

II.—ON A TEST, BY THE FREEZING-POINT METHOD, OF THE IONIZATION COEFFICIENTS DETERMINED BY THE CONDUCTIVITY METHOD, FOR SOLUTIONS CONTAINING POTASSIUM AND SODIUM SULPHATES.—BY E. H. ARCHIBALD, M. SC., 1851 Exhibition Science Scholar, Dalhousie College, Halifax, N. S.

(Communicated by Prof. J. G. MacGregor; Received September 15th, 1898.)

The experiments described below were undertaken, at the suggestion of Prof. J. G. MacGregor, for the purpose of testing the values of the ionization coefficients obtained by means of his graphical method,\* in the case of a mixture of solutions of two electrolytes with a common ion, by employing them in the calculation of the depression of the freezing-point, and comparing the calculated values with values obtained by experiment.

The time at my disposal was very limited, and in consequence I was able to make the test only in the case of equimolecular solutions of two electrolytes. Potassium and sodium sulphates were selected as the electrolytes, not because of their being the most suitable for the purpose, but because I had been observing their conductivity and had already obtained some of the requisite data.

As, in determining the depression of the freezing-point, the solutions must be at a temperature of about 0° C., it was necessary that the ionization coefficients should be determined for approximately the same temperature. Both the specific conductivities of simple solutions of the two electrolytes throughout the range of concentration of the simple solutions used in preparing the mixtures, and their equivalent conductivities at infinite dilution, had therefore to be determined for 0° C., as well as the depression of the freezing-point for the mixtures. In

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\*Trans. N. S. Inst. Sci., 9, 101, (1895-6).

addition, in order to determine how closely the depression in the case of simple solutions can be calculated by means of ionization coefficients determined by conductivity measurements, I observed the depression in the case of simple solutions also.

The work involved in making the desired test therefore included the following:—(1) The purification or testing of the materials; (2) the preparation and analysis of series of simple solutions and the preparation of the mixtures; (3) the measurement of the conductivity of series of simple solutions at 0° C.; (4) the determination of the equivalent conductivity at 0° C. of the two electrolytes at infinite dilution; (5) the calculation of the ionization coefficients of the simple solutions; (6) the measurement of the depression of the freezing-point for the simple solutions; (7) the calculation of the depression for the simple solutions by means of the ionization coefficients obtained from the conductivity measurements; (8) the measurement of the depression of the freezing-point in the case of the mixtures; (9) the determination of the ionization coefficients of the electrolytes in the mixtures, and (10) the calculation of the depression of the freezing-point of the mixtures by means of these coefficients.

#### *The Materials.*

The salts were obtained as chemically pure from Eimer and Amend of New York, and were re-crystallized carefully three times, after which treatment no appreciable impurities could be detected.

The water used was purified by Hulett's\* method, except that a block tin condenser was employed instead of a platinum one. Portions of the distillate were treated in the same manner as to exposure to air, etc., as a solution would be, and their conductivity measured. It was found to vary from  $0.88 \times 10^{-10}$  to  $0.96 \times 10^{-10}$ , expressed in terms of the conductivity of mercury at 0° C. It was kept in bottles which had been used for this purpose for several years.

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\*Journ. Phys. Chem. 1, 91, (1896).

*Preparation and Analyses of Solutions.*

The potassium sulphate solutions were prepared by adding to water a known weight of anhydrous salt which had been dried to constant weight in an air bath, so as to form a known volume of solution at 18° C. In the case of the sodium sulphate, a solution was prepared, and analysed by gravimetric determination of the sulphuric acid present in a known volume of solution. Several solutions of both salts of different concentrations were prepared in the above manner, and others were prepared from these by addition of water, their concentrations being calculated. Check analyses were made whenever any portion had gone through two or three dilutions, and if found necessary the calculated concentrations were corrected from these results.

