The Conductances of Strong Solutions of Strong Electrolytes

by

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The conductance of solutions of electrolytes has been the subject of a vast amount of experimental research and theoretical investigation. The elementary theory, due to Arrhenius, as applied to weak electrolytes remains more or less satisfactory today but it was found to present difficulties when applied to strong electrolytes. For instance, the degree of dissociation, α, determined from freezing point measurements was found to differ by as much as 5% (which is greatly in excess of the experimental error) from that determined from conductance measurements according to the relation $\alpha_c = \frac{\Lambda_c}{\Lambda_o}$ ①.* Moreover, the Ostwald dilution law $K = \frac{\alpha^2 C}{1-\alpha}$ ② fails entirely when applied to strong electrolytes, whereas it is obeyed approximately by weak electrolytes in dilute solution and more closely when activities are used instead of concentrations.

The failure to interpret experimental results by means of the Arrhenius theory indicated the necessity for a new theoretical approach to strong electrolytes. The empirical relationship of Kohlrausch (1),* the familiar square root law, $\Lambda_c = \Lambda_o - A\sqrt{c}$ ③, describes the behaviour of very dilute solutions. Any equation developed from theoretical considerations must therefore simplify to the Kohlrausch form in dilute solution. The theory of Debye-Hückel (2) resulted in an equation in which Λ is linear in $\sqrt{c}$. The new concept of complete dissociation of strong electrolytes attributed the decrease in conductance with increased concentration to a decrease in mobility of the ions. The conductance ratio, $\frac{\Lambda_c}{\Lambda_o}$, supposed by Arrhenius to represent the degree of dissociation took on a different meaning when applied to strong electrolytes - change in the conductance ratio with concentration

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* See note on Page 103.

became a measure, not of the change in the number of ions, but of the change in mobility of the ions. Shortly before the appearance of the Debye-Hückel theory, Noyes and MacInnes (3) expressed the state of opinion at that time (1920) as follows: "It seems advisable to adopt for the present the hypothesis that such substances (strong electrolytes) are completely ionised, and to attribute the decrease in the conductivity ratio wholly to a decrease of ionic mobility, and the change in the activity coefficient to some unknown effect of a physical nature."

X-ray analysis of crystals lent considerable support to the concept of complete ionisation of strong electrolytes - the units out of which the crystal lattice of a polar compound is formed are ions and no entity exists corresponding to the usual concept of a molecule. Therefore, in the solid state, salts are already completely ionized. In the act of dissolving, then, the particles breaking away from the crystal are ions, not molecules. Until a large concentration of salt is built up in the solution it is natural to assume that the solute exists as ions so that in dilute solution strong electrolytes are completely dissociated. If molecules or any such neutral particles of a strong electrolyte are to be postulated in strong solutions they must be thought of as resulting from association of ions. This is in contradistinction to our ideas on weak electrolytes where the ions result from dissociation of molecules.

The concept of complete dissociation of strong electrolytes is the fundamental tenet of the Debye-Hückel theory. A formal treatment of this theory is unnecessary here since it is to be found in any modern text book of even moderately advanced nature. Assuming complete dissociation, Debye and Hückel expressed mathematically the effect on the conductance of two properties of the solution, namely, (1) the relaxation of the ionic atmosphere due to an applied potential and (2) the electrophoretic effect. Onsager (4) extended their theory to include the effect of the Brownian movement of the ions. The combined treatment (of Debye-Hückel-Onsager) resulted in the following equation for the dependence of the equivalent conductance of a binary strong electrolyte on the concentration:

$$\Lambda_c = \Lambda_0 - \left[\frac{0.9384 \times 10^6}{(D_0 T)^{3/2}} w \Lambda_0 + \frac{28.94\,(z_+ + z_-)}{\eta_0 (D_0 T)^{\frac{1}{2}}}\right] \sqrt{(z_+ + z_-)C} \quad ④$$

where $w = (z_+ + z_-)\left(\frac{2q}{1+\sqrt{q}}\right)$ and $q = \frac{(z_+ + z_-)\Lambda_0}{(z_+ + z_-)(z_+ l_-^\circ + z_- l_+^\circ)}$.

For the special case of a uni-univalent electrolyte in water at 25° C., ④ reduces to $\Lambda_c = \Lambda_0 - [0.2273\Lambda_0 + 59.78]\sqrt{C}$ ⑤. The quantity in brackets is a constant so ⑤ is identical in form with ③. Equation ④ has been tested with electrolytes of higher valence (e. g., calcium chloride) and found to hold in very dilute solution. For aqueous solutions of uni-univalent electrolytes, the Onsager equation is obeyed up to concentrations of 2×10^{-3} N.

The Debye-Hückel-Onsager theory, then, accounted for the properties of dilute solutions of strong electrolytes: not only did it result in an equation for Λ linear in $\sqrt{C}$ but, what is also necessary, the slope of the experimental plot was equal to the calculated slope. Nevertheless, due to mathematical simplifications and the original assumptions which apply only to very dilute solutions, it is quite inadequate for strong solutions. (E. G., the equivalent conductances of silver nitrate solutions calculated from equation ⑤ become negative after a concentration of 3 N.)

It is appropriate to indicate here the assumptions or simplifications introduced by Debye-Hückel-Onsager which make the theory untenable in concentrated solutions. Among them are:

i. The series $e^x = 1 + x + \frac{1}{2!}x^2 + \frac{1}{3!}x^3 + \cdots$ ⑥ is used to develop the exponential functions; all terms after the second are neglected on the ground that they are negligible <u>except at fairly high concentrations</u>.

ii. The dielectric constant is taken to be constant. Hückel (5) attributed part of the failure of the theory for concentrated solutions to the fact that the dielectric constant is a function of the concentration

$$D = D_0 - 2\bar{\delta}c \qquad ⑦$$

where $\bar{\delta} = \frac{\delta^+ + \delta^-}{2}$, δ^+ and δ^- being the contributions of the anion and cation to the depression in dielectric constant. The dielectric constant in the immediate vicinity of an ion is greater than that of the solvent as a whole. This follows from Drude and Nernst (6) who showed thermodynamically that the electric field around an ion exerts a pressure upon the solvent and increases its density. Falchenberg (7) showed experimentally that for water up to 200 atmospheres the dielectric constant increases linearly with increase in density. It can be calculated that at a distance of 10^{-8} cm. from a univalent ion considreed to be a point charge the pressure is

9000 atmospheres which results in an 18% increase in the dielectric constant of water; at a distance of 1.7 x 10^{-8} cm. the pressure is 1000 atmospheres and corresponds to a 4% increase in dielectric constant. For concentrated solutions, a correction should therefore be applied to the Debye-Hückel theory in order to take into account this effect.

iii. It was assumed that the size of the ions could be neglected in comparison with the distance between them. This is not allowable in concentrated solutions.

For a theory of concentrated solutions to be satisfactory the simplifying assumptions introduced by Debye-Hückel must be abandoned. Using the theory as a starting point, many authors have attempted to extend its range. Onsager (4) introduced terms designed to overcome errors which entered through mathematical simplifications; and many empirical modifications were tried by others, among which the most notable are that of Jones and Dole (8)

$$\Lambda_c = \Lambda_0 - \frac{A\sqrt{c}}{1+G\sqrt{c}} - Kc \qquad ⑧$$

where A , G and K are constants, and that of Shedlovsky (9)

$$\Lambda_c = \Lambda_0 - (A+B\Lambda_0)\sqrt{c} - Cc + Dc\log c + Ec^2 \qquad ⑨$$

where A , B , C , D and E are constants. None of these equations is at all accurate at concentrations greater than 0.1 N.

A. Existence of Non-conducting Particles in Solutions.

It was soon realized that the assumption of complete dissociation might not be tenable in strong solutions where the ions are close together and hence under strong interionic attraction. To account for this Onsager introduced a factor α , the degree of dissociation into equation ④ yielding:

$$\Lambda_c = \alpha[\Lambda_0 - (A + B\Lambda_0)\sqrt{\alpha c}]$$ ⑩ .

This can be written in the form $\Lambda_c = \alpha\Lambda'$ ⑪ where $\Lambda' \equiv \Lambda_0 - (A + B\Lambda_0)\sqrt{\alpha c}$ ⑫ and is interpreted as the equivalent conductance of one equivalent of free ions at the actual ionic concentration in the solution $= \alpha c$ equiv./litre. Since $\Lambda' < \Lambda^\circ$, the degree of dissociation will be closer to unity than that calculated by Arrhenius. For equation ⑨ to be useful in evaluating the degree of dissociation it is necessary to know the value of Λ'. Two methods, both based on a series of approximations are described by MacInnes and Shedlovsky (10), Sherrill and Noyes (11) and MacInnes (12). Davies (13) gives a table of dissociation constants for a number of uni-univalent electrolytes (in water at 25° C.) calculated in the above mentioned manner. A selection of two, potassium nitrate and silver nitrate, will illustrate the degree of constancy obtained.

$c =$	0.01	0.02	0.05	0.1	0.5
			Potassium Nitrate		
$\alpha =$	0.994	0.989	0.975	0.961	
$K =$	1.40	1.38	1.32	1.37	
			Silver Nitrate		
$\alpha =$	0.993	0.989	0.973	0.957	0.883
K	1.10	1.31	1.12	1.23	1.18

In view of the approximations and assumptions made the results seem almost better than they should be - they are based on the Onsager equation ⑩ . For the higher concentrations an equation which represents the variation of conductance with concentration better, say the Shedlovsky equation ⑨, should have been used (instead of ⑩) with the concentration modified for incomplete dissociation.*

Bjerrum (14) has calculated a degree of association of ions by equating the potential energy resulting from the electrostatic forces between ions to the mean kinetic energy at various interionic distances. The extent of association of ions depends on the probability of two ions being within a certain minimum distance of each other. This probability is evaluated on the assumption that the dielectric constant in the immediate vicinity of the ions is the same as the macroscopic value, and that the ions are rigid, unpolarizable spheres. The minimum distance becomes

$$r_{min.} = \frac{\epsilon^2 |z_+ z_-|}{2DkT} \quad ⑬$$

. Ions within this minimum distance form "ion-pairs." The greater the value of $r_{min.}$, the greater is the probability of ion-pair formation because the

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[*] Two different terms are used in the literature to represent an incomplete disintegration of a salt crystal into ions; these are "the degree of dissociation" and "the degree of association." The first implies that neutral molecules exist in solution, which break up or dissociate into free ions. This is actually the modern concept of the weak or moderately strong electrolyte. Salts, however, are assumed to be completely ionized in the crystal; in dilute solution the ions are far enough apart to be essentially independent of each other; in concentrated solution there is increasing evidence for an association of ions into a neutral particle called the ion-pair. The effect on the conductance is the same whether we postulate an incomplete dissociation of a neutral molecule into ions or an associations of ions into neutral particles.

Both terms are used by different authors - for salts the term, "degree of association," should be used.

volume around a given ion in which the oppositely charged ions can be found is thereby greater. From an examination of ⑬ it is immediately apparent that ions of high valence and a medium of low dielectric constant present optimum conditions for association at a given temperature. Bjerrum calculated the degrees of association, θ, of uni-univalent electrolytes using the following expression:

$$\theta = \frac{4\pi Nc}{1000}\left(\frac{\epsilon^2}{DkT}\right)^3 Q(b) \qquad ⑭$$

where $Q(b) \equiv \int_2^b e^y y^{-4}\, dy$, and

$y \equiv \frac{\epsilon^2}{DrkT}$ and $b \equiv \frac{\epsilon^2}{DakT}$. He found that ions of small radii in highly concentrated solutions are associated to the greatest extent as is shown in Table 1.

TABLE 1

FRACTION OF ASSOCIATION (θ) OF UNI-UNIVALENT ELECTROLYTES IN WATER AT 18° C. CALCULATED BY BJERRUM (14)

	Concentration						
a (Å)	0.001	0.005	0.01	0.05	0.1	0.5	1.0 N.
2.82	0	0.002	0.005	0.017	0.029	0.090	0.138
2.35	0.001	0.004	0.008	0.028	0.048	0.140	0.206
1.76	0.001	0.007	0.012	0.046	0.072	0.204	0.0286

According to the theory of Bjerrum, then, a salt AB in solution may have a fraction of its ions associated into ion-pairs. An equilibrium may exist between the independent ions A^+, B^- and the ion-pair $[A^+B^-]^\circ$ to which the mass action law could be applied:

$$K = \frac{a_{A^+} \cdot a_{B^-}}{a_{[A^+B^-]^\circ}}$$ ⑮.

For very dilute solutions ⑮ reduces to $K = \frac{c}{\theta}$ ⑯ so that, taking into consideration ⑭, the association constant of Bjerrum becomes $K^{-1} = \frac{4\pi N}{1000}\left(\frac{e^2}{DkT}\right)^3 Q(b)$ ⑰.

The association constant then is dependent on the dielectric constant of the solvent so that for a given salt dissociation is complete in solvents having a dielectric constant above a definite value. Fuoss and Kraus (15) have tested ⑰ with their data on tetraisoamyl ammonium nitrate and find that the constants, K, calculated with the Onsager equation $\Lambda_c = \Lambda_0 - \alpha\sqrt{c} - \left(\frac{\Lambda_0}{K}\right)c$ ⑱ (⑱ is another form of ⑩.) agree remarkably well with those calculated from ⑰ where a is taken to be 6.40×10^{-8} cm. For ions of this size they prove that "dissociation is complete in all solutions of dielectric constant greater than 43.6." Therefore, these authors do not think that ion-pairs exist in aqueous solutions of salts - but the concentrations at which they worked were small and this does not preclude association in strong solutions.

Mention should be made of the evidence given by Fuoss and Kraus (16) for the existence of triple ions in an equilibrium of the type $[A^-B^+A^-]^\circ \rightleftharpoons A^- + [A^-B^+]^\circ$ ⑲ and of "ionic clusters" $[B^+A^-B^+A^-]^\circ \rightleftharpoons 2[B^+A^-]^\circ$ ⑳. These exist in solutions of low dielectric constant. Kraus and Vingee (17) give results which indicate that the electrolyte tetraisoamyl ammonium nitrate (a strong electrolyte in aqueous solution) is "highly associated even at relatively low concentrations in solvents of low dielectric constants." Despite the fact that water is a solvent of high dissociating power it is a distinct possibility (and almost a necessity) that in strong solutions where the amount of water is small compared with the amount of solute the interionic forces are great enough for association to occur.

The existence of the triple ion, $[A^- B^+ A^-]^-$, which uses an ion-pair in its formation is thought to account for the minimum in Λ-c curves for solutions of low dielectric constant. The subsequent rise in conductance is attributed to a large concentration of triple ions. This is not immediately obvious. The argument is as follows: The following equilibria exist in solution:

$$B^+ + 2A^- \rightleftharpoons [B^+A^-]^\circ + A^- \rightleftharpoons [A^- B^+ A^-]^- \qquad ㉑.$$

If the proportions of the three terms of the equilibria are taken as x, y, and z respectively, x and z are conducting, y not. At higher concentrations y decreases with respect to x and z and the conductance increases. Since no minimum is to be expected for salts in aqueous solution (silver nitrate at any rate: see Page 73) it may be expected that the concentration of triple ions is very slight in these.

In a recent paper, Hasted, Ritson and Collie (18) discuss Bjerrum-type association in strong solutions of strong electrolytes. The association constant ⑮ derived by Bjerrum and used for dilute solutions depends on concentration in an approximately linear manner. These authors state that concentrated salt solutions have conductivity values which exhibit a linear relation with concentration. They suggest that in the region where Λ is proportional to C ion association predominates. They reject Bjerrum's method of calculating the extent of association because he made a number of approximations (see Page 7) which are untenable in concentrated solutions. They attempt to evaluate a degree of association from conductivity measurements and at the same time they outline a course which might be followed in developing a theory of concentrated solutions. Since any light thrown on this complex subject will be of value I shall reproduce their treatment here despite their acknowledgment that "it appears that the amount of Bjerrum association is an extremely difficult term to estimate" and that they "cannot offer any detailed explanation....but must be content simply to offer this as a possible method of treatment of the linear variation of conductivity with concentration in concentrated solution."

They point out the anomaly of a linear dependence of conductivity on the square root of the concentration in dilute solution changing into a linear dependence on the concentration in strong solution. They cite the difficulty involved in obtaining a theoretical equation which will handle both the dilute and concentrated regions - an equation of the form $\Lambda_c = \Lambda_0 - F\sqrt{C} - HC$ ㉒ where F and H are such that the linear term HC disappears except when C is large and $F\sqrt{C}$ drops out after a concentration of say 0.02 N. is reached. The empirical equation ⑧ of Jones and Dole (8) fits these requirements to a certain extent but for this equation to satisfy the dilute region the constants A, G and K

become such as to make the linear dependence felt only after 10 N. (in practice the linear dependence occurs between 1.5 and 6 N. for the salts studied by them).

The authors feel that two equations will be necessary: I. an equation for the dilute region "tending to a constant conductivity value at concentrations greater than 1.5 M.(This statement is badly made: I think they mean "tending to a linear dependence on concentration after 1.5 M."; the linear parts of the $\Lambda - c$ curves in their figure have definite negative slopes and not zero slopes as required by the expression "constant conductivity value." II. an equation holding over the linear range where ion association is assumed to predominate. They postulate the relationship $\Lambda_c = \alpha \Lambda^*$ ㉓ where Λ^* is the value of the ordinate when the linear portion of the $\Lambda - c$ curve is extrapolated to $c = 0$. Then $1 - \alpha$ is the degree of assocation. Following is a list of the values obtained for a number of strong electrolytes in normal solution:

Electrolyte	% Associated	Temp. °C.
HCl	11	18°
NaCl	10	0° and 18°
KCl	5	18°
NaI	9	25°
KBr	5	25°
KI	5	18°
RbCl	4	18°

Electrolyte	% Associated	Temp. °C. (Cont'd)
CsCl	4	18°
$BaCl_2$	12	25°

Here no viscosity correction is applied. They question the validity of simply multiplying the conductance by the "macroscopic viscosity" and are unable to suggest any other form of correction for viscosity.

I admit, and so do the authors, that no conclusive theory or equation has been propounded but their treatment will perhaps serve to point out the extreme complexity of the subject and the futility of expecting a simple explanation for conductance. It is my belief - and the general impression given by a study of the literature on strong solutions - that this problem will not be resolved until many more experimental data of a variety of measurements are made. These can then be correlated with what at present must be pure estimates of the effects of ion association and hydration which cannot be experimentally measured by any known methods. The concluding paragraph of this paper sums up rather well the present state of opinion as to strong solutions:

"Future progress in electrolyte theory of concentrated solutions must be in an experimental evaluation of the various factors involved and by a vigorous theoretical attack on the basic problems of solute-solvent interaction."

There is evidence other than conductance data which supports the theory of incomplete dissociation of strong electrolytes, e. g., the work of Fajans (19) on refractometric measurements. At infinite dilution, where interionic forces are negligible, Heydweiler (20) had found the ionic refractivities to be additive. On the other hand, Fajans and Joos (21) report large deviations from additivity accompanying the change from infinitely dilute through strong solutions to the crystal state. The deviation from strict additivity is a result of the forces of attraction operating between the ions in solution and is observed when ions unite to form neutral molecules of a gas or crystals. The question to be answered concerning solutions is whether or not the interionic forces are strong enough to effect an actual union of oppositely charged ions into an ion-pair or similar neutral particle. The mutual action of ions on each other (measured refractrometrically) is dependent on the interionic distance. It should therefore be possible to determine from refractrometric measurements whether two ions of opposite charge can approach each other closely enough to force out solvent molecules from between them and hence form ion-pairs. This brings to the fore the problem of the meaning to be ascribed to the "distance of closest approach of ions" in solution introduced as $\mathring{a}$ into the Debye-Hückel equation. An anomalous situation arises which is treated best as follows:

In a molten salt it is to be presumed that the distance of closest approach of ions should be identical with the ionic radii. From X-ray investigations it is known that the radii of the alkali metal ions decrease in the order Cs > Rb > K > Na > Li. An oppositely directed sequence results for the "mean distance of closest approach," $\mathring{a}$, determined in the following manner:

The equation for the mean ionic activity coefficient

$$\log \gamma_{\pm} = \frac{-A z_+ z_- \sqrt{\mu}}{1 + \overset{\circ}{a} B \sqrt{\mu}} \quad (24) \qquad \text{where} \quad B = \sqrt{\frac{8\pi N^2 \epsilon^2}{1000\, DRT}} \quad \text{and} \quad A = \frac{N \epsilon^2 K}{4.406\, DRT}$$

can be rearranged into

$$-\frac{A z_+ z_- \sqrt{\mu}}{\log \gamma_{\pm}} = 1 + \overset{\circ}{a} B \sqrt{\mu} \qquad (25).$$

Using experimentally determined values of $\gamma_{\pm}$ and plotting the left hand side against $\sqrt{\mu}$ a straight line of slope $\overset{\circ}{a} B$ should be obtained. Since B is known $\overset{\circ}{a}$ can be found. The mean distance of closest approach of the ions of the alkali halides are given by Harned and Owen (22):

	Cl	Br	I
Li	4.25 Å	4.3	5.05
Na	4.0	4.1	4.2
K	3.8	3.84	3.94
Rb	3.6	3.55	3.5
Cs	3.0	2.93	2.87

This means that the effective radii decrease in the order Li > Na > K > Rb > Cs (in solution).

