however, consistent differences of secondary order in the effects of the different kinds of salts, and especially between the uni-uni- and uni-bivalent salts.

In conclusion, I take pleasure in thanking Professor A. A. Noyes for his assistance in connection with this investigation.

(CONTRIBUTIONS FROM THE LABORATORY OF PHYSICAL CHEMISTRY, UNIVERSITY OF ILLINOIS.]

THE LAWS OF "CONCENTRATED" SOLUTIONS. III.[1] THE IONIZATION AND HYDRATION RELATIONS OF ELECTROLYTES IN AQUEOUS SOLUTION AT ZERO DEGREES: A. CESIUM NITRATE, POTASSIUM CHLORIDE AND LITHIUM CHLORIDE.

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1. Purpose and Outline of the Investigation.

In undertaking a systematic extension of our knowledge of aqueous solutions of strong electrolytes into the region of "concentrated" solutions, it is natural to begin the study with the simplest type of such electrolytes, the uni-univalent salts. The salts of this type range from those such as cesium nitrate and iodide, which are slightly or not at all hydrated in solution, to those of which lithium chloride is an example, which are combined with considerable amounts of the solvent. The present investigation includes the two salts cesium nitrate and lithium chloride, which represent extremes in this respect, together with one salt, potassium chloride, which occupies an intermediate position.

For investigating the condition of these salts in solution the freezing-point method was adopted. As pointed out in a previous paper,[3] this method possesses the disadvantage that one is obliged to change two variables simultaneously, the concentration and the temperature. This difficulty can be avoided either (1) by combining measurements of heat of dilution with those of freezing-point lowering, or (2) by replacing the freezing-point method by the method of vapor-pressure lowering. For higher temperatures the latter alternative is preferable and a parallel

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[1] Contributions Nos. 1 and 2 of this series appeared in THIS JOURNAL, 32, 653 and 1636 (1910), and 33, 1461 (1911). Owing to the fact that the author was given no opportunity to correct the page proof of article No. 2, it is necessary to note the following corrections: p. 1462, for G. N. Lewis[4] read G. N. Lewis[1]; p. 1472, line 1, for (10) read (12); p. 1467, for (see p. ——) read (see p. 1471); p. 1473, Table IV, for 19° read 18°, and for f_0 read η_0; p. 1463, Note 2, next to last line, the figure 7 is omitted.

[2] Presented at the Indianapolis meeting of the Society, June 29, 1911. Abstract of a thesis presented by Mr. MacInnes to the Graduate School of the University of Illinois in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[3] *Technology Quarterly*, 21, 379–80 (1908).

investigation at 25° by that method is now in progress in this laboratory. For temperatures in the neighborhood of 0°, however, the former method involves fewer difficulties for the same degree of accuracy and was accordingly adopted.

In addition to the freezing-point data, measurements of the conductances and relative viscosities of the solutions at 0° were also made so that the degrees of ionization of the salts could be calculated. The necessary heat of dilution data will be determined in connection with another investigation as the laboratory did not possess a sufficiently accurate calorimeter at the time this investigation was made.

The results which are tabulated in the following pages include complete conductance, viscosity, density, and freezing-point data for solutions of potassium and lithium chlorides up to normal and for cesium nitrate up to half-normal. In so far as reliable data were already available in the literature, they have been employed and have been supplemented by our own measurements in order to make them complete within the above concentration range. The question of accuracy has been carefully considered and an estimate of the probable accuracy is indicated after each of the final values given in the tables. Although in some instances this estimate is to a certain extent arbitrary it is believed that the limits indicated will usually be found too large rather than too small.

2. Purification of Materials.

Cesium Nitrate.—The method of purification used was that described by Wells.[1] Cesium carbonate (Kahlbaum) was dissolved in nitric acid, iodine and hydrochloric acid added in the proportion necessary to form $CsCl_2I$ and the mixture heated. The orange colored crystals which separated upon cooling were filtered from the mother liquor and dried as far as possible by suction. The crystallization was repeated three times from hot hydrochloric acid (1 to 1). The final product was heated over a flame in a casserole to remove the iodine and excess of chlorine and the resulting cesium chloride was converted into nitrate by four evaporations with pure nitric acid. The cesium nitrate thus obtained was crystallized four times from conductivity water and the final product dried in an air bath. The product thus obtained when examined spectroscopically showed no lines except those of cesium.

Lithium Chloride.—Kahlbaum's pyridine was dried by boiling with caustic potash and then distilled. The distillate was heated with an excess of carefully dried lithium chloride (Kahlbaum) and filtered. The filtrate was placed in a distilling flask, the pyridine driven off by heating, and the residue twice evaporated to dryness with pure hydrochloric

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[1] *Am. J. Sci.*, 43, 17 (1892).

acid.[1] The resulting product was then dried at 150°. On examination it was found to be spectroscopically pure.

Potassium Chloride.—Kahlbaum's purest potassium chloride was recrystallized four times from conductivity water and dried by suction. It was always fused immediately before use.

Water.—All the water used in this investigation was conductivity water obtained from the special still[2] in this laboratory. It was collected hot and kept in thoroughly steamed bottles of "Non-sol." glass. The specific conductance of the water at 0° averaged 0.4×10^{-6} mhos.

3. Methods of Measurement.

(*a*) *The Conductance Measurements.*—A slide wire bridge of the roller type described by Kohlrausch and Holborn and furnished by Hartmann and Braun was employed in the conductance measurements. The platinum-iridium slide wire had a length of about 3 meters, the smallest scale division being 3 mm. It was calibrated against the standard resistances of the Physics Laboratory, using the method described by Kohlrausch and Holborn.[3] This calibration was repeated from time to time, whenever it became necessary to clean the wire.

The resistance coils were Hartmann and Braun's highest grade manganin coils with the high resistances wound according to the Chaperon principle. The coils were compared with the standards of the Physics Laboratory and found to be correct well within the limits of error of our measurements. A small Kohlrausch condenser[4] was used in parallel with the resistance box or the cell in all the measurements.

The alternating current was furnished by a small induction coil provided with an adjustable resistance in series with its primary coil. It was connected to the bridge through a commutating switch. Commutation either of the coil or the telephone was, however, found to be without influence upon the readings.

With the above arrangement complete silence was obtained in the telephone at the null point with all except the most dilute and the most concentrated solutions. Readings could be repeatedly checked to 1 part in 5000.

The cells, which were made of Jena Geräteglas, were of the pipet type[5] shown in Fig. 1. The internal diameter was about 15 mm. and the horizontal electrodes were 10 mm. in diameter. Three cells were employed with electrodes 75 mm., 15 mm., and 2 mm. apart, respectively. The first cell was employed for salt solutions ranging in concentration

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[1] Method of Kahlenberg and Krauskopf, This Journal, 30, 1104 (1908).

[2] The form of the still is described by Noyes and Coolidge, *Proc. Am. Acad.*, 39, 190 (1908).

[3] "Leitvermögen der Elektrolyte," p. 47.

[4] Kohlrausch and Holborn, p. 60.

[5] Similar to the cell designed by Kraus, see This Journal, 31, 732 (1909).

between N and 0.1 N, the second for those between 0.1 N and 0.005 N, while the third was used for the most dilute solutions. The electrodes were coated with platinum black and cleaned in the usual manner.

The conductance capacities at 0° of the first two cells were determined by measurements with normal and tenth-normal solutions of potassium chloride prepared exactly as directed by Kohlrausch and Holborn[1] and the values used for the specific conductances of these solutions at 0° were 0.06541 and 0.007150 mhos, respectively. The constants found by measurements with solutions prepared at two different times are as follows:

	Date, Oct. 19, 1910.		Date, Jan. 1, 1911.	
Solution.	N.	0.1 N.	N.	0.1 N.
Cell 1	3.423	3.425	3.423	3.424
Cell 2	...	0.6222	...	0.6222

The conductance capacity (0.01592) of the smallest cell was determined from that of the second cell by measurements with the same dilute solution in both. The conductance of the water was determined in a cell of the usual Arrhenius type with unplatinized electrodes 3 cm. in diameter and about 2 mm. apart. The measurements of the conductance of the water used gave results agreeing within about 2 per cent., which is sufficiently accurate.

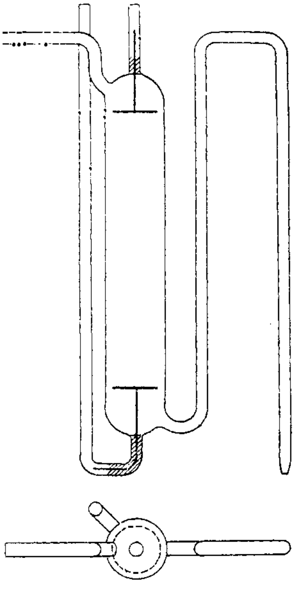

Fig. 1.

