Summary

1. The density of ammonia at two-thirds and one-third of an atmosphere has been determined and found to be 0.51161 (±0.00001) and 0.25458 (±0.00001).

2. The gas density method for the determination of atomic weights has been discussed.

3. The gas constant, R, and the limiting molal volume, v_0, have been computed by means of linear and quadratic equations of state developed on the basis of density data for ammonia as determined by the authors and by Moles and Batuecas.

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Properties of Electrolytic Solutions. I. Conductance as Influenced by the Dielectric Constant of the Solvent Medium[1]

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I. Introduction

While solutions of electrolytes in solvents of high and of intermediate dielectric constant have been studied extensively, similar solutions in solvents of very low dielectric constant have not been investigated systematically. We know only that such solutions generally are poor conductors and that the equivalent conductance falls rapidly with decreasing concentration.

In addition to a number of isolated observations on the conductance of solutions in benzene,[3] and several series of measurements relating to the conductance of complex compounds in various solvents at relatively high concentrations,[4] the literature includes two important papers by Walden and his co-workers, who investigated[5] the conductance of a variety of *salts* in benzene, ether, carbon tetrachloride and similar solvents. According to Walden's measurements, the equivalent conductance of solu-

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(1) This paper comprises a part of the subject matter of a thesis submitted by Raymond M. Fuoss in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the Graduate School of Brown University.

(2) Jesse Metcalf Fellow in Chemistry in Brown University, 1931–1932.

(3) Kablukov, *Z. physik. Chem.*, **4**, 430 (1889), hydrogen chloride in ether and in benzene; Cady and Lichtenwalter, THIS JOURNAL, **35**, 1434 (1913); Cady and Baldwin, *ibid.*, **43**, 646 (1921), heavy metal soaps in benzene; La Mer and Downes, *ibid.*, **53**, 888 (1931), conductimetric titrations in benzene; Hill, *ibid.*, **44**, 1164 (1922), silver perchlorate in benzene.

(4) Complexes in ether, Plotnikov, *Z. physik. Chem.*, **57**, 502 (1906); Ussanowitsch, *ibid.*, **124**, 427 (1926); Bruns, *Z. anorg. allgem. Chem.*, **163**, 120 (1927); complexes in bromine, Plotnikov, *Z. physik. Chem.*, **116**, 111 (1925); Finkelstein, *ibid.*, **121**, 46 (1926); Plotnikov and Jakubson, *ibid.*, **138**, 235 (1928); Plotnikov and Kudra, *ibid.*, **145**, 625 (1929); complexes in toluene, xylene, and benzene, Plotnikov and Jakubson, *ibid.*, **147**, 227 (1930); Jakubson, *ibid.*, **118**, 31 (1925); Rabinowitch, *ibid*, **132**, 83 (1928).

(5) Walden, *Bull. Acad. Imp. Sci. St. Pet.*, **7**, 934 (1913); Walden, *Z. physik. Chem.*, **147**, 1 (1930).

tions of quaternary ammonium salts in benzene falls off sharply with increasing concentration over the concentration range studied, namely, 0.1–0.03 *N*. In solvents of somewhat higher dielectric constant, the conductance passes through a minimum at moderate concentration and thereafter increases.

It is uncertain whether or not the equivalent conductance of electrolytes in benzene and similar solvents continues to fall indefinitely as the concentration decreases; the laws governing the conductance phenomenon in solvents of low dielectric constant are yet to be established. While the influence of the dielectric constant on conductance is satisfactorily accounted for by the interionic attraction theory in solvents of high dielectric constant, it is not known to what extent interionic forces are primarily concerned in solvents of low dielectric constant. Nor is it known to what extent a mass action effect may be involved. The present investigation was undertaken in order to obtain experimental information bearing on these questions.

Benzene and dioxane $\left(\overline{\mathrm{CH_2CH_2OCH_2CH_2O}}\right)$ were chosen as solvents of very low dielectric constant. Solvents of any desired higher dielectric constant were obtained by adding solvents of high dielectric constant in proper proportion. For this purpose, water and ethylene dichloride were used. The conductance phenomenon has thus been studied in mixtures of dioxane and water over a dielectric constant range from 2.2 to 79 and in mixtures of ethylene dichloride with dioxane and with benzene over the range from 2.2 to 10.4.

Tetraisoamylammonium nitrate and thiocyanate and tri-isoamylammonium picrate were employed as electrolytes; the first two are strong electrolytes, while the last is a relatively weak electrolyte. The conductances in the various pure and mixed solvents were determined over the (approximate) concentration range 0.00001–0.2 *N*, which was sufficient to establish the general characteristics of the conductance curves.

Because of the very low conductance of the more dilute solutions in solvents of low dielectric constant, the resistances were measured by means of a direct current galvanometric method. While the precision of this method is only approximately 1%, the results obtained with it are reliable within this limit as was shown by checking against results obtained by the usual alternating current method.

II. Materials

Tetraisoamylammonium Salts.—The iodide is best prepared as follows. An equivalent mixture of tri-isoamylamine and isoamyl iodide is introduced into a long tube which is then heated near the top to about 150°. As crystals of the salt form, they fall to the cooler region at the bottom, thus avoiding much of the decomposition which occurs if the salt is heated to higher temperature for an appreciable length of time. The product is washed with petroleum ether, and treated with potassium hydroxide in alcoholic solution to decompose any tertiary salt that may have formed during the heating. The salt is then precipitated by pouring the solution into water. After washing and drying, and rewashing with petroleum ether, a product is obtained which melts at 115°. This material, after several recrystallizations from a mixture of *anhydrous* ethyl acetate and petroleum ether, yielded a product melting at 136°.

Anal. Subs., 0.3499, 0.4051, 0.4530: AgI, 0.1933, 0.2240, 0.2498. Calcd. for $(C_5H_{11})_4NI$: I, 29.85. Found: 29.87, 29.88, 29.81, av., 29.86.

Tetraisoamylammonium nitrate was prepared by treating the iodide with an exact equivalent of silver nitrate in alcoholic solution. After filtering out the silver iodide, the solution was allowed to evaporate at room temperature, and the product was recrystallized from a mixture of anhydrous ethyl acetate and petroleum ether.

