

III.—ON THE CALCULATION OF THE CONDUCTIVITY OF AQUEOUS SOLUTIONS CONTAINING THE DOUBLE SULPHATE OF COPPER AND POTASSIUM, AND OF MIXTURES OF EQUI-MOLECULAR SOLUTIONS OF ZINC AND COPPER SULPHATES. — BY E. H. ARCHIBALD, B. SC., *Dalhousie College, Halifax, N. S.*

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In a paper,* read before this Society last October, I showed that for mixtures of solutions of Potassium and Sodium Sulphate, when not more concentrated than one equivalent gramme-molecule per litre, it was possible, by the aid of the dissociation theory of electrolysis, and by employing Prof. MacGregor's graphical method† for the determination of the ionization coefficients in the mixture, to calculate the conductivity within or but little beyond the limits of an error of observation. The conductivity of mixtures of solutions of Potassium and Sodium Chloride, which were measured by Bender, have been calculated by Prof. MacGregor,† who found that for mixtures of these solutions, more dilute than two equivalent gramme-molecules per litre, it was possible to calculate their conductivity within the limits of experimental error. D. McIntosh ‡ has measured and calculated the conductivity of mixtures of solutions of Potassium and Hydrogen Chloride, and found the conductivity calculable within the limits of experimental error, up to a mean concentration of one equivalent gramme-molecule per litre.

At Prof. MacGregor's suggestion I have made the observations described in this paper, to find if the conductivity is also calculable in the case of a solution containing a double salt, on the assumption that the salt does not exist as a double salt in the solution. The salt selected was the double Sulphate of Copper and Potassium.

* Transactions N. S. Inst. Science, IX. (1897), p. 291.

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

‡ Transactions N. S. Inst. Science, IX. (1896), p. 122.

The work included the purification of the salts and of water, preparation and analysis of a series of simple solutions of the constituents of the double salt and determination of their conductivity; plotting curves, giving the relation of concentration of ions to dilution for these simple solutions; preparation of the double salt and of its solutions, and measuring and calculating their conductivity. The experiments were conducted in the Physical and Chemical Laboratories of Dalhousie College.

Purification of Materials.

The salts were obtained as chemically pure, from Eimer and Amend of New York. They were carefully re-crystallized three times. No iron or other impurities could be detected in the Copper Sulphate.

The water used was purified by the method described by Hulett,* except that a block tin condenser was used instead of a platinum one. It was found to have at 18°C a conductivity varying from 0.88×10^{-10} to 0.97×10^{-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. In the case of the more dilute solutions, where the water would appreciably effect the conductivity of the solution, the conductivity of the water used in making up a solution was subtracted from the observed conductivity of that solution.

Experimental Methods.

Details as to the preparation and analysis of simple solutions and the measurement of the conductivity, will be found in the paper referred to above. I mention here only points in which the procedure of the present paper differs from the procedure of the former.

The only change in the apparatus was the use of a cylindrical electrolytic cell in measuring the more dilute solutions. This cell was about 14 cms. long, and had an internal diameter of 3.3 cms. It was provided with circular electrodes of stout platinum

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

foil, not easily bent. The stems of these electrodes were fused into small glass tubes, which passed through, and were sealed to the ebonite cover of the cell. The electrodes were kept firmly in position by means of a rubber band, passing over the cover and around the bottom of the cell. This cell, being long, and of the same diameter throughout, could, by varying the distance between the electrodes, be used for solutions extending through a wide range of dilution.

In preparing the double Sulphate of Copper and Potassium, solutions of each salt were prepared of equal molecular concentration. In the case of the Potassium Sulphate these solutions were prepared by adding a known weight of anhydrous salt (which had been dried to constant weight in an air bath) to water so as to form a solution of known volume. For the Copper Sulphate a solution was made up, analysed by determining the sulphur present, and the required concentration obtained by adding a known volume of water to a known volume of solution. Equal volumes of these solutions were then mixed, and the mixture evaporated at a temperature below 70°C. If the temperature was allowed to rise above this point, a light green substance was precipitated out, which, according to Brunner,* is a basic double salt of Copper and Potassium.

When a sufficient quantity of the double salt had been prepared, portions were weighed out and analysed for the purpose of ascertaining the composition of the crystals. The method adopted was the determination of the copper present by precipitating it in the metallic state by means of pure zinc and hydrochloric acid in a platinum crucible. The results of three determinations agreed to within 0.11 per cent and indicated crystals of the composition $\text{CuK}_2(\text{SO}_4)_2 + 6 \text{H}_2\text{O}$.

