*The probable total error involved in the measurements in this case was ±0.15 per cent.*

The theoretical principle proposed in Sec. 2 cannot be directly applied to this case for the obvious reason, again, that acetic acid vapor is associated and that its association varies with the temperature. A general theoretical study of cases complicated by phenomena of association or dissociation will be taken up in these laboratories at the earliest opportunity.

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[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASS. INSTITUTE OF TECHNOLOGY. NO. 43.]

# THE CONDUCTIVITY AND IONIZATION OF POLYIONIC SALTS.

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Received July 14, 1909.

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## 1. Outline of the Investigation.

In a previous publication from this laboratory[1] there was described an extended series of investigations on the conductivity and ionization of substances in aqueous solution through a wide range of temperature. The substances studied were, however, of the simpler ionic types, containing only univalent and bivalent ions. The purpose of this research was to extend the measurements to salts with ions of higher valence as well as to study other salts of the uni-bivalent type.

The substances investigated are potassium ferrocyanide, barium ferrocyanide, calcium ferrocyanide, lanthanum nitrate, lanthanum sulphate, potassium oxalate, calcium nitrate, potassium citrate, and potassium nitrate. Their conductivities were measured at various concentrations through a range of temperature extending from 0° to 156°, except in certain cases, when measurements could not be made at the higher temperatures, on account of partial decomposition of the salt. The temperatures employed were 0°, 18°, 25°, 50°, 75°, 100°, 128° and 156°. The concentrations studied were 2, 12.5, 50 and 100 millinormal, and in

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[1] Carnegie Institution of Washington, Publication No. 63 (1907). Briefer accounts of the work have also been given in *J. chim. phys.*, 6, 505–23 (1908); THIS JOURNAL, **30**, 335–53 (1908).

some cases also 200 and 400 millinormal. In addition, freezing-point measurements were made on a series of solutions of the same salts. The results obtained are discussed with reference to the ionization of the various salts, and its variation with the concentration, temperature, and type of salt; and also with reference to the equivalent conductances of the ions at different temperatures.

This investigation has been made possible by the financial assistance afforded by the Carnegie Institution of Washington; and to the authorities of that institution we desire to express our great indebtedness.

## 2. Description of the Apparatus and Method.

*The Conductivity Vessels.*—For all temperatures except 0°, a platinum-lined steel bomb, fitted with a quartz cup containing a flat platinum electrode, as described in the previous publications,[1] was used. The measurements at 0° and a few at 18° and 25° were made in a glass cell of the pipette form, such as has also been previously described.[2] Two such cells were used, which had different conductance capacities; and they were so made that they fitted into a silvered vacuum-jacketed tube, which, when filled with ice and water, formed the 0° bath. Readings at 25° were made both in the bomb and in one of these cells as a check. All preliminary measurements were made in the glass cells.

*Conductivity Measuring Apparatus.*—This was of the usual type. The slide-wire was calibrated by the method of Strouhal and Barus. Heavy lead wires were used; and by means of commutating switches, the measuring apparatus could be connected up to any one of the conductivity vessels. The lead-resistance was found to be 0.02 ohm, which is thus very small in comparison with the resistances measured.

*Thermometers.*—Three thermometers were used: the first for the temperatures up to 50°, the second for 75° and 100°, and the third for 128° and 156°. All were calibrated by comparison with a Baudin thermometer, certified by the Bureau of Standards in Washington.

*Heaters.*—In all the measurements with the bomb, the temperatures were secured by immersing it in a bath of pseudocumene contained in a well-jacketed cylindrical copper vessel. The bath could be heated electrically by passing a current, which could be varied at will, through a suitable heater, or cooled by flowing cold water through a coil of copper pipe immersed in the bath. In addition there was an auxiliary small electrical heater, which served the purpose of making the final adjustment of the temperatures. The bath was continually stirred by a propeller, and the temperature was kept constant within 0.02°, except perhaps at the two highest temperatures, where the variation was some-

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[1] *Loc. cit.*, p. 9, *et. seq.*

[2] *Loc. cit.*, p. 288; THIS JOURNAL, **31**, 732 (1909).

what larger. This bath and the method of procedure are the same as described in the previous publication.[1]

*Freezing-point Apparatus.*—As containing vessel a silvered vacuum-jacketed tube, about 15 cm. long and 5 cm. internal diameter, with a capacity of about 200 cc., was used. This was fitted with a cork stopper, through which passed the stem of a Beckmann thermometer, a short length of glass tubing through which passed a stirrer made of a light glass rod, and a glass tube drawn out and bent at the lower end and turned against the bulb of the thermometer. Through this tube the pipette was introduced and the samples for analysis were withdrawn. The procedure was as follows: Ice made by freezing pure water in a large test-tube was broken into small pieces in a mortar, and washed with pure water. It was then introduced into the vacuum tube in quantity sufficient to half fill it, and the tube was filled up with pure water. The stopper was put in place, and the ice and water thoroughly mixed. When the reading had been taken, some water was withdrawn by the pipette, a quantity of a cooled strong solution of the salt was added, and the whole vigorously stirred. The temperature became constant in about a minute, and remained constant to 0.001° for at least ten minutes. When temperature equilibrium had been reached, the pipette was rinsed out by withdrawing a little of the solution. A further quantity of solution, usually about 40 cc., was then withdrawn, and this was allowed to flow into a tared flask, weighed, and analyzed by an appropriate method. The withdrawal of the solution produced no effect on the reading of the thermometer. More water was added, and the whole process repeated. In this way measurements were made of the freezing points of a series of solutions of decreasing concentration.

The Beckmann thermometer was compared with a corrected Baudin standard thermometer over several ranges of about 5° between 0° and 10°. The correction amounted to about 0.1 per cent. The depressions given are all corrected values.

## 3. Preparation of the Substances and Solutions.

*Potassium Chloride.*—The salt used for determining the conductance capacity of the bomb and the glass cells was obtained by recrystallizing three times from water some analyzed C. P. salt obtained from the J. T. Baker Co. The 0.01 molal solution employed was made up by dissolving the calculated quantity of the salt in a calibrated 1000 cc. flask. A fresh solution was made up for each determination. The water used in this case and throughout this investigation had a specific conductance of $0.6 - 0.7 \times 10^{-6}$ at 18°.

*Potassium Nitrate.*—This salt was purified by repeated crystallizations from water, and was dried at 140°. The solutions were made up by dissolving the appropriate quantities of the salt in a known volume of water.

*Potassium Ferrocyanide.*—This was prepared by recrystallizing, twice from water,

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[1] *Loc. cit.*, p. 240–1.

a sample of the salt obtained from Kahlbaum. The product was light yellow in color. It contained no ferricyanide. As this salt crystallizes with water, it was necessary to determine its water content. For this purpose, a weighed portion of the purified salt was heated to 90°-100° for about 1½ hours, when it had attained constant weight; nor did it lose in weight appreciably when kept two hours at 130°, although a slight amount of decomposition had taken place, as shown by a slight bluish color. In order to make sure that the salt dried at 90° was anhydrous, it was analyzed by titration with standard potassium permanganate solution by the following procedure: A weighed portion of the potassium ferrocyanide was dissolved in 50 cc. of water: to this were added 50 cc. of "dilute" sulphuric acid (made up by dissolving 40 cc. of concentrated $H_2SO_4$ in a liter of water); this was then titrated against a solution of potassium permanganate, which had been previously standardized against pure sodium oxalate (a sample prepared "nach Sorensen," and obtained from Kahlbaum). At first it was found a little difficult to determine the end-point exactly, owing to the deep yellow color of the ferricyanide formed by the oxidation; this difficulty was surmounted by the following device: In a precisely similar flask, an approximately equivalent quantity of pure recrystallized potassium ferricyanide was dissolved in a mixture of 50 cc. water and 50 cc. "dilute" sulphuric acid. This flask was set beside that containing the solution to be titrated, when the slightest difference in tint could be detected with ease. When the end-point had been reached, potassium permanganate solution was added to the blank until it had reached the same color as the oxidized solution. The amount used up by the blank, which was always less than 0.1 g. of an approximately 0.06 normal solution, was subtracted from the first reading. A weight burette was used throughout, and it was found that a definite change of color was produced at the end-point by the addition of one drop (0.03 g.) even though an approximately 0.06 normal permanganate solution was used. The results of analyses by this method of several samples of potassium ferrocyanide dried at 90-100° gave 15.16, 15.14, 15.15, 15.16 per cent. Fe, while $K_4Fe(CN)_6$ requires 15.17 per cent. Fe: thus, potassium ferrocyanide is completely dehydrated by heating it for two or three hours at 90°. As a further check on the accuracy of this method, the potassium ferrocyanide was also analyzed by heating a weighed amount with 15 cc. concentrated sulphuric acid in a Jena glass flask until decomposition was complete.[1] When cool, water was added, and the mixture was boiled until everything went into solution: it was then passed through a Jones reductor and titrated with permanganate. A precisely similar blank experiment was made, and the permanganate used was subtracted from that used by the solution. Two such analyses gave 15.16, 15.20 per cent. Fe, in excellent agreement with those obtained by direct titration, and with the theoretical value.

The product dehydrated at 90° was used at first for the conductivity measurements; later, samples were used of the recrystallized salt partially dehydrated in a desiccator and ground, the composition of the salt being determined by titration as just described. Solutions of both kinds of samples showed the same conductances, provided that while drying the salt had not been heated above 100°. In the later experiments, use was made exclusively of the salt dried at the ordinary temperature. This possesses the advantage that the possibility of decomposition is excluded and that the salt is not hygroscopic, while the anhydrous salt takes up moisture so quickly that it is difficult to weigh it out with accuracy. The solutions were made up by dissolving weighed-out portions of the salt in a previously calibrated 1000 cc. flask.

