationship

$$\frac{\eta_1}{\eta_2} = \frac{\rho_1 t_1}{\rho_2 t_2} \tag{32}$$

where the subscripts "1" refer to the standardizing liquid, and the subscripts "2" to the solution.

The experimental values of weight per cent, molarity, density, relative viscosity, specific conductance, and equivalent conductance are recorded in Tables I and II. The data are tabulated on the basis that the conductance measurements are limited to an accuracy of 0.1 per cent and that the density figures err in the fourth decimal place.

Plots of specific conductance and equivalent conductance vs. concentration at $25.00^{\circ}C.$ and at $131.8^{\circ}C.$ are presented in Figures 6 to 11 inclusive, pages 50 to 55 inclusive.

TABLE I

CONDUCTANCES, DENSITIES AND VISCOSITIES OF AQUEOUS
SOLUTIONS OF LITHIUM CHLORATE AT 25.00°C.

Weight %	Molarity	Density gm/ml.	Relative Viscosity Water=1.000	Specific Conductance ohm⁻¹ cm.⁻¹	Equivalent Conductance mhos
0.1990	0.02188	0.9982	1.002	0.0020444	93.31
0.9036	0.1002	1.0025	1.015	0.008495	84.78
4.519	0.5121	1.0243	1.067	0.03679	71.85
7.402	0.8532	1.0420	1.110	0.05662	66.36
10.60	1.247	1.0631	1.169	0.07677	61.58
13.68	1.640	1.0834	1.229	0.09379	57.19
17.24	2.113	1.1082	1.315	0.1108	52.45
23.01	2.928	1.1505	1.472	0.1337	45.67
24.27	3.115	1.1594	1.508	0.1374	44.11
28.39	3.742	1.1915	1.642	0.1495	39.94
33.38	4.549	1.2320	1.895	0.1546	33.90
35.49	4.908	1.2502	2.019	0.1556	31.69
36.90	5.157	1.2633	2.115	0.1556	30.17
42.58	6.199	1.3160	2.594	0.1511	24.38

TABLE I (continued)

CONDUCTANCES, DENSITIES AND VISCOSITIES OF AQUEOUS
SOLUTIONS OF LITHIUM CHLORATE AT 25.00°C.

Weight %	Molarity	Density gm/ml.	Relative Viscosity Water=1.000	Specific Conductance ohm^{-1} cm.$^{-1}$	Equivalent Conductance mhos
47.61	7.185	1.3643	3.140	0.1420	19.76
50.36	7.762	1.3933	3.585	0.1346	17.35
51.68	8.047	1.4074	3.838	0.1312	16.30
55.71	8.947	1.4519	5.170	0.1189	13.29
60.88	10.19	1.5136	6.894	0.1031	10.11
65.82	11.49	1.5776	10.29	0.08639	7.521
70.43	12.80	1.6426	16.37	0.07189	5.618
74.09	13.93	1.7002	24.53	0.06010	4.313
75.06	14.27	1.7187	28.38	0.05644	3.955
80.66	16.15	1.8100	66.26	0.03928	2.432
85.44	17.95	1.8989	166.5	0.02407	1.341
88.17	19.03	1.9510	334.0	0.01644	0.8639
89.03	19.33	1.9627	-	0.01487	0.7695

TABLE II

CONDUCTANCES, DENSITIES AND VISCOSITIES OF AQUEOUS
SOLUTIONS OF LITHIUM CHLORATE AT 131.8°C.

Weight %	Molarity	Density gm/ml.	Relative Viscosity Water=1.000	Specific Conductance ohm^{-1} cm^{-1}	Equivalent Conductance mhos
1.087	0.1131	0.9407	1.013	0.03438	304.02
4.987	0.5321	0.9645	1.047	0.1303	244.79
10.57	1.169	0.9994	1.110	0.2381	203.76
15.18	1.729	1.0294	1.165	0.3099	179.28
20.17	2.374	1.0641	1.257	0.3687	155.31
25.18	3.066	1.1006	1.323	0.4184	136.50
30.13	3.794	1.1382	1.408	0.4417	116.42
35.16	4.589	1.1799	1.519	0.4630	100.89
40.77	5.548	1.2302	1.686	0.4607	83.04
46.35	6.572	1.2818	1.903	0.4451	67.72
54.15	8.165	1.3630	2.364	0.4041	49.50
59.49	9.345	1.4201	2.838	0.3703	39.62
67.57	11.40	1.5251	4.263	0.3160	27.73
72.09	12.64	1.5855	5.477	0.2920	23.09

TABLE II (continued)

CONDUCTANCES, DENSITIES AND VISCOSITIES OF AQUEOUS
SOLUTIONS OF LITHIUM CHLORATE AT 131.8°C.

