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PART ONE

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# SOME CONDUCTANCE MEASUREMENTS IN WATER

#### SOME CONDUCTANCE MEASUREMENTS IN WATER

# INTRODUCTION

The behaviour of electrolytic solutions is to-date not well understood. It is universally accepted that when a solute capable of forming a conducting solution is dissolved in a suitable solvent, it dissociates spontaneously into ions. The phenomena of electrolytic conduction have provided us with the most powerful arguments in favor of this ion concept, but, at the same time have provided much conflicting evidence with regard to the degree of dissociation. Nevertheless these phenomena do provide us with valuable means of studying the nature of electrolytic solutions. In particular we are able to infer the disposition of the ionogen (ion producer) in solution from the dependence of the conductance of the solution upon its concentration.

Numerous theories have been advanced to account for these observed variations of electrolytic conduction with changing concentrations of the solution. Two of these, the Arrhenius theory of partial dissociation, and the Debye-Huckel-Onsager theory of complete dissociation, stand prominent in providing direction toward a complete solution of the problem of electrolytic behaviour.

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# THE ARRHENIUS THEORY OF PARTIAL DISSOCIATION

The early studies of the physical chemistry of solutions brought out the fact that all normal or "ideal" solutes altered the vapour pressure and related properties (freezing point lowering, boiling point elevation, osmotic pressure) of water to the same extent provided they were dissolved in the proportion of their molecular weights. Solutes which formed conducting solutions or electrolytes were however found to have appreciably greater effects upon these colligative properties of the solutions than expected on the basis of the above rule.

To account for these deviations of electrolytic solutions from ideal behaviour, Arrhenius postulated that these solutions are comprised to varying degrees of dissociated molecules. He assumed that the degree of dissociation varied with the concentration and that it became unity at high dilutions. He further assumed that the conductivity of these solutions is determined by the fraction of the salt that is ionized. On this basis he argued that the ratio of the equivalent conductance at any concentration to that at infinite dilution was equal to the degree of dissociation (1). Thus, qualitatively, he was able to account for the deviations noted and for the additive nature of certain physical properties of these solutions. Later, he was able to show

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good quantitative agreement between the degree of dissociation obtained from his conductivity measurements with that obtained from the colligative properties of the solution, and thus demonstrated the validity of the theory, as applied to weakly dissociated solutes.

The main support for this theory came from the work of Ostwald (2). This worker assumed the law of mass action to be applicable to the dissociation process of ionogens and derived an expression for the dissociation constant of an ionogen in terms of its concentration and degree of dissociation. By substituting the Arrhenius 'conductance ratio' for the degree of dissociation in this expression, he obtained the relationship between the conductance and the concentration of the solution. He further demonstrated the soundness of this relationship for weak acid and weak base electrolytes.

It was soon observed however that for certain electrolytes the conductance ratio varied comparatively little with the concentration of the solute and that its value always remained near unity. For these 'strong electrolytes' the experimental results were found to be in poor agreement with the law of Ostwald. Other workers found similar lack of agreement between the theory and the experimental data for certain weak electrolytes. Various modification to the

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theory were proposed and although the agreement between the experimental data and these modified theories was improved for weak electrolytes, these modifications failed to account for the "anomaly of the strong ionogen".

It has since been shown that the implicit assumptions of the Arrhenius theory are that (a) the ionic mobilities do not change with concentration and (b) that the activities of the ions are equal to their concentration, and that these assumptions are very much in error. For aqueous solutions of weak electrolytes there is partial compensation of the errors introduced by these assumptions into the Arrhenius theory. The agreement observed between theory and experiment has therefore been somewhat fortuitous. If allowance is made for the variation of ionic mobilities and the ionic activities with concentration it is generally found that weak ionogens do conform with the theory of partial dissociation.

# Theory of Complete Dissociation

To account for the "anomaly of the strong ionogen" Debye and Huckel proposed that salts are completely dissociated and that electrical forces between the ions are the root of the variations of the properties of such solutions upon dilution (4). This view was put forth earlier by

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Sutherland (55) and Milner (56) but owing to the approximations which these workers made in their complex mathematical analysis of the effects of interionic forces, their theories attracted little attention. Debye and Huckel on the other hand were able to arrive at a much more satisfactory solution to this problem.

In order to calculate the quantitative effect of this ionic interaction, they postulated that each ion would attain, due to its charge, a symmetrical atmosphere of oppositely charged ions and made the following further assumptions: (1) that the Boltzman distribution function is applicable to ions, (2) that the Coulomb law of forces is also applicable and further that all other forces between the ions can be neglected, (3) that the solvent between the ions behaves as pure solvent in bulk, (4) that the resistance to motion of an ion through a solution is given by Stokes law, (5) that the solutions are sufficiently dilute that corrections for overlapping of the ionic atmospheres can be neglected, and (6) that the ions can be regarded as point charges.

The mathematical treatment of these assumptions resulted in an equation of the form  $\Lambda \equiv \Lambda_o = (A + B\Lambda_o) \sqrt{C}$  (where  $\Lambda$  and  $\Lambda_o$  are respectively the equivalent conductances at con-

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centration "C" and at infinite dilution, and A and B are constants determined by the viscosity, dielectric constant and the temperature of the solvent). This relationship is in complete agreement with the earlier empirical generalization ( $\Lambda = \Lambda_0 = K\sqrt{C}$  where K is an empirical constant) proposed by Kohlrausch (24). Onsager later showed that Stokes law does not have to be strictly applicable in the region of the ion. He also modified the above expression to correct for the effect of the natural Brownian movement of the ions upon the resistance to their motion through the solution. The expression however retained its original form (22).

Confirmation of the theory is found in the fact that for the majority of aqueous solutions (for which the requisite accurate data is available) the limiting expression is obeyed very closely up to concentrations of 0.002 equivalents per litre. At higher concentrations the measured conductances are normally greater than those predicted by the theory. This is due, in part at least, to simplifications made in the mathematical treatment of the theory. By the addition of theoretical, semi-empirical and empirical terms good agreement between theory and experiment can be had up to concentrations of 0.1 equivalents per litre.

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Notable of this treatment is the fact that the ionic atmosphere is empowered with two separate effects upon the central ion. The first effect is that, due to the opposite charges on the central ion and its atmosphere, an applied potential will tend to move the latter in a direction opposite to that in which the former moves. Thus the central ion will be retarded in its motion by the electro-viscous drag of its atmosphere. This is known as the electrophoretic effect of the ionic atmosphere. A second effect arises for an ion in motion due to the fact that the atmosphere must form continuously before it and decay behind it. The rate at which these processes occur, with respect to the velocity of the central ion, will determine the extent of asymmetry of the atmosphere about, and thereby the retarding influence upon, the parent ion. This influence on the velocity of an ion is termed the relaxation effect.

Further support for this theory lies in the experimental confirmation of the above effects. At high frequencies the central ion can be expected to oscillate within the finite time of relaxation of its atmosphere, hence the asymmetric charge distribution presumed to form about an ion in motion will not have time to form completely. In fact, if the oscillation frequency is high enough the ion

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will be virtually stationary and its atmosphere will be symmetrical. The conductance of a solution should therefore be greater at high frequencies than that observed with low frequency alternating, or with direct, current. A number of workers have observed this dispersion of conductance at high frequencies (5). Furthermore in accord with the theory at higher temperatures or lower dielectric constants this dispersion is found to occur at shorter wave lengths. (It should be mentioned, at this time, that this evidence is not nearly as conclusive as implied above. No satisfactory method has been devised to measure absolute conductances at high frequencies and the latter observations are all relative).

The conductance of an electrolyte has also been found to increase at high potential gradients (6). This Wien effect, as it is known, is interpreted as follows. At these high potential gradients (20,000 - 100,000 volts per centimeter) the ion will move so quickly that it will traverse several times the thickness of the ionic atmosphere during the time of relaxation. As a result, both the asymmetry and the electrophoretic effects will be greatly diminished if not entirely eliminated. In accord with this interpretation the Wien effect is found to be greatest under conditions where interionic forces are expected to have the largest

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influence. This is the case for concentrated solutions of high valence ions. The fact that the equivalent conductance does not extrapolate to the value at infinite dilution with increasing field strength is reconciled with the exponential nature of the ionic atmosphere. Here again the evidence is not conclusive, for it has been noted that for a number of weak acids and weak bases which are known to be very slightly dissociated the Wien effect is many times greater than is to be expected. It has been presumed that the powerful electric fields produce further ionization of the weak acid or base.

In view of the foregoing, recent researchers have been persuaded to search in non aqueous media (where discrepancies with the theory occur more frequently and are more marked) for direction toward the formulation of a more general theory. These recent researches in non aqueous media. have shown that ionogens which are strong in water often behave as weak ones in solvents of lower dielectric constant. There is therefore some doubt as to whether or not ionization can be regarded to be complete at anytime. For this reason it was felt that much is yet to be gained by high precision conductance studies in aqueous media. In this medium the Onsager equation is generally regarded to be

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valid for all strong ionogens. Any deviations observed from it are usually explained in terms of solvation. Theoretically, it is argued that since the lattice energies of salts are normally of the order of 200 kilocalories while the heats of solution are usually negligible, some process must occur to compensate for this amount of energy in order that the salts break down into ions upon dissolution. This process is termed solvation. It is further believed and has been confirmed by calculation for water (34) that the forces of solvation are electrostatic in nature. However, there is no agreement to date upon the degree of this solvation process, as determined experimentally or as postulated theoretically, to account for deviations from the Onsager equation.

