tion formula it gives values for Λ_0 which appear to be too high, if Onsager's expression is valid for sufficiently low concentrations.

The equation proposed in this paper is an extension of Onsager's theoretical equation. . It has been found to be valid up to a concentration of about tenth normal. As an extrapolation formula for most strong uni-univalent electrolytes it gives values of Λ_0 from data at concentrations which can be measured readily. These Λ_0 values will agree with values obtained from Onsager's equation applied to measurements on sufficiently dilute solutions.[9]

Summary

An equation is proposed for the relation between the equivalent conductance of strong uni-univalent electrolytes and the concentration. It has been found to agree with measurements up to about 0.1 normal in aqueous solutions. Besides theoretically calculable constants and the limiting conductance, Λ_0, it contains only one additional constant, and reduces to the limiting Onsager equation.

[9] The author has made some preliminary tests of Equation 5 on strong unibivalent electrolytes. It appears to hold in a perfectly analogous manner for these cases if the concentrations are expressed as "ionic strengths." The application of the equation to this and higher valence types will be communicated at a later date to THIS JOURNAL.

NEW YORK, N. Y.

THE ELECTROLYTIC CONDUCTIVITY OF SOME UNI-UNIVALENT ELECTROLYTES IN WATER AT 25°

BY THEODORE SHEDLOVSKY

Introduction

It has appeared important to obtain accurate values for the electrolytic conductance of solutions of a number of electrolytes. Besides providing a test for the conductivity relationships predicted by the modern theory of ionic solutions, such measurements make possible the calculation of the degrees of dissociation of certain weak electrolytes, as is shown in another paper.[1] Also, when combined with determinations of transference numbers, they give values for individual ionic mobilities. This will be the subject of a communication from this Laboratory in the near future.

With the alternating current bridge method, which has been almost universally used since Kohlrausch for measuring electrolytic conductance, a sensitivity of one part in 100,000 in the resistance readings can be readily attained. Due to various sources of error, some of which will be men-

[1] MacInnes and Shedlovsky, THIS JOURNAL, **54,** 1429 (1932).

tioned below, the accuracy of such measurements may not reach one part in 1000. In fact there are comparatively few measurements available for which a consistent accuracy of more than several hundredths of one per cent. has actually been attained.

In this paper new measurements are reported on the conductivity of several uni-univalent electrolytes in water at 25°, covering a concentration range from about 2×10^{-5} to 0.1 normal. They were obtained with an apparatus and a technique designed to give a consistent accuracy of one or two hundredths of a per cent. for the relative conductance values.

Experimental

Bridge, etc.—The alternating current bridge, oscillator, and detector used in this research have been described by the author in a previous paper.[2] With this apparatus it is possible to make measurements at several frequencies. This is important because most of the electrical errors change with the frequency, providing a useful criterion for detecting such errors.

It was shown in the earlier paper that the sources of error in the bridge (apart from the calibration of the rheostat) amounted to less than 0.002% when the direct current values of metallic resistances were compared with the corresponding a. c. measurements up to 3000 cycles. The coils in the rheostat were frequently calibrated against several Bureau of Standards standard resistances which had been certified by the Bureau of Standards, and the relative accuracy of these calibrations is a few hundredths of an ohm for the individual coils. The coils of 1000 ohms or over were immersed in a thermostat to avoid temperature fluctuations.

In measuring very dilute solutions, when cell resistances are greater than 10,000 ohms, I have found it expedient to shunt the cell with a 10,000-ohm resistance, free from reactance errors at the frequencies used. By measuring first this shunt resistance, and then the parallel combination of the cell and the shunt, the resistance of the cell is readily calculated from the relation $\rho = SR/(S-R)$ in which ρ is the desired resistance of the cell, S the resistance measurement of the shunt and R the resistance measurement of the parallel combination. Of course, the use of such a shunt method results in a loss of precision. However, S and R are both known to 0.1 ohm, since the bridge easily has that sensitivity when measuring resistances of the order of 10,000 ohms, and the calibrations of the individual coils are accurate to 0.05 ohm, as mentioned above. Consequently, an accuracy of 0.01% is retained when $S-R$, the determining factor, amounts to 1000 ohms, which corresponds to a resistance of about 90,000 ohms in the cells. That this method has the precision just stated was shown by making check measurements with shunts differing in resistance by 2000 ohms.

² Shedlovsky. THIS JOURNAL, **52**, 1793 (1930)

Conductivity Cells.—Jones and Bollinger[3] have shown in a recent paper that many cells which are commonly used in careful conductivity work suffer from a source of error inherent in the design. In such cells, in which the filling tubes are relatively close to the electrode leads, disturbing parasitic currents can flow through capacity–resistance paths, and these can produce apparent variations in cell constants. A variation of cell constant at high resistances had been observed by Parker,[4] who attributed the effect to adsorption. Jones and Bollinger have, however, definitely proved that this so-called "Parker effect" disappears when the filling tubes and electrode leads in the cells are spaced in a manner which avoids appreciable stray currents. Their new cells, which are designed with this in view, give measurements which are constant at several frequencies, indicating that this type of error has been eliminated. The measurements I have made on solutions of concentrations greater than 0.005 normal were carried out in cells of the type recommended by these authors. These cells were made from Jena 16$^{\text{III}}$ glass and the electrodes were lightly platinized.

With very dilute solutions it is desirable to use a cell of relatively large volume, so that increasing concentrations can be built up and successively measured without risk of contamination from atmospheric or other impurities. Cells of this type have been described by Weiland,[5] Kraus and Parker,[6] Hartley and Barrett,[7] and have been generally used in recent work on dilute solutions. These workers used cells consisting essentially of a flask with a pair of dipping electrodes as is represented diagrammatically in Fig. 1 (a). However, as Jones and Bollinger have pointed out, dipping electrodes may also lead to errors in conductivity measurements. The following brief analysis will make clear the reason for such errors and the direction of their effect on the measurements.

(A)   (B)

Fig. 1.

With the cell indicated in Fig. 1 (a) the total current measured in the

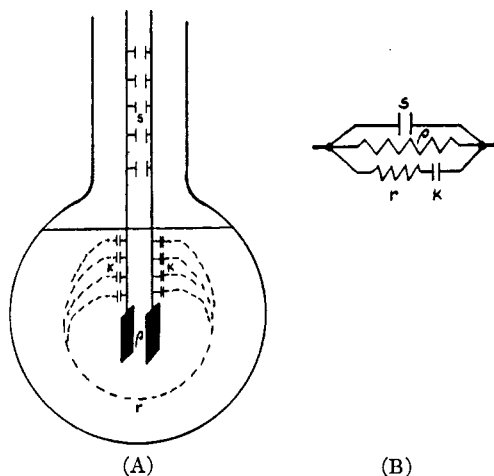[3] Jones and Bollinger, THIS JOURNAL, **53**, 411 (1931).