Weight %	Molarity	Density gm/ml.	Relative Viscosity Water=1.000	Specific Conductance ohm^{-1} cm.$^{-1}$	Equivalent Conductance mhos
78.57	14.65	1.6860	8.836	0.2578	17.59
86.56	17.42	1.8197	17.48	0.2176	12.49
93.98	20.46	1.9681	43.38	0.1650	8.064
100.0	23.11	2.0889	113.0	0.1180	5.108
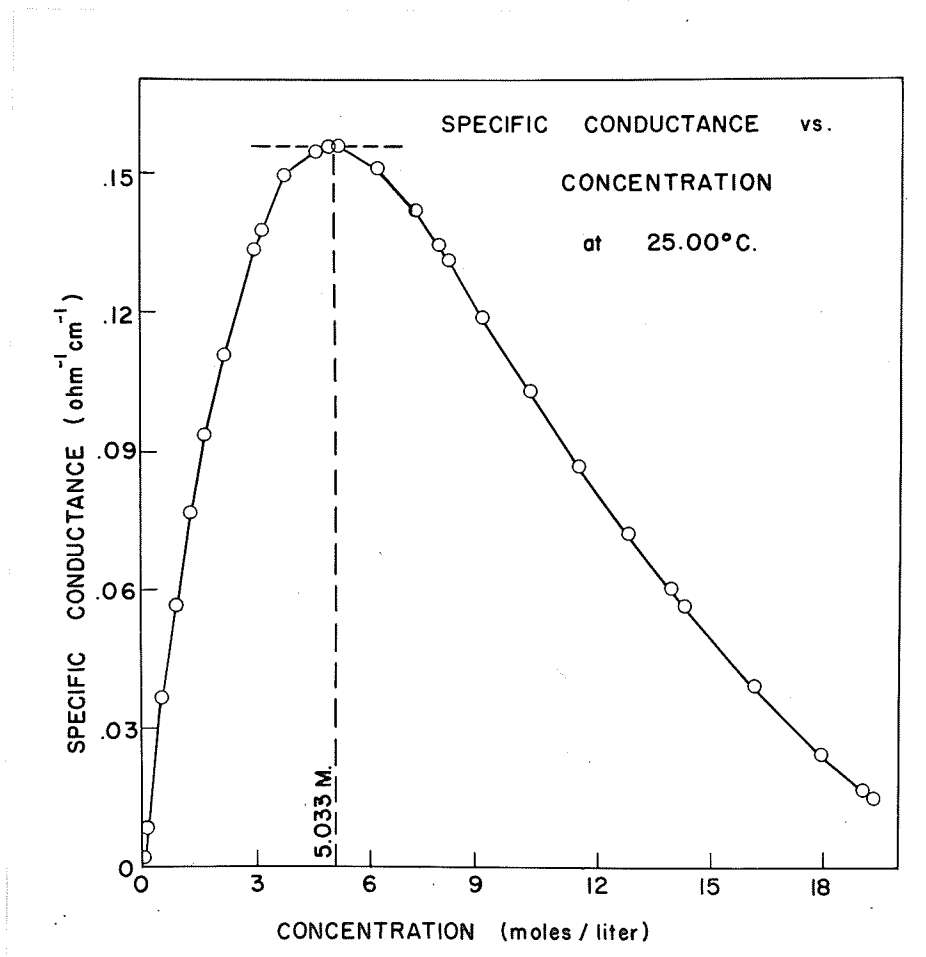
FIGURE 6
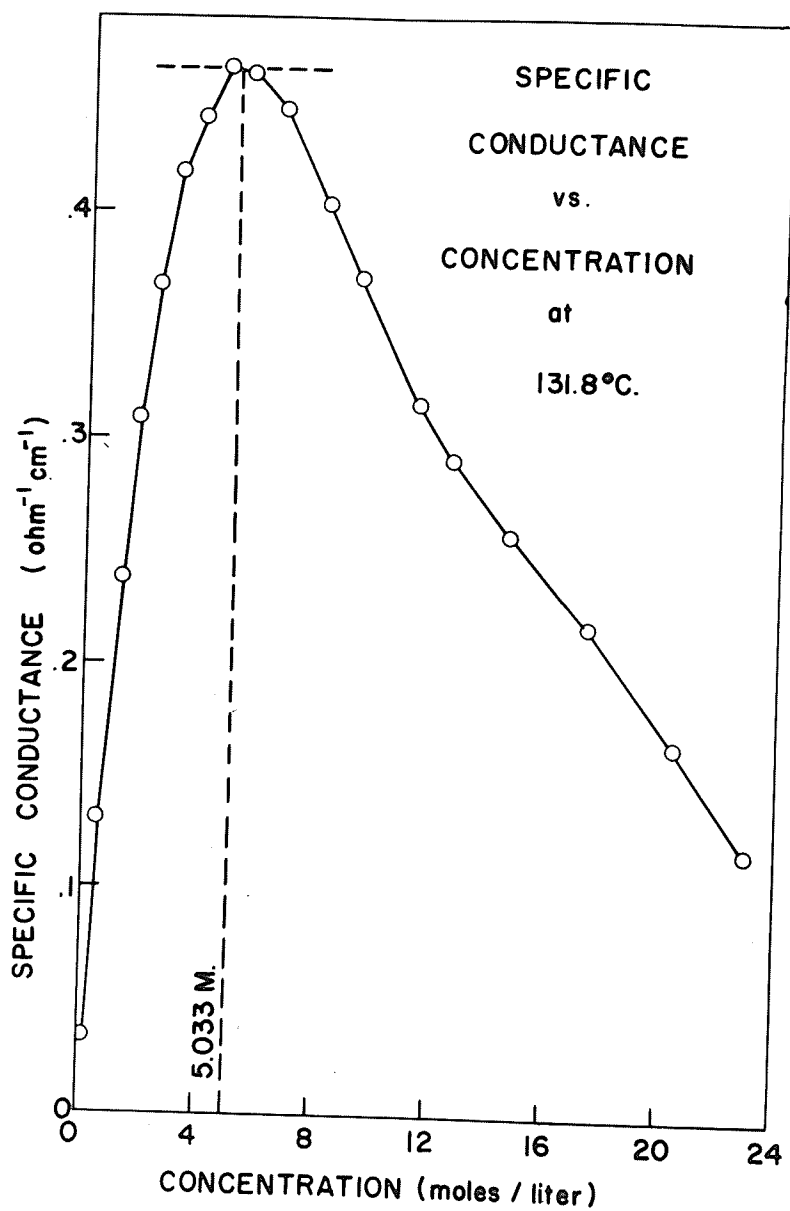
FIGURE 7

FIGURE 8

FIGURE 9

The figure shows a plot titled:

EQUIVALENT CONDUCTANCE vs. CONCENTRATION at 25.00° C.

$\Lambda^\circ = 103.28$

$\mathring{a} = 4.3 \,\mathring{A}.$

o: EXPERIMENTAL

•: CALCULATED

The x-axis is labeled CONCENTRATION (moles / liter) ranging from 0 to 20, and the y-axis is labeled EQUIVALENT CONDUCTANCE (mhos) ranging from 0 to 90.

FIGURE 10

EQUIVALENT CONDUCTANCE vs.
CONCENTRATION
at 131.8° C.