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[1] This reaction is slow, but is catalyzed by the addition of a few drops of water: even then, however, two or three hours are necessary. If the decomposition is incomplete, the subsequent addition of water produces a blue color.

*Barium Ferrocyanide.*—To a fairly concentrated solution of potassium ferrocyanide was added concentrated hydrochloric acid in quantity rather more than sufficient to set free the hydroferrocyanic acid, which was then precipitated from this solution by the addition of ether. It was filtered off, washed with ether, and dried with a suction pump. The ether compound of the free acid prepared in this way was transferred to a flask, and to it was added a suspension in water of carefully purified barium carbonate until the solution was neutral. The difficultly soluble barium ferrocyanide (mixed with a little carbonate) was filtered off, washed repeatedly with water, and finally recrystallized from boiling water. In this operation, the solution must not be boiled long, since otherwise some decomposition takes place. Light yellow crystals were thus obtained, which were dried in a desiccator and analyzed by titration just as in the case of the potassium salt, except that a little barium carbonate was added to the blank, in order more nearly to reproduce the conditions of the experiment, in which a white precipitate of barium sulphate is formed. The exact determination of the end-point is rendered more difficult by the necessity of working in very dilute solution arising from the slight solubility of the salt. A weighed sample which had been kept for 1½ hours at 85°, gave on analysis, 45.47 per cent. Ba, corresponding to 9.28 per cent. Fe; direct titration gave 9.33 and 9.36 per cent. Fe. This corresponds very closely to the composition of the monohydrate $Ba_2Fe(CN)_6 + 1H_2O$. From this, the composition of the unheated sample used in making up the solutions, was found to be represented by the formula $Ba_2Fe(CN)_6 + 6.4H_2O$, which corresponds to a molecular weight of 601.

*Calcium Ferrocyanide.*—The ether compound of hydroferrocyanic acid, prepared as described previously, was placed in a flask along with water; excess of purified calcium carbonate was added; and the solution was filtered. To the filtrate was added a large quantity of methyl alcohol, in order to precipitate the calcium ferrocyanide. It was filtered off, and dried with a suction pump. In order to purify the salt, it was dissolved in water and reprecipitated with methyl alcohol three times. The salt prepared in this manner was a light yellow powder, containing some methyl alcohol as well as water. The methyl alcohol was removed by keeping the salt for some days in an evacuated desiccator over sulphuric acid, as it was found that heating the salt always produced slight decomposition. Two separate samples were prepared in this way; they were analyzed with concordant results by precipitating the calcium as oxalate and also by titrating the ferrocyanide with permanganate. Solutions made up from these two samples, containing 2 milli-equivalents per liter, showed identical conductances.

*Potassium Oxalate.*—The two samples used were recrystallized three times from water, dried in the desiccator, powdered, and analyzed by titration with potassium permanganate. Solutions containing 2 milli-equivalents per liter made up from either sample showed the same conductance.

*Calcium Nitrate.*—A careful qualitative analysis of a sample of this salt, obtained from Eimer and Amend, showed that the amount of impurity, which consisted almost entirely of strontium, was not more than 0.1 per cent. A stock solution was made up and was analyzed by precipitating the calcium as oxalate. The various dilutions were made up by diluting the requisite weight of the stock solution up to one liter. Two separate solutions containing 2 milli-equivalents per liter gave concordant results.

*Lanthanum Nitrate.*— A sample of carefully purified lanthanum oxide was obtained through the kindness of Professors C. L. Parsons and C. James of New Hampshire State College; and to them we desire to acknowledge our indebtedness for placing this substance at our disposal. A careful qualitative analysis showed that the amount of impurities—other than rare earths—was certainly less than 0.1 per cent. We made no examination for other rare earths, but Prof. James stated that the proportion was very small. Moreover, the presence of even one or two per cent. of these similar elements would hardly effect the conductance appreciably.

The stock solution of lanthanum nitrate was made up by shaking an excess of the oxide with a solution of nitric acid of known concentration, determined by comparison with a solution of pure hydrochloric acid, which had been standardized by precipitating with silver nitrate and weighing the silver chloride. The lanthanum nitrate solution was neutral to litmus. It was analyzed by evaporating a weighed quantity and igniting to oxide, whereby it was found that the lanthanum was exactly equivalent to the nitric acid, assuming the atomic weight of lanthanum to be 139.0, as adopted by the International Atomic Weight Commission for 1908. The solutions measured were made up by dilution of the stock solution.

*Lanthanum Sulphate.*—A stock solution, about 0.25 normal in concentration, was made up in a manner exactly similar by shaking lanthanum oxide with a standardized sulphuric acid solution. The solution so obtained was slightly acid to litmus, but a comparison of the color given to methyl orange by this solution and by known solutions of hydrochloric acid showed that the hydrogen-ion concentration was between $10^{-4}$ and $10^{-5}$: this would introduce an error of only a few hundredths of one per cent. The lanthanum content was not directly determined in this case, but was calculated from the concentration of the sulphuric acid. The solutions measured were made up from the stock solution by dilution.

*Potassium Citrate.*—Two lots of this salt were prepared by recrystallizing three times, from water, samples obtained from Schuchardt. Since a large amount could only be completely dried by heating for several days with slight traces of charring, the recrystallized salt was only partially dried at 125° and dissolved in water of a known low specific conductance. The concentrations of these solutions were determined by evaporating weighed amounts to dryness in platinum dishes and heating the residue to constant weight at 150°. Solutions containing 12.5 milli-equivalents per liter, made up from two samples, showed conductances agreeing within 0.3 per cent.

## 4. Conductance Capacity of the Bomb and Glass Cells.

The conductance capacity of the bomb and glass cells (*i. e.*, the factor by which the observed conductance must be multiplied to give the specific conductance) was determined at 18° or at 25° with a freshly prepared solution of potassium chloride 0.01 normal at 18°. The values adopted for the specific conductance of this solution were those given by Kohlrausch and Holborn, namely, 0.0012243 at 18° and 0.001412 at 25°.

The conductance capacities remained almost constant during the whole course of the work. Thus, that of the bomb varied only between 1.529 and 1.523. Such variations as did occur were attributable to replatinization of the electrodes, except in one case where it was due to a slight displacement of the electrodes.

The variation of the conductance capacity of the bomb with the temperature was computed, as previously described,[1] from the dimensions of the quartz cup used.

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[1] See *loc. cit.*, p. 79. The quartz cup had an effective height of 1.80 cm. and an internal diameter of 1.35 cm. The percentage corrections applied to the 18° value of the conductance capacity for the different temperatures were as follows:

| 50°. | 75° | 100°. | 128°. | 156°. |
|---|---|---|---|---|
| —0.05 | —0.10 | —0.14 | —0.19 | —0.24 |

## 5. The Water Correction.

The amount of this correction at the higher temperatures was determined by heating pure water in the bomb, after it had been freed as far as possible from adsorbed substance by previous heating with water. The corrections applied at 100°, 128° and 156° and to the return value at 18° were derived from two such concordant experiments. The correction of the initial value at 18° was determined by measurements in a glass cell of very small conductance capacity, inasmuch as the resistance of pure water in the bomb was so high that it could not be measured with accuracy. The corrections at the other temperatures were interpolated. The specific conductance ($\times 10^6$) in reciprocal ohms of the water was thus determined to be as follows:

| 0°. | 18°. | 25°. | 50°. | 75°. | 100°. | 128°. | 156°. | 18° R. |
|---|---|---|---|---|---|---|---|---|
| 0.3 | 0.8 | 1.4 | 2.6 | 3.5 | 4.5 | 6.0 | 7.5 | 1.5 |

The appropriate corrections were subtracted from the observed conductances of the salt solutions; they form only an insignificant fraction of that conductance, except at the concentration of 2 millinormal; and even there in the worst case the correction is only about 0.3 per cent. at 18° and about 1 per cent. at 156°.

## 6. The Equivalent Conductance Values Derived Directly from the Measurements.

From the measured values of the conductance (corrected for instrumental errors in the bridge and for the resistance of the lead wires) the conductance of the water in the cell (corresponding to the specific conductance given in the preceding section) was subtracted, and the result was multiplied by the conductance capacity corresponding to the temperature in question and divided by the concentration of the solution at that temperature, so as to give the equivalent conductance of the solute. The concentration just referred to was obtained by multiplying that at 4° by the specific volume[1] of water at the temperature of the measurement, it being assumed that the expansion of even the strongest solutions measured does not differ appreciably from that of water up to 156°— a justifiable assumption.[2]

In all the experiments, the solution after the heating was brought back to 18° or to 25° and its conductance again measured, in order to see whether any considerable contamination had occurred. These return values agreed in almost all experiments[3] with the original ones within

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[1] The values used were 1.0431 at 100°, 1.0685 at 128°, and 1.0980 at 156°.

[2] See *loc. cit.*, pp. 37 and 82.

[3] The conductance of the most dilute ferrocyanide solutions changed quite noticeably with the time at the higher temperatures, so that the return values were much less concordant than usual. For this reason also, the two ferrocyanides could not be studied above 100°. The solutions of the other salts were much more stable, al-

less than 1 per cent., except in two cases, where the results were rejected and the experiment repeated. No account was taken of the return values in the calculations. Owing to the check on the measurements thus afforded, duplicate experiments were in general considered unnecessary, but these were made in some cases, as indicated in the table below.