Tetraisoamylammonium thiocyanate was prepared by dissolving the nitrate in *absolute* alcohol and adding an exact equivalent of an analyzed solution of potassium thiocyanate in absolute alcohol. After filtering and evaporating the solution, the salt was recrystallized from anhydrous ethyl acetate and petroleum ether.

Anal. Subs., 0.8857, 0.5031: AgSCN, 0.4158, 0.2350. Calcd. for $(C_5H_{11})NSCN$: SCN, 16.29. Found: 16.42, 16.34.

In the first analysis, the silver nitrate was dissolved in water; in the second, the precipitation and first washing were carried out with alcohol. Since tetraisoamylammonium thiocyanate is only sparingly soluble in water, co-precipitation of the quaternary salt apparently occurred.

It may be mentioned that the iodide is only sparingly soluble in water, the bromide may be recrystallized from water, while the chloride is extremely soluble and is very hygroscopic.

Tri-isoamylammonium picrate was prepared by adding a saturated hot alcoholic solution of picric acid to a slight excess of tri-isoamylamine. The crude product, which crystallizes from the alcohol almost completely on cooling, was recrystallized from ethylene dichloride and petroleum ether.

Dioxane was purified according to Vingee's method.[6] The technical product was cooked with caustic soda, dried over barium oxide, and subsequently distilled fractionally from sodium–lead alloy (NaPb). The middle fraction (about 90% of the total) was dissolved in liquid ammonia and treated with metallic sodium to remove various reducible impurities.[7] After boiling off the ammonia, the dioxane was redistilled and stored over sodium–lead alloy in a still from which it could be distilled directly into the conductance cells; m. p. 11.7°.

Benzene.—Thiophene-free benzene was washed with concentrated sulfuric acid, water, dilute potassium hydroxide solution and water. After drying, it was fractionally crystallized and stored in a still similar to the one used for dioxane; m. p. 5.43°.

Ethylene dichloride was distilled from phosphorus pentoxide. The middle fraction was stored over phosphorus pentoxide in one of the supply stills; b. p. 82.4° at 747 mm.

III. Apparatus and Method

Electrical Equipment.—Resistances up to 100,000 ohms were measured by the alternating current method. The apparatus was of the conventional type, comprising a drum wound bridge, a Vreeland oscillator, a set of Curtis resistance coils up to 100,000 ohms, condensers for balancing out capacity effects, a two-stage amplifier and telephones.

Higher resistances were measured by a direct current method, which essentially

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(6) Vingee, Thesis, Brown University, 1931.

(7) According to a later procedure of Vingee, the impurities are removed by boiling the dioxane with metallic sodium, after previous treatment with sodium hydroxide and desiccation with barium oxide. This procedure is much more convenient than the treatment in ammonia.

amounted to using a galvanometer as ammeter, and computing the cell resistance by Ohm's law from the current so determined and the voltage applied to the conductance cells. Two galvanometers were used. The first (G_1) had a resistance of 15.6 ohms and a sensitivity of 3×10^{-8} amp./cm., the second (G_2) had a resistance of 913 ohms and a sensitivity of 4×10^{-10} amp./cm. The galvanometers were mounted on Julius suspensions, and covered with copper shields having windows opposite the mirrors. The sensitivity of the galvanometers was determined at frequent intervals during each experiment. By means of a suitable resistance in series and shunt with the galvanometers, any input current from 10^{-4} to 10^{-8} amperes could be adjusted to give full scale deflection (25 cm.).

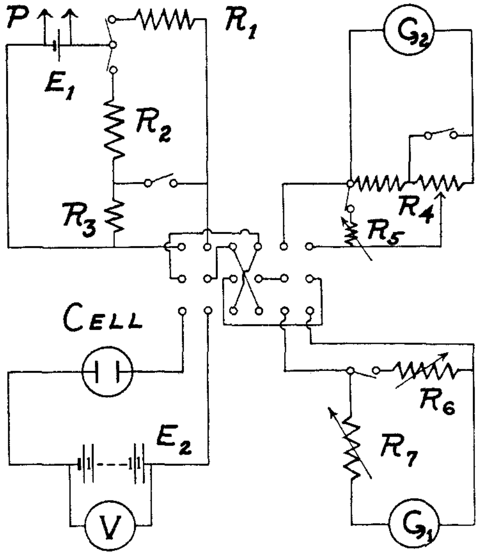

Fig. 1.—Direct current equipment: G_1, 15.6-ohm galvanometer; G_2, 913-ohm galvanometer; R_5, R_6, R_7, 0–10,000-ohm variable resistances; R_4, 1–100,000-ohm Ayrton shunt; E_1, 1.5-volt dry cell; P, potentiometer leads; R_1, 1,000,000 ohms; R_2, 10,000 ohms; R_3, 1 ohm; E_2, 150-volt storage battery; V, Weston voltmeter.

The d. c. circuit is shown in Fig. 1. Two 0–10,000 ohm resistances R_6 and R_7 were used to control the sensitivity of galvanometer G_1. An Ayrton shunt R_4 (1–100,000 ohms) was used with the high sensitivity galvanometer G_2; an auxiliary shunt R_5 (0–10,000 ohms) and a shorting switch for half of the Ayrton coil gave intermediate steps between the ten-fold sensitivity changes obtained by R_4 alone. The calibrating circuit included a dry cell E_1, potentiometer (leads) P and resistances R_1 (1,000,000 ohms), R_2 (10,000 ohms) and R_3 (1 ohm). All resistances were calibrated to 0.1%.

The reversing switch permits the average of right and left swings to be taken and avoids zero point correction as well as permanent distortion of the galvanometer suspension due to repeated full deflection in one direction. The galvanometer deflections could be read to 0.3 mm., but were not reproducible to less than 1 mm. (out of the total deflection of 250 mm.), probably due to stray currents of various kinds in the control resistances. These were reduced to a minimum by keeping the total resistance of the galvanometer circuit as high as conveniently possible. One centimeter deflection on the 913-ohm galvanometer corresponded to a resistance of 4×10^{11} ohms, and a conductance of 5×10^{-14} mhos (for a cell with a constant equal to 0.02 and using 150 volts).