O : EXPERIMENTAL

● : CALCULATED

$\mathscr{R} = 405$, $\mathring{a} = 2.7 \mathring{A}$.
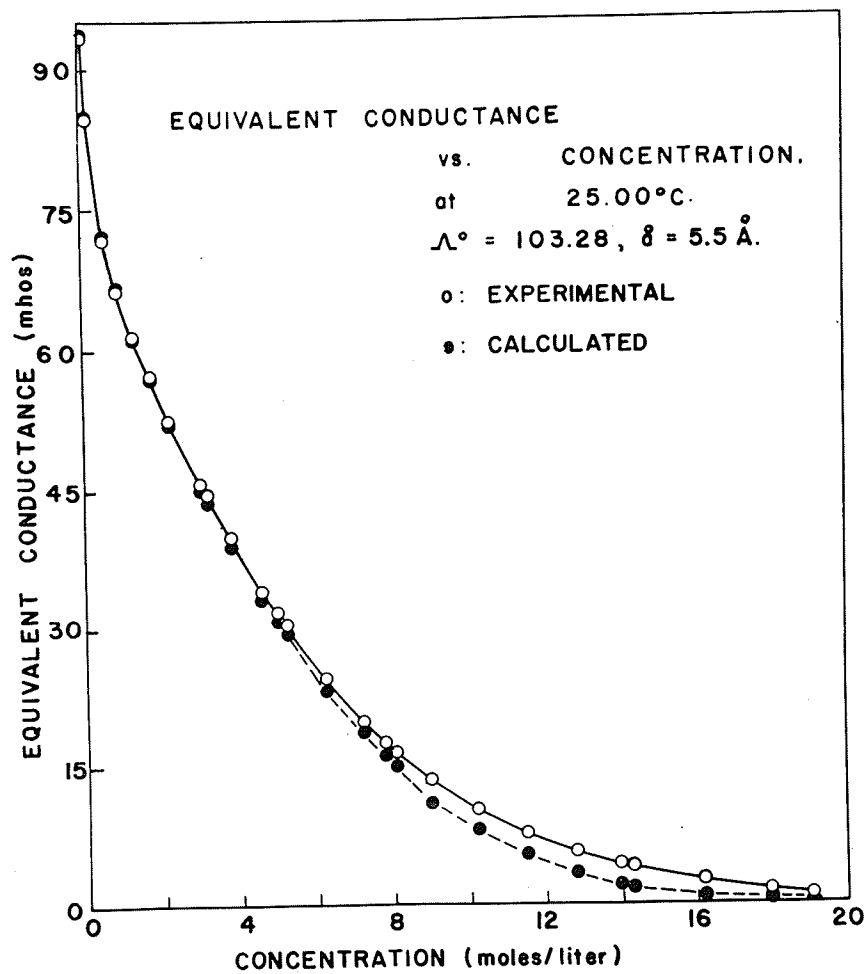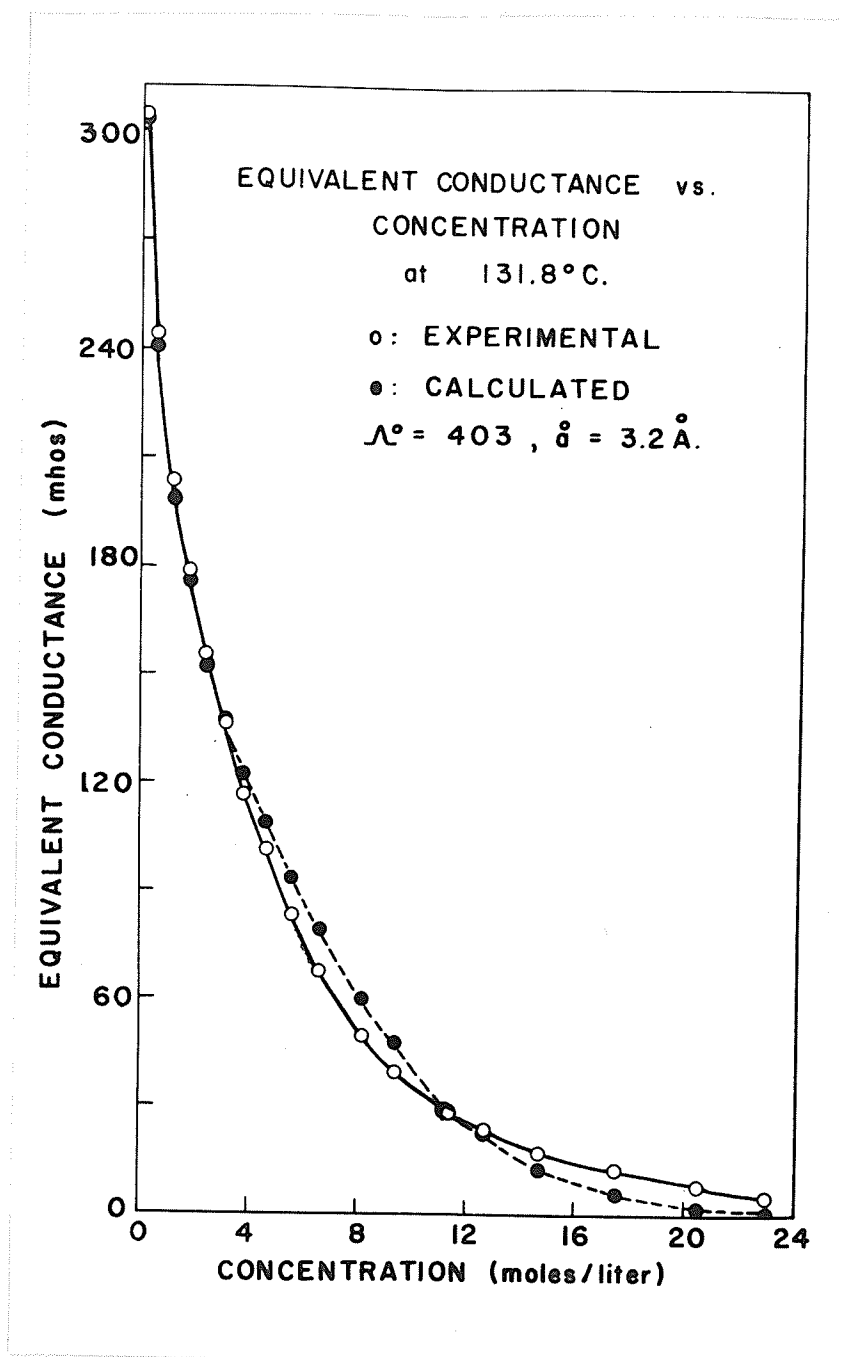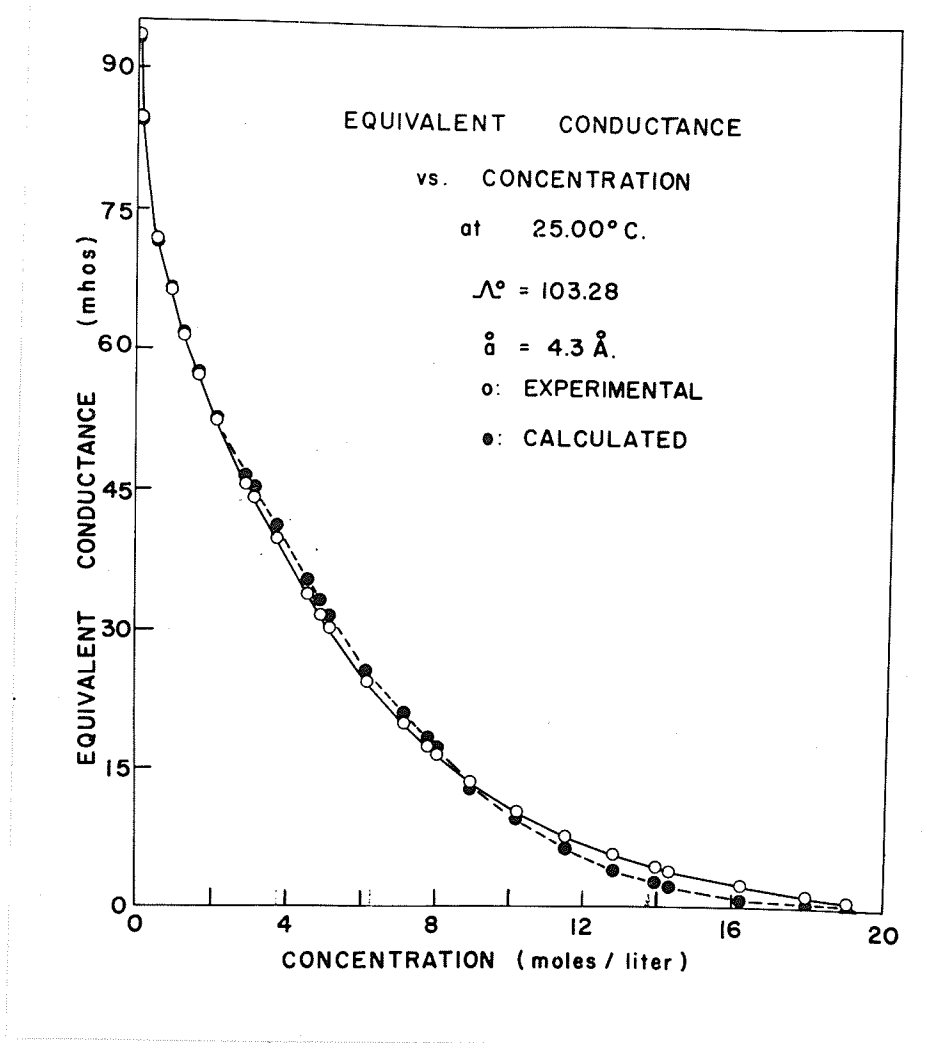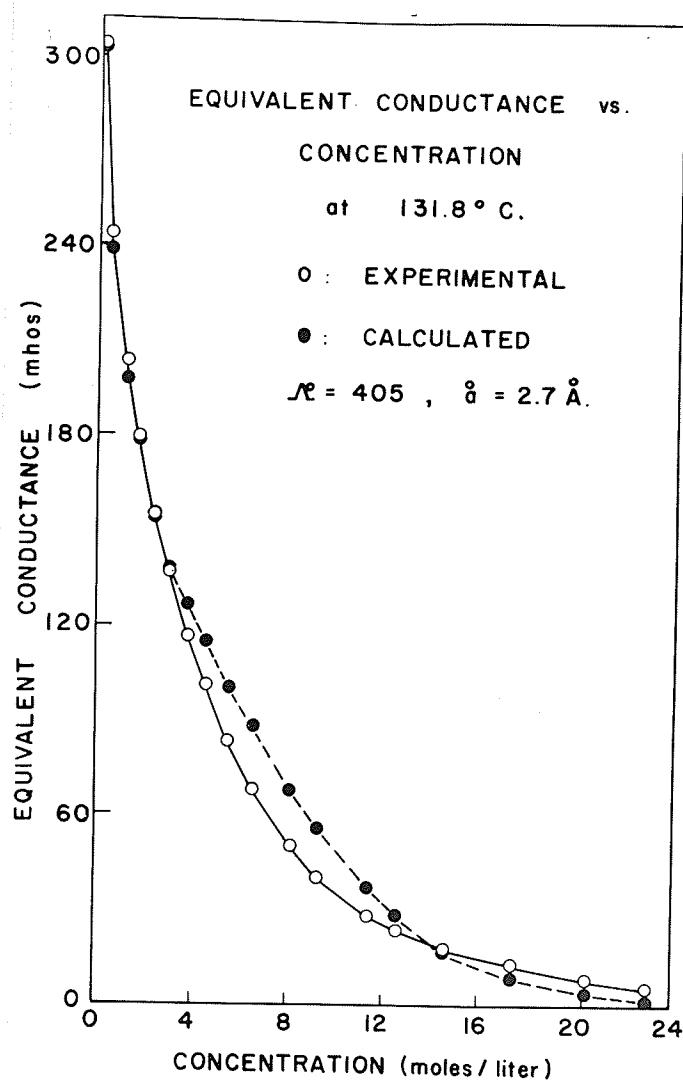
FIGURE 11