Table I contains the values in reciprocal ohms of the equivalent conductance calculated directly from the measurements in the manner described just above. These values are those of a solution whose concentration at 4° in milli-equivalents per liter is that given in the first column in the same row. In calculating the number of milli-equivalents the atomic weights used were those adopted for 1908 by the International Commission. The temperatures are those of the hydrogen-gas scale.[1] In cases where the result is a mean of concordant measurements made in different cells (the bomb and glass pipette) this is indicated by attaching to it an asterisk; where it is a mean from measurements with two independently prepared solutions in the same cell, by attaching a dagger.

The table also contains the values of the equivalent conductance ($\Lambda_0$) at zero concentration. These were obtained with the help of the expression $1/\Lambda = 1/\Lambda_0 + K(C\Lambda)^{n-1}$ by plotting the values of $1/\Lambda$ against those of $(C\Lambda)^{n-1}$, taking a value of $n$ such as would make the graph nearly a straight line, and also two other neighboring values of $n$ on opposite sides of this one. These three graphs were produced so as to intersect the $1/\Lambda$ axis, and the most probable value of the intercept chosen, representing the value of $1/\Lambda_0$. In those cases (namely, barium and calcium ferrocyanides and lanthanum sulphate) where a long extrapolation would have been necessary, the $\Lambda_0$ values were calculated by the principle of additivity from the values for the separate ions, the derivation of which will be described in a separate article. Since these

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though even with potassium oxalate a slight decomposition at the highest temperatures was noted. In the case of the lanthanum sulphate solution, some change—probably hydrolysis—took place above 128°, which rendered useless the measurements at 156°, for the conductivity decreased so rapidly with the time that no definite value could be obtained. The various return values for the concentration 12.5 show that at 25°, the conductivity gradually regained its initial value; this strengthens the idea that the salt was hydrolyzed with the formation of the very slightly soluble oxide or of a basic salt, which then, on cooling, recombined slowly with the acid. The solubility of the salt decreases with rising temperature; on this account, the measurements on the most concentrated solution could not be carried beyond 100°. The measurements with barium ferrocyanide also could not be carried to greater concentrations than 12.5, owing to the sparing solubility of the salt.

[1] In a few cases where the temperature of the measurement deviated slightly from the round temperature, the conductance was corrected by means of temperature coefficients derived from the experiments at the two nearest round temperatures.

values were not obtained directly from the measurements, they are not given in Table I, but will be found in Table II.

The measurements with potassium nitrate and potassium citrate were made in this laboratory by Mr. Roger D. Gale, to whom we are indebted for permission to include them here.

TABLE I.—EQUIVALENT CONDUCTANCE AT ROUND TEMPERATURES.

Potassium Nitrate.

Measurements by R. D. Gale.

| Concentration at 4°. | 0°. | 18°. | 25°. | 50°. | 75°. | 100°. | 128°. | 156°. |
|---|---|---|---|---|---|---|---|---|
| 0 | 81 | 126.4 | 145 | 220 | 299 | 385 | 480 | 576 |
| 2 | 78.63 | 122.5 | 140.7* | 212.7 | 290 | 370.6 | 461.8 | 551.9 |
| 12.5 | 75.28 | 117.2 | 134.9* | 203 | 276.6 | 352.1 | 436.7 | 522.4 |
| 50 | 70.67 | 109.7 | 126.3* | 189.7 | 257.8 | 327.1 | 404.8 | 479.4 |
| 100 | 67.16 | 104.5 | 120.3* | 180.4 | 244.6 | 309.7 | 381.9 | 451.3 |
| Potassium Oxalate. | | | | | | | | |
| 0 | 80.6 | 128.3 | 149 | 232 | 324 | 424 | 537 | 653 |
| 2 | 74.9 | 119.9 | 139.2†* | 216 | 300.4 | 389.9† | 490.8 | 589.1 |
| 12.5 | 69.3 | 111.1† | 129.2* | 199.3 | 275.6 | 355.2† | 441.5 | 528.2 |
| 50 | 63 | 101 | 116.5* | 178.8 | 245.6 | 313.7 | 387.1 | 454.8 |
| 100 | 59.3 | 94.6 | 109.5* | 167.2 | 228.2 | 290.6 | 356.7 | 415.4 |
| 200 | 55.8 | 88.4 | 102.3* | 155.3 | 211.7 | 266.8 | 325.5 | 378 |
| Calcium Nitrate. | | | | | | | | |
| 0 | 71.1 | 113.8 | 132 | 205 | 286 | 374 | 475 | 578 |
| 2 | 66.54 | 107.1 | 123.7† | 192 | 266.9 | 347 | 439.4 | 531.7 |
| 12.5 | 61.58 | 98.6 | 114.5† | 176.4 | 244.4 | 315.6 | 396.5 | 477.3 |
| 50 | 55.56 | 88.57 | 102.6 | 157.4 | 216.8 | 278.1 | 345.7 | 409.9 |
| 100 | 51.87 | 82.56 | 95.76 | 146.3 | 200.6 | 257 | 318.1 | 374.3 |
| 200 | 48.32 | 76.66 | 88.81 | 135.6 | 185.4 | 235.9 | 291.1 | 340 |
| Potassium Ferrocyanide. | | | | | | | | |
| 0 | 100 | 163 | 189 | 294 | 417 | 540 | ... | ... |
| 0.5 | 91.6 | .. | 171.1 | .. | .. | .. | ... | ... |
| 2 | 84.8 | 137 | 158.9* | 244 | 336 | 429.3 | ... | ... |
| 12.5 | 71 | 113.4 | 131.6* | 200.6 | 272 | 342.3 | ... | ... |
| 50 | 58.2 | 93.7† | 108.6† | 163.7† | 220.6† | 274.7† | ... | ... |
| 100 | 53 | 84.9 | 98.4 | 148.4 | 199.1 | 247.3 | ... | ... |
| 200 | 48.8 | 77.8 | 90.1 | 136 | 181.6 | 224.5 | ... | ... |
| 400 | 45.4 | 72.1 | 83.3 | 125.1 | 166.7 | 205.1 | ... | ... |
| Barium Ferrocyanide. | | | | | | | | |
| 2 | 46.9 | 75 † | 86.2*† | 127.8 | 167.2 | 204.4 | ... | ... |
| 12.5 | 30.4 | 48.8† | 56.5*† | 83.3† | 107.7† | 131.3 | ... | ... |
| Calcium Ferrocyanide. | | | | | | | | |
| 2 | 47.1 | 75.5 | 86.2* | 130 | .. | .. | ... | ... |
| 12.5 | 31.2 | 49.9† | 57.4† | .. | .. | .. | ... | ... |
| 50 | 24.1 | 38.5 | 44.4† | 64.8 | 82.4 | .. | ... | ... |
| 100 | 21.9 | 35.1 | 40.2† | 58.5 | 73.9 | 84.7 | ... | ... |
| 200 | 20.6 | 32.9 | 37.8† | 55 | 68.8 | 77.7 | ... | ... |
| 400 | 20.2 | 32.2 | 37.1† | 54 | 67.5 | 76.2 | ... | ... |

TABLE I (*Continued*).

| Concentration at 4°. | 0°. | 18°. | 25°. | 50°. | 75°. | 100°. | 128°. | 156°. |
|---|---|---|---|---|---|---|---|---|
| | | | Potassium Citrate. | | | | | |
| 0 | 77.5 | 127 | 147 | 230 | 329 | 429 | ... | ... |
| 0.5 | .. | 120.1 | 139.4† | .. | .. | .. | ... | ... |
| 2.003 | 71 | 115.4* | 134.5 | 210.3 | 294.2 | 382.7 | ... | ... |
| 5 | 67.6 | 109.9* | 128.2 | 199 | 277.2 | 358.8 | ... | ... |
| 12.5 | 62.9 | 101.8* | 118.7 | 183.8 | 254.8 | 327.4 | ... | ... |
| 51.18 | 54.4 | 87.6* | 101.9 | 157.1 | 215.5 | 273.8 | ... | ... |
| 98.62 | 50.2 | 80.9* | 94.1 | 144.2 | 197.4 | 249.8 | ... | ... |
| 301.92 | 43.5 | 69.8* | 81 | 123.5 | 168 | 211.4 | ... | ... |
| | | | Lanthanum Nitrate. | | | | | |
| 0 | 77.8 | 125 | 147 | 229 | 320 | 425 | 555 | 685 |
| 2.006 | 68.88 | 110.8 | 128.9† | 200.6 | 280.2 | 364.4 | 459.8 | 553.4 |
| 12.54 | 61.43 | 98.55 | 114.4† | 176.9 | 244 | 312.6 | 386.6 | 453.6 |
| 50.16 | 53.97 | 86.1 | 99.7 | 152.7 | 208.3 | 263 | 319.2 | 363.8 |
| 100.3 | 49.88 | 79.36 | 91.84 | 139.7 | 189.8 | 238.3 | 286 | 322.2 |
| 200.7 | 45.97 | 72.13 | 83.52 | 126.6 | 170.9 | 212.5 | 253 | 381.8 |
| 239.8 | .. | .. | 82.13 | .. | .. | .. | ... | ... |
| | | | Lanthanum Sulphate. | | | | | |
| 2 | 39.78 | 60.17 | 67.92† | 89.9 | 102.4 | 108.5 | 111.5 | 109.6 |
| 12.5 | 24.93 | 37.45 | 42.05† | 55.46 | 64.07 | 68.19 | 67.61 | ... |
| 50 | 17.2 | 25.74 | 28.77 | 37.53 | 42.51 | 43.86 | 42.29 | ... |
| 100 | 14.4 | 21.46 | 23.92 | 30.73 | 34.22 | 34.83 | 33.38 | ... |
| 200 | 12.09 | 17.86 | 19.86 | 25.07 | 27.42 | 27.47 | .. | ... |

