by the construction of an interpolation table for R and kD_2/kD_1, to be used at that wave length. The values of $\bar{r}$ and $\omega^2\bar{C}^2$ are constant for any wave length and may be obtained either by the proper calibration of the members of the circuit or by solving for one or the other by the substitution in the equation of known values of R and kD_2/kD_1. The latter known quantities must have been obtained from a series of measurements with a standard resistance. The quantities $\bar{r}$ and $\omega\bar{C}$ do not have to be precise for if approximate constant values are used throughout, the relative values of kD_2/kD_1 and R will be correct.

We wish to express our indebtedness to Professor Edward Bennett of the Department of Electrical Engineering of this University and to Dr. Ronold King of the Department of Physics of Lafayette College for their helpful advice.

Summary

A method is described which serves for the simultaneous observation of electrical conductance and dielectric constant of very dilute electrolyte solutions at high radio frequencies. The apparatus which was used may be described as being of the comparator-resonance type. It consists of three distinct units, a variable high frequency oscillator circuit, an intermediate circuit and a comparator circuit with thermocouple–galvanometer measuring system.

The mathematical theory of the circuits is considered. Dielectric constant change is calculated from a comparison of the resonance settings of the standard variable precision condenser in the comparator circuit with the conductance cell connected and disconnected. For the evaluation of electrical conductance change there are required observations of the comparator circuit galvanometer deflections, again at resonance and with the cell connected and disconnected. It is further pointed out that the method developed may be applied to the measurement of high frequency currents through other types of resistances.

MADISON, WIS. RECEIVED AUGUST 17, 1936

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, UNIVERSITY OF WISCONSIN]

The Resistance and Capacity Behavior of Strong Electrolytes in Dilute Aqueous Solution. II. The Dispersion of Electrical Conductance[1]

BY ORLAN M. ARNOLD AND JOHN WARREN WILLIAMS

Some years ago it was pointed out by Debye and Falkenhagen[2] that as a necessary consequence of the postulated existence about any central ion of an ionic atmosphere with a finite time of relaxation, there must result an electrical conductance which is dependent upon the frequency of the field which is used to measure it. If an alternating field is applied, each ion in the solution will acquire a periodic motion. If the frequency is low enough (1000 cycles, for example) there will be produced in each instant a dissymmetry in the ionic atmosphere which corresponds to the momentary velocity of the ion. But if this frequency is increased to a point where the period of oscillation of the ion becomes comparable with the time required for the formation of its atmosphere any dissymmetry of the latter, necessary for the existence of the electrical force of relaxation, will decrease. Thus, depending upon the time of relaxation of the atmosphere about any particular ion there will be a frequency at which the dissymmetry of the atmosphere no longer can be formed in the normal way, and as the frequency is increased above this value the electrical force of relaxation will diminish and the mobility of the central ion will increase until such time as the frequency has been made so high that the dissymmetry of the ionic atmosphere disappears entirely.

The results of the calculations of Debye and Hückel[3] and of Onsager[4] for the molar conductance of a solution at zero, or very low, frequency may be expressed in the form

$$\bar{\Lambda} = \bar{\Lambda}_0 - \bar{\Lambda}_{I_0} - \bar{\Lambda}_{II}$$

Here $\bar{\Lambda}$ is the molar conductance of the solution at a finite concentration, $\bar{\Lambda}_0$ is the molar conductance at infinite dilution, $\bar{\Lambda}_{I_0}$ is the electrical

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[1] A preliminary and incomplete report of this work has appeared in another place [Williams and Arnold, *Acta Physicochim., U. R. S. S.*, **3**, 619 (1935)]. This report gives as well provisional data for the dielectric constants of very dilute electrolyte solutions at two high frequencies.

[2] Debye and Falkenhagen, *Physik. Z.*, **29**, 121, 401 (1928).

[3] Debye and Hückel, *Physik. Z.*, **24**, 305 (1923).

[4] Onsager, *ibid.*, **27**, 388 (1926); **28**, 277 (1927).

force of relaxation expressed in conductance units, and $\overline{\Lambda}_{II}$ is the electrophoretic force, again expressed in conductance units. The molar conductance of the solution as a function of the frequency ω, used to measure it may be written in similar fashion as

$$\overline{\Lambda} = \overline{\Lambda}_0 - \overline{\Lambda}_{I\omega} - \overline{\Lambda}_{II}$$

in which at zero frequency, $\overline{\Lambda}_{I_\omega} = \overline{\Lambda}_{I_0}$. When at extremely high frequencies the dissymmetry of the ionic atmosphere has disappeared entirely, $\overline{\Lambda}_{I_\omega} \longrightarrow 0$, and the molar conductance approaches the limiting value

$$\overline{\Lambda} = \overline{\Lambda}_0 - \overline{\Lambda}_{II}$$

The mathematical treatment of Debye and Falkenhagen has led to the following expression for the electrical force of relaxation expressed as conductance.

