

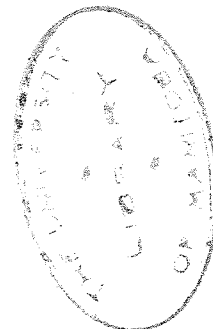
THE CONDUCTANCES OF AQUEOUS SOLUTIONS  
OF AMMONIUM NITRATE  
AT 180°C.

by

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### ABSTRACT

The specific and equivalent conductances of aqueous solutions of ammonium nitrate ranging in concentration from .1 M to that of the pure molten salt have been determined at 180°C. The special techniques employed are described.

The form of the conductance vs. concentration curves are discussed in the light of all available data on concentrated aqueous solutions. (For the most part solutions of silver and ammonium nitrate at various temperatures).

A new empirical relationship of the form  $\Lambda_c = \Lambda_a - D[\log Ca - \log c]$  where  $D$  is the slope of the  $\Lambda_c$  vs.  $\log c$  plot and the  $\Lambda_a$  is the equivalent conductance at the limiting experimental concentration  $Ca$  is described. The application of this equation to all available data on highly concentrated solutions is discussed. For silver nitrate and ammonium nitrate the range of applicability is approximately 2 M and 6 M respectively up to the limiting experimental concentration at all temperatures for which data exist.

The temperature coefficients of conductivity and the temperature vs. conductance curve are discussed.

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With appreciation to Dr. A. N. Campbell  
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**THEORETICAL INTRODUCTION.**

## I. THEORETICAL INTRODUCTION

### A. The Theory of the Electrolytic Solution.

The theory of the electrolytic solution presents itself as a major division of study within the field of physical chemistry. In the investigation of such solutions, the conductance, because of its wide range of applicability has proven to be of particular value.

What can now be termed the classical theory of electrolytic solutions was proposed by Arrhenius (1). He considered electrolytes in solution to dissociate into ions which were essentially independent of each other, and which existed in equilibrium with undissociated molecules. On this basis, the ratio  $\Lambda/\Lambda_0$  represents  $\alpha_c$  the degree of dissociation. Assuming the validity of the Ostwald dilution law, it follows that the equilibrium constant can be calculated:

$$K = \frac{\alpha_c^2 c}{1 - \alpha_c} \quad (1)$$

As applied to weak electrolytes the constancy in K was sufficient to validate the theory. In fact the theory had such overwhelming success, that it obscured a basic theoretical weakness revealed by the inconstancy of K for strong electrolytes.

Due to this failure of the Arrhenius theory, many early workers in this field were led to tentatively accept the concept of complete dissociation. A typical early statement of this view is given for example by Noyes and

MacInnes (2) wherein changes in conductance are related not to changes in the extent of dissociation, but rather to changes in ionic mobility. It was also recognized by van Laar (3) that contrary to the Arrhenius theory, ions, due to their strong electrostatic forces, were not independent of each other.

On the basis of complete dissociation Debye and Huckel (4) successfully accounted for these factors in their interionic attraction theory. They took as their model the simplest case; viz, a spherical ion surrounded by a symmetrical ionic atmosphere of opposite charge. On this basis they derived a function relating the activity and concentration. Application to the problem of conductance as extended by Onsager (5) resulted in the familiar Onsager conductance equation:

$$\Lambda_c = \Lambda_o - \left[ \frac{.9384 \times 10^6 \omega \Lambda_o}{(D_o T)^{3/2}} + \frac{28.94(Z_+ + Z_-)}{\gamma_o (D_o T)^{3/2}} \right] \sqrt{(Z_+ + Z_-)c} \quad (2)$$

where

$$\omega = (Z_+ + Z_-) \left[ \frac{2g}{1 + \sqrt{g}} \right] \quad \text{and} \quad g = \frac{(Z_+ + Z_-) \Lambda_o}{(Z_+ + Z_-) (Z_+ \lambda_o^2 + Z_- \lambda_o^2)}$$

For uni-univalent electrolytes in water at 25°C, this reduces to

$$\Lambda = \Lambda_o - \left[ 0.2273 \Lambda_o + 59.78 \right] \sqrt{c} \quad (3)$$

which is identical in form to the empirical Kohlrausch relationship (6).

The Debye-Huckel theory led to a vast amount of research in the region of the dilute solution which effectively verified the theory as



applied to this region. The fact that exact agreement was reached only for extremely dilute solutions is not surprising since the theory itself, aside from any mathematical simplifications, was derived on the basis of an infinitely dilute solution.

Attempts were made to extend the theory to higher concentrations by correcting for mathematical simplifications or accounting for factors not originally considered, but such attempts have failed to account for strong solutions.

Other workers have proposed empirical equations, such as that of Jones and Dole (7),

$$\Lambda_c = \Lambda_o - \frac{A \sqrt{C}}{1 + G \sqrt{C}} - KC \quad (4)$$

where A, G, and K are constants, and Shedlovsky's (8),

$$\Lambda_c = \Lambda_o - (A + B \Lambda_o) \sqrt{c} - Cc + Dc \log c + Ec^2 \quad (5)$$

where A, B, C, D, and E are constants. Such attempts fail to be valid beyond 0.1 N.

An excellent review of the interionic attraction theory is given by Scatchard (9), and its application to conductance by MacInnes, Shedlovsky, and Longworth (10). For detailed discussion the comprehensive work of Harned and Owen (11) is recommended.

## B. The Dissociation of Electrolytes.

The great success of the Debye-Hückel theory fully justified its assumption of the complete dissociation of strong electrolytes in dilute solution, but its application has not been confined solely to strong electrolytes, one of its greatest successes being its application to weak and moderately strong electrolytes.

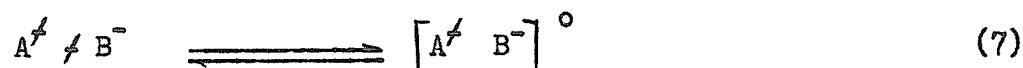
Basing their work on the Onsager theory of conductance, MacInnes (12) and MacInnes and Shedlovsky (13) arrived at a method for determining the thermodynamic dissociation constant of weak electrolytes. Likewise Gross and Halpern (14), Sherril and Noyes (15), and MacInnes (16) have developed methods of finding the dissociation constant for moderately strong electrolytes. Attempts were also made, notably by Davies (17), to extend these considerations to strong electrolytes. However, as pointed out by Redlich (18), the accuracy of such determinations decreases as the ratio of ions to molecules increases so that while it may be valid for weak electrolytes, for strong electrolytes the uncertainty becomes extremely great. Nonetheless it does represent an early attempt to account for the failure of the Debye-Hückel theory in concentrated solutions. This failure, due to the fact that short range non-symmetrical forces could not be accounted for by the Debye-Hückel theory, led to a great deal of speculation on the problem of ionic interaction.

It was to account for these short range forces that Bjerrum (19) introduced the concept of the ion-pair. On the basis of the simplest model, that of a rigid unpolarized spherical ion in a medium of fixed macroscopic

dielectric constant, neglecting all quantum forces and any solvent-solute interaction, Bjerrum was able to equate the potential energy resulting from the electrostatic forces between the ions to the mean kinetic energy at various interionic distances and to arrive at a degree of ionic association. He found the minimum distance for which association can occur to be:

$$r_{\min} = \frac{\epsilon^2 |Z_+ Z_-|}{2 DkT} \quad (6)$$

Ions approaching to within this distance form ion-pairs which are purely electrostatic in character and which can be represented by an equilibrium reaction:



It follows that  $r_{\min}$  is a maximum for ions of maximum charge in solutions of low dielectric constant. For a solution of a uni-univalent salt in water at 25°C,  $r_{\min}$  is 3.5 Å.

As originally proposed, the concept was meant to account for short range ionic forces, water molecules were not precluded from existing between the ions of a pair, and the ion-pair itself was not necessarily taken as a fixed entity. The now untenable theoretical foundation of the theory makes it difficult to arrive at any consistent physical picture on this basis.