[4] Parker, *ibid.*, **45**, 1366, 2017 (1923).

[5] Weiland, *ibid.*, **40**, 133 (1918).

[6] Kraus and Parker, *ibid.*, **44**, 2429 (1922).

[7] Hartley and Barrett, *J. Chem. Soc.*, **103**, 786 (1913).

bridge consists, when polarization is negligible, not only of the current flowing directly between the electrodes through the solution and a capacity current between the electrodes (including the leads), but there is also a parasitic current which flows from the electrode leads by electrostatic capacity to the solution and then through it. This latter current is neither constant nor directly proportional to the resistance of the solution, and thus tends to produce apparent variations in the cell constant.

The electrical circuit for the cell in Fig. 1 (a) is shown sufficiently closely for our purpose by the accompanying diagram Fig. 1 (b). Since this circuit is balanced in the bridge by a resistance and a capacity in parallel, we have the following condition at balance[8]

$$\frac{1}{R} + j\omega c = \frac{1}{\rho} + j\omega S + \frac{1}{r - j/\omega\kappa} \tag{1}$$

in which ρ is the resistance of the solution between the electrodes, S the electrostatic capacity between the electrodes including their leads, r and κ are the resistance and capacity components of the disturbing parasitic current, R is the resistance reading and c the capacity reading in the bridge, ω the angular frequency, and j the reactance operator.

Solving Equation 1 for $1/R$ we obtain

$$\frac{1}{R} = \frac{1}{\rho} + \frac{1}{r + (1/\omega^2\kappa^2 r)} \tag{2}$$

Since r depends on the resistance of the solution, it is directly proportional to ρ, that is, $r = a\rho$, where a is a constant. Thus

$$\frac{1}{R} = \frac{1}{\rho}\left(1 + \frac{1}{a + (1/\omega^2\kappa^2 a\rho^2)}\right) \tag{3}$$

which, on expansion, neglecting higher terms, gives

$$\frac{1}{R} = \frac{1}{\rho}\left(1 + \frac{1}{a} - \frac{1}{\omega^2\kappa^2 a^2\rho^2}\right) \tag{4}$$

The term $1/\omega^2\kappa^2 a^2\rho^2$ which we shall call d varies with the square of the frequency and the square of the resistance of the solution.

It is evident from this treatment that a parasitic current resulting from a path consisting of a capacity in series with a resistance such as r and κ in Fig. 1 will produce errors in the conductivity measurements if balanced, as in the usual bridge, with a resistance and a pure capacity. However, no error results from a shunting current in the cell through a pure capacity such as S in the same figure. Since the correction terms in Equations 3 and 4, arising from the disturbing parasitic current, contain factors not readily determined, it is better to design cells so as to eliminate such currents, rather than to attempt to correct for them.

Equation 4 accounts for the observation that measurements made with dipping electrodes vary with the frequency. Furthermore, if the cell

[8] See, for instance. Hague. "Alternating Current Bridge Methods." p. 71.

is calibrated with a solution having a resistance ρ_0 for which the term $1/\omega^2\kappa^2a^2\rho^2 = d_0$, measurements at higher resistances or higher frequencies will result in conductance values which are apparently too high, since d will decrease progressively with increasing resistance or frequency. And, by similar reasoning, the apparent conductances will be too low for resistances less than ρ_0.

To avoid this error I have constructed cells in which disturbing parasitic currents are not present. Such a cell is shown in Fig. 2 (a). In this design, which includes Jones and Bollinger's recommendations, the electrodes are taken out of the flask, the leads to the electrodes are separated from each other and the space between is filled not with the solution but with the oil in the thermostat. Consequently the disturbing parasitic currents are made negligible. The lead M, nearest to the flask, is connected to the terminal of the bridge which is maintained at earth potential, so that capacity effects to earth from this relatively large surface are avoided. It has been found on repeated tests that conductance values obtained with this cell are independent of frequency, between 1000 and 3000 cycles.

As an experimental proof of the electrical error due to dipping electrodes Fig. 2 (b) measurements with them have been compared with corresponding ones made in the cell shown in Fig. 2 (a), using the same solutions. The dipping electrodes were firmly set into the flask of the cell shown in Fig. 2 (a) through the ground joint x–x'. The results of the comparison are shown graphically in Fig. 3. In this plot the ordinates correspond to the ratio of values obtained with the dipping electrodes Rd and those obtained with our cell R. The abscissas correspond to the resistance as measured by the immersed electrodes. Since the readings obtained with the cell shown in Fig. 2 (a) are independent of frequency, they are considered to be correct. On this basis the curves in Fig. 3 represent the apparent variations of the cell constant of the dipping electrode with resistance at the frequency indicated. In accord with Equation 4 the variation increases with the resistance and the frequency.
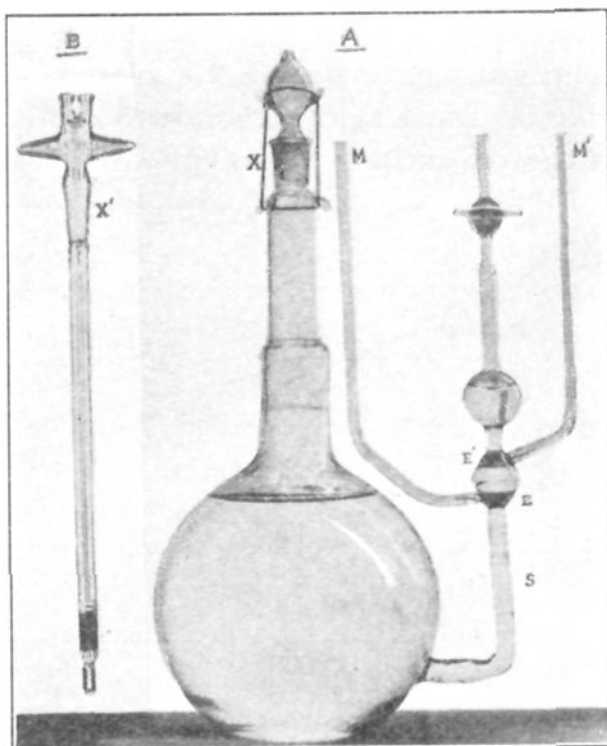

Fig. 2.

