

THE CONDUCTANCES AND FLUIDITIES OF STRONG AQUEOUS
SOLUTIONS OF AMMONIUM NITRATE AND OF SILVER NITRATE
AT 35.00°C

Being a Thesis Submitted to the
Department of Graduate Studies of
the University of Manitoba in
Partial Fulfillment of the Requirements
for the Degree of Master of Science

By

Allan Proctor Gray



September

1952

ACKNOWLEDGMENTS

The author would like to express his appreciation of the patient and understanding direction of Dr. A. N. Campbell during the performance of this research, and to acknowledge the important contribution of Dr. W. Biermann and Mr. N. Weber who so kindly calibrated the Beckmann thermometers

The author would also like to thank the Consolidated Mining and Smelting Company of Trail, B.C. for a generous grant and for permission to pursue a research in this field

Finally the author wishes to acknowledge gratefully the services and facilities made available to him by the employees of the Atomic Energy of Canada Company Limited, Chalk River, Ontario.

TABLE OF CONTENTS

<u>Part</u>	<u>Page</u>
I. INTRODUCTION	1
II. DISCUSSION OF THE LITERATURE	4
1. Conductance	5
(i) Definition	5
(ii) Development of the Method	6
(iii) Development of the Theory	9
(iv) Ammonium Nitrate	15
(v) Silver Nitrate	16
2. Viscosity and Fluidity	16
(i) Definition	16
(ii) Development of the Method	17
(iii) Development of the Theory	20
(iv) Ammonium Nitrate and Silver Nitrate	27
3. Conductance-Viscosity Relationships	27
4. The General Problem of Strong Electrolytes	32
(i) Ionic Volumes	34
(ii) Optical Properties	39
(iii) Dielectric Properties	41
(iv) Some Recent Theories	43
III. EXPERIMENTAL	48
1. Purification of Materials.	49
(i) Ammonium Nitrate	49
(ii) Silver Nitrate	50
(iii) Potassium Chloride	50
(iv) Conductance Water	50

2.	Preparation of Solutions	51
3.	Temperature Control	54
4.	The Measurement of Equivalent Conductance.	58
5.	The Measurement of Relative Viscosity.	61
6.	The Determination of Density	65
IV.	RESULTS AND TREATMENT OF THE DATA	68
1.	Specific and Equivalent Conductance.	69
2.	Viscosity and Fluidity	70
3.	Density and Apparent Molal Volume.	71
4.	The Temperature Coefficients	74
5.	The Saturated Solutions	77
V.	DISCUSSION OF THE RESULTS	93
1.	Conductance	94
2.	Viscosity and Fluidity	97
3.	Density and Apparent Molal Volume.	100
4.	The Saturated Solutions.	102
VI.	SUMMARY AND CONCLUSIONS	103
VII.	BIBLIOGRAPHY	107

INTRODUCTION

The nature of electrolytic solutions has been a classic problem since the beginnings of the science of physical chemistry. The theory of electrolytic dissociation first suggested by Arrhenius in 1887 (3), was followed by several decades of intensive study in the field which revealed a variety of new phenomena and raised many questions. The inadequacy of the theory in explaining the behaviour of the so-called "strong electrolytes" soon became apparent however, and it was realized by a number of workers that charged particles in solution must have an appreciable effect on each other which was not accounted for by the ordinary law of mass action. Various attempts to treat the problem from a mathematical viewpoint were made, but the difficulties appeared unsurmountable until in 1923, Debye and Hückel (20), on the basis of some well chosen approximations and assumptions, deduced an expression for the activity coefficient of an electrolyte in dilute solution. Their concept of an "ionic atmosphere" was soon extended to conductance and other measurable properties with the result that physical chemistry experienced a new and enthusiastic revival of interest in the problem of strong electrolytes.

The labors of a large number of workers soon verified the fundamental postulates of the theory, but then only in the extremely dilute region, so that virtually all of the subsequent experimental work was carried out in this range. Extensions

were soon made to non-aqueous solutions and considerable information was obtained on the effect of the nature of the solvent, but the constitution of solutions, even above a concentration of 0.1 molar still remained an unsolved problem.

This is essentially the situation at the present time; no adequate theory for the concentrated region has been proposed and indeed, very little experimental work on which to base such a theory is available. However, the development of new methods of investigation which are particularly suited to the concentrated range, shows great promise of yielding valuable information. The need for reliable data from the more conventional methods, including conductance measurements, has often been noted by modern workers.

With this need in mind, a study of the conductances and fluidities of strong solutions of ammonium and silver nitrates was undertaken by Dr. A.N. Campbell and Miss E.M. Kartzmark of this laboratory (16,17,18). Their data at 25.00°C and 95.0°C indicated the possibility of some interesting temperature relationships and it was decided to undertake a systematic investigation of these properties at ten degree intervals. This work therefore constitutes the first of these investigations and presents conductance data for these salts at 35.00°C and fluidity data at 25.00°C and 35.00°C.

The purpose of this thesis is thus to present these data, to describe the experimental apparatus to be used by subsequent

workers, and to review some of the more important experimental and theoretical developments which show promise of casting some light on this most difficult problem.

DISCUSSION OF THE LITERATURE

1) Conductance

(i) Definition

The conductance of a medium is defined as the reciprocal of its resistance and is therefore a measure of the conducting ability of the medium. The conductance is in general defined by the relation,

$$C = \kappa a/l \quad . \quad . \quad . \quad . \quad (1)$$

where C equals the conductance in reciprocal ohms, ohm^{-1} , usually designated as "mhos"; "a" equals the cross-sectional area of the conductor in cm^2 ; and l equals its length in cm. κ is the specific conductance and has the units $\text{ohm}^{-1} \text{cm}^{-1}$. The specific conductance represents the conductance of a centimeter cube of the material and is the most useful quantity in practical electrical work.

The physical chemist, however, being interested primarily in the behaviour of molar or equivalent quantities in electrolytic solutions, defines an "equivalent conductance" which is a measure of the conducting power of one equivalent of an electrolyte, usually in solution. The equivalent conductance is defined by the equation

$$\Lambda = 1000 \kappa^*/C \quad . \quad . \quad . \quad . \quad (2).$$

where κ^* is that part of the specific conductance due to the electrolyte; and C is the concentration of the electrolyte in equivalents per liter. The units of Λ , the equivalent conductance

are $\text{ohm}^{-1}\text{cm}^2$.

(ii) Development of the Method.

Although the determination of electrical conductivity is essentially a resistance measurement, the mechanism of electrolytic conductance is such that the ordinary methods of measurement cannot be applied to yield results of any significance unless precautions and refinements are introduced to nullify or obviate interfering effects. Reactions at the electrodes and concentration gradients due to ionic migration produce emf's which seriously affect the measured resistance on direct current; these effects are termed "polarization" phenomena.

The first significant advance in the method was made by Kohlrausch (63), who employed alternating current in a Wheatstone Bridge arrangement on the assumption that the rapid reversal of the current would alternate the polarization effects so that they would effectively cancel out. This assumption was found to be most valid when platinum electrodes were used, and particularly when these were coated with a layer of finely divided platinum or "platinum black", (55). The use of alternating current however introduced the further complicating effects of the inductance and capacitance of the cell and bridge circuit, which together with the D.C. resistance make up the A.C. reactance of such a system. The design of a bridge to yield a simple resistive reactance required many years of research and development until satisfactory bridges were built independently by Jones and

Josephs (61), and by Shedlovsky (91). The Jones bridge is now made commercially by the Leeds and Northrup Company and is critically discussed by Dike (22). The reliability of this bridge is said to be so great that the error in the measurement is dependent on the accuracy of the solution preparation.

The use of a telephone headpiece as a detector in the bridge circuit has remained the most satisfactory method since the time of Kohlrausch, the sensitivity being considerably improved in dilute solutions by the use of an audio-frequency amplifier. The A.C. current source is now commonly supplied from an audio-frequency oscillator and the measurements are generally made in a frequency range from 1000 to 4000 cycles per second. Constancy of bridge reading with variation of frequency over this range is regarded as evidence of effective elimination of polarization effects so that measurements are often made at several different frequencies.

The cell design constituted the last refinement in the method. The capacity of the cell is compensated by means of a variable condenser in the balancing arm. It was shown by Jones and Bollinger (54), that a previously unexplained variation of apparent cell constant observed by Parker (78), was due to a capacity arising from the proximity of the leads and certain parts of the solution. Cells designed by Jones and Bollinger which have leads widely separated from each other and from the solution are now universally used in conductance measurements in order to eliminate this "Parker effect."

It is apparent from equation (1) that the specific conductance cannot be measured in a cell unless its dimensions are known. It is generally impractical to attempt a direct measurement so that the cell constant, $K = l/a$, is obtained by measuring the conductance of a solution of accurately known specific conductance. The conductance of a number of KCl solutions have been accurately found by Jones and Bradshaw (56), and are conveniently employed in the cell constant determination.

In spite of the extreme accuracy of the available A.C. conductance bridges, the inherent simplicity of a D.C. resistance measurement has attracted many workers with the result that conductance measurements made with D.C. have in recent years rivalled the A.C. methods, and have obtained comparable accuracy, even in non-aqueous solvents (15,42,51).

The D.C. method depends on the determination of a difference of potential between two points in the conductor through which a known current is passing. Such a measurement in electrolytic solutions can only be made with electrodes which are reversible to one of the ions and which do not carry the current but merely act as probes. Two other electrodes are used to carry the current and are placed in large compartments at opposite ends of the tube so that no concentration changes occur in the solution between the probe electrodes. Although this D.C. method is most attractive, its use is limited to solutions for which reversible electrodes can be found, so that it is extremely unlikely that the A.C. methods will be abandoned, especially as it has

been shown that the two procedures yield the same results within the very small experimental errors.

(iii) Development of the Theory

The concentration dependence of the equivalent conductance was the first irreversible property of electrolytic solutions to be given a theoretical significance in mathematical form. The first test of any theory of solutions has always been a comparison ~~of~~ of the theoretical with the experimental change in conductance with concentration, in the range where the theory is assumed to be valid.

Workers in the aqueous conductance field early recognized the existence of two fairly definite classes of electrolytes; those with equivalent conductances decreasing with increasing concentration in such a manner that an equivalent conductance at infinite dilution, Λ_0 , could be evaluated by extrapolation of a suitable Λ -concentration plot; and those with equivalent conductances decreasing so rapidly at the lowest attainable experimental concentrations that such an evaluation could not be made. The former were termed "strong electrolytes" and included most of the simple uni-univalent inorganic salts while the latter were termed "weak electrolytes" and included organic acids and bases. That this distinction is somewhat artificial has been shown by the existence of intermediate types, such as NiSO_4 , and also by the weak behaviour of the "strong" electrolytes in solvents of low dielectric constant. Nevertheless, the

distinction is useful and the terminology is maintained.

The decrease of equivalent conductance with increasing concentration was first explained by Arrhenius (3). He assumed a decrease of the number of conducting ions in accordance with the mass-action law. On this basis Arrhenius reasoned that the quantity, Λ_c/Λ_0 should equal α_c , the degree of dissociation of the molecular salt, and hence could be substituted into the Ostwald Dilution Law to yield an equilibrium constant, thus:

$$\frac{c^2 \alpha^2}{(1-\alpha)} = K \quad \dots \dots \dots (3)$$

where $\alpha = \Lambda_c/\Lambda_0$. This equation involves approximations concerning the activity coefficients of the salts and the constancy of their mobilities with concentration, which cancel out in part. The equation thus appeared to yield correct results within the accuracy of the earliest workers.

However, as the accuracy of the measurements increased and as further evidence tended to indicate the absence of salt in molecular form in solution, it became apparent that the ratio of equivalent conductances was not a proper measure of dissociation for strong electrolytes. Hittorf (48), had furthermore early recognized the importance of the single ion contributions to conductance and in fact showed that the ion mobilities changed with concentration. Prominent chemists, including Sutherland (96), Bjerrum (11), and A.A. Noyes (74), began to adopt views more favorable to a concept of complete dissociation. However the great majority of workers followed the original theories of

Arrhenius and van't Hoff, as developed by Ostwald and Nernst.

Although a mathematical treatment of the behaviour of ions in solutions had been attempted by a number of workers, the apparent grossness of the assumptions involved and the difficulty of the treatment did not augur well for any quantitative mathematical expression of electrolytic properties. The great success of the theory of inter-ionic attraction proposed by Debye and Hückel in 1923 (20), to account for the variation of ionic activity coefficients from unity, was therefore most unexpected. Interest in the study of electrolytic solutions became intensified to such an extent that within a few years the fundamental postulates of the theory were successfully applied to virtually all the thermodynamic and irreversible properties of dilute solutions of strong electrolytes. An excellent review of the inter-ionic attraction theory, its significance and extensions has been given by Scatchard (85).

The conductance effect was given an early treatment by Debye and Hückel (21), and was later corrected and extended by Onsager (75). The Debye-Hückel-Onsager theory of conductance attributes the decrease of equivalent conductance with concentration to two factors, the time of relaxation effect and the cataphoresis effect. The former is based upon the concept of an ionic atmosphere of opposite charge being symmetrically distributed about a given ion, when the ion is at rest. However, when a force, such as an electric field, is applied to the solution, the ion migrates toward the electrode of opposite charge,

tending to move out of the ionic atmosphere which requires a finite time to reform about the ion in its changed position. The ionic atmosphere may thus be thought of as lagging behind the ion exerting a force opposing the applied force. The cataphoretic effect arises because the ion must move through a medium of opposite charge which is therefore moving in the opposite direction, exerting a retarding effect.

The success of this theory is limited to the correct form of limiting law for the equivalent conductance in the region below 0.001 N, and the correct theoretical evaluation of the limiting slope. Nevertheless, this constituted an advance of relatively revolutionary importance, especially since any of the subsequent theoretical contributions have consisted largely of improvements on, or additions to, the original derivation based on the same fundamental ideas. An excellent non-mathematical discussion of the theory, its range of validity and applications has been given by MacInnes, Shedlovsky and Longworth, (69).

So great had the interest in the problem become, that by 1934 no less than thirty different empirical and theoretical equations had been proposed (53), most of which reduced to the empirically obtained formula of Kohlrausch (64),

$$\Lambda = \Lambda_0 - A\sqrt{c} \dots \dots \dots (4).$$

The Debye-Hückel-Onsager formula was itself of this form;

$$\Lambda = \Lambda_0 - (\alpha\Lambda_0 + \beta)\sqrt{c} \dots \dots \dots (5).$$

where for binary salts α and β are functions of several universal constants, the dielectric constant, the viscosity of the solvent, the temperature, and the valences of the ions.

The most successful of these equations has been that due to Jones and Dole, (59), since it has been shown to fit the data to concentrations as high as 1 molar.

$$\Lambda = \Lambda_0 - \frac{A\sqrt{c}}{1 + N\sqrt{c}} - Bc \dots (6).$$

The equation has the disadvantage that the constants N and B are of somewhat nebulous theoretical significance. Attempts to derive an equation of this or similar form on a theoretical basis from considerations of such factors as ionic radii, and dielectric constant variation have met with some degree of success, but the problem has not yet been completely solved. N and B are still essentially empirical constants.

The Debye-Hückel-Onsager theory has thus provided a theoretical foundation upon which all subsequent workers have constructed their ideas. It must definitely be emphasized however, ~~that~~ since its derivation is based upon a time-average concept of an ionic atmosphere and is obtained by the methods of statistical mechanics that, as pointed out by Edelson and Fuoss, (24) such a treatment cannot be applied to concentrated solutions, since a time-average potential of the ionic atmosphere simply does not exist. Thus, although the many theoretical extensions to the theory, which are summarized by Harned and Owen (44), have been of value ~~at~~ to the general problem, a treatment of this nature

over the entire concentration range is not only mathematically difficult, but also fundamentally unsound. The concentrated region is consequently theoretically barren. Unfortunately, the theory of Debye-Huckel-Onsager has been so over emphasized that virtually all of the voluminous literature on conductance has been confined to the dilute region.

Although the postulate of complete dissociation is inherent in the theory and may be considered proven for dilute solutions of strong electrolytes, the often used term, "the theory of complete dissociation" is most misleading. In fact the theory has found one of its most important applications in evaluating dissociation constants of weak electrolytes in water, and of strong electrolytes in non-aqueous media. A recent determination of this nature is that of Evans and Sugden, (25). The Arrhenius theory has been by no means swept aside by Debye-Huckel-Onsager, but has in fact been rendered more useful in the light of the newer theory by workers such as MacInnes and Shedlovsky, (66,68).

In summing up, it may be said, that the Debye-Huckel-Onsager theory of conductance has made a valuable contribution to the knowledge of the mechanism of electrolytic conductance but has come far from completely solving the problem. Not only has the behaviour of concentrated solutions remained unknown but also, no method of evaluating the absolute value of the limiting conductance from theory has been devised. The limiting conductance which enters into Debye-Huckel-Onsager is thus a constant which must be determined experimentally, although usually by methods of

successive approximations based on the theory. It therefore seems that if any further progress is to be made, that the problem must be approached from a different viewpoint. It seems possible that advances could be made by investigations of the mechanism of molten salt conductance, which is probably a closer approximation to the behaviour of concentrated solutions than the treatments of the infinitely dilute region which have been proposed. Recent improvements in other methods of investigation, especially optical techniques, have shown promise of yielding important information concerning the nature of solutions in the practical range of concentrations, which are of interest to the chemist. The situation therefore, may not be as hopeless as is commonly thought. This is a view which is gradually being adopted by some of the most eminent physical chemists and it is to be hoped that the pessimistic attitude which has been prevalent regarding the possibility of further advances in electrolytic solution theory may soon be dispelled. Conductance has always been a valuable property from a theoretical standpoint and there is no reason to believe that measurements in the concentrated region may not prove to be of ultimate significance.

