VI.—On the Calculation of the Conductivity of Aqueous Solutions of Potassium-Magnesium Sulphate.—By T. C. McKay, B. A., *Dalhousie College, Halifax, N. S.*

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The measurements and calculations, the results of which are given in this paper, were made with a view to finding out whether the conductivity of solutions of the double sulphate of potassium and magnesium could be calculated on the supposition that it separates on solution in water into potassium sulphate and magnesium sulphate. The research was undertaken at the suggestion of Professor MacGregor, and carried out in the physical and chemical laboratories of Dalhousie University.

The method by which the calculation of the conductivities was made is based on the dissociation theory of electrolysis, and was devised by Professor MacGregor for the calculation of conductivities of mixtures of two electrolytes containing a common ion.[*] The writer showed in a former paper[†] that by the use of this method of calculation, the conductivity of mixtures of solutions in water of the chlorides of sodium and barium could be calculated on the supposition that the two salts exist separately in the solution. Most of the experimental methods used in the present research were described in that paper, and need not be referred to here.

The potassium sulphate used in the determinations was obtained from Eimer & Amend, New York; the magnesium sulphate, partly from Eimer & Amend and partly from Merck. All the salt obtained from the former was recrystallized once. Merck's magnesium sulphate was his guaranteed reagent, and with the exception of that used for some $MgSO_4$ solutions from .5 to 1 gramme-equivalent per litre, was not recrystallized by the writer. The salts were tested with silver nitrate for the

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[*]Trans. N. S. Inst. Sc., Vol. IX., p. 101.
[†]Trans. N. S. Inst Sc., Vol. IX., p. 321.

presence of chlorides, and with potassium ferrocyanide for iron. In none of these tests was any reaction observed. The solutions whose conductivities were measured range in the case of potassium sulphate from 1 to 0.1 gr.-eq. per litre and from 0.02 to 0.0066, and in the case of magnesium sulphate from 2 to 0.4, and from 0.025 to 0.008 gr.-eq. per litre. All the determinations by Kohlrausch which lie within these limits agree with the writer's within the latter's limits of error, except the value for the solution of magnesium sulphate of concentration 0.5, the conductivity of which, as measured by the writer, is 0.6 per cent. less than the value given by Kohlrausch. This difference was found to hold in the case of four specimens of recrystallized salt, both Eimer & Amend's and Merck's. The error of the writer's determination in this case might be 0.4 per cent.

In the first attempts to prepare the double salt, the K_2SO_4 and $MgSO_4$ were brought together in equimolecular, or nearly equimolecular proportions. In the case of the salt numbered I below the solution thus obtained was evaporated until crystals began to form. It was then allowed to cool to 75°C. and kept at a temperature varying from 60°C. to 75°C., until a large part of the salt had crystallized out. The crystals were dried on filter paper, and a portion heated in a platinum crucible to a dull red heat, until the weight was constant. The amount of SO_4 in the dry salt was then determined. The second specimen was crystallized out from a solution containing a small excess of $MgSO_4$, and was treated in a similar manner, except that the drying on filter paper was omitted. The third specimen was recrystallized according to a method given in its essentials in Dittmar's Quantitative Analysis. 87.1 grammes of powdered recrystallized K_2SO_4, together with 153.4 gms. of Eimer & Amend's chemically pure $MgSO_4 + 7 H_2O$, which had not, however, been recrystallized by the writer, were dissolved in 350 grammes of hot distilled water. The solution was made up to about 645 grammes, and after it had cooled to 50°C, put in a porcelain basin and left 24 hours. The crystals thus obtained were washed in pure water, powdered, and then dried on filter paper and by exposure to the

air. The following table shows the proportions in which the two salts were brought together, and the percentage of SO_4 obtained by analysis of the salt freed from the water of crystallization. By theory the percentage should be 65.27 :—

	K_2SO_4	$MgSO_4$	Percentage of SO_4	Difference per cent. from theoretical value.
I.	1	1.	64.31	−1.5
II.	1	1.038	65.00	−0.4
III.	1	1.13	65.47	+0.3

The error in a single analysis might be 0.2 per cent. The constitution of the specimens used was determined from two analyses. The salt used in the double salt determinations was the specimen III., and another portion of salt prepared similarly to it and which showed the same excess of SO_4. This excess was probably due to the fact that the double salt was crystallized out of a solution containing an excess of 13 per cent. of $MgSO_4$, an excess of which, however, is necessary to prevent the formation of K_2SO_4 crystals along with those of the double salt.