The complex solutions were prepared by mixing equal volumes of the constituent solutions at 18° C., the same precautions being observed for securing equality of volume of the constituents as are described in a former paper communicated to the Institute on the conductivity of these salts.\*

The concentrations of the solutions at 18° C. would, of course, be slightly less than their concentrations at 0° C., but with solutions as dilute as those which I used, the difference could hardly affect the third significant figure.† I have therefore regarded the concentrations at the two temperatures as the same.

As the method of calculation required a knowledge of any appreciable change of volume which might occur on mixing, simple solutions of each of the salts were prepared, and density determinations were made of such solutions before and after mixing. These measurements were carried out at 18° C. with Ostwald's form of Sprengel's Pycnometer. They might be in error by about 5 in the fifth decimal place. No change of volume

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\*Trans. N. S. Inst. Sci., 9, 291, (1897-8).

†From Forch's observations on the thermal expansion of solutions of potassium sulphate (Wied. Ann., 55, 100 (1895)), and Marignac's on sodium sulphate (Ann. Chim. Phys., (4), 22, 385, (1871)), I find that the difference of temperature referred to would affect the third significant figure of the concentrations only in the case of the stronger solutions examined, and in the case of these only to the extent of 1 or 2 units.—J. G. M.

was found to occur on preparing the most concentrated mixture examined, which would appreciably affect its concentration with respect to the two electrolytes, when calculated on the assumption that no such change of volume occurred.

*Method of Measuring Conductivity.*

The method used was Kohlrausch's Telephone method, and the apparatus was the same as described in the paper just referred to.

Two electrolytic cells were used, one for strong, the other for more dilute solutions. The first was U-shaped of the form shown by Ostwald in his Physico-Chemical Measurements, page 226, Fig. 178. The second was cylindrical, about 14 cm. long, with an internal diameter of 3.3 cm. It was provided with circular electrodes of stout platinum foil not easily bent. The stout wire supports of these electrodes were fused into glass tubes which passed through, and were sealed to, the ebonite cover of the cell. The electrodes were kept firmly in position by means of a rubber band passing over the cover and around the bottom of the cell. This cell being long and of the same diameter throughout, could, by variation of the distance between the electrodes, be used for solutions extending through a wide range of dilution.

The platinizing of the electrodes was carried out as described in the paper cited above.

The water-bath described in the above paper was used for these experiments also, modified, however, when working at 0° C. as follows:—A cylindrical screen made of wire gauze about 15 cm. in diameter was hung from a support so as to reach from the top, to within 6 or 8 cm. of the bottom, of the bath. Inside this, the electrolytic cell containing the solution to be measured, was placed, while outside was a mixture of snow and a very little sodium chloride. The screen thus prevented the snow from coming into contact with the cell, while the water around it could be thoroughly stirred. By varying the amount of salt the temperature could be kept within a twentieth of a degree of

zero for half an hour at a time. An error of this amount in the determination of the temperature of the solution would cause an error of about 0.1 per cent. in the determination of the resistance. The temperature of the room in which the observations were made was from 2° to 5° C. That one might be sure that the temperature of the solution to be measured had come to be that of the bath, measurements of the resistance were made at short intervals, and that reading taken which was found to be constant for successive intervals. The thermometer used was graduated to tenths of a degree centigrade, and could easily be read to twentieths. Its errors had recently been determined at the Physikalisch-Technische Reichsanstalt, Berlin.

The factor for reducing the observed conductivities to mercury units was found by plotting observed conductivities at 18° C. against concentrations, reading off from these curves the conductivity values for concentrations examined by Kohlrausch, and comparing them with his results. The value thus obtained was found to be the same for each salt and to be practically constant throughout the concentration range of my experiments. As the cell was of glass the reduction factor would not be appreciably different at 0° C. from what it was found to be at 18° C. To make sure that no change occurred in the position of the electrodes during the course of the experiments that would appreciably affect the reduction factor, every second or third solution was measured at 18° C. before reducing its temperature to 0° C., and the value of the conductivity obtained was compared with that previously obtained at the same temperature.