All conductance measurements were made at 0°, a large Dewar tube filled with a mixture of pure water and finely chopped ice (made from distilled water) being used as the constant temperature bath. This mixture was kept in constant motion by an electrically driven stirrer. Investigation of this bath with a delicate thermometer showed a temperature constant to 0.001° in all parts of the bath. The pipet cells were placed in the bath in such a manner that only the body of the cell (*i. e.*, the portion containing the solution) was immersed, the stem projecting over the edge of the Dewar tube and serving to hold the cell in position. Short leads of heavy copper wire connected the cell with the bridge, and their resistance was compensated by similar leads connecting the resistance box to the other arm of the bridge.

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[1] "Leitvermögen der Elektrolyte," p. 76. 74.422 grams of fused potassium chloride in 1000 grams of solution (weights in air).

(*b*) *The Density Measurements.*—The pycnometers used were of the Ostwald-Sprengel type, with a glass cap ground on the end of one capillary and a small bulb blown in the upper part of the other to allow for expansion of the liquid contained. This was necessary, as the pycnometer was filled at 0° and weighed at room temperature. A second pycnometer was used as a counterpoise when weighing. The capacity of the pycnometers was about 25 cc. All densities are at 0°, referred to water at 4°.

(*c*) *The Freezing-Point Measurements.*—The freezing-point measurements were made by the Equilibrium Method.[1] The freezing-point vessel was a silvered Dewar vacuum tube having a capacity of 200 cc. The Dewar tube was closely surrounded by, but not in contact with, a bath composed of a mixture of fine ice and water. Through openings in the cover were inserted a Beckmann thermometer, a glass stirrer, and a tube, *T*, which was used for withdrawing solution. In order to prevent the removal of small particles of ice, this tube was drawn out to a capillary at its lower end and to prevent the solution from rizing in this tube, air pressure was applied to it until air began to bubble from the tip. The upper end of the tube was then closed by means of a rubber tube and pinchcock.

Pure ice was prepared by placing test tubes containing conductivity water in a freezing mixture. The ice collected on the walls of the tubes, and the central portions, containing any impurities present, were poured off. The ice was then broken into small lumps in a mortar which had been previously chilled by filling it with fine ice. These lumps were placed in the Dewar tube until it was about three-fourths filled, and the solution, having about the concentration desired, was cooled to its freezing point and poured over the ice. The cover carrying the Beckmann thermometer, stirrer, and the tube *T* was then put in place, the tip of the tube *T* being close to the bulb of the thermometer but not touching it. The whole apparatus was surrounded with an asbestos shield to protect it from air currents.

Determination of the Concentration at Equilibrium.—The solution was slowly stirred and the temperature noted. During this time the thermometer was lightly tapped by an electrical hammer. As soon as a constant temperature was attained the tapper was stopped and the temperature accurately noted (R_1). A portion of about 10 cc. was then drawn off through the tube *T* and rejected. Then without allowing the solution filling the tube to fall back, the tube was connected to the stem of the conductivity cell (Fig. 1) and after filling the cell with solution, the connection with the tube *T* was closed by means of the pinchcock and the cell removed. After this, the thermometer was again read (R_2)

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[1] For reference to previous work with this method see Ostwald-Luther, "Physico-chemischen Messungen," Ed. 3, p. 281.

with the idea of using the mean between this reading and the first one, R_1, but in no instance was any difference observed in these two readings.

To determin the concentration of the solution in the conductivity cell, its specific conductance at 0° was carefully determined as described above, and the concentration obtained by interpolation from conductance measurements on solutions of known concentrations.

Calibration of the Thermometer.—The Beckmann thermometer was carefully calibrated for irregularities of bore by the usual method of a moving mercury thread. The value of a degree in terms of the standard hydrogen thermometer was found by comparison with a Beckmann thermometer newly standardized by the National Bureau of Standards. For two weeks before the beginning of the investigation and when not in use until its completion, the thermometer was kept in an ice bath in order to protect it from large changes of temperature. Each time the thermometer was used, its zero point was determined with pure ice and water. The readings of the thermometer were always made with a rizing meniscus, with the tapper temporarily stopped, and at a definit and constant room temperature, the last precaution rendering stem exposure corrections unnecessary, except in the case of the more concentrated solutions of lithium chloride. For these solutions a Beckmann thermometer standardized at the Bureau of Standards was employed and the necessary corrections for stem exposure were applied.

(*d*) *The Viscosity Measurements.*—The viscosimeter was of the Ostwald type but with the upper ends of the two tubes connected by a device similar to that employed by Archibald, McIntosh and Steele,[1] so as to prevent the entrance of warm air into the apparatus during the measurement. The upper and lower bulbs, the centers of which were at a difference of level of 16 cm., had capacities of 6.0 and 40 cc. respectively. The capillary was 10.7 cm. long and 0.055 cm. in diameter. A specially constructed support maintained the viscosimeter in a vertical position in the vigorously stirred mixture of fine ice and water which served as the constant temperature bath. The time of flow was measured by a tested stop-watch reading $^1/_5$ second.

Before each series of measurements the viscosimeter was cleaned by filling it with concentrated nitric acid containing a few drops of alcohol and allowing it to remain over night. It was then rinsed several times, first with conductivity water and then with the solution, and allowed to drain completely. A definit quantity of the solution was introduced with a pipet. The water value was determined immediately before or after that of each solution. When necessary, the solutions were

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[1] *Z. physik. Chem.*, 55, 129 (1907), see also Ostwald-Luther, "Physico-chemischen Messungen," Ed. 3, p. 233.

filtered through a previously washed hardened filter to insure freedom from small dust particles.

The potassium chloride solutions were made up from weighed quantities of the fused salt and water. The concentrations of the lithium chloride solutions were determined by conductance measurements.

Standardization of the Viscosimeter.—For a viscosimeter of the above type the relative viscosity of any solution is given by the expression

$$\frac{\eta}{\eta_0} = \frac{(D - \lambda)t}{(D_0 - \lambda)t_0}P \qquad (1)$$

in which t and t_0 are the times of flow of solution and water respectively, D and D_0 their respective densities, and λ the density of air at the same temperature. P is a correction factor, which is equal to unity if the viscosimeter obeys Poiseuille's Law exactly, but which, in general, differs slightly from unity and must be determined for each instrument.

Grüneisen[1] has shown that the correction factor, P, for any solution in a given viscosimeter is given by the equation

$$P = \frac{1 + \varphi(t_0)}{1 + \varphi\left(\frac{t\eta}{D\eta_0}\right)} \qquad (2)$$

and that the function φ has the form $e^{b/t_0^n} - 1$, the constants b and n being determined by the dimensions of the viscosimeter.

For a viscosimeter having the dimensions given above, the exponent n may without error be taken equal to unity.[2] Equation (2) consequently becomes

$$P = e^{hb} \quad (3),$$

where h is written for the expression

$$\frac{\frac{t\eta}{D\eta_0} - t_0}{\frac{t_0 t\eta}{D\eta_0}}.$$

Since the exponent hb is a small quantity the equation may be written, finally,

$$P = 1 + hb. \qquad (4)$$

In order to obtain the constant, b, for any viscosimeter it is only necessary to determin the time of flow of a solution for which η/η_0 is accurately known. For this purpose we employed a cesium nitrate solution having the composition 8.3488 grams of $CsNO_3$ per 1000 grams of water. The careful determinations of Merton[3] give this solution a relative viscosity of $\eta/\eta_0 = 0.9246$ at 0°.

Using this solution in our viscosimeter we obtained the following

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[1] *Wiss. Abhandl. Phys. Tech. Reichsanstalt,* **4,** 241 (1904).

[2] Grüneisen, *Loc. cit.,* p. 159.

[3] *J. Chem. Soc.,* **97,** 2454 (1910).

values : t_0 = 317.8 sec., t = 277.5 sec., D = 1.0618 and hence $h = -0.0010$ and b = 2.8.

(*e*) *The Weights.*—The set of weights used in this investigation was standardized at the Bureau of Standards. All the numerical data given in this paper are based upon *weights in vacuo.*

4. The Conductance and Density Data.

Cesium Nitrate.—The results of the density and conductance measurements with this salt are shown in Table I.

Cesium nitrate solutions of definit concentrations were prepared by weighing the fused salt into well steamed, glass stoppered, Erlenmeyer flasks of Jena glass, adding conductivity water and again weighing. From these solutions a series of more dilute solutions was prepared by weight. Solutions made directly from the salt are marked by asterisks in Table I. Solution No 6 was prepared from a different sample of cesium nitrate as a check. The cesium nitrate for this solution was prepared from Kahlbaum's cesium chloride by four evaporations with pure concentrated nitric acid and three crystallizations of the product from conductivity water at 0°, using centrifugal drainage.

