III.—On the Conductivity, Specific Gravity and Surface Tension of Aqueous Solutions Containing Potassium Chloride and Sulphate.—By James Barnes, B. A., Dalhousie College, Halifax, N. S.

(Communicated on May 10th, 1899, by Prof. J. G. MacGregor.)

In papers read before this Society it has been shown that it is possible, by the aid of the dissociation theory of electrolytic conduction, to predict the conductivity and other physical properties of a solution containing two¹ chlorides or two² sulphates, with data as to the conductivity and the other physical properties obtained by observations on simple solutions of these salts.

At Prof. MacGregor's suggestion, I have carried out the experiments described in this paper, with the object of testing this possibility for a solution containing a chloride and a sulphate with a common cation.

The electrolytes selected were potassium chloride and sulphate. The observations on conductivity and specific gravity were made by the writer, while <sup>3</sup>Rother's observations on surface tension were used. The observations were made in the Physical and Chemical Laboratories of Dalhousie College, Halifax, during the session of 1898–99.

Apparatus and Methods.—Chemical Analysis.

The salts were obtained from Eimer & Amend of New York, as chemically pure. They were re-crystallized twice. No traces of iron or sodium were found in the salts. For the detection of iron, the ammonium sulphocyanide test was applied; for sodium, the flame test.

The water used in making the solutions was purified by boiling ordinary distilled water with a few

McIntosh, Trans. N. S. Inst. Sci., 9, 120, 1895-6.

McKay, Trans. N. S. Inst. Sci., 9, 321, 1897-8.

<sup>&</sup>lt;sup>2</sup> Archibald, Trans. N. S. Inst. Sci., 9, pp. 291, 307, 335.

<sup>3</sup> Wied. Ann., 21, 576, 1884.

grammes of barium hydroxide in a copper boiler lined with tin, and condensing in a block tin worm. The first portion of about 200 cc. that came off, was always thrown away. The water thus purified had at  $18^{\circ}$  C. a conductivity ranging from  $.95 \times 10^{-6}$  to  $1.03 \times 10^{-6}$  expressed in <sup>1</sup>Kohlrausch's new unit (Ohm<sup>-1</sup> cm.<sup>-1</sup>)

The amount of potassium chloride in a solution was determined volumetrically by Mohr's method. Two solutions of KCl, about deci normal, were made by direct weighing of the pure fused salt. These were employed in obtaining a standard solution of Ag NO<sub>3</sub>. Weaker solutions of Ag NO<sub>3</sub> were obtained by known dilution from this standard one. Neutral potassium chromate was used as the indicator. The following results will show with what accuracy this method of titration could be performed:

				Mean		0.024457
(3)	1	cc.	"	"	• • • • •	0.02448
(2)	1	cc.	"	"		0.02445
(1)	1	cc.	solution	contained	,	0.02444

Thus it seems that results which differed from the mean value by about 0.1 per cent could be obtained.

The amount of potassium sulphate in a solution was determined gravimetrically by precipitation with barium chloride. Results in this case were found to differ about 0.1 per cent from the mean value, as shown in the following example:

(1)	1	cc.	solution	contained		0.05229
(2)	1	cc.	"	"		0.05238
(3)	1	cc.	"	"	• • • • •	0.05235
				Mean		0.05234

The burettes and pipettes used in the above analyses were calibrated by the weight of distilled water they delivered. The burettes had a capacity of 50 cubic centimetres, and were graduated to a tenth of a cubic centimetre. By means of an Erdmann

<sup>&</sup>lt;sup>1</sup> Kohlrausch u. Holborn: Leitvermögen der Elektrolyte, 1898, p. 1.

float one could read to 0.1 cc. Corrections for the volume of the water contained between every two cubic centimetre marks were found and plotted on co-ordinate paper against the reading. The pipettes were all employed as much as possible in the same way, and none required less than 40 seconds to flow out. Two flasks holding a litre and a half litre respectively, were the only ones used. These were calibrated by the weight of water they held at 18° C.