*Determination of equivalent conductivity at infinite dilution  
for 0° C.*

For this purpose a series of simple solutions of each electrolyte, of concentrations ranging from 0.01 to 0.0001 gramme-equivalents per litre, were prepared, and their conductivities were measured both at 18° C. and at 0° C. The conductivity of the water used in their preparation was also measured at both temperatures and subtracted in each case from the conductivity of

the solution. The following table gives the results of the observations together with the values of the temperature coefficients,  $(\mu_{18} - \mu_0) / \mu_{18}$ . Concentrations are expressed in gramme-equivalents of anhydrous salt per litre and conductivities in terms of  $10^{-8}$  times the conductivity of mercury at  $0^\circ$  C. The conductivities at  $18^\circ$  were tested by comparison with Kohlrausch's values, these values when plotted on coordinate paper being found to lie practically on the same curve as mine.

TABLE I.

POTASSIUM SULPHATE SOLUTIONS.				SODIUM SULPHATE SOLUTIONS.			
Concentration at $18^\circ$ C.	Equivalent Conductivity ( $\mu$ ).		$\frac{\mu_{18} - \mu_0}{\mu_{18}}$	Concentration at $18^\circ$ C.	Equivalent Conductivity ( $\mu$ ).		$\frac{\mu_{18} - \mu_0}{\mu_{18}}$
	At $18^\circ$ C.	At $0^\circ$ C.	$\mu_{18}$ .		At $18^\circ$ C.	At $0^\circ$ C.	$\mu_{18}$ .
.010	1099	687	.375	.010	907	555	.388
.008	1116	698	.375	.008	919	562	.389
.005	1142	716	.373	.005	946	577	.390
.004	1155	723	.374	.....	.....	.....	.....
.002	1180	740	.373	.002	981	596	.393
.001	1206	757	.372	.001	997	604	.394
.0008	1213	762	.372	.0008	1003	607	.395
.0006	1221	768	.371	.0006	1008	609	.396
.0005	1225	771	.371	.0005	1012	611	.396
.0004	1230	775	.370	.....	.....	.....	.....
.0002	1240	781	.370	.0002	1027	620	.396
.0001	1248	786	.370	.0001	1036	626	.396

It will be seen that the temperature coefficients for potassium sulphate solutions diminish with increase of dilution while those for sodium sulphate increase. This result\* was so

\* The results of this table are in close agreement with those obtained by Deguise (Dissertation, Strassburg, 1895), of which Mr. Archibald was not aware.—J. G. M.

unexpected that I thought it well to repeat the observations, the result being substantiated by the repetition.

It will be seen also that in both cases the coefficients reach constant values as concentration is diminished, in the case of  $\frac{1}{2} \text{K}_2 \text{SO}_4$  from a concentration of  $\cdot 0004$  on, in that of  $\frac{1}{2} \text{Na}_2 \text{SO}_4$  from  $\cdot 0006$  on. Assuming then that these values will hold for infinite dilution, the equivalent conductivities at infinite dilution for  $0^\circ \text{C}$ . may be determined from Kohlrausch's values\* for  $18^\circ \text{C}$ ., viz.,  $1270 \times 10^{-8}$  and  $1070 \times 10^{-8}$  for  $\frac{1}{2} \text{K}_2 \text{SO}_4$  and  $\frac{1}{2} \text{Na}_2 \text{SO}_4$  respectively. They were found thus to have the values  $800 \times 10^{-8}$  and  $646 \times 10^{-8}$  respectively, expressed in terms of the conductivity of mercury at  $0^\circ \text{C}$ .

*Determination of the Ionization coefficients of simple solutions.*

Both for the purpose of finding how closely the lowering of the freezing point could be calculated for simple solutions and for the purpose of determining the ionization coefficients of the electrolytes in the mixtures, it was necessary to know the ionization coefficients of a sufficiently extended series of simple solutions of the two electrolytes. The following table contains the observations of conductivity made for this purpose, together with the values of the ionization coefficients calculated on the assumption that for simple solutions they are equal to the ratios of the equivalent conductivity to the equivalent conductivity at infinite dilution. The table gives also the ionization coefficients at  $18^\circ \text{C}$ . obtained from the conductivity observations of former papers.† These quantities are not needed for the present purpose. But the knowledge of the ionization coefficients at  $0^\circ$  enables us to determine how in the case of the electrolytes under consideration the state of ionization in simple solutions varies with the temperature. Concentrations and conductivities are expressed in terms of the same units as in Table I.