(iv) Ammonium Nitrate

Although an enormous amount of conductance work of extremely high accuracy has been reported in the literature since 1930, it appears that ammonium nitrate has been largely neglected. No data could be found in the literature for

ammonium nitrate conductance except that quoted in the International Critical Tables for 18.00°C, (50) and that of Scatchard and Prentiss for 10.0°C, (87). The behaviour of the conductance of this salt therefore is not known in dilute solution either at 25.00°C or 35.00°C, although the limiting conductances may be obtained from the limiting ionic conductances and their temperature coefficients at infinite dilution, (35).

(v) Silver Nitrate

This salt has been very accurately determined by Shedlovsky in the region up to 0.1N, (92), at 25.00°C. It has been pointed out by MacInnes, Shedlovsky, and Longworth, (69), that silver nitrate is somewhat "abnormal" in that it shows no deviation from the Onsager straight line slope up to a concentration of 0.002 N whereas for the alkali halides, agreement to 0.001 N is exceptional. They also point out that the observed limiting slope of the transference number of silver nitrate is of opposite sign to that predicted on the basis of the theory. Some data on more concentrated solutions at 25.00°C are found in the International Critical Tables but appear to be of low accuracy, (50).

2) Viscosity and Fluidity.

(i) Definition

Viscosity is a measure of resistance to flow and may consequently be regarded as an internal frictional coefficient.

It is most simply defined in terms of the equation,

$$f = \eta (du/dx) \dots \dots \dots (7)$$

which is applicable to simple laminar flow. If two layers dx cm apart are moving with a difference of velocity between them of du cm sec⁻¹, then a tangential force, f dyne cm⁻² is exerted which is proportional to du/dx, the proportionality factor being η , the viscosity coefficient. The viscosity thus has the units dyne sec cm⁻², which are called poises. A commonly used unit equals 0.01 poise and is called a centipoise.

Largely through the influence of E.C. Bingham (8), who has argued that the reciprocal of the viscosity, or the fluidity, is the more fundamental quantity, data are often tabulated in these units. The unit of fluidity is the rhe; the inverse of the viscosity in poises, yields the fluidity in rhes.

(ii) Development of the Method

On the basis of his classical researches on the flow of liquids through capillary tubes, Poiseuille (79), deduced the law connecting the viscosity with the geometry of the tube, the driving pressure, and the efflux time. If a liquid with coefficient of viscosity, η , flows with a uniform velocity, at a rate of v cc. in t sec., through a narrow tube of radius r cm and length l cm, under a driving pressure of P dynes per sq.cm., then

$$\eta = \pi Pr^4 t / 8v l \dots \dots \dots (8).$$

Much subsequent work has substantiated this relation although various corrections, usually arising from conditions of non-viscous flow, have been proposed. These involve drainage, liquid head, kinetic energy, end effects, and surface tension, (4,8,47). The uncertain effect of these factors has made the determination of the absolute viscosity of a liquid extremely difficult. Ordinarily however, it is sufficient to determine only relative viscosities which, by proper design and manipulation of the capillary instrument, may be obtained to a high degree of accuracy. For this purpose modifications of the well known "Ostwald Viscometer" are most convenient.

Since the geometry of a viscometer is constant and since the average driving head of the liquid is directly proportional to the density of the liquid, provided that the same working volume is used throughout, the viscosity may be obtained from

$$\eta = Kdt \dots \dots \dots (9)$$

where d is the density, t is the efflux time and K is the viscometer constant to be determined from a measurement of the calibrating liquid. However, most workers recognize that for precise work, Poiseuille's original equation requires modification to take into account a kinetic energy term. This correction arises from the energy which must be expended in accelerating the fluid as it passes from the wide bore portion to the capillary section. The exact form of this kinetic energy term has been the subject of considerable controversy, (4,8,23,43,84).

Poiseuille's equation, including the kinetic energy correction term, can be expressed by the equation,

$$\eta = Kdt - m d/t \dots \dots \dots (10)$$

where d is the density, t , the efflux time and K and m , constants of the viscometer to be determined.

Although the constants may be found for a given viscometer by calibration with two liquids of different viscosity, it has been the practice of modern workers to design their viscometers so that the correction is negligible. In their investigations of the viscosities of dilute solutions of electrolytes, G. Jones and his co-workers, (62), made use of a viscometer having an efflux time greater than 600 seconds. By the use of photoelectric timing devices and careful consideration of the errors involved, they obtained such a high precision that the very slight kinetic energy correction was significant. However, for ordinary accuracy, (0.1%), an efflux time in excess of 200 seconds is considered sufficient to permit the elimination of the correction term, (102).

The use of an Ostwald viscometer implies the simultaneous determination of the solution densities. To eliminate this necessity, viscometers have been designed which do not require a knowledge of the density. The best known of these is that due to Ubbelohde which operates on a somewhat different principle. This viscometer and viscometry in general are well treated in Weissberger, (101).

(iii) Development of the Theory

The viscosity is a comparatively easy quantity to measure but its theoretical interpretation is one of the most difficult problems in the theory of liquids. Its importance, however, cannot be minimized, since if properly interpreted it should supply or supplement information concerning solvation, intermolecular forces, molecular aggregation and other quantities related to the internal structure of liquids and solutions. Because of this close relationship between viscosity and molecular constitution it has become an increasingly important property, particularly in colloid chemistry and the relatively new field of high polymers. The literature, both experimental and theoretical, on this subject is immense but from a theoretical standpoint significant progress has only been made on the temperature dependence of unassociated pure liquids, and on the concentration dependence in very dilute solutions of electrolytes.

Most of the early theoretical work on viscosity consisted of attempts to relate it with other simple quantities such as specific volume. These developed into ideas concerning the available free space in a liquid and many empirical and theoretical equations were proposed on this and similar postulates. Most of this work is now only of historical value and ~~is~~^{is} adequately treated in any of the standard references on viscosity, (4,8,47). The viscosity-temperature relation which has survived, largely due to its support from numerous theoretical derivations, is one

of the exponential type;

$$\eta = Ae^{E/RT} \dots \dots \dots (11)$$

This equation was first proposed by Arrhenius and first derived theoretically by Andrade,(2). It fits the data reasonably well and is moreover quite general for all non-associated liquids. The same type of equation was later derived by Eyring (26,37) on the basis of a reaction rate theory where E was assumed to be an activation energy for shear flow.

Virtually all of the subsequent theory has been based on the interpretation of E in equation (11) as being an activation energy. Numerous attempts have been made to relate E to van der Waal's constant, "a", to the latent heat of vaporization, to the internal pressure and to the latent heat of fusion. It has been most recently identified with the work of cohesion and it has been pointed out that the values are nearly identical,(38). These treatments are exceedingly complex and cannot be considered here in detail, especially since the derivations, and interpretations put on the results, are still very much a controversial matter. For example Telang,(98), has recently deduced an exponential relationship from slightly modified assumptions and obtained an activation energy approximately one third that obtained through Eyring's theory. He also deduces the value of "A" in equation (11), the so called "frequency factor". Obviously a theory which is in such a state for pure unassociated liquids is a long way from being applicable to solutions of electrolytes.

Although a theory cannot as yet be quantitatively applied to the viscosity-temperature dependence of associated liquids, some interesting empirical observations have been made. For associated liquids, the activation energy might be expected to be a function of temperature, since the association will change with temperature. Litovitz, (65), has assumed that $E = a/T^2$ so that equation (11) for associated liquids becomes

$$\eta = A e^{a/RT^3} \dots \dots \dots (12)$$

where "a" is the activation energy constant dependent on the liquid. He points out that "a" is roughly proportional to the number of OH groups in the molecule. This equation holds very well for water and some alcohols. It should be of interest to see if such an equation can fit the data for the temperature dependence of electrolytic solutions at various concentrations.

In solutions the interest is centred upon the viscosity-concentration dependence. Although it has not been found possible to deduce on theoretical grounds the absolute viscosity of any pure liquid, the "electrostatic contribution" to the viscosity due to the addition of ions has been successively developed by Falkenhagen and Dole, (27), in very dilute solutions on the basis of the inter-ionic attraction theory. An alternate treatment was subsequently proposed by Onsager and Fuoss, (77), which is considered by Harned and Owen, (44).

Dissolved salts generally increase the viscosity of water but as has been observed by a number of workers, certain salts,

including the chlorides of potassium, rubidium, cesium and ammonium, and thallos nitrate have the opposite effect, displaying so called "negative viscosity". It was found by Gruneisen, (39), that the function, $(\eta_c/\eta_0 - 1)/c$, passed through a minimum value at about semi-normal concentration whether the salt exhibited negative viscosity or not. The accurate measurements of Jones and Dole, (58), showed that in dilute solutions, the viscosity increased with the square root of the concentration in a linear manner for all salts, as predicted theoretically by Falkenhagen. Jones and Talley, (62), showed that for several salts in aqueous solution, the variation of viscosity over fairly wide ranges of concentration was given by the relation,

$$\eta_c/\eta_0 = 1 + A\sqrt{c} + Bc \dots \dots \dots (13)$$

where A is a positive constant and B is a constant, positive for salts which increase the viscosity at moderate concentrations but negative for salts which decrease the viscosity of the solvent. The evaluation of the constant "A", in terms of the ionic conductances at zero concentration, the dielectric constant, the viscosity of the solvent and the temperature, has been effected by Falkenhagen, Dole and Vernon, (27,28), with remarkable accuracy. The extended treatment of Onsager and Fuoss according to Jones and Fornwalt, (60), reduces to the relationship,

$$\eta_c/\eta_0 = 1 + A\sqrt{c} + Bc + D\log c + \dots \dots \dots (14).$$

The constant, "B", in equation (13) is empirical but highly specific and additive for the ions. Its temperature coefficient

is always positive illustrating that negative viscosity disappears at higher temperatures.

The behaviour of the viscosity in liquid systems is often qualitatively explained on the basis of known molecular properties of the systems. For example, water is known to have a fairly open quasi-crystalline structure at ordinary temperatures which successfully explains the peculiar behaviour of the physical properties of this "abnormal" substance under the influence of external variables such as temperature and pressure. It is significant that those electrolytes which exhibit negative viscosity are those possessing large, relatively unhydrated ions. The decrease of viscosity observed is therefore undoubtedly due to a partial breakdown of the quartz-like structure of the water caused by the "crowding" effect of the large ions. At higher concentrations, the viscosity again increases due to the increasing effect of the inter-ionic forces. Smaller hydrated ions probably do not affect the structure to such an extent, or if they do, the tendency is rather to increase the regular arrangement of the molecules as suggested by Bernal and Fowler,(7). This concept of the varying degrees of disorder caused by the presence of ions is supported by observations of X-ray diffraction and Raman spectra. The decrease of water viscosity with the application of pressure is also attributed to the breakdown of the structure. The classic paper of Bernal and Fowler,(7), treats the behaviour of water and of ionic solutions in terms of this structural concept in a quantitative manner.

It is interesting to note that if Eyring's interpretation of viscosity as a rate process, involving the activation energy for viscous flow, is accepted, then this flow may be considered as a thermodynamic property which may be correlated with more familiar such properties, in particular the entropy. Mason, Kampmeyer and Robinson, (71), have measured the viscosities of aqueous solutions of a number of amino acids at 25.00°C and 35.00°C and have interpreted their data with this correlation in mind. They point out that a liquid possessing a high degree of order may be expected to have a greater energy of activation for viscous flow than another liquid possessing a lower degree of order. Since entropy is related to structural order, they deduce a "differential energy of activation" which can be compared to the differential entropies of dilution. They expect that these quantities should show a parallel behaviour with changes in concentration. Their results for the amino acids are not very convincing as might be expected from the questionable applicability of Eyring's theory to solutions in an associated solvent.

Bingham (9), has demonstrated the additivity of "ionic fluidities" which he evaluates and applies somewhat in the manner of ionic mobilities according to the Kohlrausch Law. On the assumption that the potassium and chloride ions have the same ionic fluidity, since their mobilities are similar, he evaluates quantities for 1 normal solutions which he calls the "ionic elevations of the fluidity." Having obtained a set of values, Bingham then shows that the sum of the cation and anion fluidities

for any salt yields the contribution of the salt to the fluidity of the solution at 1 normal. The agreement is rather surprising since the concept of an ionic fluidity can hardly be given any physical significance. Bingham further extends this idea to other properties of electrolytic solutions and discusses the behaviour of certain specific cases. A later paper deals with additive relationships in more complicated mixed systems (10).

Theories of viscosity applied to ionic liquids, in particular molten salts, are discussed in a comprehensive review by Harrap and Heymann, (45). This review presents an interesting discussion concerning the mechanism of viscous flow in molten salts together with some evidence concerning the nature of conductivity in such systems.

The theory of viscosity for simple liquids and for solutions is obviously not in a very advanced stage of development. Some results of importance to the theory of viscosity have been obtained from studies of colloidal systems, but in general, workers in this field have adopted a somewhat different method of attack, of particular applicability to solutions of large molecules, so that their deductions do not have universal significance. The lack of theoretical support however, has not deterred workers from making use of viscosity measurements in a wide variety of investigations and applications. The close association of "internal friction" with molecular constitution is an intuitively obvious fact, so that there can be no doubt that in the development of any theory of the liquid state, the

viscosity will play an important role.

(iv) Ammonium Nitrate and Silver Nitrate

The only data to be found in the available literature for the viscosity of ammonium nitrate solutions are those obtained by F.H. Getman in 1908, (33). These results are the same as those recorded in the International Critical Tables, (50).

Some very accurate data for the viscosity of silver nitrate solutions at 25.00°C and 0.00°C have been obtained by Jones and Colvin (57) up to a concentration of 5 molar.

3) Conductance-Viscosity Relationships

Both conductance and viscosity are dynamic properties of a solution which involve the motion of molecular or ionic units relative to similar units in the solution. Consequently these two properties are closely related. This fact is not only intuitively apparent but is also shown by the appearance of an identical term for the potentials in the treatment of conductance and viscosity on the basis of the inter-ionic attraction theory. In spite of their close relationship, it should be obvious that, since conductance involves ionic migration through the bulk of the solution and viscosity involves a shearing motion of the whole of the solution, their mechanisms must be quite different.

There appears to be two different ways of looking at the

relationship between conductance and viscosity. One considers the macroscopic viscosity of a solution as representing the frictional retarding force on an ion migrating through the solution, on the assumption that Stoke's law applies to such a system. The other makes no such assumption and maintains that conductance and viscosity, though related, are two separate properties each of which must be explained on the basis of intermolecular and inter-ionic forces. These two viewpoints are not considered explicitly in the literature and the apparently indiscriminate use of one and then the other has led to a great deal of confusion concerning the role of viscosity in conductance phenomena.

For example, the viscosity of the solvent appears in the electrophoretic term in the Debye-Hückel-Onsager equation for conductance, on the assumption that Stoke's law holds for the motion of an ion in an infinitely dilute solution. In view of the other approximations made in the theory, this is not serious, but the validity of their equation in dilute solutions certainly does not constitute a rigorous test of the assumption, since the viscosity plays a relatively minor role in the limiting slope. Any error caused by the introduction of Stoke's law must be small. This constitutes an example of the first viewpoint and is perfectly legitimate, especially since there is some justification from other quarters that Stoke's law indeed yields a good approximation to the resistive force in such a solution.

The second viewpoint is exemplified by Falkenhagen's

development of the electrostatic contribution to the viscosity on the basis of the inter-ionic attraction theory, i.e. the macroscopic viscosity of the solution is calculated independently from the same assumptions used in the conductance derivation. This again is perfectly legitimate and the treatment gives excellent agreement with the experimental values in dilute solutions. The confusion arises when the very common procedure of applying a "viscosity correction" to a theoretically derived conductance equation is practised, by simply multiplying through by the macroscopic viscosity. Since the viscosity and the conductance are independently derivable from the same assumptions concerning the inter-ionic forces, it appears to this author that this amounts to allowing for the same effect twice.

The history of viscosity corrections is long and has always been controversial. The general opinion of even the earliest workers was that such a correction was inapplicable and at a number of stages the question appeared to have been settled.

G. Wiedemann in 1856 first considered the effect of viscosity on conductance. He reasoned that the conductance must be a function of the viscosity of the solvent and initiated a series of researches to show a proportionality. Arrhenius (47) and a large number of other workers increased the viscosity of solutions by the addition of organic materials such as gelatin and sucrose, and showed that no appreciable change in conductance occurred, in spite of the relatively great change in viscosity; even the solidification of the gelatin had little effect. Heber Green (47)

concluded that the ionic and physical fluidities could not be the same. The idea of a proportionality still persisted however and many workers continued to report their ionization coefficients corrected for fluidity,

$$\alpha = \frac{\Lambda_c \cdot \Phi_0}{\Lambda_0 \Phi_c} \dots \dots \dots (15).$$

The similarity of the temperature coefficients of fluidity and conductance also added support to the proportionality idea. Walden (100) worked with tetraethyl ammonium iodide in a number of organic solvents and showed that the conductance at infinite dilution was directly proportional to the fluidity, thus,

$$\eta_0 \Lambda_0 = \text{a constant} \dots \dots \dots (16).$$

This became known as "Walden's Rule". It should be noted, as pointed out by Harned and Owen, (44), that the constancy of the viscosity-conductance product is equivalent to proof of the validity of Stoke's law. It was soon shown by other workers that Walden's rule was far from universally applicable and Walden himself finally came to the conclusion that the rule holds the better, the larger the ions with respect to the solvent molecules. This is again in agreement with the postulates of Stoke's law which requires primarily that the moving particle be large with respect to the molecules of the medium, and that it be spherical. Although large ions may be expected to obey Walden's rule in various solvents or in the same solvent at different temperatures at infinite dilution, the extension to concentrated solutions

is questionable because of inter-ionic effects. In fact, Walden's rule is found to be generally inapplicable in this range.

