TRANSACTIONS

OF THE

Nova Scotian Institute of Science.

SESSION OF 1895-96.

I.—-On the Calculation of the Conductivity of Mixtures of Electrolytes. — By Prof. J. G. MacGregor, *Dalhousie College, Halifax, N. S.*

(Read 9th December, 1895.)

Arrhenius has deduced[*] as one of the consequences of the dissociation theory of electrolytic conduction, that the condition which must be fulfilled in order that two solutions of single electrolytes, which have one ion in common, and which undergo no change of volume on being mixed, may be isohydric, *i. e.*, may on being mixed undergo no change in their state of dissociation, is, that the concentration of ions (*i. e.*, the number of dissociated molecules per unit of volume) shall be the same for both. He obtained this result by combining the equations of kinetic equilibrium for the constituent electrolytes before and after mixture. As I shall have occasion to refer to these equations below, I may give them here.

Let $P_m Q$ and $P_n R$ be the general chemical formulæ for two electrolytes having the ion P in common ; let v_1 and v_2 be the

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*Ztschr. f. physikalische Chemie, ii, p. 284, (1888.)

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volumes of the solutions of these electrolytes which are mixed; let them contain N_1 and N_2 gramme-molecules of the electrolytes respectively; and let α_1 and α_2 be the respective coefficients of ionisation in the constituent solutions, and therefore, if the solutions are isohydric, in the mixture also. Then, according to the dissociation theory of electrolysis and the more general theory of solutions on which it is based, the condition that there shall be equilibrium between the undissociated and the dissociated parts of the electrolytes in the simple solutions, is expressed in the equations :—

$$c_1 \; \frac{N_1 \; (1-a_1)}{v_1} \;=\; \left(\frac{m \; a_1 \; N_1}{v_1}\right)^m \; \frac{a_1 \; N_1}{v_1},$$

$$c_2 \; \frac{N_2 \; (1-a_2)}{v_2} \;=\; \left(\frac{n \; a_2 \; N_2}{v_2}\right)^n \; \frac{a_2 \; N_2}{v_2},$$

where c_1 and c_2 are constants, *i. e.*, are independent of the values of N, v, and α. The condition that there shall be equilibrium between the dissociated and undissociated parts of each electrolyte after the mixture, in the case of isohydric solutions which do not change either in ionisation or in volume on mixing, is expressed in the following equations :

$$c_1 \; \frac{N_1 \; (1-a_1)}{v_1+v_2} \;=\; \left(\frac{m \; a_1 \; N_1 + n \; a_2 \; N_2}{v_1 + v_2}\right)^m \; \frac{a_1 \; N_1}{v_1+v_2},$$

$$c_2 \; \frac{N_2 \; (1-a_2)}{v_1+v_2} \;=\; \left(\frac{m \; a_1 \; N_1 + n \; a_2 \; N_2}{v_1 + v_2}\right)^n \; \frac{a_2 \; N_2}{v_1+v_2}.$$

It follows from the first and third of these equations, that

$$\frac{m \; a_1 \; N_1 + n \; a_2 \; N_2}{v_1+v_2} \;=\; \frac{m \; a_1 \; N_1}{v_1},$$

and from the second and fourth, that

$$\frac{m \; a_1 \; N_1 + n \; a_2 \; N_2}{v_1+v_2} \;=\; \frac{n \; a_2 \; N_2}{v_2}.$$

Hence,

$$\frac{m \; a_1 \; N_1}{v_1} \;=\; \frac{n \; a_2 \; N_2}{v_2};$$

i. e., the amount of the common ion which is dissociated per unit of volume, must be the same in both constituent solutions.

According to the dissociation theory, the specific conductivity of a mixture of two solutions of electrolytes 1 and 2, whose volumes before mixing were v'_1 and v'_2 respectively, which contained n_1 and n_2 gramme-equivalents of the electrolytes per unit of volume, whose combined volume after the mixture is $p\,(v'_1 + v'_2)$, whose co-efficients of ionisation after mixing are α_1 and α_2, and whose specific molecular conductivities at infinite dilution, under the circumstances in which they exist in the mixture, are $\mu_{\infty 1}$ and $\mu_{\infty 2}$, is given by the expression :

$$k = \frac{1}{p\,(v'_1 + v'_2)} \left(\alpha_1\, n_1\, v',\, \mu_{\infty 1} \; + \; \alpha_2\, n_2\, v_2'\, \mu_{\infty 2} \right)$$

Since in any case in which isohydric solutions are mixed without change of volume, n_1, v'_1, n_2 and v'_2 are known, α_1 and α_2 readily determinable, and p equal to unity, the specific conductivity can be calculated, provided we may assume that $\mu_{\infty 1}$ and $\mu_{\infty 2}$ have the same values in the mixture as in simple solutions. In the particular case in which equal volumes of the constituents are mixed without change of volume, the conductivity of the mixture becomes obviously the mean of the conductivities of the constituent solutions.

Arrhenius has subjected the result referred to above to a number of tests. In one he determined by experiment several series of dilute aqueous solutions of different single acids, such that if any two of the members of the same series were mixed in equal volumes, the mixture was found to have a conductivity equal to the mean of the conductivities of the constituents. Regarding the solutions of each series as shewn thereby to be isohydric among one another, he calculated the concentrations of the ions in the various solutions by the aid of Ostwald's observations of the conductivity of acids. The following table gives the result, the numbers specifying the concentration of dissociated hydrogen (in mgr. per litre) in the different solutions, and those

in each row applying to solutions found as above to be isohydric with one another:

H Cl	$(COOH)_2$	$C_4 H_6 O_6$	HCOOH	$CH_3 COOH$
151.5	152.6	......	......	......
42.3	35.1	......	......	......
22.03	21.37	19.07	.....	......
4.48	4.09	4.17	4.42	3.96
1.33	1.24	1.25	1.44	1.33
0.379	0.397	0.381	......	0.402

It will be observed that while the numbers in the various horizontal rows shew a general agreement, they differ very considerably from one another, the extreme differences ranging from 0.7 to 20.5 per cent.