The work of Fuoss and Kraus (20) on tetraisoamylammonium nitrate in dioxane-water mixtures of dielectric constant 2.1 (dioxane) to 78.54 (water) showed that ionic association occurred in solvents of dielectric constant less than 43.6. From this they deduce that in aqueous solution ion

association of the type they investigated is not present. The value of 43.6 is not a constant however, but is dependent on the particular system, although it is always in the region of 40. Thus Daly and Smith (21) in their work on KCl in mixed solvents, propose ion association in the region of dielectric constant less than 50-60. Fuoss and Kraus in later papers (22) introduced the concept of triple ions, and ion complexes. The length to which such considerations have been carried is to be gained from a recent review by Kraus (23) in which association numbers (formula weights per mole) as high as 22 are deduced. A related point of great interest is the fact that the association numbers pass through a maximum and then rapidly fall off. Kraus admits that beyond say 1 N the factors causing ion association in dilute solution may no longer be dominant. The clarification of this point awaits more extensive experimental work,

Thus from the data of Fuoss, Kraus, etc., we can say that ion complexes exist in solutions having solvents of dielectric constant less than approximately 45 and for concentrations less than 1 N. The actual nature of these complexes has not been clearly established. Due to their great complexity they must have real rather than transient lifetimes. Whether electrostatic forces alone are sufficient to explain fully such cases is an open question.

The firmest advocate of the ion-pair theory as applied to aqueous solutions is undoubtedly Kasimir Fajans, basing his convictions on his enormous series of refractometric measurements extending over almost thirty years (24). In a recent paper (25) he states, "Since 1927 the view has

been held (presumably by Fajans) that the change of the apparent molar refraction of strong electrolytes with concentration is due to the formation of combinations of oppositely charged ions coming in direct contact with each other without water molecules between them, ie. due to the formation of undissociated particles." Fajans takes these neutral particles to be bound by purely electrostatic forces, in fact he compares them to the idealized heteropolar bond. As evidence that such bond types are possible he points to gaseous NaCl. Several objections can be raised against Fajans theories. Experimentally, ion-solvent effects are significant and are difficult to distinguish from ion-ion effects. The concept of the pure bond must be regarded with scepticism since such bonds are by their nature mere abstractions. Further, it is difficult to conceive of two ions existing in intimate contact and yet showing no distortion of their electronic atmospheres, ie. not sharing electrons to some extent. Nevertheless the experimental data of Fajans are most impressive and are rightly interpreted as indicating intimate ionic interactions.

If the existence of ion-pairs in the sense used here (ie. particles involving only electrostatic forces) is admitted, there is no obvious reason why the existence of true molecular species may not also be allowed. Thus the electronegativity of silver 1.8, as compared with hydrogen 2.1, makes one wonder why molecular silver nitrate is not considered in concentrated solution whereas molecular nitric acid is. Yatsimirskii (26) claims that complexes of the type  $[\text{Ag}(\text{NO}_3)_2]^-$  exist in strong solutions. In fact Davies, Rogers, and Ubbelohde (27) on the basis of the low melting points and large

values of the entropies of fusion of the group I nitrates have suggested that ionic association may be significant in the melts. Thus for silver nitrate they suggest  $[\text{Ag}(\text{NO}_3)_2]^-$  and  $[\text{Ag}_2(\text{NO}_3)]^+$  as examples. As pointed out by the referee in a footnote, low melting points are characteristic of compounds containing irregularly shaped ions, and hence may bear no relationship to complex formation aside from purely electrostatic interactions.

From the foregoing it is obvious that the whole subject of complex formation in solution is most confusing. An unambiguous means of discriminating between simple electrostatic interactions and true bond formation, as suggested by Redlich (28), is the vibrational spectra determined by Raman and infra-red studies.

If two ions unite to form a molecule, at least one translational mode is transformed into a vibration; hence the vibration spectrum differ in the two cases. This of course is the case regardless if the ions themselves are of a type giving rise to vibration spectra (such as  $\text{SO}_4^{--}$ ,  $\text{NO}_3^-$ , etc.). The vibration spectrum of an ion is for the most part independent of its environment, but any direct interaction with other ions will modify this spectrum. Bond formation will give rise to new lines. On the other hand the complete absence of vibration spectra cannot be taken as absolute proof of complete dissociation into ions in the case of a material such as sodium chloride. Because of the great polarity of a sodium chloride bond, if it existed in solution, the Raman spectrum could be completely masked. It is possible however that the infra-red spectrum may offer less doubtful

evidence in such a case. Thus although the method is itself theoretically sound, the technique yields rather crude data as results.

The deduction of the structure of nitric acid (28) is a classic case illustrating the use of Raman spectra. It depends however on the interpretation of the spectrum of sodium nitrate. Since no vibration spectrum for sodium nitrate is found it is taken to be completely dissociated at all concentrations. For nitric acid then, lines of equal intensity to those of the sodium nitrate are assumed to be points of equal nitrate ion concentration.

The underlying assumption regarding the complete dissociation of materials such as sodium nitrate is that ion-pairs do not generate vibration spectra, hence are not true molecules, and hence can have only a statistical significance. Thus Redlich in the paper on nitric acid referred to above admits that ion-pairs undoubtedly exist. Effectively then the ion-pair is reduced to an indication of the fact that in solution ions of opposite charge come into close contact for a period of time less than their vibrational period and effectively can be considered to act as a neutral particle.

The assumption that the ion-pair is a statistical phenomenon thus leads to the structural concept of the concentrated solution which is also statistical. Evidence for definite structures in concentrated solutions exists. Thus Prins and Fontayne (29), Beck (30), and Michelsen (31), by means of X-ray diffraction detected definite regularities in the arrangement of the ions. The scarcity of such data is an indication of the great experimental difficulties involved. It

might be noted that in more dilute aqueous solutions the structure of water, originally proposed by Bernal and Fowler (32), may have significant influence on the distribution of ions. In more concentrated solutions, however, such water structures are completely disrupted.

Raman spectra also support a structural concept. A most interesting paper along this line is that of Mathieu and Lounsbury (33), which is a study of the Raman spectra of a series of metallic nitrates over a wide region of concentration. Their interpretations are based on the shifts in wave length and intensity of the lines due to the nitrate ion (no lines due to molecules of the type  $XNO_3$  being detected). At lower concentrations they explain such effects as due to the formation of ion-pairs, although the sense in which they use this term is not clear. At greater concentration however, the much more profound modifications are best explained on a structural model. The fact that changes in wave-length as well as intensity occur indicates that something more profound than a change in the concentration of some particular species has occurred. These observations are supported by the work of Freymann et al (34), and Tomitsu and Nishi (35) on the Raman spectra of ammonium nitrate at various concentrations.

The preceding discussion was made primarily with the aqueous solution in mind. It is possible however to extend these arguments to non-aqueous solutions. The "dissociating" power of a solvent is a function of its dielectric constant. As pointed out above, when the dielectric constant approaches a value around 45, some type of complex is formed. More generally the conducting properties decrease with decreasing dielectric constant of



the solvent. This is borne out by the experimental work of Walden (36). Paralleling a decrease in dielectric constant is a decrease in the maximum attainable concentration at any given temperature.

From a structural point of view, it readily follows that as dielectric constant and concentration are reduced, the possibility of a statistical structure decreases, whereas the possibility of complex formation (ion-pairs etc.) increases.

It is obvious that no firm conclusions can be drawn on the basis of the fragmentary data existing at present on ionic interaction in solution. As Redlich (37) states in his excellent review of this topic, the existence of ion-aggregates in strong solutions of strong electrolytes has not been demonstrated. Whether the concept of the ion-pair can be sustained or whether it will be absorbed in a more general theory based on statistical-structural concepts as suggested here, must await further experimental investigation.

### C. The Solvation of Ions

The solvation of ions in solution is now a generally accepted fact in spite of the great difficulties met with in determining experimentally its extent. Most work has been done on polar solvents, particularly water.

One of the principle reasons leading to the hydration theory was the anomalous conductances of the ions of the alkaline metal series. The ions of this series, have their conductances in the order  $\text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Rb}^+ < \text{Cs}^+$ . Similarly the crystallographic radii are in the order

$\text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Rb}^+ < \text{Cs}^+$ . On the other hand in the anhydrous melts of their salts, the order is reversed (37). Since the size of the ions is the only major factor influencing the conductance in such a series, the conclusion is drawn that the lithium ion has the largest and the cesium ion the smallest effective radius in solution. Hydration is the only logical explanation of such facts. Supporting evidence is to be found in the conductances of the rare earth chlorides and bromides (39). In this case again, the conductance is found to increase with increasing crystallographic radii.

Other evidence for ionic hydration exists including color changes on solution and deviations from Beers Law.

Not only has it proven difficult to determine experimentally the degree of hydration or the hydration number, but an unambiguous definition of these terms has not been established. This arises because hydration numbers are reported in two different manners, depending on the method of determination.

A first group can be taken to represent a fairly tightly held uni-molecular layer somewhat similar to the coordination complexes of the ions. It represents at any rate a minimum value. A second value larger in magnitude apparently includes all water molecules "influenced" by the ion in question. The usual conception of a hydrated ion is one surrounded by gradually less tightly held water layers. This is disputed by Sanilov (40) who allows only average hydration numbers assuming that there are no tightly held water molecules.

