IV.—On the Calculation of the Conductivity of Aqueous Solutions containing the Chlorides of Sodium and Barium. — By T. C. McKay, B. A., *Dalhousie College, Halifax, N. S.*

The object of this research was to test the possibility of calculating the conductivity of mixtures of solutions of the chlorides of sodium and barium by means of the dissociation theory of electrolytic conduction. It was undertaken at the suggestion of Prof. J. G. MacGregor, and was conducted in the Physical and Chemical Laboratories of Dalhousie College.

The method of calculation is fully described in one of Prof. MacGregor's papers.* It may suffice here to state that by a graphical treatment of the dilutions and ionic concentrations of series of simple solutions of the two electrolytes, the magnitude of the dilution of each salt, in the portion or region of a mixture which it may be supposed to occupy, can be found, together with the common value of the concentration of ions of the electrolytes in their respective regions. These having been found, their products give the ionization coefficients in the mixture, and the conductivity of the mixture is then obtained from the expression of the dissociation theory for the conductivity, viz. :—

$$k = \frac{1}{p(v_1 + v_2)}\left(a_1\, n_1\, v_1\, \mu\infty_1 + a_2\, n_2\, v_2 \mu\infty_2\right),$$

where the a's represent the ionization coefficients of the electrolytes in the mixture, the n's the concentrations of the constituent solutions (in gramme-equivalents per litre), the v's the volumes of the constituent solutions, the $\mu\infty$'s the specific molecular conductivities (*i. e.*, per gramme-equivalent) at infinite dilution, of the electrolytes in the mixture, and p the ratio of the volume of the mixture to the sum of the volumes of the constituent solu-

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* N. S. Inst. of Sci., Trasactions, Vol. IX, p. 101.

tions. The method of procedure in calculation will be more exactly described after the experimental determinations have been dealt with.

To obtain the experimental data required in the calculation, it is necessary to make up a long series of solutions of each salt and measure their conductivity. The volumes of the constituent solutions before mixing must be known, and in cases where there is an appreciable change of volume on mixing the densities of the single solutions and of the mixture must be found. These determinations will be taken up in order.

Purity of Salts.

Of the salts used the sodium chloride had been furnished by Merck, the barium chloride by Eimer & Amend of New York. The former was tested for metals of the alkali and alkaline earth groups, as well as for iron. No indication of these was found. The barium chloride was tested by heating in a Bunsen flame. No impurities were discovered in this way. A further indication that the salts were sufficiently pure for the purpose in view is given by the comparison of the conductivities with those of Kohlrausch, as shown farther on in the paper. All the salt, however, used in the experiments described here, was recrystallized once by the writer.

Purity of Water.

The water used in making up the solutions was obtained by adding potassium hydroxide, about 1 gramme to a litre, to ordinary distilled water, and redistilling by means of a copper boiler lined with tin, the distillate being collected in a block-tin worm. The conductivity of the water before the potassium hydroxide was added was about 1.87 in terms of the conductivity of mercury at $0°C \times 10^{-10}$. After distillation the conductivity ranged from 1.1 to 0.95, the latter being that of the water used for the very dilute solutions.

At an earlier stage of the experiments water was purified by methods derived from a paper by G. A. Hulett.* Instead of the

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* Journal of Physical Chemistry, Vol. I, No. 2.

platinum tube which he used, however, for condensing the water vapor, a block-tin tube was used. Generally, too, only the second distillation described by him was carried out, ordinary distilled water of a conductivity of 1.87 being treated with $Ba(OH)_2$, 50 c.c. of a saturated solution to two litres. The water distilled in this last way had a conductivity of about 1.11.

Methods of Making up Solutions.

The general plan adopted in making up a series of solutions of any salt was to dilute strong solutions by means of pipettes and measuring-flasks. In measuring off volumes of strong solutions the pipettes were rarely of smaller volume than 50 c.c. The flasks were filled to the mark when the salt solution and water added had been well mixed and had attained a temperature at or near 18°C. The calibration of the flasks and pipettes will be described in a future paragraph. Analyses were made of two or three of the solutions thus formed, of intermediate concentrations, and from these the concentrations of the other solutions of any one series were determined.