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\* Wied. Ann., 50, 406, (1893).

† Trans. N. S. Inst. Sci., 9, 291 and 307, (1897-8.)

TABLE II.

Concentration at 18°C.	Equivalent Conductivity at 0°C.		Ionization Coefficients.			
			K <sub>2</sub> SO <sub>4</sub> .		Na <sub>2</sub> SO <sub>4</sub> .	
	$\frac{1}{2}$ K <sub>2</sub> SO <sub>4</sub> .	$\frac{1}{2}$ Na <sub>2</sub> SO <sub>4</sub> .	At 18°C.	At 0°C.	At 18°C.	At 0°C.
.050	604.2	486.0	.757	.755	.733	.752
.055	598.0	480.0	.750	.748	.728	.743
.060	594.1	475.5	.745	.743	.723	.736
.070	585.4	466.5	.736	.732	.715	.722
.080	577.5	460.0	.723	.722	.703	.712
.100	564.0	448.5	.706	.705	.686	.694
.125	547.5	434.0	.. .. .	.684	.....	.672
.150	535.0	422.5	.....	.669	.....	.654
.200	516.0	403.1	.650	.645	.601	.624
.250	503.0	387.4	.634	.629	.586	.600
.300	493.0	373.5	.620	.616	.570	.578
.350	485.0	362.4	.605	.606	.556	.561
.400	478.0	353.0	.595	.598	.545	.546
.450	473.0	345.5	.587	.591	.533	.535
.500	470.0	339.6	.580	.588	.522	.525
.600	466.0	330.0	.567	.583	.506	.511
.700	464.0	324.2	.551	.580	.498	.501

It appears from these results that in the case of solutions of potassium sulphate the ionization coefficient increases very slightly with rise of temperature between 0° and 18°C from a concentration of 0.05 to one of about 0.35, and that from this concentration to one of at least 0.7 it decreases, the magnitude of the decrement increasing rapidly with the concentration, and amounting at a concentration of 0.7 to 5 per cent. In the case of sodium sulphate, the coefficient diminishes with rise of



temperature throughout the whole range of concentration observed, the amount of the decrement diminishing with increase of concentration, until at a concentration of 0.7 it is only 0.6 per cent.

*Method of measuring Depression of the Freezing-point.*

Of the different methods described for the determination of the freezing point of salt solutions, that of Loomis\* appeared to me the best, and to give the most concordant results. His method was accordingly followed in making the measurements below.

As it is most essential that the temperature of the room where the observations are made should be near zero and as constant as possible, the measurements were carried out during the winter months in a basement room of Dalhousie College building, where it was found possible to keep the temperature below 2°C and constant to within 0.5 of a degree for a couple of hours at a time. No measurements were made while the temperature of the room was above 2°C.

The thermometer was of the ordinary Beckman form, graduated to 0.01 of a degree. No reading microscope being available, I had to be satisfied with the use of an ordinary hand lens for this purpose. Nevertheless, as the divisions of the scale were about 0.6 mm. in length, I am quite satisfied that I was able to read the temperatures to at least .001 degree. The following readings of the thermometer made in an experiment for determining the freezing point of water would seem to imply that I succeeded in reading even more closely:—2.3415, 2.3410, 2.3420, 2.3415, 2.3420. Mean reading, 2.3416. Greatest divergence from mean, .0006.

The thermometer had never been calibrated, and as apparatus for this purpose was not available, I did not attempt to calibrate it myself. The length of scale used for the following measurements, however, was less than what corresponded to 1.4 degree, and for the more dilute solutions, say below 0.1

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\* Phys. Review, 1, 199 and 274 (1893) and 3, 270 (1896).

gramme-equivalent per litre, less than what corresponded to 0.2 of a degree.