#### Measurement of Specific Gravity.

The specific gravity observations were made with a pycnometer of the Ostwald-Sprengel form, holding about 22 cc. observations were made at 18° C. To obtain this temperature it was necessary, after filling the pycnometer with the solution at about this temperature, to place it in the bath described below, in which the temperature remained at 18° C. for a considerable time. After remaining in the bath fifteen minutes or more the meniscus If the meniscus now remained was adjusted to the mark. stationary for a few minutes, the pycnometer was removed. carefully cleaned and dried, and then weighed. The barometer and thermometer readings in the balance case, where the air was kept as dry as possible by means of calcium chloride, were taken, and corrections applied for the buoyancy of air. specific gravity of a certain solution of potassium chloride was found by this method to have the following values:

- (1) 1.04455
- (2) 1.04458
- (3) 1.04449
- (4) 1.04450

Mean 1.04453

Thus results which differed by about 5 in the fifth place of decimals from the mean value could be obtained.

#### Measurement of Conductivity.

The method employed by Kohlrausch with the alternating current and telephone was used.

The Wheatstone's bridge consisted of four resistance coils, which were certified by Queen & Co., of Philadelphia, to be correct to one-fiftieth of one per cent, and a platinoid bridge wire wound on a marble drum. This wire had a resistance of about 0.9 ohm, and was divided into 1000 parts, each part being capable of subdivision by the eye into tenths. It was calibrated before and after the observations, by 'Strouhal and Barus's method, ten german-silver wires of equal length, with ends firmly soldered into stout copper wire being used. Corrections were plotted against the length, and a smooth curve drawn through the points, and thus intermediate readings could be corrected. greatest correction found was 1.2 divisions. The small induction coil used had a very rapid vibrator, and was kept in an adjoining room, that its noise might not interfere with the clearness of the sound minimum in the telephone. The telephone recommended by Ostwald, and made by Ericsson of Stockholm, was used.

With these appliances the minimum point could be determined to 0.3 of a division, corresponding to an error of 0.12 per cent in the determination of the resistance at the centre of the bridge, and 0.16 per cent at the point farthest from the centre used in the experiments.

### Electrolytic Cell.

The cell in which the solutions were placed for the determination of the resistance was of the Arrhenius form, a deep cylindrical vessel, of diameter 3 cm., and depth 14 cm. The electrodes were of stout platinum foil, firmly joined by heavy platinum wire to the glass tubes. These electrodes after being well-cleaned with alcohol and a strong solution of sodium hydroxide, were platinized in a solution of platinum chloride and lead acetate. This solution was prepared from Lummer and Kurlbaum's recipe. When the electrodes had received a good coating of platinum black, they were removed and well washed in hot water.

Stout copper wires, well insulated, connected this cell with the Wheatstone bridge. They had a resistance of .023 ohm.

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

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

These wires, and also those between the induction coil and the Wheatstone bridge, were run parallel and close together to diminish any effects from self-induction.

#### Reduction Factor.

The capacity of the electrolytic cell was obtained by plotting the conductivities obtained against the concentrations. <sup>1</sup> Kohlrausch's values of the conductivity for various concentrations of the same salt were plotted to the same scale on the same coordinate paper. The ratio of the two conductivities for the same concentration gives the factor by which the observed values are reduced to the standard employed by Kohlrausch. This ratio was found to be practically the same for both electrolytes, and in the case of both, constant throughout my range of dilution.

#### Bath.

As the conductivity of a solution varies with the temperature, it was necessary to have a bath whose temperature could be kept constant for a sufficient time in which to make the measurement. Tap water, kept continually stirred by a mechanical stirrer driven by a small hydraulic motor, made an excellent bath. A thermostat was not found necessary; for, as the temperature of the room was generally near 18° C., the temperature of the bath would not change one-fiftieth of a degree in thirty minutes. The thermometer used was graduated to a fiftieth, and could easily be read to a hundredth, of a degree. This thermometer had had its errors determined at the Physikalisch-Technische Reichsanstalt, Berlin.