TABLE I.—CESIUM NITRATE SOLUTIONS AT 0.000°.

Conductance and Density Data.

No.	Moles of salt per 1000 grams of H_2O. n'.	Density 0°/4°. D.	Corrected specific conductance $\times 10^6$. $\kappa \times 10^6$.	Cell No.
1	0.5389*	1.07705	30900.0	1
2	0.4282	1.0630	26350.0	1
3	0.4427*	1.0623	26110.0	1
4	0.3346	1.0475	20420.0	1
5	0.3078	1.0425	18980.0	1
6	0.2498*	....	15740.0	1
7	0.2383*	....	15060.0	1
8	0.1612	1.0222	10700.0	1
9	0.1529	1.0215	10170.0	1
10	0.1059*	....	7262.0	2
11	0.09314*	1.0145	6461.0	2
12	0.05962	1.0074	4315.0	2
13	0.04666	1.0056	3397.0	2
14	0.01730	1.00206	1336.0	2
15	0.008877	1.0015	702.2	2
16	0.003940	....	318.0	3
17	0.001737	....	141.3	3
18	0.0004414	....	36.44	3
19	0.0002115	....	17.61	3

*Specific conductance of the water = 0.44×10^{-6} mhos.

The more dilute solutions, 0.02 N and less, were found to be readily contaminated by contact with the air and by standing for some time in the flasks. To overcome these sources of error the flasks, previously weighed, were filled with fresh, hot, conductivity water directly from the still, and allowed to stand over night. The following day they were rinsed thoroughly and then weighed, together with the required quantity of conductivity water. A portion of a freshly prepared solution of known concentration was then added and the flask and contents reweighed. By this method the flasks were not dried before the solution was made up and the impurities in the adhering water were not retained in the flask. The quantities of water and solution were adjusted so that but a small air space remained below the stopper.

The cell, after thorough cleaning and soaking out with hot, conductivity water, was filled first with the most dilute solution and afterward with the other solutions in order of their strengths.

TABLE II.—LITHIUM CHLORIDE SOLUTIONS AT 0.000°.

Conductance and Density Data.

No.	Moles of salt per 1000 grams of H_2O. n'.	Density 0°/4°. D.	Corrected specific conductance × 10^6. $\kappa \times 10^6$.	Cell No.
1	0.9990	1.0233	39200.0	1
2	0.8218	1.0193	33390.0	1
3	0.6187	1.0151	26230.0	1
4	0.3659	1.0093	16650.0	1
5	0.3561	1.0088	16260.0	1
6	0.2144	1.0054	10270.0	1
7	0.07702	1.0021	3988.0	2
8	0.04120	1.0009	2210.0	2
9	0.03337	1.0007	1801.0	2
10	0.01646	....	917.2	2
11	0.008322	....	474.2	3
12	0.002027	....	118.8	3
13	0.001039	....	61.33	3
14	(0.0005144)	....	(30.66)	3

Specific conductance of the water = 0.49 × 10^{-6} mhos.

Lithium Chloride.—Table II shows the results of the density and conductance measurements with this salt. The series of solutions of known concentrations below 0.6 N was made by dilution, as described above, of the two solutions whose analyses are given below:

Solution.	Weight of sample.	Wt. AgCl.	Moles LiCl per 1000 grams H_2O.
1	25.184	2.1754	0.6026
	25.115	2.1714	0.6032
2	99.608	0.4755	0.03331
	99.555	0.4756	0.03331

The concentrations of solutions Nos. 1, 2 and 3 were determined by analysis in the same manner.

5. The Viscosity Data.

Table III shows the results obtained in the viscosity measurements. The "uncorrected" η/η_0 values are shown in column IV. The next column contains the correction factors, obtained as explained in section 3. It will be noted that the maximum correction is only 0.2 per cent. The final corrected values are shown in the last column.

TABLE III.—VISCOSITY DATA AT 0°.

No.	n'.	$D_0°/4°$. Interpolated.	η/η_0 (uncorr.).	P.	η/η_0 (corr.).
		Potassium Chloride.			
1........	0.9991	1.0473	0.9307	0.9977	0.9286
2........	0.8010	1.0383	0.9410	0.9981	0.9392
3........	0.6020	1.0293	0.9533	0.9985	0.9519
4........	0.5160	1.0249	0.9569	0.9987	0.9557
5........	0.4063	1.0197	0.9654	0.9989	0.9643
6........	0.3015	1.0146	0.9752	0.9992	0.9744
7........	0.2118	1.0104	0.9864	0.9996	0.9860
8........	0.1042	1.0051	0.9944	0.9998	0.9842
		Lithium Chloride.			
1........	0.9776	1.0228	1.1240	1.0015	1.1257
2........	0.8710	1.0205	1.1133	1.0014	1.1150
3........	0.6036	1.0151	1.0813	1.0011	1.0825
4........	0.3508	1.0088	1.0481	1.0006	1.0488
5........	0.3247	1.0082	1.0434	1.0006	1.0441
6........	0.2540	1.0066	1.0337	1.0005	1.0342
7........	0.1077	1.0029	1.0125	1.0002	1.0127

6. The Freezing-Point Data.

Cesium Nitrate.—The data obtained with this salt are shown in Table IV. The strongest solution studied was in equilibrium with both ice and solid cesium nitrate, so that the eutectic point for this salt is —1.254° and the concentration of the saturated solution is $n' = 0.4370$ mole of $CsNO_3$ per 1000 grams of water.

All of the data shown in Table IV were treated by the method of Least Squares and the following equation obtained:

$$\Delta t = (3.426\, n' - 1.862\, n'^2 + 1.373\, n'^3) \pm 0.0019°. \quad (5)$$

The "probable error," 0.0019°, is that given by the relation, $P.\ E. = 0.675\sqrt{\Sigma D^2/10}$, where ΣD^2 is the sum of the squares of the deviations of the observed values from those calculated by means of the above equation. These calculated values, together with the deviations, are also shown in Table IV.

Lithium Chloride.—Of the data shown in Table IV, the first seven values are those of Jahn[1] corrected to the basis of the 1911 atomic weight table. The remaining values were obtained in this laboratory.

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[1] *Z. physik. Chem.*, **50**, 135 (1904).

TABLE IV.—FREEZING-POINT DATA.

No.	n'.	Δt obs.	Δt calc.	Diff.
		Cesium Nitrate.		
1	0.0185	0.067°	0.064°	—0.003°
2	0.0525	0.174	0.175	—0.001
3	0.1296	0.418	0.416	—0.002
4	0.1595	0.507	0.505	—0.002
5	0.1855	0.582	0.580	—0.002
6	0.2169	0.666	0.669	+0.003
7	0.2729	0.824	0.824	0.000
8	0.2816	0.852	0.848	—0.004
9	0.3212	0.949	0.954	+0.005
10	0.4148	1.203	1.200	—0.003
11	0.4370	1.254	1.256	+0.002
		Lithium Chloride.		
1	0.0251	*0.091°*	0.090°	—0.001°
2	0.0506	*0.179*	0.178	—0.001
3	0.0749	*0.265*	0.265	0.000
4	0.1515	*0.526*	0.527	+0.001
5	0.2042	*0.709*	0.709	0.000
6	0.2548	*0.888*	0.888	0.000
7	0.2966	*1.038*	1.038	0.000
8	0.3350	1.177	1.177	0.000
9	0.4301	1.529	1.528	—0.001
10	0.5580	(2.005)	2.012	+0.007
11	0.8218	3.053	3.054	+0.001
12	0.9990	3.790	3.789	—0.001

In order to estimate the accuracy of the data, the values of n' were plotted against values of ${}^1/_3\,(\Delta t/n' - 3.3)$ and the best smooth curve passed through the points by means of a spline. From this curve values of Δt corresponding to the first six values of n' given in Table IV were then read off. Since the remainder of the curve could not be distinguished from a straight line, linear interpolation was employed for the remaining values of n'. The Δt values thus obtained ($\Delta t_{\text{calc.}}$) are shown in Table IV, together with their deviations from the corresponding observed values. A deviation of 0.001° amounted to about 2 mm. on the scale employed.

7. Equivalent Conductances at Zero Concentration.

To determin the Λ_0 value for each salt, extrapolation was made by the method of A. A. Noyes. Values of the equivalent resistance, $1/\Lambda$, were plotted against the corresponding values of $(C\Lambda)^{n-1}$, and the value of the exponent n adjusted until a straight line was obtained. For cesium nitrate, values of these functions for the concentrations, 0.0002115, 0.0004414, 0.001737, 0.003940 and 0.008877 were employed and were calculated from the specific conductances of solutions Nos. 15, 16, 17, 18 and 19 of Table I. The value of the exponent, n, was 1.50. The

Λ_0 value thus obtained (84.0) is estimated to be known with a precision of about two units in the first decimal place.

