

II.—ON THE CALCULATION OF THE CONDUCTIVITY OF MIXTURES OF ELECTROLYTES HAVING A COMMON ION,  
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In a paper read before this Institute some months ago, Prof. MacGregor\* shewed how to obtain, by a graphical process, from observations of the electrical conductivity of a sufficient number of simple solutions 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 solution increased the differences became larger, until with a mixture of solutions containing each four grammes 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 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

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\*Trans. N. S. Institute of Science, Vol. IX, p. 101.

solutions containing sodium chloride and hydrochloric acid,—electrolytes whose ionic velocities differ from one another much more than those of sodium and potassium chlorides.

The expression for the conductivity of a mixture of equal volumes of solutions of two electrolytes 1 and 2, which contain  $n_1$  and  $n_2$  gramme-equivalents per unit of volume respectively, the ionisation coefficients of which, in the mixture, are  $a_1$  and  $a_2$ , the molecular conductivities of which at infinite dilution are  $\mu_{\infty 1}$  and  $\mu_{\infty 2}$ , and which so change in volume on mixing that the ratio of the volume of the mixture to the sum of the volumes of the constituent solutions is  $p$ , is

$$c = \frac{1}{2p}(a_1 n_1 \mu_{\infty 1} + a_2 n_2 \mu_{\infty 2})$$

In order to calculate the conductivity of such a mixture therefore, the seven quantities in this expression must be known. The ionisation co-efficients  $a_1$  and  $a_2$  are determined by the graphical process referred to above, from series of observations of the conductivities of simple solutions of the constituent electrolytes. The conductivities at infinite dilution are determined by similar observations with very dilute solutions. The concentrations may be determined by analysis, and the quantity  $p$  by density measurements.

I intended at the outset to determine all these quantities myself, in order that the data of calculation might apply to exactly the same electrolytes. But owing to the fact that the electrolytic cell, to be used in the determination of conductivities at infinite dilution, although ordered months ago, did not arrive in time, I am compelled to use Kohlrausch's values of the conductivities at infinite dilution for the electrolytes examined.

#### *Determination of Conductivities.*

Kohlrausch's well-known method with the telephone and alternating current was used. The apparatus was supplied by Queen & Co., of Philadelphia, and consisted of 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. I calibrated it by the method of \*Strouhal and Barus, and applied the corrections thus determined to the measured resistances. (The greatest correction that had to be applied during the experiments was one division).

Four coils, marked 1, 10, 100, 1000 true ohms formed part of the apparatus, and were guaranteed correct, to 0.1 per cent. The range of the resistances measured during the experiments, however, was so small that I needed to use only one of these coils (that of 100 ohms). Hence it was not necessary for me to test the relative accuracy of the coils. Nor did I need to test the absolute accuracy of the 100 ohm coil, as it was not necessary for me to express conductivities in absolute measure.

The cell used was a U-shaped one, with enlargements for the electrodes, of the kind shown in Ostwald's *Physico-chemical Measurements*, p. 226, Fig. 178. The cell and also the electrodes (each of which had an area of about 7 sq. cm.), were smaller than ordered, and the latter were so thin as to be easily bent. No change of resistance, however, could be noticed for small bendings of the plates, which could be readily detected by the eye and avoided. The induction coil was quite small, and had a specially rapid vibrator. It was kept in an adjoining room, that the noise might not disturb the operator; but, after some practice it was found that measurements could be made without difficulty, even with considerable noise. Different kinds of batteries for working the coil were tried. The most satisfactory was found to be a small dry battery, made by the Mamisburg Electric Co., of the kind used for electric bells. With this apparatus the "minimum" point on the bridge could be determined by the telephone to within  $\frac{1}{2}$  division. This, at the centre of the bridge, meant a possible error of 0.2 per cent., and at the point of the bridge farthest from the centre, used in my experiments, a possible error of 0.3 per cent.

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\*Wied. Ann., X, p. 326, 1880.