Since these forces of solvation are electrostatic in nature, it can be expected that the degree of ion-solvent interaction will depend to a large degree both upon the nature of the solvent and upon the structure of the salt. For this reason it is advisable to conduct studies of salts whose structure can be varied at will and which are universally soluble. Kraus et al have made some studies in this direction of certain quaternary ammonium salts in non aqueous media of low dielectric constant (29, 30, 31) where solvation forces

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are negligible and interionic forces predominate. Since neither theory considers the effect of the chemical nature of the solvent in accounting for the behaviour of the ionogen, it seemed to be desirable to extend this study to aqueous media where the forces of solvation are expected to be much greater and the interionic forces much smaller due to the much higher dielectric constant. In this way it was hoped that sufficient information would be made available to permit some evaluation of the part played by 'chemical forces: in determining the behaviour of electrolytic solu-The quaternary ammonium salts are generally soluble tions. while their structure can be varied as desired for the proposed Since no accurate literature data is available for the study. aqueous conductivities of tetrabutylammonium bromide, tetraethylammonium bromide, tetramethylammonium bromide and tetramethylammonium chloride these particular salts were chosen for this research.

The apparatus required for high precision conductance measurements by the alternating current technique is very elaborate. The design of both the conductance cell and the bridge network is critical since stray capacitance and inductance effects must be eliminated. The apparatus required to obtain comparable accuracy by the direct current method is vastly simpler and is free of external influences. For these reasons the latter method was chosen for this research.

#### EX PERIMEN TAL

# CONDUCTANCE WATER AND SOLVENT CORRECTION

By redistilling water from alkaline permanganate solution. it was possible to obtain water with a specific conductivity of 1 X 10-7 mhos with relative ease. The conventional methods of preparing conductance water were therefore discarded and the following procedure adopted. Ten grams of potassium hydroxide and one gram of potassium permanganate were added to five litres of distilled water in the distillation pot of the usual type of all pyrex vacuum apparatus. The pressure was reduced to 50 mm. by aspirator action and distillation commenced by the application of heat with a 'Gloscol' mantle. The usual type of vacuum receiver was modified with a three way stopcock to provide for immediate rejection of the first fraction through the aspirator, and two electrodes of shiny platinum were sealed into the receiver to provide for the requisite conductivity check upon every 50 ml. of the distillate. The specific conductivity of the distillate gradually decreased from 5 X  $10^{-5}$  mhos at the commencement of distillation to 1 X 10" at the completion. The middle fraction comprising 40 - 50 percent of the total was collected near 40°C. The bulk specific conductivity of this conductance water fell in the range 3 - 5  $\times$  10<sup>-7</sup> mhos. (The first fraction comprised approximately 20 percent of the total, while the pot residue varied from 10 - 20 percent of the total: Thus the distillate was generally only 80 percent condensed, 20 percent of it being lost through the aspirator).

The dimensions of the distillation apparatus are in no way critical, aside from the requirement for an efficient system of baffles to prevent carry-over through bumping. Since no effective means of eliminating bumping, toward the end of a distillation could be found, a column, packed with glass helices to a height of 50 cm., was employed to obviate this difficulty. To effect air tight seals, Cellogrease, previously boiled in conductance water for an hour, was used.

### THE SOLVENT CORRECTION

It is generally assumed that the conductivity of an electrolyte is equal to the sum of the conductivities of the ionogen and the solvent. Pure solvents normally have very low conductivities since in general they dissociate to inappreciable extents. To minimize any errors inherent in the assumption, it is desirable to employ solvents which are ultra pure. Ultra pure water has a specific conductivity of approximately 5 X  $10^{-9}$  mhos at  $25^{\circ}$ C but in contact with the atmosphere it rapidly absorbs carbon dioxide, which increases its specific conductivity to 8 X  $10^{-7}$  mhos at  $25^{\circ}$ C. Since it

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is difficult to prevent contact of the solution with the atmosphere a good deal of uncertainty is introduced with regard to the true solvent contribution. This difficulty can be obviated by either the use of atmospheric-conditioning boxes to enclose the measuring apparatus in carbon dioxide free air or, more simply, by employing the "equilibrium conductance water". Although some arguments can be found against the latter procedure, it was felt that this was the most reliable method to correct for the conductance contribution of the solvent. The prepared conductance water was therefore permitted to attain equilibrium with the carbon dioxide of the air.

To affect the correction for the solvent contribution to the conductance two separate methods were tried.

# (1) THE DIRECT CURRENT METHOD

Since this method requires reversible electrodes it could not be directly applied to measure pure solvent conductances. An attempt was therefore made to use a very dilute solution (approximately  $10^{-5}$  molar) of the salt under investigation as the solvent. The conductance of this dilute solution could be measured in the usual manner and subtracted from the total conductance of this solution

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to which a known amount of salt had been added. The solvent contribution is thereby eliminated upon subtraction of the conductances of the two solutions.

However, this procedure implies that the contribution of the dilute solution is independent of the concentration of the final solution being measured. This is not true and the method therefore requires an additional correction which can only be applied if the relationship between conductance and concentration is known, or if the electrolyte is strong. Since these salts showed some weak electrolyte behaviour this method was inapplicable and was subsequently abandoned.

# (2) THE ALTERNATING CURRENT METHOD

A small alternating current cell of conventional design with shiny platinum electrode was constructed and used to measure the solvent conductance. The Wheatstone bridge was constructed of General Radio components and employed a Schering Ground. To test the accuracy of this bridge the conductances of two solutions of tetramethylammonium chloride  $(20 \text{ and } 50 \times 10^{-4} \text{ molar})$  were determined with this bridge and by the direct current method. The agreement was found to be better than 2 percent which was the estimated accuracy of the alternating current method. Since the solvent corrections never exceeded 9 percent of the conductivity of the most dilute solutions measured, the overall precision attainable was therefore better than 0.02 percent.

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# PREPARATION AND PURIFICATION OF SALTS

# TETRAMETHYLAMMONIUM CHLORIDE

This salt was obtained from the Eastman Kodak firm. It was purified by recrystallization twice from nitromethane and subsequently by two further recrystallizations from methanol. Prior to use this purified salt was dried in a vacuum drying pistol at 110°C for one week.

The chloride content of the dry salt was established, by titration with silver nitrate, to be 32.34 percent (Theoretical 32.35).

# TETRAMETHYLAMMONIUM BROMIDE

This salt was also obtained from the Eastman Kodak firm. It was treated in the identical manner of the chloride.

The purified dry salt was found, by titration with silver nitrate to contain 51.88 percent bromine. (Theoretical 51.88).

#### TETRAETHYLAMMONIUM BROMIDE

Two independent samples of the tetraethylammonium bromide were used, one sample was that prepared and purified by Tink (7) while the other was Eastman Kodak product purified by four recrystallizations from methanol. Both samples dried as above were found to contain (by silver nitrate titration ) 38.02 percent bromine (Theoretical 38.02).

# TETRA-N-BUTYL BROMIDE

This salt was prepared by reacting 137 grams of redistilled n-butyl bromide (BP 101°C) with 185 grams of redistilled tri-n-butylamine (100°C at 20 mm pressure) for 20 hours in 150 millilitres of methanol at the reflux temperature of the mixture. The mixture was then diluted by addition of approximately 200 millilitres of water, and the unreacted reagents were extracted with petroleum ether. The salt was precipitated from the water-methanol solution by chilling it to -20°C. filtered on a cold Buchner funnel. and immediately dried in a vacuum oven at 80°C, over phosphorous pentoxide. (This latter step was found to be most essential. If immediate thorough drying of the prepared salt is not effected the salt invariably forms a syrup as soon as recrystallization is attempted and will not reprecipitate regardless of the solvent employed). The dried salt was then purified by three recrystallizations from benzene-petroleum ether mixture and dried in the manner of the other salts. The melting point of this product was estimated at 119.5 ±0.5°C by using a 150°C mercury-in-glass thermometer calibrated at the ice and boiling points of water. (The inaccuracy of this determination is  $\pm 0.5^{\circ}$ C). Silver nitrate titration showed the final product to contain 24.81 percent bromine: (Theoretical 24.80).

#### POTASSIUM CHLORIDE

The potassium chloride used to make up the calibrating solution was purified by three recrystallizations from conductance water. This dry recrystallized salt was placed in a platinum boat, inserted into an electrically heated silica tube, and further purified immediately prior to its use by streaming purified dry nitrogen (from which the oxygen was removed with Fieser solution (61)).over it in the molten state for 30 minutes.