To obtain solutions with smaller differences of concentration than could be conveniently got by the above method, a known quantity of one of the solutions of a series, generally a volume of 100 c.c., was placed in the dry conductivity cell and diluted by small additions of water down to the next solution in the series. 5 c.c. were generally added four or five times from a pipette. After each addition of water had been made, and the liquid well mixed, a conductivity measurement was made. An analysis of the final solution was also made if the solution was not very dilute. In that case it was assumed that the increase in the volume of the solution was equal to the volume of water added. With the stronger solutions made up in this way, the shrinkage in the combined volumes of solution and water as shown by the experimentally determined concentration of the final solution was apportioned equally among the intermediate dilutions. Judging from the course of the curves representing conductivity and concentration good results were attainable is this way up to

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a concentration of 0.6 gramme-equivalent per litre. Above that concentration the solutions, which were to be used in obtaining data for the calculations, were made up outside the cell. Two sets of solutions made in the cell in which the concentrations of the final solutions were calculated by a comparison of their conductivity with the conductivity of other solutions of approximately the same, and of known, concentration, were used to give an idea of the course of the conductivity-concentration curves between 0.7 and 1 gramme-equivalents per litre, but in none of the mixtures calculated and tabulated at the end of the paper does the determination of the ionisation coefficients require the use of these portions of the curves.

To test the validity, within the limits of experimental error, of the assumption, that, in the case of dilute solutions, the volumes of the latter are increased by the volume of water added, I made use of Kohlrausch and Hallwachs' observations of the specific gravity of solutions of sodium chloride.* For solutions whose concentration is not greater than 0.2 gramme-molecule per litre, the specific gravity may be represented to 1 in the fifth place of decimals by the equation

$$s = 1 + .04244m - .003m^2,$$

where s represents the specific gravity at 18°C and m the concentration in gramme-molecules per litre. The following is a comparison of the values obtained by this equation with those obtained by Kohlrausch and Hallwachs :—

m.	s (by formula).	s (K. & H.)
.2	1.008368	1.008358
.1	1.004214	1.004202
.05	1.002115	1.002111

Writing then k for the first constant in the formula, and l for the second, W for the weight of water in grammes, w for the weight of salt when divided by a the value of the molecular

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* Wied. Ann., 53 (1894) p. 14.

weight of the substance (in this case 58.5), and D for the density of water at 18°C, we obtain :—

$$\frac{W + a\,w}{D\,v} - 1 = \frac{kw}{v} + l\frac{w^2}{v^2}.$$

Then differentiating with respect to v, since w is a constant,

$$\frac{d\,v}{d\,W} = \frac{1}{D(1 - l\frac{w^2}{v^2})} = \frac{1}{D(1 - l\,m^2)},$$

which becomes in the above particular case

$$\frac{1}{D(1 + .003m^2)}.$$

Therefore when m is sufficiently small to make the quantity $l\,m^2$ neligible, the increase of the volume of the solution is equal to the volume of the water added, since in that case

$$\frac{1}{D}\ \frac{dv}{d\,W} = 1.$$

Calibration of Flasks, Pipettes and Burettes.

The flasks were calibrated by weighing them empty and again when filled with distilled water of known temperature up to the mark. The error in calibrating a 250 c.c. flask was determined by a large number of measurements to be possibly .03 per cent. No flasks of less volume than 200 c. c. were used in making up solutions.

With the pipettes, the weight of water of known temperature which they delivered was found. In doing this the point was always held against the receiving vessel, and the liquid which remained in the point after the delivery was removed by blowing sharply into it once. The amount of water delivered in this way was determinable to about .005 c. c.