$$\overline{\Lambda}_{I\omega} = \frac{|e_1e_2|}{3DkT}\kappa\overline{\Lambda}_0\chi(\omega, \theta, q)$$

where

$$\chi(\omega, \theta, q) = \frac{\sqrt{q}}{\left(1 - \frac{1}{q}\right)^2 + \omega^2\theta^2}\left[\left(1 - \frac{1}{q}\right)\left(\overline{R} - \frac{1}{\sqrt{q}}\right) + \omega\theta\overline{Q}\right]$$

$$\overline{R} = \frac{1}{\sqrt{2}}\sqrt{\sqrt{1 + \omega^2\theta^2} + 1}$$

$$\overline{Q} = (1/\sqrt{2})\sqrt{\sqrt{1 + \omega^2\theta^2} - 1}$$

and the other symbols have the significance usually assigned to them in the discussion of the interionic attraction theories. Thus

$$Q = \frac{(\overline{L}_1z_1 + \overline{L}_2z_1)\,z_1z_2}{(z_1 + z_2)(\overline{L}_1z_2^2 + \overline{L}_2z_1^2)}$$

$$\theta = \frac{z_1^2z_2^2}{z_2^2\overline{L}_1 + z_1^2\overline{L}_2} \times \frac{15.33 \times 10^{-8}}{kTq\kappa^2}$$

and

$$\kappa^2 = \frac{4\pi}{DkT}\frac{e^2N\gamma}{1000}\Sigma\nu_iz_i^2$$

In this article are recorded measurements of the electrical conductance of dilute aqueous solutions of potassium chloride, barium chloride, magnesium sulfate, lanthanum iodate, cerium sulfate, praseodymium sulfate and luteo chloride at the wave lengths 15, 30, 50, 75, 100, 130 and 170 meters.

High Frequency Conductance Measurements

The comparator-resonance method described in the first paper of this series[5] was employed for the measurement of the variation of conductance at the high frequencies. In order to ensure high precision the different members of the circuit were carefully calibrated as follows.

The precision condenser was calibrated by the substitution method in a heterodyne circuit for its absolute value in capacity at several different points. This condenser was calibrated twice for its linearity in capacity. The type R galvanometer was calibrated for its deflections on a circular scale by the ordinary differential direct current method. Known resistances were introduced in series with the galvanometer. From more than three hundred points over the whole range a smooth curve showing deviations from a linear relation between the current and the deflection was obtained. This curve gave the correction for the galvanometer deflections. The thermocouple in the measuring circuit and the Type R galvanometer connected to this thermocouple were calibrated for forty points on the galvanometer scale by reversing the several values of direct current through the heater of the thermocouple. This thermocouple was also calibrated in terms of microvolts in the Electrical Engineering Standards Laboratory of the University with the use of a White potentiometer. The thermocouple was twice again calibrated as located in the circuit, first with the White potentiometer and then with a microammeter. The procedure in each case was to reverse the direct current through the heater.

Careful physical measurements of size, length and position of wires in the circuit were made and independent determinations of ω, L and $\overline{C}$ showed that at resonance, $\omega L = 1/\omega\overline{C}$.

Audio Frequency Conductance Measurements

The conductance of the electrolytes at audio frequencies was determined by using the ordinary type of bridge arrangement. The measurements were accurate to 0.01% as shown by calibrations and results with standard solutions. The standard resistances were a set of Curtis-wound coils of resistance 100,000 to 1000 ohms and a dial box giving resistances from 1000 to 1 ohm. These resistances previously had been calibrated by the U. S. Bureau of Standards. Heavy connecting wire was used between members of the circuit. Careful shielding of leads was required. Two compensating condensers with capacity 3000 $\mu\mu F$ and 300 $\mu\mu F$ were used for balancing capacity in the different arms of the bridge. A Kohlrausch eleven-turn slide wire manufactured by the Leeds and Northrup Company was employed to obtain the balance point. The alternating current was furnished by a vacuum tube generator. A vacuum tube amplifier was used in the detection of the point of balance.

Design and Construction of Conductance Cells

In the selection of the conductance cells consideration had to be given to the magnitude of the resistance demanded at each of the several short wave lengths by the characteristics of the circuit. The range of values of resistance required for the highest sensitivity at each wave length was determined experimentally. Table I gives the approximate ranges at the wave lengths selected for measurements.

It has been demonstrated as well that these values are theoretically correct, using the other constants of the measuring circuit and the equation for the currents in the circuit. The ranges of the resistance for a particular wave length may be changed by variation of the characteristics of the circuit.

At the beginning of the work much attention was given to the construction and properties of the conductance cells.

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[5] Arnold and Williams, THIS JOURNAL, 58, 2613 (1936).

TABLE I

MAGNITUDE OF RESISTANCES FOR CHOSEN WAVE LENGTHS

Wave length meters	Approximate range of resistances, ohms.
170	25,000 to 75,000
130	25,000 to 75,000
100	25,000 to 100,000
75	25,000 to 65,000
50	5,000 to 20,000
30	2,500 to 7,500
15	400 to 1,600

The conductance of standard potassium chloride solutions at audio frequencies was studied in cells constructed with different kinds of glass and electrode material in a variety of shapes. Many irregularities of conductance were observed. Several important observations, later found mentioned in a publication by Jones and Bollinger,[6] were made in this preliminary work.