#### THE CONDUCTANCE MEASUREMENT

### **A PPARATUS**

#### GLASSWARE

All glassware used to collect, contain, store, or transfer the conductance water or the solutions was first cleaned with chromic acid, then treated with hot hydrochloric acid to remove the surface alkalinity, whereupon it was washed continuously under the tap for a day, rinsed several times with distilled water and conditioned with conductance water by storing the latter in it for several short periods.

#### THE CELL

Two conductance cells of the type described by Gunning and Gordon (8) were employed in this research.

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One of these drawn to one half scale is depicted on the following page. The large volume of the cells (approximately 400 ml) tends to minimize errors due to contam-The four electrodes were seated in the cell by ination. means of ground glass joints, a constant alignment being assured by means of lines etched upon the male and female members. When new, the cells were subjected to a hot hydrochloric acid treatment in order to remove surface alkalinity; they were then washed continuously for several days with tap water, rinsed several times with distilled water and conditioned with conductance water by storing the latter in it for several short periods. The cells were periodically cleaned with chromic acid solution in order to remove any slight traces of grease which might have accumuleted on the inner surfaces; after such treatment the cells were thoroughly washed with large quantities of water in order to remove any adsorbed skin left by the acid.

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THE CELL

# THE ELECTRODES

The main, current-carrying electrodes were constructed of platinum foil 1 x 2 cms. in area and joined to the copper leads by means of platinum wire. These were silver plated in a solution containing 10 g.p.l. of twice recrystallized potassium silver cyanide at a current density of 1 milliampere per square cm. for six hours, according to the manner of Brown (23). After being plated, the electrodes were placed in concentrated ammonium hydroxide in order to facilitate the removal of the cyanide and then washed with distilled water. They were then chloridized (or bromidized as required) for 30 minutes in 0.1 normal solution of potassium chloride (or bromide), made acidic with sulphuric acid, at a current density of 1 milliampere per square cm.

The probe electrodes consisted of platinum discs 8 mms. in diameter, and were completely covered with glass except for a vertical strip 1 mm. in width and 6 mms. high. These were plated in the same manner as the main electrodes. These electrodes were found to be very stable and were replated only between determinations on the different salts investigated. Before replating the electrodes were placed in concentrated ammonium hydroxide to remove the chloride layer, and were then anodized in concentrated nitric acid at 50 milliamperes to remove the silver.

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# THE ELECTRICAL CIRCUIT

The constant current device of Leroy and Gordon (9) was used to establish the potential gradient across the cell. The potential drop between the probes was compared with that across a Leeds and Northrop 1000 ohm standard resistance in series with the cell by means of a Leeds and Northrop type K2 potentiometer in conjunction with a ballistic galvonometer of sensitivity 2 X  $10^{-10}$  amperes per scale division at one meter.

# CONSTANT TEMPERATURE BATH

Thermoregulation was maintained in a heavily insulated, double-walled bath, containing about twelve gallons of light grade transformer oil vigorously stirred by a large ten bladed stirrer. The bath was heated by two blade heaters of 250 watts each and cooled by water passing through a copper coil, all placed close to the stirrer. A toluene-mercury thermo-regulator in conjunction with the control circuit described by Schiff (10) was employed to effect the temperature control. In operation, the heating and cooling conditions were so arranged that the thermoregulator was activated for a period of thirty seconds and deactivated for a corresponding period.

Temperatures were read on a mercury in glass thermometer calibrated against a standard platinum resistance

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thermometer at the National Research Laboratories at Ottawa. The variations of the bath temperature were about  $\pm 0.003^{\circ}$ , but actual fluctuations in the temperature of the solution were probably smaller than this, due to the large heat capacity of the cell.

# TECHNIQUES OF THE MEASUREMENT

# PREPARATION OF SOLUTIONS

The solutions were prepared gravimetrically by inserting a platinum boat containing the appropriate salts dried to constant weight into a flask containing the correct weight of equilibrium conductance water for the concentration desired. Since these salts are hygroscopic the platinum boats containing them were enclosed in airtight weighing bottles during the weighings. Independent checks at each concentration zone were obtained by separate measurements upon a solution composed as above and upon a solution composed by gravimetric dilution of one of approximately twice the concentration in question. All weights were corrected to vacuum.

# DENSITY DETERMINATIONS

A Shedlovsky type (12) pycnometer with the stems graduated to thousandths of a millilitre was used to determine the densities requisite for the conversion of mass to volume concentrations. This pycnometer was calibrated for volume (at  $25.00^{\circ}$ C) using conductance water (density 0.99707). The volume was found to be equal to  $26.0875 \pm 9.7 \times 10^{-4} V$ , where V is the volume in excess of the reference, expressed in thousandths of a millilitre. Thus by filling the pycnometer so that V could be read off on the stem graduations, the density was readily determinable with an accuracy better than 1 part in 50,000. In computing the volume from mass concentrations all weights were reduced to vacuum. For purposes of this calculation the assumed value of 1.6 was used for the densities of all but the tetramethylammonium chloride salt; the reported value 1.2 (11) was used for the latter.

# DETAILS OF THE MEASUREMENT

During each conductance measurement, the following procedure was observed. The cell was washed seven times with tap water, seven times with distilled water, and finally with one litre of conductivity water. It was then dried in a stream of clean, dry nitrogen supplied through a manifold to each of the electrode chambers. Meanwhile, the probe electrodes, which were kept in conductivity water when not in use, were washed with a small portion of the solution to be measured and allowed to sit in a sample of this solution for at least ten minutes. All the electrodes but one were placed in their respective chambers; into the fourth chamber was placed a filling tube having a standard taper matching the one on the filling flask. Solution was forced into the cell by nitrogen pressure; the fourth electrode was then inserted and all the electrodes carefully aligned. The cell was then placed in the oil bath and allowed to come to temperature for one hour.

To measure the conductance of the solution, the current from the constant current device was allowed to pass through the cell and the potential drop across the probe electrodes  $E_x$  and that across the standard resistance  $E_s$  was measured. The direction of the current was then reversed and the voltages were read in the reverse order. The two values of  $E_x$  were then averaged to eliminate the small static bias between the probes. This bias was found to be of the order of 0.02 millivolts.

The specific conductance of a solution, k, is defined as the reciprocal of the resistance offered by a unit centimeter cube of the solution. It can be expressed by the following equation:

where E is the voltage drop across the solution through which a current I is flowing and L is a constant dependent only upon the dimensions of the conductor. It follows that the ratio

 $E_{\mathbf{E}} = \frac{\mathbf{k}}{\mathbf{E}}$ 

where the conventional cell factor L is equal to the cell constant C multiplied by 1000.

# THE CELL CONSTANT

The value of the cell constant C was determined from the observed conductance of the hundredth demal aqueous KCl solution defined by Jones and Bradshaw (62). The conventional cell factors found for the two cells were 0.55531 and 0.54508.

# RESULTS

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# DENSI TYY

The densities of the aqueous solutions of these salts were found to be expressible within the experimental precision (and concentration range) by the general equation, d = 0.99707 - Bm where m is the molar concentration and B is 0.042, 0.009, 0.046 and 0.037 for tetramethylammonium bromide, tetramethylammonium chloride, tetraethylammonium bromide and tetra-n-butylammonium bromide, respectively.

# CONDUCTANCE

The experimental conductance values ( $\Lambda$ ) for various concentrations (C) of the above salts in water at 25.00°C are tabulated below, along with the Shedlovsky function ( $\Lambda$ \*o). The latter is given at this time for convenience. The significance of it will be discussed more fully later, at present it suffices to define this function.

$$\Lambda_{o}^{*} = \frac{\Lambda + A\sqrt{C}}{1 - B C}$$

where  $\Lambda$  and C have the significance stated above and A and B are the constants of the Debye-Huckel-Onsager equation given by:

$$= \frac{8 \,\overline{\iota} \, e^2 N}{1000 k} \left(\frac{1}{DT}\right)^{3/2} \frac{e^2}{3k(2\sqrt{2})}$$

$$^{B} = \left(\frac{8 \widehat{n} e^{2} N}{1000 k}\right)^{1/2} \left(\frac{1}{DT}\right)^{1/2} \frac{N e^{2}}{90 \widehat{n} \sqrt{1}} \frac{1}{\gamma}$$

for the case of uni-univalent salts.

where e is the electrostatic charge, N the Avogadro number, v the velocity of light, k the Boltzman constant and D and  $\eta$  the dielectric constant and viscosity respectively of the solvent at the absolute temperature T.