Of the double salt solutions referred to in the tables below, those *in italics* were made up in the cell itself by the addition of 5 c. c. of water each time in the case of the solutions above 0.1 gr.-eq. per litre, the original quantity having been 100 c.c. The other solutions were made up outside the cell and allowed to remain for some time before their conductivity was measured. To obtain equimolecular mixtures of the simple solutions, two solutions of K_2SO_4 and $MgSO_4$ were made up, of nearly the same concentration. Each of these was carefully analyzed, the difference being found to be 0.2 per cent. The proper amount of water was then added to the stronger solution to make the two equimolecular. Other solutions were made up by diluting these, the same pipette and flask being used in each case to dilute the K_2SO_4 and $MgSO_4$ solutions to the same extent. Mixtures of equal volumes were then made in order to obtain equimolecular mixtures of solutions of the two salts. The conductivities of these were measured within at most four hours after they had been made up.

Distilled water was used in making up all the solutions. In the case of the very dilute solutions, the conductivity of the water used was subtracted from the measured conductivity of the solution. The greatest value of this correction was 0.2 per cent.

The combined error in the determination of the conductivity and concentration of a double salt solution might be for solutions of concentration 0.4 gr.-eq. per litre, 0.3 per cent., for 0.8 solutions, 0.4 per cent., and for the very dilute solutions, from 0.02 downwards, 0.8 per cent. The errors in the case of the stronger simple solutions might be 0.2 per cent. greater. The error in plotting results and calculating from them by Professor MacGregor's graphical process might be 0.2 per cent.

Kohlrausch's values of the molecular conductivity at infinite dilution, were used in the calculations. They are, for potassium sulphate 1270, for magnesium sulphate 1080, expressed in terms of 10^{-8} times the conductivity of mercury at 0°C.

The following table gives the results of the measurements of simple solutions, made to secure data for the subsequent calculations. The concentrations are given in gramme-equivalents per litre at 18°C. The conductivities are for the temperature 18°C., and are expressed in terms of the conductivity of mercury at 0°C. multiplied by 10^{-8} :—

POTASSIUM SULPHATE. $\frac{1}{2}$ K$_2$SO$_4$.		MAGNESIUM SULPHATE. $\frac{1}{2}$ Mg SO$_4$.	
Concentration.	Conductivity.	Concentration.	Conductivity.
.9980	668.6		
.9509	640.5	2.017	404.7
.9078	616.9	1.922	396.1
.8688	596.1	1.837	386.6
.8327	575.6	1.759	378.4
.7975	555.0	1.687	370.9
.7604	533.2	1.622	363.6
.7264	513.1	1.388	333.1
.6955	491.5	1.324	323.4
.6671	474.1	1.266	314.9
.6662	472.8	1.212	305.9
.6251	446.1	1.001	270.6
.5889	427.3	.9384	259.0
.5568	405.8	.8837	248.3
.5281	387.2	.8345	239.0
.5029	369.6	.7913	230.7
.5016	369.7	.7520	222.1
.4992	369.4	.7050	211.8
.4542	341.0	.6636	201.8
.4166	316.4	.6268	194.4
.3852	294.9	.6146	191.1
.3580	274.9	.5805	182.6
.3347	259.0	.5510	175.9
.3344	260.1	.5227	168.8
.3136	246.1	.5224	168.9
.2954	233.5	.5028	164.8
.2991	222.3	.4997	163.6
.2645	211.4	.4751	158.3
.2514	201.1	.4545	152.9
.2508	201.2	.4356	147.8
.2091	171.0	.02516	15.43
.0999	89.43	.02359	14.61
.0200	20.76	.02220	13.91
.01668	17.70	.02097	13.32
.01430	15.32	.02012	12.76
.01001	11.00	.01678	11.07
.008340	9.226	.01438	9.679
.007706	8.581	.01260	8.659
.006680	7.509	.01121	7.861
.006706	7.517	.01009	7.273
		.01007	7.185
		.008395	6.156
		.007754	5.773

The following tables show the results of the calculation of the conductivities of the double salt solutions and of the equimolecular mixtures:

Concentration.	Concentration of ions.	Regional Dilution.		Conductivity.		
		$\frac{1}{2}K_2SO_4$.	$\frac{1}{2}MgSO_4$.	Calculated.	Measured.	Difference per cent.
DOUBLE SALT SOLUTIONS ($\frac{1}{2}$ MgK$_2$ (SO$_4$)$_2$.						
1.001	.3734	1.499	.4996	456.5	451.4	+ 1.1
.8345	.3266	1.747	.6500	398.0	393.5	+ 1.2
.6688	.2757	2.127	.8640	335.0	331.6	+ 1.0
.5019	.2191	2.768	1.216	265.5	261.6	+ 1.5
.4705	.2073	2.938	1.312	251.2	249.8	+ .6
.4429	,1976	3.113	1.403	239.3	237.3	+ .8
.4183	.1884	3.284	1.498	228.0	227.0	+ .4
.3963	.1800	3.459	1.593	218.0	216.7	+ .8
.3765	.1721	3.626	1.687	208.1	206 9	+ .6
.02004	.01408	59.34	40.42	16.79	16.73	+ .4
.01671	.01199	70.54	49.08	14.29	14.36	− .5
.01433	.01045	81.63	57.87	12.45	12.46	− .1
.01255	.009305	92.47	66.80	11.07	11.08	− .1
.01116	.008364	103.6	75.63	9.960	9.977	− .2
.01004	.007614	I14.4	84.62	9.063	9.009	+ .6
.009972	.007558	115.3	85.33	8.987	9.009	− .3
.008318	.006421	136.9	103.3	7.632	7.665	− .4
.00714	.00599	158.6	121.7	6.640	6.660	− .3
EQUIMOLECULAR MIXTURES.						
1.002	.3734	1.499	.4996	456.4	451	+ 1-2
.6690	.2757	2.127	.8640	334.9	327.8	+ 2.1
.5003	.2184	2.777	1.220	264.7	258.6	+ 2.3
.0200	.01406	59.47	40.51	16.76	16.64	+ .7
.01001	.07584	114.8	85.02	9.021	9.024	− .05