If $\overset{\circ}{a}$ is to be given the significance of "mean distance of closest approach" it must be assumed that water molecules remain between ions even at their greatest proximity. Fajans disputes this interpretation of the meaning of $\overset{\circ}{a}$ because he considers he has proof that ion-pairs do form, without intervening water molecules.

Fajans gives the following argument for his belief that ions approach close enough to each other to exclude water molecules. He compares the refractivity of 5 molal solution of lithium cloride with that of the crystal. Assuming that the ions in the solution are arranged in a similar manner (same statistical distribution) to what they are in the crystal, the interionic distance in the solution and in the crystal is proportional to the cube root of the molal volumes. From the density of the solution and of the crystal he obtains $r_{\text{sol.}} = 2.15 \times r_{\text{cryst.}}$ so that $r_{\text{sol.}} = 5.52 \times 10^{-8}$ cm. This is 2.95×10^{-8} cm. greater than $r_{\text{cryst.}}$ Since the sphere of action of the water molecule is 3×10^{-8} cm. there is room for only one water molecule between the ions and when the ions approach each other it is logical to expect that at least part of the time "direct contact" is made although "no rigorous quantitative" estimate of the extent of ion-pair formation can be made.

A comparison of the solubilities of the alkali halides led Fajans to the conclusion that, since potassium chloride is the least soluble, the potassium ion and chloride ion have the smallest tendency to be separated from the crystal into free ions. Combined with this is the fact that the vapour pressure of *equimolal* solutions of the alkali halides is a maximum for potassium chloride, that is, the lowering in vapour pressure caused by potassium chloride is less than for the other alkali halides. Therefore, he concludes that there are fewer ions in the concentrated potassium chloride solutions than in the other alkali halides and that therefore the electrolyte must be only partially dissociated. An alternative view is that the salt is completely dissociated into ions whose activity is lower than those of the other halides. But the concept of activity necessarily begs the whole question of mechanism so cannot be used to explain the properties of solutions.

Light absorption measurements also lead to evidence for the existence of neutral molecules or complex ions in solutions of weak and moderately strong electrolytes. Von Halban and Eisenbrand (23) have determined the variation of the molecular extinction coefficients with concentration for nitric acid and potassium nitrate solutions with light of several different wave lengths. The curves for potassium nitrate are simple; nitric acid gives complex curves with prominent points of inflection. The latter are attributed to the rapid rise in the ratio of the concentration of undissociated nitric acid to that of the nitrate ion as the total concentration increases. The simplicity of the potassium nitrate curves is ascribed by the authors to its complete dissociation (or what is more likely to its almost complete dissociation).

Raman spectra have also been used for determining degrees of dissociation. The relative intensities of a Raman line produced by exciting radiation from a constant source are measured. It is assumed that the intensity of a Raman line is proportional to the concentration of the ion or neutral molecule giving rise to the line. That this assumption is valid is borne out by the work of I. R. Rao (24) and N. R. Rao (25) on sodium nitrate solutions. Redlich and Bigeleisen (26) compared the intensities of the Raman line of 1048 $cm.^{-1}$ resulting from solutions of nitric acid and of sodium nitrate. They found that the intensity of the line from concentrated nitric acid solutions was not as great as that from sodium nitrate solutions of the same concentration. On the assumption that sodium nitrate is completely dissociated and that the nitrate ion concentration is the same in solutions giving rise to radiations of equal intensity they calculate the degree of dissociation of nitric acid as equal to the ratio of the concentrations HNO_3 / $NaNO_3$ for which lines of equal intensity were obtained. The following results are given:

Concentration (N)	4.51	6.60	8.90	10.30	11.89	14.23
Degree of Dissociation	0.823	0.673	0.49	0.39	0.32	0.14 .

From known activity coefficients they calculate the thermodynamic dissociation constant to be 21 ± 4, and attribute the large uncertainty to inaccuracy in the activity coefficients. More significant is the tacit assumption of the complete dissociation of the sodium nitrate solutions.

Similar work has been done on sulfuric acid solutions by N. R. Rao (27). The curves of intensity variation with concentration are most interesting. Five Raman lines have been plotted; each intensity curve passes through a maximum. These are interpreted as evidence for the existence of the following neutral molecules or ionic species: $H_2S_2O_7$, $HS_2O_7^-$, $S_2O_7^=$, H_2SO_4, HSO_4^- , $SO_4^=$.

It should be pointed out, however, that anhydrous acids are practically non-conductors, that the type of linkage between

H^+ ion (or H atom) and the rest of the molecule is quite different from the electronic linkage in salts. Therefore, the conclusion is inescapable that partial ionization prevails in the more concentrated solutions of acids. The workers on light absorption and Raman spectra assume complete ionization of salts. Whether these methods can detect an ion-pair has not been determined.

In concluding this section it is necessary to evaluate the effect of ion-pairs in strong solutions of strong electrolytes on their conductance. Few authors will dispute the existence of ion-pairs or similar neutral particles in strong solutions of strong electrolytes particularily in those solutions whose solvents have a low dielectric constants. While the ion-pair is not thought to be a neutral molecule in the usual sense of the word it does possess the property of electrical neutrality - very important from the point of view of conductance. The decrease in conductance is a result of inter-ionic forces between the free ions in the solution and of the presence of the non-conducting particles. The ion-pair is thought of as a more or less unstable union of two ions which combine for a certain length of time after which they separate and become current carriers again. For any given concentration and temperature at any instant of time there will be a constant statistical average between ions and ion-pairs. The concept of the ion-pair leads us to think of salts as always completely ionized but not necessarily completely dissociated.

B. Solvent - Solute Interaction - Hydration of Ions.

There is much evidence of a qualitative nature that many ions combine with solvent water to form hydrates: colour changes on solution, deviations from Beer's law of light absorption are two of many. The mechanism of hydrate formation is one of ion-dipole attraction - solvents such as water, ammonia and alcohol have large dipole moments and the ions have positive or negative charges. There is a definite force of attraction between these units. Indeed the process of solution seems to be dependent on this type of action - salts do not dissolve to an appreciable extent in solvents such as benzene and carbon tetrachloride because these have small dipole moment. The well-known "salting-out" effect brings to light the effect of a large concentration of ions on the solvent properties of water - non-electrolytes, such as ether, are thrown out of a saturated solution when salt is added in large quantities. The same effect is utilized in extracting organic compounds from solution in water with ether - the extraction is facilitated by the addition of salts whose ions presumably interact with the polar water molecules and decrease their solvent effect.

Comparison of the molal depression of the freezing point of water by a variety of ions gives evidence of hydrate formation. For uni-univalent electrolytes the molal depression decreases from 3.7° at infinite dilution to a minimum at about $\frac{1}{2}$ molal after which it starts to increase. The increases are slight in electrolytes which do not form hydrates. For $MgCl_2$ and $CaCl_2$ the molal depressions are larger at 1 molal than they are at infinite dilution

(5.56°). These large increases may be correlated with the fact that these salts form hexahydrates. Water is removed and the effective concentration of the solution increased accounting for the abnormally great depression of the freezing point.

Evidence for the hydration of ions is also due to Fajans and Bauer (28) who discuss the relationship of heats of hydration and apparent molar volumes to the hydration of ions. The heat of hydration for the Ag^+ is greater than the heat of hydration for the Na^+. This is interpreted as evidence for the greater hydration of Ag^+ or at least for a stronger combination between it and the water molecules. This is qualitative evidence for the concept of ion hydration. Some of the attempts to obtain quantitative results - actual hydration numbers - will now be described.

Until recently it was hoped that transference measurements would furnish the necessary information for calculating hydration numbers of ions. Nernst (29) and Washburn (30) conceived the idea of using the Hittorf technique for determining water transference by ions. A non-electrolyte in solution does not move under the influence of a potential gradient. With an electrolyte present, it is found that the concentration of the non-electrolyte is greater at one electrode than at the other. Two possibilities arise: either the non-electrolyte forms some sort of combination with the ions (characteristic of the ions) and is carried with them to different extents to the anode and cathode; or water is carried with the ions resulting in a difference in concentration at the electrodes. Washburn considers the first possibility as quite improbable and attributes the difference in concentration to transport of the water alone. The degree of hydration is then calculated from the change in concentration at the electrodes.

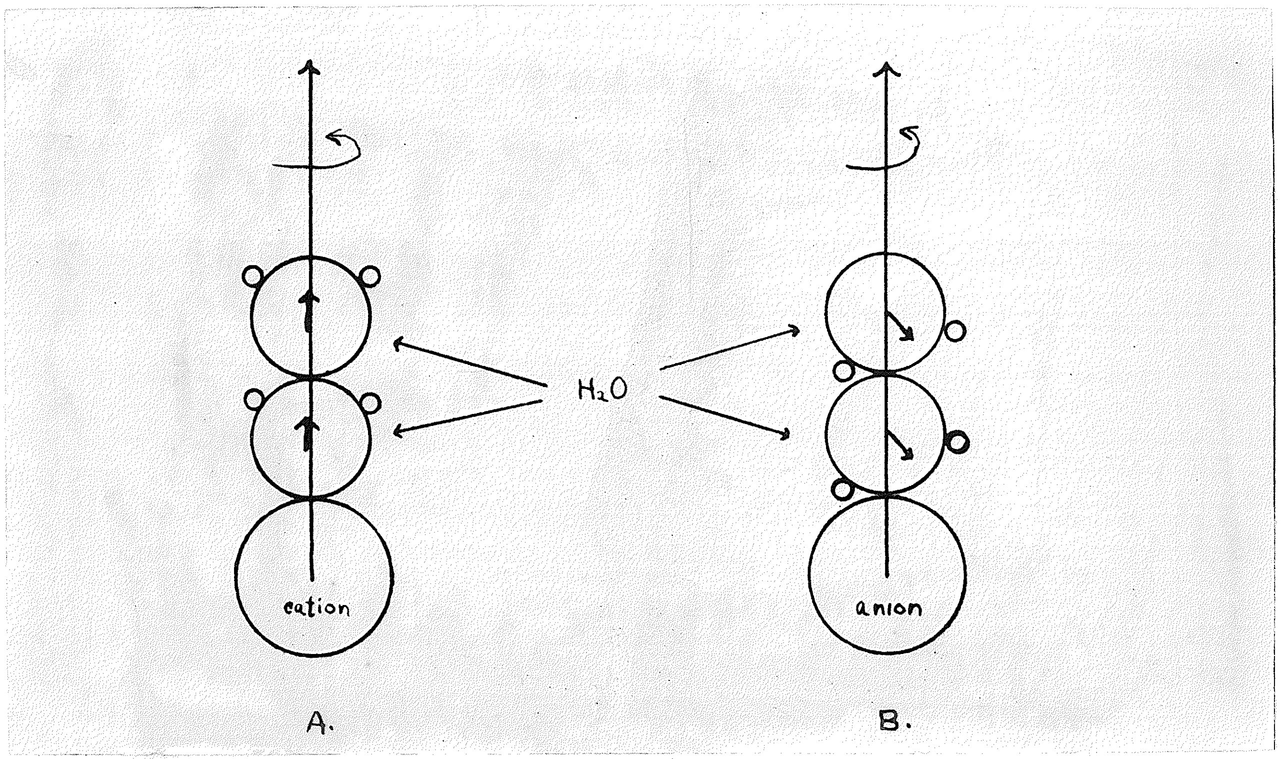
Lewis (31) developed the moving boundary technique to measure the hydration of the ions, employing the assumption that the non-electrolyte is inert. The inert material is introduced into the solution in the calibrated capillary so that its boundary with the electrolytic solution can be observed. If the ions of the solution are considered to be hydrated, one (the cation) to a greater extent than the other (the anion), water is carried through the non-electrolyte region toward the cathode in greater amount than is carried to the anode; the boundaries of the non-electrolyte region are shifted more toward the cathode than to the anode; and the difference in the shifts is a measure of the hydration of the ions.

These methods are based on the assumption that the non-electrolyte is inert. Longsworth (32) has shown that the molecules of non-electrolyte are carried along with the ions just as are the water molecules and hence the former interpretation of hydration numbers is untenable. Longsworth bases his assertion on the fact that the hydration numbers are dependent on the nature of the non-electrolyte which therefore cannot be considered to be inert. The work done by Nernst, Washburn, Lewis, etc. is not to be discredited entirely because the hydration numbers of the ions relative to each other were obtained and as such are useful to the theory of solutions.

Despite the failure to find an experimental technique successful in determining the absolute degree of hydration of ions, this property of solutions has been the subject of much speculation by authors interested in conductance of solutions. The mobility of an ion, and hence its conductance, will depend on its size and this will vary with the degree of hydration. The latter is intimately connected with the charge on the ion because the higher the electric field around it, the greater its power of combining with water. Also, for ions of equal charge, hydration will be greater the smaller the atomic volume of the ion. Depending on the nature of an ion, its effective volume in solution, i. e., the volume of the actual ion and of its hydration sheath, may be quite out of line with the crystallographic data on atomic volumes. This is actually observed with the alkali metals whose crystallographic atomic volumes decrease in the order Cs $>$ Rb $>$ K $>$ Na $>$ Li. From transference number data it is a well known fact that the mobilities of these ions in solution decrease in the same order. This must indicate, then, that Li^+ has the greatest effective volume (and hence is hydrated to the greatest extent) and Cs^+ the smallest. No other explanation for the inverted order for mobility of these ions in solution has been suggested - the concept of hydration is certainly very plausible. Emphasis is lent to the probability of ion hydration by the results of some workers on fused salts. Jaeger and Kapma (33) found that the equivalent conductances of the fused alkali nitrates decrease in order from lithium to cesium. Tubandt and Lorenz (34) observed that the specific conductances and hence the equivalent conductances of the silver and thallous halides decrease in order from chlorine to iodine. These changes are in the same order as the increase in atomic volumes of the alkali metals and of the halogens - there is no solvent present to complicate the situation by interaction with the ions.

A discussion of the work done on ion-solvent interaction should include mention of the work of Remy (35) on transference numbers. On the erroneous assumption of an unhydrated hydrogen ion which he uses as a basis for relative values of hydration numbers he comes to the conclusion that the hydration sheath of univalent ions is unimolecular in thickness. For certain ions, all indications point to a thicker layer of water molecules about the ion - among these are Li^+ and Na^+ and those of valence greater than one. The actual values reported by Remy cannot be true since they are based on an assumption now known to be incorrect (elementary texts attribute a hydration number of unity to the hydrogen ion but this open to question). His results are of value in that they give the relative degree of hydration of the ions. He found that the effective radii of the alkali metal and halide ions in solution decrease in order from Li^+ to Cs^+ and from I^- to Cl^-. This is in harmony with the relative mobilities of the ions as given on Page 23.

Hasted, Ritson and Collie (18) deal with the hydration of ions estimated from the depression in the dielectric constant of water caused by the addition of ions. These authors contend that each ion attracts a sheath of water molecules about it several layers in thickness; the dielectric properties of the closely held water molecules are different from those far from the ion. The effect decreases as the distance from the ion increases because the outer layers are less strongly held. The following diagram is postulated to show the possible hydration of a cation and of an anion:



They interpret the diagram as follows:

"An anion attracting water molecules as in B leaves them partially free to rotate and so saturates them less than would a cation which attracts them as in A. Therefore, the depression of dielectric constant is much larger for cations than anions."

They list the depressions in the dielectric constant of water caused by a number of ions and calculate the hydration numbers of cations from them on the assumption that the molecules of water in the first layer are held rigidly and thus are "effectively removed.....from playing any part in the dielectric process." Since some of the water molecules in outer layers may also be rigidly held the authors quote their hydration numbers as "minimum hydration numbers." For certain of the common cations these hydration numbers are as follows: ten water molecules for H^+, six for Li^+, four for Na^+, four for K^+, four for Rb^+, fourteen for Mg^{++}, fourteen for Ca^{++}, and twenty-two for La^{+++}. Because of the lack of rigidity in the anion-water system, they are unable to calculate hydration numbers for the anions. (In most of the literature it is assumed that anions are unhydrated but I think this must certainly be oversimplified.) From the above data it is seen that, the higher the cationic charge, the greater the capacity for water molecules and hence the greater the depression in dielectric constant. In agreement with Remy, they observe that the smaller the crystallographic ionic radius of the univalent ions, the greater the hydration number. They find that, contrary to the behaviour of most anions, the OH^- ion has a very large effect on the dielectric constant. They explain this by the assumption that the OH^- ion "can attract and saturate water molecules very easily, in a pattern similar to that of water itself, without undue disturbance of the water lattice". They mean, I think, an association with water molecules by means of the hydrogen bond.

A final observation from this excellent paper is the effect of temperature on the <u>depression</u> in dielectric constant caused by the ions. The authors found a greater depression at high temperatures than at low and infer that hydration of ions increases with temperature. I would have expected the reverse in view of the fact that the enthalpy of hydration of salts is negative. This, however, may not apply to the anthalpy of hydration of an ion in solution.

Sanoilov (36) contends that the concept of a fixed number of water molecules around an ion, in more or less stable binding, and a definite Stoke's radius is not tenable. From a consideration of the activation energy of hydration, he concludes that even the highly hydrated Li^+ does not have permanently bound water molecules. Only a mean co-ordination number can be envisaged. This need not be discouraging; it is possible to conceive of an ion-water molecule exchange in which the ion is effectively hydrated with a consequent greater effective volume and lower mobility. The result is the same whether we envisage a stable hydrated ion or one surrounded by water molecules in a loose and ever-changing array.

The hydration numbers cited by all authors cannot apply to the very concentrated solutions investigated in this research. In these, a mole fraction of approximately 0.6 for silver nitrate and approximately 0.65 for ammonium nitrate have been reached. If silver nitrate, for example, is assumed to be completely dissociated there are twelve ions (six Ag^+, six NO_3^+) for every four water molecules. Certainly "hydration sheaths" are out of the question and the picture becomes one in which the ions themselves act as the medium. The internal friction to the ions is no longer a solvent-solvent interaction: ion brushes against ion in a direct contact.

C. Effect of the Dielectric Constant of the Solvent on the Conductance.

Consider the effect produced on the conductance of a molten salt by the addition of a solvent. It is to be expected that the conductance will increase because the solvent will put greater distance between oppositely charged ions and hence decrease the electrostatic forces between them. Although the molten salt is completely ionized it probably is not completely dissociated and this is part of the function of the solvent. The dissociating power of the solvent depends on its dielectric constant; solvents of high dielectric constant produce solutions of highest conductance. (This is borne out experimentally by Walden's work (37) on the conductance of tetraethylammonium iodide in a great many solvents and is shown analytically on consideration of the Onsager equation ④ where the dielectric constant appears in the denominator of the $\sqrt{c}$ term, to be subtracted from Λ_o. A larger D decreases the value of the $\sqrt{c}$ term and hence increases the value of Λ.)

The effect of dielectric constant on the conductance is felt also in the concentration at the minimum observed in the $\Lambda - c$ curves of non-aqueous solutions - the concentration of the minimum is lower, the lower the dielectric constant. Walden (38) observed the relation $C_{\text{min.}} = k\, D^3$ ㉖ and placed the value of k as between 33 and 38 at 25° C. For aqueous solutions the minimum should lie at approximately 8 N. This has not been observed with the salts studied - indeed my results for silver nitrate solutions (Page 73) indicate no minimum in the Λ-c curve.

Factors which change the dielectric constant of the solvent such as increased concentration of solution or changes in temperature will produce changes in the ion association and hence in the conductance; thus the effect of such factors on the dielectric constant must be considered in developing a theory for strong solutions.