For water at 25.00°C with the values given by Birge (13) for the physical constants

e = 4.8025 X 10<sup>-10</sup> esu
k = 1.3804 X 10<sup>-16</sup> ergs degree <sup>-1</sup>
v = 2.9976 X 10<sup>10</sup> cm. sec.<sup>-1</sup>
N = 6.0230 X 10<sup>23</sup> mole <sup>-1</sup>
T = 273.16<sup>o</sup>A

and the values 78.54 (14) and 0.008948 (15) for the dielectric constant and viscosity of water at  $25.00^{\circ}$ C respectively, these constants become

A = 60.19 B = 0.2289

10 <sup>4</sup> c	10 <sup>2</sup> / c	<u> </u>	<u>^;</u>
100.297	10.015	111.97	120.76
99.602	9.9801	111.99	120.76
75.528	8.6907	113.06	120.69
75.091	8.6655	113.07	120.68
53.652	7.3248	114.18	120.61
50.136	7.0806	114.37	120.60
49.572	7.0407	114.42	120.60
49.427	7.0303	114.43	120.61
43.987	6.6321	114.77	120,59
36.558	6.0463	115.25	120.56
21.543	4.6415	116.60	120.67
19.567	4.4236	116.77	120.66
19.495	4.4154	116.80	120.65
14.519	3.8104	117.42	120.76
9.8883	3.1446	118.09	120.87
9.7393	3.1208	118.11	120.85
9.4074	3.0672	118.17	120.87
4.9564	2.2263	119.05	121.01
4.8926	2.2119	119.09	121.04
4.8721	2.2073	119.10	121.04
2.8873	1.6992	119.55	121.04
2.3882	1.5454	119.75	121.11
1.5006	1.2250	120.06	121.14
1.0576	1.0284	120.28	121.18
1.0359	1.0178	120.30	121.19

CONDUCTANCE OF TETRAMETHYLAMMONIUM CHLORIDE "Me\_NCl"

10 <sup>4</sup> c	$10^2 \sqrt{c}$	Λ	<u> </u>
100.20	10,010	113.39	122.21
101.19	10.059	113.35	122.22
74.837	8.6508	114.65	122.28
67.446	8.2125	115.05	122.24
49.712	7.0507	116.12	122.33
48.663	6.9759	116.17	122.32
29.157	5.3997	117.62	122.38
19.823	4.4523	118.55	122.48
10.483	3.2378	119.85	122.71
9.9303	3.1512	119.91	122.70
5.3226	2.3071	120.92	122.84
4.7196	2.1725	121.03	122.95
3.0323	1.7414	121.53	123.07
1.0203	1.0101	122.29	123.16

CONDUCTANCE	OF TETRAETHYL	AMMONIUM BROMI	DE "Et <sub>4</sub> NBr"
10 <sup>4</sup> c	10 <sup>2</sup> / c	Λ	Λ.
99.843	9.9921	101.31	109.83
101.49	10.075	101,19	109.78
52.295	7.2315	103.75	109.92
50,683	7.1193	103.78	109.88
19.956	4.4672	106.20	110.00
10.470	3.2357	107.50	110.27
10.012	3.1596	107.56	110.26
10.303	3.2099	107.51	110.25
2.1969	1.4822	109.50	110.76
3.9642	1.9910	108.93	110.63
1.2199	1.1045	109.94	110.88

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10 <sup>4</sup> C	10 <sup>2</sup> / c	Λ	Λ ο
102.70	10.134	89.276	97.640
98.951	9.9474	89.379	97.588
51.696	7.1900	92.023	97.963
49.447	7.0319	92.200	98.010
24.558	4.9556	94.189	98.286
20.669	4.5463	94.620	98.380
11.987	3.4623	95.670	98.534
10.273	3.2054	95.935	98.587
5.8553	2.4198	96.700	98.703
4.8257	2.1968	96.898	98.716
3.2342	1.7984	97.300	98.787
1.0247	1.0123	98.060	98.898

CONDUCTANCE OF TETRABUTYLAMMONIUM BROMIDE "BuanBr"
#### DISCUSSION OF RESULTS

### THE SHEDLOVSKY FUNCTION

As pointed out earlier it is possible to calculate the equivalent conductance at infinite dilution of a strong ionogen from that at any finite concentration by the Debye-Huckel-Onsager equation, which in the rearranged form gives

$$\Lambda \circ = \frac{\Lambda + A \sqrt{C}}{1 - B \sqrt{C}}$$

Furthermore in accord with the theory this calculated value should be the same at all concentrations. However, as Shedlovsky (16) pointed out, the value so obtained is not independent of the concentration but is usually a linear function of the concentration. He proposed that the above ratio be designated as  $\Lambda \circ$  and that the true limiting conductance  $\Lambda \circ$  is given by  $\Lambda \circ = \Lambda \circ = hc$  (where h is an empirical constant and c is the concentration). The empirical constant h, acquires a theoretical significance when the higher terms of the Debye-Huckel-Onsager expansion are considered. Therefore, all strong ionogens can be expected to have their "Shedlovsky functions" ( $\Lambda \circ$ ) vary linearly with the concentration. However, it is found that this equation has very limited applicability and that more generally the additional terms - DC log C +  $EC^2$  (where D and E are empirical constants) are required to represent Shedlovsky type plots. It was previously advocated that these terms, too, can be justified theoretically by considering still higher terms of the Debye-Huckel-Onsager expansion, but recent modifications of the theory (which take into account the finite size of the ion) do not favor their inclusion (17).

The Shedlovsky function  $\Lambda_0^{\dagger}$ , given in column 4 of conductance tables of the salts investigated, are plotted against concentration on the accompanying graphs. It will be seen that the curves are not linear nor can they be readily fitted to the analytical equation by the inclusion of the two extended terms. It is interesting to note that the linear term Hc would be negative in the case of the tetrabutyl, tetraethyl and tetramethylammonium bromide which is contrary to usual behaviour. In all cases the linear term would be smaller than the extended term contributions which is also different from the usual behaviour of strong electrolytes.





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Because of the large curvatures in these plots in the dilute range the Shedlovsky function is not of much value in extrapolating to infinite dilution. However large scale plots were made and the following values of  $\Lambda$  o obtained. The uncertainty in the extrapolations is estimated to be 0.1  $\Lambda$  units.

Salt	<u> </u>
Tetramethylammonium chloride	121.24
Tetramethylammonium bromide	123.27
Tetraethylammonium bromide	111.05
Tetrabutylammonium bromide	98.90

#### KOHLRAUSCH TYPE PLOTS

It has just been observed that the limiting equivalent conductances of salts determined by extrapolation of the Shedlovsky function have a measure of uncertainty associated with them. Recourse was therefore made to the Kohlrausch plot of conductivities versus the square-roots of the concentrations. These plots are illustrated in the following pages.



100√C

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The values obtained for the limiting equivalent conductances of these salts by extrapolation from the Kohlrausch plots are listed below. The experimental and theoretical slopes and the percentage deviations between these are also given. Their significance will be discussed more fully later.

Salt	Λ	Experimental Slope	Theoretical Slope	Percent Deviation
Me <sub>4</sub> NC1	123.37	100.8	87.95	14.6
Me <sub>4</sub> NBr	121.30	107.4	88.43	17.7
$\mathtt{Et}_4\mathtt{NBr}$	111.14	111.6	85.63	30.0
Bu <sub>4</sub> NBr	99.05	97.0	82.86	17.0

It can be readily observed that the limiting equivalent conductances obtained by this method are on the average O.l conductance units higher than those obtained from the Shedlovsky function plots. This is also the estimated uncertainty in the extrapolation by either method.

#### TREATMENT OF THE SALTS AS WEAK ELECTROLYTES

Although the salts do not conform to the behaviour of strong electrolytes it is still possible to treat them on the premises of the Debye-Huckel-Onsager theory. All that must be done is to make an allowance for the degree

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of dissociation. Since only the fraction dissociated  $\Theta$ , of the ionogen is capable of conducting the electric current and only the fraction  $\Theta$  is available for the ionic atmosphere effects, it is clear that for this case, the limiting equation of the theory becomes

$$\Lambda = \Theta \left[ \Lambda \circ - (A + B \Lambda \circ) \sqrt{\Theta c} \right]$$

If now the  $\bigwedge$  o value can be determined by some form of extrapolation it is possible to determine  $\Theta$ the degree of dissociation. This follows, since at the ionic concentration  $\Theta$ C the theoretical equivalent conductance is equal to

$$\Lambda \circ - (A + B \Lambda \circ) \sqrt{\Theta C}$$
$$\Theta = \frac{\Lambda}{\Lambda \circ - (A + B \Lambda \circ) \sqrt{\Theta C}}$$

whence

from which the true value for the degree of dissociation can be obtained by successive approximations starting from the "Arrhenius conductance ratio",

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An improved method of performing these approximations is that developed by Shedlovsky (18) who observed hence  $\Lambda \circ = \Lambda + \frac{\Lambda}{\Lambda_0} (A + B \Lambda \circ) \sqrt{C}$  $\Theta = \frac{\Lambda}{\Lambda \circ} \frac{A + B \Lambda \circ}{\Lambda \circ^2} \sqrt{C \Theta}$ 

if then 
$$\frac{A + B \Lambda o}{\Lambda o^{3/2}} \sqrt{C \Lambda}$$
 is represented by Z it follows  
that  $\Theta = \frac{\Lambda}{\Lambda o}$  (1+2) where the higher terms may be  
neglected. Again designating 1+2 by F,  $\Theta = \Lambda$  F.  
The mass law for a uni-univalent ionogen is given by

$$K = \frac{C \Theta^2 f^2}{1 - \Theta}$$

where K is the dissociation constant and f is the activity coefficient. Substituting for  $\Theta$  in this equation we obtain

$$\Lambda F = \Lambda \circ - \frac{F^2 f^2 \Lambda^2 c}{\kappa \Lambda \circ}$$

Thus a plot of  $\Lambda$  F versus  $F^2 f^2 \Lambda^2 C$  will be a straight line with the intercept equal to  $\Lambda o$  and the slope  $-1/K \Lambda o$ .