Many of the cells which are used for the determination of low frequency conductance are not suited at all for work at high frequencies because of arrangement of electrodes and of the proximity of mercury contact arms and filling tubes. The closeness of these arms introduces serious errors at high frequencies.

The cells finally designed for the high frequency measurements were similar to the one shown in Fig. 1. The exterior dimensions, especially with respect to electrode position and filling arms, were kept constant. This uniformity of construction was essential, first, in order that the cells would fit a standard clamp in the thermostat bath to give reproducible position from experiment to experiment, and second, in order that any capacitative effects between the electrode leads and filling arms, if not entirely eliminated, be reduced to a minimum and be nearly the same from cell to cell.

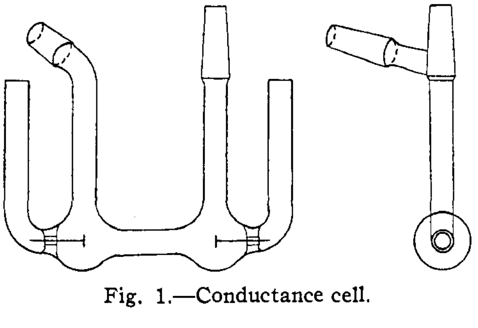

Fig. 1.—Conductance cell.

From conductance data found in standard tables, it was possible to compute the size and spacing of electrodes as well as the size of the body of a cell to be used with a given electrolyte at any of the wave lengths chosen. The cells were constructed with either Jena Geräte or Jena 16III glass. Bright platinum electrodes were employed throughout. Eight cells were so constructed.

Special seasoning of the cells was accomplished by a carefully controlled steam-bath in which the cell was first brought gradually up to the temperature of steam, after which a current of steam was forced through the cell for several hours, then the cell was caused to cool slowly. At times when the cells did not contain a solution they were kept soaking with high grade conductivity water.

Calibration of Cells.—For the determination of the ordinary cell constants a 0.01 demal solution of potassium chloride served as electrolyte. Conductance values of Parker and Parker[7] were used in these calibrations.[8] The cell constants given in Table II, obtained by means of two different standard solutions, show a maximum deviation from the average of less than one part in ten thousand except in the case of cell number eight.

Temperature Control.—A thermally insulated thermostat bath of 23 liters capacity was filled with light oil in order to avoid electrostatic disturbances common to a water-bath and to ensure as complete electrical insulation as possible for the measuring cell. The container was grounded further to reduce electrical disturbances. It was possible to maintain the temperature of the bath to 0.001 ° for a considerable length of time. The maximum deviation allowed for a measurement was 0.002 °.

Preparation and Purification of Materials.—One of the prime requisites of conductance measurements is that only pure materials be used since foreign substances are apt to give large errors from which indefinite or wrong conclusions will be drawn. This is especially true with the quantitative measurements of the small conductance effects at high frequencies. Since the frequency effect is a function of the valence of the ions involved, the presence, in small numbers, of foreign ions of the higher valence types would mask the effect of lower valence types.

Purification of Conductance Water.—The water was prepared by four or five distillations. Water, after having been distilled for general laboratory purposes, was distilled in a large block tin condenser. At the same time the steam and condensing liquid were washed by a stream of purified air. Only the middle portion of the distilled water was retained. The water was next distilled through a newly designed, all Pyrex, well-seasoned still which had a trap of direction reversing type and baffle domes for entrapping the spray. Glass dust shields protected the ground glass joints. Again only the middle portion of the water was retained. This water was then distilled in an all quartz distillation apparatus. The quartz condenser arm was air cooled. The receiver was always one of the transparent quartz flasks used in the work. The rate of distillation was maintained so that there was always an escape of steam which prevented foreign gases from diffusing back into the flask and which kept the distilled portion at nearly the boiling point. The first and last portions were always rejected. The process was sometimes repeated with the glass or quartz still. After cooling the water the quartz container was placed in a vacuum degassing tower and the evacuation was continued until the bubbling ceased. A stream of purified nitrogen was introduced into the chamber. The water, which was of exceptional quality, was found to depreciate readily in purity. Since considerable time was required to make the measurements it was decided to let the water "age" a part of a day before the solution was prepared. This procedure was followed in order that any unavoidable change of conduc-

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

[7] Parker and Parker, *ibid.*, **46**, 312 (1924).

[8] At the time the extensive and involved computations required by this work were made, the newer and more exact data of Jones and Bradshaw [*ibid.*, **55**, 1780 (1933)] were not available.

TABLE II

CELL CONSTANT DATA

Number of standard solution	Number of cell							
	1	2	3	4	5	6	7	8
2	0.043467	1.0582	0.57737	1.8265	11.498	1.1326	0.25371	8.3143
3	.043458	1.0583	.57726	1.8263	11.497	1.1323	.25371	8.3169
Av.	.043462	1.0583	.57731	1.8264	11.498	1.1324	.25371	8.3156

tance of solvent would take place before, rather than during, the measurements. The specific conductance of the aged water when used was in the vicinity of 0.360×10^{-6}.