The freezing and melting baths were each of earthenware, about 32 cm. long and with an internal diameter of about 9 cm. In the former was a mixture of snow and water with enough common salt added to keep the temperature at about  $-12^{\circ}\text{C}$ . The latter contained a mixture of snow and water, the temperature of which was about  $0.2^{\circ}\text{C}$ .

The protection bath, which was of glass 35 cm. deep and 8 cm. in diameter, was provided with a covering of felt to minimize the effect of the surrounding air. It contained a mixture of snow and water with sufficient salt added to keep the temperature from 0.3 to 0.28 degree below the freezing point of the solutions to be measured. After some experience had been gained, little trouble was found in keeping the temperature of this bath constant within a twentieth of a degree during several observations of any one solution.

The freezing tubes first tried were of the following dimensions:—the inner one 22 cm. long with an external diameter of 2.4 cm., the outer one 20 cm. long with an internal diameter of 2.7 cm., the thickness of the glass of both tubes being 1 mm. There was thus an air space of about 1.5 mm. between the tubes. This was found to be too great as shewn by its being difficult to prevent ice from forming around the bulb of the thermometer despite the most vigorous stirring. The next ones tried were as follows:—The inner tube was 28 cm. long, with an external diameter of 2.7 cm., the outer tube 26 cm. long with an internal diameter of 2.85 cm., the thickness of the glass being the same as before. There was thus an air space of about 0.7 mm. between the tubes. This was found to be hardly enough as there was a tendency for the ice to form on the walls of the tube and thus cause much delay. As I worked with 75 c.c. of solution, the greater length of these tubes allowed the solution to be immersed well into the bath, rendering it almost free from the influence of the outside temperature. The

inner tube was therefore retained and an outer tube provided of about the same length and thickness of walls, but with an internal diameter of 2.88 cm., thus leaving an air space of about 0.9 mm. between the tubes. This gave complete satisfaction. With uniform stirring no tendency was observed for the ice to form on the walls of the tube or on the bulb of the thermometer, or to freeze in a mass. The inner tube had its lower end re-entrant, as recommended by Loomis.

I should like to draw attention to the importance of having the air space between the two tubes of the proper size. If the importance of this point has been noted by former observers it has escaped me.

The hammer used for tapping the thermometer was part of a small electric bell and was covered with a piece of thick rubber tubing. It was found to be very essential to drive the hammer so that the blows on the thermometer might be of uniform strength. Some difficulty was met with in attaining that end; but by careful attention to the strength of the current what appeared to be sufficient uniformity was attained.

The stirrer was of the ordinary ring form, the upright rod passing through a glass tube, the upper end of which was constricted, and the lower so far from the solution that the wetted portion of the stirrer could not touch it. A stop on the upright rod limited the extent of the stroke so that the ring would not leave the solution, and ensured the equality of the strokes. It was worked by hand as uniformly as possible.

The over-cooling was seldom over 0.1 degree, owing doubtless to the low temperature of the room in which the observations were made. There was consequently no need of correcting for over-cooling.

The freezing point of water was determined each day before determining that of the solutions, and in the event of any appreciable change occurring in the atmospheric pressure during the observations on the solutions, the observation on water was repeated.

*Observed and Calculated Values of the Depression of the  
Freezing-point for Simple Solutions.*

The following table contains the observations of the depression of the freezing-point of simple solutions, together with observations on solutions of about the same concentration by Loomis\* and Jones† for comparison. The depressions are expressed in centigrade degrees.

TABLE III.