The source of current was a battery of 72 lead storage cells which were used when the e. m. f. was on the flat part of the discharge curve. The errors due to internal resistance of the battery and to polarization of the conductance cell (that is, in assuming that the voltage read on the Weston voltmeter *V* was the e. m. f. producing the current measured on the galvanometers) were determined and found to be less than one per cent., provided at least 150 volts were used. All lead wires were insulated by means of paraffined glass tubes, and the thermostat liquid in which the conductance cell was placed was a good grade of high flash petroleum oil. Practically no error was introduced by faulty insulation; the leakage corresponded to 1–3 mm. on the high sensitivity galvanometer in the most unfavorable cases, and was considered in the corrections.

The results of the alternating and direct current methods of measurement were compared directly for resistances of the order of 100,000 ohms. Lower resistances could not be measured with the d. c. method on account of the relatively high currents, while higher resistances could not be measured with the a. c. method without unbalancing the bridge. Indirect comparisons of the two methods were obtained, however, by measuring the ratio of the cell constants of several cells, first at low resistances (1000–10,000 ohms) by the a. c. method and second at high resistances (1–10 megohms) by the d. c. method. The a. c. and d. c. results agreed within 1% for both direct and indirect comparison.

Conductance Cells and Accessories.—The cells were constructed from Pyrex Erlenmeyer flasks by sealing side bulbs containing electrodes to the bottoms of the flasks. Long (20 × 0.8 cm.) necks with ground-glass stoppers were attached to the flasks in order to minimize the diffusion of moisture into the cells during introduction of solution. The necks were ground to fit the delivery tubes from the various solvent stills. The electrodes were lightly platinized; heavy platinization caused considerable adsorption in dilute solutions, while bright electrodes failed to give steady d. c. resistances. The cells were calibrated by comparing them against each other and against a specially constructed calibration cell whose constant was determined, using Parker's[8] data for 0.1 demal potassium chloride solution. The cell constants are given in Table I.

TABLE I

CELL CONSTANTS

Cell	Determined constant			Average
Calibration	21.626	21.635[a]		21.63
125 cc.	0.17790	0.17780	0.17769	0.1777
250 cc. (first)	.02544	.02552		.02548
250 cc. (second)	.015624	.015649		.01564
500 cc.	.19378	.19369	.19369	.1937

[a] Two separately prepared KCl solutions.

The purified solvents were stored in 3-liter Pyrex flasks, to which were sealed reflux columns and condensers. To the delivery tube of each condenser was sealed a 30-cc. bulb containing electrodes (cell constants 0.02 to 0.03), which permitted control of the specific conductance of the solvent as distilled and before admitting it to the conductance cell. Siphons from the test bulbs were provided with ground-glass joints which fitted the necks of the cells. The best figures for solvent conductance were as follows: dioxane, 5×10^{-15}; benzene, $< 3 \times 10^{-15}$; ethylene dichloride, 3×10^{-10} mhos. In each experiment, the solvent conductance was determined before adding solute and was subtracted from the observed conductance if the correction exceeded 0.5%. The cells were immersed in a thermostat kept at 25.00 ± 0.02°. When room temperature was under 25°, the necks of the cells were kept at about 35° by an electrically heated cap in order to prevent solvent from distilling into the necks. Precautions were taken to keep the glassware dry.

Method.—After making up solutions in different ways and comparing the results in order to locate and avoid any systematic errors in determining concentration, the following method was adopted. Solvent was distilled into one of the larger cells and a small portion of this was pumped by dry air pressure onto a weighed quantity of salt, in the small cell. The amount of solvent in each cell was determined by weighing. After diluting several times, the final solution (A) in the small cell was pumped into a weight buret, and increasing portions of this solution were weighed into the solvent in the first cell. For very dilute solutions, about one gram of solution (A) was weighed

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[8] Parker and Parker, THIS JOURNAL, **46**, 332 (1924).

from a pycnometer into about 60 g. of solvent in a weight buret, and this was, in turn, weighed into the first cell in six to eight portions before starting to weigh in the remainder of solution (A).

Specific gravities were determined by means of a Westphal balance, and normalities were computed from the known weight concentrations.

IV. Results

The experimental results are summarized in Tables II–XI, where c is concentration in equivalents of solute per liter of solution, and Λ is equivalent conductance. The values given in these tables were obtained by interpolation (and occasional extrapolation over a small distance) of the actual results on a large-scale log Λ–log c plot. The round concentrations chosen correspond to approximately equal steps on a log c scale, spaced at about the same ratio as the experimental dilution ratio. There are, of course, certain disadvantages in reporting only interpolated values, particularly when the interpolation function is arbitrary and *not* monotonic, but compact presentation of the large number (about fifty series of conductance measurements) of determinations could not otherwise have been achieved. For discussion and comparison, the conductance curves for the various systems investigated are shown in Figs. 2–5, where the open circles represent the *observed* values.

The conductance values for tetraisoamylammonium nitrate in dioxane are given in Table II and are shown graphically in Fig. 2 where log Λ is plotted against log c. Nine series of measurements were made in order to test the reproducibility of the results and the reliability of the methods. In the first three series covering the dilute region, the conductance at concentrations below 10^{-4} was somewhat erratic; this appeared to be due to impurities in the solvent, because the solvent conductance was about 4×10^{-13}. After re-treating the dioxane with sodium in liquid ammonia, and refluxing for about twenty hours over sodium–lead alloy, the solvent conductance was reduced to less than 2×10^{-14}. Measurements made in the dilute region with the re-treated dioxane gave consistent results. The conductance curve exhibited an unexpected complexity in structure,

TABLE II

TETRAISOAMYLAMMONIUM NITRATE IN DIOXANE

c	Λ	c	Λ	c	Λ
0.0_410	0.0_431	0.0_350	0.0_3129	0.015	0.0_3832
$.0_415$	$.0_428$	$.0_370$	$.0_3162$	$.020$	$.0_2125$
$.0_420$	$.0_427$	$.0_210$	$.0_3193$	$.030$	$.0_2261$
$.0_430$	$.0_427$	$.0_215$	$.0_3231$	$.050$	$.0_2958$
$.0_450$	$.0_430$	$.0_220$	$.0_3259$	$.070$	$.0204$
$.0_470$	$.0_434$	$.0_230$	$.0_3306$	$.100$	$.0367$
$.0_310$	$.0_4414$	$.0_250$	$.0_3376$	$.150$	$.0596$
$.0_315$	$.0_4526$	$.0_270$	$.0_3452$	$.200$	$.0768$
$.0_320$	$.0_4635$	$.010$	$.0_3569$	$.300$	$.1005$
$.0_330$	$.0_4861$				

but repeated determinations with different cells and with different methods of changing concentration were in agreement. Later, a similar structure,