It is the extension of Walden's rule to regions of finite concentration which appears to be the source of the aforementioned confusion. Since the viscosity adequately explained the variation of conductance in different solvents at infinite dilution, although only in very special cases, the practice became to correct the conductance-concentration curves by equation (16) and ascribe any deviation from constancy to "other effects". It is certain that the macroscopic viscosity of a concentrated solution does not represent the resistance offered by the solution to the migrating ions. Moreover, for ordinary electrolytes, Walden's rule does not hold, even at infinite dilution in various solvents. For example the conductances of the alkali halides in methanol are much less than in water in spite of the enormous decrease of viscosity, even when allowance is made for association.

From the above discussion it might be concluded that any consideration involving a relationship between conductance and viscosity must be viewed with some suspicion unless it be definitely demonstrated that the situation is such that the relationship may be applied. Fuoss and Kraus (32), for example, made good use of Walden's rule in estimating the limiting conductance of tetraalkyl ammonium salts in solvents of low dielectric constant where extrapolation was impossible because

of the large degrees of association. Since such large ions had been shown to obey the rule, the approximation was quite justified. Modern workers however continue to make use of a viscosity correction in conductance work, although they generally attach little importance to it. Jones and Bickford, (53), for example, apply a viscosity correction to their accurate data on KCl and LaBr_3 to test the various equations, and show that a viscosity corrected equation can be made to fit the data more accurately.

It is unfortunate that even some of the most eminent workers in the conductance field, (95), "explain" a decrease in conductance in concentrated solutions as being due to an increase in viscosity. Since an increase in the internal forces of such a solution will, in general, both decrease the conductance and increase the viscosity; to say that the decrease of conductance is explained by the increase of viscosity is to explain nothing. The authors undoubtedly consider the terminology "an increase in viscosity" to be synonymous with "an increase in internal forces", but since explanations in terms of viscosity in the past were used in a more literal sense, it would be less confusing to the student if such "explanations" were not expressed in this way.

4) The General Problem of Strong Electrolytes

Although conductance and viscosity are important properties of electrolytic solutions, their quantitative interpretation in concentrated solutions is very difficult. They also suffer from

not showing a high degree of specificity in that large classes of obviously different types of electrolytes show more or less similar behaviour with concentration. Interpretation of conductance data is further hampered by the difficulty of obtaining transference numbers at high concentrations. It appears from the current literature that if any further progress is to be made from a theoretical point of view, it will be necessary to consider each electrolyte individually in the light of its specific electronic structure, ionic radii, polarizing properties, ion-solvent interactions and the like. The manner in which electrolytes deviate from the well established Debye-Hückel limiting laws shows considerable variety, and is the starting point for any consideration concerning the specific ionic effects. Some progress has been made in this direction and, although of a highly speculative nature, some recent theoretical extensions are most encouraging.

Aside from purely thermodynamic measurements, which of course must ultimately be explained in terms of a solution model, a large body of data which promises to yield more specific information concerning the behaviour of ions in solution has been accumulating in the literature. These include optical investigations such as light absorption, Raman and infra-red spectra and refractometric investigations. Dielectric constant and dielectric dispersion measurements in electrolytic solutions are also of interest. Thermochemical quantities derived from precise measurements of densities include apparent and partial molal volumes and

apparent and partial molal expansibilities. These and other properties show promise of contributing valuable information about the behaviour of electrolytic solutions, as might be inferred by the return of a number of eminent workers to a consideration of the concentrated region after a long preoccupation with the consequences of the Debye-Hückel theory.

It is beyond the scope of this thesis and beyond the ability of the author to present a critical discussion of all of the available information. The following treatment will therefore be but a brief and incomplete summary of some of the above mentioned important properties and recent theories. The monograph of Harned and Owen, (44), considers the developments in solution theory until 1948 in a very satisfactory manner, and is recommended as a guide to the literature.

(i) Ionic Volumes

The true effective volume or radius of an ion in solution is a quantity which is of great importance in the theory of electrolytes. The mean distance of closest approach has been taken into account in extensions of the Debye-Hückel theory but is usually treated as an empirical parameter. They generally differ for each electrolyte and, as might be expected, are somewhat larger than the crystallographic distances. The distance of closest approach can be given no exact significance but the values are known to be affected by ionic hydration. It is important to notice that the mean distance of closest approach

is found to be greater than 3.5 \AA^0 for aqueous solutions of 1-1 electrolytes; a distance greater than that required for ion association on the basis of Bjerrum's theory (13). Ion association must therefore be very slight in such solutions, assuming that the theory is correct.

Precise density data allow the evaluation of the apparent and partial molal volumes of electrolytes in solution. Although, at finite concentrations, neither of these two properties can be equated to the true volume of the electrolyte in the solution, they do show some interesting additive relationships. The partial molal volumes are important quantities in thermodynamic calculations but have no advantage over the more directly obtained apparent volumes in considerations of this nature. It has often been observed that extrapolations of the apparent molal volumes to infinite dilution from \bar{V} versus \sqrt{c} plots yield values which are remarkably additive for the ions. This is true even when the extrapolation is made from data at relatively high concentrations. This is undoubtedly due to the approximately linear variation of this function with \sqrt{c} , as discovered by Masson, (72). The linear plot with \sqrt{c} was predicted theoretically by Redlich and Rosenfeld for dilute solutions on the basis of the inter-ionic attraction theory (82); although the approximate linearity at high concentrations remains unexplained. The curves are in fact somewhat S-shaped so that extrapolations made from very dilute solution density data yield somewhat different values of \bar{V}_0 , although they remain additive. The true \bar{V}_0 at infinite

dilution so obtained is identical with \bar{V}_2^0 and may be interpreted as representing the effective volume of the electrolyte at infinite dilution. For most simple salts the limiting slope agrees with that of theory, but ammonium nitrate and some others exhibit curvature in the dilute range which is generally attributed to hydrolysis, or ion association in the case of salts of higher valence type. Lacking the necessary precise density figures at high dilutions however, the extrapolations are most frequently made from higher concentrations which yield Φ_0 values somewhat larger than \bar{V}_2^0 although usually proportional to them; the additive relationships are thus maintained.

Masson extrapolated the linear equation to the concentration of the pure salt and obtained relationships between the crystallographic radii and the hypothetical value of the apparent molal volume at this concentration which indicated a simple geometric behaviour of the volume relationships in solution. Scott (88) extended this idea but used the "critical disruptive volumes" and corresponding concentrations of the solid salts in place of the ordinary crystallographic values. The critical disruptive volume is the volume of the ions when separated to a distance corresponding to the maximum cohesive forces, and marks the transition from the rigid crystal structure to the more loosely bound condition of liquids. The treatment also takes into account the possible effect of different lattice structures and predicts the approximate additivity of the slope of Masson's plot, which is observed. It appears from Scott's work that the relation

between the slope and the extrapolated value of Φ at infinite dilution is governed by the geometry of the critical disruptive state and suggests that this geometry is maintained in solutions over the range where Masson's law is valid. As Harned and Owen remark, "If this is the case, the concept of the ionic atmosphere might be replaced by a statistical lattice structure, except at high dilutions."

A paper by Fajans and Johnson, (31), is of particular importance to this investigation since it not only presents a method of evaluating the apparent volumes of individual ions, but also discusses the behaviour of ions in solution with particular reference to ammonium which, because of its presumed tetrahedral charge distribution, bears a unique relationship to the tetrahedral bonding of water.

The temperature coefficients of the partial and apparent molal volumes are respectively, the partial and apparent molal expansibilities. These quantities show an interesting specific behaviour for the various electrolytes which must be associated largely with ion-solvent effects.

A great deal of work has been done by a number of workers, in particular R.E.Gibson (34), on the compressibilities of electrolytic solutions. These yield information concerning the behaviour of solution volumes under pressure. The effect of pressure is important since its principle action will be to disrupt the internal structure of the solution leaving most of

the other characteristics relatively unaffected. Such studies thus give direct information concerning the volume relationships and allow conclusions to be drawn about the actual volume of the solute, hydration and other solvent-ion interactions.

The apparent molal properties of electrolytic solutions, their evaluation, significance and concentration dependence are reviewed by F.T. Gucker, (40,41).

It is evident that a number of methods of approach are possible in the evaluation of solute volumes. The results as deduced from crystallographic data, extrapolation of apparent molal volumes to infinite dilution, and from considerations of the expansibilities and compressibilities generally do not agree, although the differences are not great. It seems probable that the effective volumes of the ions in solution do not change greatly with concentration, at least in comparison with the volume changes produced by the disruption of the water lattice due to hydration and bulk effects. A difference between the effective radii in crystals and in infinite dilution may be attributed to the fact that the electronic systems in crystals undoubtedly interpenetrate whereas the ion at infinite dilution is totally unaffected by its far distant neighbors as indicated by the additivity of the ionic volumes. Variations in solutions of finite concentrations will be intermediate between these extremes, the greatest differences being observed for highly polarizable ions which may be distorted by neighboring ions and solvent molecules. The quantum mechanical concept of the electronic

distribution does not permit a definite radius being assigned an ion, but this does not diminish the significance of the above considerations as their usefulness has been adequately demonstrated.

(ii) Optical Properties

A property which is closely associated with molar volumes and which shows similar additive relationships is the molar refraction, (36). This quantity has the units of volume and, for radiation of infinite wave length, represents the true molecular volume of pure liquid as distinguished from the apparent volume, M/d . Refraction depends upon electronic structure and is also closely related to polarizability.

The application of this property to electrolytic solutions has been made by Kasimir Fajans in a voluminous series of refractometric investigations which have appeared in the literature over a period of thirty years, (29). Fajans has interpreted the change in apparent molar refraction with concentration as indicating the formation of undissociated particles in concentrated solutions of strong electrolytes. The relationship between the apparent molar volume and the apparent molar refraction has been discussed by Fajans (30), as well as the general behaviour of electrolytic solutions in the light of his findings.

Silver nitrate has been extensively investigated from this point of view by N. Bauer, (5), who from measurements of refraction

and refractive dispersion was able to make deductions concerning the polarizing properties, the electron distribution and solvent effects of the silver ion.

Refractometric experiments are obviously of importance, but since the distortion of the electronic atmosphere is greatly altered by its environment, ion-ion and ion-solvent effects may be difficult to distinguish. The property however is more specific to the ions than the simple volume relationships and is therefore of greater value. Considering the obvious confidence with which Fajans presents his conclusions it is surprising that Harned and Owen make no reference to his work.

The physical properties which change definitely and unambiguously for any association or dissociation in electrolytic solutions are the vibrational frequencies of the components. A method of directly observing these frequencies and hence of studying the ionic interactions over the whole concentration range is provided by Raman spectra. The vibrational frequencies of an ion are but little affected by its environment. However, a direct ionic interaction in solution results in a distinct shift or disappearance of the lines associated with the single ions. The usefulness of the method has been demonstrated by its complete elucidation of the nature of nitric acid solutions, (81). Raman spectra in conjunction with conductance and kinetic measurements have also gone a long way in interpreting the properties of sulfuric acid in solution, (105). In principle the possibilities of the method appear to be unlimited but in practice

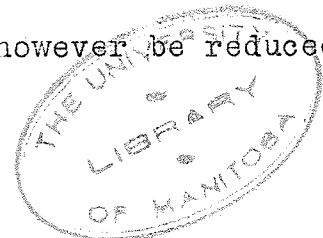
the difficulties of accurately measuring relative intensities place some restrictions on their application.

Raman spectra in general support the concept of complete dissociation for most 1-1 electrolytes including the alkali and ammonium nitrates, (93). The existing information concerning the dissociation of strong electrolytes is reviewed by Redlich (80) and by Young and Blatz (105).

(iii) Dielectric Properties

The importance of the dielectric properties of electrolytic solutions was recognized in 1926 by Hückel (49) who attempted to explain deviations from the Debye-Hückel theory on the supposition that the dielectric constant was a function of concentration. His treatment resulted in the addition of a linear term to the formula for the activity, the coefficient of which was in remarkable agreement with the experimental data. The very large effect of the dielectric constant of the solvent on the conductance behaviour of strong electrolytes was forcefully demonstrated by Fuoss and Kraus somewhat later, (32). Dielectric properties must therefore have a place of considerable importance in concentrated solutions of electrolytes where the variations must be large.

However, the experimental determination of the static dielectric constant of a conducting medium is very difficult due to the large loss angle. This factor may however be reduced



by the use of extremely high frequencies corresponding to wave lengths of the order of five cm. The experimental technique of such measurements has only recently reached a stage where results of significance can be obtained. One of the most important papers to appear in the recent literature, both from an experimental and theoretical point of view is that of Hasted, Ritson and Collie,(46). These authors have made determinations of the static dielectric constants of alkali halides in the concentrated region, and have moreover interpreted their results in terms of a hydration model. They have shown that the variation of dielectric constant is a decreasing linear relation up to 2 molar. This is explained in terms of the reorientation of a fraction of the water molecules in hydration sheaths about the ions. Above 2 molar the linear dependence does not hold and they make the significant statement that "It is possible to regard solutions in this region as ionic lattices with interspersed water molecules." They correlate the relaxation times with the macroscopic viscosities and thermodynamic entropies and make an important attempt to explain the approximately linear variation of conductance with concentration above 2 molar.

These authors consider the linear term in Huckel's theoretical extension to be made up of four factors; the van der Waals co-volume correction, the structure-breaking effect of the ions, Bjerrum-type ion association, and dielectric constant variation. They consider each of these effects in the light of their own results and all the existing pertinent data on strong electrolytes. They attribute the linear variation of conductance at high

concentrations to Bjerrum association, an explanation which they consider reasonable because of the extremely strong inter-ionic forces at short distances. In this connection they go so far as to estimate percentage association at various concentrations for the alkali halides.

The importance of such considerations to this research obviously cannot be overemphasized. Further conclusions and theoretical speculations are made by the authors which are too numerous to be considered here. For a complete appreciation of its implications the reader must be referred to the original paper.

(iv) Some Recent Theories

The theories which have been proposed since that of Debye and Hückel and its immediate extensions may be divided into two classes; those which attempt to explain variations from the limiting laws by considerations of additional effects, resulting in modifications of the original equations, and those which depart entirely from the ionic-atmosphere concept and interpret solutions on a totally different model. Since the Debye-Hückel theory is the only mathematical formulation of electrolytic properties which we possess and since its validity has been well established, the former class is by ~~xx~~ far the more populated. Relatively few radically different theories have been proposed, and these only in the most concentrated region, but as might be inferred from the previous discussion, a number of possibilities

have been considered which remain only to be put in mathematical form.

The theory of concentrated solutions from the first point of view has been thoroughly discussed by Onsager, (76). Most theories of this type are concerned with the explanation of the variation of the activity coefficient at higher concentrations. The first attempt after the consideration of the finite sizes of the ions by Debye and Hückel, was Hückel's consideration of the dielectric constant, which has already been mentioned. The addition of the linear term made the equation capable of fitting the data, with a few exceptions, up to 1 M. The addition of a further empirical squared-term allowed agreement in many cases to 4 M but the equation contained three variable parameters, the mean distance of closest approach, Hückel's parameter, "B", and the completely empirical squared-term coefficient.

Scatchard, (86), has made a very penetrating analysis of the problem and has deduced an equation for the activity coefficient of great complexity, which takes into account "molecule-molecule" as well as ion-ion and ion-molecule interaction. The molecule-molecule interaction is based on the non-ideality of non-electrolyte solutions which show significant deviations even though uncharged. Ionic volumes were estimated from crystallographic data and the dielectric constant effect was also included. The agreement with experiment was sufficient to show that the properties of the solutions are largely determined by the factors which Scatchard considered.

The suggestion of Onsager (76) that the strong, short-range repulsive forces of the ions might be accounted for by a van der Waals co-volume correction, and hence give theoretical significance to the linear and squared coefficients of the activity coefficient expression, was adopted by Van Rysselberghe and Eisenberg, (99). They achieved a theoretical result of the correct form which however led to over correction, the predicted values being too high. Harned and Owen remark, "This suggests the possibility that a combination of the co-volume effect and ionic association, which is very likely to occur in solutions of high concentration, would give a closer representation of the real conditions."

One of the most recent and most interesting attempts to extend the Debye-Hückel theory to concentrated solutions has been made by Stokes and Robinson, (94). These authors extend the early treatment of Bjerrum, (12), concerning the effect of hydration on electrolytic properties and develop an equation for the activity coefficient with two variable parameters, "a", the mean distance of closest approach and "n", a so-called "hydration number." "n" is supposed to take into account all ion-solvent interactions and is treated as the effective number of water molecules removed in the form of hydration shells about the ions. The equation represents a considerable improvement on the Debye-Hückel expression containing the linear term, in that it expresses the data to similar accuracy to ionic strengths five times as great. Moreover it is generally applicable to 2-1 electrolytes where the original equation fails badly. The hydration numbers required to fit the data are considerably higher than those usually imagined, but

Stokes and Robinson point out that it is not intended to represent the number of water molecules firmly bound to the ions but takes into account the effect of outlying layers. The values tend to indicate that anions are more hydrated than cations and also that the hydration increases with ionic size. This is exactly the reverse of the usual concept as developed by Bernal and Fowler,(7), but the authors suggest that since " n^2 " includes the effect not only of the layer adjacent to the ion but also the neighboring water molecules, these might have a greater contribution in the case of anions, and large ions of both types.

By developing a relationship between the hydration number and " a " by means of Bernal and Fowler's treatment of apparent molal volumes, Stokes and Robinson obtain a one parameter equation which represents the data with remarkable success considering the simplicity of the concept. They point out however that their equations fail badly at concentrations where the product of " n " and the molality exceeds about 10 or 15. This is to be expected since the required number of water molecules per ion simply are not available at such concentrations, and the effects of competition between neighboring ions must be considerable.