All solutions were allowed to remain in the bath ten minutes at least before observations were taken. After a few minutes another observation of the resistance was taken. This was done to insure that the solution had taken the temperature of the bath.

### Preparation of Simple Solutions.

The method adopted was to make up a few solutions of different concentrations of each salt. These solutions were care-

<sup>&</sup>lt;sup>1</sup> Kohl. u. Hol., loc. cit., p. 159, tab. 2.

fully analysed. Seventy-five cc. of a solution was introduced into the electrolytic cell, and successive dilutions prepared therein by the withdrawal of a certain volume and the addition of an equal volume of water at the temperature 18° C. This process was continued till the dilution reached that of the next formerly prepared solution, when the new one was introduced and the same process repeated. After each solution had gone through two dilutions the volume removed was analysed, the result serving as a check upon the calculated strength of the solution in the cell.

Preparation of Mixtures of Solutions.

Simple solutions of each electrolyte were prepared and analysed. These were kept in the bath till they had taken the temperature 18° C, when 50 cc. of each solution was removed, and the two mixed. The 50 cc. pipette used was thoroughly washed with a portion of the solution before the removal.

Results of Conductivity Observations on Simple Solutions.

For the purpose of calculating the ionization coefficients of the salts in the mixture, it is necessary to draw curves for simple solutions of each salt, showing the relation of the dilution to the ionic concentration. The following tables give the data for the drawing of these curves, obtained from observations on the concentrations and conductivities of a number of solutions of each salt.

The dilutions are expressed in terms of litres per gramme equivalent at 18° C. The atomic weights used were relative to oxygen (16.00) and the same as employed by <sup>1</sup> Kohlrausch. The specific conductivities are those at 18° C, expressed in terms of 10<sup>-4</sup> times Kohlrausch's new unit (Ohm<sup>-1</sup>cm.<sup>-1</sup>)

The concentrations of ions are the quotients obtained by dividing the specific conductivities by the specific molecular conductivities at infinite dilution. <sup>2</sup> Kohlrausch's values for the specific molecular conductivities at infinite dilution were used, namely, for potassium chloride  $1312 \times 10^{-4}$ , and potassium sulphate,  $1350 \times 10^{-4}$ .

<sup>&</sup>lt;sup>1</sup> Kohl. u. Hol., loc. cit., p. 205, tab. 14.

<sup>&</sup>lt;sup>2</sup> Ibid., p. 200, tab. 8.

TABLE I.—POTASSIUM CHLORIDE (KCI).

DILUTION.	SPECIFIC CONDUCTIVITY.	Concentration of Ions.
497.4	2.540	.00194
331.6	3.789	.00298
221.1	5.646	.00430
147.4	8.362	.00637
98.26	12.44	.00948
93.46	13.06	.00995
62.25	19.35	.0147
41.50	28.61	.0218
27.72	42.44	.0323
22.50	51.78	.0395
18.48	62.39	.0475
15.44	74.05	.0564
15.00	76.10	.0580
10.30	108.7	.0829
10.00	111.8	.0852
6.866	159.5	.122
4.577	234.2	.178
3.051	243.8	.262
2.024	506.1	.386
1.383	724.9	.553
1.046	939.8	.716
.922	1056	.805

TABLE II.—Potassium Sulphate ( $\frac{1}{2}K_2SO_4$ ).

DILUTION.	SPECIFIC CONDUCTIVITY.	CONCENTRATION OF IONS.
9.661	99.22	.0735
3.336	253.4	.187
2.596	313.2	.232
1.668	458.3	.339
1.298	570.3	.422

These were the only observations made upon potassium sulphate, because E. H. Archibald had made a sufficient number of observations on solutions of this salt, and his results were found to agree with mine. Archibald's results were expressed differently. The atomic weights used for determining his dilutions were relative to Hydrogen. These dilutions can be changed to the above by multiplication by the factor 1.0026. specific conductivities were expressed in terms of times the specific conductivity of mercury at 0° C. These values of the conductivity can be expressed in Kohlrausch's new unit by multiplication by  $1.069 \times 10^4$ . The new values for the concentration of ions can thus be calculated as in the former case. The following table gives the reduced results:

TABLE III.-POTASSIUM SULPHATE.