*Temperature.*

As the laboratory temperature varied considerably from day to day, the electrolytic cell was placed in a bath whose temperature was regulated by a thermostat of the kind described by Ostwald in his *Physico-chemical Measurements*, p. 59. The resistances measured were so small that a sharp "minimum" was obtained when a water bath was used. There was no necessity therefore, for a petroleum bath. The bath was stirred by a current of air from a small suction pump, and the temperature kept as near to 18°C as possible. When this temperature could not be exactly obtained, measurements of resistance were made at several near temperatures, and the temperature co-efficients found. The co-efficient was always about 2 per cent. per degree.

The thermometer used was graduated to 0.1 degree centigrade, and could be easily read to 0.05 degree. This meant a possible error of 0.1 per cent. in the determination of the resistance. The errors of the thermometer had recently been determined at the *Physikalisch-Technische Reichsanstalt*, Berlin.

*The Platinizing of the Electrodes.*

The electrodes after having been boiled in alkali and acid, were placed in a very dilute solution of chloroplatinic acid ( $H_2 Pt Cl_6$ ) and connected with a small battery, the direction of the current being frequently changed. When the electrodes had become covered with a black velvety coating, they were removed from the cell, and in order to get rid of the chloroplatinic acid which adheres strongly to the platinum black, they were washed several times with boiling water. On one occasion, in the course of the experiments, the minimum point was found to be indistinct. The plates were accordingly replatinized and distinctness found to have been regained. The experiments previously made (those on potassium chloride) may have been affected by a slight error due to defective platinizing.

*The Salts and Acids.*

The potassium and sodium chlorides, obtained as chemically pure from Eimer and Amend of New York, were further purified

by recrystallization. Solutions of them were found to be neutral and free from sulphates and magnesia. Neither potassium nor other metals could be detected in the sodium chloride with the spectroscope. Sodium, but no other metal, could be detected in a flame coloured by the potassium chloride. The hydrochloric acid was obtained as chemically pure, and gave no residue on evaporation. It was free from sulphates.

#### *The Water Used.*

The water was doubly distilled, with addition of sodium hydrate, in a tin-lined retort, and condensed in a block-tin pipe, the first part of the distillate being rejected. It was stored in bottles which had been used for this purpose for several years. It gave no residue when evaporated, was neutral, and gave no colour with Nessler's reagent.

#### *Preparation and Analysis of the Simple Solutions.*

The simple solutions were prepared by dissolving about the amount of salt required for the strongest solution, and subsequent diluting. The concentration in each case was determined by volumetric analysis. A solution of silver nitrate was used in estimating the chlorine in the potassium and sodium chlorides, and the amounts of salt present were calculated from the data thus obtained.

In making an analysis 1 c. c. (or 5 c. c.) of the solution at 18°C was drawn off by a pipette, placed in a flask, diluted, and coloured distinctly with neutral potassium chromate. Silver nitrate standardised at 18°C was run in from a burette, and a glass bulb filled with potassium chromate of the same shade as the solution being analysed, was held before the eye. The end point by this means could be seen quite sharply.

A solution of ammonia was employed for estimating the hydrochloric acid, with cochineal as an indicator.

The pipettes and burettes used were tested by weighing the water which they delivered. They were found to be accurate to 0.1 per cent.

To determine the accuracy of the volumetric analysis, a solution of sodium chloride was prepared, containing a known quantity of the pure fused salt. The results of the analyses were found to be correct to 0.1 per cent.

#### *Specific Gravity Determinations.*

The object of specific gravity determinations was the finding of  $p$  in the above expression for the conductivity. For this purpose it was necessary to find the specific gravity to the third decimal place only. Hence the determinations were made with a Mohr-Westphal balance which read to the fourth decimal place, and might be trusted in the third.

In all the mixtures examined  $p$  was found to be practically equal to unity.