### 7. Values of the Equivalent Conductance at Round Concentrations.

The values given in Table I are the conductances of solutions having the specified round concentration *at 4°*. In order to obtain values for round concentrations at the temperatures in question, corrections must be applied. For this purpose we made use of the relation between the equivalent conductance (V) and the concentration ($C$), which is given by the expression

$$C(\Lambda_0 - \Lambda) = K(C\Lambda)^n.$$

Substituting for $\Lambda$ two definite values of the equivalent conductance, $\Lambda_1$ and $\Lambda_2$, and for $C$ the two corresponding values $C_1$ and $C_2$, and dividing, we get:

$$\frac{C_1^{n-1}}{C_2^{n-1}} = \frac{\Lambda_0 - \Lambda_1}{\Lambda_0 - \Lambda_2} \cdot \frac{\Lambda_2^n}{\Lambda_1^n}.$$

This may also be written in logarithmic form as follows:

$$(n-1)[\log C_1 - \log C_2] = \log(\Lambda_0 - \Lambda_1) - \log(\Lambda_0 - \Lambda_2) + n(\log\Lambda_2 - \log\Lambda_1).$$

Reference to Table IV shows that the value of $n$ is always so close to 1.5 that in applying this expression for the reduction of the conductance values to the nearest round concentration, $n$ may be taken as 1.5 without appreciable error; the expression then reduces to

$$\log C_2 - \log C_1 = 2[\log(\Lambda_0 - \Lambda_2) - \log(\Lambda_0 - \Lambda_1)] + 3[\log\Lambda_1 - \log\Lambda_2].$$

The numerical value of the left-hand side of the above expression is known; $\Lambda_0$ and $\Lambda_1$ are known; and $\Lambda_2$ can therefore be determined. This can be done, to be sure, only by the method of approximations; but after a little practice, a very small number of trials is sufficient, and the calculation is quite rapid, since the differences between logarithms, which enter into the above expression, can be read directly from a four-place logarithm table.

The equivalent conductances at zero concentration given in Table II are smoothed-out values obtained by adding together the appropriate $\Lambda_0$ values for the separate ions, which latter values were derived from the directly determined values of Table I and the tables of the previous publication from this laboratory by means of a graphical method which will be fully discussed in the following article.

The so-reduced values of the equivalent conductance of the salts investigated are presented in Table II. It may be again stated in explanation of the table that, as in the preceding one, the concentration is expressed in milli-equivalents per liter, based on the international atomic weights for 1908 referred to oxygen as 16.00; that the temperature is the true temperature on the gas scale; and that the equivalent conductance, which has been corrected for that of the water, is expressed in reciprocal ohms, the absolute conductance capacity of the conductivity vessel having been corrected for its change with the temperature. The concentration given in the first column is in this table that at the temperature of the measurement (not that at 4° as in Table I).

TABLE II.—THE EQUIVALENT CONDUCTANCE AT ROUND CONCENTRATIONS.

| Concentration at $t^\circ$. | 0°. | 18°. | 25°. | 50°. | 75°. | 100°. | 128°. | 156°. |
|---|---|---|---|---|---|---|---|---|
| | | | | Potassium Nitrate. | | | | |
| 0 | 80.8 | 126.3 | 145.1 | 219 | 299 | 384 | 485 | 580 |
| 2 | 78.6 | 122.5 | 140.7 | 212.7 | 289.9 | 370.3 | 460.7 | 551 |
| 12.5 | 75.3 | 117.2 | 134.9 | 202.9 | 276.4 | 351.5 | 435.4 | 520.4 |
| 50 | 70.7 | 109.7 | 126.3 | 189.5 | 257.4 | 326.1 | 402.9 | 476.1 |
| 100 | 67.2 | 104.5 | 120.3 | 180.2 | 244.1 | 308.5 | 379.5 | 447.3 |
| | | | | Potassium Oxalate. | | | | |
| 0 | 79.4 | 127.6 | 147.5 | 230 | 322 | 419 | 538 | 653 |
| 2 | 74.9 | 119.9 | 139.2 | 215.9 | 300.2 | 389.3 | 489.1 | 587 |
| 12.5 | 69.3 | 111.1 | 129.2 | 199.1 | 275.1 | 354.1 | 438.8 | 524.3 |
| 50 | 63 | 101 | 116.5 | 178.6 | 244.9 | 312.2 | 383.8 | 449.5 |
| 100 | 59.3 | 94.6 | 109.5 | 167 | 227.5 | 288.9 | 353.2 | 409.7 |
| 200 | 55.8 | 88.4 | 102.3 | 155 | 210.9 | 265.1 | 321.9 | 372.1 |
| | | | | Calcium Nitrate. | | | | |
| 0 | 70.4 | 112.7 | 130.6 | 202 | 282 | 369 | 474 | 575 |
| 2 | 66.5 | 107.1 | 123.7 | 191.9 | 266.7 | 346.5 | 438.4 | 529.8 |
| 12.5 | 61.6 | 98.6 | 114.5 | 176.2 | 244 | 314.6 | 394.5 | 473.7 |
| 50 | 55.6 | 88.6 | 102.6 | 157.2 | 216.2 | 276.8 | 343 | 405.1 |
| 100 | 51.9 | 82.6 | 95.8 | 146.1 | 199.9 | 255.5 | 315.1 | 369.1 |
| 200 | 48.3 | 76.7 | 88.8 | 135.4 | 184.7 | 234.4 | 288 | 334.7 |

Table II (*Continued*).

| Concentration at *t*°. | 0°. | 18°. | 25°. | 50°. | 75°. | 100°. | 128°. | 156°. |
|---|---|---|---|---|---|---|---|---|
| Potassium Ferrocyanide. | | | | | | | | |
| 0 | 98.4 | 159.6 | 185.5 | 288 | 403 | 527 | ... | ... |
| 0.5 | 91.6 | ... | 171.1 | ... | ... | ... | ... | ... |
| 2 | 84.8 | 137 | 158.9 | 243.8 | 335.2 | 427.6 | ... | ... |
| 12.5 | 71 | 113.4 | 131.6 | 200.3 | 271 | 340 | ... | ... |
| 50 | 58.2 | 93.7 | 108.6 | 163.3 | 219.5 | 272.4 | ... | ... |
| 100 | 53 | 84.9 | 98.4 | 148.1 | 198.1 | 245 | ... | ... |
| 200 | 48.8 | 77.8 | 90.1 | 135.7 | 180.6 | 222.3 | ... | ... |
| 400 | 45.4 | 72.1 | 83.3 | 124.8 | 165.7 | 203.1 | ... | ... |
| Barium Ferrocyanide. | | | | | | | | |
| 0 | 91 | 150 | 176 | 277 | 393 | 521 | ... | ... |
| 2 | 46.9 | 75 | 86.2 | 127.5 | 166.2 | 202.3 | ... | ... |
| 12.5 | 30.4 | 48.8 | 56.5 | 83.1 | 107 | 129.8 | ... | ... |
| Calcium Ferrocyanide. | | | | | | | | |
| 0 | 88 | 146 | 171 | 271 | 386 | 512 | ... | ... |
| 2 | 47.1 | 75.5 | 86.2 | 130 | ... | ... | ... | ... |
| 12.5 | 31.2 | 49.9 | 57.4 | ... | ... | ... | ... | ... |
| 50 | 24.1 | 38.5 | 44.4 | 64.6 | 81.9 | ... | ... | ... |
| 100 | 21.9 | 35.1 | 40.2 | 58.4 | 73.7 | 84.3 | ... | ... |
| 200 | 20.6 | 32.9 | 37.8 | 55 | 68.7 | 77.5 | ... | ... |
| 400 | 20.2 | 32.2 | 37.1 | 54 | 67.5 | 76.2 | ... | ... |
| Potassium Citrate. | | | | | | | | |
| 0 | 76.4 | 124.6 | 144.5 | 228 | 320 | 420 | ... | ... |
| 0.5 | ... | 120.1 | 139.4 | ... | ... | ... | ... | ... |
| 2 | 71 | 115.4 | 134.5 | 210.1 | 293.8 | 381.2 | ... | ... |
| 5 | 67.6 | 109.9 | 128.2 | 198.7 | 276.5 | 357.2 | ... | ... |
| 12.5 | 62.9 | 101.8 | 118.7 | 183.6 | 254.2 | 326 | ... | ... |
| 50 | 54.4 | 87.8 | 102.1 | 157.5 | 215.5 | 273 | ... | ... |
| 100 | 50.2 | 80.8 | 93.9 | 143.7 | 196.5 | 247.5 | ... | ... |
| 300 | 43.5 | 69.8 | 81 | 123.5 | 167 | 209.5 | ... | ... |
| Lanthanum Nitrate. | | | | | | | | |
| 0 | 75.4 | 122.7 | 142.6 | 223 | 313 | 413 | 534 | 651 |
| 2 | 68.9 | 110.8 | 128.9 | 200.5 | 279.8 | 363.5 | 457.5 | 549 |
| 12.5 | 61.4 | 98.5 | 114.4 | 176.7 | 243.4 | 311.2 | 383.4 | 447.8 |
| 50 | 54 | 86.1 | 99.7 | 152.3 | 207.6 | 261.4 | 315.8 | 357.7 |
| 100 | 49.9 | 79.4 | 91.8 | 139.5 | 189.1 | 236.7 | 282.5 | 316.3 |
| 200 | 46 | 72.1 | 83.5 | 126.4 | 170.2 | 210.8 | 249.6 | 276.2 |
| Lanthanum Sulphate. | | | | | | | | |
| 0 | 76 | 129 | 151 | 244 | 350 | 469 | 615 | 758 |
| 2 | 39.8 | 60.1 | 67.9 | 89.6 | 101.7 | 107.2 | 109.4 | 106.6 |
| 12.5 | 24.9 | 37.4 | 42 | 55.2 | 64.6 | 67.3 | 66.3 | ... |
| 50 | 17.2 | 25.7 | 28.7 | 37.4 | 42.2 | 43.3 | 41.4 | ... |
| 100 | 14.4 | 21.4 | 23.9 | 30.6 | 34 | 34.3 | 32.5 | ... |
| 200 | 12.1 | 17.8 | 19.8 | 25 | 27.2 | 27 | ... | ... |

In only a few cases can a comparison of these results be made with those of previous investigators. In Table III are brought together such data as are comparable.