The burettes used held 50 c. c. and were graduated to tenths of 1 c. c. To calibrate them accurately it was found necessary to determine the volume of the tube for every 2 c. c., and in some cases for smaller lengths. These determinations were checked a large number of times by weighing the volumes of water between very various points on the tube. Readings could be made to .01 c. c., and the calibrations were carried nearly, if

not quite to that accuracy. In using them for making analyses volumes of 30 c. c. or over were delivered.

Analyses.

The strength of NaCl solutions was found by volumetric determination of the chlorine according to Mohr's method. Many of them also, particularly the stronger ones, were made up by weighing dry NaCl, which had been kept in a desiccator, in calibrated flasks, and filling up with water.

The $BaCl_2$ solutions were analyzed by precipitating the barium with Na_2SO_4. The barium sulphate was collected on filters and its amount determined in the ordinary way. In many cases also the amount of chlorine in the filtrate was determined volumetrically.

The volumetric analyses were not so reliable as the gravimetric, the error of the former sometimes reaching five-tenths of one per cent, though generally in the direct analyses of the chlorine, one or two tenths.

Conductivity Measurements.

The conductivity of the solutions whose strength had been determined in these various ways was measured by Kohlrausch's telephone method. The bridge wire, made of German silver, was divided into thousandths, which again admitted of easy subdivision by the eye into tenths. Of a set of four platinum resistances in the instrument, viz., 1000 ohms, 100, 10, and 1, the first two only were used. These were certified by Queen & Co., of Philadelphia, to be correct to one-fiftieth of one per cent. A number of solutions were compared with both of these resistances, and the difference between the conductivities thus measured lay within the limits of error.

To contain the solutions during the measurement of conductivity, two cells of different type were used. One was in the shape of a U-tube, the middle part being about ⅔ inch in diameter and 5 inches long, while the two arms had each a diameter of 1¾

inches. The electrodes were of stout platinum and supported by platinum wires passing through the ebonite covers of the cell. The diameter of the electrodes was $1\frac{1}{4}$ inches. The second cell was a cylindrical vessel of diameter $1\frac{1}{4}$ inches. The electrodes, whose diameter was nearly as great, were also of platinum. The platinum wires leading from them were fused into glass tubes, in the interior of which they made connection through mercury with the outside wires. The glass tubes were moveable through holes in the cover of the cell so that the distance between the electrodes could be adjusted. For any given adjustment the tubes were held in place with sealing-wax. The solutions, whose conductivity could be measured in this cell, ranged from the most dilute to, in the case of sodium chloride, about .02 gramme-equivalent per litre. The range of of NaCl solutions which could be measured in the first cell varied from 0.1 to 5 gramme-equivalent per litre. The electrodes of both cells had been platinized in a solution containing 1 grm. of platinum tetrachloride and .008 grm. of lead acetate to 30 grm. of water.

Measurements were made near the temperature 18°C, almost always within 0.3 degree of that temperature. The thermometer could be read to .01 degree, and was corrected by comparison with a standard thermometer tested at the Physikalisch-Technische Reichsanstalt, Berlin. The thermometer was kept in a separate tube in the bath; and it was found, on several occasions, by placing another thermometer in the cell itself, that the temperature of the liquid in the cell could be read off from the thermometer in the tube in almost all cases to less than 0.1 degree. Where the measurements were not made at exactly 18°, correction was made by means of the temperature coefficients given in Fitzpatrick's Table in the British Association Reports.*

The bridge wire was calibrated by Strouhal and Barus' method. The resistances for this purpose were made of German silver wires, whose ends were soldered to short pieces of thick

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* Nottingham, 1893.

copper wire. In order to draw the correction curve more
accurately, the wire was calibrated by this means in a number
of different fractions. The possible error of a conductivity
measurement, when the reading was made at the middle of the
bridge wire, was shown by a number of determinations to be
about one-tenth of one per cent. For solutions of $BaCl_2$ and
NaCl measured in the cell first described, the reading would be
made at this part of the wire if the concentration was about 0.3
gramme-equivalent. For 0.5 gramme-equivalent solutions, with
the reading at or near .64 of the length of the bridge, two-tenths
per cent, for normal solutions four-tenths. With the cell for
dilute solutions, the possible error, wherever the reading might
be made, was about six-tenths. Here other sources of error,
such as change of capacity of the cell, were greater than the
bridge error. In order to obtain a good minimum also a high
clear note from the induction coil was necessary when a very
dilute solution was in the cell, and this could not always be
obtained.