#### *Preparation of the Mixtures.*

A 50 c. c. pipette which had been carefully washed, and stood on filter-paper for some time, was rinsed out several times with one of the constituents of the intended mixture, whose composition and specific gravity had been determined. The pipette was filled to the mark, and the solution run into a clean and dry bottle. The pipette was then washed, and the other constituent placed in the bottle as before, care being taken to use the pipette in exactly the same manner in both cases. All mixtures were made at 18°C. and the same pipette was used for both solutions, in order that the mixture might consist of exactly equal volumes of them.

The conductivities of solutions were found to increase on standing, which was doubtless due to portions of the glass being dissolved. The conductivities were therefore measured as soon after the solutions were made up as possible.

#### *Capacity of the Electrolytic Cell.*

To find the factor which would reduce the observed conductivities to the standard employed by Kohlrausch, viz., the conductivity of mercury at 0°C, the following simple solutions of potassium and sodium chloride were analysed, and their conductivities measured :

POTASSIUM CHLORIDE.		SODIUM CHLORIDE.	
Concentration, (Gramme-Molecules per Litre.)	Conductivity, $\times 10^8$ .	Concentration, (Gramme-Molecules per Litre.)	Conductivity, $\times 10^8$ .
2.07	1854	2.06	1199
2.61	2281	2.56	1517
2.94	2521	2.83	1616
3.26	2767	3.37	1786
3.68	3040	3.70	1876
3.88	3187	4.29	1970
		4.69	2025
		5.12	2087

These values were plotted on co-ordinate paper with concentrations as ordinates and conductivities as abscissæ, and smooth curves were drawn between the points so as to obviate accidental errors. Conductivities were taken off these curves and compared with the numbers given by Kohlrausch\* for solutions of equal concentration, as shewn in the following table.

## POTASSIUM CHLORIDE.

Concentration (Gramme-Molecules per Litre.)	CONDUCTIVITY.		RATIO.
	Kohlrausch.	Observed.	
2	1728	1800	.960
2.5	2122	2199	.961
3	2480	2566	.966
3.5	2822	2924	.965

## SODIUM CHLORIDE.

Concentration (Gramme-Molecules per Litre.)	CONDUCTIVITY.		RATIO.
	Kohlrausch.	Observed.	
2	1209	1277	.946
2.5	1412	1500	.941
3	1584	1675	.946
3.5	1728	1815	.952
4	1846	1928	.957
4.5	1935	2000	.968
5	1991	2066	.964

\*Wied. Ann., Vol. vi, p. 146.

It will be noticed that the ratios in the above table are not the same for all solutions, but are practically the same for solutions of both salts of the same conductivity. The variation of the ratio may have been due to some unknown defect of apparatus or mode of using it; but as this source of error was equally operative in the case of solutions of both salts of the same conductivity, it would probably be equally operative also in mixtures of the same conductivity. Hence in reducing the observed conductivity of a mixture of potassium and sodium chloride solutions to Kohlrausch's standard, the factor employed was the value of the ratio for the conductivity which the mixture was found to have, this ratio being determined from the above table by graphical interpolation. Bender found a similar variation in the ratio of his conductivities of solutions of these salts to Kohlrausch's conductivities for solutions of the same strength.

On comparing the observed conductivities of solutions of hydrochloric acid with conductivities of solutions of equal concentration, as given by Kohlrausch, the ratios were found to be practically uniform and equal to 0.955. In the tables which follow all conductivities are expressed in terms of Kohlrausch's standard.

#### *Conductivities of the Simple Solutions.*

In order to obtain the data for the calculations, it is necessary to draw curves giving the relation of the dilution to the concentration of ions in the simple solutions, and therefore to know the concentrations and conductivities of sufficiently extended series of these solutions. In the case of sodium and potassium chlorides sufficient data were available for this purpose in Kohlrausch's observations. The following tables give the dilutions and ionic concentrations of solutions of these salts examined by him.