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The values of  $\Lambda$  o obtained by the Kohlrausch extrapolations have been used for the calculations required by the Shedlovsky treatment of weak electrolytes. The values of the activity coefficients which must also be known before these calculations can be made have been calculated by the equation - log f =  $0.5056\sqrt{9C}$  (46). The following tables summarize the pertinent calculations.

# TREATMENT OF THE SALTS AS WEAK IONOGENS

#### TETRAMETHYLAMMONIUM CHLORIDE

<u>104c</u>	<u> </u>	<u> </u>	$F^2 f^2 \Lambda^2 C$
100.297	119.78	•987	11)4•2
50.136	120.07	•990	61.35
19.495	120.47	•993	25.54
4.8721	120.99	•99 <b>7</b>	6.775
1.5006	121.12	•998	2.139
1.0359	121,18	•999	1.485

10 <sup>4</sup> c	<u> </u>	•	F <sup>2</sup> f <sup>2</sup> A <sup>2</sup> C
100.20	121.19	•982	116.8
74.837	121.50	•985	90.45
49.712	121.81	•987	62.67
19.823	122.26	.991	26.72
10.483	122.59	•994	14.62
5.3226	122.90	•996	7.621
3.0323	123.04	•997	4.408
1.0203	123.15	•998	1.511

TETRAMETHYLAMMONIUM BROMIDE

TREATMENT OF TETRAETHYLAMMONIUM BROMIDE AS A WEAK SALT

10 <sup>4</sup> c	<u> </u>		<mark>F<sup>2</sup>f<sup>2</sup>Λ<sup>2</sup>c</mark>
101.49	108.68	.978	96.11
50.683	109.28	•983	51.35
19.956	109.77	988	21.68
10.303	110.12	.991	11.60
3.9642	110.58	•995	4.629
1.2199	110.87	•997	1.461

10 <sup>4</sup> 0	<u> </u>	<u> </u>	F <sup>2</sup> f <sup>2</sup> A <sup>2</sup> C
102.70	96 <b>•46</b>	•974	75.71
49.447	97.43	•984	39.90
20.669	98.14	.991	17.92
10.273	98.47	•994	9.246
4.8257	98.66	•996	4.463
1.0247	98.88	•998	0,9786

TREATMENT OF TETRABUTYLAMMONIUM BROMIDE AS A WEAK SALT

The following graphs show the plots of  $\Lambda$  F as  $F^2 f^2 \Lambda^2 C$  for these salts. It will be seen that the straight lines expected for weak electrolytes were not obtained. Thus these are not typically weak electrolytes, which is in agreement with the high values of  $\Theta$  shown in the tables.



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Even though straight lines were not obtained these curves can be used as an alternate method for arriving at  $\Lambda$  o, which is the ordinate intercept.

The values thus obtained are listed below. The averages of these values and those obtained from the Shedlovsky  $\Lambda$  o plots are also given. It was felt that the Kohlrausch extrapolations tend to give slightly higher values due to the fact that a more extended extrapolation is required.

<u>Salt</u>	A o (Weak Plot)	<u> A o (Mean)</u>
Me <sub>4</sub> NCl	121.25	121.24
Me <sub>4</sub> NBr	123.25	123.26
Et <sub>4</sub> NBr	111.05	111.05
$Bu_4 NBr$	98.90	98.90

Although neither of the Shedlovsky treatments are found to be strictly applicable to these salts, excellent agreement is found between the limiting conductances determined by these two methods. Since the literature data for the conductivities of these salts in water is lacking no true comparison between the results of this research and that of other workers can be made. The only recent data available upon the aqueous conductances of tetraalkyl-

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ammonium salts (of the type considered here) is that of Daggett, Bair and Kraus (36). These workers have determined with modern precision the conductivities of tetramethylammonium picrate, tetrapropylammonium iodide, tetrabutylammonium bromide, tetraethylammonium picrate and tetraamylammonium bromide in water at 25°. McDowell and Kraus (45), on the other hand, have made similar measurements on the conductivities of tetramethylammonium picrate, potassium bromide and potassium picrate in water. Thus with the aid of the latter's data and the value 73.58 for the limiting conductance of the potassium ion, Daggett et al were able to compile ionic conductivities for the above tetraalkylammonium ions. The results of this research (a), are compared in the table below with the values calculated from Daggett's data (b).

Salt	<u> </u>	<u> </u>
Me <sub>4</sub> NCl	121.24	121.32
$Me_4NBr$	123.26	123.40
$Et_4NBr$	111.05	111.14
Bu <sub>4</sub> NBr	98.90	97.61 (c)

(c) Directly measured by Daggett.

It can be seen that, with the exception of tetrabutylammonium bromide, there is good agreement between the values obtained for  $\Lambda$  o by this research and those calculated from Daggett's data. It is of some interest to note that the value 2.02  $\Lambda$  units for  $\lambda^{\circ}Br^{-} - \lambda^{\circ}Cl^{-}$ obtained in this research agrees well with the value of 2.08  $\Lambda$  units obtained from the data of Daggett. It must however be pointed out that McDowell (45) and Daggett (36) both report values for  $\Lambda$  o KBr (152.07) and  $\Lambda$  o KCl (149.98) which are discordant from the more generally accepted values of 151.68 and 149.86 respectively (44, 49). This agreement may therefore be somewhat fortuitous. Earlier researchers have reported the value 151.9 for  $\Lambda$  o KBr (47, 48, 50) hence there does seem to be some real disagreement with the presently accepted value 1.82  $\Lambda$  units for the difference between the limiting mobilities of the Cl and Br ions. However no special significance can be attached to the difference indicated by this research since the  $\Lambda$  o values of this research are uncertain to  $0.1 \Lambda units.$ 

The wide discrepancy between the value determined by Daggett for  $\Lambda$  o BujNBr and that of this research may be accounted for on the basis of salt purity.

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Tetra-n-butylammonium bromide can be prepared quite easily, but is very difficult to purify. This is evident from the wide range of melting points which have been reported for this salt, 103.1 - 103.3°C (51), 113°C (52) 115°C (53), 118°C (40), 119.4°C (55). Sadek and Fuoss (54) have cautioned against the use of ethyl acetate as a solvent for the recrystallization of this salt. They state that this procedure is hazardous especially in humid weather, since a trace of water in the ethyl acetate leads to contamination of the salt with tetrabutylammonium acetate, and the acetate and bromide are unusually difficult to separate by recrystallization. Since Daggett gives no indication as to the purity of this salt, aside from a M.P. of 116 - 117°C (which is also the M.P. of the acetate salt) and states that the purification of the salt was effected by recrystallization from ethyl acetate until the conductances of two consecutive samples showed no variation, it is possible that his conductances measurements were made on a mixture of tetra-n-butylammonium bromide and acetate. Since the ionic mobility of the acetate ion is much less than that of the bromide (40.9 and 78.3 respectively) this could quite conceivably be the reason for the lower values reported.

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Additional doubt on the reliability of Daggett's data is found in the fact that his value 75.33 for  $\Lambda$  o for tetramethylammonium picrate was subsequently revised to 75.21 by McDowell (45) of the same laboratory. For these reasons no significance is attached to the difference observed in the behaviour of these salts. Daggett states that all the salts investigated by him obey Onsager's equation in the concentration range 0.3 to 5 X 10<sup>-4</sup>. This research indicates that the salts are somewhat weak.

The following table shows a comparison of the limiting conductances obtained in this research along with values for these and similar salts in four solvents. The numbers in parentheses give the publication references for those salts measured directly; the remaining values have been calculated from reported ionic conductances. The percentage deviations of the observed limiting slopes and those calculated from the Onsager equation are given for the experimentally determined data.