Stokes and Robinson recognize the futility of extending their treatment ~~to~~ to the highly concentrated region and introduce a radical but interesting concept of this range. They found that solutions of calcium nitrate were readily supersaturated and passed into semi-solid gels with no discontinuity in vapor pressure. This enabled them to extend their measurements to 21 M ~~wh~~

whereas the solution is normally saturated at 8.4M. This phenomenon suggested to them the possibility of treating the solutions as an adsorbent-adsorbate system and, on the basis of the Brunauer, Emmett and Teller adsorption theorem, (14), they deduced expressions for the activity coefficient. The resulting equations fit the observed data with surprising accuracy, demonstrating justification for the neglect of Debye-Hückel type ion-ion interactions which predominate in the dilute range.

EXPERIMENTAL

1) Purification of Materials

Conductance measurements in the dilute region are very greatly influenced by the presence of even minute amounts of impurities in the salts. It is therefore of great importance that the salts be purified and in particular that the water used be such that its specific conductivity indicates the absence of any conducting solutes. Water itself has a slight conductivity which may be determined and subtracted from the measured conductance of the solution where this "solvent correction" is significant, as is the case in very dilute solutions. In this work however, the specific conductances are so high that the solvent correction is completely negligible. Further, since the overall accuracy expected is no better than 0.1%, the purity of the salts is not nearly as critical in these concentrated solutions. Nevertheless, the best materials available were purified and dried according to the following methods.

(i) Ammonium Nitrate

This was part of a bulk lot obtained from the Consolidated Mining and Smelting Company during the last war. The salt was cycled through at least three crystallizations from water followed by a final recrystallization from water and ethanol. It was then placed in an oven at 80°C for twenty-four hours, removed, finely ground in an agate mortar, and replaced in the oven for an additional twenty-four hours. The grinding was repeated several times to ensure the absence of any occluded mother liquor

and the salt was finally stored in a large dessicator over sulfuric acid until required.

(ii) Silver Nitrate

The silver nitrate was that supplied by the Johnson, Matthey and Mallock Company and was adequately pure but for the presence of some water. It was felt that nothing would be gained by recrystallization and the salt was carefully fused in a platinum dish, ground in an agate mortar to a fine powder and stored over sulfuric acid in a darkened space. The resulting salt was pure white in appearance, showing no visible evidence of decomposition.

(iii) Potassium Chloride

Pure potassium chloride was necessary to make up the standard solutions for the calibration of the cells. A good reagent grade salt was recrystallized twice from water and fused in a platinum dish. The salt was then ground very finely and kept over sulfuric acid in a dessicator.

(iv) Conductance Water

KMnO_4 and KOH were added to good quality distilled water which was then redistilled from an all-pyrex distillation apparatus. The neck of the still was of such length and shape that no solid matter could have been carried over into the receiving flask. Approximately 500 mls were distilled each time and only the middle portion was collected and used for the solutions. The specific conductivity of this water was of the

order of 1.5×10^{-6} mhos which indicated accuracy entirely adequate for the concentrated solutions and for the calibration of the viscometers.

2) Preparation of the Solutions

With the exception of the four saturated cases, all the solutions were made up by weight on an analytical balance. The amount of solution necessary to fill the conductance cell, the two viscometers and the pycnometer was found to be about 60 mls and since it was claimed that the previous work had suffered somewhat by the use of a very large, coarse balance it was decided that the amount of solution would be kept to a minimum in order to utilize the increased accuracy of the finer balance. This practice also eliminated the necessity of transferring the accurately weighed salt to another container and effected a considerable economy in materials.

The weights were calibrated relatively according to the method of T.W. Richards, and again by direct comparison, piece for piece against a set calibrated six months previously by the National Research Council, Ottawa. The two calibrations agreed to within a few hundredths of a milligram, which was considered sufficient proof of the accuracy of the corrections.

The required amount of pure dry salt was placed in a previously tared weighing bottle of approximately 80 mls capacity and weighed on the balance. The bottles were handled at all times

with either Kleenex or chamois lined tongs and sufficient time was always allowed for them to come to equilibrium with the balance case. To eliminate inequalities in the balance arms, double weighing was employed and the zero point found by the method of swings. The sensitivity of the balance was determined with each weighing by displacing the rider a distance corresponding to 1 milligram and noting the change of the rest point in scale divisions. Knowing the sensitivity, the rest point and the zero point, the fourth and fifth decimal places were calculated. This procedure assured the accurate weighing of the salt to a tenth of a milligram. Since the most dilute solution required salt of the order of 500 milligrams this accuracy was more than sufficient. The fact that the empty weighing bottle was found to have the same weight to 0.1 mg from day to day, after cleaning with chromic acid and drying in an oven, was taken as evidence that the technique of the weighing was satisfactory. No increase in the weight of the salt due to adsorption of moisture was ever noticed. The density of the air was calculated from a knowledge of the temperature, humidity and atmospheric pressure, and corrections to vacuum were made in every case.

To eliminate possible bubble formation, freshly distilled conductance water was boiled in a pyrex beaker and allowed to cool. This water was then pipetted into the weighing bottle containing the salt and the solution was subsequently weighed. The mass of the resulting solution was so great that an error of a milligram or so was negligible considering the desired

accuracy, and double weighing was thought unnecessary in this case. The very significant vacuum correction was made to the weight after the solution density had been determined.

In the case of the very concentrated solutions it was found necessary to add the conductivity water to the salt while still hot in order to bring about complete solution of the salt without stirring. The solution was allowed to stand outside the balance case for 1 to 2 hours and then placed in the balance case for twenty minutes before weighing. After weighing, the solution was immediately removed from the balance case, stirred vigorously to insure homogeneity and then immediately employed in filling the instruments so as to eliminate the possibility of a concentration change on standing.

In order to obtain saturated solutions, conductance water with an excess of the salt was very efficiently stirred in an elongated tube, immersed in the thermostat, for at least three hours. At the end of this time equilibrium was assumed. It was then necessary to remove the solution from the excess salt without reprecipitation. This was done by preheating all of the apparatus which was to contact the solution to about 40°C in an oven. The solution was removed by drawing it off through a fine grain, sintered-glass filter stick which was connected through a ground glass joint to a tube in the form of a trap. Suction was applied to the open end of the trap and the solution was drawn into the tube which was then immediately detached, stoppered and replaced in the thermostat.

The saturated concentrations were determined by dilution of a weighed amount of the solution to a convenient lower concentration by weight. The specific conductance of the dilute solution was then determined in a conductance cell and from a graph of specific conductance versus weight percent, the weight percent of the dilute solution was found. By a simple calculation the weight percent of the saturated solution could then be determined. This value together with the density of the solution yielded the molar concentrations at saturation.

The standard solutions most convenient for the determination of the cell constants were 1.0N KCl and 0.1 N KCl. The vacuum weight percents of KCl in these solutions of very well known specific conductivity are given by Jones and Bradshaw, (56). The procedure was to weigh out some KCl in a weighing bottle as described above, making the weight and vacuum corrections as usual. The vacuum weight of the standard solution containing this much salt was then calculated by proportionality and by applying the buoyancy and weight corrections in reverse. The appropriate weights were then placed on the right hand pan of the balance. Sufficient water was then added or evaporated until a satisfactory balance was achieved. The solution was then thoroughly stirred and transferred to the conductance cell.

3) Temperature Control

Since the variation of conductance and viscosity with temperature is of the order of 2% per degree it was necessary

that the measurements be made under carefully controlled conditions of temperature. Three thermostats were used in this work. Two of them were water filled and used for the determination of viscosity and density at 25.00°C and 35.00°C, whereas the third was already set up in the laboratory and, being oil filled, was used for the determination of the conductance at 35.00°C. But for the use of a different mercury and glass thermoregulator, a new relay system and the adjustment to 35.00°C, the oil bath used for conductance was not altered from its condition since its use by Miss E.M Kartzmark for the 25.00°C figures. The following discussion therefore applies to the thermostats set up specifically for this work, unless otherwise stated.

The thermostats consisted of pyrex glass containers, cylindrical in shape and having a capacity of approximately 20 liters. At the low temperatures of this work it was not necessary to lag the outside of the containers so the interiors of the water thermostats were visible at all times. The growth of organic matter in the water baths was inhibited by suspending in each a ~~net~~ cotton bag containing mercuric iodide. Although it was found necessary to empty, clean, and refill the baths about every ten days, the obvious practical advantages of water as a bath fluid in this work, completely justified this slight inconvenience.

100 watt lamps served as heating elements for both the 35.00°C and 25.00°C baths. The use of a light bulb as a source of heat has a number of advantages; the heating time-lag of a lamp filament is very much shorter than that of an ordinary resistance

heater so that a finer temperature control may be achieved; the bulb presents a large surface area in a relatively small space in the bath; the periodic bright illumination of the bath by the bulb enables any dust particles in the viscometers or air bubbles in the pycnometer to be detected easily; the operation of the relay is rendered visible so that any relay failures can be immediately detected and corrected before the bath deviates greatly from its set temperature. On particularly cold days an auxiliary lamp was placed in the 35.00°C thermostat to maintain the temperature. Maximum heating efficiency is achieved when the heater is on half of the time. This condition was usually complied with.

The thermoregulators used in all three baths were constructed of pyrex glass tubing in a V-shape. One arm consisted of a test-tube top sealed into a capillary which was in turn sealed into a tube of approximately 10 mm outside diameter. This tube constituted the bend in the "V" and was joined to the other arm which was about 16 mm in outside diameter and sealed at the end. This bulb, about 25 cms long, contained the bulk of the mercury, which was purified by repeated vacuum distillations and poured into the regulator. A short piece of platinum wire was sealed in a small bore tube through the side of the regulator just below the capillary to provide an electrical contact through the mercury to the contact wire. The regulators were suspended in the baths from a cross bar so that the capillary arm was vertical and that the bulb, completely immersed, extended at a 45° angle

across the bath. The contact wire was soldered into the end of a long screw threaded through a brass head which was in turn firmly fixed in a stopper in the test-tube top. This arrangement permitted easy vertical adjustment of the wire in the capillary in adjusting the bath to temperature. A lock nut was used ~~to~~ to maintain the contact at its proper level.

The relay system to the heater was a simple mechanical type. In order to reduce sparking and consequent oxidation at the mercury contact it is desirable to reduce the current through the regulator to as small a value as possible. This may be readily accomplished by the use of a vacuum tube relay or by means of a somewhat less satisfactory high resistance mechanical type. A 5000 ohm mechanical relay operating on 6 volts D.C. was used in the regulator circuit. This together with auxiliary resistances reduced the current to below one milliamperere which was just sufficient to actuate the relay. Although slight sparking was noticeable, the regulators continued to give good performance and it was not necessary to clean them during the experimental determinations. The high resistance relay in turn actuated a mercury gravity relay which carried line voltage to the heater.

The baths were stirred by means of propeller type mechanical stirrers having in one case two, and in the other, three propellers of three inch diameter distributed along the shaft. The pitch of the blades was adjusted so that the stirring of the baths was maintained just below turbulence. The water made a

complete circuit around the circumference of the bath in a very few seconds and no difference in temperature between various parts or depths could be detected on the Beckmann thermometers. The Beckmanns themselves were calibrated by means of a platinum resistance thermometer available in the laboratory from the National Research Council so that the baths could be adjusted reliably to 25.00°C and 35.00°C

The performance of the thermostats was entirely satisfactory. The water baths, when under supervision in case of relay failures, maintained their set temperatures so that no variations could be detected on the Beckmann thermometers. The oil bath showed a maximum deviation from 35.00°C of $\pm 0.02^{\circ}$ due to the decreased stirring efficiency.

4) The Measurement of Equivalent Conductance

As has been seen, the concentration being known, the determination of the equivalent conductance of an electrolytic solution reduces simply to the determination of its electrical resistance. In this work the Campbell-Shakelton Shielded Ratio Box as supplied by the Leeds and Northrup Company was employed. This device has been discussed by Behr and Williams (6). The box, together with associated A.C. resistance boxes, variable capacitors, and an audio-frequency oscillator were arranged and shielded according to the suggestions of the Leeds and Northrup Company in their Catalog EN-95. With the exception of the tuned

audio-frequency amplifier, which was found to be unnecessary, the arrangement was identical to that described in this catalog. The apparatus had been previously set up in the laboratory by Dr. A.N.Campbell and Miss E.M.Kartzmark and had been found to be satisfactory so that an extended discussion is considered unnecessary.

The shielded ratio box includes in its assembly a Wagner earthing device to eliminate error due to capacity to ground and also a small variable air condenser for fine compensating adjustment against the capacity of the cell. The over all precision of the apparatus is claimed to be 0.1% from 10 to 11111.1 ohms. A telephone headpiece was used as a detector and found to give perfectly satisfactory minima when the apparatus was correctly balanced against external capacity and inductance effects.

Two cells of the type recommended by Jones and Bollinger (54) were employed. In order to measure the resistance of such highly conducting solutions in a cell of convenient size, it was necessary to reduce the bore of the connecting capillary to a few millimeters. The behaviour of cells with extremely high cell constants has not been reported in the literature, but in the absence of any evidence to the contrary their use was assumed justified. The two cells differed one from the other by a factor of ten in cell constant, and bearing in mind that the specific conductance had not been proved independent of cell constant for these high values, the specific conductance of a solution of unknown composition was determined in both cells and found not

to differ by more than 0.1%. This showed that at least no gross errors were caused by the use of such small bore tubes. The circular platinum electrodes were coated lightly with platinum black by the electrolysis of a solution of platonic chloride in the cells. The cell of lower cell constant was employed until the higher one was available whereafter the second cell was used exclusively.

The procedure followed was the same for all solutions whether standard, unsaturated, or saturated, and was as follows. Freshly prepared solution was pipetted into the wide bore arm of the clean, dry cell and allowed to flow through to the opposite compartment until the solution level in both arms was about 1 cm below the stop cocks. The solution was then carefully examined for air bubbles and if found satisfactory was sealed off with the stop cocks and suspended from a cross arm over the thermostat, so that the solution-containing portion of the cell was completely immersed. At least twenty minutes were then allowed for equilibration. The cell was periodically examined for air bubbles which were flushed out by alternately applying light suction and pressure to one of the arms.

The bridge, with one lead wire to the cell disconnected, was first balanced against ground and other external capacitances by means of a coarse adjustable capacity and the fine compensator included in the ratio box. When the solution had reached temperature equilibrium, the circuit was closed and the resistance and parallel capacitance alternately varied to give a

sharp minimum in the earphones. The resistance reading was then taken.

After the measurement, the cell was removed and cleaned by thorough washing with hot water and soap, followed by chromic acid solution and repeated rinsing with warm distilled water. The cell was then dried with alcohol and ether and flushed out by passing clean, dry air through it for fifteen minutes. This treatment did not alter the cell constant from time to time and was apparently quite satisfactory.

5) The Measurement of Relative Viscosity

In undertaking the determination of the viscosities of the strong electrolytic solutions of this work it was desirable to obtain a measure of accuracy comparable to that of the conductance data. As has been seen the capillary viscometer is most commonly employed in research work of this nature and has the advantage of being simple in principle and operation. However, the simple Ostwald equation commonly employed with an Ostwald viscometer cannot be used for accurate work unless care is taken to design the viscometer in such a way that errors may either be accurately compensated for, or made negligible. The latter alternative is much to be preferred and is the subject of a number of papers on viscometer design, most notable of which are by Willihnganz, McCluer, Fenske and McGrew, (102), and by G. Jones, (52).

After due consideration of the literature and of the viscous

properties of the solutions it was decided that a suitable viscometer was that designed by Cannon and Fenske for non-viscous liquids, (19, Fig. 2), and two were obtained from the H.S. Martin Glass Co. However these proved to have an unsuitable efflux time and were moreover rather fragile in construction. It was therefore decided to purchase two viscometers of the type represented in Fig. 1 of their paper and these were found to be well executed and of sturdy construction.

The drainage and kinetic energy corrections to the measurements were considered to be negligible by virtue of the rather narrow capillary diameter which gave an efflux time in excess of 200 seconds, for all of the measurements. The surface tension correction was not allowed for in such a viscometer but it was thought that the change in surface tension between the calibrating liquid, water, and an aqueous salt solution should not cause a large effect. The working volume correction was rendered negligible by the rather unique and quite sensitive method of filling the pipettes. The viscometer is inverted and the capillary arm is placed in the liquid. Suction is then applied to the wide-bore arm and the liquid is drawn to the capillary mark. This method of loading was found to be very convenient and gave quite reproducible results.

The bend in the viscometer causes it to be much less sensitive to angle of tilt from the vertical, and permitted the instrument to be supported in the bath by means of an ordinary clamp and clamp-stand separate from the thermostat and fixtures.

This reduced the transmission of vibration to the viscometer. The theory and performance of the viscometer are fully discussed by Cannon and Fenske, (19).

The viscometer should be filled at the temperature of the measurement but it was found that filling at 35.00°C, which necessitated the thermostating of the weighing bottle, resulted in no change in the efflux time so that all fillings were subsequently made at room temperature as a matter of convenience. At higher temperatures however, the change in working volume due to thermal expansion may have an appreciable effect.

Two viscometers with serial numbers 341 and 376 were used. These were calibrated with conductance water both at 25.00°C and 35.00°C. It was originally decided to use one viscometer for the 25.00°C measurement and the other for 35.00°C but it was found that the viscometer could be transferred, for example, from the 25.00°C bath, after the determination, to the 35.00°C bath and yet give the same result at the latter temperature as was obtained by filling and placing it directly in the thermostat at 35.00°C. This indicated that expansion of the solution and evaporation from the viscometer during the time from the first determination at say 25.00°C to the second at 35.00°C, were not sufficient to cause any change in the efflux time at the higher temperature. This provided an opportunity of checking the result by measuring the efflux time at both temperatures, in both viscometers, yielding four results in all.