For lithium chloride the value, $\Lambda_0 = 60.3 \pm 0.3$, was obtained in the same manner. The solutions employed for this extrapolation were Nos. 11, 12 and 13 of Table II. The value of the exponent n in the expression $(C\Lambda)^{n-1}$ was 1.53.

To potassium chloride Noyes and Coolidge[1] assign the value $\Lambda_0 = 81.4$. This was derived from the experimental data of Whetham[2] and of Kahlenberg.[3] Using the same data Johnston[4] found $\Lambda_0 = 81.9$. As the difference is considerable we decided to repeat this extrapolation and proceeded as follows:

Using Kohlrausch and Maltby's data for potassium chloride at 18°, values of $1/\Lambda$ were first plotted against values of $(C\Lambda)^{0.5}$, giving the 6 points corresponding to the concentrations 1, 2 and 5 ten-thousandths and 1, 2 and 5-thousandths normal respectively. By use of a spline, a smooth curve was made to pass through all six points. This curve, which was not far from a straight line, crossed the axis of zero concentration at the point $\Lambda_0 = 130.1$, thus giving the same value which Kohlrausch and Maltby obtained. The values 130.0 and 130.2 would, moreover, have been clearly inconsistent with the rest of the curve, so that this method of extrapolation leads, in the case of potassium chloride at all events, to the same Λ_0 value as does the one employed by Kohlrausch.

The same method of procedure was also employed with the data of Whetham and those of Kahlenberg for this salt at 0°. Only the values in the concentration interval 0.0002 to 0.03 normal were employed. Two values obtained by Kohlrausch and Holborn,[5] for the concentrations 0.01 and 0.02 normal, respectively, were also included. Using the spline, it was found that a perfectly smooth curve could be made to pass through eight of the nine points obtained from Whetham's data. The deviation in the case of the one point corresponded to an error of only 0.05 per cent. in Λ. The same curve also passed through *both* of the points obtained from the data of Kohlrausch and Holborn. Up to 0.01 normal the curve was exactly linear and it crossed the axis at a point corresponding to $\Lambda_0 = 81.0 \pm 0.1$. The points obtained from Kahlenberg's data were irregular. The "best" straight line through them did not coincide with the other line and led to a value of Λ_0 somewhere between 81.6 and 81.9. A study of the experimental methods of the two investigators indicates that Whetham's measurements were conducted with much greater care and accuracy than those of Kahlen

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[1] Carnegie Inst., Pub. No. 63, 47 (1907).

[2] *Z. physik. Chem.*, 33, 351 (1900).

[3] *J. Phys. Chem.*, 5, 348 (1901).

[4] THIS JOURNAL, 31, 1012 (1909).

[5] *Loc. cit.*, p. 204.

SUMMARY OF DATA AT ROUND CONCENTRATIONS.

TABLE V.—CESIUM NITRATE SOLUTIONS AT 0.000°. (1911 ATOMIC WEIGHTS.)

Moles of salt per 1000 grams of water. n'.	Freezing-point depression. $\Delta t \pm 0.002°$.	Density $D_{0°/4°}$. $\pm 0.01\%$.	Relative viscosity. η/η_0. $\pm 0.03\%$.	Equivalent conductance Λ. $\pm 0.1\%$.	$\frac{\Lambda}{\Lambda_0}$. $\pm 0.25\%$.	$\frac{\Lambda\eta}{\Lambda_0\eta_0}$. $\pm 0.25\%$	$\frac{\Lambda}{\Lambda_0}\left(\frac{\eta}{\eta_0}\right)^{0.826} = \gamma$. $\pm 0.30\%$.	$\frac{100(1+\gamma)n'}{55.53+(1+\gamma)n'} =$ $100N'$.
0.00000	0.000	0.9999	1.0000	(84.0 ± 0.2)	1.0000	1.0000	1.0000	0.0000
0.02500	0.086	1.0030	0.9960	75.19	0.8948	0.8912	0.8939	0.0852
0.05000	0.168	1.0061	0.9905	72.94	0.8680	0.8597	0.8651	0.1676
0.07500	0.247	1.0104	0.9846	70.96	0.8445	0.8315	0.8376	0.2476
0.10000	0.325	1.0136	0.9796	69.32	0.8249	0.8080	0.8148	0.3258
0.2000	0.622	1.0278	0.9613	65.18	0.7757	0.7456	0.7543	0.6279
0.3000	0.897	1.0414	0.9446	63.04	0.7502	0.7087	0.7190	0.9202
0.4000	1.160	1.0565	0.9291	60.88	0.7245	0.6731	0.6849	1.1992
0.5000	(1.419 ± 0.005°)	1.0710	0.9138	59.31	0.7058	0.6449	0.6582	1.4712

berg, and this fact, together with the close concordance of his values with one another and with those of Kohlrausch and Holborn, indicates that 81.0 is the most probable Λ_0 value for potassium chloride at 0°, and, if Whetham's values are as accurate as they appear to be, the uncertainty in this value should not exceed 0.2 per cent.

8. Summary of Data at Round Concentrations.

Tables V, VI and VII contain the values of the freezing-point lowerings, densities, relative viscosities, and equivalent conductances of the solutions of the three salts at round concentrations. *All* of the data in these tables are based upon the 1911 atomic weight table. In cases where the data of other observers have been employed the necessary correction to this basis has been made.

Cesium Nitrate (Table V).—The Δt values (column II) are those given by the empirical equation (5) derived in Section 6. A solution having the concentration $n' = 0.5$, to which a freezing-point lowering of $1.419 \pm 0.005°$ is assigned, is, however, a supersaturated solution. This value for Δt was obtained from equation (5), but as this involves an extension of the equation beyond the limits for which it was derived a graphical extrapolation was made as a check. For this purpose a graph of equation (5) was made on cross-section paper. A spline was then made to pass through all of the points plotted, the highest point being that for the concentration 0.4370. The portion of the spline projecting beyond this was then grasped by one man while a second man sighted along the spline from the opposit end and the first man shifted the position of the upper end until, in the judgment of the second man, it made a smooth curve with the remainder of the spline. The value of Δt for the concentration 0.5000 was then read off. This process was repeated five times with three different men and the following results obtained: 1.417°, 1.420°, 1.417°, 1.418°, 1.418°; mean, 1.4178°, which checks the value calculated from equation (5) within 0.002°. Owing, however, to the fact that it is an extrapolated value, a somewhat larger probable error has been assigned to it.

The relative viscosities shown in column IV were obtained by graphical interpolation from the accurate data of Merton.[1]

The density and equivalent conductance values are based upon the data of Table I. The values of Λ were calculated by the equation

$$\Lambda = \frac{\kappa(1000 + n'M)}{1000\, n'D}, \qquad (6)$$

in which κ is the specific conductance and M the equivalent weight.

Potassium Chloride (Table VI).—The Δt values for concentrations up to and including $n' = 0.5$ are taken from the critical compilation

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[1] *Loc. cit.*

SUMMARY OF DATA AT ROUND CONCENTRATIONS.

TABLE VI.—POTASSIUM CHLORIDE SOLUTIONS AT 0.000°. (1911 ATOMIC WEIGHTS.)

Moles of salt per 1000 grams of water. n'.	Freezing-point depression. $\Delta t \pm 0.005°$.	Density $D_{0°/4°}$. $\pm 0.05\%$.	Relative viscosity η/η_0. $\pm 0.1\%$.	Equivalent conductance Λ. $\pm 0.2\%$.	$\frac{\Lambda}{\Lambda_0}$. $\pm 0.25\%$.	$\frac{\Lambda \eta}{\Lambda_0 \eta_0}$. $\pm 0.3\%$.	$\frac{\Lambda}{\Lambda_0}\left(\frac{\eta}{\eta_0}\right)^{0.90} = \gamma$ $\pm 0.4\%$.	$\frac{100(1+\gamma)n'}{55.53+(1+\gamma)n'} = 100N'$.
0.0000	0.000°	0.9999	1.000	81.0±0.2	1.000	1.000	1.000	0.000
0.0250	0.089	1.0012	0.9985	75.54	0.9326	0.9312	0.9313	0.0868
0.0500	0.175	1.0025	0.9971	73.68	0.9096	0.9070	0.9073	0.1714
0.0750	0.262	1.0037	0.9960	72.47	0.8947	0.8911	0.8915	0.2458
0.1000	0.345	1.0049	0.9945	71.58	0.8837	0.8788	0.8793	0.3373
0.2000	0.680	1.0098	0.9866	69.51	0.8581	0.8467	0.8477	0.6611
0.3000	1.009	1.0146	0.9743	68.63	0.8473	0.8255	0.8275	0.9776
0.4000	1.335	1.0194	0.9649	67.92	0.8385	0.8091	0.8119	1.289
0.5000	1.658	1.0242	0.9574	67.32	0.8312	0.7958	0.7990	1.594
0.6000	1.983	1.0289	0.9517	66.96	0.8267	0.7867	0.7905	1.898
0.8000	2.635	1.0380	0.9394	66.23	0.8176	0.7681	0.7733	2.491
1.000	3.287	1.0472	0.9286	65.51	0.8087	0.7510	0.7569	3.067

Summary of Data at Round Concentrations.