DISCUSSION OF THE RESULTS

DISCUSSION OF THE RESULTS

A. Discussion of the Measured Quantities

The plots of specific conductance vs. concentration
at 25.00°C. and at 131.8°C. are to be found in Figures 6 and
7, pages 50 and 51. The existence of maxima in these curves
is of great theoretical interest, since its physical
significance is that a given volume of solution containing
a greater number of ions has a lower conductance at
concentrations beyond the maximum. For instance, the
conductance at 131.8°C. of a ten molar solution is the same
as that of a two molar solution despite a five fold increase
in electrolyte concentration. Such maxima are recorded
infrequently in the literature owing to the lack of
conductance investigations in the region of high concentration.
This unfortunate state of affairs has ameliorated consider-
ably in the last five years due to the revival of interest in
this topic.

It is seen at a glance from the graphs that the
maximum does not shift noticeably with a change in temperature.
This is also the result of the studies of Klotschko and
Grigorjew.[42] These authors point out that the position of the
maximum is found in the neighbourhood of the eutectic point
of the system. In fact, they seek to use the equilibrium
diagram for the system lithium chlorate - water to interpret

their results.

There is no necessary connection between the eutectic
point and the specific conductance maximum. Rather one
should regard the maximum as evidence that factors tending
to increase the conductance with rising concentration are
offset by factors opposing this increase. As the concentra-
tion increases, more ions are available; however, these ions
are in much closer proximity to one another and hence their
freedom of movement is greatly impaired through their inter-
actions. This crude picture is rendered more complex by
hydration phenomena. At high concentrations, all solvent
molecules must be tightly held by the ions. Consequently,
one would expect a large increase in viscosity, and hence
a similar decrease in conductance; such is the case in this
research. Recent theoretical speculations[51] endow liquids
with a transitory structure; the maximum thus has a possible
explanation as the incipience of the formation of a more
ordered lattice-type structure of the solution.

Graphs of equivalent conductance vs. concentration at
$25.00^{\circ}C.$ and at $131.8^{\circ}C.$ constitute Figures 8 to 11
inclusive, pages 52 to 55 inclusive. This property is the
usual function of concentration, i.e., it decreases con-
tinuously with concentration. At the higher temperature, the
entire range of concentration could be covered since all the
measurements were made above the melting point of lithium

chlorate. There are no minima in the equivalent conductance curves. The theory of the existence of such minima is discussed by Fuoss and Kraus;[52] it is based on the association of ions into non-conducting "ion-pairs" and conducting triple ions. Such entities cannot exist in lithium chlorate solutions due to the heavily hydrated cation. The very low value to which the equivalent conductance drops at 25.00°C. is most unusual. The last three figures of the data for 25.00°C. represent super saturated solutions, which were easily obtained.

In Figures 12 and 13, the equivalent conductance is plotted against the logarithm of the concentration. It was observed by Herron[33] that such a graph yielded straight line relationships from below six molar up to the highest concentration he attained. Such is not the case in this research; in both cases, the curves are seen to be of an elongated S-shape. Whether or not this should prove to have theoretical justification, it might be pointed out that the logarithmic plot of any such steadily decreasing function will tend to linearity.

Curves of fluidity vs. concentration may be seen in Figures 14 and 15, pages 65 and 66; it is apparent that Bingham's[53] rule is obeyed to quite a high concentration. The values are recorded in Tables III and IV, pages 62 to 64 inclusive. The extremely low value to which the fluidity

FIGURE 12

Λ vs. LOG₁₀C at 131.8°C.
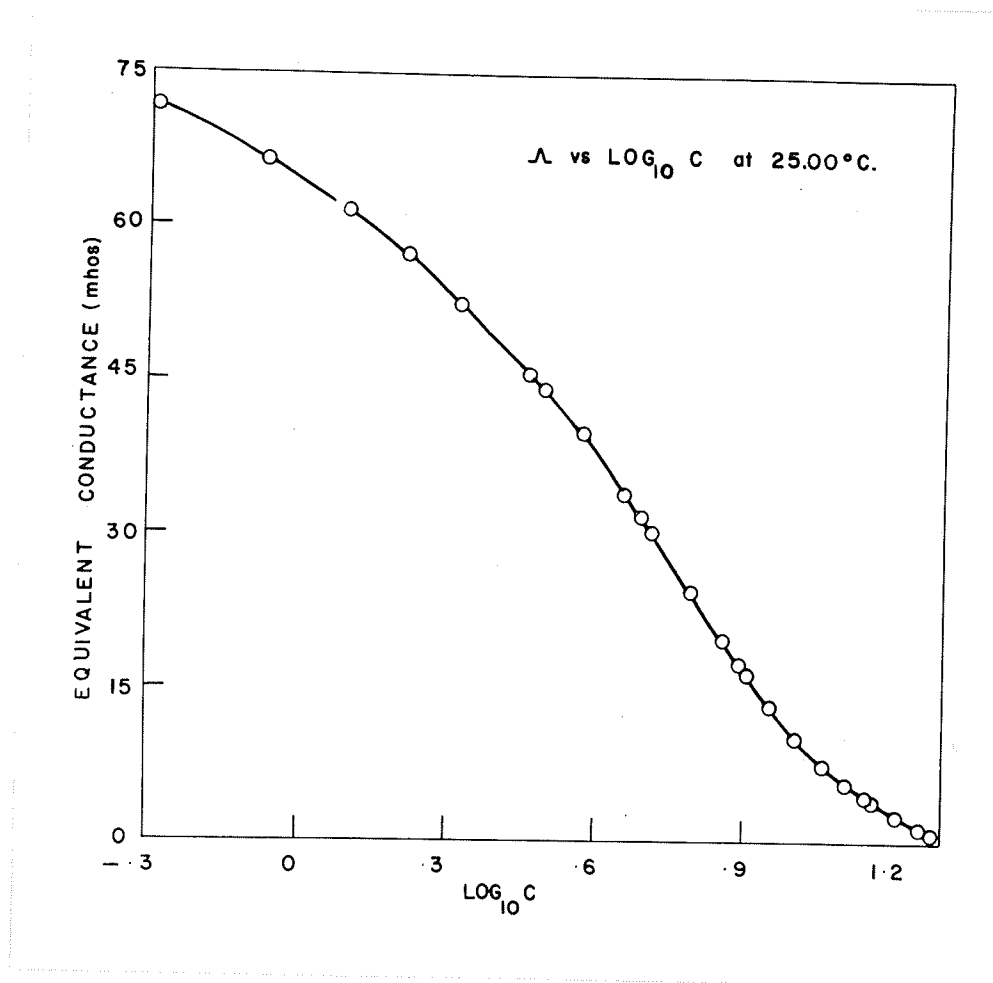
FIGURE 13

TABLE III

VALUES OF FLUIDITY AND $\Lambda \eta_r$ AT 25.00°C.