The capacity of each cell was determined by a comparison of
the conductivities of the solutions measured in it, with the values
given for corresponding solutions by Kohlrausch. The numbers
given below, under the headings NaCl and $BaCl_2$ are the ratios
of the conductivities of solutions measured in the first cell, to the
specific conductivities of corresponding solutions, as measured
by Kohlrausch.

Concentration.	Ratio.	
	NaCl.	$\frac{1}{2}BaCl_2$.
5	.2134	....
3	.2119	....
1	.2135	.2148
0.5	.2126	.2131

The mean of these ratios is .2131. This was taken as the calibration constant, and by means of it the conductivities of solutions measured in the first cell were expressed in Kohlrausch's units. The capacity of the second cell was determined in the same manner. It will be seen that the solutions above, which show the closest agreement with Kohlrausch's values, are those which could be measured near the middle of the bridge, viz., those of concentrations 0.5 and 5 gramme-equivalents per litre.

Observations on Simple Solutions.

The following tables give the concentrations and the conductivities of the simple solutions of NaCl and $BaCl_2$, by means of which the curves that show the relation between the ionic concentration and dilution were drawn.* The concentrations are expressed in gramme-equivalents per litre for the temperature of 18°C. The conductivities are expressed in terms of the conductivity of mercury at 0°C, multiplied by 10^{-8}, the temperature being also 18°C.

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* See paragraph on making up of solutions.

NaCl.		$\frac{1}{2}$ BaCl$_2$.	
Concentration.	Conductivity.	Concentration.	Conductivity.
5.013	2002	2.775	1390
3.010	1594	2.317	1245
2 005	1212	2.029	1139
1.994	1211	.6796	469.8
.9986	693.1	.6404	447.7
.7964	576.3	.6005	424.2
.5979	444.9	.5661	403.7
.5016	380.7	.5060	366.4
.4781	366.3	.4800	349.3
.4383	335.1	.4580	334.7
.4194	323.2	.4016	297.5
.4030	311.3	.3850	287.3
.3360	263.5	.3044	234.2
.2996	237.3	.2747	212.6
.2477	198.7	.2018	160.1
.2177	175.5	.1915	153.3
.2004	162.9	.01113	11.12
.1935	158.3	.00955	9.66
.1818	149.3	.00837	8.54
.01002	9.64	.00744	7.62
.00915	8.78	.00667	6.85
.00839	8.11	....	....
.00775	7.54	....	....
.00672	6.54	....	....

The conductivity of the water used in making up the above solutions did not need to be taken into account. The water used in making up the weakest NaCl solution had a conductivity equal to less than two-tenths of one per cent of the conductivity of the solution itself.

Density.

Recurring to the formula for the conductivity of a mixture of two electrolytes, given at the beginning of the paper, it will be seen that the ratio of the volume of the mixture to the sum of the volumes of the constituent solutions is required. When equal volumes are mixed as was the case in the present determinations, this ratio is equal to the ratio which the mean density of the constituent solutions has to the density of the mixture. The ratio is generally so nearly equal to 1 as to be negligible. Still its value was calculated for the mixtures of solutions above 0.2 gramme-equivalent per litre. The greatest difference from unity in the mixtures studied was .0017. The densities of the simple solutions were taken from Kohlrausch and Hallwachs' determinations in the case of NaCl, and from the British Association report before referred to in the case of $BaCl_2$. The densities of the mixtures were determined by the writer by means of Ostwald's form of Sprengel's pycnometer. The error might be about 1 in the fourth place of decimals.

Preparation of Mixtures.

The mixtures examined were in all cases mixtures of equal volumes. They were made either with the same pipette or with pipettes of equal volume. These were filled with the respective solutions at the temperature 18°C, and delivered into dry flasks or bottles.