Potassium Chloride.—The potassium chloride (Mallinckrodt, "Reagent Quality") was recrystallized four times from aqueous solutions made with the best grade of conductance water obtainable. The salt, after drying in an oven at 110° and after standing for considerable time in a closed container, was analyzed for moisture content. The salt contained 0.15% water as shown by three determinations with a maximum deviation of 0.01%. Correction was made on this basis when a standard potassium chloride solution was prepared.

Magnesium Sulfate.—The magnesium sulfate (Mallinckrodt "Reagent Quality") was further purified by recrystallizing four times from the best grade of boiled conductance water. The salt was slowly dried by placing it in a desiccator above sulfuric acid and phosphorus pentoxide and by passing a stream of purified nitrogen over it. Several sets of analyses were performed. The water content at the beginning was not constant. After the salt had stood over the pentoxide for a year an analysis was again made by the pyrophosphate method. With three determinations the average of a salt in a sample was 74.23% with a maximum deviation of 0.04%.

Lanthanum Iodate.—The lanthanum iodate was obtained through the generosity of Professor V. K. La Mer of Columbia University who furnished a sample of the purified $La(IO_3)_3$ used in a study with Goldman.[9] At the time of the measurements an analysis was made for the water content of the salt. Three determinations by the thiosulfate method gave an average of 97.40% lanthanum iodate with a maximum deviation of 0.1%. The analytical reagents were either of reagent quality or they were further purified.

Cerium Sulfate and Praseodymium Sulfate.—Samples of these salts were procured from our Division of Analytical Chemistry. Further purification of the salts was accomplished by repeated crystallizations of the salts from the best grade of conductance water. Saturated solutions of the cerium and praseodymium sulfates were prepared at 0° and then the temperature was elevated to 80° for the former and to 75° for the latter. About five-sixths of the praseodymium salt precipitated out each time, but the amount was somewhat less in the case of the cerium sulfate. The purified samples were dried carefully. Due to the small quantity of the purified salts chemical analyses were omitted and the determination of the concentrations used in the measurements was made by using conductance data given in the "International Critical Tables."

Barium Chloride.—The barium chloride (Mallinckrodt "Reagent Quality") was not purified further. However, an analysis of the usual kind for the determination of water of hydration was carried out. The average percentage of barium chloride in a sample was found to be 85.27% with a maximum variation between the three determinations of 0.05%.

Luteo Chloride.—The luteo chloride was a Kahlbaum preparation. Due to the small quantity available further purification or chemical analysis was not attempted.

Technique Used in Measurements

Preparation of Solutions.—The solutions were prepared by the volumetric method in a 500-ml. calibrated Pyrex flask which had been well-seasoned by continued soaking with conductance water. The conductance water was transferred from the quartz container in the nitrogen filled degassing chamber through a siphon into the volumetric flask, placed in another chamber which was filled with purified nitrogen gas. The sample of salt was weighed on an analytical balance which had been adjusted to a sensitivity of 0.01 mg. The same calibrated set of weights was used for all weighings throughout the experimental work. After the addition of the sample of salt to the water in the volumetric flask the latter was placed in the bath at 25.000 ± 0.002°. After temperature equilibrium had been reached the total volume was brought to the 500-ml. mark.

The Filling and Handling of Cells.—The cells were first rinsed repeatedly with the solution to be used and then filled by siphon in a chamber filled with purified nitrogen gas. Contamination of the dilute solutions with foreign gases was thus eliminated. The filled cells used in an experiment were placed in the thermostat and the audio frequency resistance of the solution in each cell was determined.

High Frequency Procedure.—To carry out the measurements at any one of the higher frequencies, the cell adapted to that particular wave length was placed in the special holder in the thermostat. The zero position of the galvanometer light beam was noted. After all parts of the high frequency circuits were adjusted to the predetermined settings for that wave length, the oscillator was started and the circuits tuned so that the maximum deflection at resonance was approximately 400.0 on the galvanometer scale. The generator was always started two or more hours before the experiment began so that stability of power output could be maintained in all of the high frequency circuits. Any lack of stability could be detected by the shift of the galvanometer light on the scale. All of the observations at the high frequencies were made after midnight in order to avoid as far as possible external electrical disturbances.

The galvanometer deflection and the precision condenser reading were recorded. The cell was then connected in parallel with the precision condenser and the galvanometer deflection and precision condenser setting at resonance were again noted and recorded. Four to ten consecutive sets of such readings were taken for a particular solution at each wave length. Besides the observations for the

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(9) La Mer and Goldman, THIS JOURNAL, 51, 2632 (1929).

solution, the same type of readings were made for two low inductive fixed resistances. The resistances were of the same order of magnitude as that for the cell with electrolyte. With any series of solutions these same fixed resistances were inserted repeatedly and observations were made at the time the solution was studied at that wave length. Thus these fixed resistances served as a check and reference for shift or disturbances from experiment to experiment. These fixed resistances were checked frequently by resistance determinations with the audio frequency bridge and were found to stay constant to well within 0.1%. It is imperative for such comparison measurements that the same cell be used for any particular wave length with a series of solutions.

