I.—On the Calculation of the Conductivity of Aqueous Solutions containing Potassium and Sodium Sulphates. — By E. H. Archibald, B. Sc., *Dalhousie College, Halifax, N. S.*

(Read November 15th, 1897.)

According to the dissociation theory of electrolysis, held by Arrhenius and others, the conductivity of a mixture of two solutions of electrolytes, 1 and 2, which have one ion in common, and which contain n_1 and n gramme-equivalents per unit of volume, is given by the expression:

$$\frac{1}{p(v_1+v_2)}\left(a_1 \, n_1 \, \mu_{\infty 1} \, v_1 + a_2 \, n_2 \, \mu_{\infty 2} \, v_2\right),$$

where v_1 and v_2 are the volumes of the two solutions mixed, p the ratio of the volume of the mixture to the sum of the volumes of the constituent solutions, $\mu_{\infty 1}$ and $\mu_{\infty 2}$ the molecular conductivities, at infinite dilution, of the respective electrolytes under the conditions in which they exist in the mixture, and α_1, α_2, the ionization coefficients of the respective electrolytes in the mixture.

The value of p in the above formula may be determined by density measurements, before and after mixing; $\mu_{\infty 1}$ and $\mu_{\infty 2}$ which for sufficiently dilute mixtures, may be considered to have

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the same values in the mixture as in the simple solutions, may be determined by conductivity measurements, to great dilution, of each electrolyte; and n_1 and n_2 may be determined by analysis. Provided, therefore, we can find the value of α_1 and α_2 the conductivity can be calculated.

In a paper communicated to this society in 1896, Professor MacGregor* explained a method for the determination of the α's in the above formula. He applied this method to some mixtures of solutions of Sodium and Potassium Chloride, examined by Bender, and found it possible to calculate their conductivity when they contained less than two gramme-molecules per litre, within the limits of experimental error. For more concentrated mixtures he found the observed values to be greater than the calculated, and the difference to increase with the concentration, till at a concentration of four gramme-molecules per litre the difference was between 3 and 4 per cent. The conductivities of mixtures of Sodium and Hydrogen Chloride solutions were measured and calculated by D. McIntosh,† who found that the conductivity of these mixtures could be calculated, within the limits of experimental error, up to a mean concentration of about one gramme-molecule per litre, and that for a mean concentration greater than this, the calculated value was greater than the observed.

The measurements, described below, were undertaken with the view of ascertaining if the conductivity was calculable, in the case of mixtures of solutions of Potassium and Sodium Sulphates, salts of more complex molecular structure than those previously examined. They were conducted in the Physical and Chemical Laboratories of Dalhousie College.

The work included purification of the salts, and of water; preparation and analysis of a series of simple solutions, and determination of their conductivity; plotting curves, giving the relation of concentration of ions to dilution for these simple solutions; preparation of the mixtures, and measuring and calculating their conductivity.

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* Transactions N. S. Inst. Science, IX (1896), p. 101.
† Transactions N. S. Inst. Science, IX (1896), p. 120.

Purification of the Salts.

The salts were obtained as chemically pure from Eimer and Amend of New York. They were carefully re-crystallized three times. After being thus treated, no impurities to any extent could be detected.

Purification of the Water.

The water used was purified by the method described by Hulett,* except that a block tin condenser was used instead of a platinum one. Water, purified by this method, had a conductivity at 18°C, varying from 0.85×10^{-10} to 0.98×10^{-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. It was neutral and left no residue on evaporation.

Preparation and Analysis of Simple Solutions.

The method adopted was to make up as concentrated a solution as it was desired to measure. This solution was carefully analysed, and from it successive multiple dilutions were prepared by adding water, all solutions being prepared at a temperature of 18°C.

A volume of fifty cubic centimetres of these solutions would be introduced into the electrolytic cell, and successive dilutions prepared from this in the cell itself, by withdrawal of a certain volume, and addition of an equal volume of water. As a check upon errors of dilution, after a portion had gone through a number of dilutions, it was taken from the cell and carefully analysed, and, if found necessary, the previous determinations of the concentration were corrected from these results.

