

III.—ON THE DEPRESSION OF THE FREEZING-POINT BY MIXTURES OF ELECTROLYTES.—BY JAMES BARNES, B. A., *Dalhousie College, Halifax, N. S.*

(Communicated by Professor J. G. MacGregor on March 12th, 1900.)

In a <sup>1</sup> paper communicated last winter to this Society, Mr. E. H. Archibald described experiments he had made to test the ionization coefficients, obtained by <sup>2</sup> Prof. MacGregor's method, for mixtures of equimolecular solutions of two electrolytes having an ion in common. With these coefficients and Van't Hoff's constant as data, he calculated the depression of the freezing-point of the mixtures; and he then compared the calculated with the experimental values. It was found that the difference between these values was, in general, equal to the arithmetic mean of the differences between the calculated and experimental values of the depressions of the constituent simple solutions, and the test was therefore concluded to be satisfactory.

At Prof. MacGregor's suggestion, I undertook similar experiments with mixtures, not of equimolecular solutions, but of solutions of different concentrations. The electrolytes selected were potassium chloride, sodium chloride, and hydrochloric acid.

In the case of mixtures of solutions which are not equimolecular Mr. Archibald's method of testing the ionization coefficients is not applicable. I found it necessary, therefore, to obtain an expression for the depression of the freezing-point for such mixtures in terms of the ionization coefficients.

In a simple solution containing  $n$  gramme-molecules of an electrolyte per litre, if  $a$  is the ionization coefficient, the number of dissociated molecules is  $na$  and the number of undissociated  $(1-a)n$ . If a molecule of this electrolyte breaks down

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<sup>1</sup> Trans. N. S. Inst. Sci., 10, 33, 1898-99.

<sup>2</sup> *Ibid.*, 9, 101, 1895-96.

into  $m$  ions, then the number of free ions is  $n m a$ , and therefore the total number of undissociated molecules and free ions in this solution is

$$(1 - a) n + n m a, \text{ or } n(1 + a(m - 1)).$$

On the assumption that a free ion produces the same amount of depression of the freezing-point as a molecule, and that in a solution the molecules are so far apart that no association of molecules occurs, if  $\delta$  is the depression of the freezing-point and  $M$  the molecular depression, *i. e.*, the depression produced by one gramme-molecule or one gramme-ion, we have

$$M = \frac{\delta}{n(1 + a(m - 1))} \dots \dots \dots (1)$$

In the case of mixtures of simple solutions, according to the above assumption,  $\Delta$  the depression of the freezing-point will be represented by the expression:—

$$\Delta = [M_1 N_1 (1 + a_1(m_1 - 1)) + M_2 N_2 (1 + a_2(m_2 - 1)) + \dots] (2)$$

where 1, 2, etc., denote the electrolytes, the  $m$ 's the numbers of ions into which the molecules of the respective electrolytes break down, the  $a$ 's the ionization coefficients in the mixture, the  $N$ 's the concentrations (in gramme-molecules per litre) of the mixture with respect to the respective electrolytes, and the  $M$ 's the depressions produced by one gramme-molecule or one gramme-ion of the undissociated and dissociated portions respectively of the electrolytes. The  $a$ 's in this expression are given by the method to be tested; the  $m$ 's in the case of the electrolytes selected can have only one value; and the  $N$ 's are of course known; but what values the  $M$ 's are to be regarded as having is doubtful. It was found for simple solutions of the three electrolytes employed, that the molecular depressions increased as the solutions became more concentrated. This appears to indicate that one molecule or one ion, when in the presence of a large number of molecules and ions, produces a greater depression than when it is in the presence of a smaller number. Thus in the case of a solution made by mixing simple solutions of different electrolytes, since the number

of molecules and ions present seems to affect the power which one molecule or ion has of lowering the freezing-point, it was assumed that the depression produced by a molecule or an ion of say, the electrolyte 1, which is surrounded by molecules and ions of this electrolyte 1 and of the other electrolytes 2, 3, etc., would have the same value as if all the molecules and ions surrounding it were of electrolyte 1. Thus the  $M$ 's of the above expression have been regarded as equal to the molecular depressions in simple solutions of the concentration  $N_1 + N_2 + \text{etc.}$

The application of this expression to the calculation of the depression in mixtures will form at once a test of the above assumption and a test of the ionization coefficients employed. I have applied it (*a*) to mixtures of potassium chloride and sodium chloride, these salts being selected because of their simple molecular structure and the approximate equality in their grade of ionization; (*b*) to mixtures of sodium chloride and hydrochloric acid, selected because of their simple molecular structure and the considerable difference in their grade of ionization; (*c*) to mixtures of potassium chloride, sodium chloride and hydrochloric acid, selected for testing in addition the method of finding the ionization coefficients in a mixture of three electrolytes.