Molarity	Relative Viscosity Water=1.000	Fluidity rhos	Equivalent Conductance mhos	$\Lambda \eta_r$
0.02188	1.002	111.7	93.31	93.47
0.1002	1.015	110.3	84.78	86.04
0.5121	1.067	104.9	71.85	76.65
0.8532	1.110	100.8	66.36	73.66
1.247	1.169	95.71	61.58	72.00
1.640	1.229	91.03	57.19	70.31
2.113	1.315	85.10	52.45	68.97
2.928	1.472	76.02	45.67	67.22
3.115	1.508	74.21	44.11	66.53
3.742	1.642	68.14	39.94	65.58
4.549	1.895	59.05	33.90	64.24
4.908	2.019	55.43	31.69	63.98
5.157	2.115	52.91	30.17	63.80
6.199	2.594	43.15	24.38	63.22
7.185	3.140	35.63	19.76	62.06
7.762	3.585	31.21	17.35	62.19
8.047	3.838	29.16	16.30	62.56
8.947	5.170	21.64	13.29	68.73
10.19	6.894	16.23	10.11	69.70
11.49	10.29	10.87	7.521	77.40

TABLE III (continued)

VALUES OF FLUIDITY AND $\Lambda \eta_r$ AT 25.00°C.

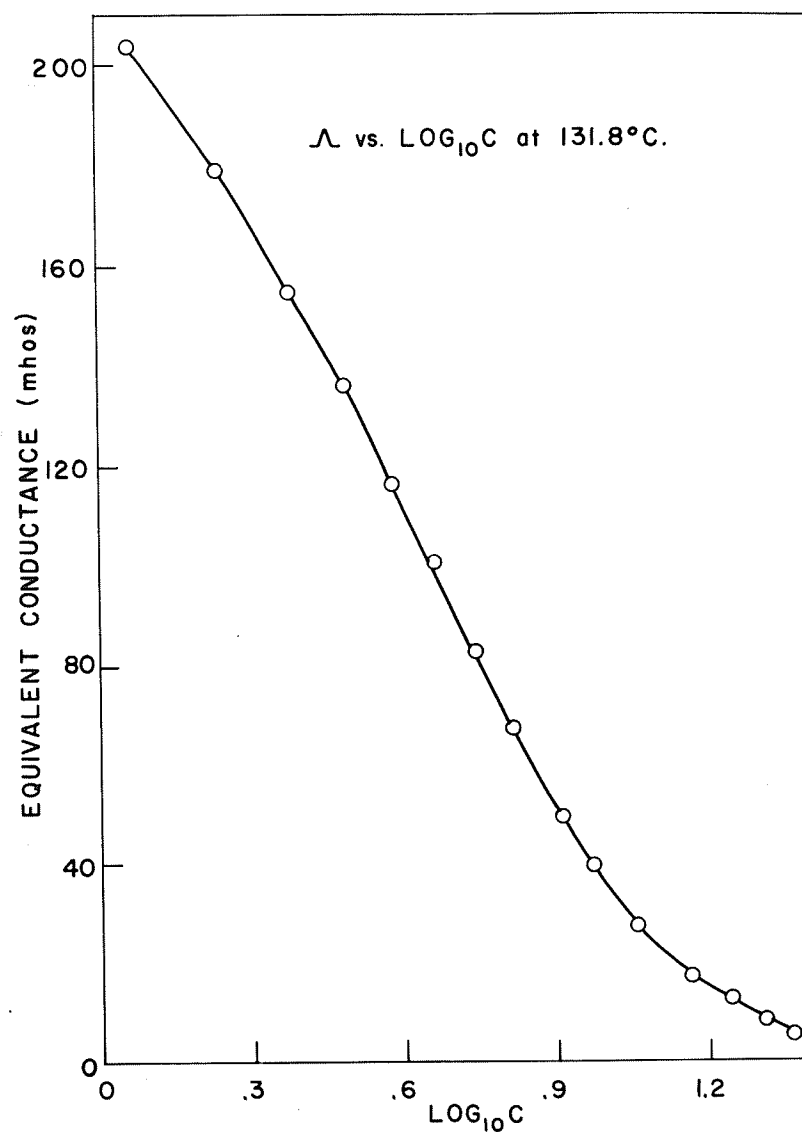| Molarity	Relative Viscosity Water=1.000	Fluidity rhos	Equivalent Conductance mhos	$\Lambda \eta_r$
12.80	16.37	6.83	5.618	91.98
13.93	24.53	4.56	4.313	105.8
14.27	28.38	3.94	3.955	112.3
16.15	66.26	1.69	2.432	161.1
17.95	166.5	0.67	1.341	223.2
19.03	334.0	0.34	0.8639	288.6
19.33	-	-	0.7695	-

TABLE IV

VALUES OF FLUIDITY AND $\wedge \eta_r$ AT 131.8°C.