Salt	Water	Nitrobenzene	Methanol	Ethanol
Me <sub>4</sub> NCl	121.25 4	39.3	121.7(37)	52.7(37)
	14.6%		23%	85%
Me <sub>4</sub> NBr	123.25 !	<b>38 •7</b>	125.4(37)	54.4(37)
	17.7%		30%	100%
Et <sub>4</sub> NCl	109.85	38.55 (40)	113.8(57)	51.9(59)
		94%	11%	62%
$\mathtt{Et}_4 \mathtt{NBr}$	111.05 :	38.0	117.6(57)	54.3(59)
	30%		16%	83%
$\mathtt{Et_4NClO_4}$	100.8	37.6 (60)	132.1(57)	62.6(59)
		26%	50%	164%
Bu <sub>4</sub> NBr	98 <b>.</b> 90 t	33.1(54)33.5(40)	96.7(54)	
	17%	88% 66%	33%	

## 1 This research.

It can be observed that in general the deviations from Onsager's equation are greater for the bromide than the chloride salts. However no general correlations between the structure of a given salt and the deviations observed for it in the various solvents is evident. It can also be seen that there is no general agreement between the observed deviations and the dielectric constant of the solvents. (The solvents are listed in order of decreasing

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dielectric constant from left to right). The large discrepancy between the values for  $\Lambda$  o Bu<sub>4</sub>NBr in nitrobenzene as reported by the two researchers should however be noted, in particular with regard to the percentage deviations. The only explanation which appears reasonable for these discordant values must lie in the purity of the salt. It is conceivable that the lack of a general correlation of the observed deviations for a given salt with its structure may also be due to impure salt. The only generalization evident from the table is that  $\Lambda$  o for each salt is found to decrease progressively from methanol to water to ethanol to nitrobenzene. This is the order of increasing viscosities of the solvents. The fact that BuaNBr does not fall in with this general rule indicates some structural dependence. Walden, who first observed a relationship between the value of  $\Lambda$  o and the viscosity of the solvent suggested that the product of these two quantities should be constant. This so-called Walden Rule will now be considered more fully in the hope that the effect of the structure of the salt upon its behaviour may be revealed.

#### WALDEN'S RULE AND IONIC SOLVATION

Stokes formula for the viscous resistance which opposes the passage of an ion of radius r, (assumed spherical) through a medium of viscosity  $\eta$  is given by

 $P = 6\pi r\eta$ 

The ionic mobility or ionic conductance of a univalent ion is given by

(where e is the charge, F the Faraday and P the viscous resistance). At infinite dilution the only retarding force acting on the ions is Stokes! force.

Hence it follows that

$$\lambda_{t}^{\circ} = \frac{eF}{1800 \pi r \eta}$$

Ions which are too large to solvate will have little or no effect upon the structure of the liquid and can therefore be expected to obey Stokes law and to have the same ionic radius in all solvents. Therefore a constant value for the product of the solvent viscosity and the ionic mobility should be obtained for these ions.

This product for uni-univalent salts can be expressed as

$$\lambda_{\underline{t}} = \frac{8.2 \times 10^{-9}}{r}$$

The empirical generalization of this is known as Walden's Rule and is more commonly expressed for the sum of the ionic mobility-viscosity products (i.e.  $\Lambda_0 \eta$  = constant). As pointed out earlier, only the large, nonsolvated ions can be expected to give good agreement with this rule. However, if ionic conductance data is available, this rule serves as a useful tool for determining specific ion-solvent interactions. The requisite transference data to compute ionic mobilities is available for aqueous and methanol solutions but is lacking for other non-aqueous media. A means of obviating this difficulty was proposed by Fowler and Kraus (43). They observed that the mobility of a large ion decreases asymptotically to a limiting value with further increase in size. They therefore assumed that the ionic conductances of the cation and anion of tetra-n-butylammonium triphenyl-borofluoride were equal. In this way they were able to arrive at the ionic conductances of all salts investigated without the aid of transport data.

In the table below the viscosity-mobility products (obtained from the data of the references cited at each value of r) have been used to determine the ionic radii of the respective ions in four different solvents. The ideal values quoted are those referred to earlier (i.e. crystal radii for the chloride and bromide ions and radii measured from atomic models (25) for the tetraalkylammonium ions.).

## TABLE OF IONIC RADII AS DETERMINED BY THE EQUATION

r	=	0.82	angstroms
		$\lambda_t \eta$	

Ion	Ideal	Water	Methanol	Acetone	Nitrobenzene
C1-	1.81	1.23(35)	2.84(35)	2.40(35)	2.04(40)
Br⊷	1.95	1.18(35)	2.54(35)	2.36(35)	2.10(40)
$Me_4N$	3.0	2.04(36)	2.15(37)	2.75(38)	2.64(41)
		2.04 t			
$\mathtt{Et}_4\mathtt{N}$	4.3	2.80(36)	2.80(39)	2.95(38)	2.77(40)
		2.80 1			
Bu <sub>4</sub> N	5.9	4.80(36)	4.0 (54)	4.02(38)	3.83(40)
		4.47 1			

( This research; based on  $\lambda \circ Cl^{-1} = 76.34(42)$ )

It will be seen that the cations show a better agreement than do the anions. Although the cations do show variations as high as 30% this is still considerably better agreement than that found for the alkali ions (63).

If it is assumed that the variation in the values of 'r' calculated in this way are due only to differences in degree of solvation, it follows that the Bu4N <sup>+</sup> ion solvates to a greater extent with water than with the other solvents; the  $Me_4N$  <sup>+</sup> ion appears to solvate to a greater extent with nitrobenzene and acetone than with the hydroxylic solvents; the  $Et_4N$  <sup>+</sup> ion appears to solvate equally with the four solvents.

If this argument is pursued further, it might be suggested that since the radius of the  $\text{Et}_4\text{N}^+$  ion remains constant no solvation occurs. If a value 2.80 is assumed for this radius, the ideal radii for the three cations could be reduced by a corresponding fraction. This yields a value of 1.95 for the Me<sub>4</sub>N<sup>+</sup> ion and 3.83 for the Bu<sub>4</sub>N<sup>+</sup> ion. These figures are in essential agreement with the values for water in the case of the Me<sub>4</sub>N<sup>+</sup> ion and for nitrobenzene in the case of the Bu<sub>4</sub>N<sup>+</sup> ion. However no great significance can be placed on these calculations

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in view of the severity of the assumptions. It may be noted that the radii of the two anions calculated for water is actually smaller than the crystallographic values. Thus the application of Stokes! law to ions may be completely unjustified.

Van Rysselberghe and Fristrom (58) pointed out that the quantity,  $\lambda_{\pm}^{\circ} \eta / D$ , where D is the dielectric constant, varied less on passing from water to methanol and isopropanol than did  $\lambda_{\pm}^{\circ} \eta$ . Butler, Schiff and Gordon confirmed this for the K, Na<sup>+</sup>, Cl<sup>-</sup> ions in water and methanol but pointed out that too much stress could not be placed on this since they found equally good agreement for the quantity  $\lambda_{\pm}^{\circ} \eta$  V, where V is the molar volume of the solvent (64). In the case of the quarternary ammonium ions it is obvious that the Van Rysselberghe relationship would show an even poorer agreement than does the straight Walden relationship. Thus it can be concluded that no simple relationship can be found connecting ionic conductances of all ions in various solvents, as has been frequently pointed out by Kreus.

# THE BJERRUM THEORY

An attempt has been made by Bjerrum to correlate the individual ionic conductances with the particular solvent. The Bjerrum model assumed that ions are rigid unpolarizable spheres acted upon by Coulombic forces in a medium of dielectric constant equal to that of the solvent. It further assumed that two ions of opposite charge approaching each other within a certain distance would associate to form ion pairs. The influences of all other ions are neglected so that this minimum distance becomes

 $r_{\min} = \frac{Z^* Z^* e^2}{2 D k T}$ 

where Z<sup>+</sup>e and Z<sup>-</sup>e are the charges on the ions, D is the dielectric constant, k the Boltzman constant and T the absolute temperature.

If the mean effective diameter of the ions is greater than this distance, no ion-pair formation is possible, while the degree of association will depend upon the difference between these quantities. Using the Boltzman law to represent the probability of finding an ion of opposite charge within the critical distance <sup>r</sup>min. Bjerrum arrived at an expression for the fraction of association, 0, for uni-univalent electrolytes.

$$\Theta = \frac{4 \pi \text{ NG}}{1000} \left(\frac{e^2}{\text{DkT}}\right)^3 \quad Q(b)$$
  
Where  $Q(b) = \int_{z}^{b} \exp \sqrt{y} = 4 \, dy$   
in which  $y = \frac{e^2}{\text{DrkT}}$  and  $b = \frac{e^2}{\text{DakT}}$ 

where 'a' is the mean effective diameter of the ions, r is the distance between the ion in question and the coion, N the Avagadro number, C the concentration in moles per litre, while exp. is the base of natural logarithms.

The significant feature of this theory is that it ignores the effects of an ionic atmosphere. Although Fuoss and Kraus have obtained considerable agreement between this theory and the data for weak electrolytes in solvents of low dielectric constant (50) the theory has been unsuccessful for aqueous solutions and for electrolytes of intermediate strength.

For water at 25°C the minimum distance of separation required to effect ionic association is cal-

culated to be 3.58 angstroms. No data for the mean ionic diameters of the tetraalkylammonium halides are known but if the values obtained from the Walden rule are used, it follows that these salts should be strong in aqueous solution. This is contrary to the observations of this research.

It can be concluded from these considerations that none of the existing theories of electrolytes adequately describes the behaviour of these salts in aqueous solution. An attempt will now be made to indicate in what direction the Onsager and Bjerrum theories might be combined in order to better represent the data.