TABLE III

TETRAISOAMYLAMMONIUM NITRATE IN DIOXANE–WATER MIXTURES

H$_2$O, % *c*	0.034 Λ	0.112 Λ	0.343 Λ	0.602 Λ	2.35 Λ
$0.0_{4}10$	$0.0_{4}30$	$0.0_{4}34$	.....	$0.0_{3}150$	0.0102
$.0_{4}15$	$.0_{4}29$	$.0_{4}33$	.....	$.0_{3}133$	$.0_{2}852$
$.0_{4}20$	$.0_{4}28$	$.0_{4}33$	$0.0_{4}61$	$.0_{3}124$	$.0_{2}745$
$.0_{4}30$	$.0_{4}29$	$.0_{4}34$	$.0_{4}60$	$.0_{3}115$	$.0_{2}618$
$.0_{4}50$	$.0_{4}33$	$.0_{4}38$	$.0_{4}60$	$.0_{3}108$	$.0_{2}496$
$.0_{4}70$	$.0_{4}37$	$.0_{4}42$	$.0_{4}62$	$.0_{3}107$	$.0_{2}431$
$.0_{3}10$	$.0_{4}442$	$.0_{4}485$	$.0_{4}670$	$.0_{3}108$	$.0_{2}374$
$.0_{3}15$	$.0_{4}560$	$.0_{4}598$	$.0_{4}761$	$.0_{3}114$	$.0_{2}322$
$.0_{3}20$	$.0_{4}676$	$.0_{4}708$	$.0_{4}863$	$.0_{3}123$	$.0_{2}292$
$.0_{3}30$	$.0_{4}902$	$.0_{4}930$	$.0_{3}109$	$.0_{3}143$	$.0_{2}261$
$.0_{3}50$	$.0_{3}132$	$.0_{3}138$	$.0_{3}156$	$.0_{3}188$	$.0_{2}231$
$.0_{3}70$	$.0_{3}166$	$.0_{3}176$	$.0_{3}202$	$.0_{3}243$	$.0_{2}224$
$.0_{2}10$	$.0_{3}204$	$.0_{3}225$	$.0_{3}272$	....	$.0_{2}227$
$.0_{2}15$	$.0_{3}247$	....	$.0_{3}380$	....	....
$.0_{2}20$	$.0_{3}279$	....	....	....	....

TABLE IV

TETRAISOAMYLAMMONIUM NITRATE IN DIOXANE–WATER MIXTURES

TABLE V

TETRAISOAMYLAMMONIUM NITRATE IN DIOXANE–WATER MIXTURES

H$_2$O, % *c*	0.331 Λ	1.242 Λ	4.01 Λ	6.37 Λ	9.50 Λ	14.95 Λ	20.23 Λ	53.0 Λ	100 Λ
$0.0_{4}15$	.....	$0.0_{3}75$	....	...	..	...	...	...	..
$.0_{4}20$	.....	$.0_{3}67$	....	...	..	...	...	...	..
$.0_{4}30$	.....	$.0_{3}58$	....	...	..	24.35	32.45	...	..
$.0_{4}50$	$0.0_{4}57$	$.0_{3}48$	....	...	5.46	22.75	31.70	...	..
$.0_{4}70$	$.0_{4}60$	$.0_{3}44$	....	...	4.84	21.55	31.05	...	..
$.0_{3}10$	$.0_{4}649$	$.0_{3}403$	0.0452	0.596	4.22	20.10	30.25	...	..
$.0_{3}15$	$.0_{4}742$	$.0_{3}376$	.0388	.494	3.61	18.35	29.10	...	..
$.0_{3}20$	$.0_{4}840$	$.0_{3}368$	.0347	.433	3.23	17.10	28.15	41.75	..
$.0_{3}30$	$.0_{3}105$	$.0_{3}368$	.0296	.363	2.76	15.40	26.65	41.50	..
$.0_{3}50$	$.0_{3}152$	$.0_{3}398$	.0245	.310	2.27	13.40	24.60	41.15	85.1
$.0_{3}70$	$.0_{3}202$	$.0_{3}442$	.0219	.256	2.00	12.15	23.15	40.80	84.7
$.0_{2}10$	$.0_{3}272$	$.0_{3}525$	.0200	.225	1.76	10.95	21.65	40.40	84.3
$.0_{2}15$	$.0_{3}372$	$.0_{3}697$	.0185	.197	1.53	9.70	19.90	39.85	83.6
$.0_{2}20$	$.0_{3}457$	$.0_{3}894$	.0180	.182	1.40	8.95	18.75	39.35	83.1
$.0_{2}30$	$.0_{3}593$	$.0_{2}131$	.0180	.167	1.25	7.97	17.20	38.55	82.1
$.0_{2}50$	$.0_{3}794$	$.0_{2}220$	.0200	.158	1.13	6.95	15.30	37.40	80.6
$.0_{2}70$	$.0_{3}992$	$.0_{2}323$	.0232	.161	1.08	6.44	14.15	36.50	79.4
.010	$.0_{2}133$	$.0_{2}495$	.0301	.175	1.07	6.05	13.05	35.45	..
.015	$.0_{2}207$	$.0_{2}844$	.0462	.214	1.13	5.75	12.10	34.10	..
.020	$.0_{2}309$	.0133	.0681	.266	1.22	5.64	11.60	33.00	..
.030	$.0_{2}646$	.0272	.128	.393	1.43	5.62	11.00	31.35	..
.050	.0200	.0675	.282	.684	1.88	5.78	10.45	29.10	..
.070	.....	.111	....	...	..	...	10.15	...	..
.100	.....	.168	.....	...	..	...	...	...	..

namely, three inflection points in the moderately concentrated region, was obtained for other systems.