Molarity	Relative Viscosity Water=1.000	Fluidity rhos	Equivalent Conductance mhos	$\wedge \eta_r$
0.1131	1.013	469.3	304.02	307.9
0.5321	1.047	454.0	244.79	256.3
1.169	1.110	428.3	203.76	226.1
1.729	1.165	408.2	179.28	208.8
2.374	1.257	378.2	155.31	195.2
3.066	1.323	359.3	136.50	180.6
3.794	1.408	337.5	116.42	164.0
4.589	1.519	312.9	100.89	153.2
5.548	1.686	281.9	83.04	140.0
6.572	1.903	249.7	67.72	128.9
8.165	2.364	201.1	49.50	117.0
9.345	2.838	167.5	39.62	112.5
11.40	4.263	111.5	27.73	118.2
12.64	5.477	86.8	23.09	126.5
14.65	8.836	53.8	17.59	155.4
17.42	17.48	27.2	12.49	218.2
20.46	43.38	11.0	8.064	349.8
23.11	113.0	4.20	5.108	577.2
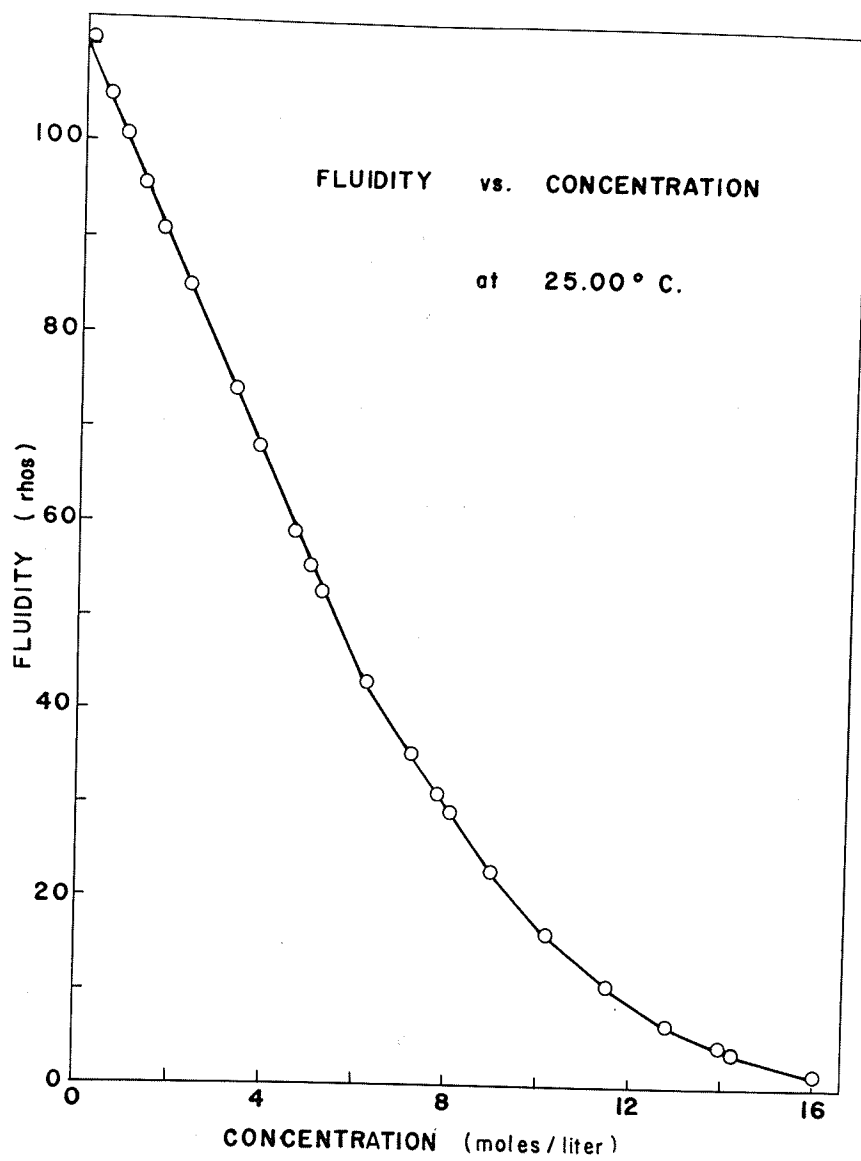
FIGURE 14
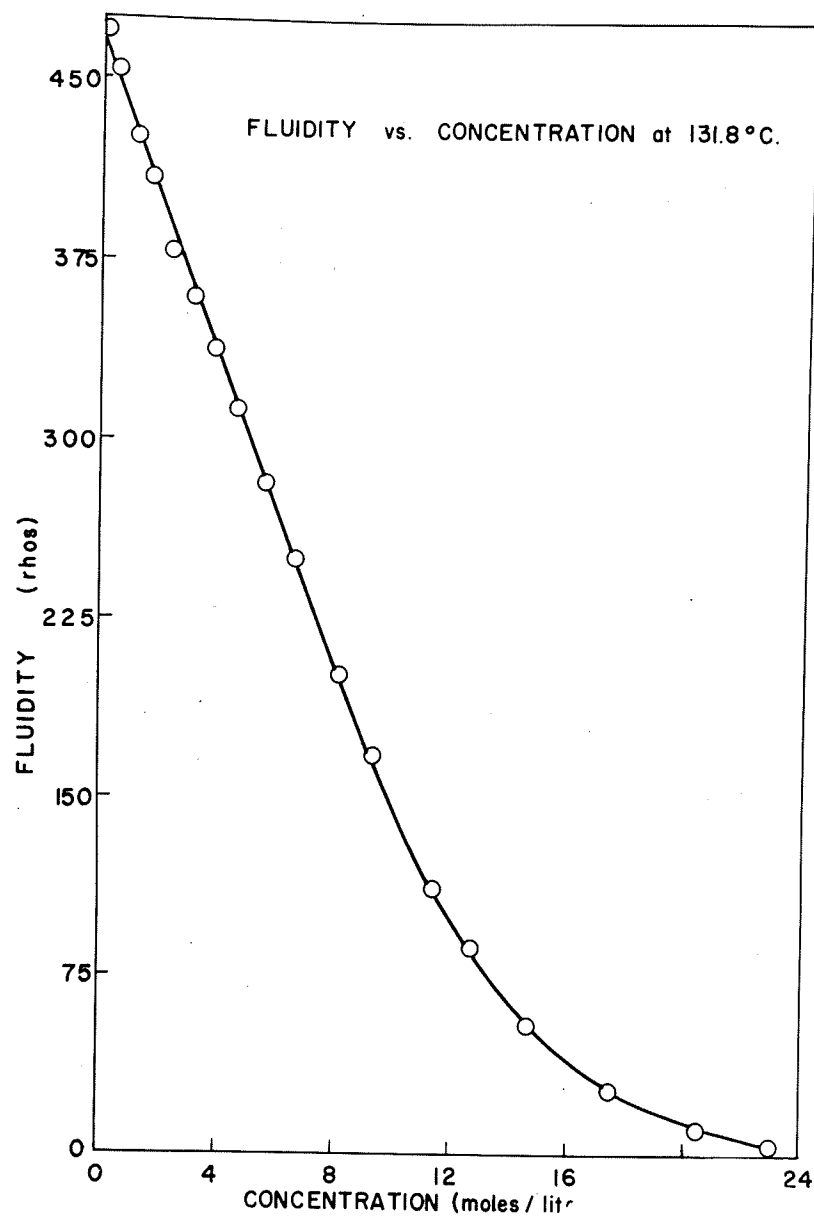
FIGURE 15

falls at 25.00°C. is most remarkable.

The absolute viscosities of all liquids decrease with rising temperature. On the other hand, the relative viscosities of electrolytic solutions increase with temperature in the vast majority of cases. For lithium salts, however, the reverse is true. This is consistent with the concept of extensive hydration of the lithium ion. One would anticipate a decrease in hydration at higher temperatures, which necessitates a greater mobility for the lithium ion.

B. Discussion of the Calculated Quantities

The experimental results of this research have been compared with conductances calculated by means of the Wishaw-Stokes and the Falkenhagen-Leist equations. These calculations are summarized in Tables V and VI; their plots against concentration are shown in Figures 8 to 11, pages 52 to 55 inclusive. On the whole, the Falkenhagen-Leist equation appears to be the more successful. In order to calculate Λ from these equations, Λ_o must be known, and a reasonable value for $\overset{\circ}{a}$, the distance of closest approach of the ions, must be assumed. Also, the dielectric constant and the viscosity of water are needed in order to obtain the theoretical constants B, B_1, and B_2. Accurate data exist for the dielectric constant[54] of water and for the viscosity.[55]

TABLE V

THEORETICAL CALCULATIONS WITH THE WISHAW-STOKES AND THE
FALKENHAGEN-LEIST EQUATIONS AT 25.00°C.

Molarity	Relative Viscosity Water=1.000	Λ_{exp}	Λ calc.		
			Wishaw-Stokes		Falkenhagen
			$\overset{\circ}{a} = 5.3\text{Å}$	$\overset{\circ}{a} = 5.5\text{Å}$	$\overset{\circ}{a} = 4.3\text{Å}$
0.02188	1.002	93.31	93.34	93.41	93.22
0.1002	1.015	84.78	85.09	85.29	84.92
0.5121	1.067	71.85	71.86	72.29	72.10
0.8532	1.110	66.36	66.17	66.66	66.84
1.247	1.169	61.58	60.73	61.26	61.86
1.640	1.229	57.19	56.30	56.83	57.81
2.113	1.315	52.45	51.34	51.86	53.23
2.928	1.472	45.67	44.30	44.77	46.69
3.115	1.508	44.11	42.94	43.40	45.42
3.742	1.642	39.94	38.56	38.49	41.32
4.549	1.895	33.90	32.58	32.97	35.47
4.908	2.019	31.69	30.27	30.63	33.18
5.157	2.115	30.17	28.69	29.04	31.60
6.199	2.594	24.38	22.71	22.97	25.57

TABLE V (continued)

THEORETICAL CALCULATIONS WITH THE WISHAW-STOKES AND THE FALKENHAGEN-LEIST EQUATIONS AT 25.00°C.