A solution of the double salt was then prepared and the concentration estimated by determination both of the copper and of the sulphur present in a definite volume of the solution, the results from the two methods agreeing to within 0.12 per cent.

* Pogg. Ann., 50, 43.

More dilute solutions were prepared from this one by adding water, and their concentrations calculated. Check analyses, however, were made after any portion had gone through a number of dilutions, and, if found necessary, the calculated concentrations were corrected from these results.

As the method of calculation required a knowledge of any appreciable change of volume which would occur on mixing simple solutions of each of the salts, of such strength as to form a solution of the same concentration as the solution of the double salt under investigation, density determinations were made of a number of such solutions, before and after mixing. These measurements were carried out with Ostwald's form of Sprengel's Pyknometer. They might be in error by about 5 in the fifth decimal place. No change of volume was found to occur on mixing the most concentrated solutions examined which would appreciably effect the calculation of the conductivity. The density of a mixture of the constituent solutions of the double sulphate was found in the case of some of the stronger solutions (the only ones tested) to be the same, within the limits of experimental error, as the density of a solution of the double salts of the same concentration.

For the simple solutions the ionization coefficient was taken to be equal to the ratio of the specific molecular conductivity to the specific molecular conductivity at infinite dilution. The values of the molecular conductivity at infinite dilution used in the calculations were:— 1280×10^{-8} , and 1100×10^{-8} for Potassium and Copper Sulphate respectively, as determined by Kohlrausch.* I was not aware, at the time the calculations were made, that he had given 1270×10^{-8} , and 1120×10^{-8} , as better values for these salts.† I have, however, repeated some of the calculations and find that the difference caused by using these later values are in all cases less than 0.06 per cent.

* Wied. Ann., Vol. 26. p. 204.

† Wied. Ann., Vol. 50 (1893), p. 406.

*Observations on Simple Solutions of Potassium and
Copper Sulphates.*

TABLE I.

POTASSIUM SULPHATE.			COPPER SULPHATE.		
Dilution.	Conductivity.	Concentration of ions.	Dilution.	Conductivity.	Concentration of ions.
400.0	1173	.002291	400.0	852	.001935
333.3	1166	.002732	333.3	832	.002266
285.7	1158	.003166	285.7	812	.002583
250.0	1152	.003600	250.0	795	.002890
222.2	1146	.004029	222.2	778	.003182
200.0	1140	.004453	200.0	763	.003465
181.8	1134	.00487	181.8	749	.00375
166.6	1130	.00530	166.6	738	.00403
150.0	1124	.00585	150.0	726	.00440
133.3	1116	.00654	133.3	713	.00486
125.0	1112	.00695	125.0	704	.00512
110.1	1104	.00783	110.1	687	.00567
100.0	1097	.00857	100.0	676	.00614
80.0	1083	.01057	80.0	651	.00737
60.00	1062	.01382	60.00	616	.00933
50.00	1046	.01634	50.00	592.0	.01076
45.00	1037	.01800	45.00	579.0	.01169
35.71	1015	.02220	35.71	545.5	.01388
30.00	997	.02596	30.00	522.5	.01583
25.00	978	.03054	25.00	497.0	.01807
20.00	960	.03748	20.00	479.6	.02180
16.66	945	.04432	16.66	465.8	.02541
15.00	936	.0487	15.00	457.5	.02773
13.33	925	.0542	13.33	447.0	.0305
12.50	918	.0574	12.50	441.8	.0321
11.01	905	.0642	11.01	431.7	.0356
10.00	895	.0699	10.00	423.5	.0385
8.00	872	.0852	8.00	403.2	.0458
6.000	840	.1093	6.000	378.1	.0573
5.000	824	.1287	5.000	359.5	.0654
4.500	815	.1414	4.500	349.9	.0707
3.571	792	.1731	3.571	329.0	.0837
3.000	775	.2018	3.000	318.0	.0963
2.500	756	.2363	2.500	304.5	.1110
2.000	736	.2877	2.000	288.2	.1310
1.500	709	.370	1.500	268.3	.1626
1.333	698	.409	1.333	261.3	.1781
1.101	679	.482	1.101	249.8	.2061
1.000	672	.525	1.000	242.1	.2200
.806	650	.630	.651	209.8	.292
.773	647	.654	.521	192.0	.335

The foregoing table, I, contains the necessary data for the drawing of the ionic concentration-dilution curves for each salt. Dilutions are expressed in terms of litres per equivalent gramme-molecule of anhydrous salt at 18°C. The conductivities are specific molecular conductivities (*i. e.* per gramme-equivalent) 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.

Observations on the Double Sulphate Solutions.