Conductance values for tetraisoamylammonium nitrate in various mixtures of dioxane and water are given in Tables III–V. Round concentrations c are given in the first columns and interpolated equivalent conductances Λ are given in the other columns. The weight percentages of water in the mixed solvents are given at the head of each conductance column. The solvent conductances are given in the last column of Table XII. These mixtures correspond to solvents whose dielectric constants range from 2.2, that of dioxane,[9] to 78.6, that of water.[10] Table III covers the low range of dielectric constant, Table IV the intermediate range, and Table V includes the conductance in water. The conductance data for these mixtures are shown on a log c–log Λ plot in Fig. 3. These curves will be discussed below but it may be pointed out here that at a concentration of 10^{-5} N the equivalent conductance changes over a million-fold as the dielectric constant of the solvent changes in the ratio of 2.2 to 78.6. It will be noted that minima appear in the conductance curves for low and intermediate values of the dielectric constant. The values of the minimum conductances and the corresponding concentrations are given in Table VI.

TABLE VI

MINIMUM CONDUCTANCES FOR TETRAISOAMYLAMMONIUM NITRATE IN DIOXANE–WATER MIXTURES

% Water	$\Lambda_{min.}$	$N_{min.}$	% Water	$\Lambda_{min.}$	$N_{min.}$
0.112	0.0_4335	0.0_418	4.01	0.0178	0.0_225
.343	$.0_4595$	$.0_440$	6.37	.159	$.0_250$
.602	$.0_3107$	$.0_480$	9.50	1.07	$.0_290$
1.242	$.0_3364$	$.0_325$	14.95	5.60	.025
2.35	$.0_2224$	$.0_370$			

In order to find whether any of the characteristics of the curves were specifically due to water, the conductance of tetraisoamylammonium nitrate was determined in ethylene dichloride and in a mixture of ethylene

TABLE VII

TETRAISOAMYLAMMONIUM NITRATE IN ETHYLENE DICHLORIDE

c	Λ	c	Λ	c	Λ
0.0_450	50.1	0.0_210	22.9	0.015	10.45
$.0_470$	47.1	$.0_215$	20.2	.020	9.90
$.0_310$	43.6	$.0_220$	18.4	.030	9.40
$.0_315$	39.6	$.0_230$	16.15	.050	8.90
$.0_320$	36.8	$.0_250$	13.80	.070	8.65
$.0_330$	33.0	$.0_270$	12.50	.100	8.40
$.0_350$	28.4	.010	11.45	.150	8.20
$.0_370$	25.6				

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(9) J. W. Williams, THIS JOURNAL, **52**, 1831 (1930).

(10) Drake, Pierce and Dow, *Phys. Rev.*, **35**, 613 (1930).

TABLE VIII

TETRAISOAMYLAMMONIUM NITRATE IN DIOXANE–ETHYLENE DICHLORIDE (22.9% $C_2H_4Cl_2$)

c	Λ	c	Λ	c	Λ
0.0_530	0.0638	0.0_450	0.0168	0.0_350	0.0086
$.0_550$	.0496	$.0_470$	.0147	$.0_370$	.0084
$.0_570$	.0417	$.0_310$	.0129	$.0_210$	.0086
$.0_410$	.0350	$.0_315$	.0112	$.0_215$	.0093
$.0_415$	.0286	$.0_320$	.0103	$.0_220$	.0103
$.0_420$	.0251	$.0_330$	.0093	$.0_230$	.0126
$.0_430$	.0209				

dichloride and dioxane with a dielectric constant of 2.45. Walden's[11] value for the dielectric constant of ethylene dichloride is 10.4. These results are given in Tables VII and VIII.

Tetraisoamylammonium thiocyanate, which is much more soluble in benzene than the nitrate, was next investigated in order to permit a com-

TABLE IX

TETRAISOAMYLAMMONIUM THIOCYANATE IN DIOXANE, IN BENZENE AND IN BENZENE–ETHYLENE DICHLORIDE (13.13% ETHYLENE DICHLORIDE)

c	Dioxane Λ	Benzene Λ	Mixture Λ
0.0_410	.....	.....	0.0_2254
$.0_415$	.....	.....	$.0_2219$
$.0_420$	0.0_434	0.0_495	$.0_2198$
$.0_430$	$.0_434$	$.0_3100$	$.0_2180$
$.0_450$	$.0_437$	$.0_3133$	$.0_2170$
$.0_470$	$.0_440$	$.0_3172$	$.0_2170$
$.0_310$	$.0_4455$	$.0_3232$	$.0_2176$
$.0_315$	$.0_4560$	$.0_3328$	$.0_2189$
$.0_320$	$.0_4666$	$.0_3412$	$.0_2207$
$.0_330$	$.0_4882$	$.0_3530$	$.0_2245$
$.0_350$	$.0_3136$	$.0_3661$	$.0_2331$
$.0_370$	$.0_3187$	$.0_3733$	$.0_2422$
$.0_210$	$.0_3257$	$.0_3810$	$.0_2544$
$.0_215$	$.0_3347$	$.0_3898$	$.0_2725$
$.0_220$	$.0_3417$	$.0_3967$	$.0_2868$
$.0_230$	$.0_3532$	$.0_2110$	.0111
$.0_250$	$.0_3735$	$.0_2137$	.0153
$.0_270$	$.0_3936$	$.0_2171$	.0195
.010	$.0_2129$	$.0_2237$	.0260
.015	$.0_2209$	$.0_2400$	.0385
.020	$.0_2331$	$.0_2634$	.0519
.030	$.0_2712$	.0130	.0794
.050	.0199	.0257	.1274
.070	.0347	.0351	.....
.100	.0617	.0463	.....

TABLE X

TRI-ISOAMYLAMMONIUM PICRATE IN ETHYLENE DICHLORIDE, IN BENZENE, AND IN BENZENE–ETHYLENE DICHLORIDE (21.2% ETHYLENE DICHLORIDE)

c	Ethylene dichloride Λ	Benzene Λ	Mixture Λ
0.0_310	....	.....	0.0_3140
$.0_315$	....	.....	$.0_3114$
$.0_320$	0.842	.....	$.0_4987$
$.0_330$	.700	.....	$.0_4813$
$.0_350$	.556	.....	$.0_4654$
$.0_370$	.475	.....	$.0_4577$
$.0_210$	.403	0.0_6269	$.0_4517$
$.0_215$	.335	$.0_6288$	$.0_4472$
$.0_220$	.293	$.0_6324$	$.0_4452$
$.0_230$	.244	$.0_6408$	$.0_4442$
$.0_250$	.194	$.0_6624$	$.0_4455$
$.0_270$	.168	$.0_6925$	$.0_4490$
.010	.1430	$.0_5154$	$.0_4556$
.015	.1220	$.0_5311$	$.0_4708$
.020	.1098	$.0_5550$	$.0_4908$
.030	.0985	$.0_4140$	$.0_3143$
.050	.0903	$.0_4566$	$.0_3320$
.070	.0891	$.0_3159$	$.0_3628$
.100	.0903	$.0_3507$	$.0_2140$
.150	.0973	.....	.....
.200	.1136	.....	.....
.300	.1310	.....	.....