DILUTION.	SPECIFIC CONDUCTIVITY.	CONCENTRATION OF IONS.
100.26	11.72	.00868
66.85	16.87	.0125
40.11	27.27	.0202
33.42	32.26	.0239
20.06	51.16	.0379
15.67	63.72	.0472
12.54	78.30	.0580
10.03	95.58	.0708
8.628	110.7	.0820
7.193	130.7	.0968
5.990	152.6	.113
4.991	179.5	.133
3.466	244.4	.181
2.888	286.2	.212
2.407	334.8	.248
2.079	380.7	.282
2.005	392.8	.291
1.444	523.8	.388
1.203	610.2	.452
1.003	716.8	.531

<sup>&</sup>lt;sup>1</sup> Trans. Roy. Soc. Can. (2), 3, Sec. 3, 69, 1897-8.

Method of Calculating the Conductivity of Mixtures.

According to the dissociation theory the specific conductivity of a mixture of two solutions of electrolytes is given by the equation

 $k = \frac{1}{p \ (v_1 + v_2)} \left( \alpha_1 v_1 n_1 \mu_{\infty 1} + \alpha_2 v_2 n_2 \mu_{\infty 2} \right)$ 

where  $v_1$ ,  $v_2$  are the volumes, and  $n_1$ ,  $n_2$  the concentrations of the solutions mixed,  $\mu_{\infty 1}$ ,  $\mu_{\infty 2}$  the specific molecular conductivities of simple solutions of the electrolytes at infinite dilution,  $\alpha_1$  and  $\alpha_2$  the ionization co-efficients of the respective electrolytes in the mixture, and p is the ratio of the volume of the mixture to the sum of the volumes of the constituent solutions. This ratio was found, for the solutions used, to be practically equal to the unity; and as the volumes of the solutions mixed were in all cases equal, the equation applicable to my experiments becomes:

$$k = \frac{1}{2}(\alpha_1 n_1 \mu_{\infty 1} + \alpha_2 n_2 \mu_{\infty 2}).$$

Of the data requisite for calculating k, the n's were obtained by chemical analysis, the  $\alpha$ 's by Prof. MacGregor's method, while the  $\mu_{\infty}$ 's, in the case of sufficient dilution, might be taken to be the same in value as in the case of simple solutions of the respective electrolytes.

## Determination of p.

As equal volumes of the simple solutions were mixed, the ratio expressed by p is equal to the ratio of the mean specific gravity of the constituent solutions to the specific gravity of the mixture. By referring to the following Table IV, it is at once seen that this ratio is practically equal to unity for the most concentrated solutions examined.

		SIMPLE SOLUTIO	ONS.		
Concentration.		SPECIFIC GRA	AVITY AT 18°.	MEAN	SP. GR. OF MIXTURE
K <sub>2</sub> SO <sub>4</sub> .	KCI.	½ K <sub>2</sub> SO <sub>4</sub>	KCl	Sp. Gr.	
.5998	.9558	1.0410	1.0445	1.0428	1.0427
.5998	.09454	1.0410	1.0045	1.0228	1.0229
.1035	.05412	1.0073	1.0026	1.0049	1.0050

TABLE IV.

Determination of Ionization Coefficients in the Mixtures.

The method of determining the coefficients of ionization of the two electrolytes in a mixture has been fully described by 1 Prof. MacGregor. Curves are drawn showing the relation of the dilution to the concentration of ions for simple solutions of each salt. From these curves the concentration of ions and the dilution in the regions of the mixture occupied by the respective electrolytes are found by a graphical process, and the products of these quantities give the ionization coefficients.

# Results of Observations and Calculations of Conductivity of Mixtures.

Table V gives the necessary data for the calculation of the conductivity of the mixtures examined, and the results obtained. The concentrations of the constituent solutions are expressed in terms of gramme-equivalents per litre at 18° C. The regional dilutions are in litres per gramme-equivalent at 18° C. The specific conductivities are expressed as in Table I. The differences between the calculated and observed values of the conductivity are given as percentages of the observed value.