Table II contains both the data for, and the results of, the calculation of the conductivity of each solution of the double sulphate examined, together with the observed values, and the differences between observed and calculated values, expressed as percentages. The concentrations of solutions are expressed in terms of equivalent gramme-molecules of anhydrous salt 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 common to the two electrolytes in a solution, and the dilutions of the electrolytes in the solution, are obtained by Prof. MacGregor's graphical method, on the assumption that a solution of double salt may be made by mixing equal volumes of equi-molecular solutions of the simple salts, and that, on mixing, the double salt does not form. The former is the number of dissociated gramme-equivalents of either electrolyte, which on that assumption would be present in the solution, divided by the volume in litres of the portion of the solution occupied by it. In any one solution it will have 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 number of gramme-equivalents present. In each solution they will 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 solution.

TABLE II.

Concentration of the Double Salt Solutions.	Concen- tration of ions in the Solution.	Dilution in the Solution.		Conductivity of Double Salt Solutions.		
		$\frac{1}{2}$ K ₂ SO ₄ .	$\frac{1}{2}$ Cu SO ₄ .	Calcu- lated.	Observed.	Differences per cent.
1.294	.4300	1.260	.284	535.9	504.1	+6.38
1.000	.3610	1.540	.460	447.0	423.5	+5.54
.909	.3350	1.682	.520	414.8	394.4	+5.17
.7500	.2875	2.000	.665	354.7	340.1	+4.29
.6666	.2615	2.226	.774	322.4	310.5	+3.83
.5000	.2072	2.910	1.090	254.9	246.3	+3.49
.4000	.1728	3.62	1.385	212.3	205.9	+3.11
.3333	.1480	4.29	1.710	181.7	176.7	+2.83
.2222	.1046	6.30	2.705	128.1	126.1	+1.59
.1666	.0816	8.32	3.68	99.85	99.21	+0.65
.1000	.0536	13.48	6.52	65.44	65.20	+0.37
.0909	.0494	14.76	7.26	60.34	60.21	+0.22
.0750	.0420	17.71	8.95	51.12	50.96	+0.31
.06666	.0379	19.80	10.21	46.13	46.26	-0.20
.05000	.0294	26.05	13.95	35.79	35.89	-0.28
.04000	.0242	32.3	17.66	29.43	29.40	+0.10
.03333	.0207	38.8	21.25	25.11	25.18	-0.28
.02222	.01455	56.5	33.5	17.64	17.59	+0.34
.01666	.01145	73.8	46.2	13.85	13.88	-0.22
.01000	.00729	119.0	81.0	8.784	8.760	+0.27
.00800	.00597	146.8	103.2	7.196	7.180	+0.22
.00750	.00565	156.0	110.5	6.797	6.776	+0.31
.00600	.00463	191.8	141.4	5.569	5.584	-0.26
.00500	.00393	228.4	171.6	4.719	4.730	-0.23

It appears from the above table that while in the case of solutions with concentration ranging from the weakest examined up to about 0.1 gramme-equivalent per litre, calculated and observed values agree within the limit of observational error. (which, as in the former paper, was estimated at 0.25 per cent), the differences between observed and calculated values for solu-

tions with concentration ranging from 0.1 to the highest examined. 1.294, are beyond the limit of error, and are much greater than the differences observed for mixtures of Potassium and Sodium Sulphate, or for any mixtures yet examined of a corresponding concentration. This result would appear therefore to support the view that the double salt does exist as such to a certain extent at any rate in solution.

Comparison of the Conductivity of Solutions of the Double Salt with Equivalent Mixtures of Solutions of its Constituents.

TABLE III.

Concentration.	Conductivity of Mixture.	Conductivity of Double Salt.	Differences per cent.
1.000	425.7	423.5	+0.52
.909	396.3	394.4	+0.48
.7500	341.2	340.1	+0.32
.6666	311.6	310.5	+0.35
.5000	246.9	246.3	+0.24
.4000	206.4	205.9	+0.24
.3333	176.4	176.7	-0.17
.2222	126.0	126.1	-0.07
.1666	99.33	99.21	+0.12
.1000	65.31	65.20	+0.16
.0909	60.29	60.21	+0.13
.07500	51.02	50.96	+0.11
.06666	46.20	46.26	-0.08
.05000	35.86	35.89	-0.08
.04000	29.45	29.40	+0.17
.03333	25.14	25.18	-0.15
.02222	17.62	17.59	+0.17
.01666	13.86	13.88	-0.14
.01000	8.770	8.760	+0.11
.00750	6.781	6.776	+0.07
.00600	5.574	5.584	-0.17
.00500	4.724	4.730	-0.12

It was thought, therefore, that it would be interesting to see to what extent a mixture of equal volumes of equi-molecular solutions of the constituents of the double sulphate of Potassium and Copper corresponded to a solution of the double salt of the same concentration. For that purpose mixtures were prepared of the same concentration as the solutions of the double salt previously examined. Table III gives the concentrations common to the mixtures and the solutions of the double salt, the observed conductivity of each, and the differences between the two values expressed as percentages. Concentrations and conductivities are expressed in terms of the same units as in Table II.