D. Effect of Temperature on the Conductance.

In general, the conductance of electrolytes rises with temperature passes through a maximum and then decreases. The low temperature approach to the maximum is almost linear and so it can be approximated by the relation

$$\Lambda_{t^\circ} = \Lambda_{25^\circ}\left(1 + \beta\left(t-25\right)\right) \qquad ㉗ .$$

The following equation is sometimes given

$$\Lambda_{t^\circ} = \Lambda_{25^\circ}\left(1 + \beta\left(t-25\right) + \delta\left(t-25\right)^2\right) \qquad ㉘$$

but in the solutions investigated by me the coefficient δ must be vanishingly small (Page 93). For aqueous solutions the temperature of the maximum is high, approximately the critical temperature of water. Sack (39) observed the maximum experimentally with aqueous copper sulfate solution. The temperature of the maximum is lower in non-aqueous solutions so many examples are known. Franklin and Kraus (40) observed maxima in a number of solutions with liquid ammonia as solvent and found that the temperature of the maximum is a function of the concentration; at higher concentrations the maximum occurs at lower temperatures. The work of Bousfield and Lowry (41) deserves mention. They found a point of inflection on the λ-t curves ($t < t_{\text{max.}}$) of sodium hydroxide solutions which they attributed to a change in the nature of the solution. For $t_{\text{inflection}} < t < t_{\text{maximum}}$ the temperature coefficient of conductance was lower than in the region $t < t_{\text{inflection}}$. Bousfield and Lowry contend that after inflection the decrease in the number of ions with increased temperature becomes appreciable with respect to the increase in mobility, so that the temperature coefficient of conductance suffers a decrease. For very dilute solutions no point of inflection exists, a fact which tends to bear out the idea of Bousfield and Lowry as to the changing degree of dissociation: dilute solutions are completely dissociated and so no point of inflection should be observed.

For very dilute solutions in which the temperature coefficients of conductance and of fluidity are very nearly equal the increase in conductance with temperature is almost entirely a result of the increased fluidity of the solutions. My results for concentrated solutions (Page 96) prove that the increase in conductance in concentrated solution with temperature is a result of other factors as well as the fluidity but it is impossible to do more than indicate what these factors are. It is to be expected that (1) the degree of hydration of the ions, (2) the degree of association of the ions and (3) the dielectric constant of the solvent will be dependent on the temperature and hence will exert a changing influence on the conductance. As my results show one at least of the above factors must oppose the fluidity because the temperature coefficient of fluidity is greater than the temperature coefficient of conductance. Until the temperature of the maximum is reached the factors opposing the fluidity must be in abeyance; at the maximum, the influence of the opposing factors cancels out, and the subsequent decrease in conductance must be attributed in part at least to an increase in ion association.

Conclusion.

No theory for strong solutions of strong electrolytes exists at present. It seems clear that, although the phenomena discussed by Debye-Hückel-Onsager will still be valid in concentrated solutions, a successful theory must consider other factors, among them

(a) ions are hydrated and their degree of hydration must change with increasing concentration;

(b) the very great likelihood that ion-pairs or other non-conducting entities exist;

(c) the dielectric constant changes at high concentrations of ions; and

(d) some sort of viscosity correction which is certainly not the macroscopic viscosity and whose nature is at present quite unknown must be applied.

These subjects have formed the main topic of this introduction. After a consideration of the work and ideas of many authors relative to these concepts we are left with a pronounced conviction of the complexity of the subject and should not be surprised that the problem is far from solved. An obvious need of experimental data provides the justification for this research.

Survey of the Literature

Survey of the Literature

The conductances of dilute solutions of silver nitrate and of ammonium nitrate have been determined by several workers at temperatures ranging from 0° to 300° C. (42, 43, 44, 45, 46, 47, 48, 49). Sachanov (50) determined the conductances and viscosities of concentrated solutions of silver nitrate at 25° C. These he used to illustrate the abnormal behaviour of strong solutions, i. e., the equivalent conductance corrected for viscosity according to $\Lambda_{corr.} = \Lambda \left(\frac{\eta_c}{\eta_0}\right)^m$ ㉙ (where $m \approx 1$) increases after a certain concentration is reached (between 4 and 8 N. for silver nitrate). This minimum occurs in all solvents of dielectric constant 6 - 82, and the position of the minimum depends on the magnitude of the dielectric constant. Sachanov used the data of Kohlrausch for ammonium nitrate at 20° C. to show that the minimum is exhibited by other salts, e. g., between 5 and 7 N for ammonium nitrate.

Rabinowitsch (51) discussed "abnormal dissociation" of aqueous solutions which results in a decrease in equivalent conductance with dilution. He cited many examples of this behaviour in non-aqueous solvents and observed that solvents of dielectric constant between 10 and 80 give normal equivalent conductance curves, and exhibit abnormality only after the viscosity correction is applied.

On the basis of determinations of equivalent conductances and viscosities of solutions of the cadmium halides, he stated that abnormal dissociation occurs which he attributed partly to "over-correction" (viscosity correction), and partly to the fact that ionic mobility does not remain strictly proportional to the fluidity but changes more slowly. He found minima in the $\Lambda_{corr.}$ - C curves for silver nitrate solutions at a dilution of $V = 0.25$ l./mole at 25° C., and at $V = 0.35$ l./mole at 100° C. He proposed "true" abnormal dissociation to explain the displacement with the temperature, i. e., an actual increase in the equivalent conductance with increased concentration in strong aqueous solutions. He suggested that those factors which cause true abnormal dissociation in non-aqueous solutions operate in aqueous solutions at high concentrations. He gave extensive data on the conductances of solutions of silver nitrate and of ammonium nitrate at 100° C. (concentrations varying between 15 and 0.1 N), but due to experimental difficulties introduced by the elevated temperature, he claimed accuracy of only 1%.

Shedlovsky (52) gave an empirical extension of the Onsager equation and tested it with concentrations 0.001 - 0.1 N. He determined conductances at 25° C. of solutions of silver nitrate at concentrations 2×10^{-5} to 0.1 N with great accuracy and determined Λ_0 for silver nitrate by extrapolation to be 133.32 mhos. This value is to be preferred to the older one of Harkins (46) because of the greater accuracy of the measurements.

Robinson and Davies (53) discussed equations relating equivalent conductance and concentration in separate ranges and applied them to the conductance of silver nitrate among others:

(1) Onsager's limiting equation, < 0.001 N,

(2) $\Lambda = \Lambda_0 - b(\sqrt{c} - c + 0.001)$, between 0.002 and 0.02N, and

(3) $\Lambda = \Lambda_0 - b \cdot f(c)$, $>$ 0.02 N, where $f(c) = \sqrt{c} - c(c - 0.001)$, an empirical universal function.

The data for silver nitrate are anomalous, and the anomaly is attributed to incomplete dissociation. They determined the equivalent conductance of 0.1 N silver nitrate at 25° C. to be 109.14 mhos, and calculated $K = \frac{f^2\alpha^2c}{1-\alpha}$ 1.5 at 25° C., and 1.2 at 18° C.

Jones and Colvin (54) determined with great accuracy the viscosities and densities of solutions of silver nitrate at 25° C. from 0.002 - 5.000 N.

References to trichloroacetic acid are few. Wightman and Jones (55) determined the conductances of solutions of trichloroacetic acid at dilutions 8, 32, 128, 512, 1024, and 2048 litres at temperatures 0°, 15°, 25°, and 35° C. The conductance at infinite dilution was determined to be 355.94 mhos at 25° C., assuming that dilution of 1024 litres results in complete dissociation, i. e., $\Lambda_{1024} = \Lambda_0$.

Dawson and Crann (56) gave values for the conductances and viscosities of solutions of trichloroacetic acid in the concentration range 0.01 to 0.5 N at a temperature of 25 ± 0.01° C. Using Kendall's value for the limiting equivalent conductance of potassium trichloroacetate they calculated Λ_0 for the acid to be 384.6 mhos.

Kendall and Gross (58) determined the specific conductivity and the viscosity of anhydrous trichloroacetic acid at 60° C.

From the foregoing it is apparent that the conductances of strong solutions of silver nitrate, of ammonium nitrate, and of trichloroacetic acid have not been investigated accurately. Most of the work has been done on solutions weaker than 0.1 N, the lowest concentration at which I proposed to work. Apart from the data of Sachanov on silver nitrate and ammonium nitrate, any work done at higher concentrations was at temperatures other than 25° and 95° C. and the data were obtained by the Kohlrausch method without bridge refinements. Temperature control was also poor. The earlier data thus do not have the accuracy of values obtained with modern technique. The values of Sachanov were obtained in the same manner so a repetition of the range investigated by him is justified and the discrepancies found between my data and his are to be considered real and due to inaccuracies in his method.

In discussing their results all authors seem to agree that a correction for the decreased mobility of the ions with increased concentration is necessary, and, although no-one has suggested a suitable form of the viscosity correction, it is generally assumed that the simple direct proportionality correction is not applicable. Considerable discussion is made of the anomalous behaviour of concentrated solutions of strong electrolytes, i. e., the apparent increase in the equivalent conductance when corrected for viscosity in the heretofore accepted form with increased concentration. While some authors (50 and 51) have attempted to explain the minimum in the $\Lambda_{corr.}-C$ curve as due to some property of the concentrated solution (incomplete dissociation) it seems clear that the anomaly is the result of a correction inappropriately applied.

No work has been done on the conductance of strong solutions of trichloroacetic acid. Dilute solutions have been investigated by Wightman and Jones and Dawson and Crann but their results are open to question. While their experimental technique appears to be good their values are greatly different from those obtained by me. In the light of my own experience I would attribute their errors to factors inherent in the dilute solutions. This will be discussed further in a later section (Page 79). It is sufficient to point out here that the values quoted by these authors for the limiting equivalent conductance of trichloroacetic acid are in error.

In summation, the conductances of dilute solutions of the electrolytes in question have been dealt with extensively within the limits of the earlier experimental techniques. No accurate data exist for concentrated solutions.

Nature of the Problem

The Nature of the Problem

It is obvious from a review of the literature that the study of the conductances of solutions more concentrated than 0.1 N has been neglected. The International Critical Tables give data for silver nitrate in the concentration range up to 8.46 N at 25° C., and for ammonium nitrate up to 7.5 N at 18° C. The literature reference is omitted but the data resemble those of Sachanov (50). The extended Debye-Hückel theory accounts for the behaviour of strong electrolytes up to a concentration of 0.1 N, but no theoretical treatment and no empirical extension of existing theories is even remotely successful in the higher concentration range.

In this research it was desired to obtain good experimental data at high concentrations. The electrolytes chosen were silver nitrate and ammonium nitrate, selected because of their high solubility (9.709 and 11.282 N, respectively at 25° C.) and because of their relatively low melting points. The latter factor was considered because it is expected to carry this research to concentrations increasing to 100% solute in the molten condition. (This will be possible since the melting points lie well below the critical temperature of water.) It was decided to carry out the research first at 25° C. because at this temperature fewer complications in technique arise. Then, to take advantage of the higher solubility, the temperature was to be raised to 95° C. which would make possible the investigation of solutions of higher concentration (14.02 N and 14.81 N. for silver nitrate and ammonium nitrate respectively.

In conductance literature it has been customary to attempt to correlate conductance with viscosity measurements because the change in mobility of the ions (and hence in conductance) may be due in part at least to change in fluidity of the solutions and, although measurement of viscosity does not necessarily measure the resistance to the motion of the ions, it was decided to obtain data on the viscosity of strong solutions at 25° C. and 95° C. These data would make possible the calculation of temperature coefficients of fluidity and of conductance which might throw further light on the problem of concentrated solutions.

To compare strong with weak electrolytes, it was thought desirable to investigate the conductance and viscosity of acetic acid at 25° C. over the complete concentration range. Trichloroacetic acid was also chosen as supposedly an electrolyte of intermediate strength, although this has turned out to be a misconception. It was decided to investigate it at 25° C. and 60° C., the latter temperature making accessible the complete range of concentration. These data were to be used in the conventional Dilution Law treatment (Ostwald).

Experimental Technique

enough to contain the amount of solution desired so that no transfer was necessary.

The potassium chloride used as secondary standard in determining the cell constants was B. D. H. Analar reagent. It was re-crystallized twice and ignited in a platinum crucible in order that it might be absolutely dry before it was weighed.

The acetic acid, a Canadian Industries Ltd. product of high degree of purity (99.8%), was used without further purification since the analysis indicated only the presence of water.

B. Conductance Measurements

(1) The Bridge

A Campbell-Shackleton Bridge, especially designed for this type of measurement by the Leeds and Northrup Company, was used. It was assembled and operated in accordance with their specifications for which they claim an accuracy of ± 0.05%. The detector used was an ordinary telephone head-piece without amplification which is unnecessary in these strong solutions. Further details are given in the Leeds and Northrup pamphlet "Directions for Capacitance and Conductance Bridge using No. 1553 Shielded Ratio Box."

(2) The Conductance Cells

Seven of the conductance cells employed were of the design recommended by Jones and Bollinger (59). The eighth was a vertical cell which would exhibit the Parker effect (60) if solutions of high resistance were measured in it. The Parker effect introduces an error in measurement due to a shunt path for the current along the filling tubes of the cell which are parallel to and close to the solution between the electrodes. This second path for the current is more effective for solutions whose resistance is high but is negligible for highly conducting solutions. To overcome the effect, Jones and Bollinger designed a cell whose filling tubes were far apart, about 15 cms., and they recommended that cells be tested by obtaining measurements at different frequencies. All of the cells used gave no change in resistance with change in frequency (from 500 - 5000 cycles) so were concluded to be of proper design.

Diagrams of the conductance cells used (about three-quarters of actual size) appear in Figures 1 and 2. The frequency used in the actual measurements was 1000 cycles. Sharp minima were obtained in the head-phones (readings of 1 in 10,000 were clearly audible so errors due to polarization were absent). Some of the cells had platinized electrodes, but the cells of very high constant were used without platinization. There was no difference in the values obtained with both types: the minima were sharp in all cases.

All authors recommend that the cells be filled with distilled water when not in use, i. e., they should not be allowed to dry. The same results were obtained whether the cells were dried or not, so, since it was more expedient to fill the cells when dry, they were first rinsed thoroughly with distilled water and then dried with pure alcohol and ether.

(3) The Cell Constant

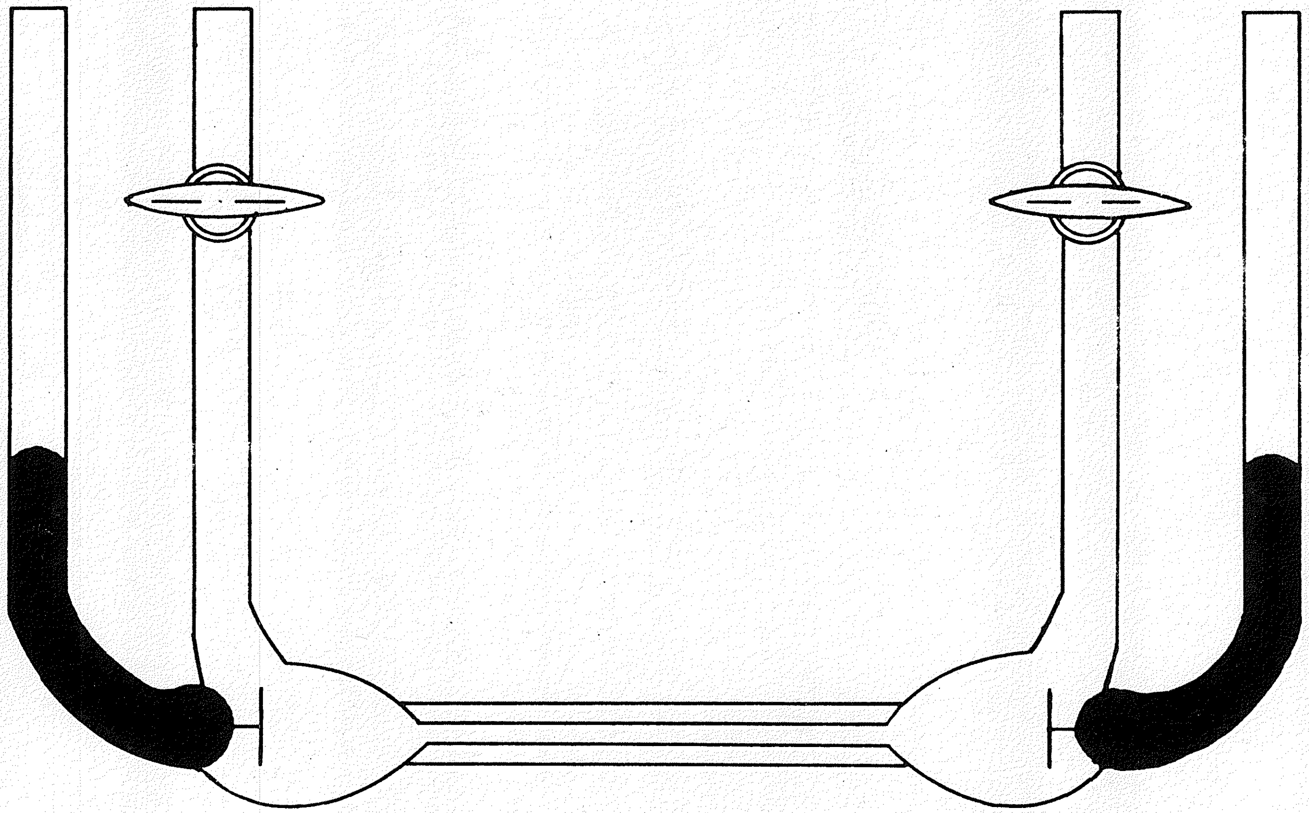


FIGURE 1. CONDUCTANCE CELL

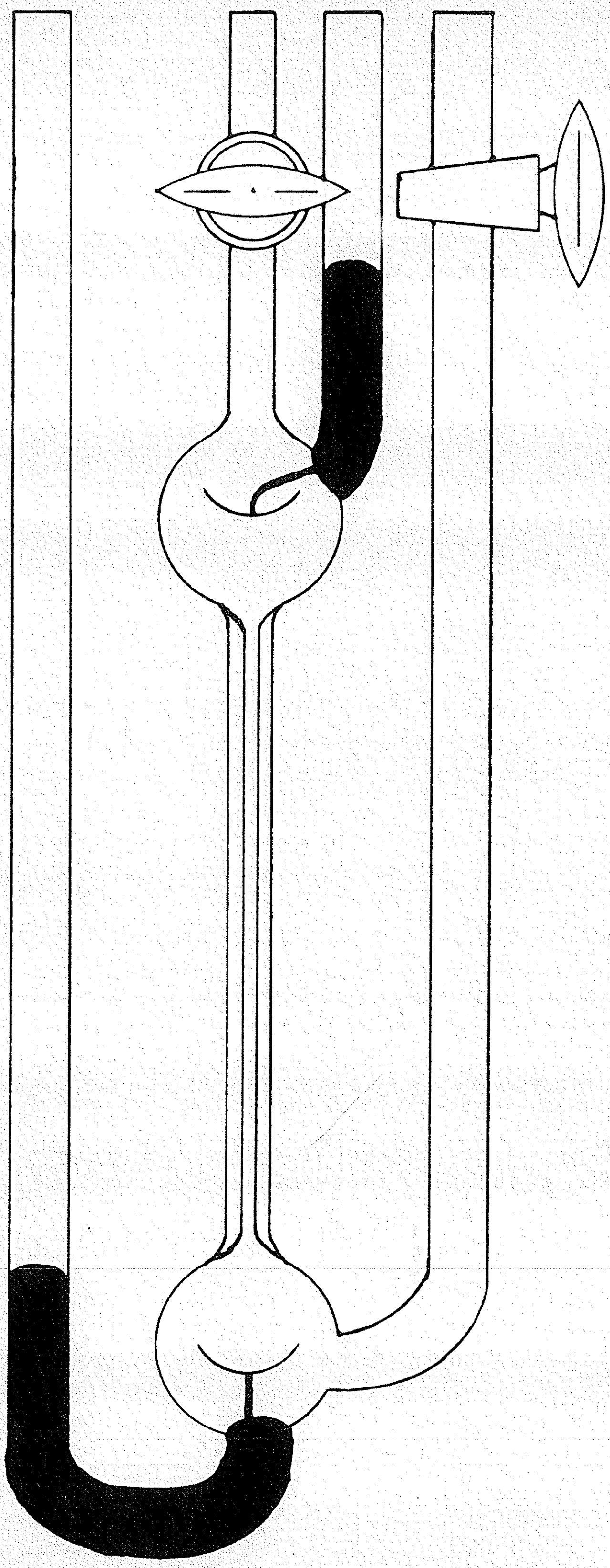


FIGURE 2. CONDUCTANCE CELL

The cell constants were determined using twice recrystallized potassium chloride which was ignited in a platimum dish before weighing. The solutions were made up according to the specifications of Jones and Bradshaw (61) who have determined the specific conductances of the solutions described at 0°, 18°, and 25° C. The solutions are defined as follows:

71.1352 grams of potassium chloride per 1000 grams of solution in vacuum: conductivity x 10^6 at 25° C. = 111342 mhos

and

7.41913 grams of potassium chloride per 1000 grams of solution in vacuum: conductivity x 10^6 at 25° C. = 12856.0 mhos.