The concentration of the solutions was determined by gravimetric analysis, the quantity of salt in solution being estimated from the amount of Barium Sulphate precipitated by Barium Chloride, when added in slight excess to a known

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* Journ. Phys. Chem., Vol. I, p. 91.

volume of the solution to be analysed.   The following results
will show with what accuracy such analyses could be carried
out :—

(1.)	K_2SO_4 in 5c.c. of solution	= 0.2174	gram.
(2.)	" " "	= 0.2178	"
(3.)	" " "	= 0.2179	"
		Mean = 0.2177	"
(1.)	Na_2SO_4 in 5c.c. of solution	= 0.2365	"
(2.)	" " "	= 0.2369	"
(3.)	" " "	= 0.2370	"
		Mean = 0.2368	"

It would seem that the result might be in error by about
0.14 per cent.

In the case of the Potassium Sulphate, standard solutions
were made up from weighed quantities of the salt, which had
been dried to constant weight in an air bath.

Preparation of the Mixtures.

For convenience in calculating, the mixtures were made up
of equal volumes of the constituent solutions. All mixtures
were prepared at a temperature of 18°C, the constituent solu-
tions being kept, for about 20 minutes previously to mixing, in a
water bath, the temperature of which was kept as near 18°C as
possible, by means of a thermostat. A 50 c.c. pipette was used to
measure out the volumes.; the same pipette being used for both
solutions, and care being taken to use the pipette in the same
manner in both cases. During outflow, the point of the pipette
was allowed to rest against the side of the vessel, and when
outflow had ceased it was slightly blown into without removing
the point.

All pipettes used were calibrated by weighing the water they
delivered. None were used in the experiments, in which the
time of outflow was less than 40 seconds.

Determination of the Conductivity.

The Kohlrausch method with the telephone and alternating current was used. The measuring apparatus consisted of four resistance coils, and a german-silver bridge wire, about three metres long, wound on a marble drum. The wire was divided into 1000 parts, and had a resistance of about 1.14 ohms. It was calibrated by the method of Strouhal and Barus,* the corrections thus obtained being plotted against length on co-ordinate paper, and the correction for any point on the wire taken off this curve.

The resistance coils were marked 1, 10, 100, and 1000 ohms. As I used only one coil (that of 1000 ohms), and as it was not necessary to express the conductivities in absolute measure, I did not need to know the relative accuracy of the coils, or the absolute value of the one used.

Two electrolytic cells were used, one for solutions more concentrated than 0.1 equivalent gramme-molecules per litre, the other for solutions more dilute. They were of the U-form, shown by Ostwald in his Physico-Chemical Measurements, page 226, fig. 178.

The electrodes were of stout platinum foil, not easily bent, circular in form, and about 3.5 cm. in diameter. Care was taken to have the electrodes always in as nearly the same position in the electrolytic cell as possible. No change of resistance could be observed for small differences in position, such as could be detected by the eye, and avoided.

The induction coil was small, and had a very rapid vibrator. It was kept in a box stuffed with cotton wool, that the noise might not interfere with the determination of the sound minimum in the telephone. A Leclanché cell was found most convenient for working the coil. With this arrangement the minimum point on the bridge-wire could be determined to within 0.3 of a division. This would allow an error of 0.12 per cent in the determination of the resistance at the centre of the bridge,

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* Wied. Ann., x (1880), p. 326.

and 0.15 per cent at the point farthest from the centre, used in my experiments.

Platinizing the Electrodes.

The electrodes, after being washed in boiling alkali and acid, were placed in a solution prepared from a recipe given by Lummer and Kurlbaum, and referred to by Kohlrausch.* This solution consists of 1 part platinum chloride, 0 008 of acetate of lead, and 30 of water. They were then connected with the terminals of two Bunsen cells arranged in series, the direction of the current being frequently changed. When the electrodes had become covered with a velvety coating of platinum black, they were removed from the solution and thoroughly washed with boiling water to remove all traces of the chloroplatinic acid. The platinizing can be done much more quickly with the above solution than with the chloroplatinic acid alone.

Reduction Factor.

To find the factor, which would reduce the observed conductivities to the standard employed by Kohlrausch, (the conductivity of mercury at 0.C), the values of the conductivity for a series of solutions of each salt, which were measured for the purposes of calculation, were plotted against the concentration (gramme-equivalents per litre), and conductivities corresponding to the concentrations examined by Kohlrausch, taken off these curves and compared with the values given by him. The ratio of these values was found to be practically constant for each salt through as wide a range of dilution as it was necessary for me to measure.