Procedure in Calculation.

In making a calculation of the conductivity of any mixture, the conductivities and concentrations of the single solutions were first plotted on coordinate paper. From the curves thus obtained

the conductivities at regular intervals were read off and divided by the value of $\mu\infty$ for that salt, Kohlrausch's values being employed, viz., for sodium chloride 1030 and for barium chloride 1150, the conductivity unit being the same as hitherto. The quotients thus obtained were taken to be the values of the ionic concentrations. These last, divided by the corresponding dilutions, were plotted against the dilutions, and from the curves thus obtained, by Prof. MacGregor's graphical process, the common value of the ionic concentration of the electrolytes in their respective regions in the mixture and their dilutions throughout these regions, were found. The products of the latter values and the former gave the corresponding ionization coefficients. The plotting was done on very various scales as was necessary in order to plot all the curves so that readings could be made to 0.1 per cent. The calculation of the conductivity required three readings from the curves representing ionic concentration and dilution. Supposing these curves correct, the error involved in making these readings might amount to 0.15 or 0.2 per cent.

Results of Calculations.

The following table gives the results of the calculation of the conductivity of the mixtures. The first two columns give the concentration in gramme-equivalents per litre of the NaCl and $BaCl_2$ solutions before mixing, their volumes being then equal. The third, fourth, and fifth columns give the ionic concentrations and the dilutions of each salt in its portion of the mixture, each of these being expressed in terms of the units and quantities before described. The sixth and seventh columns give the specific conductivity at 18°C, in terms of 10^{-8} times the specific conductivity of mercury as calculated, and the value of the same determined experimentally. The eighth column gives the excess of the calculated over the measured value expressed in fractions of 1 per cent of the latter.

Concentration.		Concen-tration of ions in the Mixture.	Dilution in Mixture.		Conductivity.		
NaCl.	½ BaCl$_2$.		NaCl.	½ BaCl$_2$.	Calcu-lated.	Measured.	Differ-ence per cent.
3.012	2.029	1.282	.4439	.3283	1373	1380	—.5
2.007	2.775	1.195	.4886	.3672	1304	1310	—.5
2.007	2.029	1.079	.5580	.4322	1167	1171	—.4
.9986	.3044	.4501	1.601	1.315	474.8	473	+.4
.7964	.3044	.3853	1.903	1.586	407.8	407.6	+.1
.5979	.6404	.4084	1.658	1.574	445.2	444.9	+.1
.4994	.4048	.3128	2.377	2.009	337.7	339.8	—.6
.4994	.3044	.2852	2.641	2.289	307.9	307.4	+.2
.4013	.4048	.2803	2.688	2.275	304.0	304.9	—.3
.4013	.3044	.2457	3.098	2.635	270.6	270.8	—.1
.00602	.01113	.00757	123.9	116.8	8.577	8.56	+.2
.01002	.00667	.00756	116.9	124.0	8.166	8.159	+.1
.01002	.01113	.00961	96.54	90.85	10.38	10.36	+.2
.00602	.00667	.00582	162.9	153.3	6.36	6.322	+.6

In the case of solutions of from 0.3 to 0.5 gramme-equivalent per litre, which can be measured in the first cell, under the most favorable circumstances, the combined error of conductivity and analysis may amount to about 0.3 per cent. In the case of normal solutions it may reach 0.6 per cent, and in the case of very dilute solutions 0.6 per cent also. Hence, except in the case of the first solution of the above table and one other, the differences of the last column are all within the limits of experimental error. Also, the number of positive differences is about the same as the number of negative, and except that in the three strongest solutions they are all negative, and in the

four weakest all positive, the differences exhibit the alternation of sign which we would expect if they were due to accidental errors.

The results of the experiments, therefore, lead the writer to conclude that it is possible, by means of the dissociation theory, to calculate the conductivity of mixtures of solutions of the chlorides of sodium and barium at least for solutions whose concentrations are not above 2 gramme-equivalents per litre.