In actual practice only 100 grams of solution was made, a calculated aliquot of potassium chloride was weighed (to a tenth of a milligram) and the solution weighed to a milligram. No data are available on the specific conductance of any suitable material for a secondary standard at 95° C. and 60° C., so it was necessary to apply the correction for the change in geometry of the cell with the increased temperature. Washburn (62) discusses the necessary correction and shows that, for cells which have a long capillary separating the electrodes, the changes in length and in cross section of the capillary due to the expansion of the glass are the only errors of moment. The change in area of the electrodes is neglibly small. (See the end of this section for a detailed account of the Washburn correction.) The result: multiply the cell constant at 25° C. by the coefficient of linear expansion of Pyrex glass and by the temperature interval to obtain the correction to be applied to the cell constant at 25° C.

The cell constants at 25° C. determined experimentally and their corresponding values at 95° C.and at 60° C. are given below:

TABLE 2

COMPARISON OF THE CELL CONSTANTS DETERMINED AT 25° C. WITH THOSE CALCULATED AT 95° C. and AT 60° C.

Cell Constant at 25° C.	Cell Constant at 60° C.	Cell Constant at 95° C.
33.64	-	-
38.42	-	-
148.94	-	-
210.86	-	210.82
511.72	-	511.6
1133.9	-	1133.7
1156.9	-	1156.7
1293.56	1293.44	-

The change in cell constant with temperature is very small. Using the corrected value for the cell constant at 60° C., it was possible to determine the specific conductance of the Jones and Bradshaw solution. The 0.1 demal solution (containing 7.41913 g. KCl in 1000 g. of solution in vacuo and made up as described on Page 45) was found to have a specific conductance of 0.02186 mhos at 60° C., a value which agrees favourably with that (0.021853 mhos) obtained by Lelong, Tartar, Lingefelter, O'Loane and Cadle (63) who employed the same procedure.

(These results are listed here rather than in a later section because they are a result of the experimental technique of determining cell constants and have no direct bearing on the main results of this research.)

<u>The Washburn Correction (62)</u>

The cell constant (Z) is the ratio of the length (ℓ) of solution between the electrodes to the area (a) of the electrodes (for cells in which the connecting tube is of greater cross section than the electrodes) or to the area of the cross section of the solution if the connecting tube is a capillary, i. e.,

$$Z = \ell / a$$ ㉚ .

Differentiating with respect to temperature gives

$$\frac{dZ}{dt} = \left(a\frac{d\ell}{dt} - \ell\frac{da}{dt}\right) / a^2$$ ㉛ .

Now $$\frac{d\ell}{dt} = \beta(\ell + s) - \gamma s$$ ㉜

where β = coefficient of linear expansion of Pyrex glass,

ℓ = length between electrodes,

s = length of electrode posts, and

γ = coefficient of linear expansion of platinum.

For cells which have a long capillary separating the electrodes, equation ㉜ simplifies to $\frac{d\ell}{dt} = \beta\ell$ ㉝ .

Now $$\frac{da}{dt} = 2\beta a$$ ㉞ *.

Hence $$\frac{1}{Z}\frac{dZ}{dt} = \frac{a}{\ell}\cdot\frac{1}{a}\left(\ell\beta - \frac{\ell}{a}\cdot 2\beta a\right) = -\beta$$ ㉟ .

---

*The simplification in ㉝ is obvious: equation ㉞ may be proved as follows:

$C = 2\pi r$ where C = circumference of the tube and r = radius of the tube.

(Cont'd on following page)

(4) The Thermostat

The earlier part of this work was done at 25.00 ± 0.01° C. in a thermostat filled with paraffin oil as recommended by Davies (64) (water introduces a capacity effect). The cells were allowed to remain in the thermostat until a constant reading was obtained on the bridge. The fluctuation in the temperature of the thermostat was only ± 0.01°, a temperature change not large enough to produce detectable fluctuation in bridge readings.

The later part of the work was done at 95.0 ± 0.05° C. with Stanolax, a hydrocarbon oil of high boiling point and low vapour pressure, as thermostatic fluid. Three Archimedean stirrers were used and the bath was insulated with about two inches of asbestos powder and an inch of felt. A cover was made with

---

$$\frac{dc}{dt} = c\beta = 2\pi r\beta$$

$$a = \pi r^2 = \frac{1}{2} c r$$

$$\frac{da}{dt} = \frac{1}{2}\left(c\frac{dr}{dt} + r\frac{dc}{dt}\right) = 2\pi r\frac{dr}{dt}$$

$$= \frac{1}{2}\left(2\pi r\frac{dr}{dt} + r\, 2\pi r\beta\right)$$

$$= \pi r\frac{dr}{dt} + \pi r^2\beta$$

$$\therefore \pi r^2\beta = \pi r\frac{dr}{dt}$$

$$\text{Then } a\beta = \frac{1}{2}\frac{da}{dt}$$

$$\therefore \frac{da}{dt} = 2a\beta.$$

suitable perforations for leads, etc., and it too was covered with an inch of felt. With these precautions the fluctuations in temperature were no more than ± 0.05°.

When this research was started, a platinum resistance thermometer was not available. The 25° C. setting was obtained using a National Bureau of Standards mercury-in-glass thermometer which was checked at 32.383° C. by the transition temperature of the equilibrium

$$Na_2SO_4 \cdot 10H_2O \rightleftharpoons Na_2SO_4 + 10H_2O \qquad ㊱$$

determined by Dickinson and Mueller (65). The 25° C. setting has since been checked with a platinum resistance thermometer and was found to be 25.00 ± 0.01° C. The mercury-in-glass standard thermometer was found to be in excellent accord with the platinum resistance calibration at 60° C. (actually 59.99° C.) and was assumed to be correct at 95° C.

(5) The Nature of the Solutions

The salt solutions investigated at 25° C. were made up by weight. Approximately 100 ml. of solution was made; the salt was weighed to a tenth of a milligram, the solution to a centigram using as a counterpoise a flask of the same volume. The density of the solution was determined in a manner to be described later. Sufficient information was then known to calculate the normality. The accuracy of the concentration expressed as weight percent is therefore ± 0.005% but since the normalities of the solutions are dependent on the densities (accurate to ± 0.05%) these concentrations are accurate to ± 0.05%.

At 95° C. a different procedure was necessary due to the formation of air bubbles in the cell and pycnometer. Boiling the solvent alone did not remove the dissolved air so it was found necessary to make the solution of freshly boiled water and to boil it briefly. This resulted in the loss of an unknown amount of water which made it necessary to analyse the solutions. Some were analysed in the conventional manner: deposition of silver from potassium cyanide solution for silver nitrate and the Kjeldahl determination of ammonia for ammonium nitrate. The latter method gave results reproducible to only ±0.15%. The electrochemical analysis (of silver nitrate solutions) was abandoned because it was impossible to attain the desired accuracy. The method, although a standard one, gives results which are not sufficiently reproducible for the purpose in hand, when double cyanide is used as the electrolyte. If this electrolyte is not used the deposit is loose and non-adherent. Analysis by conductometric titration with standard sodium chloride solution (and a calibrated burette) was next tried. While the burette could be read to 0.02 ml. it was felt that the graphical determination of the equivalent volume could be read to little better than ± 0.5%. The method of analysis finally used is described below.

This method consisted in determining the specific conductance at 25° C. and comparing it with the values previously obtained in the 25° C. phase of the work. Analytical interpolation gave the weight percent, and density at 95° C. allowed of calculating the normality and dilution at the latter temperature.

This method was used in analysing both silver nitrate and ammonium nitrate solutions. The accuracy of the analyses is thus limited to that of the measurements of specific conductance at 25° C. and to the accuracy of the density measurements at 95° C. These quantities were determined to an accuracy of ± 0.05%: the accuracy of the analysis may then be estimated at ± 0.05%. The actual concentrations have been expressed to four significant figures.

The acetic acid solutions were analysed with standard (carbonate free) sodium hydroxide solution. The volumetric apparatus (flasks and burettes) was calibrated and methyl orange used as indicator. The results of the analyses were reproducible to ± 0.05%.

The trichloroacetic acid solutions were made up by distilling the acid into a weighed flask (200 ml. capacity, weighed to a centigram against a counterpoise of the same volume). The system was completely dry and protected from the moisture in the atmosphere by a drying tube of calcium chloride. After collecting the acid, the flask was stoppered and weighed. Conductance water was added and the solution weighed again. The densities were determined. This method was possible at both temperatures because the solutions did not need to be boiled to expel dissolved air at the relatively low temperature of 59.99° C. Here, the acid was weighed only to a centigram but large amounts were distilled (say 40 grams). Hence, the weighing was sufficiently accurate.

(6) The Conductance Water

Because of the very high specific conductance of the salt solutions ($\geq$ 0.01277 mhos), special conductance water was not necessary. Instead, a good quality distilled water having specific conductance equal to 5.28 x 10^{-6} mhos was used. Water to be used for the trichloroacetic acid solutions of low specific conductance was distilled from alkaline potassium permanganate solution and was found to have a specific conductance of 0.9 x 10^{-6} mhos. A solvent correction was applied to the conductance of those acid solutions in which the conductance of the solvent was significant. (True specific conductance = measured specific conductance of the solution − 0.9 x 10^{-6}. The solutions to which this correction was applied are marked with an asterisk in Tables 5 and 6.)

C. Density and Viscosity Measurements

A Weld pycnometer, calibrated with water at 25°, 60° and 95° C., was used for density determinations. The data for the density of water were taken from Volume 3, Page 24 of the International Critical Tables (1929 ed.). They read as follows: 0.99707_{39} g./ml. at 25° C., 0.9832_4 g./ml. at 60° C. and 0.9686_5 g./ml. at 95° C. It will be noticed that the figures for the two higher temperatures have been determined to four significant figures only. This no doubt is due to the difficulty of obtaining absolute temperature control. Obviously this source of error and the inevitable loss of water by vaporization are the factors which limit the accuracy of my density determinations at these temperatures. At 25° C. approximately 10 ml. quantities of solution, say between 10 and 30 grams, were weighed against a counterpoise to 0.1 mg. At the higher temperatures the weighings could be reproduced to 1 mg. only due to evaporation of the solution while in the thermostat. This represents higher accuracy than I claim (± 0.05%) but I feel that despite the fact that the weighings were reproducible to 1 in 10000 to 30000 the concentrations of the solutions change an indeterminate amount (with the stronger solutions particularly) and this makes it impossible to claim the accuracy suggested by that of the weighings.

In the viscosity measurements an Ostwald viscometer calibrated with water and possessing a run-time of 100 - 400 seconds was employed. The Couette correction (66) and the Hagenbach correction (67) were not applied. These are corrections to the Poiseuille equation governing viscosity:

$$\eta = \frac{\pi r^{4} p t}{8 l v}$$ ㊲

where η= dynamic viscosity of the liquid (poise),

v= volume of liquid ($cm.^3$),

l= length of capillary tube (cm.),

t= time (secs.),

p= pressure difference between the ends of the tube ($dynes/cm.^2$) and

r= radius of tube (cm.).

The Poiseuille equation applies only stream-line flow in narrow tubes and assumes no acceleration along the axis of the tube. The Couette correction is applied to correct for acceleration in the initial part of the tube: l is increased by a factor k,r where k = 1.64 usually. A portion of the pressure difference is used in giving kinetic energy to the liquid. This makes necessary the kinetic energy or Hagenbach correction: let P = total pressure difference, P_1 = the effective pressure difference used in overcoming viscosity. Then $P_1 v$ = work done per second against viscosity and $\frac{v^3 d}{\pi^2 r^4}$ = the kinetic energy imparted per second. The total loss of energy $Pv = P_1 v + \frac{v^3 d}{\pi^2 r^4}$ ㊳ so the effective pressure $P_1 = P - \frac{v^2 d}{\pi^2 r^4}$ ㊴. Experimentally, the correction for kinetic energy $= \frac{k_2 v^3 d}{\pi^2 r^4}$ where k_2 = a constant called the Hagenbach coefficient which is characteristic of the viscometer used and must be evaluated by calibration. Equation ㊲ then becomes:

$$\eta = \frac{\pi P r^4}{8 v (l + k_1 r)} - \frac{k_2 v d}{8 \pi (l + k_1 r)} \qquad ㊵ .$$

Authors are not agreed upon the values to be used for k_1 and k_2; 1.64 and 1.12 are usually taken but many others have been proposed. It is generally agreed that the flow time (for an Ostwald viscometer) should be between 100 and 200 seconds. Schulz (68) takes into consideration the volume of efflux and quotes a range of 1/100 ml./sec. to 1/200 ml./sec. The viscometers used by me have a volume of efflux of 2.5 ml. and should therefore have a flow time between 250 and 500 seconds. The concensus of opinion is that for measurements other than the most precise it is sufficient to choose a calibrating fluid of approximately the same viscosity as the one to be measured and a viscometer designed to give a long flow time. According to Ostwald Luther (69) "Die obernerwähnte Korrektur für kinetische Energie kommt bei diesem Eichverfahren nur als Differenz für beide Flüssigkeiten Zur Geltung. Die

Eichflüssigkeit wählt man so, dass $\eta : \eta_0$ etwa zwischen 0.5 und 2, allenfalls auch 0.3 und 3 liegt."

A third error inherent in the use of the Ostwald viscometer is the drainage error but in comparative measurements this error cancels out since it common to the calibrating fluid and to the fluid being measured. (Here the surface tensions of the fluids are assumed equal.)

The viscosity figures have been quoted to four significant figures as have the density data - I therefore claim an accuracy of ± 0.05%.

Experimental Results

Experimental Results

The main results of direct experiment of this research are summarized in Tables 3, 4, 5, and 6.

The results for silver nitrate, ammonium nitrate, and acetic acid at 25° C. have already appeared in my Master's Thesis but should be included here to make this a complete survey of the research problem. The entire investigation of trichloroacetic acid and the 95° C. work on the other electrolytes were done following the Master's Thesis.

In the table are given the weight percent, normality, mole fraction, specific conductance, equivalent conductance, density, and viscosity (relative to water) of the solutions investigated.

The corresponding graphs of equivalent conductance vs. concentration appear in Figures 3, 4, and 5.

TABLE 3

SPECIFIC CONDUCTANCES (κ), EQUIVALENT CONDUCTANCES (Λ), DENSITIES (d), AND VISCOSITIES (η) OF SILVER NITRATE SOLUTIONS

A. AT TEMPERATURE OF 25.00° C

Concentration Wt. %	Concentration Normality	Concentration Mole Fraction	Specific Conductance (mhos)	Equivalent Conductance Λ	Density (g./ml.) d	Relative Viscosity (Water 1.000)
1.680	0.1000	0.001829	0.01091	109.1	1.011	1.009
15.01	1.004	0.02084	0.07815	77.82	1.137	1.074
26.74	1.998	0.04683	0.1303	64.20	1.276	1.177
36.41	3.028	0.07901	0.1665	54.97	1.413	1.307
44.02	4.000	0.1141	0.1940	48.50	1.544	1.472
50.71	5.029	0.1553	0.2168	43.14	1.685	1.658
59.28	6.006	0.2099	0.2316	38.55	1.810	1.890
61.30	7.012	0.2461	0.2413	34.70	1.943	2.170
65.61	8.011	0.2956	0.2501	31.20	2.075	2.505
69.45	9.010	0.3470	0.2522	27.99	2.203	2.998
71.59	9.709	0.3811	0.2523	26.1	2.298	3.330

TABLE 3 (CONT'D)

SPECIFIC CONDUCTANCES (κ), EQUIVALENT CONDUCTANCES (Λ), DENSITIES (d), AND VISCOSITIES (η) OF SILVER NITRATE SOLUTIONS

B. AT TEMPERATURE OF 95.0° C

Concentration			Specific Conductance (mhos)	Equivalent Conductance (mhos)	Density (g./ml.)	Relative Viscosity (Water 1.000)
Wt. %	Normality	Mole Fraction				
0.9363	0.0534	0.001002	0.0159	298.3	0.9696	0.993
18.57	1.220	0.02419	0.2107	172.7	1.116	1.122
29.70	2.189	0.04481	0.3235	147.8	1.252	1.263
36.95	2.967	0.06216	0.3880	130.8	1.364	1.425
50.74	4.829	0.1093	0.4978	103.1	1.617	1.797
60.46	6.591	0.1621	0.5594	84.86	1.852	2.280
69.54	8.830	0.2422	0.6014	68.10	2.157	3.107
73.38	9.906	0.2926	0.6070	61.27	2.293	3.590
79.45	11.876	0.4095	0.5981	50.34	2.540	4.262
82.33	14.02	0.5817	0.5619	40.07	2.816	-

TABLE 4

SPECIFIC CONDUCTANCES (κ), EQUIVALENT CONDUCTANCES (Λ), DENSITIES (d), AND VISCOSITIES (η) OF AMMONIUM NITRATE SOLUTIONS

A. AT TEMPERATURE OF 25.00°C

Concentration			Specific Conductance (mhos)	Equivalent Conductance (mhos)	Density (g./ml.)	Relative Viscosity (Water 1.000)
Wt. %	Normality	Mole Fraction				
0.800	0.100	0.001813	0.01227	112.95	1.001	0.991
7.810	1.004	0.01925	0.1017	101.32	1.029	0.960
15.06	1.993	0.04056	0.1833	91.95	1.059	0.952
21.91	2.982	0.06437	0.2513	84.28	1.089	0.977
28.74	4.020	0.09226	0.3085	76.78	1.120	1.009
34.93	5.014	0.09806	0.3507	70.00	1.149	1.061
41.01	6.036	0.1557	0.3809	63.12	1.178	1.144
46.54	7.015	0.1912	0.3979	56.73	1.206	1.234
51.98	8.011	0.2311	0.4036	50.36	1.234	1.366
57.31	9.043	0.2762	0.3973	43.93	1.262	1.531
62.14	10.004	0.3225	0.3819	38.19	1.289	1.776
68.49	11.282	0.3921	0.3538	31.3	1.319	2.170

TABLE 4 (CONT'D)

SPECIFIC CONDUCTANCES (κ), EQUIVALENT CONDUCTANCES (Λ), DENSITIES (d), AND VISCOSITIES (η) OF AMMONIUM NITRATE SOLUTIONS

B. AT TEMPERATURE OF 95.0° C.

Concentration			Specific Conductance (mhos)	Equivalent Conductance (mhos)	Density (g./ml.)	Relative Viscosity (Water 1.000)
Wt. %	Normality	Mole Fraction				
0.728	0.0878	0.001591	0.02689	306.1	0.9656	-
1.605	0.1940	0.004195	0.05340	275.3	0.9677	1.016
8.041	0.9963	0.02489	0.2340	234.8	0.9918	1.054
12.12	1.525	0.03032	0.3526	213.6	1.007	1.076
19.90	2.576	0.05476	0.4780	185.6	1.036	1.142
29.96	3.600	0.08156	0.6007	166.9	1.069	1.217
31.12	4.221	0.09942	0.6528	154.7	1.086	1.296
38.13	5.325	0.1342	0.7218	135.6	1.118	-
45.89	6.632	0.1809	0.7695	116.0	1.157	1.555
53.12	7.950	0.2340	0.7775	97.79	1.198	1.777
57.50	8.740	0.2703	0.7694	88.02	1.217	1.913
64.65	10.12	0.3403	0.7317	72.43	1.253	2.381
64.81	10.16	0.3422	0.7321	72.06	1.255	2.365
69.54	11.13	0.3970	0.6897	61.98	1.281	2.705
79.74	13.31	0.5420	0.5598	42.06	1.336	3.89
79.92	13.38	0.5456	0.5539	41.40	1.341	-
85.58	14.81	0.6492	0.4251	28.70	1.385	4.29

TABLE 5

SPECIFIC CONDUCTANCES (κ), EQUIVALENT CONDUCTANCES (Λ), DENSITIES (d), AND VISCOSITIES (η) OF TRICHLOROACETIC ACID SOLUTIONS

A. AT TEMPERATURE OF 25.00°C.

	Concentration			Specific Conductance (mhos)	Equivalent Conductance (mhos)	Density (g./ml.)	Relative Viscosity (Water 1.000)
	Wt. %	Normality	Mole Fraction				
☆	-	0.001026	-	0.0003755	365.9	0.9972	1.004
☆	-	0.001016	-	0.0003552	349.6	0.9972	-
☆	-	0.01018	-	0.003729	366.5	0.9979	-
☆	-	0.01072	-	0.003672	342.6	0.9979	-
	0.00728	0.04460	0.000725	0.01574	352.9	1.001	1.017
	1.640	0.1010	0.002390	0.03390	335.7	1.005	-
	2.460	0.1521	0.003539	0.04926	323.8	1.009	-
	15.32	1.009	0.01956	0.2090	207.0	1.076	1.405
	16.57	1.099	0.02140	0.2186	198.9	1.083	1.449
	22.95	1.566	0.03179	0.2443	156.0	1.115	1.623
	29.00	2.044	0.04308	0.2481	121.4	1.152	1.885
	41.56	3.116	0.07272	0.2110	67.72	1.225	2.508
	48.62	3.777	0.09448	0.1763	46.68	1.269	2.961
	56.52	4.568	0.1254	0.1317	28.83	1.321	3.567
	65.22	5.513	0.1713	0.08047	14.60	1.381	4.407
	69.57	6.015	0.2013	0.05698	9.473	1.413	4.925
	73.36	6.523	0.2366	0.03693	5.662	1.445	5.512
	77.79	7.029	0.2786	0.02157	3.069	1.476	6.218
☆	84.09	7.859	0.3684	0.006497	0.8268	1.527	7.604
☆	90.30	8.721	0.5067	0.0009259	0.1062	1.578	11.368

☆ Solvent correction applied.