Results

Conductance at Audio Frequency.—Although the determination of conductance at an audio frequency (1000 cycles), was not the chief object of the measurements being reported, it was part of the necessary procedure for each solution, since these data furnish a basis for reference. To illustrate the accuracy of these results data may be given for the reference potassium chloride solutions. For 0.005 normal potassium chloride the values of the observed molar conductance are 143.63 and 143.61 for two experiments as compared to Shedlovsky's[10] observed value 143.64 and his calculated value 143.65. For 0.002 normal potassium chloride in another experiment the observed value was 145.83 as compared to Shedlovsky's observed value 145.79 and calculated value 145.81.

Theoretical Values of High Frequency Change of Conductance.—In order to interpret the experimental observations it was necessary to calculate the changes in conductance of standard potassium chloride solutions at the different frequencies. It is assumed in the interpretation of the observations made with higher valence type salts that the small changes to which potassium chloride solutions are subject obey the Debye–Falkenhagen equation. This assumption has been made by other observers. The theoretical values were calculated for the other salts studied.

Because of the difficulty in adaptation and because of desire for greater accuracy the interpolation table given by Debye and Falkenhagen[2] for the ratio $\bar{\Lambda}_{I_\omega}/\Lambda_{I_0}$ at definite values of q and $\omega\theta$ was not used.

The predicted conductance changes were calculated by using an equation given in the introduction. In addition to certain universal constants ($T = 298$, $e = 4.770 \times 10^{-10}$, $D = 78.54$, $k = 1.371 \times 10^{-16}$), it was necessary to have figures for the limiting molar conductances, $\bar{\Lambda}_0$ of the several salts. The following figures were obtained from standard sources of reference: KCl, 149.82; $BaCl_2$, 282.13; $MgSO_4$, 267.0; $La(IO_3)_3$, 336.8; $Ce_2(SO_4)_3$, 953.9; $Pr_2(SO_4)_3$, 945.5; $Co(NH_3)_6Cl_3$, 540.0. The mobility of the luteo ion, $Co(NH_3)_6{}^{+++}$, is somewhat uncertain.[11] The value 104.6 for $^1/_3$ $Co(NH_3)_6{}^{+++}$ was deduced from conductance data given by Harkins, Hall and Roberts.

The experimental work was arranged in three series of experiments, as shown in Table III. Here are presented theoretical and experimental values for the increase of molar conductance $\bar{\Lambda}_{I_0} - \bar{\Lambda}_{I_\omega}$ of the different salts at the several high frequencies used in the measurements. Thus, these data indicate the amount by which the limiting molar conductance is changed due to changes in the electrical force of relaxation produced by the application of the fields of high frequency. It is also possible to obtain at once values for $\bar{\Lambda}_{I_\omega}$, and $\bar{\Lambda}_{I_\omega}/\bar{\Lambda}_{I_0}$ if it is desired to express the changes in this way.

Example of the Calculation of the Conductance from the Experimental Observations.—In order to illustrate the method by which the data of the foregoing tables have been obtained, the observations in the case of the 0.0006443 molar magnesium sulfate solution at 50 meter wave length are considered in detail. Galvanometer deflections with the cell in the circuit and with the cell out of the circuit are given in Table IV, Part A. Here the two columns at the right give the deflections corrected for the zero of the galvanometer as recorded in column two at the left. Part B of the same table gives average deflection values for the cell and fixed resistances.

In Part C are found the ratios of the galvanometer deflections with and without the cell or fixed resistance in the circuit for an experiment (14) with the standard potassium chloride solution and for an experiment (18) with the magnesium sulfate solution. The same cell and fixed resistances were used in both runs.

Any shift in the zero of the galvanometer after the beginning of the observations or any shift due to other disturbances from experiment to experiment should be detected through the ratios observed for the standard fixed resistances. Thus,

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(10) Shedlovsky, THIS JOURNAL, **54**, 1411 (1932).

(11) Harkins, Hall and Roberts, *ibid.*, **38**, 2643 (1916).

TABLE III

INCREASE OF MOLAR CONDUCTANCE WITH CHANGE OF FREQUENCY[a]