Some further essential details of the design of the cell shown in Fig. 2 (a) are as follows. The flask, of transparent quartz, has a capacity of 1 liter. The cell proper is made of Jena 16^{III} glass connecting to the flask through a graded seal S. The electrodes E, E' are truncated hollow cones of platinum foil, the outer surfaces of which are completely sealed to the glass. They are platinized only to a dull gray color, which is sufficient to avoid polarization at the concentrations used in this cell. Electrical contact is made with the electrodes through the mercury cups M, M', which are amply spaced to avoid parasitic shunting currents. To eliminate temperature errors the leads from the cups extend into two short test-tubes of mercury supported in the thermostat. Two additional leads connect these tubes to the bridge. Three cells of this design of somewhat different dimensions have been used in measuring dilute solutions of potassium chloride and sodium chloride. The conductance values obtained in all three were entirely consistent with each other.
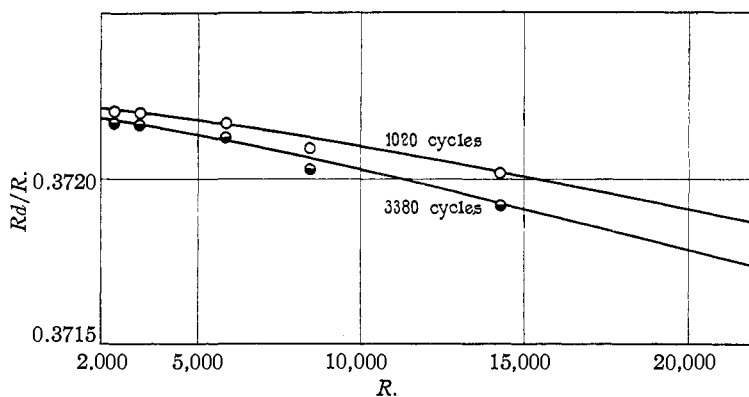

Fig. 3.

Temperature Control.—The temperature of the solutions measured was controlled by immersion of the cells in an electrically operated thermostat filled with a light mineral oil. Jones and Josephs[9] pointed out that appreciable errors may result from the use of water in the thermostat in measurements with alternating currents. The regulator consists of a hollow-walled cylindrical steel tube filled with about 300 cc. of mercury, connecting to a glass capillary in which is set the regulating needle. By use of a radio tube arrangement, similar to that described by Beaver and Beaver,[10] sparking at the mercury surface is entirely avoided. The heater consists of bare manganin wire wound non-inductively on an insulated frame around the regulator. The temperature of the thermostat, which remained constant to $\pm0.001°$, was set accurately at $25°$ ($\pm0.001°$) with

[9] Jones and Josephs, THIS JOURNAL, **50**, 1065 (1928).

[10] Beaver and Beaver, *Ind. Eng. Chem.*, **15**, 359 (1923).

the aid of a carefully calibrated platinum resistance thermometer, which serves as a temperature standard in this Laboratory. It is of the strain-free type, with a resistance of about 25 ohms and is provided with a special thermostated Mueller thermometer bridge and a sensitive galvanometer.

Purification of Materials

Conductivity Water.—The conductivity water was obtained by redistilling distilled water from alkaline potassium permanganate in a still similar to the one described by Kraus and Dexter.[11] The precautions suggested by these authors were carefully observed. In this apparatus the steam from the evaporator passes through a settling chamber in which traces of spray are separated from the vapor. This vapor then passes to a condenser where it is partially condensed. The large volume of uncondensed vapor carries with it most of the carbon dioxide and other gaseous impurities. The condensed water was collected out of direct contact with air in a 15-liter "Vitreosil" quartz flask.[12] This flask was fitted with an air-tight block tin cover carrying block tin pipes for collecting and withdrawing the water. The conductivity water in this container was protected from atmospheric impurities by a set of "guard" bottles, containing sulfuric acid and strong potassium hydroxide solution, followed by a long tube filled with soda lime. The specific conductance of the water was between 0.1 and 0.4×10^{-6} mhos.

Sodium and Potassium Chlorides.—The best obtainable c. p. salts were crystallized once by absorbing pure hydrochloric acid gas in a hot saturated solution which was gradually cooled to $0°$. After centrifuging, the product was recrystallized from conductivity water, again centrifuged, and dried in a clean electric oven. Two samples of potassium chloride were prepared by four crystallizations from conductivity water, but no difference was observed between the conductance of solutions made with them and with the samples prepared as above. The purified salts were fused in platinum under vacuum in an electric furnace. When potassium chloride and particularly sodium chloride is fused in air, the resulting product is slightly alkaline, as can be seen from a pink fringe around a crystal placed in a few drops of distilled water containing a trace of phenolphthalein. However, fusing the salts in vacuum avoids this difficulty, probably by removing traces of water quickly enough to prevent appreciable hydrolysis at the high temperatures.

Potassium Nitrate and Silver Nitrate.—The c. p. salts[13] were recrystallized several times from conductivity water, centrifuged, dried and fused as above. The fused salts gave negative tests with phenolphthalein and with acidified potassium iodide and starch solution, showing that no loss or decomposition of nitrate took place.

A "Richard's bottling apparatus,"[14] was used in handling the fused salts, since they are more or less hygroscopic. With this apparatus[15] it is possible to fuse salts in a controlled atmosphere, and to transfer them into glass-stoppered weighing bottles where they may be kept without risk of contamination from the air.

Hydrochloric Acid.—Constant boiling hydrochloric acid was prepared from c. p.

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[11] Kraus and Dexter, THIS JOURNAL, **44**, 2469 (1922).

[12] In the measurements on hydrochloric acid (dilute) the conductivity water was collected directly from the still into the cell. Its conductivity was always less than 2×10^{-7}.

[13] A pure sample of silver nitrate was kindly supplied by Dr. Vinal of the Bureau of Standards. This sample was recrystallized once from conductivity water.

[14] T. W. Richards and H. G. Parker, *Proc. Am. Acad. Arts Sci.*, **32**, 59 (1896).