Concentration gr.-eq. / litre.	Depression of Freezing-point.		Observer.
	K <sub>2</sub> SO <sub>4</sub> .	Na <sub>2</sub> SO <sub>4</sub> .	
.03949	.0975	.....	Jones.
.04	.0952	.0974	Loomis.
.050	.1185	.1191	Author.
.055	.1296	.1304	"
.0579	.1397	.....	Jones.
.060	.1407	.1416	Author.
.070	.1629	.1638	"
.07556	.1792	.....	Jones.
.080	.1851	.1856	Author.
.10	.2307	.....	Jones.
.10	.2271	.2297	Loomis.
.100	.2285	.2286	Author.
.116	.2655	.....	Jones.
.19685	.42525	.....	"
.20	.4317	.4340	Loomis.
.200	.4322	.4330	Author.
.250	.5295	.5300	"
.300	.6240	.6252	"
.350	.7196	.7157	"
.40	.8134	.8141	Loomis
.400	.8128	.8100	Author.
.450	.9063	.8968	"
.500	.9950	.9875	"
.60	1.1672	1.1604	Loomis.
.600	1.170	1.155	Author.
.700	1.341	1.323	"

\* Phys Review, 3, 277, (1896).

† Ztschr. f. phys. Chem., 11, 536, (1893).

It will be seen, especially if the above results be plotted, that all three sets of observations agree very well with one another, but that mine agree better with Loomis's than with those of Jones. Their agreement with Loomis's is very close.

The following table contains the observed and calculated values of the freezing-point depressions for simple solutions, with the differences expressed as percentages of the observed values. In the calculations Van 't Hoff's constant was taken to be 1.86, and the expression used for the depression was

$$\Delta = 1.86 (1 + 2\alpha) N/2,$$

where N is the concentration of the solution in gr.-equivalents per litre.

TABLE IV.—DEPRESSION OF FREEZING-POINT.

Concentra. (gr.-eq. / l.)	Potassium Sulphate Solutions.			Sodium Sulphate Solutions.		
	Observed.	Calculated.	Diff. per cent.	Observed.	Calculated.	Diff. per cent.
.050	.1185	.1168	-1.4	.1191	.1164	- 2.3
.055	.1296	.1277	-1.5	.1304	.1272	- 2.5
.060	.1407	.1387	-1.4	.1416	.1379	- 2.6
.070	.1629	.1604	-1.5	.1638	.1591	- 2.9
.080	.1851	.1818	-1.8	.1856	.1803	- 2.9
.100	.2285	.2241	-1.9	.2286	.2221	- 2.9
.200	.4322	.4259	-1.5	.4330	.4181	- 3.4
.250	.5295	.5250	-0.8	.5300	.5115	- 3.5
.300	.6240	.6227	-0.2	.6252	.6015	- 3.8
.350	.7196	.7200	+0.1	.7157	.6907	- 3.5
.400	.8128	.8169	+0.5	.8100	.7782	- 3.9
.450	.9063	.9131	+0.8	.8968	.8663	- 3.4
.500	.9950	1.0118	+1.7	.9875	.9532	- 3.5
.600	1.170	1.209	+3.3	1.155	1.128	- 2.3
.700	1.341	1.406	+4.9	1.323	1.303	- 1.5

The above table shews the degree of accuracy with which the depression of the freezing-point can be calculated in the case of simple solutions. If the ionization coefficients for the mixtures are determined by Prof. MacGregor's method as closely as they are for the simple solutions by putting  $\alpha = \mu/\mu_{\infty}$ , the differences between the calculated and observed values of the depressions in the case of the mixtures may be expected to be no greater than those of the above table.

*Depression of the Freezing-point by the Mixtures.*

The following Table contains the observed and calculated values of the depression of the freezing-point in the case of the mixtures examined. The observations were made in the manner described above. The calculations were made by the following formula for which I am indebted to Professor MacGregor:—

$$\Delta = 1.86 (1 + \alpha_1 + \alpha_2) N/2$$

where  $\alpha_1$  and  $\alpha_2$  are the ionization coefficients of the respective electrolytes in the mixture and  $N$  the number of gramme-equivalents per litre in the solutions mixed, which were in all cases equimolecular. This expression may be readily obtained as follows:—In each litre of the mixture there will be  $N/4$  gramme-molecules of each electrolyte. There will therefore be  $(1 - \alpha_1) N/4$  and  $(1 - \alpha_2) N/4$  undissociated gramme-molecules of the respective electrolytes, and, if we assume the ionization in each case to be complete,  $3\alpha_1 N/4$  and  $3\alpha_2 N/4$  free gramme-ions. Hence the total number of undissociated gramme-molecules and free gramme-ions will be  $(1 + \alpha_1 + \alpha_2) N/2$ , and the expression for the depression will consequently be as above.