In their classic paper on the structure of water, Bernal and Fowler (32) proposed a hydration model based on the manner in which the various ions are coordinated with the water molecules. The resultant hydration number at least represents a minimum value. They deduced this to be four for all monovalent ions in dilute solution. More recently Mishchenko (41), on the same basis, employing a slightly different water model, has arrived at a different series of values; viz, Li 4; Na 6; K 8; Rb 8; Cs 8; F, Cl, Br, 8. These values are obviously contrary to what is expected on the basis of the conductance data previously cited. They really have value only in indicating the extent to which a unimolecular layer may go.

In one of the most interesting of recent papers on the entire field of electrolyte solutions, Hasted, Ritson, and Collie (42) attempt to evaluate hydration numbers from considering the depression in the dielectric constant of water produced by the addition of ions. They assume that the first layer is tightly held and yet they do not deny that water molecules in outer layers may also be rigidly held. Some of their values are as follows;  $H^+$  10;  $Li^+$  6;  $Na^+$  4;  $K^+$  4;  $Rb^+$  4;  $Mg^{++}$  14. These values are in keeping with the order of hydration as derived from conductance data and are best considered as minimum values.

The determination of transference numbers, particularly by the moving boundary technique developed by Lewis (43), seemed to offer a means of determining hydration numbers. The hydration number was found by using an inert material to measure the change in water concentration at each

electrode, but, the values so obtained were only relative since as Longworth (44) pointed out, the hydration numbers were dependent on the particular inert material employed; in effect, the inert material was not inert. Likewise the values of Remy (45) based on a value of one for the hydrogen ion can only be taken as relative values.

The above considerations are really applicable only to dilute solutions. Their application to concentrated solutions, in which the number of ions may exceed the number of water molecules, is not possible. On the other hand the nature of the ion-solvent interaction is of interest, since if water molecules are rigidly held by ions, there will be great competition to hold these water molecules in concentrated solutions.

#### D. Effect of Temperature on Conductance.

The equivalent conductance of an electrolytic solution increases with temperature to a maximum value and then falls off. In the case of aqueous solutions the maximum occurs close to the critical temperature of water (46). For non aqueous solutions it occurs at lower temperatures and is in many cases a function of the concentration.

For silver nitrate and ammonium nitrate solutions up to 95°C, Campbell and Kartzmark (47) have shown that the conductance varies almost linearly with temperature, and can be represented by the equation

$$\Lambda_{t^{\circ}} = \Lambda_{25^{\circ}} [1 + \beta(t^{\circ} - 25^{\circ})] \quad (8)$$

where  $\beta$  is the temperature coefficient of conductance.

Noyes (48) has also observed such linear relationships extending in some cases as high as  $160^{\circ}\text{C}$ .

The reasons for such behaviour are not clear. As shown by the work of M. E. Bednas on silver nitrate solutions at  $221.7^{\circ}\text{C}$  and the present work on ammonium nitrate solutions at  $180^{\circ}\text{C}$ , the linear relationship disappears beyond  $95^{\circ}\text{C}$ .

Any increase in temperature will alter the mobility, extent of "association", degree of hydration (assumed), and dielectric constant of the solvent all in a manner such as to favor an increase in conductance. That such a complex series of factors should allow a linear relationship to exist considering the non-linear fluidity relationship is indeed strange.

Further, the nature of the opposing forces accounting for the existence of a maximum are not clear. They may of course be related to the solvent itself since for water as noted, the maximum is close to the critical temperature.

This aspect of the problem however remains vague on the basis of existing data.

#### E. Conclusions.

From the inconclusive nature of the discussion it follows that no firm conclusions on the true nature of the concentrated electrolytic solution can be drawn. Nonetheless it is encouraging to note the revival of interest in this relatively neglected aspect of solution chemistry.

There are already several plausible theoretical approaches to this problem and it is hoped that work along these divergent paths will eventually lead to a unified theoretical foundation to this fundamental problem.

SURVEY OF THE LITERATURE

## II. SURVEY OF THE LITERATURE

The conductance of dilute solutions of ammonium nitrate has been investigated by several workers at a series of temperatures (49) (50) (51).

Rabinowitsch (52) gives data on the conductance of ammonium nitrate solutions at 100°C over the range .1 N to 15 N, accurate to 1%.

Much more accurate data at 95°C have been obtained in this laboratory (47). Likewise, accurate data at 25° (53) and 35° (54) were obtained.

No data exist in the literature for conductance of ammonium nitrate solutions at elevated temperatures and concentrations.



NATURE OF THE PROBLEM

### III. NATURE OF THE PROBLEM

As even the most casual survey of the literature of conductance will reveal, the concentrated solution has been almost completely neglected. One of the few cases in which a study over the complete concentration range has been made is that of sodium hydroxide (55). Such an electrolyte is not characteristic however, since the hydroxyl ion interacts too readily with the water structure in aqueous solution.

In view of this dearth of data, it was decided in this laboratory to undertake a comprehensive survey of the conductance and viscosity of suitable electrolytic solutions at a series of temperatures such that eventually the complete concentration range could be covered. For this purpose the salts ammonium nitrate (m.p.  $169.6^{\circ}\text{C}$ ) and silver nitrate (m.p.  $212^{\circ}\text{C}$ ) were chosen. Their melting points are sufficiently low to allow a complete coverage of the concentration range.

Preceding workers have determined the conductance and viscosity of solutions of ammonium nitrate and silver nitrate at  $25^{\circ}\text{C}$  (53),  $35^{\circ}\text{C}$  (54), and  $95^{\circ}\text{C}$  (47). The conductance of silver nitrate solutions over the complete range at  $221.7^{\circ}\text{C}$  has been determined by M. E. Bednas (unpublished). The present work on the conductance of ammonium nitrate solutions over the complete range at  $180^{\circ}\text{C}$  thus represents a completion, for the moment at any rate, of the conductance work on this particular pair of electrolytes. The viscosity data for these later two remain undetermined pending development of a suitable technique.

## EXPERIMENTAL TECHNIQUE

#### IV. EXPERIMENTAL TECHNIQUE

##### A. Purity of Materials.

The ammonium nitrate was obtained in bulk from the Consolidated Mining and Smelting Company, Trail, B.C. It was re-crystallized twice from water, dried over porous plates, and stored over sulphuric acid in a desiccator.

The potassium chloride used as a standard in the determination of the cell constants was a Merk reagent grade product. It was fused in a platinum dish and stored over sulphuric acid.

##### B. Conductance Measurements.

###### (1) The Bridge.

The bridge employed was a Campbell-Shackleton Bridge as designed by the Leeds and Northrup Company. Detection was made by means of a telephone head-piece. The accuracy claimed by the manufacturers was  $\pm 0.05\%$ . Detailed specifications are given in the Leeds and Northrup pamphlet "Directions for Capacitance and Conductance Bridge using No. 1553 Shielded Ratio Box."

###### (2) The Conductance Cells.

Three types of conductance cell were employed in this research. For use in the bomb (q.v.) in determining the conductances of the ammonium nitrate solutions, a compact vertical cell as shown in Figure I was used. Such cells would be expected to show the Parker effect (56), i.e., errors in measurement due to shunt currents set up in the filling tubes which

run parallel to the solution between the electrodes, but for highly conducting solutions as used here, such effects are negligible.

A second type of cell was used in determining the conductance of the anhydrous melt. It is shown in Figure 2 along with its filling apparatus.

The third type of cell was used for analyses at 25.000°C. It was a horizontal type of cell with filling tubes widely separated.

The cells were not platinized. After use, the cells were flushed with water and washed with alcohol and then ether and stored dry.

### (3) The Cell Constant.

The cell constants were determined using potassium chloride as a standard. The solutions were made up according to the specifications of Jones and Bradshaw (57), on the basis of their defined solutions which at 25°C are as follows:

71.1352 grams of potassium chloride  
per 1000 grams of solution in vacuum:  
conductivity  $\times 10^6 = 111342$  mhos.

and

7.41913 grams of potassium chloride  
per 1000 grams of solution in vacuum:  
conductivity  $\times 10^6 = 12856.0$  mhos.

In actual practice only 1000 grams of solution were made up. The salt was weighed to 0.005% (for a .1 N solution) and the solution to 0.002%.