[15] This excellent apparatus, which is essential for accurate work with hygroscopic materials, has not come into as general use as might be desired.

acid in the manner described by MacInnes and Dole.[16] The barometric pressure corresponding to the fraction of acid collected was carefully noted, and the concentration of the product was thus determined from the data of Foulk and Hollingsworth.[17] Analyses were also made by differential potentiometric titrations (through a sodium hydroxide solution) against benzoic acid and potassium hydrogen phthalate with the procedure described by MacInnes and Cowperthwaite.[18] The three methods agreed well within 0.01%. Although the distilled acid, which was stored in small glass-stoppered Pyrex flasks, showed no appreciable change in concentration on standing for several weeks, fresh samples were taken for making up the solutions used in this work.

Determination of Cell Constants.—The "Jones and Bollinger"[3] cell for moderately concentrated solutions (cell B) was calibrated with a 0.1 "demal" solution of potassium chloride, containing 7.47896 g. of potassium chloride and 1000 g. of water (weighed in air). The specific conductance of this solution according to Parker and Parker[19] is 0.0128524 at $25°$. This value has been taken as the basis for all the conductance measurements reported in the present paper.

Another "Jones and Bollinger" cell (C) had a resistance of less than 600 ohms when filled with 0.1 "demal" potassium chloride solution. But since it is best to measure cell resistances of over 1000 ohms to retain the full sensitivity of the bridge, the cell C was calibrated by intercomparison with cell B. The ratio between measurements in these two cells remained constant to 0.01% over a wide range of resistances with solutions of different electrolytes, i. e., no "Parker effect" was observed. The cell constants showed only slight variations with time over a period of two years. In that time the constant of cell B, K_B, varied between 24.706 and 24.712; and that of cell C, K_C, varied between 7.6342 and 7.6357. In computing the conductance values obtained in these cells, which were calibrated at intervals of two or three months, the most recent calibration was always used.

The cell constants of the "flask" cells Fig. 2 (a) which were used in measuring the very dilute solutions, were determined at the end of each run in these cells by intercomparison with cell C. Also for these cells no "Parker effect" was observed. For three cells of this type the constants were (1) 0.70652, (2) 0.51247, (3) 0.58915; cell (1) was used in series a, b, d, e on potassium chloride, and series a, b on sodium chloride; cell (2) was used in series f on potassium chloride and series c, d, e, f on sodium chloride; cell (3) was used in all the other dilute series.

Preparation of Solutions.—Solutions at round concentrations of 0.1, 0.05, 0.02, 0.01, 0.005 and in some cases 0.07 normal at $25°$ (gram moles per liter of solution at $25°$) were made up by weight, using the density data given in the "International Critical Tables." The glassware was cleaned with hot dichromate–sulfuric acid solution, thoroughly rinsed with distilled water, steamed out, and dried with air which had been passed through towers of fused calcium chloride followed by a long cotton filter. After determining the dry weight of the flasks, they were again rinsed with several samples of conductivity water before being used for making up the solutions.

Weighing.—Three balances were used for weighing in this research. A large Christian Becker chainomatic balance with a capacity of 10 kilos and an average sensitivity of 0.5 mg. was used in weighing water for the solutions. A Christian Becker analytical balance, with a sensitivity of 0.05–0.1 mg. was used for weighings corresponding to loads between 10 and 150 g. A Kuhlman microbalance with a sensitivity of 0.001 mg. was used for weighing small quantities of solutes. All weighings were made by

[16] MacInnes and Dole, THIS JOURNAL, **51**, 1119 (1929).

[17] Foulk and Hollingsworth, ibid., **45**, 1220 (1923).

[18] MacInnes and Cowperthwaite, ibid., **53**, 555 (1931).

[19] Parker and Parker, ibid., **46**, 332 (1924).

the tare and substitution method, and were corrected to vacuum. The weights for the large and micro balances were carefully calibrated to the same basis against a standard set which was certified by the Bureau of Standards.

Procedure

Measurements above 0.005 Normal.—The conductivities of solutions above 0.005 normal, which were made up to round concentrations of 0.005, 0.01, 0.02, 0.05, 0.07 and 0.10 normal,[20] were determined in cells B and C. These cells were periodically cleaned with dichromate–sulfuric acid mixture, followed by very thorough rinsing with distilled water, and finally with conductivity water, with which they were also kept filled when not in use. Occasionally, when it was suspected that the cells had been contaminated with grease, they were cleaned with alcohol and ether before receiving the usual cleaning treatment.

The procedure was to rinse the cell used in a particular measurement with six or eight portions of the solution, and then to let the cell stand, filled with solution, for fifteen to thirty minutes. The cell was then refilled with solution and immersed in the thermostat, where it attained thermal equilibrium within about fifteen minutes, after which its resistance remained constant. Refilling the cell and repeating the measurement usually gave the same resistance value, but several fillings of the cell with check measurements were always made.

For transferring the solution from the storage flask into the cells used for the more concentrated solutions, the ground-glass stopper of the flask was replaced by a two-holed rubber stopper into which were fitted a short glass tube and a long U-shaped glass tube, the latter reaching to the bottom of the flask. The tubes were, of course, previously cleaned and dried. The outside end of the U-tube was connected to the cell, and the solution was forced into it with a sufficient pressure of purified air.

The solvent correction for the solutions measured in this manner is relatively small. It was determined by finding the conductivity of a sample of the water used in making up the solution in a cell similar in design to cells B and C, but having large electrodes and a cell constant of about 0.037. The conductance of the water used for these solutions, since it was not completely protected from the carbon dioxide in the atmosphere, was between 0.5 and 0.8×10^{-6} mhos, usually about 0.6×10^{-6}. However, this value corresponds to about only 0.1% of the conductivity of a 0.005 normal solution for the electrolytes measured.