The following is a synopsis of the work involved:—Purification of materials;—construction and calibration of the instruments used in the conductivity and freezing-point observations;—preparation and analysis of a series of simple solutions of the three electrolytes;—determination of the specific molecular conductivities at infinite dilution for  $0^\circ\text{C.}$ ;—observations on the conductivity at  $0^\circ$  for the series of simple solutions;—calculation of the ionization coefficients at  $0^\circ$  from the conductivity observations;—measurement of the depression of the freezing-point of the simple solutions;—calculation of the molecular depression for each solution of the three electrolytes;—preparation of mixtures of two and of the three electrolytes;—measurement of the depression of the freezing-point of the mixtures;—

determination of the ionization coefficients of the electrolytes in the mixtures;—calculation of the depression of the freezing-point in the mixtures.

The experiments were carried out during the session of 1899-1900 in Dalhousie College, Halifax.

*Materials, Apparatus and Methods.*

The salts and acids were obtained from Merck. The salts were recrystallized once, and it was found that solutions of them, and also of the acid, had conductivity values showing satisfactory agreement with the values as given by <sup>1</sup> Kohlrausch. These electrolytes were therefore considered sufficiently pure for the purpose. The water used in making the solutions was purified by the method described in my former <sup>2</sup> paper, and it had a conductivity at 18°C. of about  $0.95 \times 10^{-6}$  expressed in terms of Kohlrausch's new <sup>3</sup> unit ( $\text{ohm}^{-1} \text{ cm.}^{-1}$ ).

The solutions of potassium and sodium chloride were prepared by direct weighing; the salts being first dried to constant weight in an air-bath. The hydrochloric acid solutions were analysed volumetrically by means of a standardized solution of potassium hydroxide with phenol-phthalein as indicator. All burettes and pipettes used in the preparation and analysis of these solutions were calibrated by the weight of distilled water they delivered, and the flasks by the weight of water they held at 0°C.

Observations were made on the specific gravity at 18°C. of the simple solutions and their mixtures with a pycnometer of the Ostwald-Sprengel form. These observations were made to obtain the knowledge whether or not there was any change of volume on mixing the simple solutions. It was found that with solutions of the concentrations used, there was no appreciable change, and it was assumed that such would also be the case at 0°.

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<sup>1</sup> Kohlrausch u. Holborn : *Leitvermögen der Elektrolyte*, 1898, pp. 159, 160, tab. 2.

<sup>2</sup> *Trans. N. S. Inst. Sci.*, 10, 49, 1898-99.

<sup>3</sup> Kohl. u. Holb., *loc. cit.*, p. 1.

Conductivities were determined by Kohlrausch's method with the alternating current and telephone. The Wheatstone's bridge consisted of four coils, two of which, the 100 and 1000 ohms, were the only ones used. These coils were correct at 17.5°C. and had a temperature coefficient of 0.000267 per centigrade degree per ohm. The correction for temperature was applied when the observations were made in the basement room referred to below. The platinoid bridge wire was calibrated by the method proposed by <sup>1</sup>Strouhal and Barus with ten german silver wires of equal length. A telephone made by Ericsson of Stockholm, and an inductorium made after a plan of Ostwald's and giving a clear high note were employed. For a detailed account of the pycnometer, and of the instruments employed in the conductivity observations, with the methods used, see my paper referred to above.

Three electrolytic cells of two types were used. One, with the shape of a U-tube, was employed for the stronger solutions of the hydrochloric acid. The other two were of the Arrhenius form. One of these, with electrodes at a distance from one another of about  $\frac{1}{2}$  cm., was used for the weak solutions employed in the determination of the specific molecular conductivities for 0°C.; the other with electrodes at a distance of about 5 cm., for the stronger solutions of the two salts. The electrodes were all of stout platinum foil firmly fixed to the platinum wire and glass connections, so that the capacity of the cell once determined would remain the same throughout a series of experiments. These electrodes were platinized in a solution prepared from <sup>2</sup>Lummer and Kurlbaum's recipe. The reduction factor of each of these cells, by which the observed conductivities were reduced to the standard employed by Kohlrausch, was obtained by comparing the values determined for two carefully prepared solutions of potassium chloride, with the values given by <sup>3</sup>Kohlrausch for the same concentrations. Data for the

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<sup>1</sup> Wied. Ann., 10, 326, 1880.