Table VII.—Lithium Chloride Solutions at 0.000°. (1911 Atomic Weights.)

Moles of salt per 1000 grams of water n'.	Freezing-point depression. Δt.		Density $D_{0°/4°}$. $\pm 0.05\%$.	Relative viscosity $\eta/\eta_\circ$. $\pm 0.2\%$	Equivalent conductance Λ. $\pm 0.1\%$.	$\frac{\Lambda}{\Lambda_\circ}$ $\pm 0.35\%$.	$\frac{\Lambda\,\eta}{\Lambda_\circ\eta_\circ}$. $\pm 0.4\%$	$\frac{\Lambda}{\Lambda_\circ}\left(\frac{\eta}{\eta_\circ}\right)^{0.94} = \gamma$. $\pm 0.4\%$.	$\frac{100(1+\gamma)n'}{55.53+(1+\gamma)n'}$, = 100 N'.
0.0000	0.000°	±0.002°	0.9999	1.000	60.3±0.3	1.000	1.000	1.000	0.000
0.0250	0.090		1.000^5	1.003^0	54.5^4	0.904^3	0.907^0	0.906^9	0.0858
0.0500	0.177		1.001^2	1.006^0	52.9^6	0.878^1	0.883^4	0.883^0	0.1693
0.0750	0.265		1.002^0	1.008^8	$51.9^{\bar{0}}$	0.860^6	0.868^2	0.867^7	0.2516
0.1000	0.351		1.002^5	1.011^8	51.0^7	0.846^8	0.856^8	0.856^2	0.3331
0.2000	0.694		1.005^0	1.026^0	48.3^9	0.802^3	0.823^2	0.821^9	0.6519
0.3000	1.049		1.007^4	1.040^8	46.6^7	0.773^8	0.805^4	0.803^4	0.9649
0.4000	1.416		1.010^0	1.055^7	45.3^0	0.751^1	0.793^1	0.790^6	1.273
0.5000	1.791	±0.004°	1.012^3	1.069^2	44.0^0	0.729^6	0.780^2	0.777^1	1.575
0.6000	2.174		1.014^6	1.081^9	42.8^9	0.711^2	0.769^5	0.765^9	1.872
0.8000	2.966		1.018^6	1.107^2	41.4^3	0.686^9	0.760^6	0.756^0	2.467
1.000	3.792		1.023^4	1.128^2	40.0^2	0.663^6	0.748^7	0.743^4	3.044

published recently by Noyes and Falk[1] and are based chiefly upon the data of Jahn. The value for $n' = 1$ is that of Raoult[2] and the values for $n' = 0.6$ and 0.8 are interpolated.

The density data are interpolated from the results of Freund.[3]

The viscosity data are based upon the values of Table III.

Of the equivalent conductance values those for $n' = 0.025$, 0.1 and 1.0 are based upon the data of Kohlrausch and Holborn.[4]

The remaining values were interpolated from the data of Kahlenberg.[4]

Lithium Chloride (Table VII).—The Δt values are those obtained by interpolation as explained on page 1696.

The density and equivalent conductance values are based upon the data in Table II, and the viscosity values upon those in Table III.

9. Comparison of the Three Salts.

The Degree of Ionization.—In order to estimate the degrees of ionization of the salts, the expression $\gamma = \Lambda/\Lambda_0(\eta/\eta_0)^m$ was employed. The deduction of this relation, the evidence in its favor and the derivation of the numerical values of the "fluidity exponent," m, have all been discussed in the preceding communication of this series.[4] The values of γ thus obtained are shown in column VIII of Tables V, VI and VII.

It will be noted that the values for cesium nitrate are the lowest and those for potassium chloride the highest of the three salts. The figures in columns VI and VII, respectively, permit a comparison with the values for γ which one would obtain (1) by neglecting the viscosity influence and (2) by taking the fluidity exponent equal to unity.

The Mole Fractions and Freezing-Point Lowerings.—In order to compare the effects of the three salts upon the freezing point, values of the mole fraction, N', for each salt were plotted against the corresponding values of the freezing-point lowering. The mole fractions were calculated by means of the equation

$$N' = \frac{(1 + \gamma)n'}{1000/18 + (1 + \gamma)n'}, \tag{7}$$

and the values of $100\,N'$ are given in the last column of Tables V, VI, and VII.

For an "ideal solution" the relation connecting the freezing-point lowering and the mole fraction, N', of the solute was deduced in the first paper of this series.[5] If water is the solvent and if the solution is only moderately concentrated, the following equation is a sufficiently exact numerical statement of this relation.

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[1] THIS JOURNAL, **32**, 1011 (1910).

[2] *Z. physik. Chem.*, **27**, 659 (1898).

[3] *Ibid.*, 66, 508 (1909).

[4] *Loc. cit.*

[5] *Loc. cit.*, equation 127, p. 667 (and p. 1636).

$$N' = 0.00969\,(\Delta t - 0.00425\Delta t^2). \qquad (8)$$

A comparison of this equation with the freezing point data for non-electrolytes has already been made.[1] It will be recalled that the data for the simpler alcohols and for chloral hydrate were in good agreement with the above equation.[2] Of the other non-electrolytes for which data were available, the deviation, with one exception, was always in the direction which would result if the solute were hydrated in solution. The only pronounced deviation in the opposite direction, a deviation which would occur if the solute were partially associated, was found in the case of glycocoll, a substance for which association, due to partial neutralization, is to be expected.

A solute, which gives freezing-point lowerings in accordance with equation (8) and hence presumably one which is neither associated, dissociated, nor hydrated, will be called a "normal solute." Fig. 2 shows the curve of a "normal solute," together with the curves given by the three salts. In this figure values of the mole per cent. 100 N' are taken as ordinates and values of Δt as abscissas. The dotted lines crossing these curves are iso-concentration lines, that is, lines showing the positions of equal values of n' for the three salts. The same relations are shown more exactly in Table VIII. This table shows ($\Delta t_{\text{obs.}}$) the freezing-point lowerings of each salt for the concentrations (n') given at the top of the table; and also the corresponding values ($\Delta t_{\text{n.s.}}$) which a "normal solute" would give at the concentration $(1 + \gamma)\,n'$, the values for γ being those given in column VIII of Tables V, VI and VII.

TABLE VIII.—THE THREE SALTS COMPARED WITH A "NORMAL SOLUTE".

n'.	0.05	0.1	0.2	0.3	0.5	1.0
			$CsNO_3$.			
$\Delta t_{\text{obs.}}$	0.168°	0.325°	0.622°	0.897°	1.419°	(2.6)°
$\Delta t_{\text{n.s.}}$	0.173	0.336	0.650	0.953	1.528	(2.9)
$\Delta t_{\text{obs.}} - \Delta t_{\text{n.s.}}$	—0.005	—0.011	—0.028	—0.056	—0.109	—(0.3)
			KCl			
$\Delta t_{\text{obs.}}$	0.175°	0.345°	0.680°	1.009°	1.658°	3.287°
$\Delta t_{\text{n.s.}}$	0.177	0.348	0.684	1.013	1.656	3.209
$\Delta t_{\text{obs.}} - \Delta t_{\text{n.s.}}$	—0.002	—0.003	—0.004	—0.004	0.002	0.078
			LiCl.			
$\Delta t_{\text{obs.}}$	0.177°	0.351°	0.694°	1.049°	1.791°	3.792
$\Delta t_{\text{n.s.}}$	0.175	0.344	0.675	1.000	1.636	3.183
$\Delta t_{\text{obs.}} - \Delta t_{\text{n.s.}}$	0.002	0.007	0.019	0.049	0.155	0.609

If both the ions and un-ionized molecules of the salts were "normal

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[1] *Technology Quarterly*, **21**, 373 (1908).