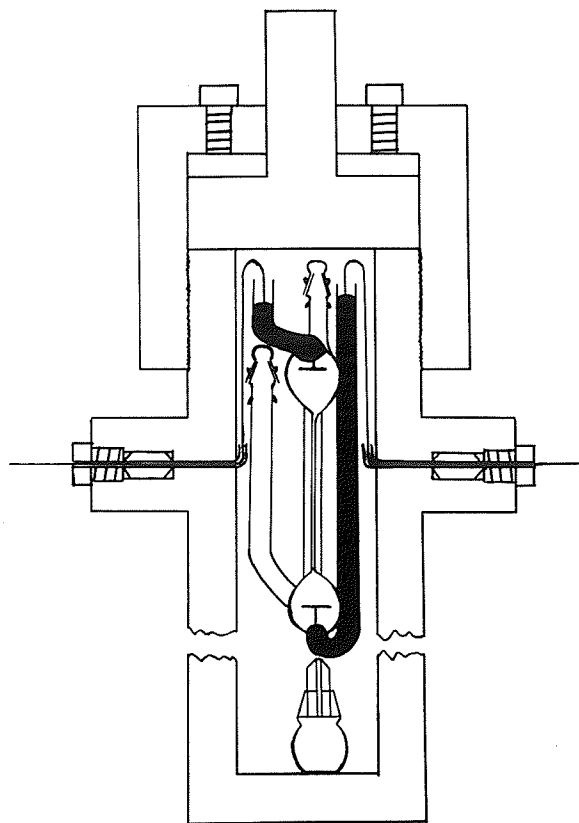


Figure 1  
Bomb, conductance cell, and pyknometer

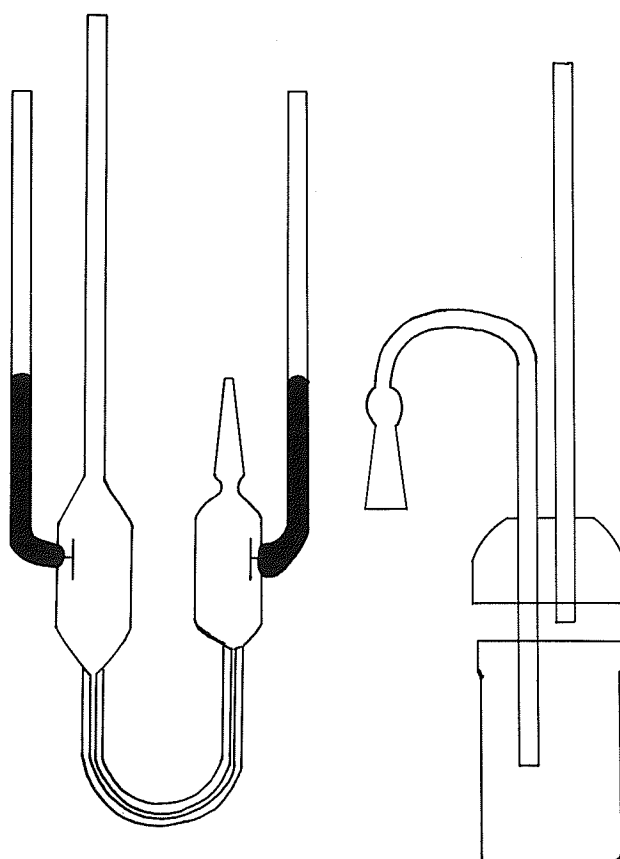


Figure 2  
Apparatus for molten salts

Since no standard existed at 180°C for the determination of cell constants, it was necessary to apply a correction to the value found at 25°C. Such corrections due to geometry changes of the cell are discussed by Washburn (58), and in the present case reduce to a simple linear expansion correction.

This is readily seen by considering the effect of temperature changes on the cell constant (Z). The latter is defined as the ratio of the length (l) of solution between the electrodes, to the effective areas (a) of solution between the electrodes.

$$\text{ie. } Z = l/a \quad (9)$$

Differentiating with respect to temperature gives

$$\frac{dZ}{dt} = \frac{1}{a} \frac{dl}{dt} = \frac{1}{a^2} \frac{da}{dt} \quad (10)$$

$$\text{But } \frac{dl}{dt} = \beta (l + s) - \gamma s \quad (11)$$

Where  $\beta$  = Coefficient of linear expansion of Pyrex glass,  
 $s$  = Length of electrode posts, and  
 $\gamma$  = Coefficient of linear expansion of platinum.

For cells having a long capillary separating the electrodes, (11) reduces to

$$\frac{dl}{dt} = \beta l \quad (12)$$

$$\text{Also } \frac{da}{dt} = 2\beta a \quad (13)$$

$$\text{Hence } \frac{dZ}{dt} = \frac{1}{a} \beta l \approx \frac{1}{a^2} \cdot 2\beta a = 2\beta \frac{Z}{a} \quad (14)$$

Thus the cell constant at 180° was equal to the product of the cell constant at 25°C, the coefficient of linear expansion of Pyrex glass, and the temperature interval. The resultant correction was of the order of .5%

The cell constants were periodically redetermined.

#### (4) The Bomb.

Since the solutions in this research were all above their normal boiling points at 180°C, the conductance cell and density bottle were enclosed in a bomb. For this purpose a standard steel bomb was obtained from the American Instrument Company. The electrical leads were enclosed in Teflon tubing for insulation, and the bomb made air-tight by crushing soapstone cones together under pressure. The bomb is shown in Figure I indicating the placement of the cell and density bottle.

#### C. The Thermostat.

The thermostat employed (Figure 3) was designed by M.E. Bednas. It consisted of a rectangular copper tank of approximately eight gallon capacity. This was set in an outer steel tank insulated with an inch of powdered asbestos. This entire set up was enclosed in a wooden box with



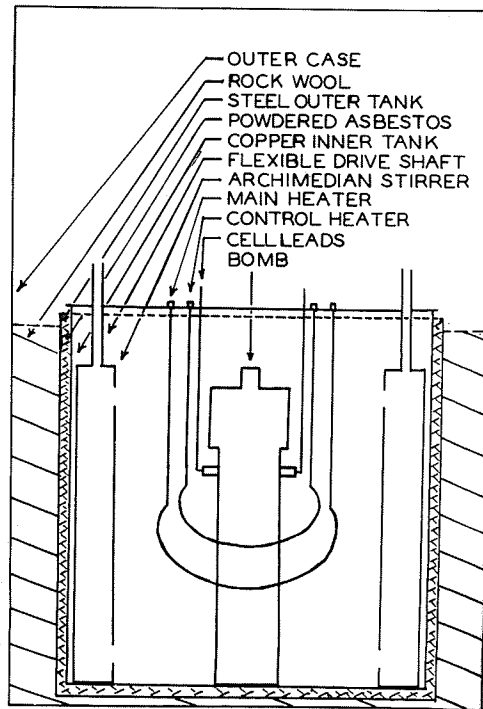


Figure 3  
Thermostat

hinged doors on front and a hinged top. Rock wool was packed between the box and steel tank.

The thermostat fluid was Sturbinol 65 supplied by the Imperial Oil Company.

The thermostat was heated by means of two copper tube heaters, one large heater maintaining a falling temperature at 180°C, and a smaller one acting as a control through a mercury in steel regulator connected to a standard relay.

The large heater eventually burned out and was replaced by two immersion type engine block heaters which proved to be satisfactory.

Two large Archimedean stirrers were sufficient to achieve very efficient stirring.

Temperature was measured with a Beckmann thermometer which was frequently calibrated against a standard platinum resistance thermometer. As an added precaution to guard against violent fluctuations in the Beckmann calibration, a mercury in glass thermometer reading in tenths was calibrated and set beside the Beckmann.

It was possible to maintain the temperature within  $\pm .05^{\circ}\text{C}$ . Due to the thickness of the bomb, the actual fluctuations of temperature in the solutions themselves would be even less.

#### D. Preparation of Aqueous Solutions.

The solutions were prepared by weight up to saturation at room temperature. In each case 100 ml. of solution was prepared. The salt was weighed out to a tenth of a milligram and the solutions to a milligram.

This introduces an error due to weighing of the order of 0.005%.

To prepare solutions beyond the saturation point at room temperature, a special technique was employed. The components to prepare approximately 100 grams of solution at the approximate weight per cent desired were placed in a flask, heated to bring about solution, and finally refluxed to drive off air which might later form air bubbles in the cell and thus cause an infinite resistance to be set up.

The flask containing the solution was then transferred to a small oil bath kept at a temperature sufficient to maintain complete solution. By means of ground glass joints, it was possible to connect an outlet from the solution flask to a receiving vessel (density bottle or conductance cell); employing special clamps, it was then possible to immerse the entire system in the oil bath. Naturally each vessel had a small second outlet coming above the surface of the bath. During immersion, it was possible by gently applying suction and compression to the inlet of the solution flask, to achieve a reasonable degree of final mixing. (Care was taken that no bubbles were generated during this step.)