Molarity	Relative Viscosity Water=1.000	Λ_{exp}	$\Lambda_{calc.}$		
			Wishaw-Stokes		Falkenhagen
			$\overset{\circ}{a}= 5.3A.$	$\overset{\circ}{a} = 5.5A.$	$\overset{\circ}{a} = 4.3A.$
7.185	3.140	19.76	18.27	18.49	20.99
7.762	3.585	17.35	15.78	15.96	18.33
8.047	3.838	16.30	14.63	14.80	17.10
8.947	5.170	13.29	10.63	10.74	12.65
10.19	6.894	10.11	7.723	7.752	9.441
11.49	10.29	7.521	5.005	5.043	6.304
12.80	16.37	5.618	3.035	3.055	3.953
13.93	24.53	4.313	1.964	1.973	2.632
14.27	28.38	3.955	1.681	1.690	2.271
16.15	66.26	2.432	0.6831	0.6850	0.9695
17.95	166.5	1.341	0.2577	0.2571	0.3862
19.03	334.0	0.8639	0.1241	0.1234	0.1920
19.33	-	0.7695	-	-	-

TABLE VI

THEORETICAL CALCULATIONS WITH THE WISHAW-STOKES AND THE FALKENHAGEN-LEIST EQUATIONS AT 131.8°C.

Molarity	Relative Viscosity Water=1.000	Λ_{exp}	$\Lambda_{calc.}$		
			Wishaw - Stokes		Falkenhagen
			å = 3.2A. Λ_0 = 403	å = 3.6A. Λ_0 = 399	å = 2.7A. Λ_0 = 405
0.1131	1.013	304.02	304.62	303.76	304.29
0.5321	1.047	244.79	240.22	243.31	238.59
1.169	1.110	203.76	198.34	203.75	197.73
1.729	1.165	179.28	175.66	181.87	178.04
2.374	1.257	155.31	152.78	159.31	154.85
3.066	1.323	136.50	137.54	144.29	141.05
3.794	1.408	116.42	123.24	129.84	128.03
4.589	1.519	100.89	109.27	114.26	115.24
5.548	1.686	83.04	93.92	99.72	100.89
6.572	1.903	67.72	79.54	84.68	87.20
8.165	2.364	49.50	60.09	64.20	68.12
9.345	2.838	39.62	47.93	51.33	55.73
11.40	4.263	27.73	29.75	31.81	36.18
12.64	5.477	23.09	22.25	23.74	27.81

TABLE VI (continued)

THEORETICAL CALCULATIONS WITH THE WISHAW-STOKES AND THE
FALKENHAGEN-LEIST EQUATIONS AT 131.8°C.

Molarity	Relative Viscosity Water=1.000	Λ_{exp}	$\Lambda_{calc.}$		
			Wishaw – Stokes $\overset{o}{a} = 3.2A.$ $\Lambda_o= 403$	Stokes $\overset{o}{a} = 3.6A$ $\Lambda_o= 399$	Falkenhagen $\overset{o}{a} = 2.7A$ $\Lambda_o= 405$
14.65	8.836	17.59	12.86	13.78	16.20
17.42	17.48	12.49	5.948	6.348	8.411
20.46	43.38	8.064	2.175	2.288	3.334
23.11	113.0	5.108	0.7684	0.7963	1.014

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The only doubtful parameter at $25.00^{\circ}C$. is the distance of closest approach. Two sets of calculations were made with the Wishaw-Stokes equation using slightly different values of this parameter. The results indicate that $\overset{\circ}{a}$ is a parameter of which considerable adjustment is permissible. To obtain a good fit with experimental data using the Falkenhagen-Leist equation, a significantly different value of $\overset{\circ}{a}$ must be used. It will be remembered that different values of $\overset{\circ}{a}$ (4.3, 4.8, and 5.2 A) were required to obtain successful theoretical calculations for lithium chloride.[19,22,24]

At the higher temperature, the usual difficulty of not knowing Λ_o is an additional handicap. For each value of $\overset{\circ}{a}$, I have used a slightly different value of Λ_o. The agreement at $131.8^{\circ}C$. is much less spectacular than that at $25.00^{\circ}C$., but in view of the uncertainty in Λ_o, better results can hardly be expected.

Although Stokes maintains that $\overset{\circ}{a}$ is temperature independent, a smaller value of $\overset{\circ}{a}$ has been used for the higher temperature in each instance. This procedure is probably justifiable. I have elsewhere alluded to the fact that the extent of ion hydration decreases with a rise in temperature. It is therefore reasonable to assume that the effective radius of the hydrated lithium ion is smaller at the higher temperature, and hence the distance of closest approach of the ions must be smaller. Even if this were not

so, the attached water molecules must be more mobile at the
higher temperature; they would then be more easily pushed
aside, and the proximity of the electrical centers would
increase. Further, at both temperatures, a concentration
is soon reached where the number of ions and of solvent
molecules becomes comparable. At this point, there is no
longer sufficient water to maintain extensive hydration,
and consequently $\overset{\circ}{a}$ must become smaller.

The values of $\Lambda \eta_r$ have been calculated and are
presented in Tables III and IV, pages 62 to 64 inclusive.
As usual, the product drops rapidly, passes through a minimum,
and then rises to a high value. Similar behaviour is
experienced at both temperatures. If the two theoretical
equations were obeyed over the entire range of concentration,
it is apparent from the form of the equations that
should decrease continuously. The concentrations at which
the product begins to increase correspond roughly to that
region in which the two equations encounter serious
difficulties.

It is not the position of a person of my limited
capabilities and inexperience to decide which of the equations
is theoretically preferable. When expanded, the Wishaw-Stokes
equation has four terms; the Falkenhagen-Leist equation has
three terms. The values of the terms which differ are not
comparable. The difference in mathematical form is due

to the use by Wishaw and Stokes of a Boltzmann distribution

function, and by Falkenhagen and Leist of an Eigen-Wicke

distribution function in the treatment of the relaxation

effect.

SUMMARY AND CONCLUSIONS

SUMMARY AND CONCLUSIONS

Experimental data on the conductance, density, and viscosity of aqueous solutions of lithium chlorate have been obtained over the complete range of concentration at 25.00°C. and at 131.8°C.

The maximum of the curve of specific conductance vs. concentration does not shift noticeably with change in temperature. There are no minima in the equivalent conductance curves. The exponential relationship between concentration and equivalent conductance discovered by Herron is not applicable to the results of this research.

Theoretical calculations have been made with the recently published equations of Wishaw and Stokes, and of Falkenhagen and Leist. Of these two treatments, the latter appears to be slightly more satisfactory.

Bingham's fluidity rule is obeyed to a concentration of six molar at 25.00°C. and to nine molar at 131.8°C. The relative viscosity of the solutions decreases with a rise in temperature; this is the reverse of the usual effect. Evidence of a strongly hydrated lithium ion is thereby furnished.

The distance of closest approach of two ions has not been found to be independent of temperature. Theoretical justification is given for this viewpoint.

The present research is offered in the hope that it will help to stimulate the recently revived interest in the phenomena encountered in concentrated solutions of strong electrolytes.

TABLE OF SYMBOLS

TABLE OF SYMBOLS

A, A^*, B — Empirical or theoretical constants.
B^*, D, E

$a, \overset{\circ}{a}$ — Distance of closest approach of two ions in cms. and Angstrom units respectively.

a — Effective area of cross-section in an electrolytic cell.

B, B_1, B_2 — Constants in Stokes-Robinson equation.

C — Concentration in moles per liter.