[2] *E. g.*, for a 1.089 weight-normal solution, equation (8) gives $\Delta t = 1.987°$. For a solution of ethyl alcohol of this concentration Raoult (*l. c.*) found $\Delta t = 1.990°$.

solutes" the corresponding values of Δt would all be identical and the four curves of Fig. 2 would coincide. That they are far from doing so is evident from the figure and from the data of Table VIII. The difference in the behaviors of electrolytes in their effect upon the freezing point is a well known fact, which has been emphasized recently by the extensive investigations of H. C. Jones and his co-workers. Jones attributes this difference to the different degrees of hydration of the electrolytes and attempts to calculate the approximate degrees of hydration by assuming that the difference between the observed freezing-point lowering and that required by the laws of the infinitly dilute solution is due entirely to hydration. That such a procedure is theoretically

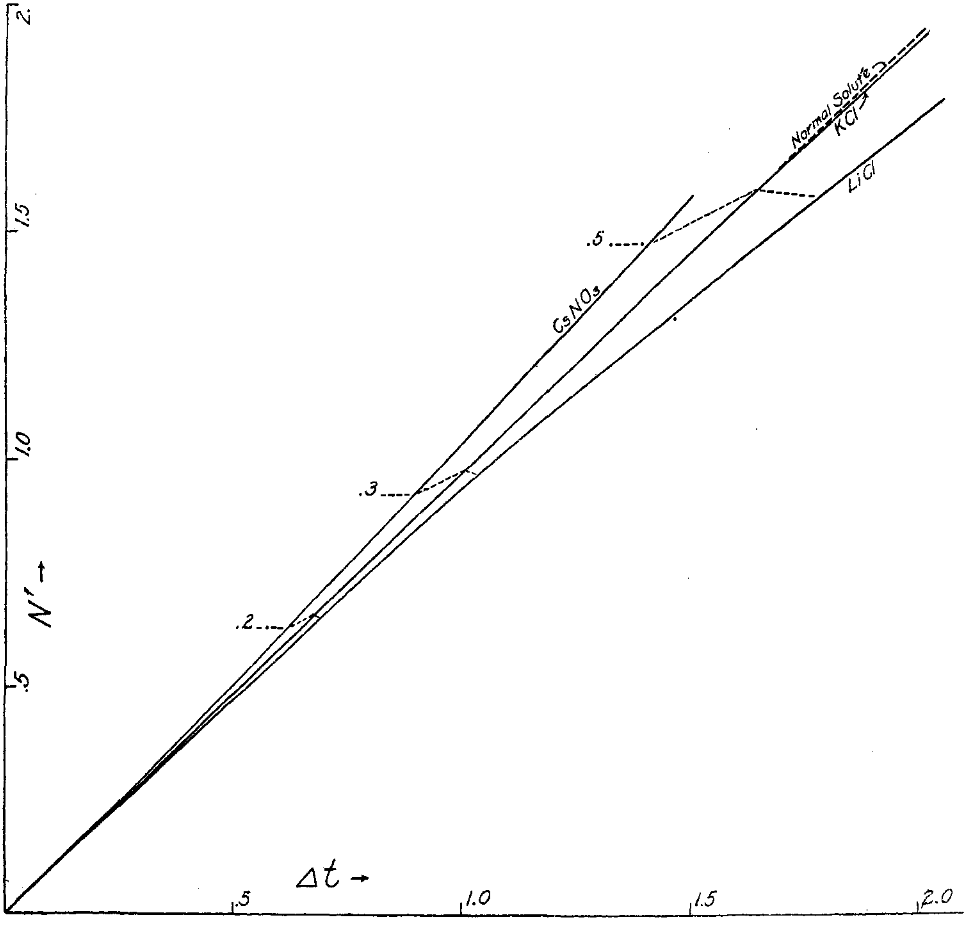

Fig. 2.

unjustifiable and leads to improbable and even absurd results has already been pointed out.[1]

It was hoped that the present investigation might lead to some less objectionable method of estimating the degree of hydration of an electrolyte in solution and, as explained in the introduction, the two salts cesium nitrate and lithium chloride were included in the first experiments because, while both belong to the simplest type of electrolytes, they represent opposit extremes as regards their degrees of hydration. Let us therefore examin the results of the investigation, with this object in mind.

Turning to Fig. 2 and to Table VIII, and considering first the behavior of potassium chloride, it will be noted that, up to a concentration of about 0.5 mole of potassium chloride per 1000 grams of water, the behavior of this salt is (within the experimental error) in exact agreement with the assumptions, (1) that it is unhydrated, and (2) that both the ions and the un-ionized molecules are "normal solutes," each producing upon the freezing point the same effect as would be produced by an equal number of alcohol molecules, for example.[2]

Are these two assumptions, therefore, to be considered as justified? This question must seemingly be answered in the negative: (1) because we have independent evidence[3] that the ions of potassium chloride are hydrated and (2) because if ions and un-ionized molecules *both* behave as "normal solutes;" the mass-action law becomes a thermodynamic necessity;[4] while we know that it is not even approximately obeyed by this salt. It seems probable, therefore, that there are two influences at work in the case of strong electrolytes. One of these, which is probably closely connected with the "abnormal" behavior which produces the deviation from the mass-action law, operates to produce too small a freezing-point lowering.[5] The other, the hydration influence, naturally operates to produce too great a depression of the freezing point, and in the case of potassium chloride it happens that these two effects exactly counterbalance each other and make the salt apparently exhibit the behavior of a normal solute.

Turning now to cesium nitrate, it is evident that if deviation from the

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[1] *Technology Quarterly*, 21, 367 (1908). For example, in a liter of a 4 molal solution of H_2CrO_4, Jones finds that "41.75 mols" (four significant figures!) of water are "combined" with the solute, and this in spite of the fact that *a liter of a 4 molal H_2CrO_4 solution contains only 36.5 moles of water altogether.*

[2] This is, of course, equivalent to the statement that the degree of ionization of this salt as calculated from conductivity data agrees exactly with the value calculated from the freezing-point lowering.

[3] *Loc. cit. Technology Quarterly*, and THIS JOURNAL, 31, 322 (1909).

[4] Cf. Article No. 2 of this series, THIS JOURNAL, 33, 1461–2 (1911).

[5] This point will be discussed in more detail after some investigations now in progress have been brought to a conclusion.

behavior of the "normal solute" could be ascribed wholly to hydration, this salt must be negatively hydrated. From Table VIII it is clear that the deviation is quite appreciable even at such a low concentration as 0.1 normal. From what has just been said regarding potassium chloride, however, it will be readily understood that in the case of cesium nitrate the hydration is entirely lacking or is too small to compensate for the abnormal behavior referred to above, so that the freezing-point curve is what we might expect for a salt which is unhydrated but which exhibits towards the mass-action law the well known behavior of the strong electrolytes.

Turning finally to lithium chloride, its behavior evidently indicates a comparatively high degree of hydration.

If we consider now the question of the calculation of the degrees of hydration of potassium and lithium chlorides, we meet with numerous difficulties. Evidently deviation from the behavior of the "normal solute" cannot be made the basis for such a calculation because this would give a negative hydration to cesium nitrate. The least objectionable method would probably be to first correct the data for the three salts to the same temperature, 0°, with the aid of heat of dilution data; and then by studying the ions and un-ionized molecules separately, by methods previously indicated,[1] obtain functional relations connecting activity and concentration for each kind of molecules. From these data a curve for the "normal unhydrated strong electrolyte" might perhaps be established, which could be made to serve as the basis for calculating the degree of hydration of another electrolyte which deviated from it. Before such a method can be employed, however, further investigation will be required in order to secure the necessary data. Meanwhile, we can make what may be called the "best guess" in the following manner:

Assume that the cesium nitrate curve of Fig. 2 is the normal curve for an unhydrated uni-univalent salt and assume further that the abnormal behavior which causes the deviation of this curve from that of the "normal solute" affects the other salts to an equal extent. Then if we neglect for the present the differences in temperature and in the degrees of ionization of the salts, the degree of hydration can be calculated from the following equation,

$$N'_{\mathrm{CsNO_3}} = \frac{n'(1+\gamma)}{55.53 + n'(1+\gamma) - hn'}, \tag{9}$$

in which h is the number of moles of water combined with one mole of the salt in question at the concentration n' moles per 1000 grams of water, at which concentration its degree of ionization is γ. $N'_{\mathrm{CsNO_3}}$ is the mole fraction of cesium nitrate in a solution which gives the same freezing-point lowering as the salt in question. $N'_{\mathrm{CsNO_3}}$ can be obtained graph-

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[1] THIS JOURNAL, **32,** 492–3 (1910).

ically from Fig. 3. Such a calculation gives for a 0.5 normal solution, h = about 9 for KCl and about 18 for LiCl, figures whose order of magnitude is doubtless correct.

It is our intention to continue this work until, of the uni-univalent salts, the iodides, nitrates and chlorides of cesium, potassium, sodium and lithium have been included.