TABLE 5 (CONT'D)

SPECIFIC CONDUCTANCES (κ), EQUIVALENT CONDUCTANCES (Λ), DENSITIES (d), AND VISCOSITIES (η) OF TRICHLOROACETIC ACID SOLUTIONS

B. AT TEMPERATURE OF 59.99° C.

Concentration			Specific Conductance (mhos)	Equivalent Conductance (mhos)	Density (g./ml.)	Relative Viscosity (Water 1.000)
Wt. %	Normality	Mole Fraction				
1.530	0.09273	0.001659	0.04430	477.7	0.9906	1.042
22.57	1.513	0.03108	0.3152	208.3	1.095	1.473
33.64	2.369	0.05296	0.3056	129.0	1.151	1.786
53.14	4.108	0.1112	0.1982	48.24	1.263	2.603
73.83	6.344	0.2373	0.05297	8.350	1.404	4.053
75.75	6.560	0.2563	0.04011	6.115	1.415	4.160
84.01	7.607	0.3668	0.01074	1.412	1.480	5.208
100.0	9.795	1.000	2.5×10^{-8}	2.6×10^{-6}	1.601	8.445

TABLE 6

SPECIFIC CONDUCTANCES (κ), EQUIVALENT CONDUCTANCES (Λ), DENSITIES (d), AND VISCOSITIES (η) OF ACETIC ACID SOLUTIONS AT 25.00°C.

	Concentration			Specific Conductance (mhos)	Equivalent Conductance (mhos)	Density (g./ml.)	Relative Viscosity (Water 1.000)
	Wt. %	Normality	Mole Fraction				
*	10.30	1.735	0.0330	1.74×10^{-3}	1.003	1.011	1.197
*	20.19	3.437	0.0733	1.83×10^{-3}	5.31×10^{-1}	1.024	1.407
*	30.15	5.206	0.1150	1.61×10^{-3}	3.09×10^{-1}	1.036	1.640
*	38.79	6.751	0.1600	1.31×10^{-3}	1.94×10^{-1}	1.044	1.833
*	48.04	8.423	0.221	9.47×10^{-4}	1.12×10^{-1}	1.052	2.038
*	57.32	10.106	0.287	6.14×10^{-4}	6.08×10^{-2}	1.058	2.259
*	67.10	11.883	0.380	3.33×10^{-4}	2.80×10^{-2}	1.063	2.473
*	76.52	13.585	0.494	1.32×10^{-4}	1.79×10^{-3}	1.065	2.635
*	87.09	15.415	0.670	2.30×10^{-5}	3.55×10^{-4}	1.062	2.449
	99.76	17.360	0.990	2.30×10^{-7}	3.99×10^{-6}	1.044	1.263

* Solvent correction applied.

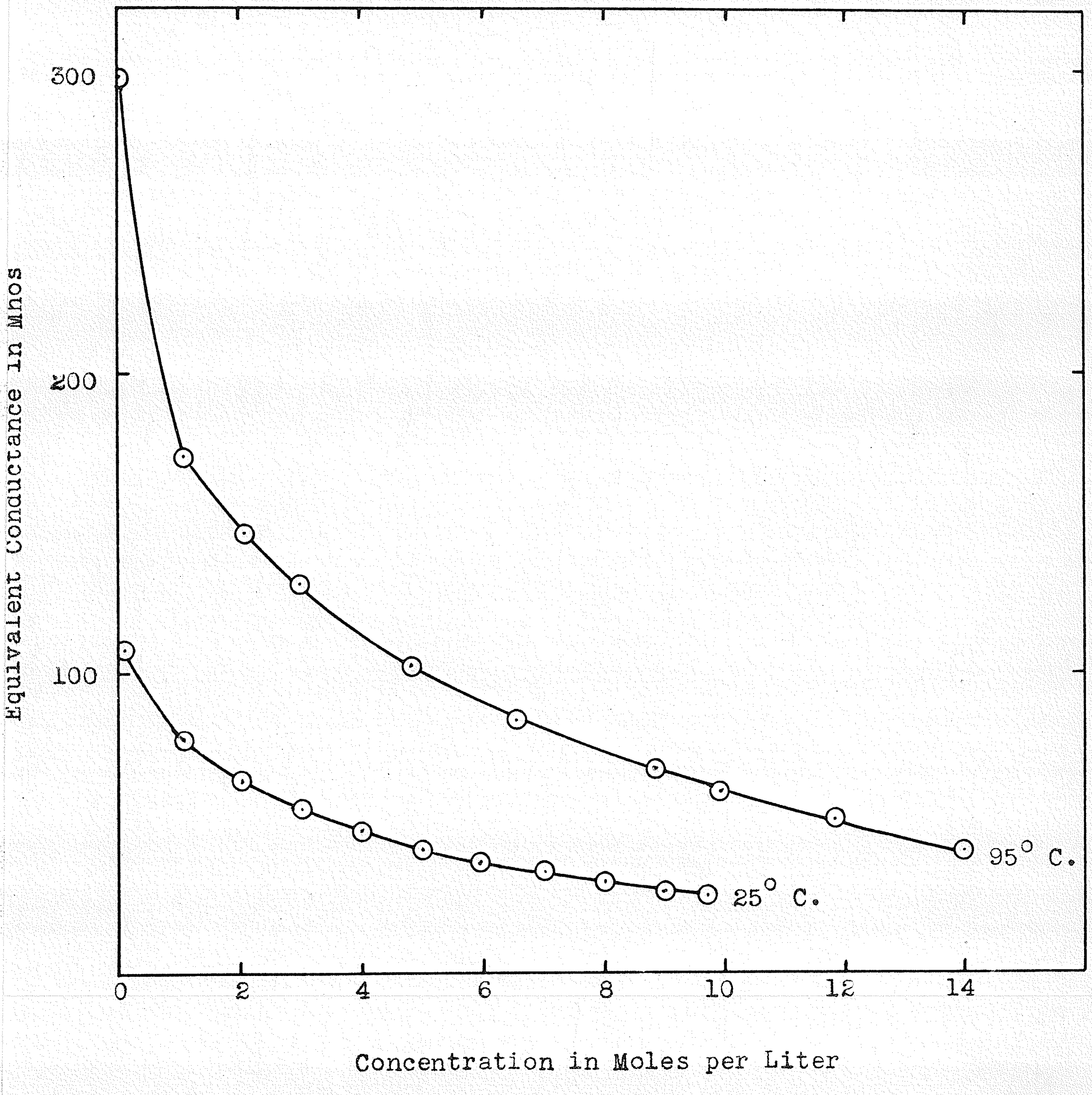


FIGURE 3. CONDUCTANCE VS. CONCENTRATION FOR SILVER NITRATE

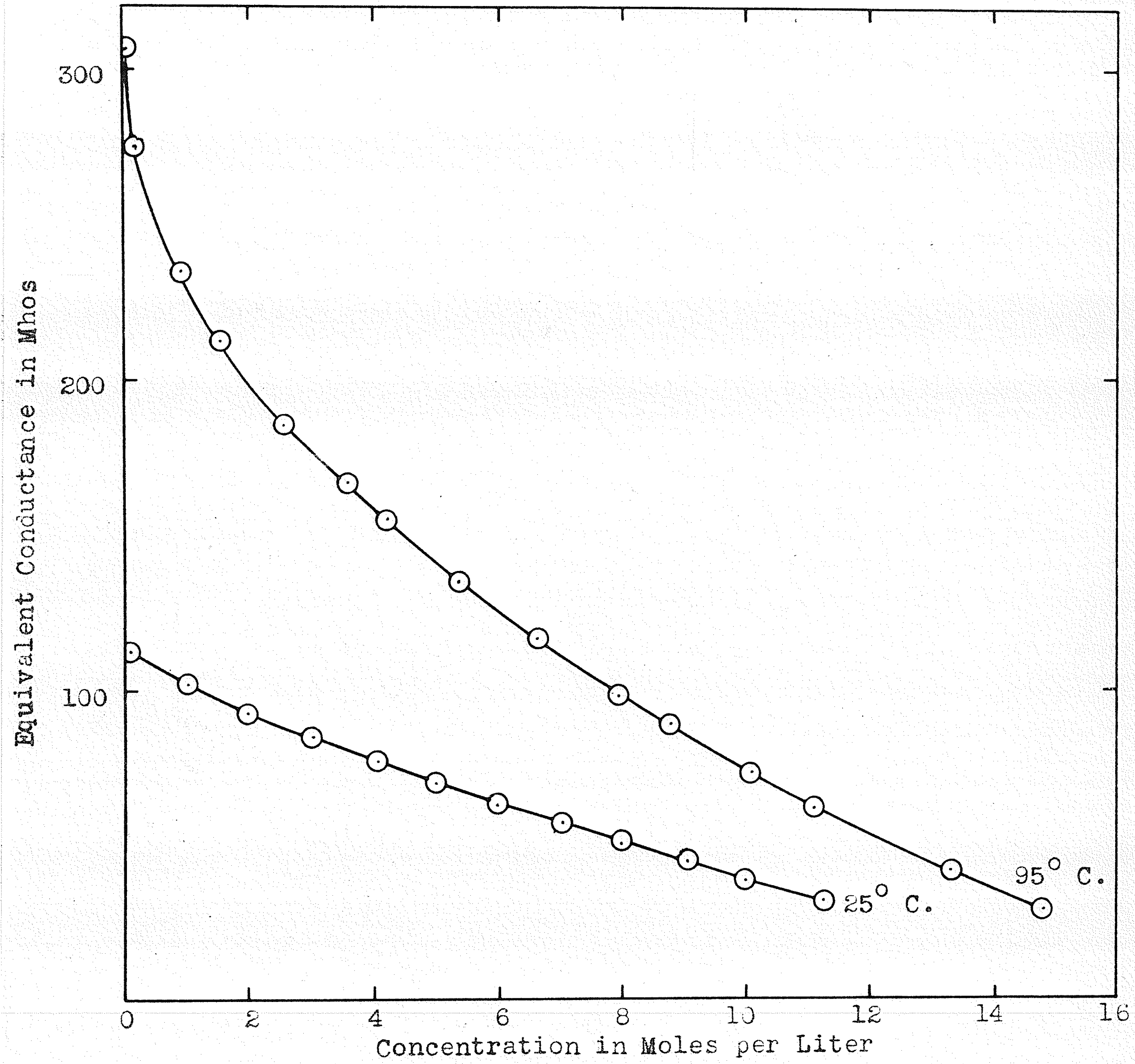


FIGURE 4. CONDUCTANCE VS. CONCENTRATION FOR AMMONIUM NITRATE

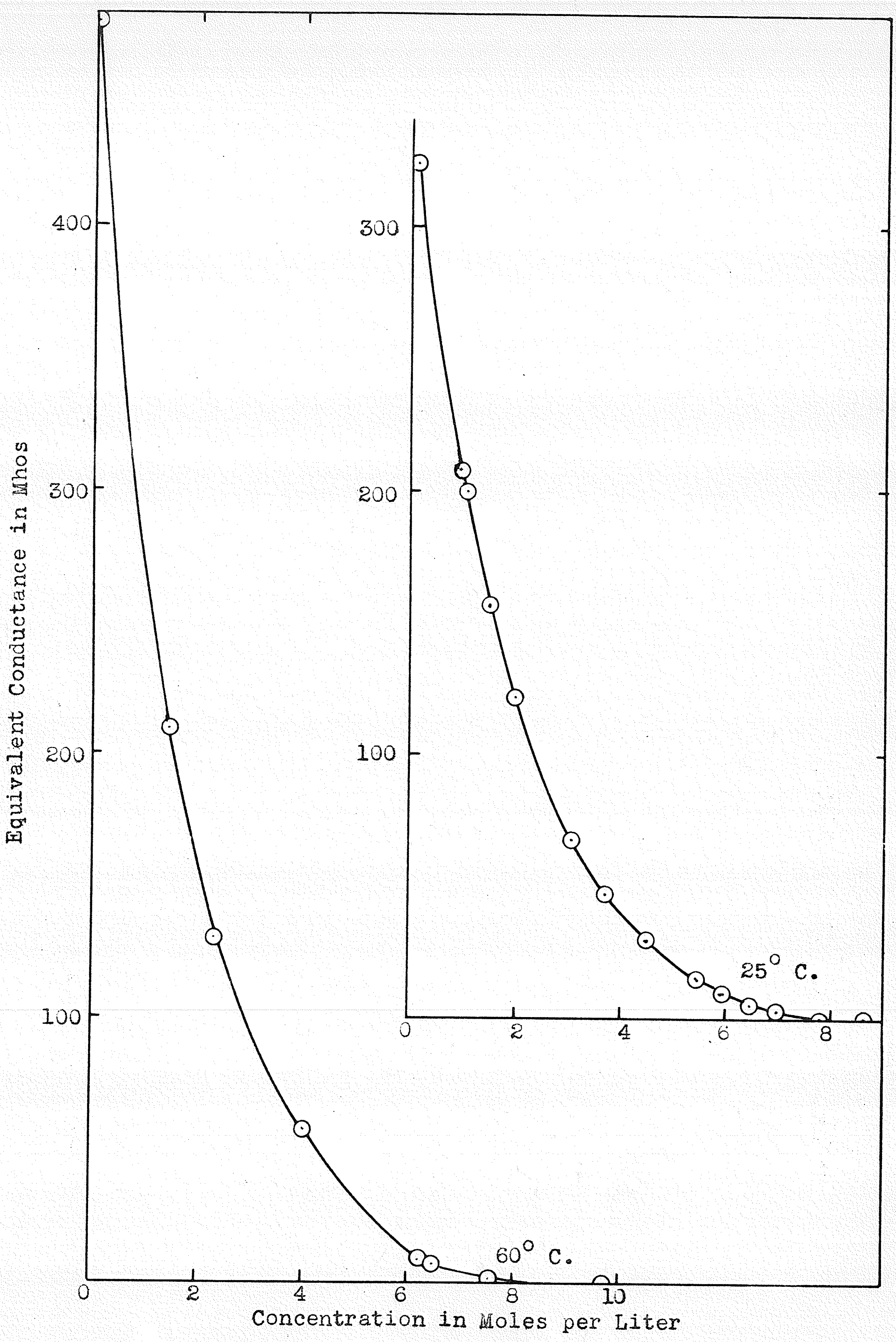


FIGURE 5. CONDUCTANCE VS. CONCENTRATION FOR TRICHLOROACETIC ACID

Discussion of the Results

Discussion of the Results

A. Estimation of Accuracy

In the preceding section I have given an estimation of the accuracy of each measurement together with a description of it. These estimates are compiled below:

concentration of solutions: ± 0.05%;
temperature control: ± 0.01°C. at 25°C.,
± 0.05°C. at 95°C. and
± 0.01°C. at 60°C.;
accuracy of the conductance bridge: ± 0.05%;
density: ± 0.05%; and
viscosity: ± 0.05%.

I think it impossible to predict the influence of errors in these measurements on the final conductance figures. The only alternative is to compare my results wiht literature values. For the more concentrated solutions no such values exist at the temperatures investigated by me. However, Shedlovsky (9) quotes a value of 109.10 mhos for the equivalent conductance of 0.1 N silver nitrate solution at 25.00° C. He claims an accuracy of "one or two hundredths of a percent" and his description of his apparatus and technique leave no doubt of the validity of this statement. I, therefore, used the 0.1 N silver nitrate solution as a check on my apparatus and experimental technique. Using cells of widely different cell constants and solutions made up afresh for each determination I consistently obtained the value of 109.1 ± 0.01 mhos for 0.1 N silver nitrate at 25.00° C. Considering the excellent agreement with the literature value of at least six determinations of the equivalent conductance of 0.1 N silver nitrate solution, I deem it permissible to claim an overall accuracy of at least ± 0.05 for the 25° C. measurements. The greater difficulty attendant on the 95° C. measurements would require a less ambitious estimation of accuracy in these. However, as with the 25° C. data, these were found to lie on a smooth conductance-concentration curve drawn to an enlarged scale which would detect slight errors, if present. Of necessity, these plots are greatly reduced in the figures given here.

Data do exist in the literature with which to compare my density values. The following is a table comparing my density results at 25° C. with those of Jones and Colvin (54) for silver nitrate solutions and with those compiled from the literature and listed in the International Critical Tables (70) for ammonium nitrate and acetic acid solutions. (A very large number of authors are concerned with these data; it would serve no real purpose to list them individually here.) Finally, the density values for trichloroacetic acid solutions are compared with those calculated from the equation proposed by Mameli (71):

$$d = d_W + 0.00505p + 0.000006119p^2 + 0.0000001038p^3 \quad ㊶$$

where d_W = density of water at 25° C. and

p = weight percent of the solution.

TABLE 7

COMPARISON OF THE DENSITY DATA AT 25.00° C. OBTAINED IN THIS RESEARCH WITH LITERATURE VALUES

A. Silver Nitrate

Normality	Density (g./ml.) Jones & Colvin (54)	Density (g./ml.) This Research
0.10	1.01118	1.011
(1.0)	1.13643	1.135
2.0	1.27363	1.275
(3.0)	1.40942	1.410
(4.0)	1.54407	1.544

B. Ammonium Nitrate

Normality	Density (g./ml.) International Critical Tables (70)	Density (g./ml.) This Research
1.004	1.029	1.029
1.993	1.060	1.059
2.982	1.089	1.089
4.020	1.119	1.120
5.014	1.149	1.149
6.036	1.178	1.178
7.015	1.205	1.206

C. Acetic Acid

Normality	Density (g./ml.) International Critical Tables (70)	Density (g./ml.) This Research
1.735	1.011	1.011
3.437	1.025	1.024
5.206	1.036	1.036
6.751	1.044	1.044
8.423	1.052	1.052
10.106	1.058	1.058
11.883	1.063	1.063
13.585	1.065	1.065
15.415	1.063	1.062
17.360	1.045	1.044

TABLE 7 (CONT'D)

COMPARISON OF THE DENSITY DATA AT 25.00° C. OBTAINED IN THIS RESEARCH WITH LITERATURE VALUES

D. Trichloroacetic Acid

Wt. %	Density (g./ml.) Equation Proposed By Mameli (71)	Density (g./ml.) This Research
.00728	.998	1.000
1.64	1.005	1.005
2.46	1.009	1.009
15.32	1.076	1.076
16.57	1.083	1.083
22.95	1.117	1.115
29.00	1.151	1.152
41.56	1.225	1.225
48.62	1.269	1.269
56.52	1.321	1.321
65.22	1.381	1.381
69.57	1.413	1.413
73.36	1.442	1.445
77.79	1.476	1.476
84.09	1.527	1.527
90.30	1.579	1.578

B. Discussion of the Measured Quantities

Smooth conductance-concentration curves were obtained for all the electrolytes studied: the equivalent conductance decreases with concentration. No minima exist in the curves despite the high concentrations investigated at 95° C. (14.02 N for silver nitrate, 14.81 N for ammonium nitrate, and 9.79 N for trichloroacetic acid) and linearity appears to be present in the ammonium nitrate curve at 95° C. and at 25° C. at the maximum concentrations. This is more clearly shown by means of the following table in which the experimental values are compared with those calculated from the slope of the conductance-concentration curve between the two highest concentrations, assuming that the linearity persists into the weaker regions:

TABLE 8

COMPARISON OF EXPERIMENTAL VALUES OF EQUIVALENT CONDUCTANCE OF AMMONIUM NITRATE SOLUTIONS WITH THOSE CALCULATED ON A LINEAR (Λ VS. C) BASIS

A. AT 95° C.

Normality	$\Lambda_{calc.}$ (mhos)	$\Lambda_{exp.}$ (mhos)
11.13	61.96	61.99
10.12	70.45	72.44
8.74	82.72	88.04

B. AT 25° C.

Normality	$\Lambda_{calc.}$ (mhos)	$\Lambda_{exp.}$ (mhos)
9.043	43.38	43.93
8.011	48.94	50.36

Linearity is observed for the last three measurements at 95° C. A similar result is obtained at 25° C. for here again the last three points lie on a straight line. In the case of silver nitrate, the approach to linearity is less marked.