One of the salient weaknesses of these two theories stems from the assumption that the ions can be considered to be under Coulombic forces exclusively. The application of the Boltzman distribution function and the neglect of possible asymmetric distribution of charge on ions of finite size may also be questioned. Fowler has shown that for higher valent electrolytes the Coulomb law becomes incompatible with the Boltzman distribution (19).

Stokes has enjoyed a measure of success in

modifying the Onsager theory for ions of finite size (17). He arrived at effectively the same expression which was suggested on empirical grounds by Hasted and Ritson in their survey of strong electrolytes:

$$\Lambda = \Lambda \circ - (\underline{A + B} \land \circ) \sqrt{C}$$

$$1 + B \overset{\circ}{a} \sqrt{C}$$

where 1<sup>+</sup> Ba is the familiar "corrective factor" to the Debye limiting law for activity coefficients at finite concentrations, B a theoretical constant and a a "disposable parameter" representing the distance of closest approach for the ions. The success of this treatment is limited to electrolytes which are strong in the light of the Onsager theory, and therefore cannot be applied to the salts investigated here. To fit the results of this research to this theory negative values for a must be assumed. These are physically meaningless. Therefore consideration of the finite size of the ions alone is insufficient to account for the observed deviations from the Onsager theory.

Another factor which has been neglected by the Onsager theory and the Bjerrum theory is the possible polarization of one ion by the fields of neighbouring ions.

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It has been observed that the deviations from the Onsager equation for alkali metal salts increase with increasing atomic number, - which is in the same order as increasing polarizabilities of these ions (64). The explanation usually given for the order of deviation from Onsager equation neglects the polarizability and is attributed solely to the degree of solvation. It is true that the "so called" mean ionic radii as calculated from the Debye-Huckel expression from electromotive force measurements does decrease with increasing atomic number, and that the Stokes' law treatment by Onsager would likewise be less applicable the higher the atomic number. Eley has suggested that ions could destroy the normal structure of water (28). If the Li<sup>+</sup> ion is the most hydrated of the alkali metal ions then Eley's suggestion implies that it would have the largest disruptive effect upon the structure of the water. This is because the six water molecules postulated to solvate with the Li + ion would be distributed in an octahedral form and therefore be least compatible with the tetrahedral structure of water. Since this should be reflected in a marked alteration of the viscosity of the water in the immediate vicinity of the hydrated ion, it might be concluded that the Li + ion should show the

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largest deviations from the Onsager equation, in direct contradiction to what is observed.

It is thus apparent that solvation itself cannot account for the deviation from the Onsager theory and that some consideration should be given to the polarizabilities of the ions, which likewise follow the same order as these deviations. Further support for this suggestion is found in the observation that the deviations for a given salt increase with decreasing dielectric constant of the solvent, as does the polarizability of the salt.

Some support for this concept is provided by the results of the investigations of Kraus et al (29, 30, 31). The following table shows their data for some of the salts in ethylene chloride along with the dissociation constant (K).

Salt	<u> </u>	λο	KX10 <sup>4</sup>
$\operatorname{EtPh}_3\operatorname{PClO}_4$	66.03	26.8	3.60
$EtPh_3AsClO_4$	65.69	26.5	3.45
Bu4NPL	57.40	26.2	2.28
Bu <sub>4</sub> PPi	57 •27	26.1	1.60
Bu <sub>4</sub> As Pi	57.14	25.9	1.42
Bu3SPI	62.31	31.1	0.449
Ph <sub>2</sub> IPi	62.50	31.3 <del>]</del>	0.0233
$Ph_2IClO_4$	70,42	31.2	0.155
Pr <sub>4</sub> NPi	62.66	31.5	1.94
Me <sub>4</sub> NPi	73.81	42.6	0.32

(Me methyl, Et ethyl, Pr propyl and Ph phenyl groups)

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Kraus discovered that the central atom had little effect on the ion conductances but that it was the dominant factor in determining the ion and ion pair equilibrium. It can also be seen from the two alkyliodonium salts that the co-ion also has little effect upon the conductance but that it has a marked effect on the dissociation constant. These observations certainly indicate that some attention must be given to the charge distribution on the ions and their effect upon one another.

Furthermore, it can be seen from the table that the structure of the salt plays an important role in determining the degree of dissociation of the salt. This is evident from the fact that although both the  $Bu_3S^+$ ion and the  $Pr_4N^+$  ion are of approximately the same size (12 carbon atoms each) they display a marked difference in their tendencies to associate with the picrate ion, as can be observed from the respective dissociation constants.

If it is assumed that the planar structure of the  $Bu_3SPi$  salt and the tetrahedral structure of the  $Pr_4NPi$  salt are retained by the cation upon ionization then it is possible that steric hindrance could affect the degree

of association. Consistent with this argument is the fact that the linear  $Ph_2IPi$  has a dissociation constant approximately 5% as large as that for the planar  $Bu_3SPi$  (Again both cations have 12 carbon atoms). This suggests that storic hindrance as well as charge distribution effects may influence ionic association.

If the structure of the ion can effect the degree of association then perhaps the location of the centre of the charge on the ion may also be important. Existing theories always assume the charge density is greatest at, and its distribution symmetrical about the centre of the ion.

The work of Kraus et al on the aqueous conductivities of long-chain, asymmetric quarternary ammonium ions has shown that for the case of the uni-univalent octodecyl- and hexadecyl-tri-methylammonium salts, the experimental Kohlrausch slopes approach or exceed the theoretical Onsager slopes for <u>bi</u>-univalent salts (32, 33). This unusual behaviour might be accounted for on the basis of a non-uniform charge distribution. Thus, if it is assumed that due to the opposite direction of motion of the cation to its atmosphere, the cation may become

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oriented so that it will travel with the part having the largest charge density in the rear. Since the long chain might be expected to have the least charge density, it could travel foremost. This would in turn produce an asymmetry in the ionic atmosphere which would be additional to that considered by the Onsager treatment.

Although this suggestion cannot be tested quantitatively, an order of magnitude of the effect can be estimated.

From the Debye theory the time of relaxation for a uni-univalent electrolyte in water is approximately equal to 6 X  $10^{-11}/C$  seconds at  $25^{\circ}C$  (C = concentration in moles per litre) while the thickness of the ionic atmosphere (1/K becomes equal to 3 X  $10^{-8}/\sqrt{C}$  centimeters: Now the mobility of all ions is of the order of 5 X  $10^{-4}$  cm per second. Thus the asymmetry produced by an ion in motion can be approximated to be  $10^{-4}/\sqrt{C}$ percent and this small asymmetry of the ionic atmosphere causes approximately  $20\sqrt{C}$  percent decrease in the mobility of the ion. Thus at a concentration of  $10^{-4}$ moles per litre, the ionic atmosphere is asymmetric by only 0.01 percent and yet causes the equivalent conduc-

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tance of the ions to be decreased by 0.20 percent.

At concentration of  $10^{-4}$  molar the thickness of the ionic atmosphere is 300 angstroms, while the sizes of the long chain salts referred to above are of the order of 10 angstroms, thus an asymmetry of the order of 1 percent is possible (in the extreme) which, by the argument above, could cause a 20 percent decrease in the equivalent conductance. Since it is not possible to estimate the true effect of the substituent long chain it can merely be suggested that such a concept of a structural asymmetric charge distribution might account for the anomalies mentioned.

# SUMMARY

(1) The conductivities of aqueous solutions of  $Me_4NCl_{,}Me_4NBr_{,}Et_4NBr$  and  $Bu_4NBr_{,}have been determined at 25.00°C in the concentration range <math>10^{-4}$  to  $10^{-2}$  molar with a precision of 0.02%.

(2) The limiting conductances  $\Lambda$  o for these salts have been determined with an accuracy of 0.1%. They were 123.26, 121.24, 111.05 and 98.90 for Me<sub>4</sub>NBr, Me<sub>4</sub>NCl, Et<sub>4</sub>NBr and Bu<sub>4</sub>NBr respectively.

(3) The data has been considered from the point of view of the Onsager theory of strong electrolytes using both the Kohlrausch  $\Lambda$ - $\sqrt{C}$  relationship and the Shedlovsky function. Poor agreement was found with these theories which indicated that the electrolytes were not completely "strong".

(4) Application of the Shedlovsky treatment for weak electrolytes indicated that these electrolytes were not typically "weak".

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(5) The data has been used to criticize the "socalled" Walden Rule and the simple Bjerrum picture of ion pair formation.

(6) The results have been considered along with those of Kraus to suggest methods of combining the Onsager concept of ionic atmosphere with the Bjerrum concept of ion pair formation. It has also been suggested that consideration be given to the polarizability and the asymmetry of charge distribution on the ion in future theories.

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PART TWO

CONDUCTANCES IN NITROMETHANE

### CONDUCTANCES IN NITROMETHANE

#### INTRODUCTION

At the outset of this investigation it was hoped that conductances of the quaternary ammonium halides could be measured both in aqueous and in nitromethane solution so that comparisons could be made.