Wave length					170	130	100	75	50	30	15
Salt	Concn., molar	$\bar{\Lambda}_0$	$\bar{\Lambda}_{I_0}$		$\bar{\Lambda}_{I_0}-\bar{\Lambda}_{I\omega}$	$\bar{\Lambda}_{I_0}-\bar{\Lambda}_{I\omega}$	$\bar{\Lambda}_{I_0}-\bar{\Lambda}_{I\omega}$	$\bar{\Lambda}_{I_0}-\bar{\Lambda}_{I\omega}$	$\bar{\Lambda}_{I_0}-\bar{\Lambda}_{I\omega}$	$\bar{\Lambda}_{I_0}-\bar{\Lambda}_{I\omega}$	$\bar{\Lambda}_{I_0}-\bar{\Lambda}_{I\omega}$
First Series											
No. of cell used					8–5	8–5	8–5	8–5	5	4	6
KCl	0.00500	149.82	2.412	T	0.003	0.005	0.007	0.012	0.027	0.068	0.211
$BaCl_2$	.00280	282.13	10.522	T	.008	.012	.024	.044	.096	.253	.804
				E	.09	.07	...	...	...	...	.96
$MgSO_4$	.00387	267.0	30.248	T	.021	.031	.052	.083	.176	.475	1.611
				E	.051	.035	...	...	...	.72	...
Second Series											
No. of cell used					5	5	5	5	4	6	7
KCl	0.00200	149.82	1.524	T	0.009	0.016	0.026	0.043	0.086	0.181	0.377
KCl	.00197	149.82	1.513	T	.010	.016	.026	.045	.087	.182	.379
$BaCl_2$	.00112	282.13	6.653	T	.033	.056	.094	.163	.325	.696	1.502
				E	.19	.03	...	.54	...	...	1.67
$MgSO_4$	.00155	267.0	19.132	T	.065	.105	.176	.301	.627	1.450	3.488
				E	.06	.45	.51	.52	...	...	3.65
Third Series											
No. of cell used					5	5	5	5	4	7	7
KCl	0.000985	149.82	1.070	T	0.025	0.040	0.062	0.096	0.161	0.268	0.432
KCl	.00100	149.82	1.079	T	.025	.039	.061	.094	.159	.267	.431
$BaCl_2$	.000561	282.13	4.708	T	.090	.147	.230	.360	.620	1.061	1.762
				E	.20	.41	.18	.54	.73	1.01	1.70
$MgSO_4$	.000774	267.0	13.528	T	.166	.277	.448	.721	1.326	2.466	4.443
				E	...	.27	.62	1.08	1.54	2.41	...
$MgSO_4$	.000644	267.0	12.340	T	.219	.354	.556	.881	1.542	2.696	4.554
				E	...	.19	.40	.46	1.91	2.43	4.88
$La(IO_3)_3$	.000445	336.8	10.726	T	.231	.373	.580	.888	1.512	2.546	4.156
				E	.18	.56	...	.78	2.25	2.56	5.52
$Ce_2(SO_4)_3$	.000366	953.9	93.448	T	.428	.725	1.153	2.010	4.053	8.896	19.868
				E	.60	.38	1.01	1.47	3.47	8.96	18.85
$Pr_2(SO_4)_3$	.000366	945.5	92.522	T	.392	.719	1.143	1.992	4.050	8.883	19.857
				E	..	.65	1.54	1.85	3.88	9.75	20.33
$Co(NH_3)_6Cl_3$	.000253	540.0	12.211	T	.299	.476	0.731	1.123	1.864	3.065	4.890
				E	.44	.83	0.51	1.78	...	5.49	6.04

[a] T indicates theoretical value; E indicates experimental value.

this added information obtained by using the fixed resistances R18 and R17 made it possible to correct the magnesium sulfate values for any deviation or shift taking place during an experiment. Part D of Table IV shows the ratios of the fixed resistances referred to the values obtained in experiment 14 as standard. The average ratio 1.0027 is the factor by which the magnesium sulfate ratio is corrected to 0.5303. It is to be regarded as a coincidence that the thermocouple correction exactly cancels the adjustment in opposite sense for the galvanometer. The thermocouple correction is determined from calibration curves in which the square of the current through the thermocouple heater is plotted as a function of the galvanometer deflection. The next step is to evaluate these current ratios for the two solutions in terms of the relative ohmic resistances. The relative values of resistance are obtained from the relation[5]

$$\frac{I_2^2}{I_1^2} = \frac{\bar{r}_1^2}{\left(r_2 + \dfrac{R}{1 + \omega^2C^2R^2}\right)^2} = \frac{kD_2}{kD_1}$$

From the portion of the interpolation table which forms Part E of Table IV, the ratios for potassium chloride and magnesium sulfate (Part D) are identified with the relative resistances 12,792 and 12,504, respectively. By using the theory of Debye and Falkenhagen the actual resistance in the cell at 50 meters for the potassium chloride solution is calculated to be 13,422 ohms. By direct proportion, using this ohmic resistance

TABLE IV

INTERPRETATION OF EXPERIMENTAL OBSERVATIONS

Part A

No. of cell or R placed in circuit	Zero of galv.	Deflection of galv. without R or cell corrected for zero	Deflection of galv. with cell or R corrected for zero
C4	0.6	402.0	212.4
		401.4	212.4
		401.4	212.4
R18	.6	401.4	242.9
		401.2	242.8
		400.2	242.4
R17	.6	400.2	243.6
		400.2	243.6

Part B

Av. defl. of galv. without cell	Av. defl. of galv. with cell	Av. defl. of galv. without R18	Av. defl. of galv. with R18	Av. defl. of galv. without R17	Av. defl. of galv. with R17
401.6	212.4	400.9	242.7	400.2	243.6

Part C

No. of expt.	Cell solution	Ratio of galv. defl. conductance cell	Ratio of galv. defl. resistance R18	Ratio of galv. defl. resistance R17
18	$MgSO_4$	0.5289	0.6053	0.6087
14	KCl	.5367	.6071	.6101

Part D

No. of expt.	Salt	Ratio with R18	Ratio with R17	Av.	Ratio with conductance cell
14	KCl	1.0000	1.0000	1.0000	0.5367
18	$MgSO_4$	1.0030	1.0023	1.0027	.5303