## POTASSIUM CHLORIDE.

DILUTION.	CONCENTRATION OF IONS.	DILUTION.	CONCENTRATION OF IONS.
2	0.3861	0.400	1.7311
1	0.7467	0.333	2.0328
0.666	1.0885	0.285	2.3131
0.500	1.4164		

## SODIUM CHLORIDE.

DILUTION.	CONCENTRATION OF IONS.	DILUTION.	CONCENTRATION OF IONS.
2.30	0.3257*	0.500	1.1738
2.00	0.3689	0.400	1.3709
1.80	0.4036*	0.333	1.5378
1.64	0.4378*	0.285	1.6776
1.50	0.4732*	0.250	1.7920
1.20	0.5752*	0.222	1.8783
1.13	0.6109	0.200	1.9320
1.00	0.6777	0.182	1.9596
0.666	0.9456		

\*Obtained through Prof. MacGregor's interpolation formula, Trans. N. S. Inst. Sci., Vol. IX, p. 112.

In the case of hydrochloric acid, sufficient data were not available. I therefore made a series of measurements of the concentrations and conductivities of solutions of this acid, the results of which are given in the following table :

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 following table contains values of the dilution and concentration of ions in hydrochloric acid solutions, obtained in

part by graphical interpolation of the above observations, and in part by the aid of Kohlrausch's tables :—

Dilution.	Concentration of Ions.	Obtained.	Dilution.	Concentration of Ions.	Obtained.
2.000	0.4310	Kohlrausch	0.500	1.3600	Observed
1.666	0.5090	"	0.444	1.4660	"
1.428	0.5840	"	0.400	1.5685	"
1.250	0.6567	"	0.364	1.6516	"
1.111	0.7269	"	0.333	1.7229	Kohlrausch
1.000	0.7943	"	0.286	1.8379	Observed
0.800	0.9557	Observed	0.250	1.9132	"
0.666	1.1031	"	0.222	1.9746	"
0.571	1.2370	"			

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

*Results of Observations on Mixtures.*

*(A).—Sodium and Potassium Chlorides.*

The following series of mixtures of potassium and sodium chloride solutions were examined :

CONCENTRATION (GRAMME-MOLECULES PER LITRE.)		CONDUCTIVITY $\times 10^8$
K Cl.	Na Cl.	
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
3.46	3.20	2160
3.80	2.23	1877

\*Wied. Ann., Vol. xxvi, p. 204.

The following table contains a statement of the measured and calculated values of the conductivities of the above mixtures, with the concentrations of the constituent solutions, and the data necessary for the calculations, viz., the dilutions of the respective electrolytes and their ionic concentrations, in the mixtures, these data being obtained by Prof. MacGregor's graphical process. The measured values of the conductivity were obtained from the above observations by graphical interpolation.

Constituent Solutions (Gramme-molecules per Litre.)		Dilution in the mixture.		Concentration of Ions in the Mixture.	Conductivity, $\times 10^8$		Difference, Per Cent.
K Cl.	Na Cl.	K Cl.	Na Cl.		Calculated.	Measured.	
3.75	5.12	.247	.143	2.013	2312	2469	-6.4
3.50	"	.234	.156	1.993	2276	2420	-6
3.00	"	.205	.1855	1.950	2202	2313	-4.8
2.50	"	.175	.216	1.890	2109	2190	-3.7
2.00	"	.151	.239	1.822	2013	2049	-1.7
3.88	5.00	.26	.14	2.014	2323	2481	-6.4
"	4.50	.291	.151	1.998	2295	2429	-5.5
"	4.00	.335	.166	1.980	2292	2377	-3.6
"	3.50	.388	.182	1.955	2261	2324	-2.7
"	3.00	.462	.205	1.916	2227	2260	-1.4
"	2.50	.573	.227	1.864	2174	2189	-0.7
"	2.00	.750	.250	1.788	2096	2116	-1.0
3.46	3.12	.412	.2295	1.848	2130.5	2160	-1.3
2.23	3.80	.2432	.2824	1.68	1875.5	1877	-0.08
2.87	4.69	.225	.202	1.924	2177	2222	-2

The results of Bender's experiments, as calculated by \*Prof. MacGregor, are given below for comparison.