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[11] Walden, *Z. physik. Chem.*, **70**, 569 (1909).

parison of conductance values in different solvents of very low dielectric constant. Interpolated conductance data are given in Table IX for solutions of the thiocyanate: in dioxane, column 2; in benzene, column 3 and in a mixture of benzene and ethylene dichloride, with a dielectric constant of 2.8, column 4.

It was considered desirable, for purposes of comparison, to determine the characteristics of the conductance curve of a weak salt. Accordingly, tri-isoamylammonium picrate was investigated in benzene, in ethylene dichloride and in a mixture of these solvents having a dielectric constant of 3.1. The results are given in Table X.

The temperature coefficient of the conductance of tetraisoamylammonium nitrate in dioxane was determined at several concentrations, over the temperature range 18–35°. The results are summarized in Table XI. The concentration M for each series is given as moles of salt per kilo of solvent, and may be converted to normality by means of the equation

$$d = 1.029 - 0.0248\,M - 0.00105\,(t - 25°)$$

where d is the density, M weight concentration and t the temperature. The temperature coefficients are all positive, and decrease with increasing temperature. They depend markedly on concentration: the average

TABLE XI

TEMPERATURE COEFFICIENTS FOR TETRAISOAMYLAMMONIUM NITRATE IN DIOXANE

t, °C.	$\Lambda \times 10^4$	$100\,\Delta \log \Lambda/\Delta t$	t, °C.	$\Lambda \times 10^4$	$100\,\Delta \log \Lambda/\Delta t$
	$M = 0.001064$			$M = 0.01038$	
18.40	1.573		18.58	4.35	
		1.91			2.48
23.93	2.005		23.80	5.87	
		1.71			2.29
29.49	2.497		29.29	7.84	
		1.62			2.22
34.95	3.061		34.75	10.37	
	$M = 0.002313$			$M = 0.0557$	
18.36	2.072		18.76	98.5	
		2.23			1.99
23.91	2.755		23.96	125	
		2.10			1.90
29.47	3.606		29.50	159	
		1.91			1.76
34.80	4.557		34.65	196	
	$M = 0.00773$			$M = 0.1111$	
18.42	3.43		18.53	334	
		2.51			1.61
23.81	4.68		23.50	402	
		2.28			1.55
29.31	6.26		29.55	499	
		2.18			1.47
34.85	8.25		34.71	550	

value of $\Delta \log \Lambda/\Delta t$ has a maximum at about 0.02 N, from which it decreases slowly toward higher and rapidly toward lower concentrations.

For purposes of comparison, the dielectric constants of the various mixtures together with those of the pure solvents are given in Table XII.[12]

TABLE XII

DIELECTRIC CONSTANTS

Composition of solvent		Dielectric constant	Solvent conductance
$C_4H_8O_2$	H_2O		
100.0	0.0	2.20	$0.0_{13}2$
99.89	.112	2.25	$.0_{13}3$
99.66	.343	2.3	$.0_{13}5$
99.40	.602	2.4	$.0_{13}5$
98.76	1.242	2.6	$.0_{12}2$
97.65	2.35	2.9	$.0_{11}8$
95.99	4.01	3.5	$.0_{9}2$
93.63	6.37	4.4	$.0_{8}28$
90.50	9.50	5.8	$.0_{7}44$
85.05	14.95	9.0	$.0_{6}17$
79.77	20.23	12	$.0_{6}30$
47.0	53.0	37	$.0_{6}90$
0.0	100.0	78.6	$.0_{5}25$
$C_4H_8O_2$	$C_2H_4Cl_2$		
77.13	22.87	2.45	$.0_{11}65$
0.00	100.0	10.4	$.0_{9}3$
C_6H_6	$C_2H_4Cl_2$		
100.0	0.0	2.28	$.0_{13}1$
86.87	13.13	2.8	$.0_{12}1$
78.76	21.24	3.1	$.0_{11}43$

V. Discussion

The conductance of tetraisoamylammonium nitrate in dioxane is shown graphically in Fig. 2, where the logarithms of equivalent conductance and of concentration are plotted as ordinates and abscissas, respectively. This curve is typical of solutions of strong electrolytes in solvents of very low dielectric constant. The conductivity falls off continuously, although at varying rate, to concentrations well below 10^{-4} N. Indeed, if measurements had been carried only to this concentration, it might have been inferred that the conductance was approaching zero as the limiting value. Actually, however, below 10^{-4} N, the rate of decrease diminishes and there is evidence of a minimum in the conductance curve in the neighborhood of 2×10^{-5} N. What form the conductance curve may have at concentrations below the minimum point in the solvents of lowest dielectric constant could not be ascertained by the method employed in this investigation. Measurements in solvents of slightly higher dielectric constant, however,

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(12) For the dielectric constants of the mixtures, we are indebted to Mr. G. S. Hooper, of this Laboratory, who kindly carried through a series of measurements for us.

indicate that, after passing through a minimum point, the conductance increases with decreasing concentration in regular manner.

The curve at higher concentration is quite complex, since it exhibits three inflection points. The decreasing slope of the curve with increasing concentration at high concentrations may be accounted for on the assumption that the ion mobilities are decreasing, owing to the rapidly increasing viscosity of the solutions. Although the viscosities were not measured, it was quite evident that the viscosity of these solutions increases rapidly with increasing concentration. The complex structure of the remainder of the curve remains unaccounted for. Such a structure is seemingly found only in the case of the strongest electrolytes and is not dependent upon the particular solvent employed, so long as the dielectric constant is sufficiently low. Thus, a similar curve is found for tetraisoamylammonium thiocyanate in dioxane (Fig. 4, Curve V) and for the same salt in benzene (Fig. 4, Curve IV). On the other hand, a weaker electrolyte, tri-isoamylammonium picrate, yields a curve in which inflection points are absent (Fig. 5, Curve V).