TABLE III.—COMPARISON OF THE CONDUCTIVITY RESULTS OF DIFFERENT INVESTIGATORS.

| | Potassium Nitrate at 18°. | | Potassium Oxalate at 18°. | | Calcium Nitrate at 18°. | |
|---|---|---|---|---|---|---|
| Concentration. | N. and J. | K. and M.[1] | N. and J. | K. and G.[2] | N. and J. | K. and G.[2] |
| 2 | 122.5 | 122.6 | 119.9 | 120.53 | 107.1 | 106.5 |
| 50 | 109.7 | 109.86 | 101 | 100.83 | 88.6 | 88.41 |
| 100 | 104.5 | 104.79 | 94.6 | 94.84 | 82.6 | 82.48 |
| 200 | ... | .... | 88.4 | 88.62 | 76.7 | 75.94 |

| | Potassium Ferrocyanide at 25°. | | | Calcium Nitrate at 25°. | |
|---|---|---|---|---|---|
| Concentration. | N. and J. | Jones.[3] | Walden.[4] | N. and J. | Jones[5] |
| 2 | 158.9 | 151.2 | 156.6 | 123.7 | 124.8 |
| 12.5 | 131.6 | 132 | 131 | 114.5 | 113.1 |
| 50 | 108.6 | 107.9 | 108 | 102.6 | 102.4 |
| 100 | 98.4 | 98.2 | ... | 95.8 | 95.4 |
| 200 | ... | ... | ... | 88.8 | 86.8 |

It will be seen that the results of Kohlrausch and Grüneisen on potassium oxalate and calcium nitrate agree closely with ours, except at the concentration of 2 millinormal where the divergence is about 0.5 per cent., and except in the case of the 200-millinormal calcium nitrate solution, where the two values differ by nearly 1 per cent.

With reference to the effect of temperature on the conductance, it is worthy of note that lanthanum sulphate at concentrations from 0.0125–0.2 normal exhibits a maximum conductance at about 100°, owing to the fact that the rapid decrease in ionization there begins to over-compensate the increase in the ion conductances. Such maxima have often been observed before, but not we believe at so low a temperature in the case of a neutral salt.

## 8. Change of the Equivalent Conductance with the Concentration.

It has been shown in the previous publication[6] that in the case of the di-ionic and tri-ionic substances investigated the variation of the equivalent conductance ($\Lambda$) with the concentration ($C$) can be expressed, at least approximately, by an equation of the form $C(\Lambda_0 - \Lambda) = K(C\Lambda)^n$, by assigning to the exponent $n$ values varying somewhat with the nature of the salt and with the temperature, but almost always lying between the limits of 1.40 and 1.50. It is therefore of much interest to determine

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[1] Kohlrausch and Maltby, *Landolt-Bornstein-Meyerhoffer Tabellen*, p. 744

[2] Kohlrausch and Grüneisen, *Ibid.*, 745–746.

[3] Interpolated and corrected from Jones' values, *Carnegie Institution Publication*, No. 46, 1907.

[4] Interpolated from Walden, *Z. physik. Chem.*, 2, 49 (1888).

[5] Interpolated and corrected from the values of Jones and Jacobson, *Am. Chem. J.*, 40, 355 (1908).

[6] *Loc cit.*, 337.

the applicability of this principle to the salts of higher valence types. The following table contains the values of $n$ which make the results best conform to the foregoing function. These were determined, in connection with the derivation of the $\Lambda_0$ values of Table I, by the graphical method described at the beginning of the preceding section. The error in this determination of the $n$ values is probably not greater than 0.05. In the cases of calcium and barium ferrocyanides and of lanthanum sulphate the $n$ values were derived with the help of special plots of a similar character; on these plots the $\Lambda_0$ value obtained by the additivity principle was included, and the value of $n$ which gave a straight line passing through this point and most nearly through the point corresponding to the two most dilute solutions. The error in these values is probably somewhat greater than in those determined without the use of the $\Lambda_0$ value.

TABLE IV.—VALUES OF THE EXPONENT $n$ IN THE FUNCTION $C(\Lambda_0 - \Lambda) = K(C\Lambda)^n$.

| Substance. | Valence-product. | No. of ions. | 0°. | 100°. | 156°. |
|---|---|---|---|---|---|
| $KNO_3$ | 1 × 1 | 2 | 1.4 | 1.4 | 1.4 |
| $K_2C_2O_4$ | 1 × 2 | 3 | 1.4 | 1.5 | 1.5 |
| $Ca(NO_3)_2$ | 2 × 1 | 3 | 1.45 | 1.5 | 1.5 |
| $K_3C_6H_5O_7$ | 1 × 3 | 4 | 1.55 | 1.55 | ... |
| $La(NO_3)_3$ | 3 × 1 | 4 | 1.45 | 1.5 | 1.5 |
| $K_4Fe(CN)_6$ | 1 × 4 | 5 | 1.5 | 1.5 | ... |
| $Ba\ Fe(CN)_6$ | 2 × 4 | 3 | 1.55 | .... | ... |
| $Ca_2Fe(CN)_6$ | 2 × 4 | 3 | 1.5 | .... | ... |
| $La_2(SO_4)_3$ | 3 × 2 | 5 | 1.55 | 1.5 | ... |

It is thus evident that for all these salts at all temperatures from 0° to 156°, as for all the salts previously studied, the exponent $n$ has a value differing little from 1.5, in spite of the fact that these salts are of very different ionic types. This remarkable fact will be more fully considered in its relation to the ionization of salts.

It should, however, be stated that in the case of the salts of the higher ionic types no value of the exponent $n$ can be found which will make the function in question represent the results accurately. This was best illustrated by the plots of $1/\Lambda$ against $(C\Lambda)^n$ that were made for potassium ferrocyanide at 18°.[1] These plots showed that, although the graph for the exponent 1.45 is the one that is most nearly linear between the concentrations 2 and 100, yet even it has a double curvature with a point of inflexion lying within the range of concentrations plotted. For higher values of $n$, the point of inflexion is displaced in the direction of smaller concentrations. The plots that have been made for other salts also show curvature of a similar character even in the case of those of a simpler type, although with these it is smaller in amount and therefore

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[1] *Cf.* Fig. 1, p. 1011.

exerts less influence. This matter will be more fully discussed in a later communication from this laboratory.

## 9. Ionization Values.

In Table V are given the ratios (multiplied by 100) of the equivalent conductances at the various equivalent concentrations to that at zero concentration at each temperature. According to the ionic theory, these ratios are equal to the percentage values of the ionization of the substances. With reference to the absolute accuracy of these values it should be remembered that there may be considerable error in the conductances at zero concentration, especially in the cases of the ferrocyanides. The third figure, though of no absolute significance, is retained in order to show better the relative values at different concentrations and temperatures.

TABLE V.—THE CONDUCTANCE RATIO ($100\Lambda/\Lambda_0$) AND PERCENTAGE IONIZATION OF THE SALTS.

| Concentration. | 0°. | 18°. | 25°. | 50°. | 75°. | 100°. | 128° | 156°. |
|---|---|---|---|---|---|---|---|---|
| Potassium Nitrate. | | | | | | | | |
| 0 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| 2 | 97.3 | 97 | 96.9 | 97.2 | 97 | 96.4 | 95 | 94.9 |
| 12.5 | 93 | 92.8 | 93 | 92.7 | 92.5 | 91.5 | 89.8 | 89.7 |
| 50 | 87.5 | 86.8 | 87.1 | 86.6 | 86.2 | 85 | 83.1 | 82.1 |
| 100 | 83.1 | 82.8 | 82.9 | 82.4 | 81.8 | 80.4 | 78.4 | 77.2 |
| Potassium Oxalate. | | | | | | | | |
| 0 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| 2 | 94.5 | 94 | 94.5 | 93.9 | 93.1 | 92.9 | 90.9 | 89.9 |
| 12.5 | 87.3 | 87.2 | 87.7 | 86.7 | 85.4 | 84.5 | 81.7 | 80.4 |
| 50 | 79.4 | 79.2 | 79.1 | 77.8 | 76 | 74.5 | 71.4 | 68.9 |
| 100 | 74.7 | 74.3 | 74.3 | 72.6 | 70.6 | 69 | 65.6 | 62.8 |
| 200 | 70.3 | 69.5 | 69.5 | 67.4 | 65.5 | 63.2 | 59.9 | 57 |
| Calcium Nitrate. | | | | | | | | |
| 0 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| 2 | 94.4 | 95 | 94.6 | 95 | 94.6 | 93.7 | 92.5 | 92.2 |
| 12.5 | 86.4 | 87.6 | 87.6 | 87.3 | 86.5 | 85.3 | 83.1 | 82.4 |
| 50 | 78.9 | 78.8 | 78.5 | 77.8 | 76.7 | 75 | 72.3 | 70.4 |
| 100 | 73.7 | 73.5 | 73.3 | 72.3 | 71 | 69.2 | 66.5 | 64.2 |
| 200 | 68.7 | 68.3 | 68 | 67 | 65.5 | 63.5 | 60.8 | 58.3 |
| Potassium Ferrocyanide. | | | | | | | | |
| 0 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| 0.5 | 93.2 | ..... | 92.2 | ..... | ..... | ..... | ..... | ..... |
| 2 | 86.3 | 85.8 | 85.8 | 84.5 | 83.1 | 81.2 | ..... | ..... |
| 12.5 | 72.2 | 71 | 71 | 69.4 | 67.2 | 64.5 | ..... | ..... |
| 50 | 59.2 | 58.7 | 58.6 | 56.7 | 54.5 | 51.6 | ..... | ..... |
| 100 | 53.9 | 53.2 | 53 | 51.3 | 49.1 | 46.5 | ..... | ..... |
| 200 | 49.7 | 48.8 | 48.6 | 47.1 | 44.8 | 42.1 | ..... | ..... |
| 400 | 46.2 | 45.3 | 45 | 43.3 | 41.1 | 38.5 | ..... | ..... |