<sup>&</sup>lt;sup>1</sup> Trans. N. S. Inst. Sci., 9, 101, 1895-6.

TABLE V.

Concentr Constituent		Concentrat'n of Ions in Mixture.	Regional	Dilution.	Specific	Conduct Mixture.	ivity of
$\frac{1}{2}$ K <sub>2</sub> SO <sub>4</sub>	KCl.	Conce of I Mix	½ K <sub>2</sub> SO <sub>4</sub>	KCl.	Observed	Calcu- lated.	Diff. per cent.
.7707	.4941	.405	1.36	1.91	536.2	537.2	+0.18
"	.09454	.264	2.22	3.03	354.1	354.5	+0.11
"	.05412	.251	2.37	3.18	337.9	337.8	-0.03
"	.01018	.235	2.55	3.43	317.9	317.2	-0.22
.5998	.9558	.528	1.01	1.45	684.0	695.9	+0.27
"	.09454	.220	2.76	3.69	295.5	296.1	+0.20
"	.05412	.206	2.98	3.89	275.5	276.4	+0.32
"	.01018	.190	3.25	4.28	255.3	255.3	土0.00
.3853	.2470	.218	2.79	3.73	288.7	289.9	+0.41
"	.02706	.138	4.75	5.97	184.0	184.6	+0.32
.2999	.2470	.193	3.21	4.23	258.6	257.7	- 0.35
.1035	.9558	.400	1.38	1.94	524.3	525.2	+0.17
. "	.4941	.233	2.58	3.47	303.4	303.8	+0.16
"	.05412	.0611	11.8	14.3	81.51	81 37	+0.18
"	.01018	.0431	17.4	20.4	58.42	58.27	-0.26
.05175	.02706	.0324	24.2	27.6	43.48	43.50	+0.05
"	.00509	.0231	24.7	39.4	31.11	31.04	-0.23

From this table it appears that the difference between the calculated and observed values of the conductivity for all the mixtures examined, is within, or but little beyond, the limit of the error of observation, which is estimated at about 0.25 per cent.

It might be well to note that in each series having a constant concentration of potassium sulphate, the differences seem to change from a negative to a positive per cent.<sup>1</sup>

Considering the many sources of error in the calculations of the conductivity, the agreement between the observed and calculated values is very satisfactory, and leads one to draw the conclusion that the conductivity of mixtures of solutions of these

<sup>1</sup> Note by the communicator of the paper .- Mr. Barnes points out that in series of mixtures whose constituent solutions have in the case of one electrolyte the same concentration  $(n_1 \text{ say})$  in all, and in that of the other a variable concentration  $(n_2 \text{ say})$ , the excess (e) of the calculated over the observed value of the conductivity increases with  $n_2$ , being usually negative for small values of  $n_2$  and positive for larger values. At first sight it might appear that he had over-estimated his limit of error, and that the conductivity was thus shown to be calculable only for a particular value of  $n_2$  in each case. There are, however, two sources of error which will account for this regular progression in the relative magnitude and sign of the e's, viz., (1) The employment, of the quotients of the specific equivalent conductivity by the specific equivalent conductivity at infinite dilution  $(\mu/\mu_{\infty})$  as the values of the ionization coefficients (a) for simple solutions, and (2) the impossibility of drawing with perfect accuracy the dilution-ionic-concentration curves. The more concentrated the solutions the greater will  $\mu/\mu_{\infty}$  differ from a; and the greater the liability to error in the drawing of the curves the greater the possible error in the determination of the ionization coefficients of the electrolytes in the mixture. The dilution-ionic-concentration curves are nearly rectilinear for very weak and for strong solutions but curve rapidly in the region of moderate dilution, and it is in this region that it is most difficult to draw them accurately. Hence in the case of strong solutions, the magnitude and sign of the e's will be determined largely by the error due to using values of  $\mu/\mu_{\infty}$  as the ionization coefficients of the simple solutions. In the case of moderately dilute solutions they will be determined by both sources of error. In the case of dilute solutions neither source of error will have so large an effect on the result. Hence a regular progression of the e's the same in kind, may be expected in different series of mixtures of strong solutions of two given electrolytes; a regular progression may be expected also in series of moderate dilution, but since the error due to inaccurate drawing of curves will depend on the portion of the curve which is used, it may be different in kind for different series; and in sufficiently dilute solutions no regular progression is likely to occur, The most of Mr. Barnes' series are of moderate dilution, and in all of them the e's show a regular progression of the same kind, as they would if the errors involved did not conflict in sign, or if the error due to the one source were large relatively to that due to the other. His series of dilute solutions exhibit the same progression in the e's, but they consist of only two mixtures each. In my calculations of the conductivity of mixtures of NaCl and KCl solutions (Trans N. S. I. S., 9, 116), the three more concentrated series showed a progression of the e's of the same kind, the two weakest series showed no progression. In Mr. McIntosh's calculations (Ibid., 9, 132), for HCl and NaCl, the two stronger series gave a progression of the same kind, the weakest no progression. And in Mr. Archibald's calculations (Ibid., 9, 299), for  $K_2SO_4$  and  $Na_2SO_4$  solutions, the four stronger series gave progressions of the e's, differing in kind, and the three series of weaker solutions gave either a very doubtful progression or no progression at all. All these results are thus consistent with the assumption that this regular progression in the e's is due mainly at least to the two sources of error mentioned above.