<sup>2</sup> Wied. Ann., 60, 315, 1897.

<sup>3</sup> Kohl. u. Holb., *loc. cit.*, p. 159, tab. 2.

determination of the reduction factors were available only at  $18^{\circ}$ , but as the cell was of glass its value at  $0^{\circ}$  would not be practically different from that at  $18^{\circ}$ .

The water bath used in the observations of the conductivity at  $18^{\circ}$  was the same as that described in my former paper. In the case of the observations at  $0^{\circ}$  the bath was modified so that the temperature could be kept constant at  $0^{\circ}$  by means of pieces of ice floating in it, while the water was kept continually stirred. The ice was prevented from coming in contact with the cell by placing around the cell a cylindrical screen of wire gauze 17 cm. in diameter, and reaching to within 10 cm. of the bottom of the bath. By the addition or the removal of pieces of ice from the salt water, the temperature of the bath could easily be kept within one twenty-fifth of a degree for a sufficient time to make the measurement of conductivity. The observations were made in a basement room of the college, where the temperature, during the winter months, was generally below  $6^{\circ}\text{C}$ . The thermometer used was graduated to a fiftieth of a centigrade degree and its zero point was determined by the writer. Each solution was brought to about  $0^{\circ}$  before it was placed in the cell, and while in the cell successive observations of the conductivity were made to insure that the temperature of the bath had been taken.

The method employed for finding the freezing-point of the solutions was the same in principle as that proposed by <sup>1</sup>Loomis. The size of the protection bath was larger than that used by Loomis, and the stirring was done mechanically.

The thermometer used was of the Beckmann form. It was graduated to a hundredth of a degree, and could be read to a thousandth by aid of a small microscope, mounted on an upright stand. This thermometer was at a certain place on its stem firmly fixed in the cork of the inner freezing-tube (the freezing-tubes consisted of an inner and outer tube, the inner containing the solution whose freezing-point was measured) so that when in position its bulb was within 2 cm. of the bottom of the tube.

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<sup>1</sup> Phys. Review, 1, 199, 1893 and 9, 257, 1897.

This inner freezing-tube was 28 cm. in length and 2.8 cm. in diameter and had its lower end re-entrant. The outer tube was 25 cm. in length and 3.15 cm. in diameter. The thickness of the glass being about 1 mm., there was an air space of about 1.5 mm. between the tubes. This space was found to be quite sufficient to prevent the formation of ice on the wall of the tube. The inner tube was supported in the outer by means of two rubber bands, one at the top and the other at the bottom. These bands also prevented the walls from touching one another. The length of the tubes allowed the solution to be well submerged in the protection bath and therefore almost freed it from the influence of the outside temperature.

In the determination of the freezing-point of a solution these tubes were surrounded by a mixture of salt water and pieces of ice, contained in a vessel of glass 35 cm. high and 11 cm. in diameter (called the protection bath). The cover for this vessel was one taken from the protection bath of a Beckmann apparatus. The glass of this vessel was  $\frac{1}{2}$  cm. thick and was covered with asbestos paper that the effect of the temperature of the room might be lessened. It was found necessary to keep this bath at a constant temperature within a fiftieth of a degree, if values of the freezing-point agreeing with the mean value to less than a thousandth of a degree were desired. This was obtained by keeping the bath continually stirred. Any change of temperature was quickly recorded by means of a thermometer graduated to a fiftieth of a degree. The temperature of the bath could be raised by the addition of water at the temperature of the room, or lowered by the addition of pieces of ice, snow when obtainable being preferable.