By the application of pressure on the inlet tube of the solution flask, solution was forced first into the density bottle. Upon completion of the filling the whole system was lifted from the bath and the density bottle removed, rapidly capped, and placed in the bottom of the bomb. The conductance cell was now connected up as the receiving vessel, the system immersed, and the cell filled as before. It was removed when full and placed in the bomb. Finally a portion of the solution was forced over into a weighing bottle.

The various operations were carried out as rapidly as possible to minimize changes in concentration of the hot solution during the procedure. At higher concentrations the bomb itself was heated to prevent salt coming out of solution. The bomb was sealed rapidly and placed in the thermostat.

The sample drawn off into the weighing bottle was weighed, diluted to 100 ml. and reweighed. Its specific conductance at 25°C was then determined. From the data of Campbell and Kartzmark (53) on the conductance of ammonium nitrate at 25°C, it was thus possible to interpolate to get the weight per cent of the solution. This procedure introduced an uncertainty of the order of  $\pm 0.05\%$  into the calculated weight per cent. (ie. the uncertainty involved in the work at 25°C.).

#### E. Densities.

In the determination of densities, a Weld pyknometer of 10 ml. capacity was employed. The pyknometer was calibrated with water at 25°C and with glycerol at 180°C. On the basis of the water calibration at 25°C, the volume at 180°C was calculated using the formula:

$$V_{180^{\circ}} = V_{25} (1 \mp \gamma t) \quad (15)$$

where  $t$  was the temperature interval and  $\gamma$  was the coefficient of cubical expansion of Pyrex glass.

The two calibrations checked to 0.1% which was satisfactory.

In each case the pyknometer was weighed to a tenth of a milligram but no density is quoted to more than four figures due to the inherent difficulties and uncertainties involved in determining densities at such great concentrations and at such high temperatures.

#### F. Measurements with the Anhydrous Salts.

The anhydrous salt required an approach differing from that used for aqueous solutions. A bomb was not employed in determining the conductances, since at its melting point anhydrous salt has a vapour pressure sufficiently low to permit the work to be done in the open laboratory. The cell used is shown in Figure 2 along with the filling apparatus.

A charge of ammonium nitrate was placed in the bottle, and the apparatus connected through its ground glass joints. The whole set up was then immersed in an oil bath maintained at approximately  $175^{\circ}\text{C}$ . When the charge had melted, it was forced over into the cell by the alternate application of suction and compression. When the electrodes were completely immersed in molten salt, the cell was removed from the small bath and clamped (less the filling apparatus) into the large thermostat.

Obviously temperature control in this case is not as good as when a steel bomb is used.

The density of the anhydrous melt was done as before in a Weld pyknometer immersed in a small oil bath. Several determinations were made and a mean value taken.

## EXPERIMENTAL RESULTS

## V. EXPERIMENTAL RESULTS

The experimental data of this research are shown in Table I which lists the weight per cent, normality, density, specific conductance, and equivalent conductance of ammonium nitrate solutions at 180°C.

Plots of specific conductance and equivalent conductance vs. concentration are shown in Figures 4 and 6 respectively along with other plots which are explained in a later section.

TABLE I

Conductances and Densities of Aqueous  
Ammonium Nitrate Solutions at 180.0°C

<u>Weight %</u>	<u>Specific Conductance in Mhos.</u>	<u>Density g/ml.</u>	<u>Molarity</u>	<u>Equivalent Conductance in Mhos.</u>
0.7984	0.0474	0.8919	0.0890	532.3
8.5160	0.3752	0.9276	0.9868	380.2
16.077	0.6192	0.9571	1.922	322.2
24.028	0.8172	0.9935	2.982	274.0
24.028	0.8165	0.9955	2.988	273.3
32.141	0.9718	1.030	4.136	235.0
38.692	---	1.062	5.133	---
38.692	1.058	1.061	5.128	206.1
45.215	1.100	1.099	6.207	177.2
50.190	1.119	1.121	7.029	159.2
54.907	1.122	1.145	7.854	142.9
58.590	1.118	1.166	8.534	131.0
61.995	1.104	1.184	9.170	120.4
66.71	1.063	1.218	10.15	104.7
66.85	1.050	1.213	10.13	103.7
71.20	1.014	1.231	10.95	92.60
76.42	0.9338	1.272	12.14	76.92
78.84	0.8828	1.290	12.70	69.51
83.78	0.7881	1.322	13.84	56.94
85.15	0.7817	1.326	14.11	55.40
88.50	0.7003	1.355	14.98	46.75
100.00	0.433	1.44	18.0	24.1