salts up to an average concentration of 0.8 gramme-equivalent per litre at least, can be predicted within the limit of error of my observations.

Specific Gravity and Surface Tension.

Prof. MacGregor¹ has proposed, in the case of simple solutions of electrolytes, so dilute that the ions and the undissociated molecules may be regarded as without mutual action, to express any of their physical properties, such as specific gravity, surface tension, &c., by the following formula:

$$P = P_w + k (1-\alpha) n + l \alpha n$$

where P is the numerical value of the property for the solution,  $P_w$  that of the same property for water under the same physical conditions, n the concentration expressed in gramme-equivalents per unit volume,  $\alpha$  the ionization coefficient of the electrolyte in the solution, and k and l constants, called ionization constants.

He has also shown how to predict the value of any such property for a mixture of simple solutions, by the aid of the jonization constants determined for the simple solutions.<sup>2</sup>

<sup>&</sup>lt;sup>1</sup> Trans. N. S. Inst. Sci , 9, 219, 1896.

<sup>&</sup>lt;sup>2</sup> Note by the communicator of the paper.—The fact that values of k and l in the above formula can be found which make the formula represent the observed values of a property for simple solutions of an electrolyte has of course little theoretical interest. The ionization coefficient,  $a_i$  is a complex function of the concentration, n. If expressed in terms of powers of n the expression would involve several powers. (See Trans. N. S. I. S., 9, 112). The above expression for P is thus equivalent to an expression in terms of three or more powers of n with coefficients which are functions of constants determined by the electrical character of the electrolyte and of two additional arbitrary constants. As the concentration curves of specific gravity and surface tension for solutions are but slightly curved, it is thus to be expected that the above expression would represent them. It is of theoretical interest, however, to find whether, when the ionization constants for any property have been determined for simple solutions of two electrolytes, it is possible to predict the value of the property for mixtures by the method referred to. For (1) there are no arbitrary constants in the expression by which the prediction is made, (2) the expression itself is derived from the dissociation theory, and (3) the ionization coefficients of the electrolytes in the mixture, involved in the expression, are determined by a direct application of that theory. I think it well to make this remark because several reviewers of former papers have written under the apprehension that the k's and l's of the expression for the value of a property for a mixture (see p. 65 of this paper) were arbitrary constants determined by the observations on the mixtures. They are, however, the ionization constants already determined by observations on simple solutions. J. G. M.

In what follows I endeavor to ascertain whether or not the above formula is applicable to the specific gravity and surface tension of simple solutions of KCl and K<sub>2</sub>SO<sub>4</sub> and whether or not it is possible to predict the values of these properties for mixtures of such solutions.