Water can be regarded as both a protonic and an aprotonic solvent: It can therefore be expected to solvate with either the cations or the anions of a solute. Nitromethane on the other hand is an aprotonic solvent only, and would be expected to interact preferentially with the cations of the solute. Furthermore, since nitromethane has a fairly high dielectric constant, (approximately one-half that of water) it would also be expected that salts would dissociate to a large degree in this medium. Thus an investigation of the behaviour of the tetraalkylammonium salts in water and in nitromethane should afford the opportunity to correlate the observed deviations from the present theories with the structure of the salt in terms of the chemical nature of the solvent. However, it was di scovered that the silver-silver halide electrodes were too soluble in nitromethane solutions of these tetraalkylammonium salts to effect satisfactory potential drop measurements. Since this was rather unexpected, a comprehensive investigation was carried out to determine the cause of this electrode dissolution phenomenon.

### PURIFICATION OF NITROMETHANE

Since impurities in nitromethane could conceivably form some complex with the silver halide of the electrodes this possibility was investigated first. The problem of purifying nitromethane, first by fractional distillation under reduced pressure, and finally by fractional recrystallization, is aptly discussed by Tink (7). However, it was found that with an increase in the reflux ratio from 75% to 85%, fewer fractional recrystallizations were required to obtain ultimate purity. The take-off pressure and temperature of the still were not altered from h5 mm and 30°C respectively.

## TEST OF PURITY OF NITROMETHANE

The ultimate test of the purity of the nitromethane obtained in this manner was based upon the attainment of an invariant freezing point. The resistances of two thermistors were determined at the freezing points of water, carbon tetrachloride and mercury from the values of the voltage applied and the current flowing through them. The two thermistors employed were found to obey resistancetemperature relations given by:

> $\log R_{T_1} = 1703.2/T = 0.6831$  $\log R_{T_2} = 1725.6/T = 0.7342$

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The freezing point of the nitromethane was determined with this arrangement. A value of  $2h_{4.9}^{\circ}$  was obtained for the invariant point with each of the thermistors which confirmed the accuracy of their calibrations. Application of the usual freezing point depression equations with the available thermal data for nitromethane indicated a maximum impurity of 5 X 10<sup>-4</sup> mole percent. This agreed with the results obtained by Karl Fisher titration for water.

### DETERMINATION OF PHYSICAL CONSTANTS OF NITROMETHANE

Since there is lack of agreement in the literature on the values for the density, viscosity and dielectric constant of nitromethane, these were redetermined in this laboratory. The temperature of these determinations was read on a mercury in glass thermometer calibrated against a platinum resistance thermometer at the National Research Council in Ottawa.

## DENSITY

This determination was made at  $25.00 \pm 0.005^{\circ}$ C using the pycnometer described in the previous section. The density was found to be 1.1314 in agreement with the most recent literature value 1.1314 of Walden and Birr (66). The lower values reported 1.1300 (69) 1.13015, 1.1306 (67) 1.13125 (71) and 1.1311 (74) were probably determined for less pure nitromethane.

## VISCOSITY

The viscosities of nitromethane saturated with water, water saturated with nitromethane, as well as pure nitromethane were determined at  $25.00 \pm 0.005^{\circ}$ C with the usual type of modified Ostwald viscometer. The following table summarizes the data obtained. The viscosities reported are the average values relative to 8.95 and 5.45 millipoise for water and methanol respectively.

Solvent	Density	Wt % H20	(millipoises)
CH3NO2	1.131	0.001	6.32
$CH_{3}NO_{2}$ (Sat.)	1.12	1.89	6.14
H <sub>2</sub> 0 (Sat.)	1.01	88.8	9•38

It is notable from the table that the addition of water to nitromethane decreases the viscosity of the latter while the converse is true for the reverse case. The values reported for the viscosity of nitromethane in millipoises are 6.203 (67) 6.11 (68) 6.19 (69) 6.31 (70) and 6.27 (71). Thus it is seen that the highest value reported agrees well with that determined here. Again the probable reason for the lower values reported is that the nitromethane was impure.

# DIFLECTRIC CONSTANT

The author is indebted to Mr. R. Gordon of the Pulp and Paper Research Institute for carrying out this determination. Acetone purified by the method of Reynolds and Kraus (38), D = 20.47, was used to calibrate a General Radio Type No. 716-C Schering Capacitance Bridge by the substitution method. For the temperature range  $20 = 25^{\circ}$ C the dielectric constant of nitromethane was found to be expressible by the relationship D = 36.7 = 0.16 (t = 25.00°C). This agrees well with the most recent literature value 37 given by Latley and Gatly (72). Some indication was also obtained that the dielectric constant increases rapidly with slight traces of water. This can account for the higher values 39 (67) and 40.4 (73) reported earlier.

#### THE ELECTRODE DISSOLUTION PHENOMENON

In order to study the dissolution of silver halide in nitromethane solutions of the tetraalkylammonium halides, the following experiments were performed. Exactly  $1.2 \times 10^{-5}$ equivalents of the appropriate silver halide was electrodiposited on a given platinum electrode. The electrode was placed in 15 cc of the solution under investigation and the time required for complete solution of the silver halide noted. No stirring was employed. The results are summarized in the following table:

Solutions	Effect
0.5 cc Et <sub>3</sub> N in 15 cc CH <sub>3</sub> NO <sub>2</sub>	nil
0.5 cc EtBr in 15 cc CH <sub>3</sub> NO <sub>2</sub>	nil
0.25 cc of each of above in 0.15 cc. CH <sub>3</sub> NO <sub>2</sub>	complete solution 2 hrs.
10 <sup>-2</sup> molar CH3NO2 Solution of Et <sub>4</sub> NBr	complete solution $\frac{1}{2}$ hr.
10 <sup>-2</sup> molar CH <sub>3</sub> NO <sub>2</sub> Solution of Bu <sub>1</sub> NBr	complete solution $\frac{1}{2}$ hr.
10 <sup>-2</sup> molar CH <sub>3</sub> NO <sub>2</sub> Solution of Me <sub>4</sub> NBr	complete solution 2 hrs.
10 <sup>-2</sup> molar CH <sub>3</sub> NO <sub>2</sub> Solution of Me <sub>4</sub> NCl	complete solution 2 hrs.
$10^{-2}$ molar CH <sub>3</sub> NO <sub>2</sub> Solution of Et <sub>4</sub> NCl	complete solution 1 hr.

No dissolution was apparent for similar cases in water or methanol. For similar solutions in acetone the times required to effect the dissolution of a similar amount of electroplated silver halide from the electrodes were found to be slightly greater than those given above. These results suggested that the dissolution of silver halide in the above instances might be due to the formation of the  $AgX_2^-$  complex. To test this inference a study of the dependence of the rate of solution of AgCl in nitromethane solutions of Et<sub>li</sub>NCl was made.

## RATE STUDY PROCEDURE

The four main current carrying electrodes previously described were chloridized in series to convert 7.2 X  $10^{-5}$  equivalents of the plated Ag to AgCl. These Ag - AgCl electrodes were washed with distilled water, dried and rinsed in the purified nitromethane and

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then immersed simultaneously into a nitromethane solution of Et, NCl of known concentration at room temperature. After approximately 10% of the AgCl had been dissolved (noted visually) one of the electrodes was removed from the solution and the exact time of immersion was noted. The other electrodes were removed after approximately 20, 50 and 75% of the AgCl was dissolved respectively. The AgCl remaining on the respective electrodes was then dissolved in NH, OH, suitably diluted and reprecipated in a colloidal state for nephelometric determination. A Fisher Electrophotometer was calibrated to read the concentrations of these colloidal suspensions of AgCl in terms of the percentage light transmission through them. In this way it was possible to draw a rate curve (i.e. amount dissolved vs time) for each concentration. From these curves the times taken to dissolve 10<sup>-5</sup> equivalents of AgCl in nitromethane solutions 226, 200, 150, 100, 86, 75, 65 and 50 X 10<sup>-4</sup> molar in Et<sub>11</sub>NCl were found to be 8, 10, 18, 40, 54, 71, 94 and 160 minutes respectively. This data when subjected to the usual reaction rate expression R = kc<sup>n</sup> (where R is the rate of the reaction, k the reaction constant, c the concentration and n the order of the reaction) yields the values n = 2 and k = 0.15 equivalents litres<sup>-2</sup>.

It should be pointed out that these values were determined under conditions similar to that which exists during a conductance

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determination; there was no stirring of the solution and hence the rates determined are not "true rates of dissolution" of AgCl in nitromethane solutions of  $Et_{\downarrow}NCl$  at room temperature. Nevertheless these results do strongly support the postulate that dissolution of silver halides occurs in nitromethane halide solutions through formation of a  $AgX_2^-$  complex. Furthermore they illustrate the degree of uncertainty which is introduced in direct current conductance measurements of nitromethane halide salt solutions. Further research is being carried out in this laboratory with a different arrangement of reversible Ag-AgX electrodes to obviate this difficulty.

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