The results given in Table III show that in the case of the weaker solutions the differences are within the limits of experimental error, but that in the case of the first four solutions the errors of observation would need to be of opposite sign for the two solutions in each case in order to account for the differences observed. In the stronger solutions, therefore, the conductivity of the mixture would appear to be greater than the conductivity of the equally concentrated solutions of the double salt. This might be due to the molecules of the double salt not having become broken up in solution, to the extent that they are in a mixture of solutions of its constituents. Similar results for Potassium Chrome Alum have been observed by Jones and Mackay.*

Observations on Solutions containing Zinc and Copper Sulphates.

As the large differences between the calculated and observed values of the conductivity, in the case of the double sulphate solutions, were still unaccounted for, I thought it advisable to see how closely it was possible to predict the conductivity of mixtures of equi-molecular solutions of each of the constituents of the double salt with some other sulphate with which it does not form a double salt of the same nature as the Potassium

* Am. Chem. Jour., Vol. XIX., No. 2, p. 83.

Copper salt. For this purpose Zinc Sulphate was selected to be associated with Copper Sulphate and Sodium Sulphate with Potassium Sulphate.

In Table IV are given the data for the drawing of the ionic concentration-dilution curve for Zinc Sulphate. Conductivities, dilutions and concentrations of ions are expressed in terms of

TABLE IV.

ZINC SULPHATE.		
Dilution.	Conductivity.	Concentration of ions.
100.0	684	.00633
80.0	665	.00770
66.66	647	.00899
50.00	610	.01129
40.00	582	.01347
33.33	555	.01541
25.00	520	.01925
22.22	508	.02117
20.00	500	.02314
16.66	484.0	.0269
13.33	463.0	.0322
12.50	455.0	.0337
10.00	430.4	.0399
8.00	414.0	.0479
6.666	400.0	.0556
5.000	375.0	.0694
4.000	354.5	.0821
3.333	341.0	.0947
2.500	317.0	.1174
2.222	309.0	.1287
2.000	302.0	.1398
1.666	290.5	.1614
1.333	270.6	.1879
1.176	260.8	.2052
1.000	248.5	.2300

the same units as in Table I. In calculating the concentration of ions, the value of the molecular conductivity at infinite dilution was taken to be 1080, according to Kohlrausch's* determination.

Mixtures of equal volumes of equi-molecular solutions of Zinc and Copper Sulphates were then prepared, and their conductivity measured. In Table V are given the necessary data for the calculation of the conductivity of each mixture examined, together with the observed and calculated values and the differences expressed as percentages. The different values are expressed in terms of the same units as in Table II.

TABLE V.

Concentration of the Constituent Solutions.		Concentration of ions in the Mixture.	Dilution in the Mixture.		Conductivity of Mixture.		
$\frac{1}{2}$ Zn SO ₄ .	$\frac{1}{2}$ Cu SO ₄ .		$\frac{1}{2}$ Zn SO ₄ .	$\frac{1}{2}$ Cu SO ₄ .	Calculated.	Observed.	Differences per cent.
1.000	1.000	.2252	1.032	.968	245.1	245.4	-0.12
.850	.850	.2006	1.212	1.140	215.6	215.3	+0.13
.7500	.7500	.1832	1.382	1.284	199.4	199.7	-0.15
.6000	.6000	.1562	1.744	1.588	170.1	170.5	-0.23
.5000	.5000	.1354	2.080	1.920	147.5	147.3	+0.12
.4000	.4000	.1144	2.600	2.400	124.6	124.5	+0.08
.2000	.2000	.0674	5.22	4.79	73.30	73.20	+0.13
.1000	.1000	.0393	10.22	9.78	42.76	42.83	-0.16
.0850	.0850	.0346	12.10	11.42	37.68	37.63	+0.13
.0750	.0750	.0314	13.80	12.86	33.82	33.88	-0.17
.06000	.06000	.02618	17.26	16.06	28.50	28.55	-0.17
.05000	.05000	.02245	20.70	19.30	24.05	24.01	+0.16
.04000	.04000	.01866	26.1	24.0	20.32	20.36	-0.19
.02000	.02000	.01105	51.6	48.4	12.03	12.05	-0.15
.01250	.01250	.00753	82.1	77.9	7.837	7.830	+0.08

* Wied. Ann. Vol. xxvi (1885), p. 195.