Temperature.

All conductivity measurements were made at 18°C. To insure this condition, the cell containing the solution to be measured was placed in a water-bath, the temperature of which was regulated by a thermostat, of the form recommended by Ostwald in his Physico-Chemical Measurements, p. 59, fig. 42. The regulating liquid, which was water, was enclosed in a brass

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* Wied. Ann., LX (1897), p. 315.

tube, about 35 cm. long and 4 cm. in diameter, bent so as to form three sides of a square. Two vanes fixed at an angle of 45° near the bottom of the bath, to a vertical axis, which was turned by a small hydraulic motor, kept the water of the bath well stirred. The thermometer used was graduated to fiftieths of a degree, and could easily be read to hundredths. Its readings were compared with those of another, whose errors had recently been determined to hundredths of a degree at the Physikalisch-Technische Reichsanstalt, Berlin. With this apparatus the temperature of the bath could be kept constant to within a fiftieth of a degree, for half an hour at a time. A variation of one-fiftieth of a degree might cause an error of 0.05 per cent in the determination of the resistance.

That one might be sure that the temperature of the solution to be measured had come to be that of the bath, two or more determinations of the resistance were always made at intervals of about five minutes, and that reading taken which was found to be the same for successive intervals.

Data for the Calculations.

For the simple solutions the ionization coefficient (α) was taken to be equal to the ratio of the specific molecular conductivity to the specific molecular conductivity at infinite dilution. Kohlrausch's values for the specific molecular conductivity at infinite dilution were used. They were taken to be 1280×10^{-8} and 1060×10^{-8} for Potassium and Sodium Sulphate respectively, as determined by him.[*]

The value of p in the above formula was found by density measurements before and after mixing. These measurements were carried out with Ostwald's form of Sprengel's pyknometer. Measurements, accurate to one in the fourth place of decimals, which was beyond the degree of accuracy required, could be made without much difficulty. The value of p was found to be practically equal to unity for the most concentrated solutions examined.

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[*] Wied. Ann., Vol. XXVI., p. 204.

Results of Observations on Simple Solutions.

For the purposes of calculation it was necessary to draw curves for each salt, showing the relation of dilution to ionic concentration. It was therefore necessary to know the concentrations and conductivities of a sufficiently extended series of dilutions of each salt. The following table gives the dilution, conductivity, and concentration of ions of each solution examined.

POTASSIUM SULPHATE.			SODIUM SULPHATE.		
Dilution.	Conductivity.	Concentration of ions.	Dilution.	Conductivity.	Concentration of ions.
20.00	959	.0375	20.00	784	.0370
15.62	934	.0467	15.62	771	.0466
12.50	918	.0574	12.50	753	.0568
10.00	898	.0702	10.00	734	.0692
8.605	893	.0811	7.047	663	.0888
7.173	879	.0957	5.882	651	.1044
5.973	856	.1119	5.313	648	.1150
4.977	839	.1316	3.692	623	.1592
3.456	791	.1787	2.918	598	.1933
2.880	771	.209	2.431	583	.226
2.400	753	.245	2.022	562	.262
2.073	741	.279	1.689	541	.302
2.000	737	.288	1.408	521	.349
1.440	707	.384	1.176	496	.397
1.200	689	.449	1.016	478	.443
1.000	672	.525	.847	456	.507

The dilutions are expressed in terms of litres per equivalent gramme-molecule at 18°C. The conductivities are specific mole-

cular conductivities at 18°C, expressed in terms of 10^{-8} times the specific conductivity of mercury at 0°C. The concentrations of ions are the ratios of the specific molecular conductivity to specific molecular conductivity at infinite dilution, divided by the dilution.

Results of Observations on Mixtures.

The following table contains both the data for, and the results of, the calculation of the conductivity of each mixture examined.