10. Cesium Nitrate and the Mass Action Law.

In 1902 W. Biltz published[1] a set of freezing-point data for aqueous solution of cesium nitrate. From these data he calculated, in the usual manner, a set of values for the degree of ionization of the salt in the different solutions studied. On substituting these values in the Ostwald Dilution Law, $\gamma^2/(1-\gamma)V=K$, he found that the values of K thus obtained did not exhibit the usual regular variation with concentration shown by other electrolytes, but showed irregular variations about a mean value of 0.34, throughout the concentration range 0 to 0.43 normal. The values of 100 K which he thus obtained are shown in column VIII of Table IX. From these results Biltz drew the following conclusions: "Das Cäsiumnitrat folgt dem Massenwirkungsgesetze exakt..... Cäsiumnitrat ist demnach der erste starke Elektrolyt, dessen Dissoziationsverhältnisse genau bekannt sind. Dadurch ist zugleich die Annahme widerlegt, dass die Abweichungen von dem Massenwirkungsgesetze durch die Anwesenheit von Ionen in grösserer Zahl prinzipiell bedingt sind. Der Grad der Dissoziation hat, wie man auch schon aus dem zuerst gegebenen Versuchsmaterial ersehen konnte, keinen erkennbaren Einfluss auf der Grösse der Abweichungen, vorausgesetzt, dass man γ aus Gefrierpunktserniedrigungen berechnet."

The results obtained in the present investigation do not confirm the data given by Biltz and the conclusions to which they lead regarding the behavior of this electrolyte with reference to the Law of Mass Action are also somewhat different from those arrived at by Biltz. In view of the frequent citations to the "exceptional" behavior of this salt which one meets in the literature,[2] this question will be considered in the light of the results obtained in our investigation.

Comparison with Biltz's Values.—Column I of Table IX gives the compositions of the solutions investigated by Biltz, column IV contains the corresponding freezing-point lowerings found by him, and column V

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[1] *Z. physik. Chem.*, 40, 218 (1902).

[2] *E. g.*, Abegg's "Handbuch der Anorganischen Chemie," Band II (1), p. 450; Weinstein's "Thermodynamik und Kinetik der Körper," Band III (2), p. 716. Morgan's "The Elements of Physical Chemistry," p. 319. Wegscheider in his recent paper, "On the Anomaly of the Strong Electrolytes and the Limits of the Validity of the Dilution Law" (*Z. physik. Chem.*, 69, 627 (1909)), discusses Biltz's results at some length and dissents from the latter's conclusion with respect to the influence of the ions upon the deviation from the Mass Action Law.

TABLE IX.

No.	I. n'. Mole $CsNO_3$ per 1000 g. water.	II. V_B 17.5°/17.5°. Biltz.	III. V. 0°/4°. W. and M.	IV. Δt_B. Biltz.	V. $\Delta t \pm 0.002°$ W. and M.	VI. $\frac{\Delta t_B}{0.0185n'} - 1 = 100\gamma_B$.	VII. $\frac{\Delta t}{0.0186n'} - 1 = 100\gamma$.	VIII. $\frac{100\gamma_B^2}{(1-\gamma_B)V_B} = 100K_B$.	IX. $\frac{100\gamma^2}{(1-\gamma)V} = 100K$.
1	0.00766	130.7	130.5	0.028	0.028	98.0	96.0 ± 14.0	33	18.0 ± 70.0
2	0.0194	51.6	51.6	0.070	0.068	95.0	88.0 ± 6.0	35	13.0 ± 8.0
3	0.0465	21.6	21.6	0.164	0.157	90.7	81.0 ± 2.0	(41)	16.6 ± 3.0
4	0.0988	10.2	10.17	0.331	0.322	81.0	75.0 ± 1.0	34	22.1 ± 1.6
5	0.1421	7.09	7.09	0.460	0.453	75.0	71.5 ± 0.8	32	25.3 ± 1.2
6	0.2100	4.81	4.81	0.662	0.650	70.4	66.4 ± 0.5	35	27.2 ± 0.8
7	0.2987	3.39	3.40	0.907	0.894	64.1	60.9 ± 0.4	34	27.6 ± 0.6
8	0.3861	2.62	2.64	1.125	1.124	57.5	56.4 ± 0.3	(30)	27.6 ± 0.4
9	0.4339	2.33	2.356	1.267	1.248	57.8	54.6 ± 0.2	34	27.9 ± 0.4
10	(0.5000)	....	2.05	...	(1.419 ± 0.005°)	....	52.6 ± 0.2	..	28.6 ± 0.8

shows the freezing-point lowerings given by our empirical equation (5). A comparison of the two sets of data shows that from a concentration of 0.05 molal up, all of Biltz's values differ from ours by from 0.01° to 0.02°, except in the case of solution number 8, for which the values are identical.[1]

The Ostwald Dilution Law.—If an electrolyte is assumed to be a *normal solute* and the solution be sufficiently dilute, its degree of ionization would be given by the equation

$$\gamma = \Delta t/k_F n' - 1, \qquad (10)$$

where k_F is molal freezing-point lowering. The theoretical value for k_F as computed from the relation, RT^2_0/L_0 is 1.86° for water. This value is moreover confirmed by the recent careful freezing-point measurements of Bedford,[2] who found for cane sugar solutions the value 1.86° and for potassium chloride solutions the value 3.72° = 2 × 1.86°, at high dilutions.

At the time of Biltz's investigation, 1.85° was the generally accepted value for k_F and he employed this value in calculating the degree of ionization of the cesium nitrate in the solutions investigated by him. His results for 100 γ are shown in column VI of Table IX. If, however, we employ the value 1.86° and use the values for Δt given in column V, we obtain for 100 γ the values shown in column VII. The deviation which would be caused by the probable error in the corresponding value of Δt is also indicated after each value in this column.[3] It is evident that below 0.05 normal the values are too uncertain to be relied upon. Those above 0.3 normal will also be somewhat in error from the fact that equation (10) is applicable only to dilute solutions.

In order to test the mass-action law for cesium nitrate solutions, Biltz substituted the values for γ from column VI and the values for V from column II in the Ostwald Dilution Law,

$$\gamma^2/(1 - \gamma)V = K, \qquad (11)$$

and obtained the values for 100 K_B given in column VIII. These values evidently vary irregularly and rejecting Nos. 3 and 8, Biltz adopted 0.34 as the mean value for K.

If the values for γ given in column VII and the values for V of column III be employed, the values for 100 K shown in column IX are obtained. After each value in this column is given the deviation[4] which would be produced by the probable error in the corresponding value of Δt.

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[1] Biltz rejected the value for this solution in computing his mean value of K, see column VIII.

[2] *Proc. Roy. Soc. London* (*A*) 83, 454 (1910).

[3] These deviations are computed from the relation $\delta\gamma = \delta(\Delta t)/1.86n'$.

[4] These deviations are computed from the equation

$$\delta K = \left(K + \frac{\Delta t}{0.93} - \frac{2}{V}\right)\frac{\delta(\Delta t)}{3.72n' - \Delta t}. \qquad (12)$$

The values for K are shown graphically in curve IV of Fig. 3. Values of n' are plotted as ordinates and those of K as abscissas, using the scale 1 unit = 0.025 as ordinates and 1 unit = 0.0286 as abscissas. Through each point is drawn a double-headed arrow whose length is equal to the probable error of the location of the point. An inspection of this curve shows that K increases fairly rapidly up to a concentration of about 0.2 normal and from thence up to 0.5 normal it is nearly constant.

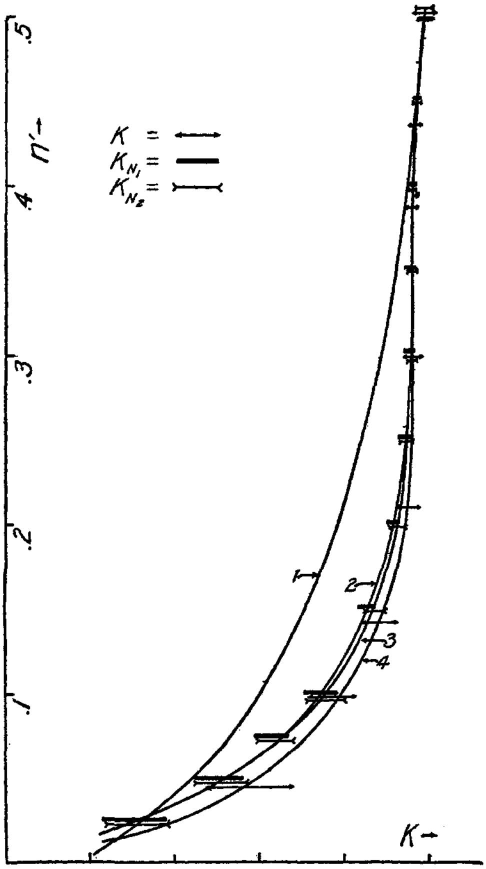

Fig. 3.