Each viscometer was filled directly from the weighing bottle by inverting the instrument and drawing solution through a fine grained filter stick to the capillary mark or above it, by means of suction applied through a rubber tubing attached to the wide bore arm. The tubing was then clamped and by squeezing it in the vicinity of a pin-hole, sufficient air was admitted to the viscometer to allow the solution level to drop slowly to the mark. Excess fluid was then brushed from the end of the capillary arm and the viscometer was inverted and placed in the appropriate thermostat. The instrument was supported in the bath by an ordinary testtube clamp and was aligned by inspection, since it was found that even quite obvious displacements from the vertical produced no change in the efflux times. The solution was carefully inspected for dust particles in the strong light of the thermostat heaters.

After allowing fifteen minutes for equilibration, the solution was drawn above the upper mark and the time taken for efflux from the upper to the capillary marks. Two stopwatches were used which were periodically checked against station WWV, Washington, and found to be reliable for periods well in excess of the efflux times. The measurement was repeated until at least three consecutive readings were in agreement to 0.2 sec, which was the practical limit of the stopwatches. The first viscometer was then transferred from one bath to the other and vice versa. Each was again allowed to come to equilibrium and the procedure was repeated.

When satisfactory results had been obtained, the viscometers were rinsed out with tap water, filled with chromic acid solution and allowed to stand for approximately two hours. They were then rinsed again with tap and distilled water and finally about two liters of hot distilled water were drawn through a filter stick into the viscometers to insure thorough cleansing and the elimination of dust particles. Clean, dry air was then passed through them momentarily and they were placed inverted in an oven at 80°C . The air and oven treatments were alternated until the instruments were dry, at which time they were wrapped in Kleenex in readiness for the next run.

The viscometer constants were checked frequently with conductance water and showed no variation over the period of this work.

6) The Determination of the Density

In this determination a simple Weld pycnometer was employed. Although this instrument is not capable of the highest accuracy, it has many practical advantages over the more elaborate and time consuming methods which are commonly employed for high precision measurements, (67,103).

The pycnometer had a capacity of approximately 25 ml. No advantage would have been gained by the use of a larger bottle since uncertainties due to adsorption of moisture on large surfaces become considerable beyond 30 ml. The constant volume of

the pycnometer was obtained by thrusting the plug into the neck so that excess liquid could be squeezed out and wiped from the capillary top. The cap was provided to minimize evaporation losses.

The technique employed in the use of this pycnometer was exactly that of Weissberger,(101). The pycnometer was filled from a pipette and placed capped in the 25.00° thermostat for 20 minutes. The plug was then inserted and the pycnometer allowed to remain in the bath a few minutes before it was removed, wiped dry with a chamois, and capped again. It was then allowed to stand in the balance case for at least 20 minutes before weighing. Some Uranyl acetate was kept in the balance case to eliminate electrostatic interaction between the bottles and the balance.

An additional pycnometer was used as a tare and double weighings were always carried out. By a determination of the rest point, zero point and the sensitivity by the method of swings, the weight was calculated to 5 decimal places. The appropriate buoyancy corrections were made from a knowledge of the temperature, pressure and humidity. Corrections to the weights were made on the basis of the calibration against the set which had been previously calibrated by the National Research Council, Ottawa.

When the weight at 25.00° had been determined, the pycnometer was placed in the 35.00° thermostat. Some additional solution

was added to provide an excess to be forced from the neck by the insertion of the plug. After twenty minutes, the procedure was repeated as for the 25.00° weighing. The volume of the pycnometer being known from previous calibrations with water at both 25.00° and 35.00°, the densities of the solutions were readily calculated.

A considerable amount of preliminary work was done in calibrating and testing the accuracy of the pycnometer. The very accurate results of Adams and Gibson,(1) for ammonium nitrate solutions at 25.00°C were fitted to an equation by Gucker,(41) thus providing a convenient means of checking the accuracy of the pycnometer. A number of solutions of ammonium nitrate were made up by weight and their densities determined by the above procedure at 25.00°. An approximate molar concentration was then calculated and substituted into Gucker's equation yielding an accurate value of d_4^{25} to within ± 0.00002 gr/ml. This result was then compared with the experimental value found directly. A similar equation due to Jones and Colvin for silver nitrate,(57), was used to check the experimental points for this salt up to 5 molar at 25.00°C. No direct checks on the accuracy of the 35.00°C figures were available, but since the 35.00° volume calibration was just as reproducible as that at 25.00°, it was assumed that the density figures themselves should be of comparable accuracy.

RESULTS
AND
TREATMENT OF THE DATA

1) Specific and Equivalent Conductance

The design of the Campbell-Shakelton ratio box is such that the specific conductances are calculated from the formula,

$$k = \frac{K(10,000.0 - R)}{R \times 10^4} \dots (17)$$

where k is the specific conductance, $\text{ohm}^{-1}\text{cm}^{-1}$; K is the cell constant, cm^{-1} ; and R is the reading at balance of the resistance box, ohm.

Since the solutions were made up by weight, the volume concentration was not directly known, but was calculated from the equation,

$$C = \frac{10p_1d}{M_1} \dots (18)$$

where C is the concentration in equivalents per liter; p_1 , the weight percent of solute; d , the solution density, gr cm^{-3} ; and M_1 is the molecular weight of the solute, gr. Knowing C and k the equivalent conductances were then calculated from equation (2).

The experimental data as calculated from equations (2), (17) and (18) are presented in Tables I and II. All values are recorded to the first doubtful figure guided by the assumptions that the conductance data is limited to 0.1% accuracy by the apparatus itself and that the density figures are significant to the fourth place. The variation of the equivalent conductance with molar concentration is shown graphically in Figs. 1 and 2,

the 25.00°C figures of Campbell and Kartzmark being included for comparative purposes. The variation of the specific conductance with molar concentration for NH_4NO_3 and AgNO_3 is also shown in Figs. 3 and 4, the 25.00°C and 95.0°C results of Campbell and Kartzmark being presented also to illustrate the temperature variations, in particular the behaviour of the maxima.

2) Viscosity and Fluidity

As pointed out by Hatschek, (47), the question of the applicability of the viscometer corrections may be settled by calibrating the viscometers with two different known standards or with the same standard at two temperatures. Provided that the variation in viscosity between the two calibrations is of the same magnitude as that between a standard and the unknowns, constancy of the viscometer constants for the two calibrations indicates that it is safe to assume that the corrections are negligible in this range.

The efflux times for pure water in viscometer 341 for 25.00°C and 35.00°C were respectively, 405.0 ± .1 secs and 328.5 ± .1 secs. Using the viscosity values of Bingham for pure water, 0.8937 centipoises at 25.00°C and 0.7225 at 35.00°C, the viscometer constant was respectively found to be 0.0022132 and 0.0022125. Similarly for viscometer 376, with efflux times of 363.2 and 294.3 secs at 25.00° and 35.00°, the values were 0.0024679 and 0.0024696. This agreement is well within the

experimental error and is moreover well within the variations of the published figures for the absolute viscosities of water, more recent figures being somewhat different from the long accepted data of Bingham. Using these values of the viscometer constants therefore, all viscosity data were calculated from equation (9).

The fluidity being simply the reciprocal of the viscosity in poises, was then calculated from

$$\phi = \frac{100}{\eta} \dots \dots \dots (19)$$

where ϕ is the fluidity in rhes and η the viscosity in centipoises.

All the pertinent viscosity data, including the original efflux times are tabulated for the two salts at 25.00° and 35.00° in Tables III, IV, V and VI. The fluidities are plotted in Figs. 5 and 6 together with the results of Campbell and Kartzmark at 25.00°C.

3) Density and Apparent Molal Volume

The density relative to water at 4°C, which is the most conveniently evaluated density, is given by the relationship,

$$d_4^t = m/V \dots \dots \dots (20)$$

where d_4^t is the density at temperature t relative to water at

$d_4^{\circ}C$, $gm\ ml^{-1}$; m is the mass of the substance in grams; and V is the volume of this mass in mls.

The pycnometer calibrations, using $d_4^{25} = 0.99707$ and $d_4^{35} = 0.99406$ for water, yielded volumes of 26.6343 mls at 25.00° and 26.6361 mls at 35.00°. After several dozen trials, the technique of the measurement was perfected so that any single calibration rarely differed from these mean values by more than 0.0005 mls. Since all calibrations and measurements were made in the same location, W , the weight, was substituted for m , the mass, in equation (20).

The empirical equation of Gucker (41) for the densities of ammonium nitrate solutions at 25.00°C up to saturation is:

$$d_4^{25} = 0.997077 + 0.032628C - 9.63 \times 10^{-4} C^{3/2} - 4.73 \times 10^{-5} C^2. \quad (21)$$

This equation represents the experimental data of Adams and Gibson (1) to two parts in the fifth decimal place. The experimental densities for six ammonium nitrate solutions determined in a single day are presented in Table VII, together with values calculated from equation (21).

It should be noted that the density is implicitly contained in C , the concentration, through equation (18) and hence, in principle, equation (21) should be solved by successive approximations. However, since the experimental values were very close first approximations, this was not necessary.

TABLE VII.

Weight % NH ₄ NO ₃	Normality	d ₄ ²⁵	
		Experimental	Calculated
1.4812	0.1856	1.00305	1.00305
1.7248	0.2163	1.00403	1.00404
6.2710	0.8010	1.02251	1.02249
10.048	1.3031	1.03803	1.03809
15.537	2.0599	1.06124	1.06124
24.759	3.4075	1.10167	1.10165

The density data for the determinations at 25.00°C and 35.00°C are contained in Tables III, IV, V and VI. For comparative purposes, Table III also contains the values calculated from equation (21). Calculated values for AgNO₃ at 25.00°C for concentrations up to 5 molar were also obtained from the equation of Jones and Colvin (57);

$$d_4^{25} = 0.997074 + 0.141956C - 0.002603C^{3/2} \dots (22)$$

These values are included in Table IV.

The apparent molal volume is readily calculable from the density data by means of the expression:-

$$\Phi = M_1/d_0 - 1000(d - d_0)/Cd_0 \dots (23)$$

where M_1 is the molecular weight of the solute; C , the molar concentration; d , the density of the solution, gm ml^{-1} ; and d_0 is the density of the solvent, gm ml^{-1} . The apparent molal volumes of ammonium nitrate solutions at 25.00°C have been very accurately determined by Adams and Gibson (1) and by Gucker, (41). The apparent molal volumes of silver nitrate at 25.00°C have been determined by Bauer, (5). The agreement of these values with those found here is dependent on the agreement of the density figures which have already been compared. The density data differ from their accurate results by as much as two units in the fourth decimal place and consequently the molal volume data presented in Table VIII for 35.00°C are quoted to only as many figures as this error justifies. The probable errors in the apparent molal volume, determined on the assumption that the 35.00°C density figures were of comparable accuracy to those at 25.00°C , were calculated and included in the table.

4) The Temperature Coefficients

The true temperature coefficient, ω , of a quantity, q , is defined by the differential expression,

$$\omega = 1/q \cdot dq/dt \dots \dots \dots (24)$$

This coefficient may be evaluated graphically from a temperature versus "q" plot at any given value of q or t , simply by measuring the slope at the corresponding point and dividing by the value of

"q" at that point. Alternatively and more accurately, an analytical expression for "q" in terms of t and known constants may be obtained and the coefficient found in the form of a second analytical expression by differentiating the first with respect to t, and dividing by "q". If the form of the equation is known it is a simple matter to fit the data and obtain the constants by one of the standard procedures, such as the method of least squares, (70,104).

It is well known that the variation of conductance with temperature may be expressed by means of a virial equation, usually of the form,

$$\Lambda_t / \Lambda_{25} = 1 + a(t - 25) + b(t - 25)^2 + \dots \quad (25)$$

where a and b are constants to be determined.

As has been discussed, there is no generally applicable formula for the temperature dependence of viscosity or fluidity but it is generally agreed, both on empirical and theoretical grounds that it should contain an exponential expression of the form, $e^{E/RT}$.

The proper evaluation of the virial coefficients of equation (25) and the determination of the temperature dependence of the fluidity must be left until further data are obtained in the range between 35.00° and 95.0°C. In this work, the procedure followed by Campbell and Kartzmark in the determination of "coefficients" between 25.00° and 95.0°C was adopted. The

variation of both the equivalent conductance and the fluidity between 25.00°C and 35.00°C was assumed to be linear and linear temperature coefficients were evaluated.

The coefficients were obtained at different concentrations by plotting the experimental figures for conductance and fluidity on graph paper of such size that one division represented the experimental error, and by determining the values at even concentrations at both temperatures, by graphical interpolation. These values are tabulated in Table IX. The curves through the points fitted the data extremely well so that no appreciable error was introduced by evaluating the coefficients at concentrations somewhat removed from the experimental points. This was checked by evaluating a series of coefficients at experimental points, and also by repeating the graphing and interpolating independently. Neither of these procedures yielded coefficients significantly different from those obtained at even concentrations. The linear coefficients were obtained from the equation:

$$\omega = (q_{35} - q_{25})/10q_{25} \dots (26)$$

The results are presented in Table X. Since the ratio of the temperature coefficient of fluidity to the temperature coefficient of equivalent conductance was thought to be of some interest by Campbell and Kartzmark, this ratio is also included.

5) The Saturated Solutions

With the exception of the preparation of the solutions and the determination of the concentrations, which have already been described, the saturated solution data was obtained and treated in the same manner as indicated above. However, since these results are of special interest from the point of view of solubilities, and since they are probably not of comparable accuracy, they are not included in tables with the other solutions but are presented separately in Table XI.

DENSITIES AND SPECIFIC AND EQUIVALENT CONDUCTANCES
OF AQUEOUS AMMONIUM NITRATE SOLUTIONS
AT 35.00°C.

TABLE I

Concentration		d_4^{35} gm/ml	κ mho cm ⁻¹	\wedge mho cm ²
Wt. %	Molarity			
0.4324	0.0538	0.9958	0.00823	153.1
7.9779	1.0234	1.0269	0.1222	119.4
12.963	1.6940	1.0461	0.1881	111.0
14.533	1.9104	1.0523	0.2068	108.2
18.352	2.4504	1.0688	0.2528	103.2
28.572	3.9749	1.1136	0.3545	89.17
38.071	5.5065	1.1579	0.4210	76.46
47.424	7.1318	1.2038	0.4554	63.86
50.378	7.6705	1.2188	0.4590	59.84
59.457	9.4086	1.2667	0.4465	47.46
66.012	10.749	1.3035	0.4141	38.52

DENSITIES AND SPECIFIC AND EQUIVALENT CONDUCTANCES
 OF AQUEOUS SILVER NITRATE SOLUTIONS
 AT 35.00°C.

TABLE II

Concentration		d_4^{35} gm/ml	κ mho cm ⁻¹ .	Λ mho cm ²
Wt. %	Molarity			
1.6612	0.0986	1.0082	0.01306	132.5
20.051	1.4023	1.1882	0.1197	85.37
24.350	1.7757	1.2389	0.1413	79.55
36.551	3.0322	1.4094	0.1983	65.41
42.849	3.8230	1.5158	0.2252	58.91
45.764	4.2306	1.5705	0.2372	56.06
51.422	5.1064	1.6874	0.2590	50.71
51.844	5.1784	1.6970	0.2606	50.32
57.194	6.1438	1.8250	0.2782	45.28
64.283	7.6633	2.0253	0.2954	38.55

EXPERIMENTAL AND CALCULATED DENSITIES AND VISCOSITY DATA FOR AMMONIUM NITRATE

AT 25.00°C.

TABLE III

Molarity	Exptl. Density gm ml ⁻¹	Calc. Density gm ml ⁻¹	Efflux Time 341	Efflux Time 376	η Centi-poise 341	η Centi-poise 376	Mean Fluidity Rhes
0.0000	0.99707	0.99707	405.0	363.2	0.8937	0.8937	111.9
0.0540	0.99883	0.99883	403.9	362.0	0.8925	0.8924	112.0
1.0261	1.02957	1.02951	379.3	339.6	0.8640	0.8630	115.8
1.7009	1.05028	1.05029	369.0	330.0	0.8574	0.8554	116.7
1.9184	1.0567	1.0569	366.5	328.0	0.8568	0.8555	116.8
2.4611	1.0735	1.0734	362.4	324.6	0.8607	0.8601	116.2
3.9940	1.1190	1.1187	364.0	325.8	0.9012	0.8998	111.1
5.5346	1.1637	1.1636	382.9	342.4	0.9859	0.9834	101.6
7.1685	1.2100	1.2101	423.4	378.8	1.1335	1.1314	88.30
7.7100	1.2251	1.2252	443.6	396.1	1.2024	1.1976	83.35
9.4584	1.2734	1.2734	534.2	478.7	1.5050	1.5045	66.46
10.8027	1.3100	1.3098	648.5	582.8	1.8795	1.8844	53.13

EXPERIMENTAL AND CALCULATED DENSITIES AND VISCOSITY DATA FOR SILVER NITRATE

AT 25.00° C.

