



LVIII. On the calculation of the conductivity of mixtures of electrolytes having a common ion

Douglas McIntosh

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form better suited to itself if it had been allowed to do so, as it is in commerce. This consideration must affect, not only the efficiency, but also the curves which Fleming and Petavel obtained for the variations in the luminous intensity.

Further, this action of the arc in modifying the wave form may throw some light on the discrepancy between the efficiency of alternate current arcs as determined in the laboratory and that stated to be obtained in practice.

When an arc is run in the laboratory a large resistance is almost certain to be put in series with it to ensure that degree of steadiness which is essential to exact measurement, and hence the arc cannot alter the wave form. In the commercial use of arcs, on the contrary, the circumstances are widely different. In this case, for economic reasons, the arc must form a large percentage of the total "reactance" of the circuit, and therefore can easily alter the wave to the form required for the greatest efficiency.

It is interesting to note that the wave form giving the best result for the arc is almost exactly the opposite to that giving the best efficiency for transformers. In the former case a flat-topped wave is best, while for the maximum efficiency of transformers an exceedingly peaked wave is best, as lately found by Dr. Rössler.

This points to the building of alternators for use with transformers in such a way as to give peaked wave-forms.

In the case of the arc the building of machines to give the most efficient wave form is not so necessary, since, generally, the arc itself has the power of automatically converting *any* wave form into the one best suited to its requirements. Nevertheless, when the arc has to run in series with a large resistance it is of the utmost importance for obtaining the best efficiency that the machine should give a flat-topped wave.

City and Guilds of London Central Technical College,
April 2, 1896.

LVIII. *On the Calculation of the Conductivity of Mixtures of Electrolytes having a common Ion.* By DOUGLAS MCINTOSH, *Physical Laboratory, Dalhousie College, Halifax, N.S.**

IN a paper published in the April number of this Magazine (*supra*, p. 276) Prof. MacGregor showed how to obtain, by a graphical process, from observations of the electrical conductivity of a sufficient number of simple solutions

* Abstract of a paper read before the Nova Scotia Institute of Science on the 13th of April, 1896. Communicated by the Secretary of the Institute.

of two electrolytes having a common ion, the data necessary for the calculation of the conductivity of a solution containing both electrolytes, according to the dissociation theory of electrolytic conduction; and in order to test this theory he calculated the conductivities of a series of mixtures of solutions of sodium chloride and potassium chloride, which had been measured by Bender. He found that for dilute solutions his calculations agreed with Bender's observations within the limits of experimental error; but that as the strength of the solutions increased the differences became larger, until with a mixture of solutions containing each four grammes-molecules per litre of salt (the strongest solutions with which Bender worked) a difference of 3.6 per cent. was found. The method of calculation assumed that the ionic velocities of the constituent electrolytes were not changed by the mixing; and Prof. MacGregor attributed the differences between the calculated and observed values to the change which, as he pointed out, would probably be produced in these velocities by mixture.

At his suggestion I have made the observations and calculations described in this paper with the object of determining (1) what the differences between the observed and calculated values are, in the case of mixtures of sodium and potassium chloride solutions of greater strength than those examined by Bender; and (2) how the calculated and observed values are related in the case of solutions containing sodium chloride and hydrochloric acid—electrolytes whose ionic velocities differ from one another much more than those of sodium and potassium chlorides.

Preparation of Solutions and Determination of Conductivities.

The paper of which this is an abstract contains a full statement of the experimental methods employed and the precautions taken to secure accuracy. It will be sufficient here to make a general statement merely.

The salts and acid used were purchased as chemically pure, and the former re-purified by crystallization. They were found by the usual tests to be free from probable impurities. The water was doubly distilled and was also tested.

Simple solutions of salt or acid having been prepared their concentration was determined by volumetric analysis, the pipettes and burettes used having been tested by weighing the water they delivered. The volumetric analyses were found to be accurate to 0.1 per cent. when applied to solutions specially prepared by the mixture of exactly determined quantities of salt and water.