TABLE V (*Continued*).

| Concentration. | 0°. | 18°. | 25°. | 30°. | 75°. | 100°. | 128°. | 156°. |
|---|---|---|---|---|---|---|---|---|
| Barium Ferrocyanide. | | | | | | | | |
| 0 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| 2 | 51.5 | 50 | 49 | 46 | 42.2 | 38.8 | ..... | ..... |
| 12.5 | 33.4 | 32.5 | 32.1 | 30 | 27.2 | 25 | ..... | ..... |
| Calcium Ferrocyanide. | | | | | | | | |
| 0 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| 2 | 53.5 | 51.7 | 50.4 | 48 | ..... | ..... | ..... | ..... |
| 12.5 | 35.5 | 34.2 | 33.6 | ..... | ..... | ..... | ..... | ..... |
| 50 | 27.4 | 26.4 | 26 | 23.8 | 21.2 | ..... | ..... | ..... |
| 100 | 24.9 | 24 | 23.5 | 21.6 | 19.1 | 16.5 | ..... | ..... |
| 200 | 23.4 | 22.5 | 22.1 | 20.3 | 17.8 | 15.1 | ..... | ..... |
| 400 | 23 | 22.1 | 21.7 | 19.9 | 17.5 | 14.9 | ..... | ..... |
| Potassium Citrate. | | | | | | | | |
| 0 | 100 | 100 | 100 | 100 | 100 | 100 | ..... | ..... |
| 0.5 | ..... | 96.4 | 96.4 | ..... | ..... | ..... | ..... | ..... |
| 2 | 93 | 92.6 | 93 | 92 | 92 | 90.8 | ..... | ..... |
| 5 | 88.6 | 88.2 | 88.7 | 87.3 | 86.5 | 85 | ..... | ..... |
| 12.5 | 82.4 | 81.7 | 82.1 | 80.5 | 79.4 | 77.7 | ..... | ..... |
| 50 | 71.3 | 70.4 | 70.7 | 69.1 | 67.4 | 65 | ..... | ..... |
| 100 | 65.7 | 64.8 | 65 | 63 | 61.4 | 59 | ..... | ..... |
| 300 | 57 | 56 | 56 | 54.2 | 52.2 | 50 | ..... | ..... |
| Lanthanum Nitrate. | | | | | | | | |
| 0 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| 2 | 91.4 | 90.4 | 90.4 | 89.9 | 89.5 | 88.1 | 85.6 | 84.3 |
| 12.5 | 81.6 | 80.4 | 80.4 | 79.2 | 77.7 | 75.3 | 71.8 | 68.8 |
| 50 | 71.6 | 70.2 | 70 | 68.3 | 66.3 | 63.3 | 59.2 | 55 |
| 100 | 66.3 | 64.7 | 64.4 | 62.5 | 60.5 | 57.3 | 53 | 48.6 |
| 200 | 61 | 58.8 | 58.6 | 56.7 | 54.4 | 51.1 | 46.7 | 42.4 |
| Lanthanum Sulphate. | | | | | | | | |
| 0 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| 2 | 52.3 | 46.6 | 45 | 36.8 | 29 | 22.9 | 17.8 | 14 |
| 12.5 | 32.8 | 29 | 27.8 | 22.6 | 18.5 | 14.3 | 10.8 | ..... |
| 50 | 22.6 | 20 | 19 | 15.3 | 12.1 | 9.2 | 6.7 | ..... |
| 100 | 18.9 | 16.6 | 15.8 | 12.5 | 9.7 | 7.3 | 5.3 | ..... |
| 200 | 15.9 | 13.8 | 13.2 | 10.2 | 7.8 | 5.7 | ..... | ..... |

## 10. Ionization in Relation to Type of Salt, Concentration, and Temperature.

Previous studies of the ionization of salts have led to the conclusion that at any definite concentration salts of the same ionic type have roughly the same degree of ionization, and that for salts of different types the ionization decreases rapidly when the product of the valences of the constituent ions increases.[1] It is of interest to determine the applica-

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[1] For a discussion of this matter, see Noyes, "Physical Properties of Aqueous Solutions in Relation to the Ionic Theory," *Technology Quarterly*, **17**, 300 (1904); *Science*, **20**, 582 (1904); abstract in *Z. physik. Chem.*, **52**, 635; see also *Carnegie Institution Publication*, No. **63**, pp. 342-343 (1907).

tion of these principles to the salts which we have investigated, especially to those of high valence-product. To bring out the relations involved, the percentage ionization values at 18° and 100° at the salt concentration of 0.1 normal and at the ion-concentration[1] of 0.05 normal for all the salts studied in this and the preceding investigations (up to these concentrations) are brought together in Table VI. The table also contains in the last two columns the ionization values at such a concentration of the salt that the ion of higher valence has a concentration of 0.05 formula weight or mol per liter. The significance of these values will be considered below.

TABLE VI.—IONIZATION IN RELATION TO VALENCE TYPE.

| | | Percentage ionized. | | | | | |
|---|---|---|---|---|---|---|---|
| | | Salt concentration 0.1 normal. | | Ion concentration 0.05 equivalent per liter. | | Conc. of ion of higher valence 0.05 mol per liter. | |
| Salt. | Valence-product. | 18°. | 100°. | 18°. | 100°. | 18°. | 100°. |
| KCl | 1 × 1 | 86 | 81 | 89 | 83 | 89 | 83 |
| $KNO_3$ | 1 × 1 | 83 | 80 | 86 | 84 | 86 | 84 |
| NaCl | 1 × 1 | 84 | 82 | 87 | 85 | 87 | 85 |
| $AgNO_3$ | 1 × 1 | 81 | 79 | 85 | 82 | 85 | 82 |
| $NaC_2H_3O_2$ | 1 × 1 | 79 | 75 | 83 | 80 | 83 | 80 |
| *Mean* | 1 | 83 | 80 | 86 | 83 | 86 | 83 |
| $K_2SO_4$ | 1 × 2 | 72 | 69 | 75 | 68 | 68 | 61 |
| $K_2C_2O_4$ | 1 × 2 | 74 | 69 | 78 | 73 | 72 | 66 |
| $Ca(NO_3)_2$ | 2 × 1 | 73 | 69 | 77 | 73 | 72 | 66 |
| $Ba(NO_3)_2$ | 2 × 1 | 68 | 66 | 71 | 69 | 64 | 62 |
| *Mean* | 2 | 72 | 68 | 75 | 71 | 69 | 65 |
| $K_3C_6H_5O_7$ | 1 × 3 | 65 | 59 | 67 | 61 | 57 | 50 |
| $La(NO_3)_3$ | 3 × 1 | 65 | 57 | 67 | 58 | 56 | 47 |
| *Mean* | 3 | 65 | 58 | 67 | 60 | 57 | 49 |
| $MgSO_4$ | 2 × 2 | 45 | 31 | 43 | 28[2] | 36 | 24[2] |
| $K_4Fe(CN)_6$ | 1 × 4 | 53 | 46 | 53 | 46 | 45 | 37 |
| $La_2(SO_4)_3$ | 3 × 2 | 17 | [illegible]7 | 10[2] | 5[2] | 10[2] | 5[2] |
| $Ca_2Fe(CN)_6$ | 2 × 4 | 24 | 16 | 23 | 14[2] | 21 | 14[2] |

It will be seen that the various salts of the uni-bivalent and uni-trivalent types, like the uni-univalent ones previously considered, have ionization values at the same concentration which do not differ more than a few per cent. from one another, again confirming the principle that the degree of ionization of salts is primarily determined by the ionic type.

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[1] That is, at such a concentration of the salt that the concentration of the positive ion (or of the negative ion) is 0.05 equivalent per liter.

[2] Relatively inaccurate values.

For the salts of still higher type, such comparisons are not possible as yet. Table V shows, however, that the ionization relations of the salts with valence-products 6 and 8 differ from those of salts of lower type in the respect that at the highest concentrations the ionization changes very little with the concentration. Thus the ionization of calcium ferrocyanide is nearly independent of the concentration at concentrations ranging from 100 to 400 milli-equivalents per liter. This behavior may perhaps be due to complex-ion or intermediate-ion formation.