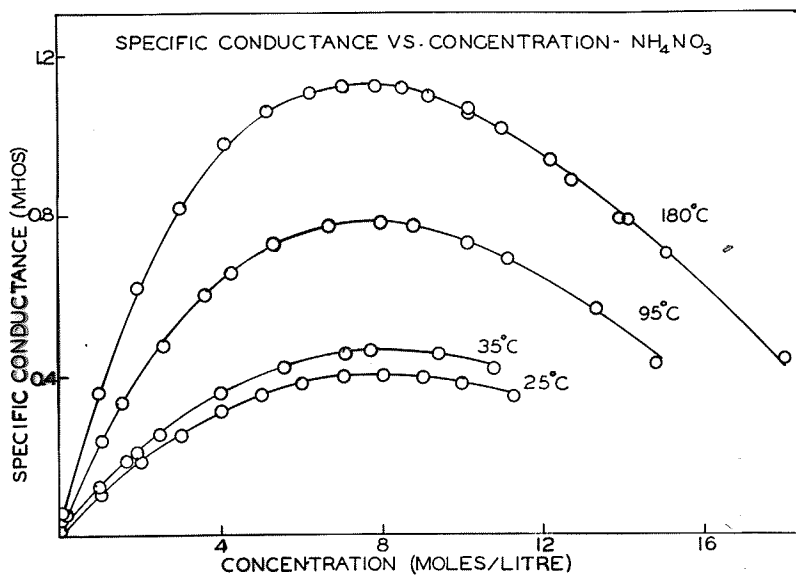


Figure 4  
Specific conductance vs. concentration for ammonium nitrate

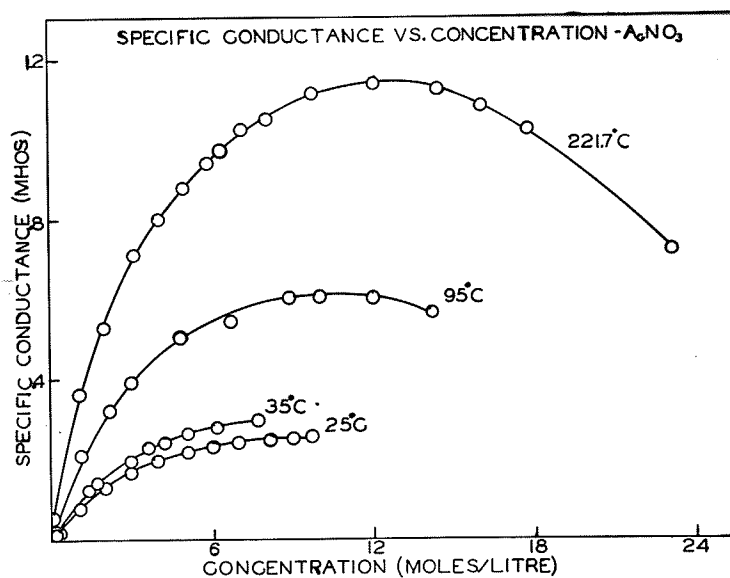


Figure 5  
Specific conductance vs. concentration for silver nitrate

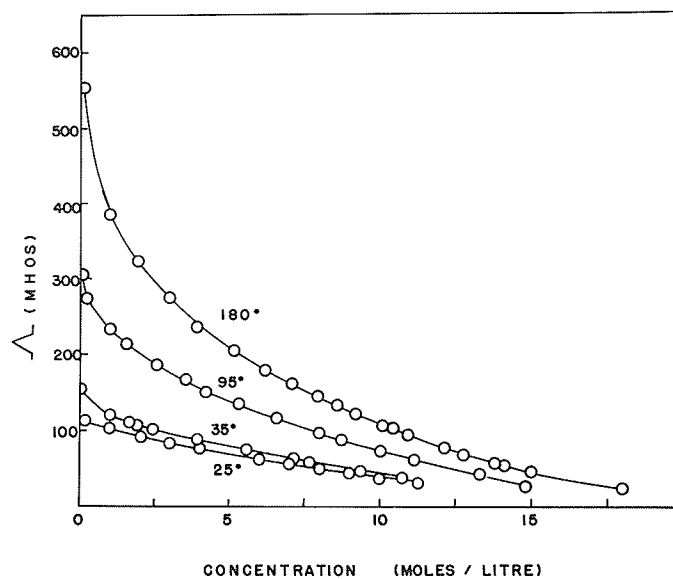


Figure 6  
Equivalent conductance vs. concentration for ammonium nitrate

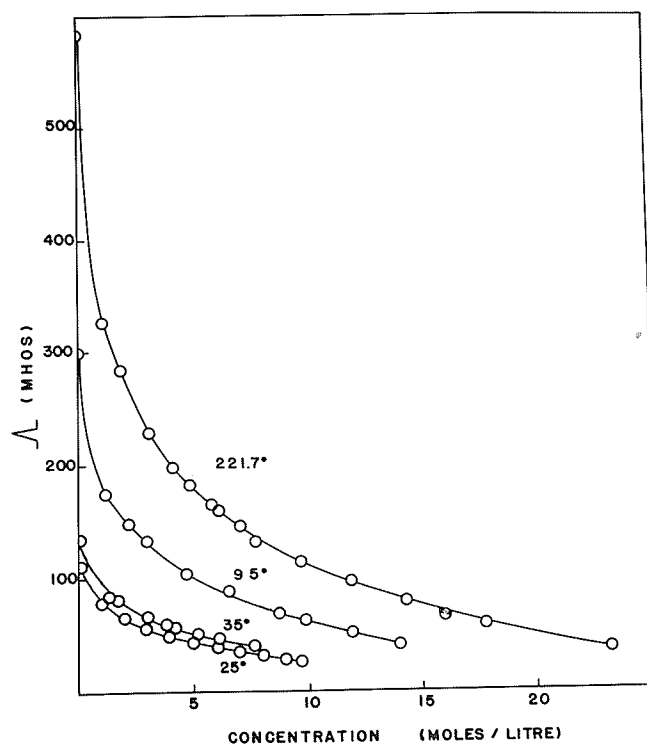


Figure 7  
Equivalent conductance vs. concentration for silver nitrate

## DISCUSSION OF THE RESULTS

## VI. DISCUSSION OF THE RESULTS

### A. Estimation of Error.

Wherever possible, the uncertainties involved in any value have been indicated.

There are three major sources of error, viz., the weight per cent, the density, and the temperature.

For those solutions prepared exactly by weight, the error involved was  $\pm 0.005\%$ . On the other hand for those solutions for which analyses were required the error in weight per cent was  $0.05\%$ .

The densities are not given to anything beyond four figures i.e. to  $0.1\%$ .

As will be shown later, the average temperature coefficient of conductance over the range of  $95^{\circ}\text{C}$  to  $180^{\circ}\text{C}$  is approximately  $0.006$  mhos per degree. Thus the error involved in a temperature uncertainty of  $\pm .05^{\circ}$  is negligible when compared to the other sources of error.

Thus the limiting value of the error is determined by the densities.

### B. Discussion of the Measured Quantities.

Since the present work represents the conclusion of the first phase at any rate of a series of investigations (53), (54), (47) of the conducting properties of silver and ammonium nitrates over a wide temperature interval (from  $25^{\circ}\text{C}$  to above the melting point of the salt) it is

considered best to present all the data so that they may be readily compared. The conductances of ammonium nitrate solutions have been determined at 25°C, 95°C, and 18°C. Silver nitrate solutions have been determined at 25°C, 35°C, 95°C and 221.7°C.

In Figures 4 and 5 are plotted the specific conductances vs. concentration at all four temperatures for ammonium nitrate and silver nitrate respectively. The maximum in each curve is seen to shift towards higher concentration with increasing temperature. Thus the maximum specific conductance of ammonium nitrate at 180°C is 1.122 mhos at 7.62 molar whereas at 95°C it is 0.787 mhos at 7.28 molar. Similarly for silver nitrate at 221.7°C the maximum shifts from 1.136 mhos at 12.11 molar to 0.607 mhos at 10.7 molar at 95°C. (The method of evaluating these maxima is discussed later).

The significance of these maxima is not as yet clear. Such a maximum is a region in which those factors tending to increase the conductance as the concentration is increased are just balanced by factors opposing an increase in conductance. As the concentration increases, the number of ions available to conduct increases. At the same time however, the ions are in closer contact, and hence their mobility or effective numbers are decreased through their interactions. The shift of the maxima towards higher concentration is thus not surprising since a temperature increase would be expected to reduce the ionic interactions.

This simple picture is complicated by hydration effects. As the temperature increases it would be expected that the extent of hydration

would decrease. Hasted, Ritson, and Collie (42), on the contrary, suggest that hydration increases with temperature. At high concentration however, the number of water molecules available is such that all would be tightly held by the ions. Ionic hydration therefore may have little meaning at high concentration.

In Figures 6 and 7 are plotted the equivalent conductance vs. the molarity at all four temperatures for ammonium nitrate and silver nitrate respectively. The conductance is seen to drop off rapidly with increasing concentration, approaching linearity at high concentration. No minima are observed in the curves.

Of much greater interest are the plots of equivalent conductance vs. logarithm of concentration. This quite empirical plot yielded straight line relationships from below 6 N up to the highest concentration attained. In some cases the straight line could be extended to 2 N. Figures 8 and 9 show this plot for ammonium nitrate and silver nitrate respectively.

It follows from this relationship, that the data can be represented by an equation; viz,

$$\Lambda_c = \Lambda_x + D \log c \quad (16)$$

where  $\Lambda_x$  is the value of  $\Lambda$  at  $\log c = 0$  or  $c = 1$ . Since this form is inconvenient, a different form has been used, ie.

$$\Lambda_c = \Lambda_a - D [\log c_a - \log c] \quad (17)$$

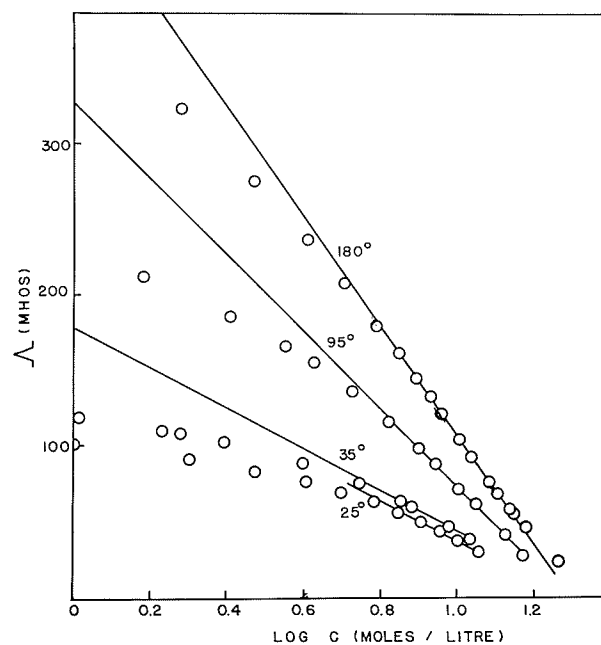


Figure 8  
Equivalent conductance vs. logarithm concentration for ammonium nitrate

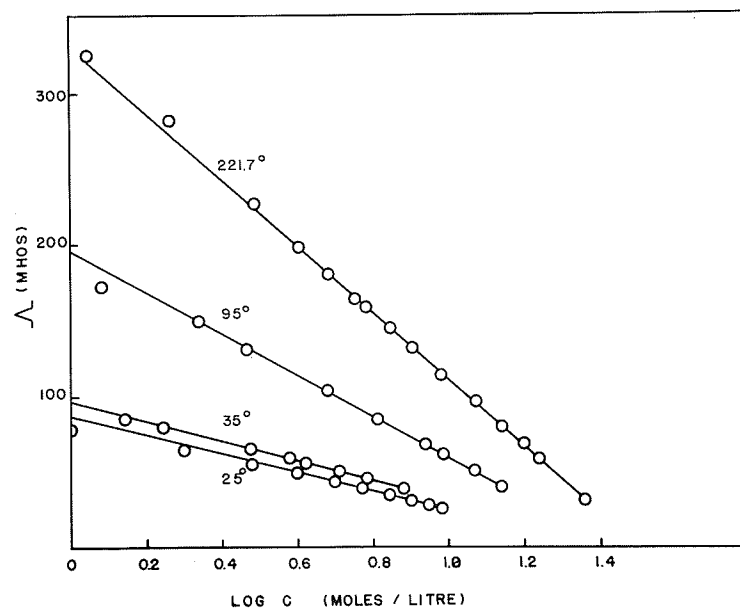


Figure 9  
Equivalent conductance vs. logarithm concentration for silver nitrate

where  $\Lambda_a$  is the equivalent conductance at the limiting experimental concentration  $c_a$ . In some cases however, particularly for the molten salts, the  $\Lambda_a$  value has been extrapolated so as to give a value which actually lies on the line (effectively it becomes an empirical constant).