The first column of Table V gives the concentration of the solutions mixed, in gramme-equivalents of anhydrous salt per litre at 18°C. The fifth and sixth columns give the ionization coefficients of the respective electrolytes in the mixture at 0°C as determined by Prof. MacGregor's method. The second, third and fourth give the quantities obtained directly by this method, viz., the common concentration of ions, and the dilutions of the respective electrolytes in the mixture. (By the concentration of

ions in the mixture is meant the number of dissociated gramme-equivalents of either electrolyte in any volume of the mixture divided by the volume of that portion of the mixture which may be regarded as occupied by it. The dilutions of the electrolytes in the mixture are the volumes of such portions divided by the number of gramme-equivalents of the electrolytes they contain. The product of these two quantities for each electrolyte gives the ionization coefficient of such electrolyte in the mixture.) The data of the other columns are sufficiently specified by the headings.

TABLE V.

Concentration of constituent solutions at 18°C. (gr.-eq. per l.)	Concentration of ions in mixture at 0°C.	Dilution in Mixture at 0°C.		Ioniza. Coeffts. in Mixture at 0°C.		Depression of Fr.-point.		
		$\frac{1}{2}$ K <sub>2</sub> SO <sub>4</sub> .	$\frac{1}{2}$ Na <sub>2</sub> SO <sub>4</sub> .	K <sub>2</sub> SO <sub>4</sub>	Na <sub>2</sub> SO <sub>4</sub> .	Observed	Calculated.	Diff. per cent.
.050	.0377	20.04	19.96	.7555	.7525	.1187	.1166	— 1.8
.055	.0410	18.22	18.14	.7470	.7437	.1299	.1274	— 1.9
.060	.0443	16.72	16.60	.7407	.7354	.1411	.1382	— 2.1
.070	.0509	14.40	14.18	.7330	.7218	.1634	.1598	— 2.2
.080	.0574	12.60	12.40	.7232	.7118	.1854	.1812	— 2.3
.100	.0698	10.18	9.92	.7106	.6924	.2284	.2235	— 2.1
.150	.0998	6.73	6.60	.6717	.6587	.3327	.3250	— 2.3
.200	.1266	5.10	4.90	.6457	.6203	.4324	.4215	— 2.5
.250	.1528	4.10	3.90	.6265	.5959	.5295	.5166	— 2.4
.300	.1784	3.46	3.21	.6173	.5727	.6246	.6110	— 2.2
.400	.228	2.63	2.37	.5996	.5404	.8096	.7961	— 1.7
.500	.227	2.12	1.88	.5872	.5208	.9885	.9802	— 0.8
.600	.327	1.79	1.54	.5853	.5036	1.1604	1.1657	+ 0.5
.700	.376	1.54	1.31	.5790	.4926	1.3300	1.3489	+ 1.4

If we compare the percentage differences of the above table with the corresponding differences in the case of the constituent simple solutions (Table IV, p. 45), it will be seen that the former are in general equal to the arithmetic means of the latter. Hence the depressions of the freezing-point of the mixtures have been calculated with the same degree of accuracy as those of the simple solutions.

The test which has thus been applied to Prof. MacGregor's method of determining the ionization coefficients in a solution containing two electrolytes with a common ion, and which the method has completely satisfied, is, however, not a severe one. It was intended, after the experiments on equimolecular solutions, to take up mixtures of solutions of different concentration with respect to the two electrolytes. Unfortunately I was prevented from doing so by lack of time.

In conclusion, I wish to express my thanks to Prof. MacGregor for valuable suggestions kindly given.