Measurements of Very Dilute Solutions.—The conductivities of the most dilute solutions were measured in the "flask" cell Fig. 2 (a). The cell, which was thoroughly cleaned in the manner described below, was partially filled with about 950 cc. of fresh conductivity water. The solvent was then swept out for several minutes with purified nitrogen entering through the stopcock and escaping through the neck of the flask. (The stopcock and ground-glass stopper in the "flask" cell were lubricated with a trace of thick, purified vaseline. This was prepared by distilling off the more volatile components of white vaseline under a vacuum, and the viscous residue was extracted repeatedly with hot conductivity water.) The cell with the water was then weighed, and the quantity of solvent was determined by subtracting the weight of the empty dry cell. After introducing mercury into the tubes leading to the cell electrodes, the cell was placed in the thermostat and connected to a source of purified nitrogen. etc., in the manner shown in Fig. 4. The mercury cup E_1, which is nearest to the flask and makes contact with the lower electrode in the cell proper (W), was connected to the bridge terminal at the junction of the rheostat and detector. Owing to the relatively large surface of the

[20] Check series of solutions were kindly prepared by Mr. Donald Belcher of this Laboratory.

flask, it has an appreciable capacity to earth. However, by connecting E_1 to the terminal which is at earth potential when the bridge is balanced, no capacity current to earth is likely from this source. The ground-glass stopper (S) was held in place with a rubber band. By means of the three-way stopcock A, the cell could be connected either to a source of purified nitrogen under a pressure, regulated by the reduction valve V, or to the atmosphere through the guard train D. With this arrangement (T open and A as in Fig. 4), the valve V was set so that a slight pressure was established in the flask (F). This pressure was regulated to force solution into the cell proper (W) past the electrodes, half filling the bulb (B) when the stopcock A was subsequently turned so as to connect T to the atmosphere (through D). Thus the cell W could be alternately filled and emptied by turning A to the proper position. With A set as in Fig. 4, the liquid in the flask could be stirred with purified nitrogen by lifting the stopper S slightly.
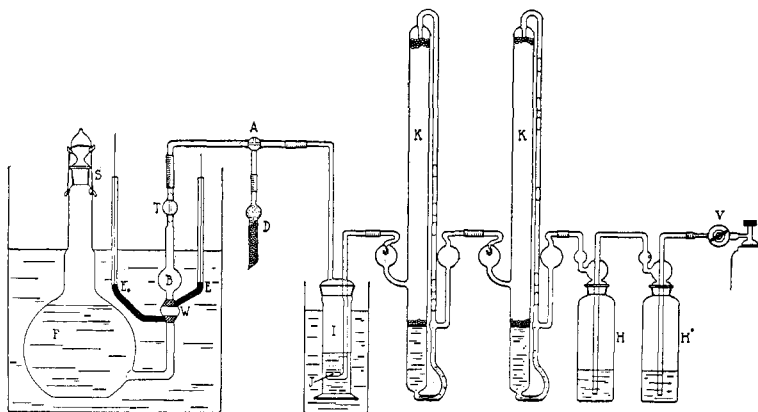

Fig. 4.

The purification train for the nitrogen consists of two gas scrubbing bottles containing sulfuric acid (H, H'), two scrubbing towers (K) of the type recommended by Kraus and Parker,[21] filled with strong potassium hydroxide solution, and finally the glass filter bottle (I) which contains conductivity water and is immersed in the thermostat. In this bottle, the gas passed through the sintered glass membrane (J) in fine bubbles, and is thus saturated with water vapor at the temperature of the thermostat.

The guard train (D) consists of a tube of sulfuric acid, and a long soda lime tube. The purpose of this train is to prevent atmospheric impurities from diffusing into the cell when it is opened to the air by the stopcock A.

After the conductivity water in the "flask" cell had reached thermal equilibrium in the thermostat, the cell proper (W) was filled, as described above, by manipulating the stopcock (A) with the stopcock (T) open. Then (T) was closed and the resistance was measured. This procedure was repeated a number of times to make sure that a reliable, constant value was obtained.

Then, with the ground-glass stopper (S) removed and a slow stream of nitrogen passing through the flask, an increment of solute was quickly added and the stopper replaced. This was added in the form of salt fused in tiny platinum cups, which were dropped into the flask, or in the form of solution of known concentration which was added from a weight buret. Two weight burets were used, one having a capacity of 1.5 cc. and the other 75 cc. Both burets were made from Pyrex glass. In the case of the

21 Kraus and Parker, THIS JOURNAL, 44, 2432 (1922).

platinum cups, containing 20 to 90 mg. of fused salt, and the micro buret, containing a maximum of 1.5 cc. of solution, the required weighings were made on the micro balance to 0.001 or 0.002 mg. When the larger buret was used, at least 5 g. of solution was added, and the weighings were made on the analytical balance to 0.1 mg. The small platinum cups were handled with platinum-tipped tongs, the micro buret with clean, oil-free chamois, and the larger buret with clean silk gloves. For the most dilute solutions the quantities of solid required were too small to weigh accurately. In such cases small quantities of solution of known concentration were added from the micro weight buret. However, most of the values given for potassium chloride, sodium chloride and potassium nitrate were obtained with the use of the platinum cups. These weighed about 0.25 g., their exact weight being determined for each run. They were readily cleaned by rinsing in a stream of distilled water and heating to incandescence over a Bunsen burner until no color was imparted to the flame. The small amounts of salt were fused in the cups in the manner already described. After the addition of an increment of solute, the stopcock T was closed, the flask cell was disconnected, removed from the thermostat, and thoroughly shaken until all the added solute was well distributed. Then the flask was replaced in the thermostat, reconnected, and, by manipulating (A), (T) and (S), the cell proper was filled and emptied numerous times, and the solution stirred with gas. After thermal equilibrium had again been established. the solution was measured, as described above, with several refillings of the cell proper (W). This precedure was repeated until several concentrations had been built up and measured. In the case of some very low concentrations, especially with hydrochloric acid, it was found that the measured resistance for a particular filling of C changed with time. It is supposed that this effect was due to adsorption or slight contamination from the Jena glass of which the cell proper is constructed (the flask itself being of quartz). However, since the relative volume of the cell proper is small, this effect on the solution as a whole was probably negligible. In any case, reproducible values were always obtained by taking the readings immediately on filling (W), or by taking readings over a period of time and extrapolating to zero time. The level of the solution in the bulb (B) or in the flask had no detectable effect on the measurements.

After the conductance of the last solution had been determined in this apparatus, it was again measured in cell C. Using the result of this measurement, it was possible to check the constant of cell (W) at the end of each series of determinations.

Before starting a new run, the flask cell was completely cleaned inside and outside. Most of the oil adhering to the outside of the cell was removed with warm soap solution. The mercury cups were cleaned out with nitric acid. All grease was finally removed with ether, the flask and cell were completely filled with warm sulfuric acid–dichromate mixture and allowed to stand overnight. It was then thoroughly rinsed with distilled water by letting at least 5 liters flow through it, entering at the stopcock and leaving through the neck of the flask. The quartz flask was then further cleaned with steam, and rinsed with several portions of conductivity water. The outside of the flask and also the mercury cups were dried and the apparatus was ready for the next run.