TABLE IV

Molarity	Exptl. Density gm ml ⁻¹	Calc. Density gm ml ⁻¹	Efflux Time 341	Efflux Time 376	η Centi-poise 341	η Centi-poise 376	Mean Fluidity Rhes
0.0000	0.99707	0.99707	405.0	363.2	0.8937	0.8937	111.9
0.0989	1.0112	1.0110	402.5	360.8	0.9005	0.9005	111.0
1.4077	1.1928	1.1926	374.4	335.0	0.9881	0.9862	101.3
1.7830	1.2440	1.2440	371.2	332.2	1.0217	1.0200	97.96
3.0458	1.4157	1.4156	371.9	332.3	1.1648	1.1612	86.00
3.8399	1.5225	1.5226	379.4	339.6	1.2779	1.2761	78.30
4.2526	1.5779	344.6	1.3427	74.48
5.1313	1.6953	1.6952	401.2	358.8	1.5048	1.5014	66.52
5.2027	1.7049	1.7047	403.2	360.9	1.5209	1.5187	65.80
6.1730	1.8336	428.0	382.9	1.7363	1.7330	57.65
7.6996	2.0349	482.6	431.2	2.1727	2.1658	46.10

VISCOSITY DATA FOR AMMONIUM NITRATE

AT 35.00°C

TABLE V

Molarity	Density gm ml ⁻¹	Efflux Time 341 sec	Efflux Time 376 sec	Viscosity Centi- poise 341	Viscosity Centi- poise 376	Mean Fluidity Rhe
0.0000	0.99406	328.5	294.3	0.7225	0.7225	138.4
0.0538	0.99575	327.9	293.8	0.7224	0.7221	138.5
1.0234	1.0269	313.6	280.7	0.7125	0.7114	140.5
1.6940	1.0461	307.6	275.4	0.7119	0.7110	140.5
1.9104	1.0523	306.5	274.5	0.7136	0.7129	140.2
2.4504	1.0688	305.2	273.2	0.7216	0.7207	138.7
3.9749	1.1136	310.4	277.6	0.7648	0.7630	131.0
5.5065	1.1579	329.1	294.8	0.8430	0.8424	118.7
7.1318	1.2038	366.1	328.0	0.9750	0.9746	102.6
7.6705	1.2188	383.3	342.9	1.0336	1.0315	96.85
9.4086	1.2667	462.4	413.9	1.2960	1.2941	77.21
10.749	1.3035	559.5	501.7	1.6136	1.6141	61.96

VISCOSITY DATA FOR SILVER NITRATE

AT 35.00°C

TABLE VI

Molarity	Density gm ml ⁻¹	Efflux Time 341 sec	Efflux Time 376 sec	Viscosity Centi- poise 341	Viscosity Centi- poise 376	Mean Fluidity Rhe
0.0000	0.99406	328.5	294.3	0.7225	0.7225	138.4
0.0986	1.0082	326.9	292.8	0.7292	0.7286	137.2
1.4023	1.1882	307.9	276.1	0.8094	0.8098	123.5
1.7757	1.2389	306.2	274.0	0.8393	0.8378	119.3
3.0322	1.4094	308.1	274.8	0.9608	0.9560	104.3
3.8230	1.5158	314.8	1.0557	94.72
4.2306	1.5705	318.7	1.1074	90.30
5.1064	1.6874	332.5	297.5	1.2412	1.2390	80.64
5.1784	1.6970	334.1	299.0	1.2544	1.2523	79.78
6.1438	1.8250	354.1	316.7	1.4297	1.4266	70.02
7.6633	2.0253	397.4	355.4	1.7807	1.7766	56.24

THE APPARENT MOLAL VOLUMES OF NH_4NO_3 AND AgNO_3 SOLUTIONS AT 35.00°C

TABLE VIII

AMMONIUM NITRATE				SILVER NITRATE			
C	\sqrt{C}	d_{35}^4	Φ	C	\sqrt{C}	d_{35}^4	Φ
1.0234	1.011	1.00269 ⁰	48.2 ± .2	1.4023	1.184	1.1881 ⁹	31.6 ± .1
1.6940	1.301	1.0460 ⁷	49.6 ± .1	1.7757	1.332	1.2388 ⁸	32.2 ± .1
1.9104	1.382	1.0523 ⁰	49.9 ± .1	3.0322	1.741	1.4093 ⁸	33.22 ± .06
2.4504	1.565	1.0687 ⁹	49.9 ± .1	3.8230	1.955	1.5157 ⁶	33.73 ± .05
3.9749	1.994	1.1136 ²	50.27 ± .05	4.2306	2.057	1.5705 ⁴	33.93 ± .04
5.5065	2.347	1.1578 ⁶	50.60 ± .04	5.1064	2.259	1.6873 ⁷	34.32 ± .03
7.1318	2.671	1.2037 ⁶	50.95 ± .03	5.1784	2.276	1.6969 ⁵	34.36 ± .03
7.6705	2.770	1.2188 ¹	51.05 ± .03	6.1438	2.479	1.8249 ⁷	34.85 ± .03
9.4086	3.067	1.2667 ⁰	51.38 ± .02	7.6633	2.768	2.0253 ²	35.53 ± .03
10.749	3.278	1.3034 ⁹	51.57 ± .02				

CONDUCTANCES AND FLUIDITIES OF NH₄NO₃ AND AgNO₃ AT EVEN CONCENTRATIONS
AT 25.00°C AND 35.00°C.

TABLE IX

Molarity	AMMONIUM NITRATE				SILVER NITRATE			
	^ 25		Q 25		^ 35		Q 35	
	^ 25	Q 25	^ 35	Q 35	^ 25	Q 25	^ 35	Q 35
1.00	101.3	115.8	120.0	140.5	77.8	104.8	127.9
2.00	91.9	116.8	107.4	140.0	64.2	95.8	76.4	116.4
3.00	84.2	115.1	98.1	136.5	55.2	86.2	65.7	104.6
4.00	76.9	111.1	88.9	130.8	48.5	76.8	57.6	92.7
5.00	70.1	105.3	80.6	123.1	43.2	67.9	51.2	81.7
6.00	63.4	98.2	72.5	114.0	38.6	59.1	46.0	71.4
7.00	56.8	89.8	64.9	104.0	34.8	51.3	41.4	62.2
8.00	50.4	80.8	57.4	93.1	31.2	44.0	37.2	53.4
9.00	44.2	71.1	50.3	81.8	28.0	37.3	33.4
10.00	38.4	61.1	43.4	70.4	29.9
11.00	51.1	36.9	59.1

LINEAR TEMPERATURE COEFFICIENTS OF CONDUCTANCE AND FLUIDITY
BETWEEN 25.00°C AND 35.00°C.

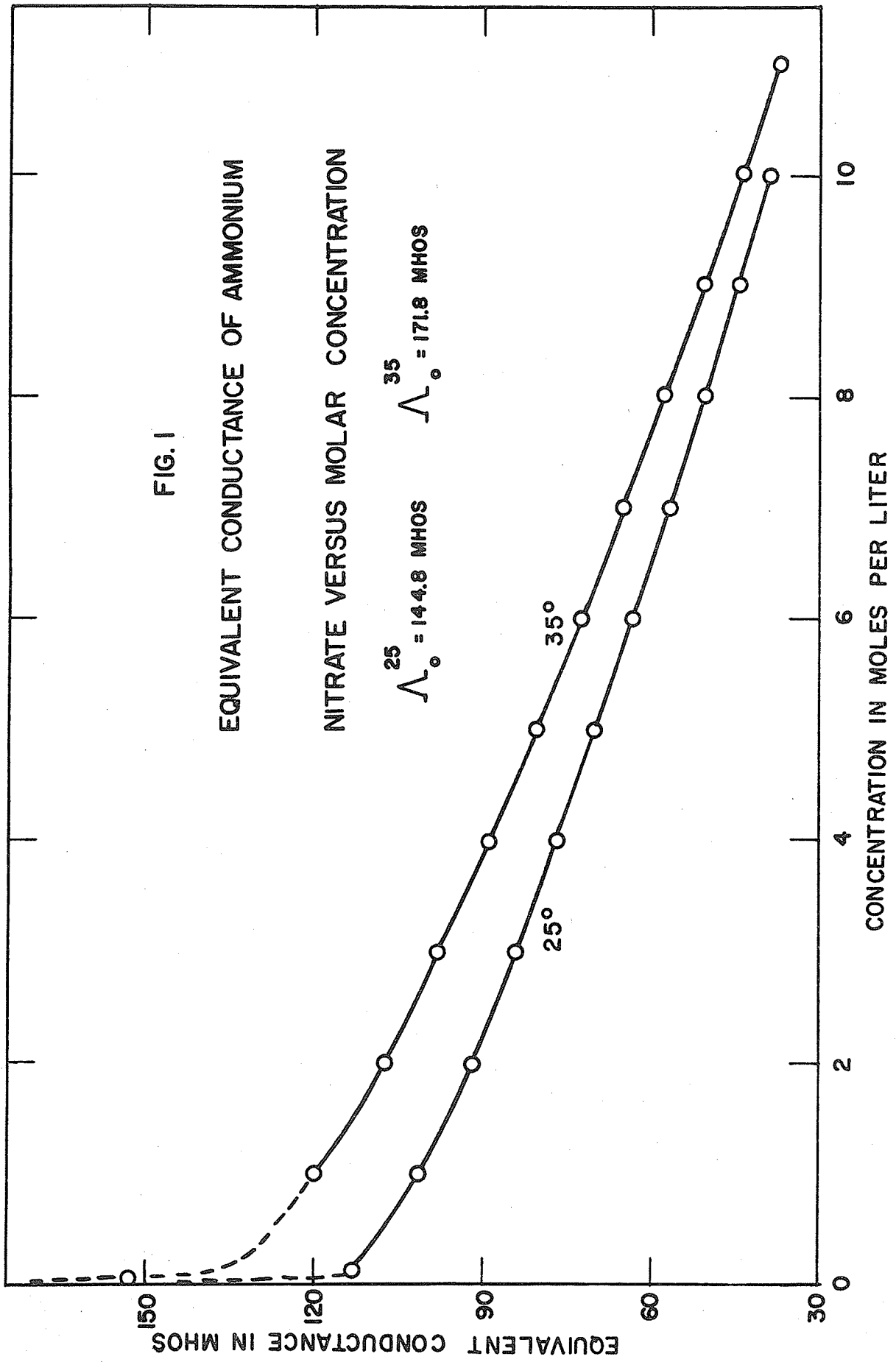
TABLE X

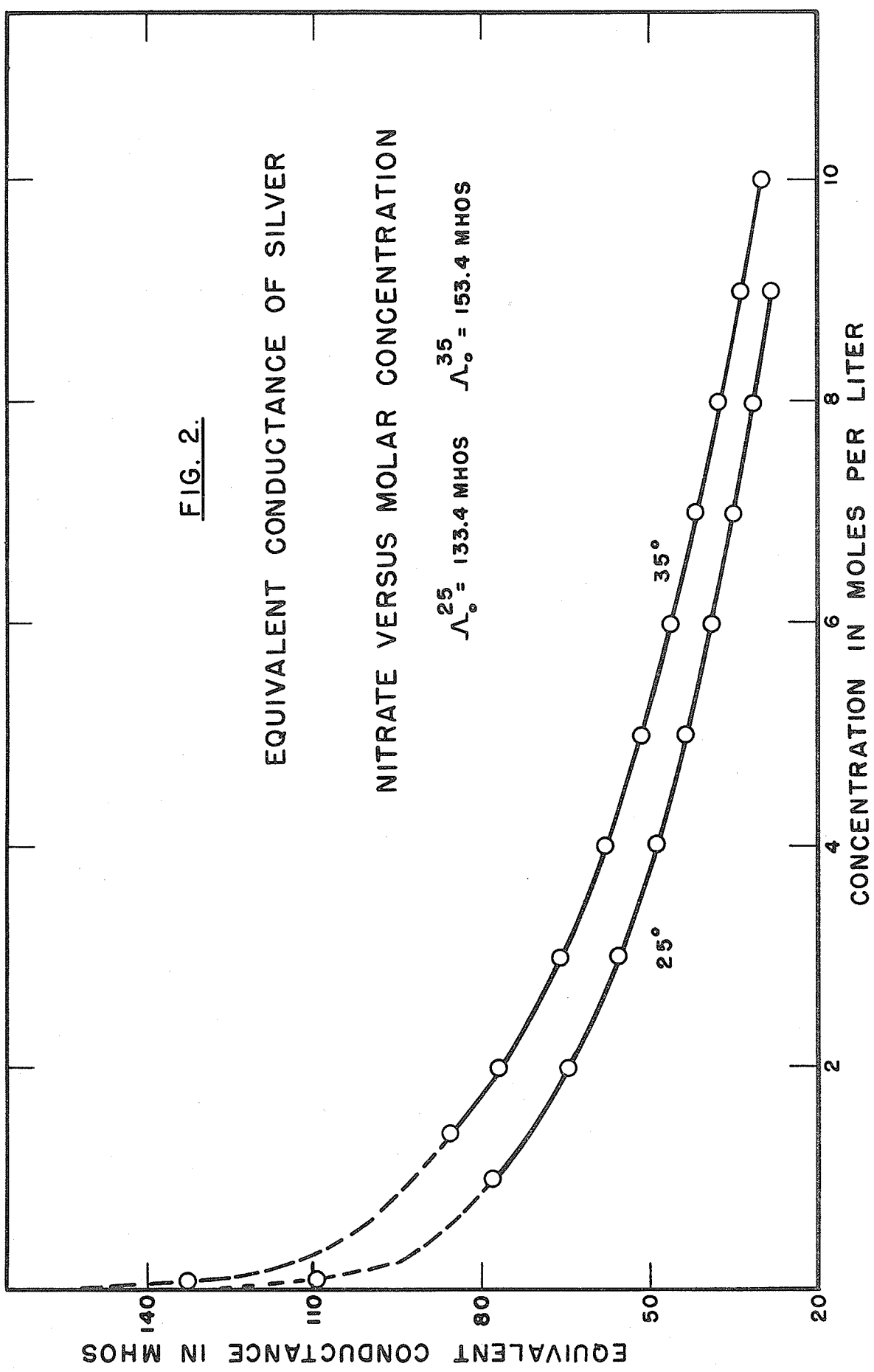
Molarity	AMMONIUM NITRATE			SILVER NITRATE		
	Coefficient of:		γ/β	Coefficient of:		γ/β
	Fluidity γ	Conductance β		Fluidity γ	Conductance β	
0.00	2.37×10^2	1.86×10^2	1.27	2.37×10^{-2}	1.88×10^{-2}	1.26
1.00	2.14	1.85	1.16	2.20
2.00	2.00	1.69	1.18	2.15	1.90	1.13
3.00	1.86	1.65	1.13	2.13	1.90	1.12
4.00	1.77	1.56	1.13	2.07	1.88	1.10
5.00	1.69	1.50	1.13	2.03	1.85	1.10
6.00	1.62	1.44	1.13	2.08	1.92	1.08
7.00	1.58	1.43	1.10	2.12	1.95	1.09
8.00	1.53	1.39	1.10	2.14	1.92	1.11
9.00	1.50	1.38	1.09	1.93
10.00	1.53	1.30	1.18

CONCENTRATION, DENSITY, CONDUCTANCE AND FLUIDITY DATA FOR SATURATED SOLUTIONS AT 25.00°C AND 35.00°C.

TABLE XI

Salt	t°C	Wt. %	Lit. Wt. %	d	Lit. d	Molarity	K	Λ	g
NH ₄ NO ₃	25.00	67.3	67.6	1.3174	1.3197	11.08	0.3519	31.76	50.05
	35.00	71.5	71.6	1.3384	1.3394	11.95	0.3702	30.98	48.06
AgNO ₃	25.00	71.0	71.0	2.3019	2.3021	9.62	0.2509	26.10	33.25
	35.00	75.4	75.4	2.4530	10.90	0.2943	27.00	33.09