The platinum stirrer for the freezing-tube was of the common ring shape, having wound around its ring a thin platinum wire, which would rub against the wall of the tube and thereby prevent the formation of an ice sheath. With constant stirring there was found no tendency for the ice to mass itself together and float to the surface, but it could be seen moving through the whole solution in tiny glistening particles. The stirrer for the

protection bath was of thick brass wire with two rings, one for the upper and the other for the lower portion. Both these stirrers were worked mechanically by means of one of Henrici's hot air motors placed at a distance of about 3 metres from the freezing-point apparatus. By means of a light belt this motor turned a small wooden wheel placed over the protection bath. A connecting-rod connected this wheel to a slider on a vertical guiding rod; and to this slider also were attached the two stirrers. Any range of stroke could be obtained by varying the distance of the connecting-rod from the centre of the wheel. As about 70 cc. of solution were used, a stroke of 11 cm. was required to cause the ring of the stirrer in the freezing-tube just to touch the bottom of the tube and reach to within  $\frac{1}{2}$  cm. of the surface of the solution. Thus all solutions were throughout uniformly stirred, and as the stroke of the engine was quite constant every solution was stirred in exactly the same manner.

Another glass vessel of the same dimensions as the protection bath contained salt water and ice at a temperature of about  $-10^{\circ}\text{C}$ . (called the freezing bath). The purpose of this bath was to reduce the solution in the freezing-tube to about 0.3 degree below the freezing-point.

The hammer of a common electric bell covered with a piece of rubber tubing, and supported on a frame over the freezing-point apparatus, was used for tapping the thermometer. A current from an Edison-Lalande cell had sufficient strength to give rapid and vigorous blows.

The following method of <sup>1</sup>Raoult's was employed for determining the elevation above the temperature of the protection bath, of the convergence temperature of this apparatus, *i. e.*, the temperature finally assumed by a solution which is being stirred and has no ice in it, when it comes into thermal equilibrium with the protection bath. The freezing-point of water was first obtained. The ice formed in this observation was then melted and the freezing-tubes containing the water returned to the protection bath and the stirring begun. With the protection

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<sup>1</sup> Ztschr. f. Phys. Chem., 27, 636, 1898.



bath kept constantly at  $0^{\circ}$  the temperature of the water in the freezing-tubes at first fell rapidly, then more slowly, till it remained constant at  $0.05^{\circ}$ . This experiment was repeated with the same result, and thus the convergence temperature was shown to be  $0.05$  degree above the temperature of the protection bath. In all experiments, therefore, the temperature of the protection bath was adjusted so as to be  $0.05$  degree below the freezing-point of the solution. It was also found with water that the protection bath required to be this same amount ( $0.05$  degree) below the freezing-point in order that the value of the freezing-point, with a very small quantity of ice present, might agree with that obtained with a large amount of ice.

The method of carrying out an observation of the freezing-point was as follows:—The freezing-tube was filled with the solution up to a mark on the glass (about 70 cc.) It was then placed in the freezing bath where it remained till the temperature was lowered with constant stirring to about  $0.3$  degree below the freezing-point of the solution, this point having been determined by a preliminary experiment. The freezing-tubes were now quickly removed to the protection bath which was at the required temperature ( $0.05$  degree below the freezing-point of the solution), and the stirring started. After ten minutes time, in which the solution had risen to within  $0.1$  degree of its freezing-point, a small crystal of ice was introduced through a glass tube in the cork. As the particles of ice gradually formed throughout the solution the mercury in the thermometer rose, and in about a minute assumed a fixed position. The tapping was begun and continued for half a minute when both it and the stirring were stopped, the microscope brought into position and a reading made. After again stirring and tapping, the thermometer was read again, this reading acting as a check upon the former. Care was taken to keep the protection bath constant at the required temperature throughout both these readings. The tubes were now removed, the ice melted, and the same operation repeated for a second observation.

As a change in the atmospheric pressure would cause a corresponding change in the thermometer, the freezing-point of the water used was determined about every three hours. The temperature of the room was kept as low and as constant as possible during the experiments, and no observation was made when it was above 5°C.

Since the freezing of my solutions was started about 0.1 degree below the freezing-point, the amount of ice formed was so small that the correction usually applied for the change in concentration, and, therefore, in the depression, comes within my limit of error. Thus the results are recorded without any correction.

*Simple Solutions.*

With the electrolytes K Cl, Na Cl, and H Cl, there is only one possible way for their molecules to dissociate, namely, into two ions. Hence expression (1) reduces to

$$M = \frac{\delta}{n(1+a)} \dots \dots \dots (3)$$

For the determination of the values of M, the other quantities,  $\delta$ ,  $n$  and  $a$  are obtained from observations on simple solutions;  $a$  being taken equal to the ratio of the specific molecular conductivity to the specific molecular conductivity at infinite dilution. As the solutions are at a temperature of about 0°C. in the determination of the freezing-point, the ionization coefficients should be obtained at approximately the same temperature. For this purpose measurements were made of the conductivity at 0°, both of solutions of the range of concentration used in the observations of the freezing-point and also of very dilute solutions of the electrolytes. These latter measurements are required for the determination of the specific molecular conductivities at infinite dilution for 0°C.