Results

All the conductance values here presented are on the basis of a specific conductance of 0.0128524 for a 1/10 "demal" potassium chloride solution at $25°$.[19] Such a solution contains 7.47896 g. of potassium chloride in 1000 g. of water (weights in air vs. brass).

The equivalent conductances are defined as $\Lambda = 1000\ L/C$, L being the measured specific conductance, and C the concentration in equivalents per

liter of solution at 25°. The molecular weight values given in the "International Critical Tables" have been used throughout. Except in the case of the hydrochloric acid solutions, the conductance of the solvent has been subtracted from the measured specific conductances.
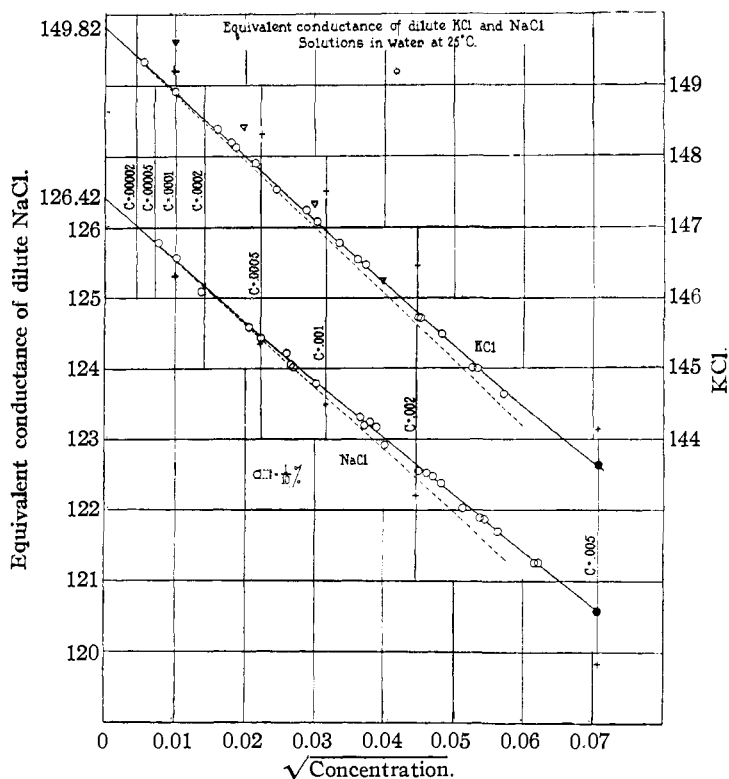

Fig. 5.—O, Shedlovsky; ∇, Grindley and Davies; +, Jeffery and Vogel.

Tables I to V give the results of the measurements on the dilute solutions (below 0.005 normal). The average values of the measurements at the round concentrations between 0.1 and 0.005 normal are given in Tables VI and VII. These two tables also give the conductivity values corresponding to round concentrations between 0.002 and 0.0001 normal, graphically interpolated from the data on the dilute solutions. Graphs corresponding to the data in the tables are shown in Figs. 5 to 8, in which the equivalent conductance is plotted against the square root of the concentration. On these graphs, the dotted lines represent the theoretical slopes (A) calculated from Onsager's conductance equation,[22] which, however, is a limiting expression, strictly only valid at infinitesimal concentrations. *It can be seen from these figures that the Onsager equation yields,*

[22] Onsager. *Physik. Z.,* **28**, 277 (1927).

TABLE I

EQUIVALENT CONDUCTANCES OF POTASSIUM CHLORIDE AT 25°

Series	$C \times 10^4$	Λ	Series	$C \times 10^4$	Λ
f	0.32576	149.33	d	11.321	146.76
f	1.0445	148.91	e	14.080	146.46
f	2.6570	148.38	d	15.959	146.26
e	3.3277	148.19	b	20.291	145.72
b	3.5217	148.12	e	20.568	145.71
c	4.6948	147.89	d	23.379	145.48
a	6.0895	147.52	a	27.848	145.00
e	8.4200	147.23	e	28.777	144.99
c	9.2856	147.07	b	32.827	144.64

$$\Lambda_0 = 149.82$$

TABLE II

EQUIVALENT CONDUCTANCES OF SODIUM CHLORIDE AT 25°

Series	$C \times 10^4$	Λ	Series	$C \times 10^4$	Λ
e	0.59441	125.79	f	15.306	123.17
e	1.1283	125.57	d	16.271	122.91
d	1.8985	125.09	b	20.348	122.54
d	4.2677	124.58	c	21.253	122.51
f	5.0056	124.44	f	22.275	122.47
c	6.7898	124.21	a	23.388	122.37
a	6.9196	124.21	b	26.538	122.02
d	7.1846	124.05	c	28.988	121.88
b	7.3843	124.02	−	29.806	121.87
f	9.2243	123.78	a	31.862	121.70
c	13.448	123.31	c	37.367	121.26
b	13.868	123.19	a	38.776	121.26
a	14.466	123.24			

$$\Lambda_0 = 126.42$$

TABLE III

EQUIVALENT CONDUCTANCES OF HYDROCHLORIC ACID AT 25°

Series	$C \times 10^4$	Λ	Series	$C \times 10^4$	Λ
a	0.28408	425.01	a	7.5404	421.66
c	0.81181	424.75	b	15.768	419.88
b	1.7743	423.82	a	18.766	419.64
a	3.1863	423.43	c	25.614	418.32
c	3.4227	423.22	b	29.943	417.98
b	5.9146	422.42			

$$\Lambda_0 = 426.04$$

TABLE IV

EQUIVALENT CONDUCTANCES OF POTASSIUM NITRATE AT 25°

Series	$C \times 10^4$	Λ	Series	$C \times 10^4$	Λ
a	0.69820	144.17	b	12.119	141.53
a	1.7613	143.62	a	16.468	140.91
a	3.8888	142.98	b	24.219	140.17
b	5.8651	142.61	b	36.724	139.08
a	8.6853	141.97			

$$\Lambda_0 = 144.92$$

<div align="center">

TABLE V

EQUIVALENT CONDUCTANCES OF SILVER NITRATE AT 25°

</div>

Series	$C \times 10^4$	Λ	Series	$C \times 10^4$	Λ
a	0.27575	132.91	a	7.5380	130.82
b	0.72453	132.64	b	10.026	130.45
a	1.0710	132.48	b	12.297	130.10
a	3.5387	131.58	a	14.530	129.86
b	4.6704	131.46	b	29.054	128.44