CONCENTRATION (GRAMME-MOLECULES PER LITRE.)		CONDUCTIVITY.		DIFFERENCE, PER CENT.
K Cl.	Na Cl.	Measured.	Calculated.	
2.0	2.0	1445	1458	+0.90
3.0	2.0	1823	1808.6	-0.79
2.0	3.0	1664	1660	-0.24
3.0	3.0	2007	1988.7	-0.91
2.0	4.0	1858	1849.3	-0.47
3.5	4.0	2303	2239.2	-2.77
4.0	4.0	2432	2345.3	-3.56

\*Trans. N. S. Institute of Science, Vol. ix, p. 101.

The two sets of observations agree very well together, the differences between calculated and observed values being of the same sign and in general for mixtures of about the same mean concentration, of approximately the same magnitude.

The two series of mixtures of strong solutions shew that the differences increase rapidly as the constituent solutions are more and more nearly saturated, reaching in the case of practically saturated solutions 6.4 per cent.

(B.)—*Sodium Chloride and Hydrochloric Acid.*

The conductivities of the following series of mixtures of hydrochloric acid and sodium chloride solutions were measured :

CONSTITUENT SOLUTIONS CONCENTRATION : GRAMME-MOLECULES PER LITRE.		CONDUCTIVITY OF MIXTURE, $\times 10^8$ .
Na Cl.	H Cl.	
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 following table contains in columns 1 and 2 the concentrations of the solutions of hydrochloric acid and sodium chloride which were mixed, and in column 7 the measured conductivities of the mixtures, obtained by graphical interpolation from the above observations. The 3rd, 4th and 5th columns give the common concentration of ions and the respective dilutions of the electrolytes, in the mixture, as determined by Prof. MacGregor's graphical process. The 6th column gives the calculated values of the conductivity, and the 8th the excesses of the calculated over the observed values expressed as percentages.

Constituent Solutions. Concentration (Gramme-molecules per litre.)		Concentration of Ions in the Mixture	Dilution in the Mixture.		Conductivity of Mixture, $\times 10^8$ .		Differ- ences per cent.
H Cl.	Na Cl.		H Cl.	Na Cl.	Calcu- lated.	Mea- sured.	
2	2.02	1.272	.539	.451	3020	3008	+0.4
2.5	"	1.392	.592	.398	3489.5	3456	+1.0
3.0	"	1.485	.636	.354	3885	3888	-0.08
3.5	"	1.570	.668	.322	4233.5	4260	-0.6
4.0	"	1.665	.700	.290	4622.3	4580	+1.0
4.5	"	1.740	.726	.264	4944	4880	+1.3
1	1.04	.744	1.031	.892	1751	1752	-0.005
1.5	"	.916	1.215	.708	2373	2332	+1.7
2.0	"	1.062	1.345	.578	2928.3	2900	+0.9
2.5	"	1.196	1.431	.492	3428.5	3398	+0.9
3.0	"	1.324	1.495	.428	3906	3872	+0.9
3.5	"	1.440	1.545	.378	4340.7	4316	+0.6
4.0	"	1.538	1.585	.338	4715	4700	+0.3
4.5	"	1.628	1.616	.307	5055	5036	+0.4
.4	.607	.392	1.450	1.844	829.8	838	-1.0
.5	"	.436	1.636	1.656	983.4	976	+0.8
.6	"	.474	1.794	1.500	1125.5	1116	+0.8
.7	"	.508	1.922	1.372	1255.	1250	+0.4
.8	"	.544	2.022	1.272	1384.7	1388	-0.2
.9	"	.582	2.121	1.173	1524.6	1525	-0.025
1.0	"	.620	2.195	1.099	1658.6	1656	+0.16
1.1	"	.655	2.267	1.027	1787.6	1784	+0.2
1.2	"	.692	2.322	.972	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 shew 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 shew 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 1 gramme-molecule per litre, and that in the case of solutions of greater mean concentration, the calculated value is greater than the observed.