In a recent paper by Wetmore (72) the equivalent conductances of molten silver nitrate between temperatures of 210° and 330° C. are given. When these conductance values are plotted against the temperature (Figure 6) a straight line is obtained. If this is extrapolated to 95° C. the equivalent conductance of super-cooled silver nitrate is obtained for the temperature of my work, viz., $\Lambda = 5.3$ mhos. In a hitherto unpublished paper by Wetmore (73) an equation for the density of silver nitrate is given as $d = 3.867 + 0.001(300 - t)$ ㊷ whence d at 95° C. = 4.072. From this the normality of anhydrous (super-cooled) silver nitrate at 95° C. = 23.96 N. When this figure is plotted along with my own data (Figure 7) it is seen that the curvature is very slight after 12 N and no maximum or minimum is indicated.

The specific conductance of silver nitrate appears to be passing through a maximum at the saturation point at 25° C. (9.709 N). At 95° C. the maximum is actually observed at 10 N. For ammonium nitrate the maximum occurs at 8 N at both temperatures which seems significant since the maximum for silver nitrate at 25° C. may well be 10 N (as at 95° C.) if such a concentration could be realized. The specific conductance-concentration curves are shown for the two salts in Figure 8. In both cases the rate of attainment of the maximum is much greater at the higher temperature,

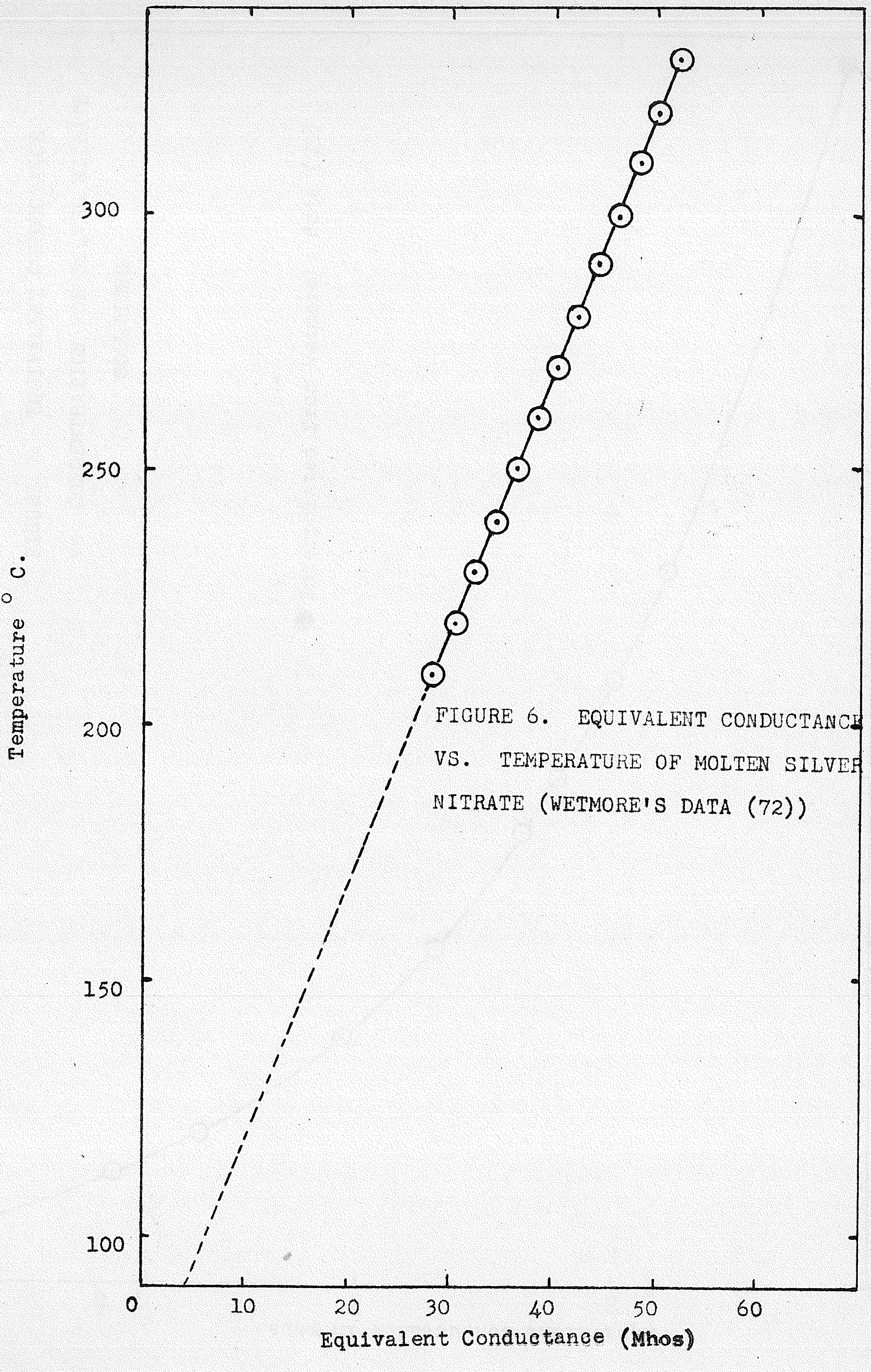


FIGURE 6. EQUIVALENT CONDUCTANCE VS. TEMPERATURE OF MOLTEN SILVER NITRATE (WETMORE'S DATA (72))

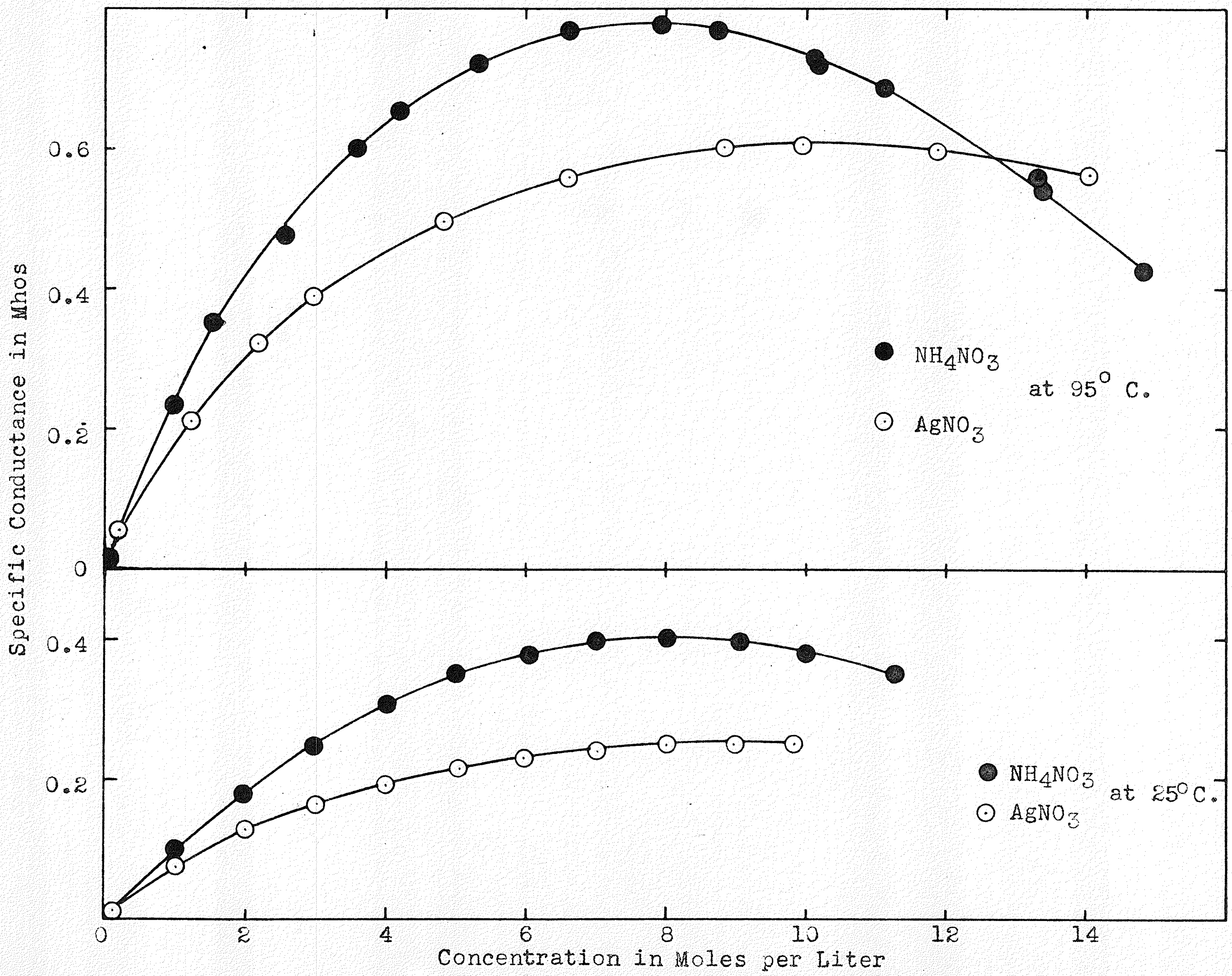


FIGURE 8. SPECIFIC CONDUCTANCE VS. CONCENTRATION

that is, the curves are steeper. No such maximum is observed in the weak electrolyte, acetic acid, over its complete range of concentration, but trichloroacetic acid exhibits a maximum at approximately 1.5 N at both temperatures studied.

The densities and viscosities of silver nitrate solutions have no particular interest, but ammonium nitrate exhibits the phenomenon of "negative viscosity" at 25° C., that is, the viscosity is less than that of the solvent, water. The depression in the viscosity of water persists until a concentration of 3 N is reached. Negative viscosity is not observed at 95° C. Acetic acid at a mole fraction of 0.5 passes through a maximum density and a corresponding macimum viscosity. The densities and viscosities of trichloroacetic acid solutions increase normally with concentration.

The absolute viscosities of all liquids decrease with rise in temperature; the relative viscosities of electrolytic solutions on the other hand increase with rise in temperature. This must mean, then, that the viscosity of water decreases more rapidly than does that of the solution. For solutions of non-electrolytes, however, the converse is true (74). My results for silver nitrate and ammonium nitrate show normal behaviour but trichloroacetic acid solutions behave like solutions of non-electrolytes. Table 9 gives a comparison of the relative viscosities at the temperatures 25°, 60° and 95° C.

TABLE 9

COMPARISON OF THE RELATIVE VISCOSITIES OF SOLUTIONS AT 25° C., 60° C. AND 95° C.

	A. Silver Nitrate		B. Ammonium Nitrate		C. Trichloroacetic Acid	
N	η_c/η_0 @ 25°	η_c/η_0 @ 95°	η_c/η_0 @ 25°	η_c/η_0 @ 95°	η_c/η_0 @ 25°	η_c/η_0 @60°
1	1.07	1.10	0.96	1.05	1.40	1.30
2	1.17	1.23	0.95	1.10	1.88	1.67
3	1.31	1.43	0.97	1.17	2.47	2.10
4	1.47	1.62	1.00	1.26	3.13	2.60
5	1.66	1.85	1.06	1.37	4.02	3.20
6	1.90	2.14	1.14	1.47	4.91	3.82
7	2.16	2.44	1.23	1.62	6.21	4.60
8	2.51	2.82	1.37	1.78	7.95	5.65
9	2.98	3.17	1.53	2.00	-	-
10	-	-	1.76	2.35	-	-
11	-	-	2.08	2.67	-	-

It remains to discuss the conductance data of trichloroacetic acid. This has been left to the last because it requires amplification. The highest concentrations were investigated first. Enough water was added just to dissolve the amount of acid distilled. After the conductance and other measurements were made the solution was diluted by weight and the consequent solution measured. No more than two dilutions were performed on the same original solution because errors would accumulate. When the dilute region was reached, a large discrepancy was found to exist between my values and those of Wightman and Jones (55). This region was repeated twice and the deviation from their values found to be real.

Wightman and Jones calculated the equivalent conductance at infinite dilution to be 355.94 mhos at 25° C., which is scarcely more than that of the limiting conductance of the hydrogen ion at that temperature. This would give a value close to zero for the conductance of the trichloroacetate ion. The limiting conductance of most organic ions lies between 30 and 40 mhos. The above authors used Kohlrausch's values for the specific conductance of potassium chloride solutions in determining the constants of their cells. The values of Kohlrausch are in too close agreement with those of Jones and Bradshaw (61) to account for the systematic error in the values of Wightman and Jones. It may perhaps have been an error in dilution or, what is more significant in view of my results in very dilute solution, it may have been due to hydrolysis of the trichloroacetic acid according to the equation

$$CCl_3COOH + HOH \longrightarrow CHCl_3 + H_2CO_3 \qquad ㊸ .$$

This phenomenon accounts for my inability to obtain reproducible results in the very dilute region. The graph of Λ vs. $\sqrt{C}$ (Figure 9) gives a straight line up to a dilution of 25,000 mls. This straight line extrapolates to 387.5 mhos at zero concentration. Determinations at dilutions greater than 25,000 mls. gave varying results; and the extent of variation seemed to depend on the

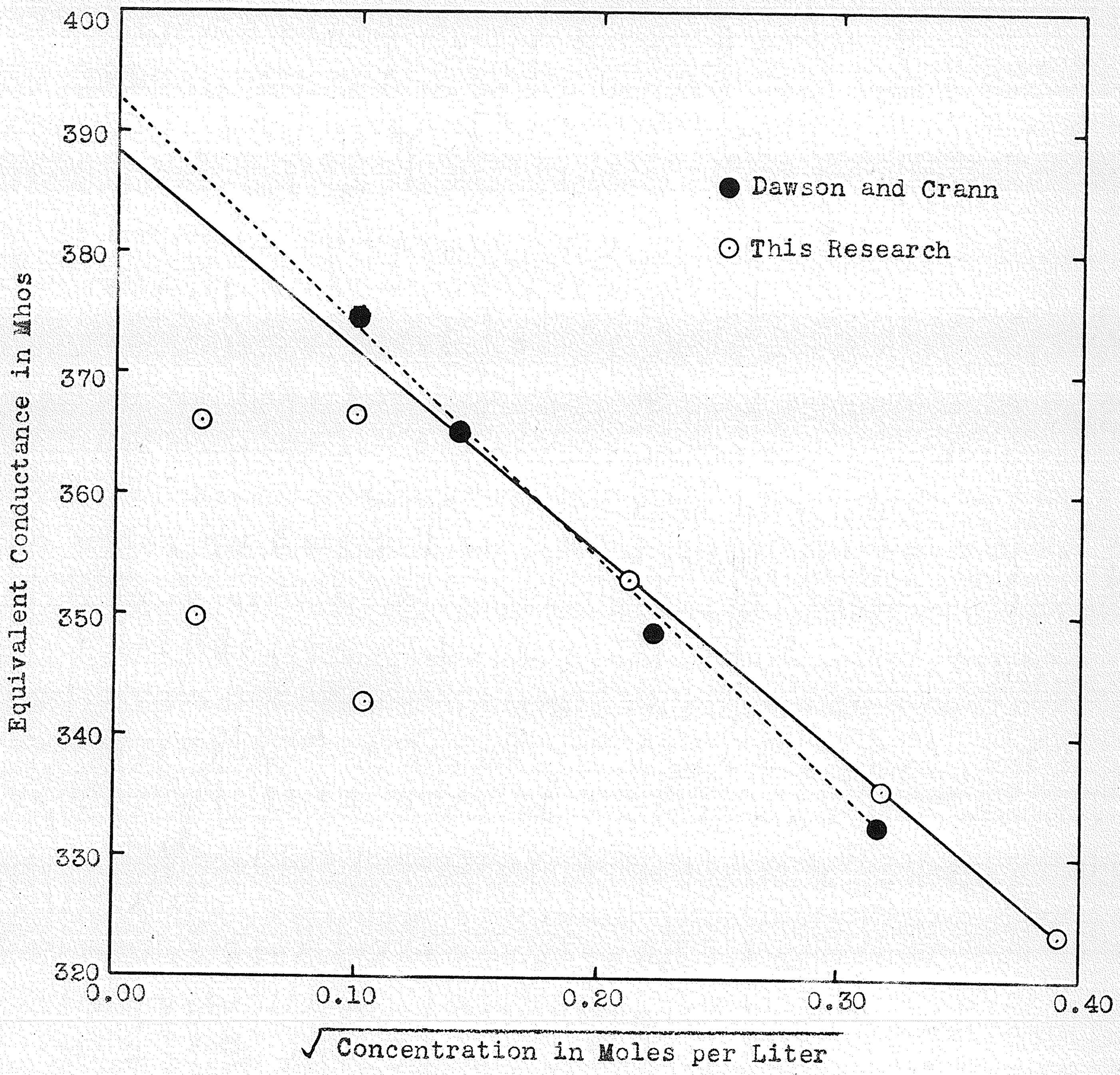


FIGURE 9. EQUIVALENT CONDUCTANCE VS. $\sqrt{C}$ FOR TRICHLOROACETIC ACID AT 25° C.

length of time which had elapsed between making up the solution and determining the conductance. No exact investigation of the time factor was carried out because the dilute range had no real interest to the problem at hand. The values of Dawson and Crann (56) have been plotted on the same graph; the best straight line through these gives Λ_0 equal to 392 mhos. Kendall's (57) value for the limiting conductance of potassium trichloroacetate is 111.2 mhos which gives a calculated value of 111.2 - 73.5 + 349.82 = 387.5 mhos for Λ_0 of the acid, which is identical with mine. The limiting ionic conductance thus becomes 37.7 mhos for the trichloroacetate ion.

Since I had determined the limiting equivalent conductance, it was possible to calculate the so-called degree of dissociation, $\alpha = \frac{\Lambda_c}{\Lambda_0}$ ①, and the dissociation constant, $K = \frac{\alpha^2 c}{1-\alpha}$ ②. It is true that this treatment is considered to be old-fashioned. Nevertheless, it does apply to weak electrolytes in dilute solution and it is of interest to investigate trichloroacetic acid in this light. This acid is weak in strong solution - the question arises as to whether a range exists over which the Dilution Law holds. For this reason Table 10 is presented including the same calculations for acetic acid.

TABLE 10

THE "DEGREE OF DISSOCIATION" (α) AND THE DISSOCIATION CONSTANT (K) FOR ACETIC ACID AND TRICHLOROACETIC ACID AT 25° C.

A. ACETIC ACID

Normality	Equiv. Cond.	α	K
1.735	1.003	2.58×10^{-3}	1.15×10^{-5}
3.437	5.31×10^{-1}	1.37×10^{-3}	6.42×10^{-6}
5.206	3.09×10^{-1}	7.95×10^{-4}	3.29×10^{-6}
6.761	1.94×10^{-1}	4.99×10^{-4}	1.68×10^{-6}
8.423	1.12×10^{-1}	2.89×10^{-4}	7.03×10^{-7}
10.106	6.08×10^{-2}	1.56×10^{-4}	2.46×10^{-7}
11.883	2.80×10^{-2}	7.20×10^{-5}	6.16×10^{-8}
13.585	1.79×10^{-3}	4.61×10^{-6}	2.9×10^{-10}
15.415	3.55×10^{-4}	9.11×10^{-7}	1.3×10^{-11}
17.360	3.99×10^{-6}	1.03×10^{-8}	1.8×10^{-15}

B. TRICHLOROACETIC ACID

Normality	Equiv. Cond.	α	K
0.0446	352.9	0.9106	0.4158
0.1009	335.7	0.8664	0.5647
0.1521	323.8	0.8356	0.6483
1.0096	207.0	0.5342	0.6180
1.099	198.9	0.5133	0.5939
1.566	156.0	0.4026	0.4260
2.044	121.4	0.3133	0.2915
3.116	67.72	0.1748	0.1157
3.777	46.68	0.1205	6.236×10^{-2}
4.568	28.83	0.0744	2.732×10^{-2}
5.5125	14.60	0.03768	7.817×10^{-3}
6.015	9.947	0.02567	4.077×10^{-3}
6.523	5.662	0.01461	1.411×10^{-3}
7.029	3.069	0.00792	3.812×10^{-4}
7.859	0.827	0.00213	3.573×10^{-5}
8.721	0.106	0.000274	6.548×10^{-7}

It is immediately apparent that no constancy is obtained for strong solutions of weak electrolytes.