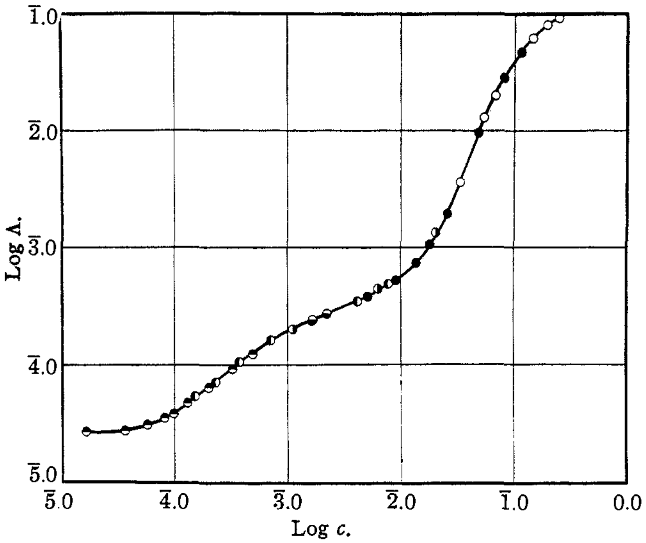

Fig. 2.—Tetraisoamylammonium nitrate in dioxane.

Incidentally, it may be pointed out that conductance values as determined by the alternating and by the direct current method are in excellent agreement. In Fig. 2, the open circles represent points determined by the alternating current method, while the other circles represent points determined by the direct current method. The black circles and the various half-shaded circles represent independent series of direct current measurements in which the methods of carrying out the dilution were varied. As may be seen from the figure, the various determinations are consistent. We may conclude, therefore, that the direct current method yields reliable results and that, even in solvents of dielectric constant as low as 2.2, the conductance curve passes through a minimum at very low concentration.

The influence of the dielectric constant of the solvent medium as well as the influence of specific factors upon the conductance of solutions is of considerable interest. By the methods employed, it was possible to extend the measurements to concentrations sufficiently low to permit determination of the general course of the curve at concentrations below the minimum point. This is well illustrated in Fig. 3 for solutions of tetraisoamylammonium nitrate in varying mixtures of dioxane and water. Dioxane was purposely selected as solvent, since it is completely miscible with water and thus permits of a continuous increase of the dielectric constant of the medium from that of dioxane, 2.2, to that of water 78.6. The composition of various mixtures in weight percentages of water is indicated on the figure.

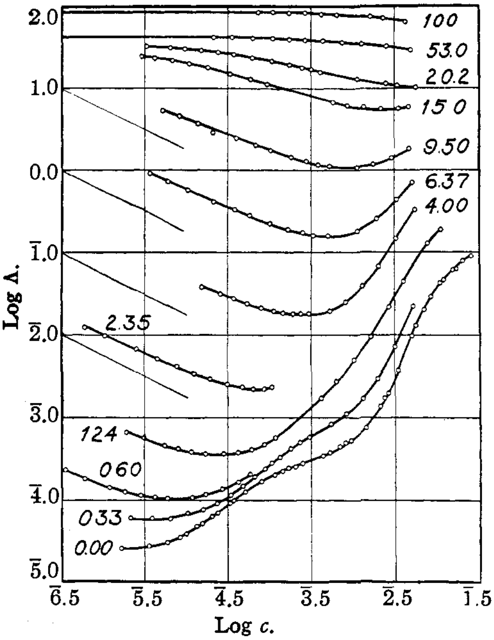

Fig. 3.—Tetraisoamylammonium nitrate in dioxane–water mixtures. (Weight per cent. of water given opposite corresponding curve.)

It will be seen from the figure that, on addition of water to dioxane, the conductance is increased and the complex structure of the curve at higher concentration becomes less pronounced and ultimately disappears. The eccentricities in the conductance curve at higher concentration, while still noticeable at a concentration of 1.24% of water, have disappeared when the concentration of water reaches 4.0%. In the meantime, the minimum point has shifted toward higher concentration, namely, from 2×10^{-5}, in pure dioxane ($D = 2.2$), to 3×10^{-3} N at 4% of water ($D = 3.5$). As the dielectric constant of the medium increases with increasing concentration of water, the minimum point shifts more and more toward higher concentration and becomes less and less pronounced in that the approach from the high concentration side becomes less steep. It ultimately disappears for a mixture containing 20% of water ($D = 12$). The form of the conductance curve beyond the minimum point (toward lower concentration) remains unchanged as the dielectric constant increases and is practically linear on a logarithmic plot. For mixtures having dielectric constants above 12, the conductance curves are displaced chiefly by an increase of conductance in the more concentrated region and the curves approximate those of strong electrolytes in water.

There is no sharp shift in the conductance curve on the initial addition of water. The controlling factor seems to be the dielectric constant of the medium, for the form of the curves and the value of the conductance at a given concentration is practically the same whether the change in dielectric constant is brought about by the addition of water or of ethylene dichloride.

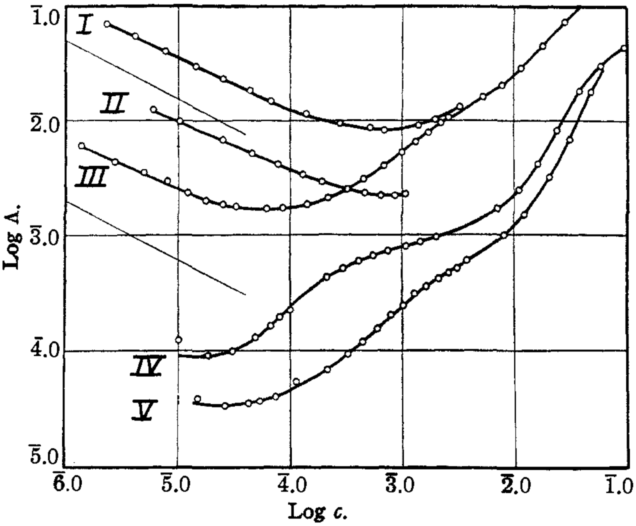

Fig. 4.—I, Tetraisoamylammonium nitrate in dioxane containing 22.9% ethylene dichloride; II, tetraisoamylammonium nitrate in dioxane containing 2.35% water; III, tetraisoamylammonium thiocyanate in benzene containing 13.13% ethylene dichloride; IV, tetraisoamylammonium thiocyanate in benzene; V, tetraisoamylammonium thiocyanate in dioxane.