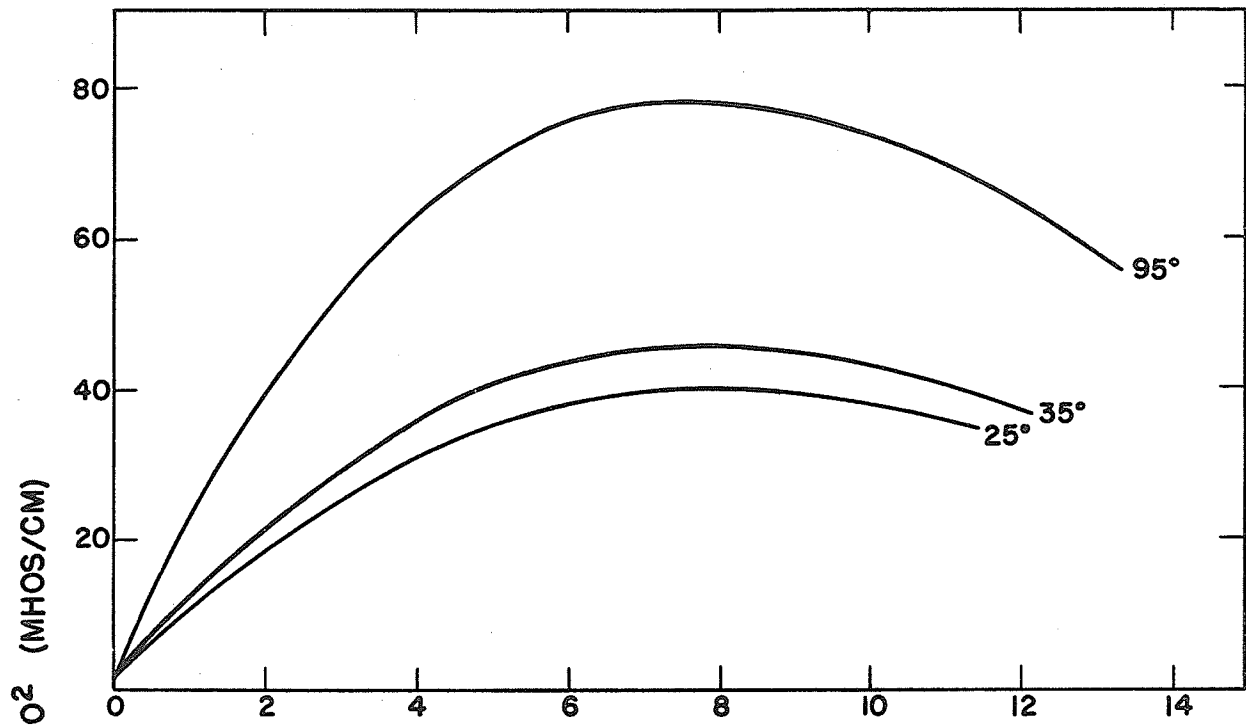


FIG. 3 NH_4NO_3 SPECIFIC CONDUCTANCE VERSUS MOLARITY

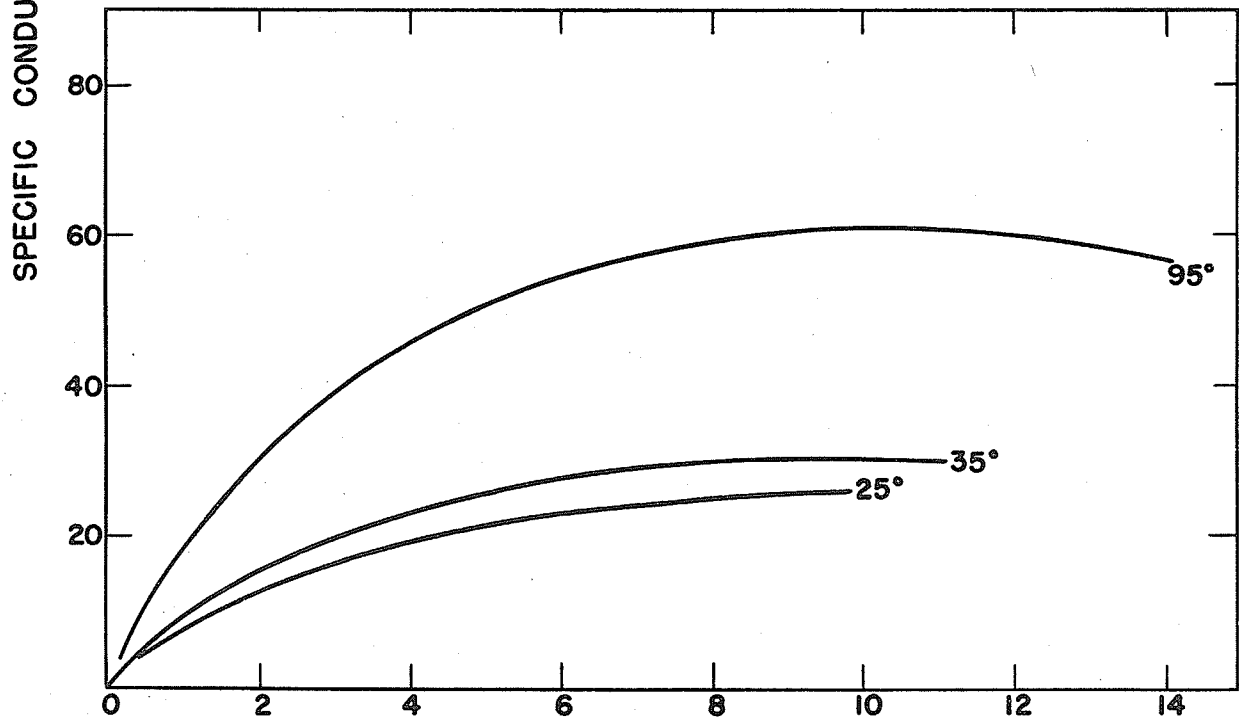


FIG. 4 AgNO_3 SPECIFIC CONDUCTANCE VERSUS MOLARITY

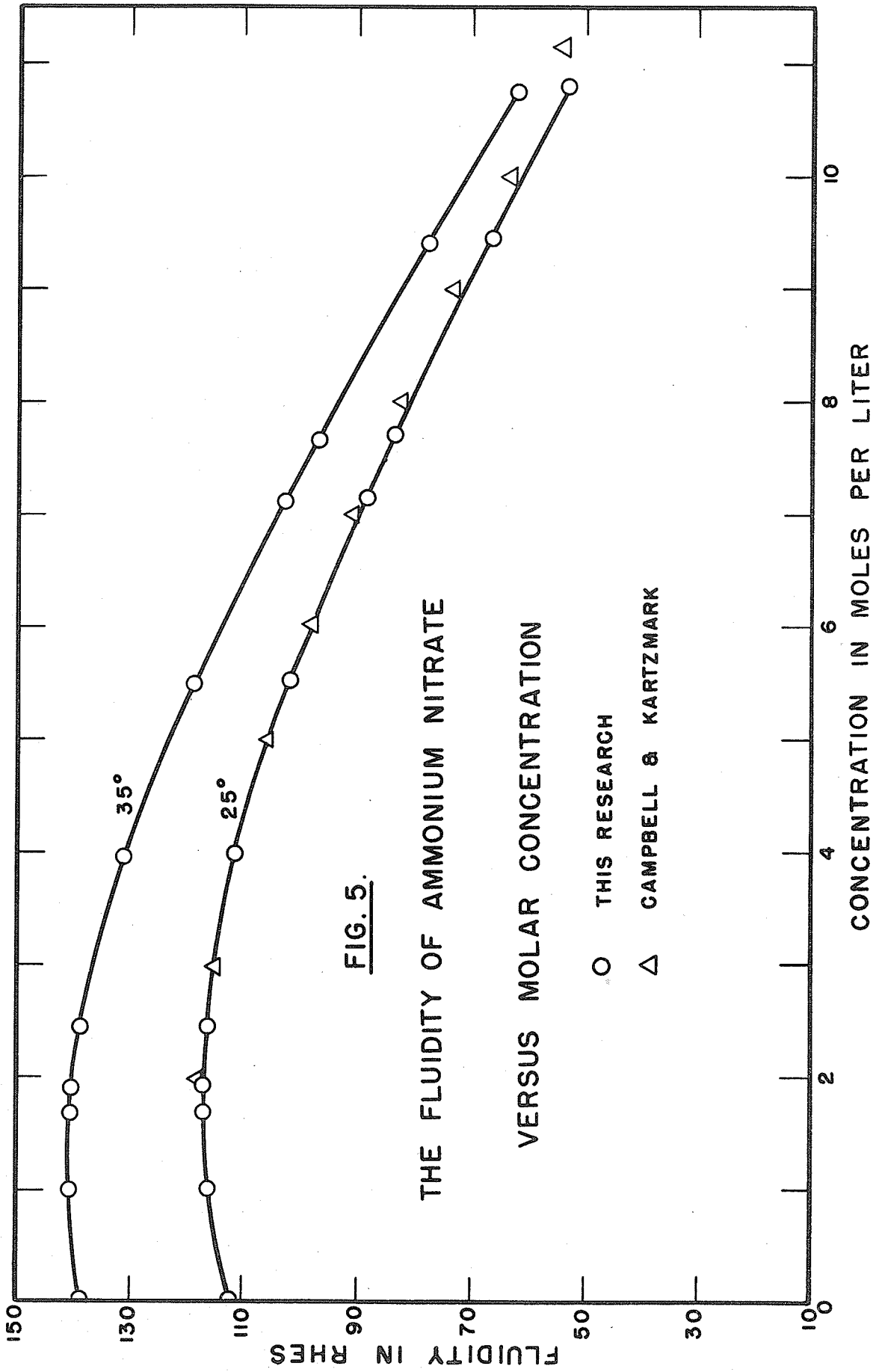


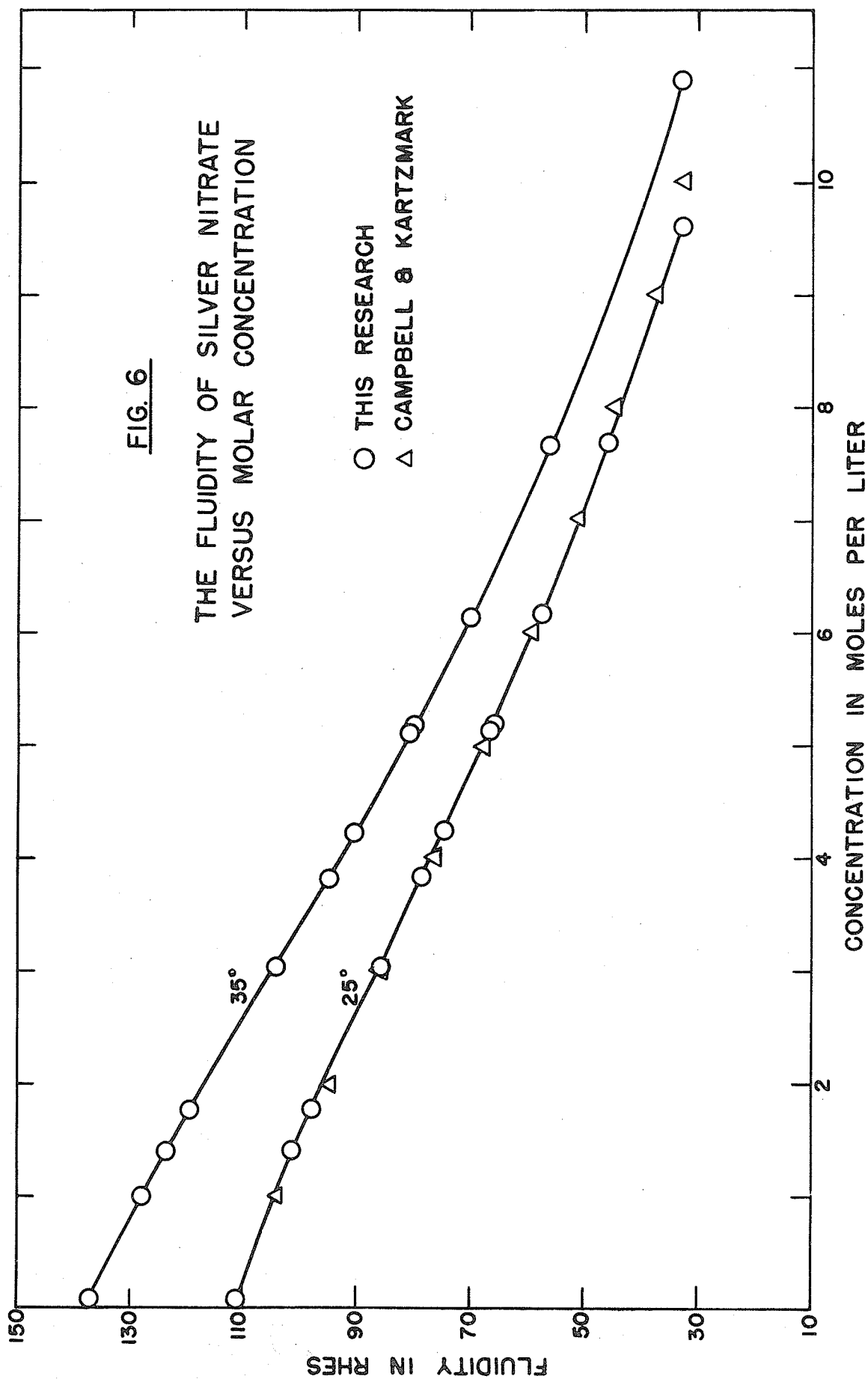
FIG. 5.

THE FLUIDITY OF AMMONIUM NITRATE
VERSUS MOLAR CONCENTRATION

○ THIS RESEARCH

△ CAMPBELL & KARTZMARK

CONCENTRATION IN MOLES PER LITER



DISCUSSION OF THE RESULTS

1) Conductance

The variation of equivalent conductance with concentration at 35.00°C is seen to be similar to that at 25.00°C . The approximately linear variation at high concentrations persists although a noticeable increase of curvature may be detected on a large scale plot. The trend to increasing curvature with increasing temperature is evident from the data at 95.0°C where the deviations from linearity are quite pronounced. The equivalent conductances of ammonium nitrate are numerically greater than those of silver nitrate and tend to linearity at a lower concentration. The values at infinite dilution were obtained from the published ionic conductances and their temperature coefficients (35) and are included in Figs. 1 and 2 to demonstrate the great variation in the dilute solution range.

Figs. 3 and 4 illustrate the behaviour of the specific conductance with increase of concentration. The occurrence of a maximum is of great interest since its physical meaning is that a ml of solution containing a greater number of ions has a lower conductance at concentrations past the maximum. At 95.00°C for example, the specific conductance of a 12 molar solution is approximately the same as a 4 molar solution in spite of a three fold increase in electrolyte concentration. This phenomenon was often noted in the early literature (97) and interpreted as the "interplay of ionization and concentration." It has only been observed infrequently in the modern literature (73) because of the lack of conductance work in the concentrated region. It

seems probable that the existence of a maximum indicates the association of ions in some manner or other. In view of the present ideas on the structure of concentrated electrolytic solutions, the maximum might be explained as a manifestation of the gradual formation of a more ordered lattice-like structure of the ions. In this connection it is interesting that the maxima occur at substantially the same concentration with rise in temperature, and in fact appear to move toward higher dilution. This behaviour is not contradictory to the view that dissociation normally increases with rising temperature, since the decrease in dielectric constant, and variations in ion-solvent effects might well compensate for the increase in thermal energy. In fact it was the conclusion of early workers on independent evidence that electrolytic dissociation decreased at higher temperatures, (97). Some authors would undoubtedly attribute the decrease in specific conductance to the increase in viscosity, but as has been pointed out, this does not constitute an explanation at all, especially since the variation of viscosity in no way parallels that of the conductance.

It should be noted that this behaviour of the specific conductance at high concentrations indicates that minima in the equivalent conductance curves are not to be expected according to the empirical rule of Walden,

$$D^3/c_{\min} = \text{a constant } (- 3 \times 10^4) \dots (27)$$

even if the necessary high concentrations were attainable, (for

water, $D = 78.5$). An examination of equation (2) shows that the evaluation of the equivalent conductance at increasing concentration amounts to taking an increasingly smaller fraction of the specific conductance. The rate at which the specific conductance decreases past the maximum is so great that the effect of taking an increasingly smaller fraction of a quantity which is itself decreasing, results in a decreasing equivalent conductance. Since the relative decrease in κ appears to be greater at the higher temperatures, it is unlikely that a minimum would occur at temperatures where extremely high concentration is possible.

The theoretical explanation of the minima in equivalent conductance curves by Fuoss and Kraus (32), is based on the formation of conducting triple ions in competition with non-conducting ion-pairs. The effect of high concentration in an aqueous medium would probably render this effect negligible in favor of larger aggregates of correspondingly lower mobility, whereas in moderate concentrations the dielectric constant of the inter-ionic solvent is sufficiently great to prevent association of any sort.

The linear temperature coefficients of ammonium nitrate solutions decrease continuously with increasing concentration. A comparison with those estimated by Campbell and Kartzmark, (18), shows that their values between 25.00° and 95.0° are somewhat lower. This indicates a slight deviation from exact linearity in such a direction that the second virial coefficient of the

conductance-temperature equation should be negative, though small. It must be emphasized however, that, in view of the probable 0.1% error in the conductance figures and the small differences in the conductance in a ten degree range, these coefficients may well be in error by 2 to 4%, the error being greatest for the highest concentrations.

The silver nitrate temperature coefficients are constant with concentration over the whole range within the estimated error and, moreover, are essentially the same as those deduced by Campbell and Kartzmark. The conductance of silver nitrate solutions therefore appears to be an almost exactly linear function of the temperature at all concentrations studied in this investigation. Lacking accurate figures in the dilute range it is impossible to ascertain the temperature dependence here, so that the possibility of a somewhat different behaviour below about 2 molar is not excluded. The coefficients at infinite dilution are calculated from the corresponding ionic temperature coefficients tabulated by Glasstone, (35), which are claimed to be applicable over a ten degree range from 25.00°C.

2) Viscosity and Fluidity

The viscosity data for 25.00°C and 35.00°C are tabulated in Tables III, IV, V and VI, to a number of figures which appears unjustified in view of the ^{lack of} agreement between the results obtained in the two different viscometers. This was done to illustrate the fact that, but for the exception of two runs, the viscosity

as obtained with viscometer 341 was higher than that from 376. The reproducibility of the efflux times was better than ± 0.2 seconds and the difference cannot be accounted for on the basis of any error in the experimental procedure. Drainage effects and other errors should be approximately the same for two viscometers of identical construction with the exception of the kinetic energy correction, which depends on the efflux time. However this correction was demonstrated to be negligible, which is further supported by the agreement of the most dilute solution results. It can only be concluded that a higher accuracy cannot be expected from viscometers of this design and that the differences are due to structural inadequacies of the viscometers themselves. Nevertheless, since the differences are systematic, the viscosities at different temperatures are still comparable, provided the same viscometer is used. The procedure of taking the mean values for the evaluation of the fluidities appears to be justified since interest is primarily centred upon the relative values at the different temperatures.

The fluidity data for ammonium nitrate lie very well along a smooth curve at both temperatures (Fig. 5), exhibiting a maximum between 1.7 and 2.0 molar at 25.00°C and between 1.2 and 1.5 molar at 35.00°C. The fluidities approach linearity at the higher concentrations, the 35.00°C curve being the more linear. The data of Campbell and Kartzmark (18) for 25.00°C are included and show considerable deviations from the smooth plot, especially above 6 molar where their figures lie uniformly high by about 3%.

An independent check on the fluidity figures may be obtained for ammonium nitrate by virtue of the linearity at the high concentrations. The fluidities of the saturated solutions at 25.00°C and 35.00°C were plotted as horizontal lines on a large scale graph and the linear lines extrapolated to intersect. The concentrations at intersection were for 25.00°, 11.11 molar and for 35.00°, 11.97 molar. These compare very favorably with 11.08 and 11.95 molar obtained independently by the conductance method. This was considered adequate evidence for the accuracy of the results.