The mixtures in all cases consisted of equal volumes of the constituent solutions. In preparing them the same pipette was used for both solutions in exactly the same way, having been washed out before use in each case with a portion of the solution with which it was to be filled. In all cases solutions were prepared and analysed at 18° C.

The method employed in the observations of conductivity was that of Kohlrausch with alternating current and telephone, the apparatus consisting of a bridge-wire of german-silver about 3 metres long, wound on a marble drum, a set of resistance-coils (of which I needed to use but one), a small induction-coil with a very rapid vibrator, and an ordinary Bell telephone. I calibrated the bridge-wire by the method of Strouhal and Barus, and was able to determine resistances to within from 0.2 to 0.3 per cent.

The electrolytic cell was of a U-shape, and was placed in a water-bath kept at or near 18° C. by a thermostat and stirred by a current of air. Its temperature was read by a thermometer graduated to 0.1 degree Centigrade, and capable of being read easily to 0.05 degree. Its errors had recently been determined at the Physikalisch-technische Reichsanstalt Berlin. When the bath could not be kept at 18° C., the temperature coefficient was determined. In the platinizing of the electrodes, and in the whole procedure of the determination of the conductivity, I followed carefully the recommendations of Kohlrausch's recent papers.

As I was to employ Kohlrausch's observations as data in the calculations, I reduced all my observations of conductivity to his standard (the conductivity of mercury at 0° C.). The factor requisite for this purpose was determined by comparing my own observations for certain solutions with the values given by him for the same solutions. This factor I found (as Bender had also) to vary somewhat with the conductivity of the solution used in finding it, but not with the nature of the solution. I therefore found its values as given by using a series of solutions of different conductivities; and in reducing the observed conductivity of a mixture to Kohlrausch's standard I used the value of the factor corresponding to the conductivity of the mixture. All observations given below are expressed in terms of Kohlrausch's standard.

Results of Observations on Mixtures.

The following tables give the concentrations of the constituent solutions of the mixtures examined and the observed conductivities of the mixtures : —

(A).—Sodium and Potassium Chlorides.

Constituent Solutions (gramme-molecules per litre).		Conductivity $\times 10^3$.
KCl.	NaCl.	
3.88	5.12	2494
3.20	"	2326
2.49	"	2187
1.93	"	2029
3.88	5.12	2494
"	4.28	2404
"	3.37	2316
"	2.56	2196
"	2.06	2124

(B).—Sodium Chloride and Hydrochloric Acid.

Constituent Solutions (gramme-molecules per litre).		Conductivity $\times 10^3$.
NaCl.	HCl.	
2.02	4.55	4932
"	3.89	4492
"	3.29	4089
"	3.19	4073
"	3.06	3958
"	2.66	3623
"	2.56	3489
"	2.34	3323
1.04	4.55	5069
"	3.97	4682
"	3.80	4315
"	3.10	3989
"	2.86	3696
"	2.18	3112
"	2.11	3025
"	1.93	2824
"	1.58	2427
"	1.15	1928
0.607	1.120	1813
"	0.970	1620
"	0.815	1412
"	0.730	1296.5
"	0.603	1114
"	0.485	952

The Data for the Calculations.

The method of calculating the conductivity of the mixtures was that described by Prof. MacGregor in the paper referred to above. It requires as data the change of volume on mixing (if not negligible), the conductivities of sufficiently extended series of the simple solutions of about the same dilution as the solutions mixed, and the molecular conductivities of the simple solutions at infinite dilution.

Specific gravity determinations showed that the change of volume on mixing was in all cases so small as to produce no practical effect on the calculated value of the conductivity.

Kohlrausch's tables* of the conductivity of solutions of sodium and potassium chlorides furnished sufficient data for calculating the conductivity of mixtures of these salts; but I found it necessary to make additional observations on solutions of hydrochloric acid. They are as follows:—

Concentration (gramme-molecules per litre).	Molecular Conductivity $\times 10^8$.	Concentration (gramme-molecules per litre).	Molecular Conductivity $\times 10^8$.
1.58	2550	2.80	2065
1.93	2403	2.88	2052
2.11	2347	3.15	1960
2.18	2305	3.29	1914
2.24	2290	3.39	1890
2.46	2245	3.60	1789
2.51	2192	3.83	1726
2.56	2164	4.13	1636
2.66	2141	4.55	1534
2.78	2090	4.87	1456

The values of the specific molecular conductivity at infinite dilution for potassium chloride, sodium chloride, and hydrochloric acid respectively, were taken to be 1220×10^{-8} , 1030×10^{-8} , and 3500×10^{-8} according to Kohlrausch's determination †.