*Determination of the Specific Molecular Conductivities at Infinite Dilution for 0°C.*

A series of simple solutions varying in concentration from .01 to .0001 in the case of the salts, and from .01 to .001 for the

acid, were prepared and their conductivities measured at 18° and at 0°. The conductivity of the water used in the preparation of these solutions was measured at both temperatures, and its value subtracted in each case from the conductivity of the solution. Considerable care was required with these dilute solutions to obtain good results. The electrodes were thoroughly washed with a portion of the solution before placing them in the cell. Both the solutions and the water used were exposed as little as possible to the air, and the measurements were taken immediately after a solution was made. The measurements were repeated three times, and the mean of the values obtained was taken as the most probable value.

The following Table I gives the values thus obtained, and the ratio  $\frac{\mu_{18} - \mu_0}{\mu_{18}}$ , where  $\mu_{18}$  and  $\mu_0$  are the specific molecular conductivities at 18° and 0° respectively. The concentrations are expressed in gramme-molecules per litre at 0°, and the specific molecular conductivities in terms of this unit and of  $10^{-4}$  times Kohlrausch's new unit of conductivity.

TABLE I.

Concentration.	Sp. Mol. Cond. at 18°C. ( $\mu_{18}$ ).	Sp. Mol. Cond. at 0°C. ( $\mu_0$ ).	$\frac{\mu_{18} - \mu_0}{\mu_{18}}$ .
K Cl. (74.59).			
.010	1224	775	.367
.005	1244	787	.367
.001	1278	809	.367
.0005	1284	814	.366
.0002	1293	821	.365
.0001	1298	824	.365
Na Cl. (58.50).			
.010	1023	638	.379
.005	1049	651	.380
.001	1075	664	.382
.0005	1084	670	.382
.0002	1094	676	.382
.0001	1098	679	.382
H Cl. (36.46).			
.010	3706	2595	.300
.005	3731	2608	.301
.002	3753	2625	.301
.001	3757	2626	.301

The ratio  $\frac{\mu_{18} - \mu_0}{\mu_{18}}$  appears to increase as the concentration diminishes, except in the case of potassium chloride where it decreases. This peculiarity is also shown in the values as calculated by means of <sup>1</sup>Dégusne's data. The agreement between Dégusne's conductivity values at 0° and the above for the solutions of concentration .01 is very close, but with the dilute solutions it is not so good. It was found impossible to obtain

<sup>1</sup> Kohl. u. Holb., *loc. cit.*, p. 199, tab. 7.

concordant results with solutions of greater dilution than those above. It is seen, however, that the ratio appears to reach a constant value in these dilute solutions, and the writer has assumed that the value of this ratio for the solution of concentration .0001 of the salts and .001 of the acid would hold for infinite dilution.

Table II gives the values of the specific molecular conductivities at infinite dilution for 0° obtained from Kohlrausch's values at 18° by aid of the above ratios. The conductivities are expressed as in Table I.

TABLE II.

Electrolyte.	Specific Molecular Conductivity at Infinite Dilution.	
	For 18°C.	For 0°C.
K Cl.....	<sup>1</sup> 1312	833
Na Cl.....	<sup>1</sup> 1103	682
H Cl.....	<sup>2</sup> 3774	2638

*Determination of the Ionization Coefficients at 0°C. for Simple Solutions.*

For this purpose the specific conductivities at 0°C. for series of simple solutions of each electrolyte were found. These conductivity values are also necessary for the drawing of the curves showing the relation between the concentration and the conductivity; these curves being required in the determination of the ionization coefficients in the mixtures.

Table III contains the observed values and also the ionization coefficients calculated therewith. The concentrations are expressed in gramme-molecules per litre at 0°C., and the conductivity in terms of 10<sup>-4</sup> times Kohlrausch's new unit.

<sup>1</sup> Kohl. u. Holb., *loc. cit.*, p. 200, tab. 8.

<sup>2</sup> Wied. Ann., 50, 385, 1893.

TABLE III.