Now the Ostwald Dilution Law has no theoretical basis except for very dilute solutions and it is exactly in this region that it is not obeyed by cesium nitrate according to the above calculation. If we wish to study this equilibrium for concentrations above 0.1 normal a more general law for chemical equilibrium should be employed, one which, at least, does not contain the assumption that the solution is dilute.

The Law for Chemical Equilibrium in an Ideal Solution.—The general law for chemical equilibrium is an "ideal" or "perfect" solution and is expressed by the equation[1]

$$\frac{N_A^a \, . \, N_B^b \ldots}{N_M^m \, . \, N_N^n \ldots} = K_N. \qquad (13)$$

This differs from the Ostwald Dilution Law only in the substitution of *mole fractions* in place of *volume concentrations*. For the dissociation of a binary electrolyte it assumes the form

$$N_i^2/N_U = K_N \qquad (14)$$

where N_i is the mole fraction of each ion and N_U the mole fraction of the un-ionized molecules.

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[1] For a derivation of this equation see Contribution No. 1, of this series, THIS JOURNAL, **32**, 668 (1910).

If the solvent is water and the degree of ionization of the salt is γ_N and its concentration is n' moles per 1000 grams of water we have

$$N_i = \frac{\gamma_N n'}{55.53/A + (1 + \gamma_N)n'} \tag{15}$$

and

$$N_u = \frac{(1 - \gamma_N)n'}{55.53/A + (1 + \gamma_N)n'} \tag{16}$$

and equation (14) becomes

$$\frac{\gamma_N^2 n'}{[55.53/A + (1 + \gamma_N)n'](1 - \gamma_N)} = K_N \tag{17}$$

in which A is the association factor for water, *i. e.*, 18 A is the average molecular weight of the water at the temperature in question.

Calculation of γ_N.—In order to calculate γ_N from the freezing-point data, we will make use of the relation connecting the freezing-point lowering and mole fraction of the solute in the case of an "ideal" solution. If water is the solvent and the solution is only moderately concentrated we have seen above (p. 1703), that equation (8) is a sufficiently exact numerical statement of this relation. If we replace N', the mole fraction of the solute, by $\frac{in'}{1000/18 + in'}$ this equation takes the form

$$in' = (\Delta t/1.858)\ (1 + 0.0055\Delta t). \tag{18}$$

If the electrolyte were a normal solute and were not hydrated, the van't Hoff i or the "mole number" would be equal to $1 + \gamma_N$ and we could therefore employ this equation in order to obtain the degree of ionization of such an electrolyte. Now, as we have seen above, cesium nitrate is probably the least hydrated of all electrolytes and if we apply equation (18) to the data for this salt, we obtain the values for the per cent. of ionization, $100\gamma_N$, which are shown in column II of Table X.

TABLE X.

I. n'.	II. $100\gamma_N$.	III. $100K_N$. $A = 2$.	IV. $100K_N$. $A = 3$.	V. $100\gamma'$. $\pm 0.3\%$.	VI. $100K'_N \pm 0.1\%$. $A = 3$.
0.0250	82.0±4.0	3.4 ±0.8	5.1 ±1.2	89.4	9.2
0.0500	80.0±2.0	5.6 ±0.6	8.4 ±0.9	86.5	13.6
0.0750	77.0±1.0	7.0 ±0.4	10.5 ±0.6	83.8	15.9
0.1000	75.0±1.0	8.4 ±0.4	12.5 ±0.6	81.5	17.6
0.1500	71.3±0.7	9.5 ±0.2	14.3 ±0.3	....	....
0.2000	68.0±0.5	10.2 ±0.18	15.2 ±0.27	75.4	22.8
0.2500	64.8±0.4	10.49±0.14	15.60±0.21	....	....
0.3000	61.7±0.3	10.57±0.10	15.71±0.15	71.9	27.2
0.3500	59.1±0.3	10.63±0.10	15.80±0.15	....	....
0.4000	57.0±0.3	10.67±0.08	15.81±0.12	68.5	29.4
0.4500	55.3±0.2	10.84±0.06	16.08±0.09	....	....
0.5000	(53.6±0.5)	11.1 ±0.26	16.40±0.39	65.8	31.4

Values of K_N.—We will now substitute these values in equation (17) and calculate the equilibrium constant K_N. Before we can do this, however, it will be necessary to assign some value to the association factor A. This factor is, however, not a constant but is a function of n' and is connected with it in such a way that as n' increases A probably decreases, so that even if we knew the value of A accurately for pure water and employed this value in our equation, we should not expect to find a constant value for K_N even if the Mass Law were obeyed, but a slowly increasing value as the concentration increases. Authorities agree that water at 0° is composed chiefly of double and triple molecules so that A is probably not less than 2 or greater than 3. Two series of values for 100 K_N have therefore been computed, one upon the basis that $A = 2$, column III, and the other upon the basis that $A = 3$, column IV.[1] These values are shown graphically in curves II and III, respectively, in Fig. 3, values of n' being plotted as ordinates and values of 100 K_N as abscissas using the scale, 1 unit = 0.025 as ordinates and 1 unit = 0.0111 and 0.0164, respectively, as abscissas.

An inspection of these curves shows that between 0.2 and 0.5 normal 100 K_N increases slowly (from 10.2 to 11.1 for $A = 2$ and from 15.2 to 16.4 for $A = 3$). The direction of the curve in the more dilute solutions, however, indicates that at high dilutions K_N must have a very different value.

The Equilibrium "Constant" Computed from Conductivity Data.—By employing the equation $\gamma = \Lambda/\Lambda_0(\eta/\eta_0)^{0.826}$ for calculating the degree of ionization we obtained the values for γ given in column V of Table X. It will be noted that they are uniformly larger than those obtained from the freezing-point data.

If these values be substituted in equation (17), the values for the equilibrium constant, K'_N, given in column VI of Table X, are obtained. These are shown graphically in curve I of Fig. 3. As in the other curves of this figure, the scale for the abscissa was 1 unit = 0.1 of the value of K'_N for $n' = 0.5$. The values of K'_N increase continuously with n' which is the normal behavior for a strong electrolyte.

Conclusion.—The characters of the curves shown in Fig. 3 are in general the same. Curve I, however, shows a fairly gradual rise of K throughout its whole course, while the other curves show a rapid rise at first, followed by a very slow rise, so slow in fact that it is perhaps within the experimental error. There is, however, some indication that from 0.4 normal on, a more rapid rise again occurs in the case of curves II and III. Although between 0.2 and 0.4 normal K_N appears to be reasonably con-

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[1] The probable errors given for these values of K are computed from the relation

$$\delta K_N = [K_N + 0.0192A\ \Delta t - 0.036A\ n'] \frac{0.54\delta(\Delta t)}{2n' - 0.54\Delta t}. \qquad (19)$$

stant, the remainder of the curve (II or III) clearly will not justify the statement that the mass-action law is obeyed by this salt when γ is obtained from freezing-point data. With cesium nitrate, therefore, as with the other strong electrolytes, the freezing point method cannot be relied upon to give correct values for γ, for the validity of the mass-action law is implicitly assumed whenever γ is calculated by this method.

11. Summary.

1. The freezing point lowerings, densities, relative viscosities, and equivalent conductances of solutions of cesium nitrate, potassium chloride, and lithium chloride at 0° have been investigated and a complete set of these data are given in Tables V, VI, and VII. The data extend to normal solutions in the case of potassiun and lithium chlorides and to 0.5 normal in the case of cesium nitrate.
2. The cryohydric point for cesium nitrate is —1.254°.
3. When the freezing-point curves (Fig. 2, mole fraction of solute plotted against freezing-point lowering) for the three salts are compared with the curve of the "normal solute," potassium chloride is found to agree exactly up to about 0.5 normal, lithium chloride deviates decidedly in the direction of hydration while cesium nitrate deviates decidedly in the opposit direction. The conclusion is drawn that deviation from the behavior of a "normal solute" (an unhydrated non-electrolyte) cannot serve as a basis for the calculation of the degree of hydration of an electrolyte. Another method for making this calculation is outlined and, as a provisional result, about 9 molecules of water are found to be in combination with one of KCl and about 18 with one of LiCl in a half normal solution of the electrolyte.
4. The freezing-point data for cesium nitrate are compared with the data of Biltz and his conclusion, that this salt obeys the Mass Action Law, is only partially substantiated.

URBANA, ILL.

[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, No. 199.]

THE WEIGHT OF A FALLING DROP AND THE LAWS OF TATE. X. THE DROP WEIGHTS OF SOME FURTHER ASSOCIATED AND NON-ASSOCIATED LIQUIDS, AND THE SURFACE TENSIONS AND CAPILLARY CONSTANTS CALCULATED FROM THEM.

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The associated and non-associated liquids used in this research were selected for the following purposes: (1) The further testing of the new