It is also evident from Table VI that the ionization of a salt with a higher valence-product is at the same concentration always less than that of one with a lower valence-product. In seeking for a more definite relation between the degree of ionization and the type of salt, we may compare the proportion of the various salts existing in the un-ionized state either (1) in solutions in which their ions are present at the same equivalent concentration, thus insuring the same quantity of free electricity in the solution (though not the same distribution of it); or (2) in solutions in which the ion-particles are present in equal number and are therefore similarly distributed throughout the same volume. The latter of these two methods seems distinctly the more rational. Thus, if we compare potassium chloride and magnesium sulphate in solutions where the ions have the same molal (instead of the same normal) concentration, we have, considering the matter from a molecular standpoint, conditions that are apparently absolutely identical except that singly charged ions are in the second case replaced by doubly charged ones. In the case of salts, like potassium chloride and sulphate, whose molecules dissociate into a different number of ions, comparable conditions can not be so fully nor so simply realized. The following basis of comparison seems, however, fairly satisfactory. In order to compare, for example, potassium chloride and potassium sulphate at an ion concentration of the former of 0.05 normal, we should in strictness employ a solution of potassium sulphate in which the $K^+$ ion and the $SO_4^{=}$ ion both have a concentration of 0.05 mol per liter, since this solution would differ from the potassium chloride solution only in the respect that the singly charged $Cl^-$ ions are replaced by an equal number of doubly charged $SO_4^{=}$ ions. Now such a solution can not be prepared without introducing at the same time some other positive ion; but, if we disregard the effect of introducing such a foreign ion, we can realize the conditions just referred to by taking such quantities of potassium sulphate and another sulphate (say sodium sulphate) that the $K^+$ ion and $Na^+$ ion concentrations are both equal to 0.05 mol per liter (when the $SO_4^{=}$ ion concentration will, of course, also be 0.05 mol per liter). The question then becomes, What is the proportion of un-ionized $K_2SO_4$ in this mixture? Now experimental investigations[1] have shown that the degree of ionization of each salt in such a mixture is the same as if it were alone present with an equivalent ion-concentration equal to the sum of those of the two separate salts (thus equal to 0.1 normal in the example just cited or 0.05 molal for the $SO_4^=$ ion). For the purpose in question, we should therefore derive the degrees of ionization of salts of different valence types by considering solutions in which the ion of the higher valence has some definite *molal* concentration.

The ionization values ($\gamma$) so derived were given in the last two columns of Table VI, while those corresponding to the same normal concentration were given in the two preceding columns of that table. In Table VII the corresponding values of 100 ($1 - \gamma$) are brought together, the mean value being taken for all the salts of each valence type. The quotients of these values by the valence-product ($v_1v_2$) are also given.

TABLE VII.—RELATION OF THE UN-IONIZED FRACTION TO VALENCE-PRODUCT.

| | At equimolal ion-concentrations = 0.05. | | | | At equinormal ion-concentrations = 0.05 | | | |
|---|---|---|---|---|---|---|---|---|
| | 100 $(1 - \gamma)$. | | 100 $(1 - \gamma)/v_1v_2$. | | 100 $(1 - \gamma)$. | | 100 $(1 - \gamma)/v_1v_2$. | |
| $v_1v_2$. | 18°. | 100°. | 18°. | 100°. | 18°. | 100°. | 18°. | 100°. |
| 1 × 1 | 12 | 17 | 14 | 17 | 14 | 17 | 14 | 17 |
| 2 × 1 | 31 | 35 | 16 | 18 | 25 | 29 | 13 | 15 |
| 3 × 1 | 43 | 51 | 14 | 17 | 33 | 40 | 11 | 13 |
| 4 × 1 | 55 | 63 | 14 | 16 | 47 | 54 | 12 | 14 |
| 2 × 2 | 64 | 76 | 16 | 19 | 57 | 72 | 14 | 18 |
| 3 × 2 | 90 | 95 | 15 | 16 | 90 | 95 | 15 | 16 |
| 4 × 2 | 79 | 86 | 10 | 11 | 77 | 86 | 10 | 11 |

It is evident that under these conditions an approximate proportionality exists between the un-ionized fraction and the valence-product, at any rate for values of the latter between 1 and 4 inclusive; and that this is true whether the comparison is made at equimolal or equinormal ion concentration, but more nearly so in the former case. The rule seems to hold with as great a degree of accuracy as the other rule that at the same concentration salts of the same ionic type are ionized to the same extent.[2]

The law of the variation of the ionization with the concentration must, of course, correspond to that governing the change of conductance with

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[1] Arrhenius, *Z. physik. Chem.*, **31**, 218 (1899). Much work on this subject has been done by a number of Canadian investigators. For a discussion of the matter see Noyes, *loc. cit.*

[2] It is remarkable that this principle applies to the *un-ionized fraction* of the salt rather than to the *concentration of its un-ionized part.* It can readily be shown that the latter (expressed in equivalents) is proportional to the quantity $(1 - \gamma)/\gamma$ (instead of to $(1 - \gamma)$) for salts of the types 1 × 1, 1 × 2, 1 × 3, etc.; and therefore that this quantity increases much more rapidly than the valence-product.

the concentration which was considered in Section 8. Expressed in terms of the ionization $\gamma$ this concentration function becomes

$$C(1-\gamma) = K(C\gamma)^n,$$

where $n$ has values varying somewhat with the salt and the temperature, but only between the comparatively narrow limits of 1.4 and 1.55. This principle, which had been previously verified mainly in the case of di-ionic and tri-ionic salts has been shown by the results of this research to apply also to tetra- and penta-ionic salts. Thus it holds true for lanthanum nitrate, potassium citrate and potassium ferrocyanide, for which the exponent required by the mass-action law would be either 4 or 5. Here again, therefore, the concentration function is found to be independent of the number of ions into which the salt dissociates, showing that mass action has no appreciable influence in determining the equilibrium between the ions and the un-ionized part of salts.

Reference to Table V shows that the ionization of every salt investigated decreases steadily with rising temperature between 0° and 156°, and, moreover, that the rate of decrease is greater the higher the value of the valence product. The rate of decrease is also more rapid, the higher the temperature. All these effects, which are, of course, greater at the higher concentrations, are more clearly shown in Table VIII, which gives for each type of salt at a concentration of 0.1 normal the mean values of $-10^3\Delta\gamma/\Delta t$, which represent the average decreases in percentage ionization caused by a rise of 10° in temperature. The salts considered are those included in this investigation.

TABLE VIII.—TEMPERATURE COEFFICIENTS OF IONIZATION.

| Valence-product. | No. of salts studied. | Values of $-10^3\Delta\gamma/\Delta t$ for interval | | |
|---|---|---|---|---|
| | | 0°–50°. | 50°–100°. | 100°–156°. |
| 1 × 1 | 1 | 0.2 | 0.4 | 0.6 |
| 1 × 2<br>2 × 1 | 2 | 0.5 | 0.6 | 1 |
| 3 × 1<br>1 × 3 | 2 | 0.6 | 0.9 | 1.5 |
| 1 × 4 | 1 | 0.5 | 0.9 | ... |
| 3 × 2 | 1 | 1.2 | 1 (?) | ... |
| 2 × 4 | 1 | 0.7 | 0.9 | ... |

## 11. The Freezing-point Data.

In the case of all the salts (except potassium nitrate, potassium citrate, and barium ferrocyanide) whose conductances were measured, the lowering produced by them in the freezing point of water was also determined. This was done by the method described in Section 2. The data of the experiments are contained in Table X. The numbers given in the column headed $\Delta t$ are the freezing-point lowerings (corrected for error in the thermometer) of solutions of concentration $C$, the concentration in this case being given in milli-equivalents of salt per 1000 grams of water. The measurements with lanthanum sulphate were made by Mr. Roger D. Gale.

TABLE IX.—FREEZING POINT DATA.

| Potassium Ferrocyanide. | | | | Calcium Ferrocyanide. | | Potassium Oxalate. | |
|---|---|---|---|---|---|---|---|
| First series. | | Second series. | | | | | |
| *C.* | Δ*t.* | *C.* | Δ*t.* | *C.* | Δ*t.* | *C.* | Δ*t.* |
| 763 | 0.915 | 262 | 0.368 | 387 | 0.21 | 109 | 0.245 |
| 647 | 0.798 | 207 | 0.297 | 330 | 0.183 | 181 | 0.393 |
| 500 | 0.626 | 144 | 0.215 | 227 | 0.135 | 120 | 0.261 |
| 329 | 0.439 | 93 | 0.143 | 164 | 0.1 | 90 | 0.197 |
| 227 | 0.32 | 55 | 0.089 | 108 | 0.07 | 55 | 0.117 |
| 166 | 0.235 | 30 | 0.052 | 74 | 0.05 | 37 | 0.077 |
| 113 | 0.165 | ... | ..... | ... | ..... | 28 | 0.047 |

| Calcium Nitrate. | | Lanthanum Nitrate. | | Lanthanum Sulphate.[1] | |
|---|---|---|---|---|---|
| *C.* | Δ*t.* | *C.* | Δ*t.* | *C.* | Δ*t.* |
| 242 | 0.551 | 197 | 0.377 | 82 | 0.053 |
| 163 | 0.37 | 129 | 0.235 | 67 | 0.043 |
| 122 | 0.287 | 89 | 0.173 | 124 | 0.088 |
| 93 | 0.213 | 53 | 0.103 | 110 | 0.074 |
| 58 | 0.126 | ... | ..... | 124 | 0.082 |
| ... | ..... | ... | ..... | 93 | 0.066 |

## 12. Discussion of the Mol Number *i* as Derived from Freezing Point and Conductivity.

The freezing point lowerings at round concentrations of the solution were obtained by plotting the observed lowerings against the concentrations as given in Table IX, drawing the best representative curve through the points and interpolating. This curve was in every case very nearly a straight line, and the deviations of the separate observations from it scarcely ever exceeded 0.002°. The interpolated values so obtained are given in Table X in the third column, headed Δ*t*. The first and second columns give the corresponding concentration expressed in milli-equivalents and in formula weights per 1000 grams of water. The fourth column contains the ratio of the freezing-point lowering to the latter concentration. The fifth column shows the values of the mol number *i* calculated from this ratio by dividing it by 1.858, which apparently is the best value for the molal freezing-point lowering.[2] The sixth column gives the corresponding values of *i* calculated from the conductance ratio $\Lambda/\Lambda_0$ at 0° (as given in Table V) by the expression $i = 1 + (n - 1)(\Lambda/\Lambda_0)$, *n* being the number of mols of ions that would be produced by the complete dissociation of one formula weight of the

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[1] Owing to the relatively small solubility of this salt, measurements could be made only in dilute solutions; they cannot be considered very accurate, since the freezing-point depression caused by this salt is so small.