The fluidity-concentration dependence of silver nitrate, (Fig. 6), differs considerably from that of ammonium nitrate. The curves are S-shaped and show a tendency to flatten out at high concentrations. The data of Campbell and Kartzmark (18), are again included and, though taken from a smoothed plot, their results show deviations from this work.

The linear coefficients of fluidity evaluated between 25.00° and 35.00° and tabulated in Table X, show a behaviour roughly parallel to that of the conductance coefficients, as shown by the approximate constancy of their ratios. The ratios, γ/β , are surprisingly constant considering the probable error of from 4 to 8%. The fluidity coefficients are markedly different from those evaluated by Campbell and Kartzmark, illustrating the non-linear dependence of fluidity on temperature. The assumption of linearity between 25.00°C and 35.00°C is perhaps not serious and some comparisons may be made.

The apparent constancy of the ratio with concentration was pointed out by Campbell and Kartzmark, but an observation of perhaps greater significance is that the ratio is the same for both silver nitrate and ammonium nitrate, indicating a proportionality between the two coefficients, at least for these two salts. This shows that above 2 molar the factors which cause an increase of conductance with temperature have a proportional effect on the fluidity. The differences between the values for conductance and for fluidity are to be expected since each phenomenon proceeds by a different mechanism. Nevertheless, the close relationship is clearly demonstrated, and it is probable that a mathematical treatment would contain an identical term for both conductance and fluidity as was found in the Falkenhagen derivation for dilute solutions.

3) Density and Apparent Molal Volume

The excellent agreement of the preliminary density determinations of ammonium nitrate solutions as shown in Table VII, seemed to indicate that an accuracy to a few parts in the fifth place should be attainable in this work. However, an examination of the experimental results and comparison with the calculated figures, show that differences in the fourth place are quite common. Since all the precautions and corrections for fifth place accuracy were diligently observed, it is difficult to explain these errors in the light of the excellent early results of Table VII. However, since the method involves

the forcing of excess liquid from the pycnometer by means of a ground glass plug, it seems possible that the increased viscosity of the more concentrated solutions might render this operation less and less reproducible as compared to the calibrating liquid, water. This contention is supported by the good agreement of the dilute solutions and of the preliminary ammonium nitrate solutions where the viscosity was approximately equal to that of water. Moreover, since the diameter of the plug capillary was approximately 1mm, a simple calculation will show that, in order to obtain fifth place accuracy with a pycnometer of 25 ml capacity, the allowable error in wiping the excess from the plug must not exceed about 1 mm height in the capillary. This is obviously quite difficult and subject to considerable human error. It seems, therefore, that an accuracy better than 1 part in 10,000 cannot be expected from such a pycnometer as pointed out in Weissberger's latest edition of "Physical Methods."

Although the density data are quite accurate enough for use in evaluating the viscosities and the volume concentrations, they are not sufficient to allow the ultimate calculation of the partial molal volumes. Partial molal quantities are most reliably determined through the corresponding apparent molal quantity, which, in the case of volume, is very sensitive to errors in density. The apparent molal volumes of ammonium and silver nitrate solutions at 35.00°C are presented in Table VIII. Estimated errors are included on the assumption that the probable error in the densities is 2 parts in the fourth decimal place.

A plot of these figures against \sqrt{C} shows that the behaviour is normal for 1-1 electrolytes, the curve being less steep and higher than the apparent molal volumes at 25.00°C which have been accurately determined, (1,5).

The curves are not linear but have an elongated S-shape. The accurate 25.00°C data of Adams and Gibson (1) were fitted to a three term equation by Gucker, (41) from which he evaluated the partial molal volumes. The density figures of this work at 35.00°C are neither sufficiently numerous nor sufficiently accurate to allow such a procedure to be carried out.

4) The Saturated Solutions

The data for the saturated solutions together with corresponding literature values, where obtainable, are included in Table XI. The literature figures were obtained from the International Critical Tables (50) and from Seidell's "Solubilities of Inorganic and Metal Organic Compounds", (90). The concentrations at saturations appear to agree well with those in the literature, although the densities show considerable differences. This is not surprising since the difficulties in determining the densities are multiplied in the case of the saturated solutions. It may be that the results of this work constitute an improvement on the older data but it is difficult to say, in view of the possibility of super-saturation.

SUMMARY AND CONCLUSIONS

The equivalent conductances of concentrated solutions of ammonium and silver nitrates have been determined up to saturation at 35.00°C with a probable error of 0.1%. The equivalent conductances behave in a normal manner for strong electrolytes in aqueous solution, being approximately linear with the first power of the concentration, though slightly convex to the concentration axis.

The viscosities and fluidities of these same solutions have been determined both at 25.00°C and 35.00°C with a probable error of 0.2%. Ammonium nitrate solutions exhibit the phenomenon of "negative viscosity" which tends to disappear at higher temperatures, the viscosity minimum or fluidity maximum, shifting towards higher dilution. The silver nitrate fluidities decrease continuously with concentration, the curve showing less tendency to linearity at high concentrations than that for ammonium nitrate.

The densities of the solutions at both temperatures have been determined with an apparent error of 0.02%. Apparent molal volumes have been calculated from these figures at 35.00°C and have been shown to be greater than those at 25.00°C and to have less positive slope with the square root of the concentration.

The concentrations of the saturated solutions of both salts at 25.00°C and 35.00°C have been determined by the conductance method and have been shown to be in good agreement with

the published data.

The linear temperature coefficients of fluidity and conductance for both salts have been evaluated between 25.00°C and 35.00°C and an approximate constancy of the ratio of fluidity coefficient to conductance coefficient has been observed beyond 2 molar. The ratio appears to have the mean value of 1.12 for both salts in spite of a considerable difference in the individual coefficients.

A survey of the literature has revealed that, although far from being expressible in mathematical form, the theory of strong solutions of strong electrolytes has made some notable advances. With the continued improvement of some of the newer experimental methods there is every reason to believe that the problem may yet find an adequate solution.

Much of the apparent contradiction and confusion in the literature concerning effects such as hydration and ion association, is dispelled if the basic concepts of these phenomena as described by the individual investigators are kept in mind. The physical pictures of hydration as described by Bernal and Fowler, by Hasted, Ritson and Collie, and by Stokes and Robinson are all quite different and their conclusions therefore should not be considered contradictory. Similarly, Bjerrum's concept of ion association and that envisaged by Fajans, for example, are not the same thing. Definite conclusions about these phenomena cannot be reached until some agreement is reached upon what is the proper definition of "hydration" and

what is the nature of an "ion-pair."

Conductances and fluidities are properties which of themselves cannot be expected to yield a theoretical picture, but, in conjunction with new developments and improved techniques, they may yet play an important part in the ultimate solution of the problem.

BIBLIOGRAPHY

- (1) Adams, L.H., and Gibson, R.E., J. Am. Chem. Soc., 54, 4520 (1932).
- (2) Andrade, E.N. da C., Phil. Mag., 17, 497, 698, (1934).
- (3) Arrhenius, S., Z. Physik. Chem., 1, 631 (1887).
- (4) Barr, G., "A Monograph of Viscometry," Oxford University Press,
London, 1931.
- (5) Bauer, N., "Dissertation", University of Michigan, 1941.
- (6) Behr, L., and Williams, A.J., Proc. Radio Inst. Eng., June 1932.
- (7) Bernal, J.D., and Fowler, R.H., J. Chem. Phys., 1, 515 (1933).
- (8) Bingham, E.C., "Fluidity and Plasticity," McGraw-Hill Book Co.
New York, N.Y., 1922.
- (9) Bingham, E.C., J. Phys. Chem., 45, 885 (1941).
- (10) Bingham, E.C., and Foley, R.T., J. Phys. Chem., 47, 511 (1943).
- (11) Bjerrum, N., Kgl. Danske Vidensk. Selskabs Skrifter (7) 4, 1
(1906).
- (12) Bjerrum, N., Medd. Vetenskapsakad. Nobelinstit., 5, 1 (1919).
- (13) Bjerrum, N., Kgl. Danske Vidensk. Selskab., 7, No. 9 (1926).
- (14) Brunauer, S., Emmett, P.H., and Teller, E., J. Am. Chem. Soc., 60,
309 (1938).
- (15) Butler, J.P., Doctorate Thesis, University of Toronto, 1950.
- (16) Campbell, A.N. and Kartzmark, E.M., Can. J. Research, B, 28:43. (1950)
- (17) Campbell, A.N. and Kartzmark, E.M., Can. J. Research, B, 28:161
(1950).
- (18) Campbell, A.N. and Kartzmark, E.M., Can. J. Chem., 30, 132 (1952).
- (19) Cannon, M.R., and Fenske, M.J., Ind. and Eng. Chem., Anal. Ed.,
10, 299 (1938).
- (20) Debye, P., and Hückel, E., Physik. Z., 24, 185 (1923).
- (21) Debye, P., and Hückel, E., Physik. Z., 24, 305 (1923).

- (22) Dike, P.H., Rev.Sci.Instruments, 2, 379 (1931).
- (23) Dorsey, N.E., Phys.Rev., 28, 833 (1926).
- (24) Edelson, D. and Fuoss, R.M., J.Am.Chem.Soc., 72, 306 (1950).
- (25) Evans, C.C., and Sugden, S., J.Chem.Soc., 270, Feb. (1949).
- (26) Eyring, H., J.Chem.Phys., 4, 283 (1936).
- (27) Falkenhagen, H. and Dole, M., Z.Physik.Chem., (B), 6, 159 (1929).
- (28) Falkenhagen, H. and Vernon, E.L., Phil. Mag., (7) 14, 537 (1932).
- (29) Fajans, K., Trans.Faraday Soc., 23, 357 (1927).
- (30) Fajans, K., J.Chem.Phys. 9, 283 (1941).
- (31) Fajans, K., and Johnson, O., J.Am.Chem.Soc., ~~64~~ 668 (1942).
- (32) Fuoss, R.M., and Kraus, C.A., J.Am.Chem.Soc., 55, 2387 (1933).
- (33) Getman, F.H., J.Am.Chem.Soc., 30, 721 (1908).
- (34) Gibson, R.E., Sci. Monthly, 46, 103 (1938).
- (35) Glasstone, S., "Textbook of Electrochemistry", D.Van Nostrand Co.
New York, N.Y. 1942, p. 56
- (36) Glasstone, S., "Textbook of Physical Chemistry", D.Van Nostrand
Co. Inc. N.Y., 1947, p. 528.
- (37) Glasstone, S., Laidler, J.L., and Eyring, H., "The Theory of Rate
Processes", McGraw-Hill Book Co. Inc., N.Y. 1941.
- (38) Grunberg, L. and Nissan, A.H., Trans.Far.Soc., Feb. 125 (1949).
- (39) Grüneisen, E., Wiss.Abhandl.physik.-tech. Reichsanstalt, 4, 239
(1905).
- (40) Gucker, F.T., Chem.Rev., 13, 111 (1933).
- (41) Gucker, F.T., J.Phys.Chem., 38, 307 (1934).
- (42) Gunning, H., and Gordon, A.R., J.Chem.Phys., 10, 126 (1942).
- (43) Hall, H.T., and Fuoss, R.M., J.Am.Chem.Soc., 73, 265 (1951).
- (44) Harned, H.S., and Owen, B.B., "The Physical Chemistry of
Electrolytic Solutions", Reinhold Pub. Corp., N.Y. 1950.

- (45) Harrap, B.S., and Heymann, E., Chem. Rev., 48, 45 (1951).
- (46) Hasted, J.B., Ritson, D.M., and Collie, C.H., J. Chem. Phys., 16,
1 (1948).
- (47) Hatschek, E., "The Viscosity of Liquids", D. Van Nostrand Co.,
N.Y., (1928).
- (48) Hittorf, W., Pogg. Ann., 89, 177 (1853); 98, 1 (1856); 103, 1
(1858); 106, 337, 513 (1859).
- (49) Hückel, E., Physik. Z., 26, 93 (1925).
- (50) International Critical Tables, McGraw-Hill Book Co., N.Y. 1930.
- (51) Jervis, R.E., Doctorate Thesis, University of Toronto, 1952.
- (52) Jones, G., J. Am. Chem. Soc., 60, 1691 (1938).
- (53) Jones, G., and Bickford, C.F., J. Am. Chem. Soc., 56, 602 (1934).
- (54) Jones, G., and Bollinger, G.M., J. Am. Chem. Soc., 53, 411 (1931).
- (55) Jones, G., and Bollinger, D.M., J. Am. Chem. Soc., 57, 280 (1935).
- (56) Jones, G., and Bradshaw, B.C., J. Am. Chem. Soc., 55, 1780 (1933).
- (57) Jones, G., and Colvin, J.H., J. Am. Chem. Soc., 62, 338 (1940).
- (58) Jones, G., and Dole, M., J. Am. Chem. Soc., 51, 2950 (1929).
- (59) Jones, G., and Dole, M., J. Am. Chem. Soc., 52, 2245 (1930).
- (60) Jones, G., and Fornwalt, H.J., J. Am. Chem. Soc., 57a, 2041 (1935).
- (61) Jones, G., and Josephs, R.C., J. Am. Chem. Soc., 50, 1049 (1928).
- (62) Jones, G., and Talley, S.K., J. Am. Chem. Soc., 55, 624 (1933).
- (63) Kohlrausch, F., Z. Physik. Chem., 2, 561 (1888).
- (64) Kohlrausch, F., Wiss. Abhandl. physik.-tech. Reichsanstalt, 3,
219 (1900).
- (65) Litovitz, T.A., J. Chem. Phys., 20, 1088 (1952).
- (66) MacInnes, D.A., J. Am. Chem. Soc., 48, 2068-72 (1926).
- (67) MacInnes, D.A., and Dayhoff, M.O., J. Am. Chem. Soc., 74, 1017 (1952).

- (68) MacInnes, D.A., and Shedlovsky, T., J. Am. Chem. Soc., 54, 1429 (1932).
- (69) MacInnes, D.A., Shedlovsky, T., and Longworth, L.G., Chem. Rev.,
13, 29 (1933).
- (70) Margenau, H., and Murphy, C.M., "The Mathematics of Physics and
Chemistry", D. Van Nostrand Co. Inc., N.Y. 1943.
- (71) Mason, L.S., Kampmeyer, P.M., and Robinson, A.L., J. Am. Chem. Soc.,
74, 1287 (1952).
- (72) Masson, O., Phil. Mag., 8, 218 (1929).
- (73) Mead, D.J., and Fuoss, R.M., J. Phys. Chem., 49, 480 (1945).
- (74) Noyes, A.A., Science, 20, 584 (1904).
- (75) Onsager, L., Physik. Z., 27, 388 (1926): 28, 277 (1927).
- (76) Onsager, L., Chem. Rev., 13, 73 (1933).
- (77) Onsager, L., and Fuoss, R.M., J. Phys. Chem., 36, 2689 (1932).
- (78) Parker, H.C., J. Am. Chem. Soc., 45, 1366, 2017 (1923).
- (79) Poiseuille, J.L.M., Mem. savants etrangers, 2, 433 (1846).
- (80) Redlich, O., Chem. Rev., 39, 333 (1946).
- (81) Redlich, O., Chem. Rev., 44, 1 (1949).
- (82) Redlich, O., and Rosenfeld, P., Z. Phys. Chem. A155, 65 (1931).
- (83) Reilly, J. and Rae, W.N., "Physico-Chemical Methods", D. Van
Nostrand Co. Inc. N.Y. Vol. I 1943.
- (84) Riemann, W., III, J. Am. Chem. Soc., 50, 46 (1928).
- (85) Scatchard, G., Chem. Rev., 13, 7 (1933).
- (86) Scatchard, G., Chem. Rev., 19, 309 (1936).
- (87) Scatchard, G., and Prentiss, S.S., J. Am. Chem. Soc., 54, 2696 (1932).
- (88) Scott, A.F., J. Phys. Chem., 35, 3379 (1931).
- (89) Shedlovsky, T., J. Am. Chem. Soc., 52, 1793 (1930).
- (90) Seidell, A., "Solubilities of Inorganic and Metal Organic
Compounds.", D. Van Nostrand Co. Inc., N.Y. 1940.

- (91) Shedlovsky, T., J. Am. Chem. Soc., 52, 1793 (1930).
- (92) Shedlovsky, T., J. Am. Chem. Soc., 54, 1411 (1932).
- (93) Simons, L., Soc. Sci. Fennica Commentationes Phys. Math., No. 9
(1934).
- (94) Stokes, R.H., and Robinson, R.A., J. Am. Chem. Soc., 70, 1870 (1948).
- (95) Strong, L.E., and Kraus, C.A., J. Am. Chem. Soc., 72, 166 (1950).
- (96) Sutherland, W., Phil. Mag., (6), 14, 1 (1907).
- (97) Taylor, H.S., "A Treatise on Physical Chemistry", D. Van Nostrand
Co., N.Y. 1925, p. 526.
- (98) Telang, M.S., J. Chem. Phys., 17, 536 (1949).
- (99) Van Rysselberghe, P., and Eisenberg, S., J. Am. Chem. Soc., 61,
3030 (1939).
- (100) Walden, P., Zeit. Physik. Chem., 55, 246 (1906).
- (101) Weissberger, A., "Physical Methods of Organic Chemistry",
Vol. I., Interscience Publishers Inc., N.Y. 1945
- (102) Willihnganz, E.A., McCluer, W.B., Fenske, M.R., and McGrew, R.V.,
Ind. and Eng. Chem., Anal. Ed., 6, 231 (1934).
- (103) Wirth, H.E., J. Am. Chem. Soc., 59, 2549 (1937).
- (104) Worthing, A.G., and Geffner, J., "Treatment of Experimental
Data," John W. Wiley and Sons Inc. N.Y. 1943.
- (105) Young, T.F., and Blatz, L.A., Chem. Rev., 44, 93 (1949).