It is most significant that the conductance of trichloroacetic acid in dilute solutions is very high, while in concentrated solutions it is very low and, in the anhydrous state, less than that of water. My value for the specific conductance of anhydrous trichloroacetic acid at 60° C. equals 2.5×10^{-8} mhos, approximately four times greater than the value obtained by Kendall and Gross (58): 0.62×10^{-8} mhos. Since my result is greater than theirs it must be assumed that theirs is closer to the fact and that a slight trace of water was present in my "anhydrous" acid. I am confident that the amount of water in the acid used to make up the solutions was negligibly small since had there been more than a trace of water my value for the anhydrous acid would have been very much higher. Evidence for this lies in the enormous leap in conductance observed on the addition of a small amount of water to the anhydrous acid: compare the change in Λ between 100% acid and 84% acid, viz., 2.6×10^{-6} and 1.412 mhos respectively, and that between 84% acid and say 53% acid, viz., 1.412 and 48.24 mhos respectively. A property less sensitive to a trace of water is the viscosity of the acid: my value of 0.0396 poises at 60° C. compares favourably with that of Kendall and Gross, 0.0397 poises.

The behaviour of trichloroacetic acid emphasizes the fundamental difference between such an electrolyte and the salts, silver nitrate and ammonium nitrate. The latter have been studied to 82% salt and 85% salt respectively.

From the evidence in Figure 7, it appears that the equivalent conductance of salts (of silver nitrate, at any rate) decreases with concentration to the anhydrous electrolyte along a smooth curve - no minimum or maximum is indicated. The approach to linearity is explained by Hasted, Ritson and Collie (18) on the assumption that on diluting concentrated solutions the predominating factor is change in ion association, the effect of the inter-ionic forces being more or less constant in this region of high concentration. Trichloroacetic acid, on the other hand, is un-ionized in the pure state or at any rate to a smaller extent that conductance water. When water is added, the molecules ionize and a sharp increase in conductance results. It is not until an addition of about 40% water, however, that the trichloroacetic acid becomes comparable with the strong electrolytes. At higher dilutions, the conductances of the acid solutions begin to exceed those of the salts, due of course to the greater speed of the hydrogen ion.

C. Discussion of the Derived Quantities

Since the conductance of an electrolyte is dependent on the number and velocity of the ions, the conductance increases with rise in temperature. The increase in velocity of the ions is in part a result of the increase in fluidity of the solution. If the fluidity were the only factor influencing the speed of the ions the change in conductance with temperature should be equal to the change in fluidity with temperature, i. e., the temperature coefficient of the fluidity should equal the temperature coefficient of conductance. That this is not the case is shown in the following table for the two salts and the acid (Table 11). These coefficients are actually <u>average</u> coefficients over the wide temperature ranges (25° - 95° C., 25° - 60° C.).

TABLE 11

CALCULATION OF TEMPERATURE COEFFICIENTS OF FLUIDITY (γ) AND CONDUCTANCE (β) AND THE RATIO γ/β.

A. SILVER NITRATE

Normality	Abs. Fluidity		Equiv. Cond.		Average Coeff. of Fluidity	Average Coeff. of Conductance	γ/β
	25° C	95° C	25° C	95° C			
0.00	111.0	334.0	-	-	0.0283	-	-
0.1	110.9	334.0	109.1	278	0.0287	0.0222	1.39
1.0	104.2	318.1	77.8	182	0.0295	0.0190	1.55
2.0	94.9	272.7	64.2	151	0.0268	0.0190	1.41
3.0	85.6	230.3	55.0	130	0.0242	0.0195	1.24
4.0	76.0	202.4	48.5	116	0.0237	0.0195	1.22
5.0	67.6	178.1	43.1	101.5	0.0234	0.0198	1.18
6.0	59.2	159.0	38.6	90.0	0.0241	0.0191	1.26
7.0	51.6	139.2	34.7	81.5	0.0243	0.0190	1.27
8.0	44.7	121.5	31.2	74.0	0.0246	0.0198	1.24
9.0	37.3	106.0	28.3	67.0	0.0263	0.0199	1.31
10.0	32.2	92.8	26.1	60.0	0.0313	0.0187	1.67

TABLE 11 (CONT'D)

CALCULATION OF TEMPERATURE COEFFICIENTS OF FLUIDITY (γ) AND CONDUCTANCE (β) AND THE RATIO γ/β.

B. AMMONIUM NITRATE

Normality	Abs. Fluidity 25°C	Abs. Fluidity 95°C	Equiv. Cond. 25°C	Equiv. Cond. 95°C	Average Coeff. of Fluidity	Average Coeff. of Conductance	γ/β
0.00	111.9	334.0	-	-	0.0283	-	-
0.100	112.9	330.7	112.9	306.0	0.0275	0.0244	1.13
1.004	116.5	312.1	101.3	234.0	0.0240	0.0187	1.28
1.993	117.6	300.9	91.9	199.7	0.0222	0.0167	1.33
2.982	114.5	285.4	84.3	177.3	0.0214	0.0158	1.35
4.020	110.9	269.4	76.8	158.0	0.0190	0.0151	1.26
5.014	105.4	249.2	70.0	140.5	0.0195	0.0144	1.35
6.036	97.8	228.8	63.1	124.5	0.0192	0.0139	1.38
7.015	90.7	207.4	56.7	110.5	0.0185	0.0136	1.36
8.011	81.9	186.5	50.4	97.4	0.0182	0.0133	1.37
9.043	73.1	164.5	43.9	84.5	0.0179	0.0132	1.36
10.004	63.0	145.2	38.2	73.8	0.0186	0.0133	1.40
11.282	51.6	120.1	31.3	60.2	0.0190	0.0132	1.44

TABLE 11 (CONT'D)

CALCULATION OF TEMPERATURE COEFFICIENTS OF FLUIDITY (γ) AND CONDUCTANCE (β) AND THE RATIO γ/β

C. TRICHLOROACETIC ACID

Normality	Abs. Fluidity 25°C	Abs. Fluidity 60°C	Equiv. Cond. 25°C	Equiv. Cond. 60°C	Average Coeff. of Fluidity	Average Coeff. of Conductance	γ/β
0.00	111.9	213.3	-	-	0.0259	-	-
1.0	79.5	164.5	207.0	304.0	0.0306	0.0134	2.28
2.0	60.1	130.1	125.0	152.0	0.0333	0.00617	6.75
3.0	46.0	105.0	72.0	92.0	0.0366	0.00793	5.93
4.0	35.1	86.0	40.0	52.0	0.0415	0.00857	4.84
5.0	28.5	71.0	21.0	27.5	0.0426	0.00884	4.82
6.0	22.8	58.0	9.5	12.5	0.0443	0.00902	4.91
7	18.0	47.0	-	-	0.0460	-	-
8	14.0	37.5	-	-	0.0479	-	-
8.75	11.1	31.8	-	-	0.0535	-	-

In all cases the average coefficient of fluidity, γ , is greater than the average coefficient of conductance, β ; hence, the ratio γ/β is greater than one. It is significant that the ratio is approximately constant for the two salts which would indicate that there is some other constant factor opposing the increase in conductance due to the increase in fluidity. The fluctuation in the ratio γ/β with increasing concentration is less than the progressive changes in γ and β individually. The equations

$$\begin{aligned} \Lambda_{95^\circ} &= \Lambda_{25^\circ}(1+\beta(70)) \quad \text{and} \quad & f_{95^\circ} &= f_{25^\circ}(1+\gamma(70)) \\ \Lambda_{60^\circ} &= \Lambda_{25^\circ}(1+\beta(35)) & f_{60^\circ} &= f_{25^\circ}(1+\gamma(35)) \end{aligned} \tag{44}$$

were used in the above calculation. Actually, the change in the conductance with temperature is said to be expressed by equation ㉘ but as my results show (see Page 93) terms in t higher than the first can be neglected as far as conductance is concerned and therefore the coefficients of conductance are exact, or practically so. For fluidity, however, the calculation on the basis of linearity is, of course, an approximation tenable only over a more restricted range than the 70° and 35° intervals used here. However, since the main object of this research was to obtain conductance values for the highest concentrations possible, it was necessary to use the higher temperature. Investigations are being carried out in connection with this research at 35° C. and subsequent 10° intervals over which the approximation to linearity may be more justifiably used.

Trichloroacetic acid presents a very different relationship between average temperature coefficient of conductance and average temperature coefficient of fluidity. The fluidities of these solutions at 25° C. are very much lower and decrease to a greater extent with concentration than is observed with either of the two salts. Between 1.0 N and 8 N the fluidity of silver nitrate solutions decreases from 104.2 to 44.7 rhos; that of ammonium nitrate from 116.5 to 81.9 rhos; whereas that of trichloroacetic acid decreases from 79.5 to 14 rhos. This is a factor of 5.7 for the acid as compared with 2.3 and 1.4 for silver nitrate and ammonium nitrate respectively. The low fluidities at the high concentrations of trichloroacetic acid are due to the existence of a preponderance of molecules, possibly associated molecules, in the solution. The large increase in fluidity as compared with that of the salts over the same range of concentration is due to the enormous increase in ionization of the acid as the concentration decreases.

The average temperature coefficients of fluidity are higher for trichloroacetic acid solutions than for the salt solutions - in the former, there is a relatively greater increase in fluidity with temperature, particularly at the higher concentrations. Possibly this is due to a lower degree of association of the acid molecules at the higher temperature.

The change in conductance with temperature is complicated by the partial ionization of the acid. Up to a concentration of 3 N the conductances of trichloroacetic acid solutions are considerably greater than the conductances of the salts, a result of course of the highly conducting H^+ present in a region of almost complete dissociation. At higher concentrations the conductance of the acid becomes very much smaller than that of the salts: it is a weak electrolyte. The average temperature coefficient of conductance is smaller for the acid than for the salts, approximately one-half as great. This is significant since the average temperature coefficient of fluidity of the acid is twice that of the salts. The factor retarding the increase in conductance due to increased fluidity is thus much greater in the case of trichloroacetic acid. This may be summarized by comparing the ratio γ/β for the two types: γ/β (acid) $=$ 4 x γ/β (salt).

Fluidity data (as yet unpublished) for silver nitrate and ammonium nitrate solutions of 2, 3, 4, and 5 N have been made available to me by Gray (75) for the purpose of discussion. Since an extensive theory of viscosity of liquids has been built around the exponential formula of Reynolds (76) $\eta = A e^{B/T}$ (45) it seemed to me of interest to treat my viscosity data in this manner. It was more expedient to use fluidity data since there have been compiled in another connection (Page 85) so the equation used was actually $\varphi = A^{-1} e^{-B/T}$ (46). If fluidity varies with temperature in this manner the plot of log φ vs. $\frac{1}{T}$ should be linear. Figures 10 and 11 show that for solutions of silver nitrate and of ammonium nitrate this exponential relationship is not observed. The non-linearity is real: it is impossible to draw these plots as straight lines because the accuracy of the results will not allow such a gross error to be applied to them. It would seem then that (45) applies only to pure liquids and

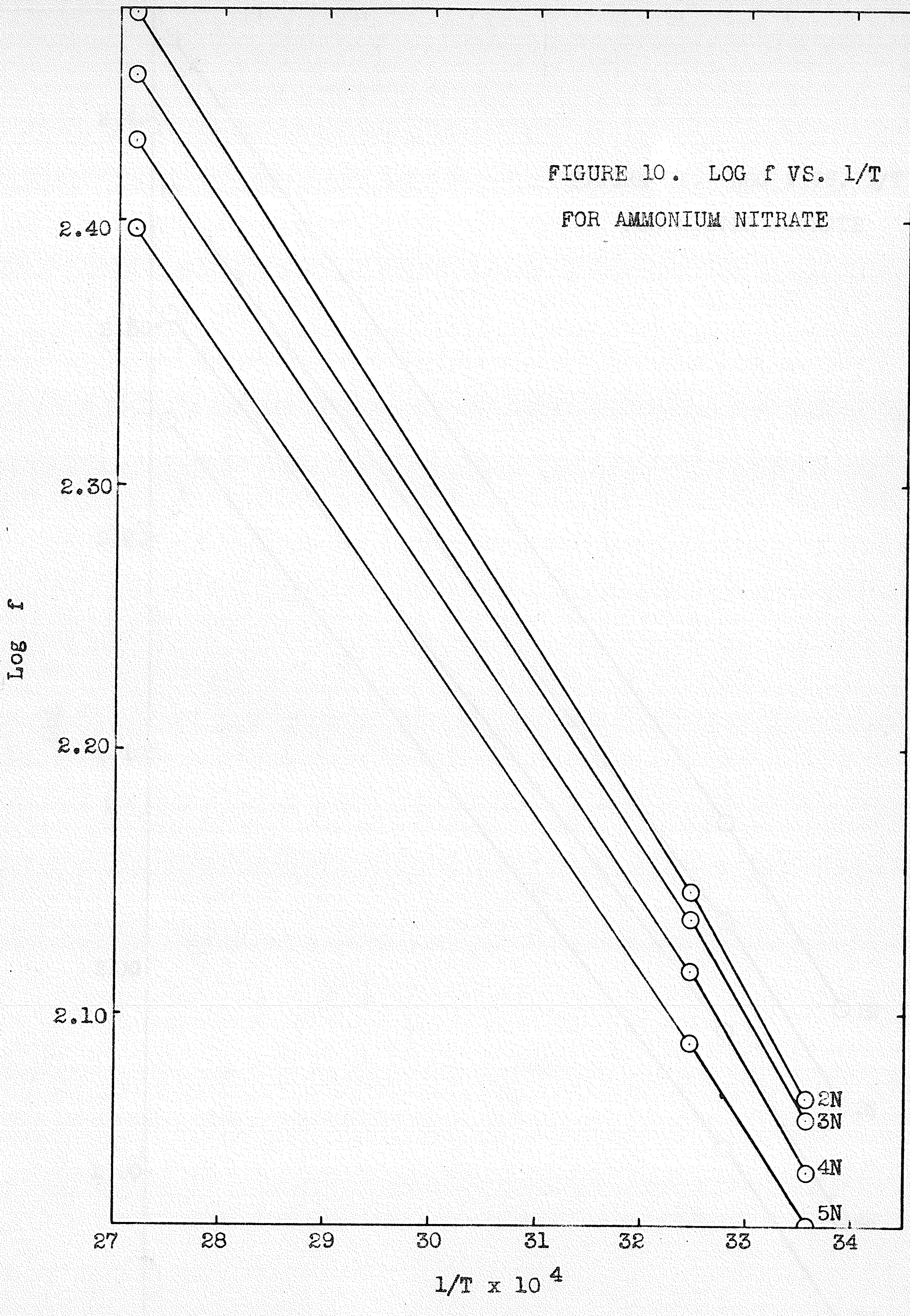


FIGURE 10. LOG f VS. 1/T FOR AMMONIUM NITRATE

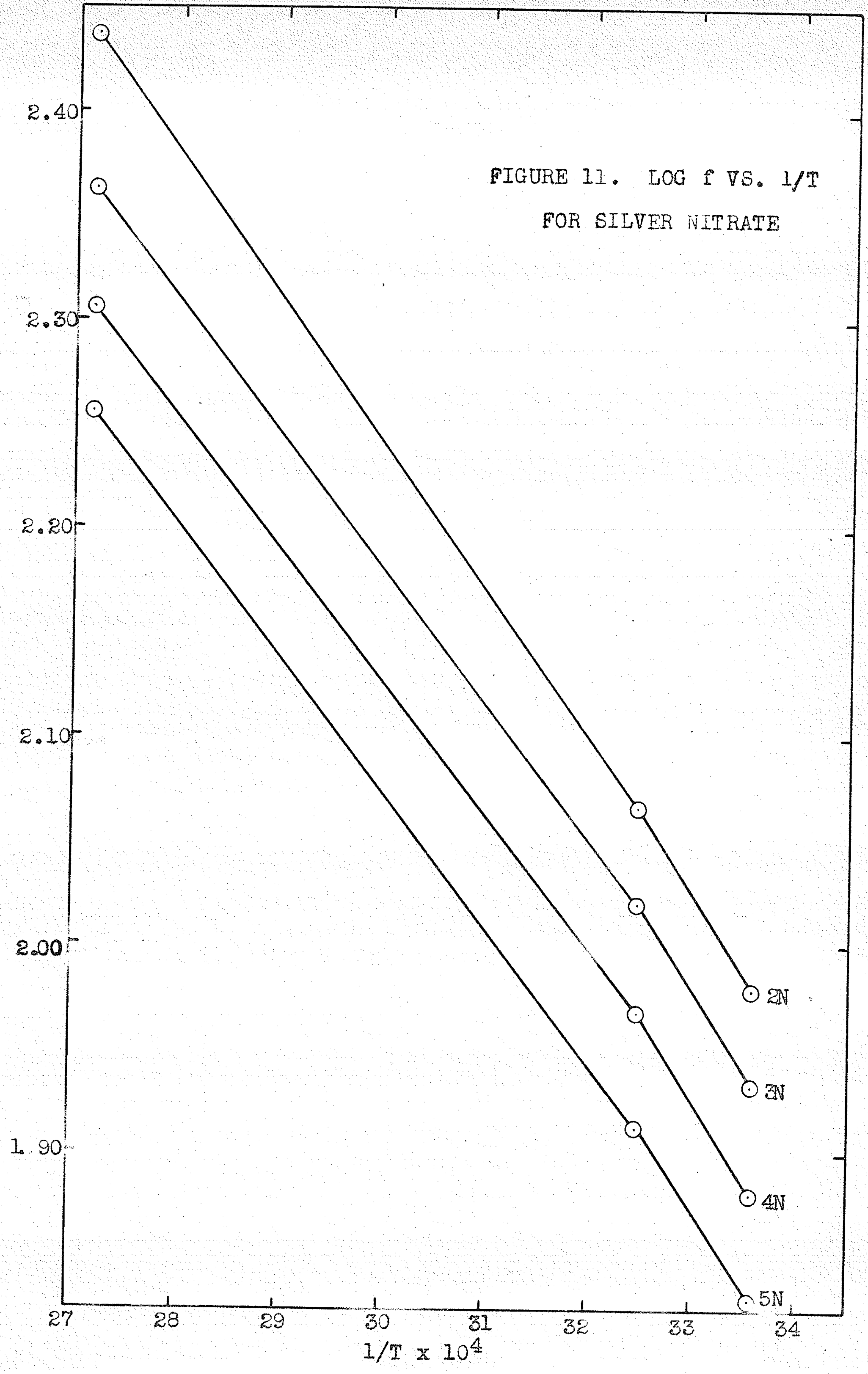


FIGURE 11. LOG f VS. 1/T FOR SILVER NITRATE

not to solutions. Partington's (77) intensive survey of the literature of viscosity (up to 1949) contains no information that would dispute the above observation.