These results show that in the case of solutions containing equi-molecular quantities of Zinc and Copper Sulphate up to 1 gramme-equivalent per litre, the calculated and observed values of the conductivity agree within the limits of observational error.

Observations on Solutions Containing Sodium and Potassium Sulphate.

Table VI contains the results of calculations and observations on some mixtures of equal volumes of equi-molecular solutions of Sodium and Potassium Sulphates, of the same range of concentration as those of the Copper-Potassium Sulphate solutions and Zinc-Copper mixtures examined. The data for the drawing of the ionic concentration-dilution curve for Potassium Sulphate

TABLE VI.

Concentration of the Constituent Solutions.		Concentration of ions in the Mixture.	Dilution in the Mixture.		Conductivity of Mixture.		
$\frac{1}{2}$ K ₂ SO ₄ .	$\frac{1}{2}$ Na ₂ SO ₄ .		$\frac{1}{2}$ K ₂ SO ₄ .	$\frac{1}{2}$ Na ₂ SO ₄ .	Calculated.	Observed.	Differences per cent.
1.000	1.000	.483	1.096	.904	570.0	568.5	+0.26
.909	.909	.448	1.202	.998	528.1	526.6	+0.29
.750	.750	.384	1.432	1.234	451.9	452.8	-0.19
.6666	.6666	.351	1.605	1.395	413.3	414.4	-0.26
.5000	.5000	.276	2.105	1.895	323.8	324.6	-0.24
.4000	.4000	.228	2.60	2.40	267.7	267.2	+0.19
.2000	.2000	.1254	5.14	4.86	147.1	147.3	-0.13
.1000	.1000	.0696	10.06	9.94	81.40	81.49	-0.11
.0800	.0800	.0571	12.56	12.44	66.82	66.70	+0.18
.0750	.0750	.0540	13.40	13.26	63.12	63.02	+0.15
.0600	.0600	.0441	16.76	16.56	51.60	51.67	-0.13
.0500	.0500	.0372	20.16	19.84	43.48	43.51	-0.07

are given in Table I. Similar data for Sodium Sulphate are given in my previous paper.* As the above data, in the case of the Potassium Sulphate, are better than those given in my previous paper, I have thought it well to make new observations and calculations on these mixtures. Concentrations, dilutions, concentrations of ions, and conductivities, are expressed in terms of the same units as in Table II.

The results of this table show that the calculated and observed values of the conductivity of mixtures of equimolecular solutions of Potassium and Sodium Sulphates agree within the limits of observational error, at least up to a concentration of 1 gramme-equivalent per litre. The observations of my former paper, in which the mixtures examined were not equi-molecular in concentration, gave a similar result.

Conclusions.

An examination of Tables II, V, and VI, will show, that in the case of the Potassium-Copper sulphate solutions, the differences between the observed and calculated values of the conductivity, are all of the same sign and positive from a concentration of 0.1 to one of 1.294 equivalent gramme-molecules per litre, that the differences increase with the concentration, reaching in the case of the strongest solution examined 6.38 per cent.

For the mixtures of Sodium and Potassium Sulphates and of Zinc and Copper Sulphates examined, the difference for a like concentration are not greater than 0.30 per cent. Now, errors are caused in the calculations by taking the ionization coefficients to be the ratios of the specific molecular conductivity at infinite dilution, which is rigorously true only for infinitely dilute solutions, and also by taking the value of the specific molecular conductivity at infinite dilution for an electrolyte in a mixture to be the same as the value found by observations on the simple solutions, which is strictly true only for infinitely

* Loc. cit.

dilute mixtures. But the fact that the differences are so large where a double salt may exist, would seem to furnish evidence for the assumption, that in the more concentrated solutions of the double Sulphate of Potassium and Copper, the molecules of the double salt are not all broken up, but exist to some extent as a double salt in the solution.

For solutions of the Copper-Potassium sulphate, more dilute than 0.1 equivalent gramme-molecules per litre, as for the Zinc-Copper and Sodium-Potassium sulphate mixtures, through as wide a range of dilution as here examined, the differences are within the limit of observational error and change sign frequently, which seems to show that they are due to accidental errors. It is thus possible to calculate the conductivity of these solutions and mixtures; and it would follow that, as far as the conductivity measurements can show, for the more dilute solutions of Copper-Potassium sulphate there is no double salt existing as such in the solutions.