Part E

R	R^2	$\omega^2C^2R^2$	$\frac{R}{1+\omega^2C^2R^2}$	$\left(r_2+\frac{R}{1+\omega^2\bar{C}^2R^2}\right)$	$\left(r_2+\frac{R}{1+\omega^2\bar{C}^2R^2}\right)^2$	$\frac{kD_2}{kD_1}$
12,500	156.25 × 10^6	6396.1	1.9540	7.3445	53.942	0.5302
12,525	156.88	6421.7	1.9501	7.3406	53.884	.5308
....	....	....	....	....	....	...
12,775	163.20	6680.6	1.9120	7.3025	53.327	.5363
12,800	163.84	6706.8	1.9082	7.2987	53.271	.5369

for the potassium chloride solution and the two relative values given in the table, the actual ohmic resistance for the magnesium sulfate solution is calculated to be 13,120 ohms. But the resistance of the magnesium sulfate solution in the same cell at the audio frequency was 13,235 ohms, therefore an increase in conductance has been observed. Interpreted in terms of molar conductance the quantities $\bar{\Lambda}_0$ and $\bar{\Lambda}_\omega$ are found to be 225.62 and 227.53, respectively. Then

$$\bar{\Lambda}_\omega - \bar{\Lambda}_0 = \bar{\Lambda}_{I_0} - \bar{\Lambda}_{I\omega} = 1.91$$

The theoretical value of $\bar{\Lambda}_{I_0}$ is 12.34. Thus $\bar{\Lambda}_{I_\omega} = 12.34 - 1.91 = 10.43$. If the data for a given solution are referred to figures for several standard potassium chloride solutions the above procedure must be repeated.

Discussion

Since the appearance, in 1928, of the quantitative theory describing the dispersion of electrical conductance for dilute solutions of strong electrolytes there have been published the results of a number of experimental researches intended to test the validity of the theory. Reference may be made to important contributions in this field by Sack,(12) Zahn,(13) Rieckhoff,(14) Brendel,(15) Deubner,(16) M. Wien,(17) Malsch,(18) Gärtner,(19) and others. In some cases it was possible to measure only the order of magnitude of the conductance increase at a single high frequency, in others

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(12) Sack, *Physik. Z.*, **29**, 627 (1928).

(13) Zahn, *Z. Physik*, **51**, 350 (1928).

(14) Rieckhoff and Zahn, *ibid.*, **53**, 619 (1929); Rieckhoff, *Ann. Physik*, [5] **2**, 577 (1929).

(15) Brendel, Mittelstädt and Sack, *Physik. Z.*, **30**, 576 (1929); Brendel and Sack, *ibid.*, **31**, 345 (1930); Brendel, *ibid.* **32**, 327 (1930).

(16) Deubner, *ibid.*, **30**, 946 (1929); **33**, 223 (1932); *Ann. Physik*, [5] **5**, 305 (1930).

(17) Wien, *Physik. Z.*, **31**, 793 (1930); *Ann. Physik*, [5] **11**, 429 (1931).

(18) Malsch, *Physik. Z.*, **33**, 19 (1932); *Ann. Physik*, [5] **12**, 865 (1932).

(19) Gärtner, *Physik. Z.*, **32**, 919 (1931).

complications served to render difficult any interpretation in terms of the theory, but in the main the results of these studies have been consistent with the requirements of the theory.

It has been our plan to make, in extremely dilute aqueous solutions of strong electrolytes, a more systematic study of the theory than has hitherto been attempted. Thus, instead of confining our attention to observations of the behavior of the solutions at one, or at most, several wave lengths, we have sought to make the measurements over a considerable frequency range. Again, we have been interested in a comparison of the magnitude of the conductance increase for electrolytes of as many different valence types and ion sizes as conveniently possible. To a lesser extent we have been able to study the effect of concentration changes in the solution of some of the salts. The results of the experimental work are compared with the requirements of the theory in Table III.

It is at once evident that the agreement between theory and the results of our experiments at each of the seven wave lengths is as good as can be expected when the difficult nature of the measurements is considered. The influence of variation in the valence type of the dissolved salt in changing the values of $\bar{\Lambda}_{I_0} - \bar{\Lambda}_{I_\omega}$ in the dilute solutions is consistent with the requirements of the theory. Thus, at any one wave length, barium chloride solutions show much less actual increase in conductance than do solutions of salts of higher valence types. The lanthanum iodate and luteo chloride solutions (3–1 valence type) show more significant increases and, when the relative concentration is taken into consideration, the magnesium sulfate solutions (2–2 valence type) show an even greater dispersion. The increased conductance is so pronounced in the case of the cerium sulfate and praseodymium sulfate in solution (3–2 valence type) that it can be measured with a very considerable degree of accuracy.