[2] See Roth, *Z. physik. Chem.*, 63, 445 (1908).

salt. The next column contains the percentage difference between the two values of $i$; and the last column contains values of the freezing-point lowering calculated by multiplying the values of $i$ in the sixth column by 1.858 C. Values of $i$ were also calculated by the freezing-point formula derived by Washburn,[1] but up to the concentrations involved, the results given by the two formulas are identical.

TABLE X.—FREEZING-POINT LOWERINGS AT ROUND CONCENTRATIONS, AND VALUES OF THE MOL NUMBER $i$.

| Concentration. | | Freezing point lowering | | Mol number $i$ | | | $\Delta t$ calculated from conductivity. |
|---|---|---|---|---|---|---|---|
| Milli-equiv. | Formula wts. $C$. | $\Delta t$. | $\Delta t/C$. | from freezing pt. | from conductivity. | Per cent. diff. | |
| | | | Potassium Oxalate. | | | | |
| 50 | 0.025 | 0.108 | 4.32 | 2.32 | 2.59 | −12 | 0.12 |
| 100 | 0.05 | 0.215 | 4.3 | 2.31 | 2.49 | − 8 | 0.231 |
| 200 | 0.1 | 0.43 | 4.3 | 2.31 | 2.4 | − 4 | 0.446 |
| | | | Calcium Nitrate. | | | | |
| 50 | 0.025 | 0.112 | 4.48 | 2.41 | 2.58 | −7 | 0.12 |
| 100 | 0.05 | 0.224 | 4.48 | 2.41 | 2.47 | −2 | 0.229 |
| 200 | 0.1 | 0.449 | 4.49 | 2.41 | 2.37 | +2 | 0.44 |
| | | | Potassium Ferrocyanide. | | | | |
| 50 | 0.0125 | 0.083 | 6.64 | 3.57 | 3.37 | +6 | 0.079 |
| 100 | 0.025 | 0.154 | 6.16 | 3.32 | 3.16 | +5 | 0.147 |
| 200 | 0.05 | 0.286 | 5.72 | 3.08 | 2.99 | +3 | 0.278 |
| 400 | 0.1 | 0.519 | 5.19 | 2.79 | 2.85 | −2 | 0.53 |
| | | | Calcium Ferrocyanide. | | | | |
| 50 | 0.0125 | 0.035[1] | 2.8 | 1.51 | 1.55 | −3 | 0.036 |
| 100 | 0.025 | 0.065 | 2.6 | 1.4 | 1.5 | −7 | 0.07 |
| 200 | 0.05 | 0.121 | 2.42 | 1.3 | 1.47 | −13 | 0.136 |
| 400 | 0.1 | 0.215 | 2.15 | 1.16 | 1.46 | −27 | 0.271 |
| | | | Lanthanum Nitrate. | | | | |
| 50 | 0.0167 | 0.1 | 6 | 3.23 | 3.15 | +3 | 0.097 |
| 100 | 0.0333 | 0.193 | 5.79 | 3.12 | 2.99 | +4 | 0.189 |
| 200 | 0.0667 | 0.381 | 5.71 | 3.07 | 2.83 | +8 | 0.351 |
| | | | Lanthanum Sulphate. | | | | |
| 50 | 0.0083 | 0.03[2] | 3.6 | 1.94 | 1.9 | +2 | 0.029 |
| 100 | 0.0167 | 0.068 | 4.08 | 2.2 | 1.76 | +20 | 0.054 |

A comparison of the two series of $i$ values (or of the observed and calculated values of $\Delta t$) in the foregoing table shows that in general differences exist which largely exceed the experimental error. For potassium oxalate, calcium nitrate, and potassium ferrocyanide, in 0.1 formular solution, the deviations are small (not more than 2½ per cent.); but in the more dilute solution the deviations are much larger, and they lie in opposite directions in the cases of the first two salts on the

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[1] *Jahrbuch für Radioaktivität*, **5**, 504, *et seq.* (1908); *Tech. Quart.*, **21**, 373 (1908).

[2] It is obvious that this figure and those derived from it cannot lay claim to any great percentage accuracy; they are included, however, for the sake of completeness.

one hand and of potassium ferrocyanide on the other. The striking constancy at different concentrations of the values for potassium oxalate and calcium nitrate which prevails in spite of the decreasing ionization seems to show that the mol number is not proportional to the freezing point lowering in these cases. For the other three salts the deviations are not large in the more dilute solutions, but become so in the more concentrated ones. The general agreement would not therefore be improved by any change in the values of $\Lambda_0$, for if such a change lessened the divergence at some concentrations, it would increase it at others. It is to be remembered, however that the $\Lambda_0$ values for the salts of higher valence type like lanthanum nitrate and potassium ferrocyanide may be in error by several per cent. Yet to give a satisfactory explanation of the discrepancy does not seem possible at the present time.

## 13. Summary.

In this article have been presented the results of measurements of the conductivity of aqueous solutions of nine salts at a number of different concentrations and temperatures (between 0° and 156°). The salts studied were selected so as to include a variety of valence types; thus one of the salts (potassium nitrate) was uni-univalent, two (potassium oxalate and calcium nitrate) were uni-bivalent, two (potassium citrate and lanthanum nitrate) were uni-trivalent, while the remainder (potassium, calcium, and barium ferrocyanides and lanthanum sulphate) were of still higher types.

A study of these results, with reference especially to the ionization of the substances, has shown that the following principles, previously derived mainly through the consideration of salts of the uni-univalent and uni-bivalent types, apply also to those of higher types.

The equivalent conductance ($\Lambda$) and the degree of ionization ($\gamma$) of salts vary with the concentration according to approximately the same law, whatever may be the ionic type of the substance or the temperature. This law is expressed in all cases by a function of the form

$$C(\Lambda_0 - \Lambda) = K(C\Lambda)^n \text{ or } C(1 - \gamma) = K(C\gamma)^n,$$

where K and $n$ are constants for a definite salt at a definite temperature, and where the exponent $n$ has values which vary with the specific nature of the salt or with the temperature only within narrow limits (between 1.4 and 1.55 in the cases here studied) and without reference to the number of ions into which the salt molecule dissociates.

For different salts of the same ionic type at any definite concentration and temperature the degree of ionization is approximately the same.

For salts of different ionic types, the un-ionized fraction of the salt at any definite concentration of the ions and at a definite temperature is roughly proportional to the product of the valences of the ions.

The ionization decreases in all cases steadily with rising temperature, the decrease being more rapid the higher the temperature and the greater the valence-product of the ions of the salt.

The freezing point lowerings caused by most of the same salts were also determined; and from each of these lowerings the mol number $i$ (that is, the number of mols resulting from one formula weight of salt) was calculated and compared with the mol number derived from the conductivity by the well-known expression, $i = 1 + (n - 1)(\Lambda/\Lambda_0)$. Between the two $i$ values considerable differences, far exceeding the experimental error (often of 5–10 per cent. in 0.05–0.2 normal solution), were found to exist, of which we are able to offer no explanation.

BOSTON, July, 1909.

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[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY. No. 44].

# THE CHANGE OF THE EQUIVALENT CONDUCTANCE OF IONS WITH THE TEMPERATURE.

BY JOHN JOHNSTON.

Received July 14, 1909.

In connection with a research on the electrical conductivity of salts of higher ionic type,[1] it was necessary to determine the value of the equivalent conductance ($\Lambda_0$) at infinite dilution at eight temperatures ranging from 0° to 156°. The conductance values obtained by actual measurement in extremely dilute solutions are not reliable, unless they are made with great care in a specially constructed apparatus, by means of which access of air or other impurity to the solution is prevented. Even in the case of 0.002 normal solutions it is often difficult to obtain completely concordant results. Recourse was therefore had to extrapolation from higher concentrations, using the function which has been previously employed in this laboratory, *viz.*, $1/\Lambda = 1/\Lambda_0 + K\,(C\Lambda)^{n-1}$, where $\Lambda$ is the equivalent conductance at the concentration $C$, and $K$ is a constant. A value of $n$ was chosen so that the graph obtained by plotting the values of $1/\Lambda$ against those of $(C\Lambda)^{n-1}$ was nearly a straight line, and two other graphs corresponding to neighboring values of $n$ on opposite sides of the first line were also drawn. The value of $1/\Lambda_0$ is obtained by determining the most probable point at which these three graphs cut the $1/\Lambda$ axis.

For the salts of simpler type it had been found that lines very nearly straight were obtained with values of $n$ not far different from 1.45; but for the salts of higher types it appears to be impossible to obtain a straight line between the concentrations 0.1 and 0.002 normal, no matter what

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[1] THIS JOURNAL, 31, 987 (1909).