D, D_0 — Dielectric constant of solution and solvent respectively.

$\mathcal{D}$ — Debye-Hückel function.

e — Charge on proton; base of natural logarithms.

F — Function in Stokes-Robinson equation equal to

$$\frac{e^{0.2929 Ka} - 1}{e^{0.2929 Ka}}$$

f — Activity.

K — Cell constant; equilibrium constant.

k — Boltzmann constant.

ℓ — Length between electrodes of electrolytic cell.

n — Number of ions of a given type per cubic cm.

N — Avogadro's number.

q — Falkenhagen's term equal to $\frac{1}{2}$ for 1:1 electrolytes.

R — Resistance in ohms.

s — Length of electrode posts in electrolytic cell.

t — Centigrade temperature; time in seconds.

T Absolute temperature.

u, v Ionic velocities.

V Volume in cubic cms.

$\Delta x/x$ Falkenhagen's relaxation effect.

α Degree of dissociation.

α^{*} Empirical constant.

β Coefficient of linear expansion of Pyrex glass.

β' Coefficient of linear expansion of platinum.

γ Coefficient of cubical expansion of Pyrex glass.

δ^{+}, δ^{-} Ionic contributions to dielectric constant.

ϵ Dielectric constant of solvent.

η_{0}, η_{r} Viscosity of solvent and solution respectively.

κ Specific conductance, Ionic atmosphere term.

Λ Equivalent conductance.

Λ_{0} Equivalent conductance at infinite dilution.

ρ Density in gms. per cm.

BIBLIOGRAPHY

BIBLIOGRAPHY

1. Debye, P., and Hückel, E., Physik. Z., 24, 185, 305 (1923).

2. Onsager, L., Physik. Z., 27, 388 (1926).

3. Onsager, L., Physik. Z., 27, 288 (1926).

4. Onsager, L., Physik. Z., 28, 277 (1927).

5. Onsager, L., and Fuoss, R. M., J. Phys. Chem., 36, 2689 (1932).

6. Shedlovsky, T., J. Am. Chem. Soc., 54, 1405 (1932).

7. Jones, G., and Bickford, C. F., J. Am. Chem. Soc., 56, 602 (1934).

8. Scatchard, G., Chem. Rev., 13, 7 (1933).

9. MacInnes, D. A., and Shedlovsky, T., J. Am. Chem. Soc., 54, 1429 (1932).

10. MacInnes, D. A., Shedlovsky, T., and Longsworth, L. G., Chem. Rev., 13, 29 (1933).

11. Harned, H. S., and Owen, B. B., "The Physical Chemistry of Electrolytic Solutions," Reinhold Pub. Corp., N. Y., 1950.

12. Hasted, J. B., Ritson, D. M., and Collie, C. H., J. Chem. Phys., 16, 1 (1948).

13. Hückel, E., Physik. Z., 26, 93 (1925).

14. Bjerrum, N., Kgl. Danske Vidensk. Selskab., 7, No. 9 (1926).

15. Kraus, C. A., J. Phys. Chem. 60, 129 (1956).

16. Falkenhagen, H., Leist, M., and Kelbg., G., Ann. Physik, 6, (11), 51 (1952).

17. Stokes, R. H., J. Am. Chem. Soc., 75, 4563 (1953).

18. Stokes, R. H., and Robinson, R. A., J. Am. Chem. Soc., 76, 1991 (1954).

19. Wishaw, B. F., and Stokes, R. H., J. Am. Chem. Soc., 76 2065 (1954).

20. Stokes, R. H., Rev. Pure Appl. Chem., 5, 60 (1955).

21. Stokes, R. H., and Robinson, R. A., "Electrolyte Solutions," Butterworths Sci. Pub., London, 1955.

22. Falkenhagen, H., and Leist, M., Naturwiss., 41, 570 (1954).

23. Eigen, M., and Wicke, E., Naturwiss., 38, 453 (1951).

24. Fuoss, R. M., and Onsager, L., Proc. Natl. Acad. Sci., U.S., 41, 274 (1955).

25. Wells, A. F., "Structural Inorganic Chemistry," Clarendon Press, Oxford, 1945.

26. Redlich, O., Chem. Rev., 39, 333 (1946).

27. Bernal, J. D., and Fowler, R. H., J. Chem. Phys., 1 515 (1933).

28. Stokes, R. H., and Robinson, R. A., J. Am. Chem. Soc., 70, 1870 (1948)

29. Brunauer, S., Emmett, P. H., and Teller, E., J. Am. Chem. Soc., 60, 309 (1938).

30. Campbell, A. N., and Kartzmark, E. M., Can. J. Research, 828, 43 (1950).

31. Campbell, A. N., Gray, A. P., and Kartzmark, E. M., Can. J. Chem., 31, 617 (1953).

32. Campbell, A. N., and Kartzmark, E. M., Can. J. Chem., 30, 128 (1952).

33. Campbell, A. N., Kartzmark, E. M., Bednas, M. E., and Herron, J. T., Can. J. Chem., 32, 1051 (1954).

34. Campbell, A. N., Debus, G. H., and Kartzmark, E. M., Can. J. Chem., 33, 1508 (1955).

35. Campbell, A. N., and Debus, G. H., Can. J. Chem., 34, 1232 (1956).

36. Campbell, A. N., and Kartzmark, E. M., Can. J. Chem., 33, 887 (1955).

37. Kraus, C. A., and Burgess, W. M., J. Am. Chem. Soc., 49, 1226 (1927).

38. Jones, G., and Josephs, R. C., J. Am. Chem. Soc., 50, 1049 (1928).

39. Parker, H. C., and Parker, E. W., J. Am. Chem. Soc., 46, 312 (1924).

40. Jones, G., and Bradshaw, B. C., J. Am. Chem. Soc., 55, 1780 (1933).

41. Scatchard, G., Prentiss, S. S., and Jones, P. T., J. Am. Chem. Soc., 56, 805 (1934).

42. Klotschko, M. A., and Grigorjew, I. G., Akad. Wiss. (U.S.S.R.), Nachr. Abt. physik.-chem. Analyse, 21, 288 (1950). A German translation may be obtained from the Library of the National Research Council, Ottawa, Canada.

43. Potilitzin, A., J. Russ. Phys. Chem. Soc., 16, 840(1883).

44. Campbell, A. N., and Griffiths, J. E., Can. J. Chem., 34, 1647 (1956).

45. Scott, W. W., "Standard Methods of Chemical Analysis," D. Van Nostrand Company, Inc., New York, 1950.

46. Griffiths, J. E., Master's Thesis, University of Manitoba, 1956.

47. Jones, G., and Bollinger, G. M., J. Am. Chem. Soc., 53, 411 (1931).

48. Parker, H. C., J. Am. Chem. Soc., 45, 1366, 2017 (1923).

49. Washburn, E. W., J. Am. Chem. Soc., 38, 2431 (1916).

50. Cannon, M. J., and Fenske, M. R., Ind. Eng. Chem. Anal. Ed., 10, 299 (1938).

51. Frank, H. S., and Evans, M. W., J. Chem. Phys., 13, 507 (1945).

52. Fuoss, R. M., and Kraus, C. A., J. Am. Chem. Soc., 55, 2387 (1933).

53. Bingham, E. C., "Fluidity and Plasticity," McGraw-Hill Book Company, New York, 1922.

54. Akerlof, G. C., and Oshry, H. I., J. Am. Chem. Soc., $\underline{72}$, 2844 (1950).

55. Hardy, R. C., and Cottington, E. M., Natl. Bureau Standards (U.S.), Research Paper RPL1994. J. Res. Natl. Bur. Standards, $\underline{42}$, 573 (1949).