Concentration. ( <i>m</i> ).	Specific Conductivity at 0°C. ( <i>k</i> ).	Ionization Coefficients at 0°C. ( <i>a</i> ).
K Cl.		
.03	22.73	.910
.05	37.15	.892
.08	58.32	.875
.10	71.83	.862
.20	138.5	.832
.30	204.5	.819
.40	268.1	.804
Na Cl.		
.03	18.34	.896
.05	29.92	.877
.08	46.93	.860
.10	58.03	.850
.20	111.2	.815
.30	161.0	.787
.40	208.9	.765
H Cl.		
.03	76.43	.966
.05	126.1	.956
.08	198.9	.942
.10	246.1	.933
.20	480.3	.910
.30	710.6	.898
.40	933.4	.884

*Determination of the Values of M.*

The following Table IV contains the values of the depression of the freezing-point of the simple solutions. These values, being the means of three observations, are given to four places of decimals. It also contains the values of the lowering (*M*) produced by each gramme-molecule or gramme-ion of the electrolyte

in the solution, calculated by expression (3) with the data given in this Table and in Table III. The concentrations are expressed as in former tables and the depressions in centigrade degrees.

TABLE IV.

Concentration. ( <i>n</i> ).	Depression of Freezing-point. ( $\delta$ ).	Molecular Depression. ( <i>M</i> ).
K Cl.		
.03	.1060	1.85
.05	.1752	1.85
.08	.2776	1.55
.10	.3458	1.86
.20	.6795	1.86
.30	1.0171	1.86
.40	1.3487	1.87
Na Cl.		
.03	.1072	1.89
.05	.1768	1.88
.08	.2824	1.90
.10	.3515	1.90
.20	.6885	1.90
.30	1.0292	1.92
.40	1.3646	1.93
H Cl.		
.03	.1078	1.83
.05	.1786	1.83
.08	.2835	1.83
.10	.3552	1.84
.20	.7138	1.87
.40	1.4553	1.93

By comparing Loomis' values of the depression of the freezing-point with these values, it will be seen, that the agreement in many cases is very close. If both results are plotted the curve, formed by joining the points given by the above values,

will be a little above that obtained from Loomis' values. As mentioned above, the molecular depression increases as the solutions become stronger.

According to Van't Hoff's theory the value of the molecular depression should be 1.86. <sup>1</sup>Loomis found experimentally that, with a large number of non-electrolytes in aqueous solutions, the molecular depression was 1.86 for the dilute solutions. In the case of the electrolytes used above, with the ionization coefficients determined by the conductivity method, the values of the molecular depression are seen to be grouped around this value. The divergence from this value may partly be accounted for by the use of the doubtful values of the specific molecular conductivities at infinite dilution for 0°, employed in the calculations of the ionization coefficients.

*Mixtures of Solutions of Two Electrolytes.*

Since equal volumes of simple solutions of two electrolytes, having one ion in common, were mixed, and the molecules of the electrolytes used dissociate each into two ions, expression (2), as there was no change of volume on mixing, reduces to :

$$\Delta = \frac{1}{2} [M_1 n_1 (1 + a_1) + M_2 n_2 (1 + a_2)] \dots \dots \dots (4)$$

in which  $n_1$  and  $n_2$  are the concentrations of the simple constituent solutions. For the calculation of  $\Delta$  the depression of the freezing-point of the mixture by this expression, the  $n$ 's are known, the  $a$ 's are obtained by the modification of Prof. MacGregor's method fully described in my former <sup>2</sup> paper, and the  $M$ 's in the manner referred to above.

*Results of the Calculations.*

Table V gives the data necessary for the calculation of the depression of the freezing-point of mixtures of potassium chloride and sodium chloride, and of sodium chloride and hydrochloric acid. It also shows the agreement of the calculated with the observed values. The concentrations, molecular depressions of the constituent solutions, and the depressions of the freezing-points of the mixtures are expressed as in Table IV.

<sup>1</sup> Phys. Review, 9, 257, 1899.

<sup>2</sup> Trans. N. S. Inst. Sci., 10, 124, 1899-1900.



TABLE V.