The observations of specific gravity requisite for this purpose were made by the writer in the way described above.

On surface tension Rother's observations were used. They were made at 15°C and his values are therefore not strictly comparable with calculated values based on ionization coefficients for 18°C. I have, however, reduced a few of the ionization coefficients of the salts to 15°C, by using 'temperature coefficients, and found that the difference between the values for the two different temperatures is not sufficient to cause any appreciable error in my calculated results. Rother's paper has sufficient data for determining the concentration in gramme-equivalents per litre, with atomic weights as used in Table I. Rother regards his observations as possibly in error by +5 to +8 in the third place of decimals. The surface tension of the water he used was 7.357.

The following table, VI, contains the ionization coefficients for simple solutions, used in the calculations. They were obtained either from direct observations on the conductivity of the solution or by interpolation of the results of Tables I—III. The concentrations are expressed in gramme-equivalents per litre at 18°C.

<sup>&</sup>lt;sup>1</sup>Kohl. u. Holb., loc. cit., pp. 195-199, Table 7.

TABLE VI.

K	C1.	½ K <sub>2</sub>	SO <sub>4</sub> .
Concentration.	Ionization Co- efficient.	Concentration.	Ionization Co- efficient.
.01018	.932	.0517	.756
.05412	.880	.1035	.710
09454	.854	.2098	.666
.2185	.817	.2999	.626
.3400	.794	.3209	.617
.4941	.780	.3853	.603
.6851	.769	.4277	.594
.9558	.749	.5817	.569
1.046	.743	.5998	.566
1.085	.742	.7047	.558
1.428	.723	.7707	.549
2.138	.705	.8000	.545
		1.2125	.526

Determination of the Ionization Constants.

The values of the ionization constants (k and l) for either property of either salt were found by the method of least squares from the data of Tables VII and VIII for the four weakest solutions, for the specific gravity and surface tension respectively. The values thus found were employed in calculating the values of the properties of the various mixtures.

Results of the Calculations on Simple Solutions.

Tables VII and VIII contain the results of the calculations from the above formula for the two properties.

The concentrations are expressed as in the tables above.

TABLE VII. Specific Gravity at 18° C. referred to Water at 18° C.

	K Cl.				$\frac{1}{2}$ K $_2$	SO <sub>4</sub> .	
k = .045	k = .045775, $l =$		048251.	k = .062	2911.	l =	073959.
Concentration.	Observed Value.	Calculated Value.	Difference.	Concentration.	Observed Value.	Calculated Value.	Difference.
.01018	1.00045	1.00049	+0.044	.0517	1.00374	1.00369	-0.045
.05412	1,00259	1.00259	±0.0 <sub>4</sub> 0	.1035	1.00731	1.00732	$+0.0_{4}1$
.09454	1.00452	1.00454	$+0.0_{4}2$	.2999	1.02088	1.02093	$+0.0_{4}5$
.2185	1.01045	1.01044	-0.041	.3853	1.02683	1.02680	-0.043
.4941	1.02351	1.02357	+0.046	.5998	1.04097	1.04149	$+0.0_{3}5$
.9558	1.04453	1.04554	$+0.0_{2}1$	.7707	1.05266	1.05457	$+0.0_{2}2$
1.085	1.05066	1.05166	+0.021				

TABLE VIII,
SURFACE TENSION AT 15° C.

	K Cl.				½ K <sub>2</sub>	SO <sub>4</sub> .	
k = .250	67.	l=	.12272.	k = .123	802.	l = .15919.	
Concentration.	Observed Value.	Calculated Value	Difference.	Concen- tration.	Observed Value.	Calculated Value.	Difference.
.3400	7.411	7.408	-0.003	.2098	7.389	7.388	-0.001
.6851	7.460	7.461	+0.001	.3209	7.402	7.404	+0.002
1.0459	7.518	7.520	+0.002	.4277	7.419	7.419	±0.000
1.4280	7.584	7.583	-0.001	.5817	7.441	7.440	-0.001
2.1829	7.705	7.707	+0.002	.7047	7.458	7.458	±0.000
				.8000	7.459	7.471	+0.012
				1.2125	7.529	7.529	上0.000

From Table VII it seems that the specific gravity of solutions of these salts between the concentration of about 0.01 and 0.5 can be calculated by aid of the formula and with the values of k and l given, while for surface tension (Table VIII) the calculation seems possible from a concentration of 0.2 to 1.0.