The most striking result of this research has been left to the end. This is the closely linear relationship between equivalent conductance and temperature. Values exist in the literature (78) for the conductance of ammonium nitrate at 0° C. and 18° C. at concentrations 2, 3, 4, and 5 N. These, together with my values at 25° C. and 95° C., and Gray's (75) at 35° C. have been plotted in Figure 12. Higher concentrations have been investigated at only three temperatures but these give straight lines also. The linearity is observed for silver nitrate solutions as well at concentrations 2, 3, 4, and 5 N (Figure 13). Here again, only three temperatures have been investigated. Following is a comparison of the experimental values at 95° C. with those calculated from the slope of the $\Lambda - t$ plot:

Silver Nitrate

Norm.	Λ 95° C. (exp.)	Λ 95° C. (calc.)
2	151.0	151.4
3	130.0	129.3
4	116.0	116.4
5	101.5	101.6

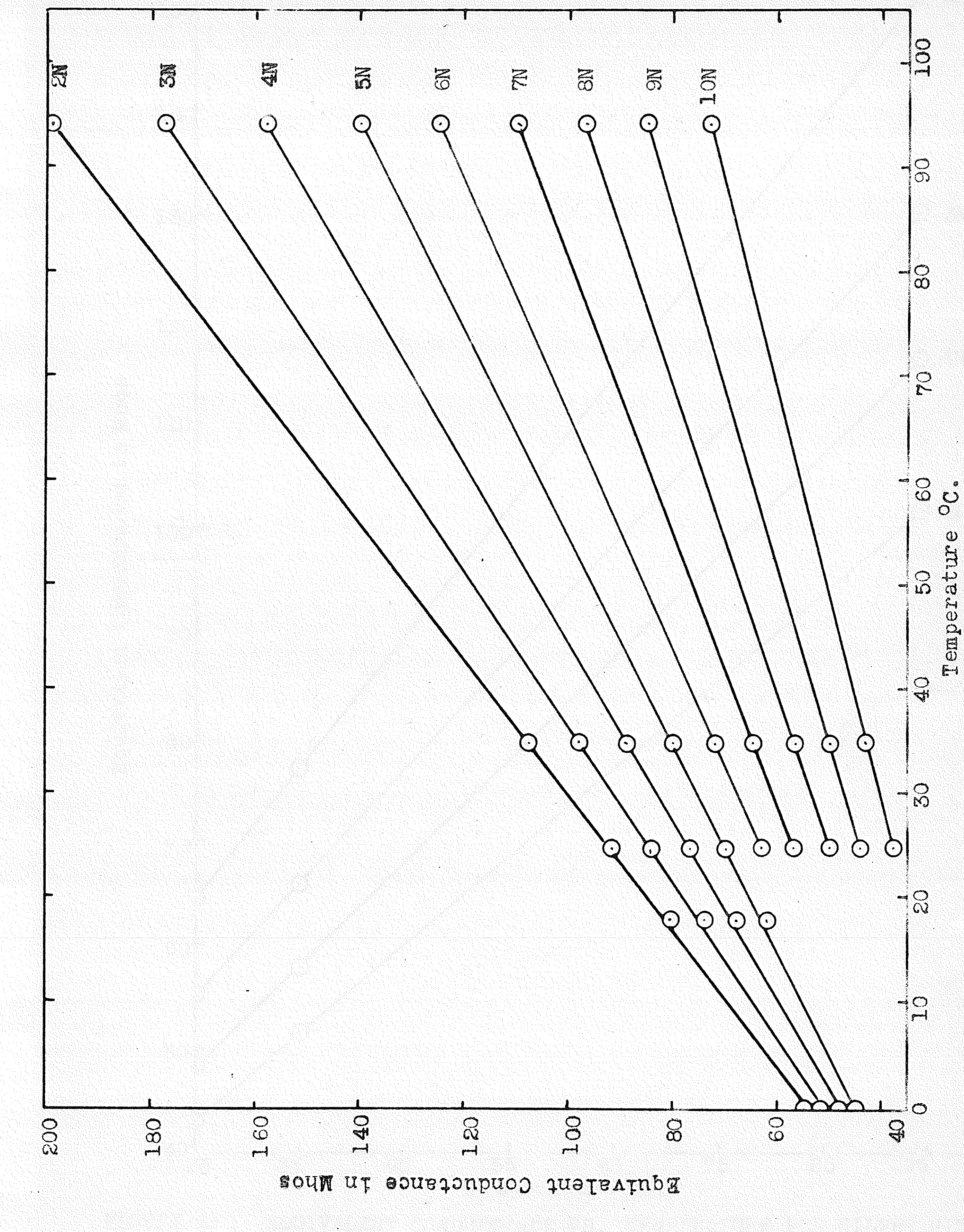


FIGURE 12. EQUIVALENT CONDUCTANCE VS. TEMPERATURE FOR AMMONIUM NITRATE

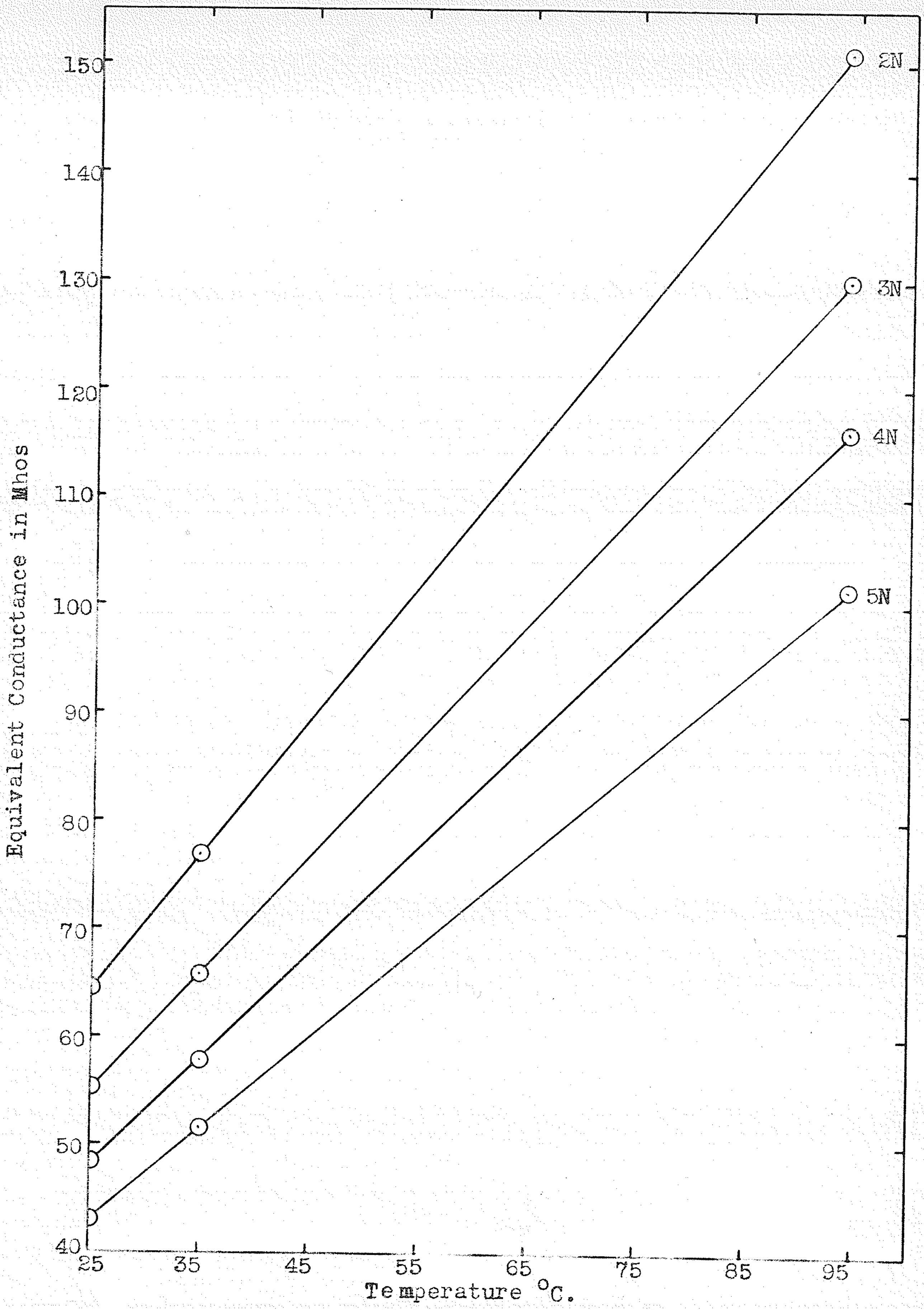


FIGURE 13 . EQUIVALENT CONDUCTANCE VS. TEMPERATURE FOR SILVER NITRATE

Ammonium Nitrate

Norm.	Λ 95° C. (exp.)	Λ 95° C. (calc.)
2	199.5	199.6
3	177.7	177.3
4	158.0	158.4
5	140.5	141.3
6	125.3	125.5
7	110.0	109.8
8	96.7	97.2
9	84.3	84.6
10	73.0	72.2

The agreement is very good. The earlier calculation of the temperature coefficient of conductance based on ㊹ was therefore justifiable. The fluidities of the corresponding solutions have been plotted at the temperatures investigated for both salts (Figures 14 and 15). No linearity is obtained. This emphasizes the fact that there are factors other than fluidity concerned in the conductance of solutions.

My results are not isolated cases. Noyes (47) measured the conductances of dilute solutions of silver nitrate and other electrolytes at a series of temperatures between 0° C. and 306° C. In these the linearity is preserved to about 160° C.; the curve then passes through a maximum and the temperature coefficient of conductance becomes negative. The linear relationship, then, is not confined to silver nitrate and ammonium nitrate in strong solutions. On the other hand, Bousfield and Lowry (41) obtained

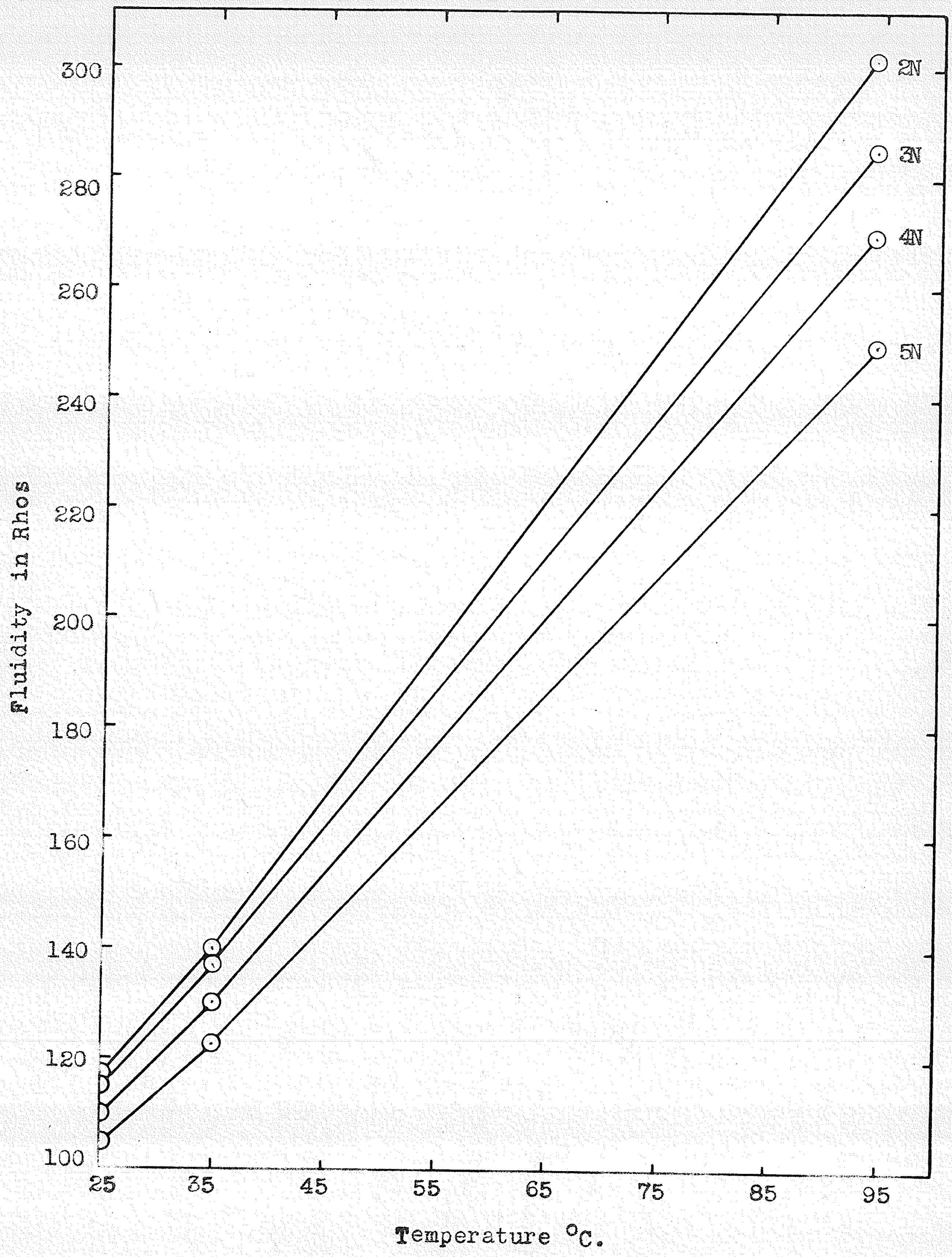


FIGURE 14. FLUIDITY VS. TEMPERATURE FOR AMMONIUM NITRATE

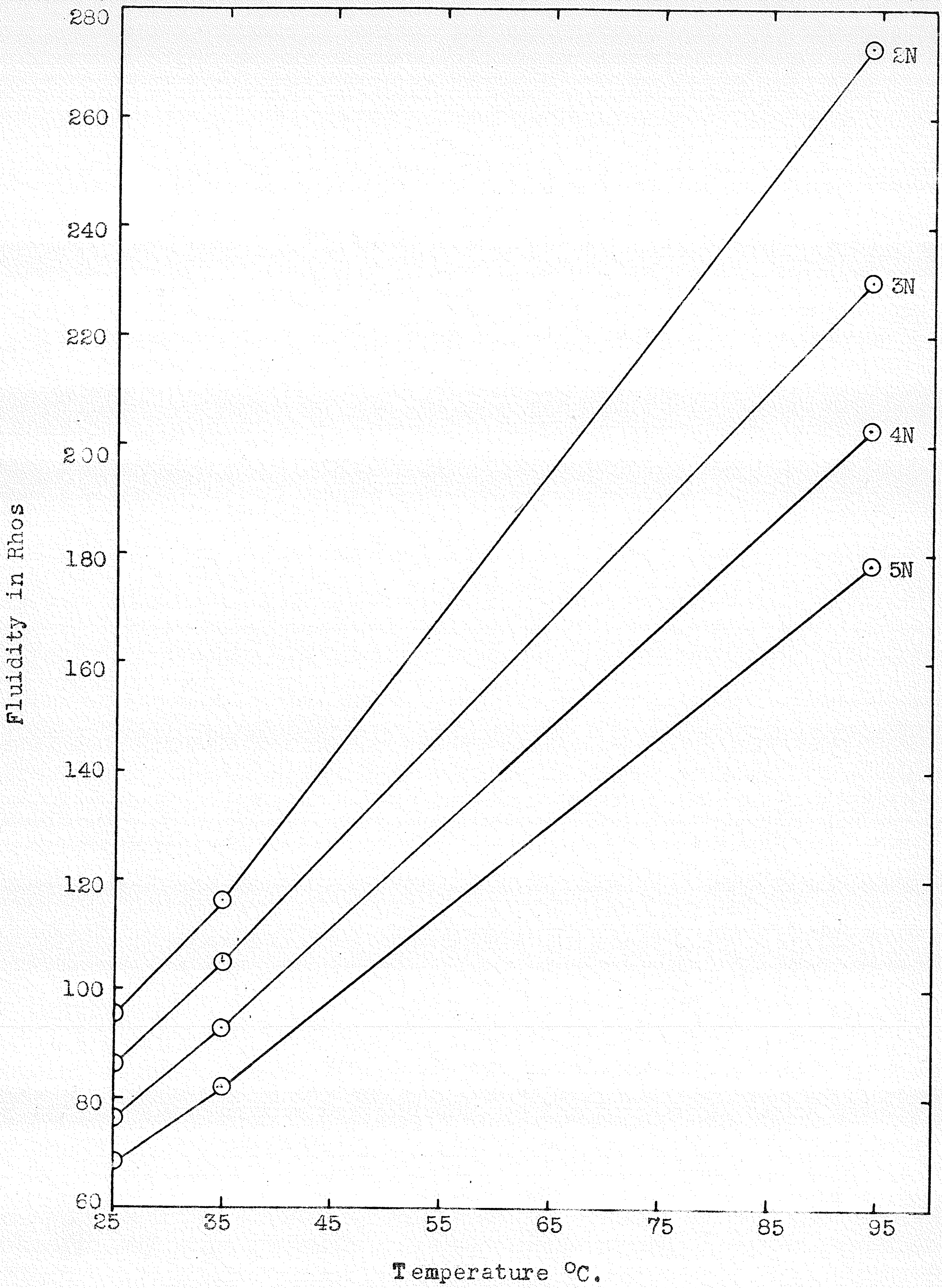


FIGURE 15. FLUIDITY VS. TEMPERATURE FOR SILVER NITRATE

a point of inflection in Λ-t curves (of sodium hydroxide) at low concentrations and no linearity at higher concentrations. This is probably due to the more complex nature of the electrolyte.

The reason for the direct proportionality between conductance and temperature is not apparent to me. Certainly, it is not a direct consequence of the change in fluidity because the fluidity-temperature relationship is not linear. That the compensating factors should change in such a way as to produce linearity in the Λ vs. t curve is indeed strange, particularly over such a large range of concentration (1 - 10 N for ammonium nitrate). An enumeration of the factors involved would include:

(1) change in hydration of the ions with temperature,
(2) change in dielectric constant of the medium with temperature,
(3) change in the number of ions with temperature,
(4) change in activity of the ions with temperature and
(5) change in fluidity of the solutions with temperature.

It must be emphasized that the existence of a linear relationship between Λ and t for any one concentration is sufficiently remarkable but that the linearity should persist over a range of concentration is still more remarkable because the magnitude of each of the determining factors above will vary with the concentration as well as with the temperature. In the present state of theory and of experimental knowledge it is impossible to do more than to note these factors: any quantitative treatment is impossible.

Conclusion

Conclusion

Good experimental data on the conductances of strong solutions of ammonium nitrate and of silver nitrate at 25° C. and 95° C., of acetic acid at 25° C., and trichloroacetic acid at 25° C. and 60° C. have been obtained. The densities and viscosities have also been determined at the temperatures indicated.

Graphs have been drawn to show the variation of specific and equivalent conductances with concentration. The specific conductances of silver nitrate and of ammonium nitrate solutions were found to pass through a maximum: the maxima for each salt occur at the same concentration at both temperatures. The equivalent conductance curves are smooth and tend to linearity at the highest concentrations with no minima indicated.

Temperature coefficients of conductance and of fluidity have been calculated on a linear basis; the ratio of coefficient of conductance to coefficient of fluidity is always greater than unity and appears to be constant. This indicates that factors other than the fluidity of the solutions determine the conductance of the solutions. The variation of equivalent conductance of silver nitrate and of ammonium nitrate with temperature is shown to be linear, a most interesting result. No such linearity is observed in the fluidity-temperature curves of the salts although their curvature is not very great.

A theoretical treatment of the linear relationship between conductance and temperature is impossible since there must be a large number of factors involved, many of which cannot as yet be experimentally determined. The value of this thesis lies, then, in its experimental data which are more accurate than any hitherto obtained in a field almost untouched by recent workers. A theory for strong electrolytes in strong solutions is very greatly needed but little can be done without more experimental data with which to work. The nature of strong solutions must be most complex; it will therefore be necessary to make a variety of measurements in order to describe completely such solutions. I therefore submit my work as a contribution to a field which may become the subject of intensive study in the future.

Table of Symbols

Table of Symbols

The symbols listed here, with their meaning and units, are those which occur throughout the thesis. Symbols used in a specific case and not referred to again (e. g., Washburn correction, Page 47) are identified when used and not included herein.

α = degree of dissociation.

K = dissociation constant (moles/litre).

K^{-1} = association constant (litres/mole).

Λ_c = equivalent conductance at concentration c equivalents per litre (mhos).

Λ_0 = limiting equivalent conductance at infinite dilution (mhos).

l_+^0 = limiting equivalent conductance of cation at infinite dilution (mhos).

l_-^0 = limiting equivalent conductance of anion at infinite dilution (mhos).

z_+, z_- = valence of the cation, anion.

T = absolute temperature (° K.).

t = temperature (° C.).

D_0 = dielectric constant of solvent (unitless).

D = dielectric constant of solution (unitless).

η_0 = viscosity of solvent (poise).

η = viscosity of solution (poise).

f = fluidity (rhos).

ϵ = charge on the electron in electrostatic units.

k = Boltzmann constant ($= 1.380 \times 10^{-16}$ ergs/degree).

r= distance between two ions (cms.).

$\mathring{a}$= mean distance of nearest approach (cms.).

a= ionic radius (cm.).

a_{A^+}, a_{B^-}, $a_{[A^+B^-]^\circ}$= activity of the ions A^+, B^- and the ion pair $[A^+B^-]^\circ$.

β= temperature coefficient of conductance (mhos/degree C.).

γ= temperature coefficient of fluidity (rhos/degree C.).

d= density (g./ml.).

N= normality (equivalents of solute/litre of solution).

μ= ionic strength ($= \frac{1}{2}\sum c_i z_i^2$).

Note: ○ equation number.
() Bibliography reference.

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