RESULTS OF THE CALCULATIONS,

(A) *Sodium and Potassium Chlorides.*

The following table contains in columns 1 and 2 the concentrations of the constituent solutions in the mixtures. Column 3 gives the calculated values of the conductivity;

* 'British Association Reports' (1893), p. 148.

† Wiedemann's *Annalen*, xxvi. p. 204.

column 4 the observed values obtained by graphical interpolation from the observations given above; and column 5 the excesses of the calculated over the observed values expressed as percentages:—

Constituent Solutions (gramme-molecules per litre).		Conductivity $\times 10^6$.		Difference per cent.
KCl.	NaCl.	Calculated.	Measured.	
3.75	5.12	2312	2460	—6.4
3.50	"	2276	2420	—6
3.00	"	2202	2313	—4.8
2.50	"	2109	2190	—3.7
2.00	"	2013	2049	—1.7
3.88	5.00	2323	2481	—6.4
"	4.50	2295	2429	—5.5
"	4.00	2292	2377	—3.6
"	3.50	2261	2324	—2.7
"	3.00	2227	2260	—1.4
"	2.50	2174	2189	—0.7
"	2.00	2096	2116	—1.0

The differences of the above table agree very well with those found by Prof. MacGregor* in the case of the mixtures examined by Bender, being of the same sign and, in general, for mixtures of about the same mean concentration, of approximately the same magnitude. The results seem, therefore, to be worthy of confidence, and they show clearly that the differences between the calculated and the observed values increase rapidly as the constituent solutions become more and more nearly saturated, reaching in the case of practically saturated solutions 6.4 per cent.

(B) *Sodium Chloride and Hydrochloric Acid.*

The following table gives the results in the case of mixtures of solutions of sodium chloride and hydrochloric acid:—

* *Supra*, p. 285.

Constituent Solutions (gramme-molecules per litre).		Conductivity of Mixture $\times 10^3$.		Difference per cent.
HCl.	NaCl.	Calculated.	Measured.	
2	2.02	3020	3008	+0.4
2.5	"	3489.5	3456	+1.0
3.0	"	3885	3888	-0.08
3.5	"	4233.5	4260	-0.6
4.0	"	4622.3	4580	+1.0
4.5	"	4944	4880	+1.3
1	1.04	1751	1752	-0.005
1.5	"	2373	2332	+1.7
2.0	"	2928.3	2900	+0.9
2.5	"	3428.5	3398	+0.9
3.0	"	3906	3872	+0.9
3.5	"	4340.7	4316	+0.6
4.0	"	4715	4700	+0.3
4.5	"	5055	5036	+0.4
.4	.607	829.8	838	-1.0
.5	"	983.4	976	+0.8
.6	"	1125.5	1116	+0.8
.7	"	1255	1250	+0.4
.8	"	1384.7	1388	-0.2
.9	"	1524.6	1525	-0.025
1.0	"	1658.9	1656	+0.16
1.1	"	1787.6	1784	+0.2
1.2	"	1917.1	1913	+0.2

It will be seen that in the series of weakest solutions, the differences between calculated and observed values are of such small magnitude and show such alternation of sign as to warrant the conclusion that they are due chiefly to accidental errors. In the two series of stronger solutions the differences are more irregular in magnitude and the alternation of sign is much less marked, the most of the differences being positive. The above results, therefore, seem to show that even in the case of two electrolytes with a common ion which differ so markedly in ionic velocity from one another as sodium chloride and hydrochloric acid, the dissociation theory enables us to calculate the conductivity of solutions containing both, within the limits of experimental error, up to a mean concentration of about one gramme-molecule per litre, and that in the case of solutions of greater mean concentration the calculated value is greater than the observed.