#### Mixtures of Solutions.

For a solution containing two salts, the equation for the value of a property, if there is no change of volume on mixing, is of the form

$$\begin{split} \mathbf{P} = \mathbf{P}_w + (k_1(\mathbf{1} - \pmb{\alpha}_1) n_1 + l_1 \pmb{\alpha}_1 n_1) \frac{v_1}{v_1 + v_2} \\ + (k_2 \, (\, \mathbf{1} - \pmb{\alpha}_2) \, n_2 + l_2 \pmb{\alpha}_2 n_2) \, \frac{v_2}{v_1 + v_2} \, , \end{split}$$

where the n's are the concentrations of the constituent solutions, the  $\alpha$ 's the ionization coefficients of the respective electrolytes in the mixture, and the v's the volumes of the constituent solutions, the electrolytes being indicated by 1 and 2.

The ionization coefficients of the salts in the mixture are obtained by the before-mentioned-graphical method from the same curves as were used in the conductivity determinations for mixtures of solutions of these salts. The k's and l's are the ionization constants obtained for the simple solutions, and given in Tables VII and VIII.

For the specific gravity measurements, equal volumes of the constituent solutions were mixed; while Rother mixed equal weights of the simple solutions. He, however, gives sufficient data for the calculation of the concentration and volume of the constituent solutions.

The following table contains the requisite data for determining the values of the two properties from the above equation, and also, for the comparison of the results thus calculated with the observed values. The volumes of the constituent solutions in Table X, are expressed in litres at 18°C. The concentrations are expressed as in the former tables.

TABLE IX. Specific Gravity at 18° C. referred to Water at 18° C.

Concentration of Constituent Solutions.		Ionization (in Mix	Coefficients xture.	Observed Value.	Calculated Value.	Difference.
1 K2SO4.	K Cl.	1 K2SO4	K Cl. oso		Obse	
.1035	.01018	.750	.879	1.00389	1.00393	+0.04 4
	.05412	.721	.874	1.00497	1.00496	$-0.0_{4} 1$
.7707	.09454	.586	.800	1.02899	1.02899	±0.0 <sub>4</sub> 0
.5998	.9558	.533	.766	1.04271	1.04341	+0.03 7

TABLE X.
SURFACE TENSION AT 15° C.

Constituent Solutions.				Ionization Coefficients		Observed Value.	Calculated Value.	nce.
Conceatration.		Volu	me.	in Mixture.		serv	lcula Va	Difference.
½ K <sub>2</sub> SO <sub>4</sub> .	K Cl.	½ K2SO4.	K Cl.	½K2SO4.	к съ.	් ට	ු 	
.7243	.2718	.49124	.50902	.581	.769	7.438	7.435	- 0.003
.2423	.7483	.50535	.49466	.569	.788	7.447	7.430	-0.017
.8917	.6869	.49330	.50693	.535	.763	7.471	7.475	+0.004
.4921	1.7115	.51100	.48989	.470	.742	7.527	7.529	+0.002
1.1936	1.4158	.49646	.50354	.445	.740	7.554	7.550	-0.004

According to Table IX it appears that the specific gravity of a solution of these salts from an average concentration of about 0.05 to 0.5 can be calculated by the above formula, and with the above values of the ionization constants.

From Table X this formula applies for surface tension of solutions of these salts from a concentration of 0.5 to 1.3.

## Summary of Results.

According to the above results it is possible, by the aid of the dissociation theory and with data obtained from the simple solutions, to predict the conductivity, specific gravity and surface tension, of fairly dilute solutions of potassium chloride and potassium sulphate, within the limit of experimental error.