<div align="center">

$\Lambda_0 = 133.32$

TABLE VI

EQUIVALENT CONDUCTANCES (25°). OBSERVED AND COMPUTED VALUES AT ROUND CONCENTRATIONS

</div>

Concn.	Λ, KCl Calcd.	Obs.	Λ, NaCl Calcd.	Obs.	Λ, HCl Calcd.	Obs.
0.0001	148.89	148.90	125.54	125.56	424.46	424.53
.0002	148.52	148.56	125.19	125.21	423.82	423.86
.0005	147.77	147.80	124.48	124.50	422.58	422.62
.001	146.95	146.93	123.71	123.72	421.23	421.24
.002	145.81	145.79	122.64	122.67	419.34	419.27
.005	143.65	143.64	120.60	120.58	415.75	415.68
.01	141.36	141.32	118.45	118.43	411.96	411.88
.02	138.39	138.34	115.67	115.65	407.06	407.12
.05	133.33	133.33	110.89	110.88	398.79	398.97
.07	....	....	....	....	395.42	395.33
.10	128.94	128.90	106.73	106.68	391.78	391.20
$A = 0.2274\Lambda_0 + 59.79$			93.85	88.53	156.70	
B			94.9	89.5	165.0	
Λ_0			149.82	126.42	426.04	

$$\Lambda_0 = \frac{\Lambda + 59.79\sqrt{C}}{1 - 0.2274\sqrt{C}} - BC$$

<div align="center">

TABLE VII

EQUIVALENT CONDUCTANCES (25°) OF SILVER AND POTASSIUM NITRATES AT ROUND CONCENTRATIONS

</div>

Concn.	Λ, AgNO$_3$	Λ, KNO$_3$	Concn.	Λ, AgNO$_3$	Λ, KNO$_3$
0.0001	132.46	144.02	0.01	124.72	135.78
.0002	132.08	143.53	.02	121.37	132.37
.0005	131.32	142.73	.05	115.20	126.27
.001	130.47	141.80	.07	....	123.52
.002	129.32	140.54	.10	109.10	120.36
.005	127.16	138.44	Λ_0	133.32	144.92

in each case, the limiting slope which is approached by the curves representing the actual measurements.

An empirical extension of Onsager's equation applicable to solutions of strong uni-univalent electrolytes up to about 0.1 normal has been presented in the preceding paper.[23]　The equation proposed is

[23] Shedlovsky, THIS JOURNAL, **54**, 1405 (1932).

$$\Lambda_0 = \frac{\Lambda + \beta \sqrt{C}}{1 - \alpha \sqrt{C}} - BC \tag{5}$$

which differs from Onsager's theoretical limiting equation by the term BC. Λ is the equivalent conductance, Λ_0 is the equivalent conductance at infinite dilution, C is the equivalent concentration, α and β[24] are Onsager's theoretically computed constants depending on the solvent and the temperature, and B is an empirical constant. As has been shown in the preceding paper,[23] Equation 5 is suitable for obtaining Λ_0 values for hydrochloric acid, potassium chloride and sodium chloride, by applying the equation to the conductivity data with Λ_0 and B as the adjustable constants.
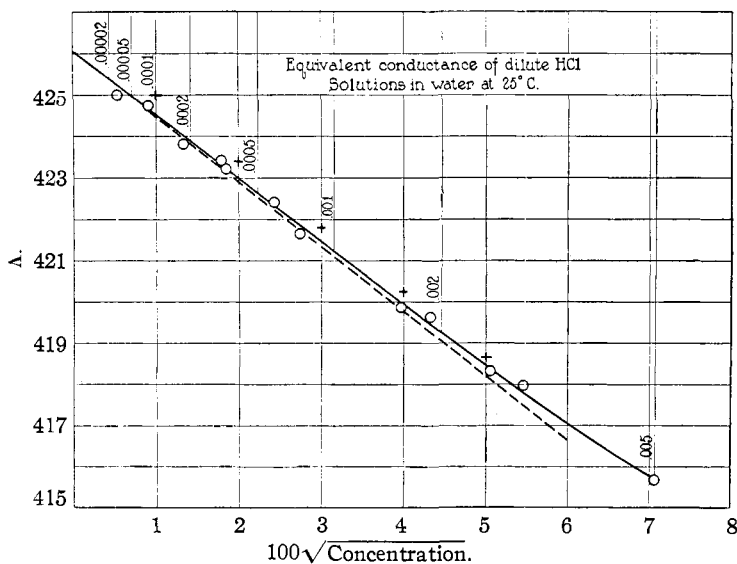

Fig. 6.—O, Shedlovsky; +, Parker.

The limiting values thus obtained agree with the graphical extrapolations, using the measurements on the more dilute solutions in the plots shown in Figs. 5 and 6. The agreement between the observed Λ values for hydrochloric acid, potassium chloride and sodium chloride and those calculated from Equation 5 is indicated in Table VI.

The Λ_0 values for the solutions of potassium nitrate and silver nitrate were obtained by linear extrapolations from the plots of results from the measurements on the most dilute solutions. These plots are shown in Fig. 7. For these substances Equation 5 does not quite fit the observed values. In the case of hydrochloric acid, sodium chloride, and potassium chloride, positive deviations from Onsager's limiting equation, which increase with rising concentration, are observed even below 0.001 normal

[24] At 25° in water $\alpha = 0.2274$; $\beta = 59.79$.