In order to test this equation, the slopes were evaluated from a large scale plot, and a comparison of calculated and observed values of the equivalent conductance were made for each of the eight sets of data. These values along with the deviations are given in the Tables II to IX inclusive.

The tables show that the calculated conductances differ from the observed values by not more than 2 units over a considerable extent of the high concentration region. The points representing the molten salts are seen to show the greatest variance. Whether this is due to the experimental error involved in their determination which admittedly is considerable or whether this indicates a true deviation from linearity awaits a thorough investigation of 80-100% region.

It has proven difficult to find other data with which to test this linear relationship. Data for sodium hydroxide over the complete concentration range at 18° when plotted showed a positive deviation from linear behaviour over the entire range. However in view of the anomalous conductance of the hydroxyl ion, this is not surprising.



TABLE II.

 $\text{NH}_4\text{NO}_3$  $t = 180.0^\circ\text{C.}$ 

Slope = -342

 $\Delta a = 19.0$ 

Molarity	$\Delta$ calc.	$\Delta$ obs.	( $\Delta$ calc- $\Delta$ obs.)
18.0	19.0 (ext.)	24.1	- 5.1
14.98	46.28	46.75	- 0.47
14.11	55.15	55.40	- 0.25
13.84	58.02	56.94	+ 1.08
12.70	70.81	69.51	+ 1.30
12.14	77.51	76.92	+ 0.59
10.95	92.84	92.60	+ 0.24
10.13	104.41	103.7	+ 0.71
10.15	104.12	104.7	- 0.58
9.17	119.2	120.4	- 1.2
8.534	129.9	131.0	- 1.1
7.854	142.2	142.9	- 0.7
7.029	158.7	159.2	- 0.5
6.207	178.1	177.2	+ 0.9
5.128	205.5	206.1	- 0.6
4.136	237.4	235.0	+ 2.4
2.988	285.7	273.3	+ 12.4
2.982	286.0	274.0	+ 12.0
1.922	351.3	322.2	+ 29.1
0.9868	450.2	380.2	+ 70.0
0.0890	807.5	532.3	+ 275.2

TABLE III

AgNO<sub>3</sub>:

t = 221.7°C.

Slope = -218

 $\Delta a = 32.4$ 

Molarity	$\Delta$ calc.	$\Delta$ obs.	( $\Delta$ calc - $\Delta$ obs.)
23.19	32.4 (ext.)	31.00	/ 1.4
17.71	57.97	57.54	/ 0.43
16.01	67.48	67.71	- 0.23
14.32	78.05	78.34	- 0.29
11.98	94.92	94.78	/ 0.14
9.761	114.3	113.2	/ 1.1
8.124	131.7	129.6	/ 2.1
7.097	144.5	144.2	/ 0.3
6.159	157.9	157.5	/ 0.4
5.763	164.2	163.4	/ 0.8
4.900	179.6	179.8	- 0.2
4.076	197.0	197.0	0.0
3.130	222.0	227.2	- 5.2
1.868	270.9	283.0	- 13.0
1.119	319.3	325.2	- 5.9
0.0965	551.5	581.9	- 30.4

TABLE IV.

NH<sub>4</sub>NO<sub>3</sub>:

t = 95.0°C.

Slope = -252

 $\Delta$  a = 30.3

Molarity	$\Delta$ calc.	$\Delta$ obs.	( $\Delta$ calc. - $\Delta$ obs.)
14.81	30.3	28.71	✓ 1.59
13.31	41.99	42.07	- 0.08
11.13	61.60	61.99	- 0.39
10.12	72.01	72.44	- 0.31
8.74	88.02	88.04	- 0.02
7.95	98.4	97.81	✓ 0.59
6.632	118.2	116.0	✓ 2.2
5.325	142.3	135.6	✓ 6.7
4.221	167.7	154.7	✓ 10.0
3.600	185.1	166.9	✓ 18.2
2.576	221.7	185.6	✓ 35.9
1.525	279.1	213.6	✓ 65.5
0.9963	325.7	234.8	✓ 90.9
0.194	504.8	275.3	✓ 229.5

TABLE V.

AgNO<sub>3</sub>: $t = 95^{\circ}\text{C.}$ 

Slope = -134

 $\Delta a = 41.0$ 

Molarity	$\Delta$ calc.	$\Delta$ obs.	( $\Delta$ calc- $\Delta$ obs.)
14.02	41.0 (ext.)	40.08	$\neq$ 0.92
11.88	50.64	50.35	$\neq$ 0.29
9.906	61.22	61.28	- 0.06
8.83	67.9	68.12	- 0.22
6.591	84.92	84.88	$\neq$ 0.04
4.83	103.01	103.1	- 0.09
2.97	131.32	130.8	$\neq$ 0.52
2.189	149.1	147.8	$\neq$ 1.3
1.220	183.0	172.7	$\neq$ 10.3
0.0534	365.1	298.3	$\neq$ 66.8



TABLE VI.

 $\frac{\text{NH}_4\text{NO}_3}{3}$  $t = 35^\circ\text{C.}$ 

Slope = -136

 $\Delta a = 39.7$ 

Molarity	$\Delta$ calc.	$\Delta$ obs.	( $\Delta$ calc- $\Delta$ obs.)
10.75	39.7 (ext.)	38.52	$\neq$ 1.18
9.409	47.59	47.46	$\neq$ 0.13
7.6705	59.63	59.84	- 0.21
7.1318	63.94	63.86	$\neq$ 0.06
5.5065	79.22	76.46	$\neq$ 2.76
3.9749	98.48	89.17	$\neq$ 9.31
2.4504	127.14	103.2	$\neq$ 23.94
1.9104	141.8	108.2	$\neq$ 33.6
1.6940	151.4	111.0	$\neq$ 40.4
1.0234	188.7	119.4	$\neq$ 69.3
0.0538	352.7	153.1	$\neq$ 199.6

TABLE VII.

AgNO<sub>3</sub>:

t = 35°C.

Slope = -65

 $\Delta a = 39.2$ 

Molarity	$\Delta$ calc.	$\Delta$ obs.	( $\Delta$ calc- $\Delta$ obs.)
7.663	39.2 (ext.)	38.55	≠ 0.65
6.144	45.43	45.28	≠ 0.15
5.1784	50.26	50.32	- 0.06
5.1064	50.66	50.71	- 0.05
4.2306	55.97	56.06	- 0.09
3.8230	58.83	58.91	- 0.09
3.0322	65.38	65.41	- 0.03
1.7757	80.47	79.55	≠ 0.92
1.4023	87.15	85.37	≠ 1.78
0.0986	162.1	132.5	≠ 29.6

TABLE VIII.

 $\text{NH}_4\text{NO}_3$ : $t = 25^\circ\text{C.}$ 

Slope = - 129

 $\Delta a = 31.3$ 

Molarity	$\Delta$ calc.	$\Delta$ obs.	( $\Delta$ calc- $\Delta$ obs.)
11.282	31.3 (ext.)	31.3	0
10.004	38.01	38.19	- 0.08
9.043	43.64	43.93	- 0.29
8.011	50.42	50.36	/ 0.06
7.015	57.85	56.73	/ 1.12
6.036	66.3	63.12	/ 3.18
5.014	76.7	70.00	/ 6.7
4.020	89.06	76.78	/ 12.28
2.982	105.8	84.28	/ 21.92
1.993	128.34	91.95	/ 36.39
1.004	166.8	101.32	/ 65.48
0.100	295.9	122.7	/ 173.2

TABLE IX.

AgNO<sub>3</sub>:

t = 25°C.

Slope = -59

 $\lambda_a = 26.1$ 

Molarity	$\lambda$ calc.	$\lambda$ obs.	( $\lambda$ calc - $\lambda$ obs.)
9.709	26.1 (ext.)	26.1	0
9.010	28.02	27.99	≠ 0.03
8.011	31.03	31.20	- 0.17
7.012	34.44	34.70	- 0.26
6.006	38.41	38.55	- 0.14
5.029	42.96	43.14	- 0.18
4.000	48.83	48.50	≠ 0.33
3.028	55.97	54.97	≠ 1.00
1.998	66.60	64.20	≠ 2.40
1.004	84.24	77.82	≠ 6.42
0.100	143.4	109.1	≠ 34.3



Plots were also made of the data of Rice and Kraus (59) on potassium and cesium formate at 50.5°C. These seemed to show linear relationships at high concentrations, although the data are not extensive enough to be unambiguous.