Concentration of the Constituent Solutions.		Concentration of ions in the Mixture.	Dilution in the Mixture.		Conductivity of Mixture.		
$\frac{1}{2}K_2SO_4$.	$\frac{1}{2}Na_2SO_4$.		$\frac{1}{2}K_2SO_4$.	$\frac{1}{2}Na_2SO_4$.	Calculated.	Observed.	Difference per cent.
1.000	2.000	.637	.7940	.6030	746.0	735.0	+ 1.47
.8263	"	.605	.8463	.6510	707.2	699.7	+ 1.06
.9915	1.998	.635	.7959	.6050	743.4	738.4	+ 0.67
"	1.667	.588	.8742	.6790	687.7	682.9	+ 0.68
"	1.427	.554	.9441	.7440	648.0	645.4	+ 0.40
"	.9982	.482	1.096	.9060	564.7	565.9	− 0.21
.4957	.9975	.3760	1.473	1.272	438.5	436.8	+ 0.38
"	.6658	.3105	1.837	1.634	363.6	364.4	− 0.21
"	.4996	.2740	2.112	1.908	320.9	322.1	− 0.37
.4166	.5050	.2572	2.281	2.077	300.6	301.2	− 0.19
.3333	"	.2360	2.509	2.304	276.0	275.5	+ 0.18
.2500	"	.2141	2.795	2.576	250.3	249.5	+ 0.31
"	.2525	.1544	4.121	3.840	180.5	180.9	− 0.22
"	.1683	.1332	4.933	4.554	155.7	155.2	+ 0.32
"	.1262	.1210	5.463	5.024	141.5	141.3	+ 0.14
.1000	.1010	.0700	10.02	9.870	81.89	81.90	− 0.01
"	.0800	.0631	11.18	11.03	73.81	73.71	+ 0.13
"	.06734	.0598	12.01	11.86	69.96	.70.05	− 0.12
"	.05050	.0542	13.33	13.20	63.40	63.49	− 0.14
.04000	"	.03485	22.28	21.95	40.76	40.83	− 0.17
.02500	"	.02860	26.96	26.25	33.45	33.36	+ 0.26
.01500	"	.02570	30.63	30.50	30.05	30.12	− 0.23

The concentrations of solutions are expressed in terms of equivalent gramme-molecules per litre at 18°C. The conductivities are specific conductivities at 18°C expressed in terms of 10^{-8} times the specific conductivity of mercury at 0°C. The concentration of ions (column 3) common to the two electrolytes in the mixture and the dilutions of the electrolytes in the mixture (columns 4 and 5) are obtained by Prof. MacGregor's graphical process.* The former is the number of dissociated gramme-equivalents of either electrolyte present in the mixture, divided by the volume in litres of the portion of the solution occupied by it. In any one mixture it has the same value for both electrolytes. The latter are the volumes in litres of the portions of the solution occupied by the respective electrolytes divided by the numbers of gramme-equivalents present. In each mixture they have different values for the two electrolytes. The product of the former into the value of the latter in the case of either electrolyte gives the ionization coefficient for that electrolyte in the mixture.

It will be seen from the above table that the differences range from 1.47 per cent to 0.12 per cent, that the greater differences are for the stronger solutions, and that in the case of these solutions all the differences but one have the same sign.

For more dilute mixtures than 0.7 equivalent gramme-molecules per litre, the differences are within or but little beyond the limit of the error of an observation, which would be about 0.25 per cent. The sign also changes frequently. The differences in these cases are therefore probably due to accidental errors.

In the case of the stronger solutions, it was to be expected that the differences would be beyond the limit of error, as the ionization coefficients (α) were taken to be the ratios of the specific molecular conductivity to the specific molecular conductivity at infinite dilution, and this is rigorously true only for infinitely dilute solutions. Also the value of the specific molecular conductivity at infinite dilution for an elecrolyte in a

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* *Loc. cit.*, p. 108.

mixture can be taken to be exactly the same as the value found by observations on the simple solutions only in the case of infinitely dilute mixtures.

The fact that for mixtures of nearly saturated solutions of these salts, the difference between the calculated and observed values is only 1.47 per cent, while for solutions of KCl and NaCl as near saturation, the difference is about 5 per cent, as determined by MacGregor* and again by McIntosh*, would seem to indicate that in the case of this class of salts, the magnitude of the differences depends on the amount of salt in the solution, not on the nearness to saturation.

It would appear from the above results that for mixtures of solutions of these salts not more concentrated than 0.8 equivalent gramme-molecules per litre, it is possible, by the aid of the dissociation theory, to calculate the conductivity within, or but little beyond, the limit of the error of observation.

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*Loc. cit.