However, in solutions of potassium nitrate and silver nitrate the corresponding deviations have small negative values at first and then become positive, but increase more slowly than is observed for solutions of the chlorides. It therefore appears that a compensating effect is present in these solutions, whose direction is such as might be produced by a slight progressive association of silver nitrate and of potassium nitrate. If this explanation is correct, these salts appear to be somewhat weaker electrolytes than sodium chloride, potassium chloride and hydrochloric acid. However, a more detailed consideration of the conductivity data on silver nitrate and potassium nitrate solutions from this viewpoint will be reserved for a future communication.
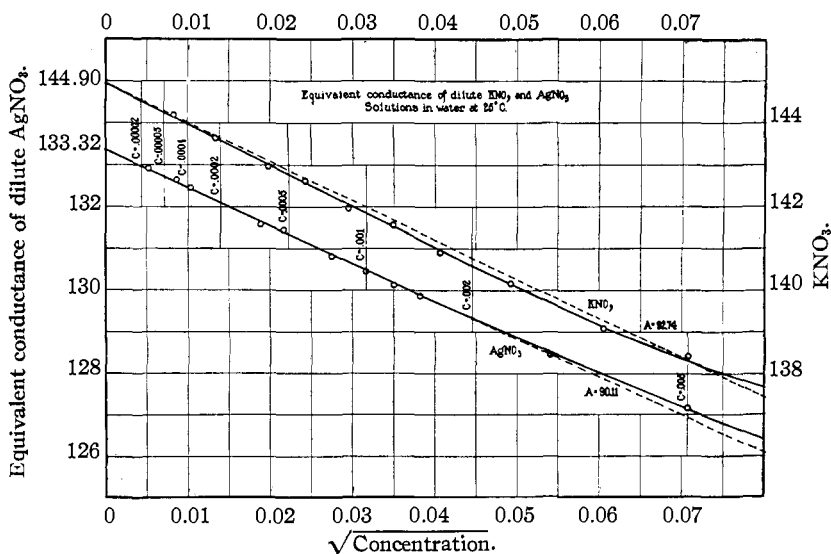

Fig. 7.

In Figs. 5 and 6 some recent measurements at 25° by other workers are compared with my results. The triangles (Fig. 5) indicate conductance values obtained by Grindley and Davies[25] on potassium chloride solutions, and the crosses, values reported by Jeffery and Vogel[26] for potassium chloride and sodium chloride. The crosses (Fig. 6) indicate values obtained by Parker[27] on hydrochloric acid solutions recomputed to the conductance basis of the present measurements. The discrepancies between the new measurements and those of the other workers are probably due, in part at least, to the use of dipping electrodes, whose disadvantage has been discussed in the early part of this paper. In the case of the measurements of

[25] Grindley and Davies, Trans. Faraday Soc., **25**, 129 (1929).

[26] Jeffery and Vogel, J. Chem. Soc., 1715 (1931).

[27] Parker, THIS JOURNAL, **45**, 2017 (1923).

Jeffery and Vogel, there may have been also appreciable earth capacity errors, since these authors apparently did not use an "earth-balancing circuit" in their bridge.
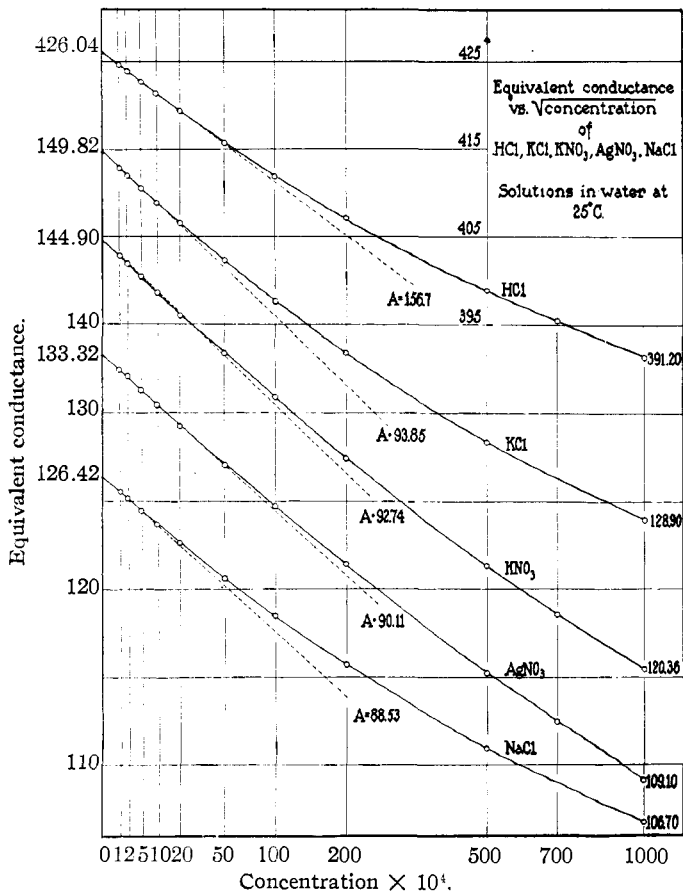

Fig. 8.

Addendum.—After this paper had been submitted to THIS JOURNAL, measurements on the conductance of lithium chloride solutions in water at 25° were completed. The results are summarized in the table below. The equivalent conductance of this salt can be represented accurately up to a concentration of 0.07 N by the equation

$$115.00 = \frac{\Lambda + 59.79 \sqrt{C}}{1 - 0.2274 \sqrt{C}} - 89.1\ C$$

The salt was prepared as follows. Lithium carbonate was precipitated from a solution of C. P. lithium chloride with redistilled ammonium carbonate. The carbonate was washed several times with hot water and then

dissolved in distilled hydrochloric acid. The lithium chloride thus formed was crystallized, ignited to remove the volatile impurities, and then recrystallized twice from conductivity water acidulated with pure hydrochloric acid. With the aid of the Richards bottling apparatus the final product was fused in platinum in an atmosphere of dry hydrogen chloride and cooled in vacuum. The product was found to be neutral.

EQUIVALENT CONDUCTANCE OF LITHIUM CHLORIDE AT 25°

C	Λ obs.	Λ calcd.	C	Λ obs.	Λ calcd.
0	....	115.00	0.032581	102.34	102.30
0.00047210	113.18	113.18	.009836	107.33	107.35
.0023455	111.04	111.05	.018515	104.91	104.92
.0058846	108.91	108.92	.049942	100.10	100.06
.0107786	107.03	107.03	.064021	98.70	98.70
.0199375	104.64	104.61	.10000	95.83	96.19

The author wishes to express his thanks to Dr. D. A. MacInnes for his kind suggestions in connection with this work.

Summary

1. The accurate measurement of the conductance of very dilute solutions with a new type of cell is described.

2. It is shown that the use of "dipping electrodes" for accurate conductivity measurements may lead to errors.

3. Measurements of the equivalent conductances of aqueous solutions of sodium chloride, potassium chloride, hydrochloric acid, silver nitrate, and potassium nitrate at 25° are given in the concentration range 0.00003 to 0.1 N.

4. These measurements confirm the Onsager conductance equation as a limiting equation.

5. The measurements on the conductances of the chlorides can be expressed, within experimental error, to about 0.1 N by an extension of the Onsager equation containing, besides Λ_0, only one empirical constant The measurements on solutions of the nitrates, however, show deviations from this equation which may be due to partial association.

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