Concentrations, Constituent Solutions <sup>a</sup> at 0°C.		Ionization Coefficients in Mixture at 0°C.		Molecular Depression in Mixture.		Depression of Freezing-point of Mixture.		Difference.
K Cl. ( $n_1$ ).	Na Cl. ( $n_2$ ).	K Cl. ( $a_1$ ).	Na Cl. ( $a_2$ ).	K Cl. ( $M_1$ ).	Na Cl. ( $M_2$ ).	Observed Value.	Calculated Value.	
.05	.03	.902	.886	1.85	1.89	.1406	.1415	+ .0009
"	.06	.890	.878	1.85	1.89	.1942	.1937	- .0005
"	.08	.883	.866	1.85	1.90	.2283	.2289	+ .0006
"	.10	.878	.863	1.85	1.90	.2648	.2638	- .0010
"	.20	.854	.834	1.86	1.90	.4361	.4345	- .0016
"	.40	.829	.807	1.86	1.90	.7709	.7716	+ .0007
.30	.03	.840	.825	1.86	1.90	.5661	.5655	- .0006
"	.06	.838	.820	1.86	1.90	.6164	.6167	+ .0003
"	.08	.835	.818	1.86	1.90	.6519	.6501	- .0018
"	.10	.833	.816	1.86	1.90	.6856	.6840	- .0016
"	.20	.827	.798	1.86	1.91	.8546	.8531	- .0015
"	.40	.813	.775	1.87	1.93	1.1924	1.1937	+ .0013

TABLE V—(Continued).

Concentrations, Constituent Solutions at 0°C.		Ionization Coefficients in Mixture at 0°C.		Molecular Depression in Mixture.		Depression of Freezing-point of Mixture.		Difference.
Na Cl. ( $n_1$ ).	H Cl. ( $n_2$ ).	Na Cl. ( $\alpha_1$ ).	H Cl. ( $\alpha_2$ ).	Na Cl. ( $M_1$ ).	H Cl. ( $M_2$ ).	Observed Value.	Calculated Value.	
.05	.03	.883	.960	1.89	1.83	.1436	.1428	-.0008
"	.05	.877	.958	1.89	1.83	.1786	.1783	-.0003
"	.08	.866	.952	1.90	1.83	.2307	.2315	+.0008
"	.10	.860	.947	1.90	1.83	.2654	.2665	+.0011
"	.20	.836	.924	1.90	1.85	.4438	.4432	-.0006
"	.40	.800	.908	1.91	1.88	.8057	.8034	-.0023
.30	.03	.825	.919	1.90	1.86	.5752	.5738	-.0014
"	.05	.824	.919	1.90	1.86	.6103	.6090	-.0013
"	.08	.820	.919	1.90	1.87	.6617	.6624	+.0007
"	.10	.815	.918	1.90	1.87	.6984	.6967	-.0017
"	.20	.797	.907	1.91	1.89	.8748	.8755	+.0007
"	.40	.770	.894	1.93	1.93	1.2450	1.2436	-.0014

It is difficult to estimate the limit of error of the above observations. The observed values are in all cases means of at least three observations, which were found to differ from their mean values in different cases by very different amounts up to 0.001 degree. There are also many sources of error in the calculations and they do not admit of exact valuation. As a rough estimate the limit of error due to both observation and calculation may probably be put at 0.0015 degree.

If this estimate is approximately correct, the above table shows that the agreement between the observed and calculated values is very satisfactory for both mixtures of potassium chloride and sodium chloride, and of sodium chloride and hydrochloric acid.

*Mixtures of Solutions of Three Electrolytes.*

In the case of mixtures of the three electrolytes used as equal volumes of the simple solutions were mixed, and there was no change of volume on mixing, and as each molecule of these electrolytes breaks down into two ions, expression (2) becomes

$$\Delta = \frac{1}{3} [M_1 n_1 (1 + a_1) + M_2 n_2 (1 + a_2) + M_3 n_3 (1 + a_3)] \dots (5)$$

where the  $n$ 's are the concentrations of the constituent solutions. Thus in any mixture the  $n$ 's are known, the  $M$ 's can be obtained as above, and the  $a$ 's can be determined by the method given below.

*Determination of the Ionization Coefficients in Mixtures of Three Electrolytes.*

<sup>1</sup> Professor MacGregor has shown how to obtain equations sufficient for finding the ionization coefficients in a mixture of any number of electrolytes having a common ion, and how to solve them by a graphical procedure. As in the case of mixtures of two electrolytes, <sup>2</sup> I have, in the present case also, transformed

<sup>1</sup> Trans. Roy. Soc. Can. (2), 2, 69, 1896-97.

<sup>2</sup> Trans. N. S. Inst. Sci., 10, 124, 1899-1900.

Professor MacGregor's equations so as to express them in terms of regional conductivities and concentrations.