The columns in order give (1) the concentrations, in grammeequivalents per litre, of the double salt solutions, or of the

constituent simple solutions of the equi-molecular mixtures, as the case may be; (2) their concentrations of ions; (3) the dilutions, in litres per gramme-equivalent, of the respective salts in the regions of the solutions occupied by them, determined by the graphical process referred to above, on the hypothesis that the salts exist separately, (4) the values of the conductivities as measured, and (5) as calculated, and (6) the excess per cent. of the former values over the latter.   The concentrations of ions, that is the ionization coefficients divided by the dilutions, and the conductivities, are given in terms of the units before specified.   The solutions, the values of whose concentrations are printed in italics, were made up in the cell.

In the case of the double salt solutions from 1 gr.-eq. per litre down to 0.4, the values of the conductivities are less than they would be if the salts were separated, as judged from the values calculated on that hypothesis.   For this range of solutions the signs in the last column are all positive, and the differences are beyond the limits of error, though in two cases not much beyond. With the first four solutions the excess of the calculated values does not differ much, though the fourth is unexpectedly high. On the first addition of water to the 0.5019 solution, the difference becomes much smaller and continues so as water is added. Moreover, with most of the solutions from 0.5 to 0.37, that is, with the solutions which were diluted in the cell, the conductivity rose after the water had been added and mixed.   In these cases the last value observed was taken as the conductivity of the solution.   Thus the first measurement of the conductivity of the 0 4075 solution gives a value 1 per cent. less than the calculated value ; but the last two measurements of the same solution taken half an hour later give a value only 0.6 per cent. less.   In the case of the 0.4183 solution, however, no change was noticed. The effect is as if the addition of water, and possibly also the stirring of the solution, caused the double salt to undergo rapid dissociation.   But it may have been due to the thorough mixture of the original solution and the water added, requiring time.

In the case of the dilute solutions the differences are within limits of error, although their signs are not entirely satisfactory

most of the signs being negative. The results of these measurements seem to show that at such dilution the double salt is separated into its components.

The conductivities of the strong double salt solutions seem to be greater than the conductivities of corresponding mixtures, though in the case of dilute solutions they agree.

A fact which makes the writer somewhat suspicious of the trustworthiness of the measurements of the mixtures of strong solutions is that the density of these mixtures was found to be less than the mean density of the constituent solutions, amounting at the concentration 0.8 to a difference of 0.1 per cent. The error of a density measurement might be 0.03 per cent. The density of the double salt solutions was found to be equal to the mean density of the K_2SO_4 and $MgSO_4$ solutions of the same strength. The following are the measurements on which these statements are based. With the exception of those for the $MgSO_4$ solutions, the values of which are taken from Kohlrausch and Hallwachs' determinations, they were made by the writer.

½ K_2SO_4.		½ $MgSO_4$.		Double Salt.		Equimolecular Mixtures.	
Gr.-eq. per litre.	Sp. Grav. at 18°.	Gr.-eq. per litre.	Sp. Grav. at 18°.	Gr.-eq. per litre.	Sp. Grav. at 18°.	Gr.-eq. per litre.	Sp. Grav. at 18°.
.8327	1.0567	1.	1.05863	1.001	1.0633	.8019	1.0503
.7975	1.0539	.5	1.02987	.8345	1.0531	.6690	1.0422
.6688	1.0456	.25	1.01518	.6688	1.0427	.5003	1.0317
.5029	1.0344	.01	1.00063	.3744	1.0243	......	......
.5016	1.0340	......	.....	.0998	1.0040	......	......
.2508	1.0173	......	......	.02004	1.0015	.....	......
.01001	1.0006	.....	......	.01004	1.0004	......	.....

The results of the double salt measurements lead the writer to conclude that in dilute solutions the double salt entirely separates, but that in strong solutions the two component salts are at least partly united.