Thus for ammonium nitrate and silver nitrate solutions, at any rate, a most interesting relationship connecting the equivalent conductance and concentration has been demonstrated in the high concentration region. Whether this logarithmic relationship has a general validity must await the availability of further experimental data.

#### C. Discussion of the Derived Quantities.

It remains to discuss the temperature dependence of conductance. As was previously noted, the conductance of ammonium and silver nitrate solutions up to 95°C was an almost linear function of temperature. However as can readily be seen from Figures 10 and 11 for ammonium nitrate and silver nitrate respectively, this relationship becomes invalid somewhere beyond 95°C. The Figures are drawn showing linear relationships between the values at 95°C and those at 221.7°C or 180°C, but this is merely for convenience, since the intermediate range has not been investigated and hence the shape of the curve is unknown.

Likewise for convenience the temperature coefficients of conductance  $\beta$ , at each normality, have been calculated as defined by the equation

$$\Lambda_{t^{\circ}} = \Lambda_{95^{\circ}} [1 + \beta (t - 95)] \quad . \quad (18)$$

These average values are given in Table X.

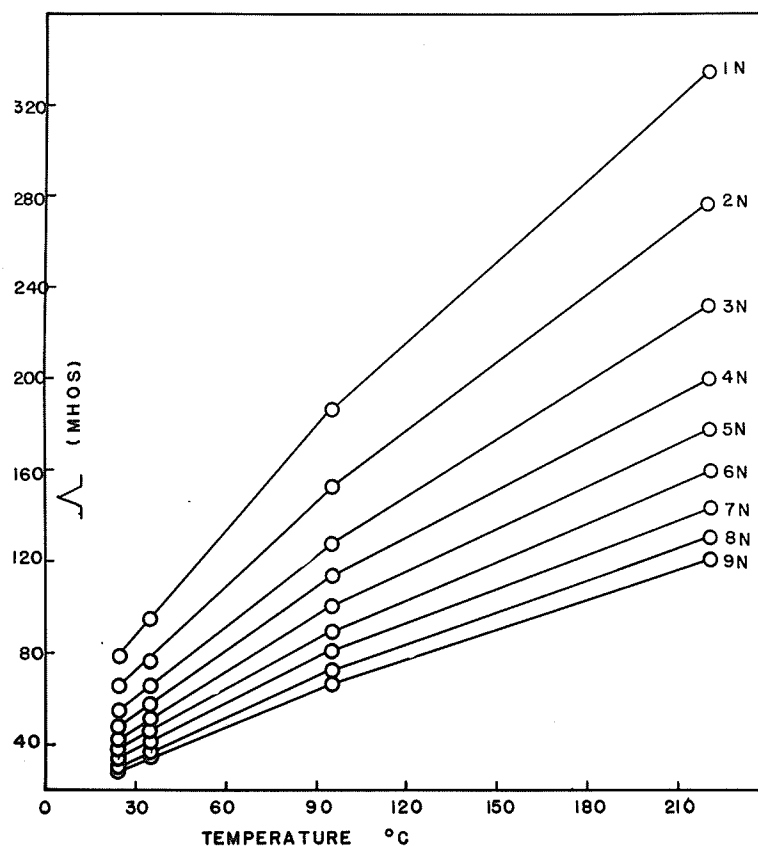


Figure 10  
Equivalent conductance vs. temperature for silver nitrate

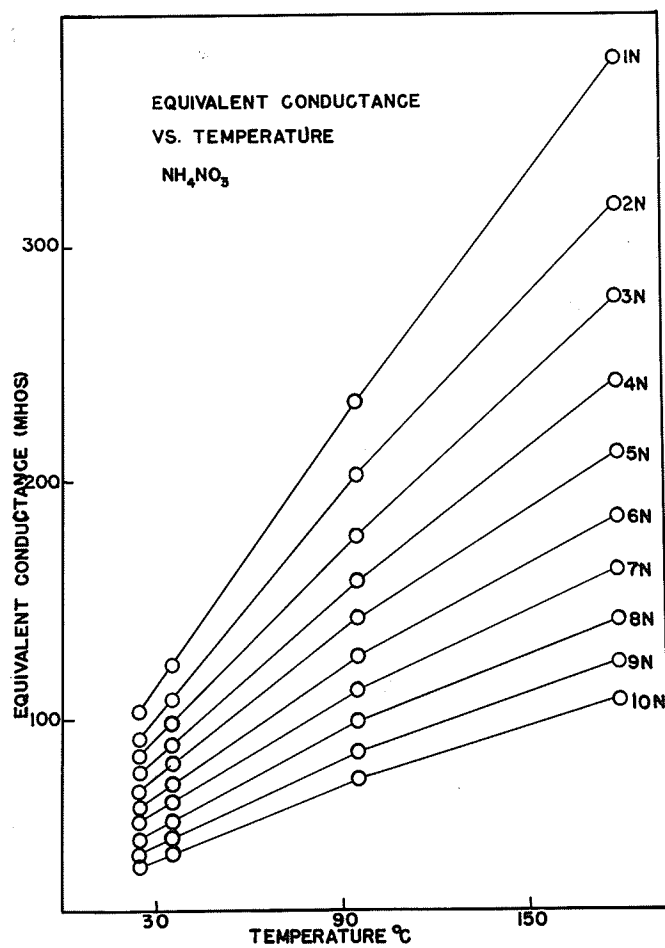


Figure 11  
Equivalent conductance vs. temperature for ammonium nitrate

TABLE X.

Temperature Coefficients of Conductance,  
 Between 95° and 221.7° ( $\text{AgNO}_3$ ) and  
 Between 95° and 180.0° ( $\text{NH}_4\text{NO}_3$ ).

<u>Concentration in Moles/litre</u>	<u>Temperature Coefficient</u>	
	<u><math>\text{AgNO}_3</math></u>	<u><math>\text{NH}_4\text{NO}_3</math></u>
1	0.00626	0.00743
2	0.00642	0.00672
3	0.00627	0.00676
4	0.00599	0.00640
5	0.00606	0.00584
6	0.00619	0.00556
7	0.00620	0.00531
8	0.00634	0.00517
9	0.00645	0.00526
10	--	0.00509

CONCLUSION

## VII. CONCLUSIONS

Experimental data on the conductance and density of ammonium nitrate solutions over the complete concentration range at 180°C have been obtained.

A comparison of the data of this research with those of previous workers has shown that the maximum on the specific conductance vs. normality curves shifts towards higher concentration with temperature.

The exponential approach to linearity of plots of equivalent conductance vs. concentration was verified by the discovery of a linear relationship between log concentration and equivalent conductance. This linear plot extended over a very wide concentration range up to the anhydrous salt.

An equation could thus be set up of the form

$$\Lambda_c = \Lambda_a + D \log C$$

to represent the data over the linear portion of the curve. The validity of this relationship for salts other than ammonium nitrate and silver nitrate has not been demonstrated due to the absence of appropriate data.

Average temperature coefficients of conductance were calculated on a linear basis for comparative purposes. They were found to be much smaller than the corresponding values over the range 0 - 95°C where a true linear relationship exists.

The great confusion in the theoretical treatment of solutions of

strong electrolytes has been indicated in the introduction. The present work is thus offered in the hope that with a sufficient body of data existing, greater efforts will be made to supply a consistent theoretical treatment.

## TABLE OF SYMBOLS

TABLE OF SYMBOLS

Symbols identified and used in specific cases are not included

here.

$\Lambda_c$  = equivalent conductance at concentration  $c$  equivalents per litre (mhos).

$\Lambda_o$  = limiting equivalent conductance at infinite dilution (mhos).

$\alpha_c$  = degree of dissociation.

$K$  = dissociation constant (moles/litre).

$l_+^\circ$  = limiting equivalent conductance of cation at infinite dilution (mhos).

$l_-^\circ$  = limiting equivalent conductance of anion at infinite dilution (mhos).

$Z_+, Z_-$  = valence of cation, anion.

$T$  = absolute temperature (°K).

$t$  = temperature (°C).

$D_o$  = dielectric constant of solvent.

$D$  = dielectric constant of solution.

$\eta_o$  = viscosity of solvent (poise).

$\eta$  = viscosity of solution (poise).

$e$  = charge on the electron in electrostatic units.

$k$  = Boltzmann constant (ergs/degree).

$\beta$  = temperature coefficient of conductance (mhos/degree C).



ACKNOWLEDGEMENT

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