The measurements are much less complete as regards the effect of concentration change, but again, insofar as our experiments extend, this influence is entirely consistent with the predictions and requirements of the dispersion theory. The data for barium chloride and magnesium sulfate solutions are the only ones which are now involved. The change of conductance with frequency is very small at the higher concentrations in the wave length region in which these studies were made. The theory predicts that in order to observe large changes of conductance at the higher concentrations it will be necessary to measure the effects at much higher frequencies than were available to us. However, this shift of the critical frequency range toward the shorter wave lengths is indicated clearly by the experimental data for both barium chloride and magnesium sulfate solutions, with the more pronounced increases in conductance being observed in the solutions of lower concentration. For the study of the effect of changes in concentration measurements of Wien[17] with magnesium sulfate and barium ferricyanide solutions at 10, 20 and 40 meters are especially deserving of mention.

The significance of experiments of the type made by us now can be suggested. In the interionic attraction theories the fundamental idea is that the ions cannot be distributed at random in a solution, since, owing to the coulomb forces, there must be an excess of positive ions in the neighborhood of a negative ion and *vice versa*. Thus each ion is considered to be surrounded by a symmetrical ionic atmosphere with distribution of charge depending upon the square root of the concentration. It order to explain the ordinary conductance behavior of an electrolyte solution the number of the ions and their mobilities must be considered. The interionic attraction theory describes the effect of the electrical forces on the ionic mobilities by assuming the ionic atmosphere to have a definite time of formation and relaxation. On the basis of this assumption, if a constant current passes through such a solution the average distribution of ions is changed and the ionic atmosphere loses its central symmetry, but if a high frequency voltage, with time necessary for one vibration comparable to the time of relaxation, is applied, the dissymmetry of the atmosphere is greatly reduced and a conductance larger than that measured at ordinary low frequencies ought to result. If the experimentally observed conductances show satisfactory agreement with the requirements of the dispersion theory, as they do in the cases investigated by us, it can be claimed that the existence of such an atmosphere about each ion with finite time of relaxation, is definitely proved.

According to the theory the time of relaxation of the atmosphere (which is responsible for the dispersion effect) depends only on the mobilities of the ions and the forces between them. Thus, only the valence of the ions, the viscosity and dielectric constant of the solvent, and certain other physical factors are involved. If we wish to investigate whether or not in an ionic solution the chemical nature of the solvent and the affinities of ions play an important role, experiments of the type described above in which these factors are varied can give valuable information. In the experiments here reported a nearly ideal ionic behavior is observed, but it is probably accounted for because only extremely dilute aqueous solutions were considered. But even if the chemical nature of the solvent and the affinities of the ions are predominant factors, such experiments as these are still of significance because they explain and predict the behavior of ideal electrolytes and make possible a measure of the deviations from ideality in the actual solution.

Summary

1. A quantitative experimental study of the dispersions of the electrical conductance for strong electrolytes of several valence types in extremely dilute aqueous solutions has been made. The conductance of these solutions was observed at frequencies corresponding to the seven wave lengths, 15, 30, 50, 75, 100, 130 and 170 meters. In addition, observations were made at the frequency 1000 cycles.

2. The results of the experiments have been compared with the requirements of the dispersion theory. They are found to be in satisfactory quantitative agreement, indicating once more that in all probability the purely physical interionic attraction theory does adequately explain and describe the behavior of an ideal electrolyte.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

The Thermodynamics of Cadmium Chloride in Aqueous Solution from Electromotive Force Measurements[1]

BY HERBERT S. HARNED AND MARGARET E. FITZGERALD

Measurements of the electromotive forces of the cell

$$\mathrm{Cd{-}Cd_xHg}\ (11\%)\ |\ \mathrm{CdCl_2}(m)\ |\ \mathrm{AgCl{-}Ag} \qquad (1)$$

have been made at 5° intervals from 0 to 40°, inclusive, and throughout a cadmium chloride concentration range of 0.0005 to 1 *M*. From the results, the standard potential of the cell, E_0, the activity coefficients and other thermodynamic properties of cadmium chloride have been computed.

Experimental Procedure

The silver–silver chloride electrodes of the kind designated by Harned[2] as type (2) were used. The cadmium amalgam was prepared from pure redistilled Kahlbaum cadmium and distilled mercury. The amalgam electrodes containing 11% of total cadmium were made individually in each cell vessel.

Mercury and an excess of cadmium were introduced in a suitable glass vessel which was then evacuated. This mixture was placed in a water-bath at 60° for fifteen minutes, and was shaken frequently. The saturated amalgam formed in this manner was allowed to flow through a sealed tube into the amalgam electrode compartments of four cells where it covered the sealed in platinum wires which made contact with the external leads. Since this operation was carried out *in vacuo*, the amalgam was free of oxide. In the case of cells containing dilute solutions ($m < 0.05$ *M*) the silver chloride electrode was immersed in the same compartment as the amalgam. On the other hand, with higher concentrations of solution the life of the cell was found to be considerably increased by separating the electrode compartments by means of a tube and a stopcock which was closed at times when actual measurements were not in progress.

A standard concentrated stock solution was made from a high-grade carefully purified cadmium chloride and conductivity water. Its strength was found by gravimetric determination of its chloride content. More dilute solutions were prepared by adding weighed amounts of the standard solution to water. The cell solu-

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(1) This communication contains material from a Dissertation presented to the Graduate Faculty of Yale University in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1936.

(2) Harned, THIS JOURNAL, 51, 416 (1929).