This is well illustrated in Fig. 4, Curves I and II. The first curve is that of solutions of tetraisoamylammonium nitrate in a mixture of dioxane and ethylene dichloride ($D = 2.45$) and the second in a mixture of dioxane and water ($D = 2.9$). Both curves have a minimum point in the neighborhood of 10^{-3} N and both curves are practically linear and parallel at lower concentrations. The ethylene dichloride mixture is a considerably better conductor than the water mixture, but this is in a large measure due to the much lower viscosity of the former mixture. Curve III, Fig. 4, is for tetraisoamylammonium thiocyanate in an ethylene dichloride–benzene mixture, of dielectric constant 2.8, and it will be noted that the curve approximates that of tetraisoamylammonium nitrate in a dioxane–water mixture, of dielectric constant 2.6 (Curve 1.24, Fig. 3), except for a vertical displacement, presumably due to the difference in solvent viscosities. Curves IV and V, Fig. 4, represent the conductance of tetraisoamylammonium thiocyanate in benzene and dioxane, respectively. The structure of the two curves is much the same and, at low concentrations, the conductance values in the more fluid benzene are the higher. Quite unexpectedly, therefore, specific influences due to the solvent medium are absent, if we leave out of account viscosity effects.

The conductance curve of tri-isoamylammonium picrate, a weak electrolyte, differs markedly from that of strong electrolytes. This will be evident on comparing Curve V, Fig. 5, for this electrolyte in benzene with Curves IV and V, Fig. 4, for tetraisoamylammonium thiocyanate in benzene and dioxane or with the curve for tetraisoamylammonium nitrate in dioxane, Fig. 2. It will be noted that the conductance of tri-isoamylammonium picrate in benzene is far below that of tetraisoamylammonium thiocyanate in the same solvent at corresponding concentrations. Thus, at 10^{-3} N, the conductance of the first electrolyte in benzene is approximately 2.5×10^{-7}, while that of tetraisoamylammonium thiocyanate is 10^{-3}. As the dielectric constant of the solvent medium is increased by adding ethylene dichloride to benzene, the conductance is largely increased. This is evident on comparing Curve V, Fig. 5, with Curve IV, Fig. 5, where the solvent contains 21% of ethylene dichloride ($D = 3.1$).

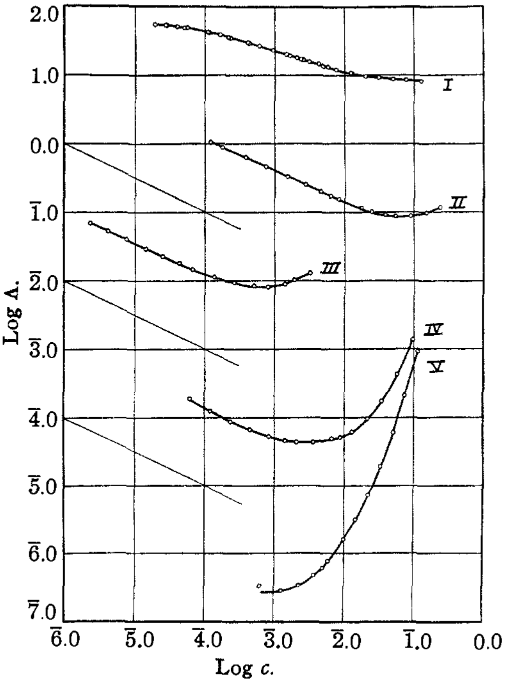

Fig. 5.—I, Tetraisoamylammonium nitrate in ethylene dichloride; II, tri-isoamylammonium picrate in ethylene dichloride; III, tetraisoamylammonium nitrate in dioxane containing 22.9% ethylene dichloride; IV, tri-isoamylammonium picrate in benzene containing 21.2% ethylene dichloride; V, tri-isoamylammonium picrate in benzene.

The difference in the behavior of a quaternary and a ternary salt at higher dielectric constant is well illustrated by Curves I and II, Fig. 5, for tetraisoamylammonium nitrate and for tri-isoamylammonium picrate, respectively, in ethylene dichloride. Curve III, for tetraisoamylammonium nitrate in a dioxane mixture containing 23% of ethylene dichloride, lies far above Curve IV, for the picrate in benzene containing 21% of ethylene dichloride. The dielectric constants of the solvents are, respectively, 2.45 and 3.1. As in the case of the strong salts, however, the minimum for the tertiary ammonium picrate shifts to higher concentrations with increasing dielectric constant and, at the same time, the slope of the curve, toward higher concentration, decreases. This phenomenon is characteristic of the transition from solvents of low to those of high dielectric constant.

One of the striking results of this investigation, best illustrated in Fig. 3 but also evident from Figs. 4 and 5, is the fact that, at concentrations below the minimum point, the curves as plotted are approximately parallel until the conductance reaches a value in the neighborhood of 1.0. This is illustrated in Fig. 3 by the curves for mixtures containing from 0.60 to 9.50% of water, as well as by Curves II, III and IV of Fig. 5 and Curves I, II and III of Fig. 4. The slope of the curves toward lower concentrations approaches a value of approximately minus 0.5, which is indicated by the straight lines drawn in the figures. Since, in the figures, logarithms of the equivalent conductance are plotted against logarithms of the concentration, it follows that the curves conform approximately to a simple equation $\Lambda = A/C^{1/2}$, where A is constant. One should expect such a relation for a binary electrolyte if the conductance were determined by ionization according to the law of mass action. A theoretical discussion of the foregoing and other results is reserved for a future paper.

Summary

1. The conductances at 25° of the following systems have been determined over the concentration range 0.2–0.00001 N: tetraisoamylammonium nitrate in dioxane, water, ethylene dichloride and various mixtures of ethylene dichloride and of water with dioxane; tetraisoamylammonium thiocyanate in dioxane, benzene and a mixture of benzene and ethylene dichloride; and tri-isoamylammonium picrate in ethylene dichloride, benzene and a mixture of these two solvents.

2. It is shown that, at sufficiently low concentrations, the equivalent conductance increases with dilution, even in solvents of very low dielectric constant.

3. The influence of the dielectric constant on conductance has been determined over the range from dioxane to water and it has been found that, viscosity excepted, specific influences due to the solvents are not conspicuously present.

4. The behavior of strong and weak electrolytes is compared.

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