In the case of mixtures of three electrolytes the transformed equations are as follows :—

$$k_1 = \frac{\mu_{\infty 1}}{\mu_{\infty 2}} k_2 = \frac{\mu_{\infty 1}}{\mu_{\infty 3}} k_3, \dots \dots \dots (6)$$

$$\frac{N_1}{C_1} + \frac{N_2}{C_2} + \frac{N_3}{C_3} = 1, \dots \dots \dots (7)$$

$$\left. \begin{aligned} k_1 &= f_1(C_1), \\ k_2 &= f_2(C_2), \\ k_3 &= f_3(C_3), \end{aligned} \right\} \dots \dots \dots (8)$$

where 1, 2, and 3 denote the electrolytes, the *k*'s the specific conductivities of the electrolytes in the regions which they respectively occupy in the mixture, (these conductivities having the same values as in simple solutions of equal concentrations), the  $\mu_{\infty}$ 's the specific molecular conductivities at infinite dilution, the *N*'s the concentrations of the mixture with respect to each electrolyte, and the *C*'s the regional concentrations, which in the case of dilute solutions are the concentrations of the constituent isohydric solutions.

We have thus six equations for the determination of three *k*'s and three *C*'s.

These equations can be solved by a graphical process. In the first place the values of the specific conductivities of electrolyte 2, (*k*<sub>2</sub>), are multiplied by the constant  $\frac{\mu_{\infty 1}}{\mu_{\infty 2}}$ , and those of electrolyte 3, (*k*<sub>3</sub>), by  $\frac{\mu_{\infty 1}}{\mu_{\infty 3}}$ . Equations (8) are now employed by drawing curves having as abscissæ the values of the specific conductivities, and the corresponding values of the concentrations as ordinates. Three points are now found by inspection, one on each curve, having a common abscissa, according to equations (6),

and ordinates, ( $C_1$ ,  $C_2$  and  $C_3$ ), whose values when substituted in equation (7), satisfy this equation. By this method we have found  $k_1$ ,  $C_1$ ,  $C_2$  and  $C_3$ ; and  $k_2$  and  $k_3$  are easily obtained from equations (6). The  $a$ 's, the ionization coefficients in the mixture, are then determined from the relation,  $a = \frac{k}{\mu_\infty C}$ .

*Results of the Calculations.*

The following Table VI contains the results of the calculations by expression (5); also the experimental values obtained for the depression of the freezing-point of mixtures of solutions of potassium chloride, sodium chloride and hydrochloric acid. The results in all the columns are expressed as in Table V.

TABLE VI.

Concentration, Constituent Solutions at 0°C.			Ionization Coefficients in Mixture at 0°C.			Molecular Depression in Mixture.			Depression of Freezing-point of Mixture.		Difference.
K Cl. ( $a_1$ ).	Na Cl. ( $a_2$ ).	H Cl. ( $a_3$ ).	K Cl. ( $a_1$ ).	Na Cl. ( $a_2$ ).	H Cl. ( $a_3$ ).	K Cl. ( $M_1$ ).	Na Cl. ( $M_2$ ).	H Cl. ( $M_3$ ).	Observed Value.	Calculated Value.	
.05	.06	.05	.890	.874	.962	1.85	1.89	1.83	.1878	.1892	+ .0014
"	.10	.08	.875	.860	.944	1.85	1.90	1.83	.2712	.2705	- .0007
"	.20	.10	.853	.838	.931	1.86	1.90	1.85	.4070	.4094	+ .0024
.30	.08	.10	.840	.825	.919	1.86	1.90	1.86	.5515	.5537	+ .0022
"	.10	.20	.833	.814	.913	1.86	1.90	1.87	.6952	.6943	- .0009
"	.20	.30	.821	.790	.904	1.86	1.91	1.89	.9290	.9274	- .0016

The calculated values in this Table will have a greater possible error than those in Table V, due to the greater number of experimental data required. In the observed values the possible error is the same as before. Considering the many sources of error in both these values the above agreement between them is very satisfactory.

*Conclusions.*

The above results show that in the case of mixtures of solutions of potassium chloride and sodium chloride, and of sodium chloride and hydrochloric acid, and of all three, it is possible, with the ionization coefficients obtained by the method referred to above, and on the assumption that the molecular depression of an electrolyte in a mixture is the same as it would be in a simple solution of the same total concentration, to predict the depression of the freezing-point within the limit of the error involved in observation and calculation.