He found also that two solutions of ammonium acetate and acetic acid respectively, which were determined in the above way to be isohydric with one another, contained, according to Kohlrausch, amounts of the ion $CH_3 COO$ which were in the ratio 1 : 0.79, a ratio which is only very roughly equal to unity.

So far as result is concerned, these tests are not satisfactory; but the lack of agreement may have been due to various causes: (1) the data for calculation may have been defective, (2) the change of volume which would doubtless occur on mixing, even with very dilute solutions, may have been too great for the application of Arrhenius's deduction, and (3) the difference between the values of μ_∞ in simple solution and in a mixture, may be too great to admit of the identification of isohydric solutions by the method employed.

On the other hand, Arrhenius has calculated* the conductivities of two dilute solutions containing in each case given quantities of two acids, employing for this purpose a series of approximations based on his own observations of isohydric

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*Wiedemann's Annalen, xxx, p. 73 (1887).

solutions of the acids ; and the calculated values were found to agree with those observed to within 0.5 and 0.2 per cent. respectively. So far as result is concerned, this forms a much more satisfactory test than those mentioned above ; but the number of calculations is too small to exclude the possibility of accidental agreement.

The calculation of the conductivity of a mixture of electrolytes is so severe a test of the ionisation theory of electrolysis that I have thought it well to try its possibility on a larger scale, especially as a considerable body of material is available for this purpose in the observations of the conductivity of mixtures of solutions of potassium and sodium chlorides made by Bender*. The present paper contains the results of calculations of the conductivities of mixtures determined experimentally by him.

METHOD OF CALCULATION.

In order to make such calculations by Arrhenius's method, it would be necessary to make a preliminary determination of a number of isohydric solutions of the two salts, and to restrict the calculations to very dilute solutions. They may be made however, without such preliminary experiments, and without such restriction, by employing a more general form of Arrhenius's deduction.

Two electrolytes, which have a common ion and are in a state of equilibrium in the same solution, may be regarded as occupying definite portions of the volume of the solution. If we apply the equilibrium conditions to the parts of the solutions occupied by the respective electrolytes, as well as to the whole solution, we obtain equations which, *mutatis mutandis*, are identical with those obtained by Arrhenius, as indicated above, for the isohydric solutions and their mixture. Thus, if in the equations of equilibrium given above, we take v_1 and v_2 to be the portions of the volume of the mixture occupied by the respective electrolytes, and α_1 and α_2 to be their co-efficients of ionisation in the

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*Wiedemann's Annalen, XXII, p. 197, (1884).

mixture, the above equations express the conditions which must be fulfilled that there may be equilibrium between the dissociated and undissociated portions of each electrolyte, both in the part of the mixture occupied by it and throughout the whole volume of the mixture. The result :

$$\frac{m \; a_1 \; N_1}{v_1} = \frac{n \; a_2 \; N_2}{v_2},$$

states that in a mixture of solutions of two electrolytes which have a common ion, and are in a state of equilibrium, the concentration of the ions of the respective electrolytes per unit volume of the portions of the mixture occupied by them, must be the same.

With the aid of this result we can find the ionisation co-efficients of the constituents of mixtures such as Bender examined. For if v'_1 and v'_2 are the volumes of the constituent solutions before mixing, and n_1, n_2 the numbers of gramme-molecules per unit of volume which they contain, it gives us the equation :

$$\frac{a_1 \; n_1 \; v_1'}{v_1} = \frac{a_2 \; n_2 \; v_2'}{v_2} \dots\dots (1)$$

We have also

$$v_1 + v_2 = p \; (v_1' + v_2') \dots\dots (2)$$

and as the co-efficients of ionisation are functions of the dilution only, at constant temperature, we have

$$a_1 = f_1 \left(\frac{v_1}{n_1 \; v_1'} \right) \dots \dots (3)$$

$$a_2 = f_2 \left(\frac{v_2}{n_2 \; v_2'} \right) \dots\dots (4)$$

Of the quantities involved in these equations, n_1, n_2, v_1', v_2' are known, and p may be determined by density measurements before and after mixture. The form of the functions in (3) and (4) may be determined if measurements of the conductivities of sufficiently extended series of simple solutions of the constituent electrolytes are made. We have thus four equations with but four unknown quantities.

If we employ the symbol V to represent the dilution $(v/n\, v')$ we may write the above equations as follows :—

$$\frac{a_1}{V_1} = \frac{a_2}{V_2} \dots\dots\dots\dots\dots\dots\dots (1)$$

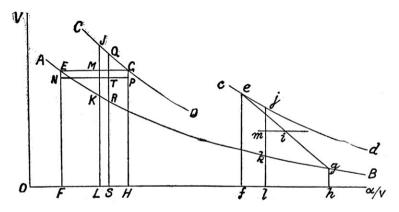$$V_1 + \frac{n_2\, v_2'}{n_1\, v_1'}V_2 = p\Big(V_1' + \frac{n_2\, v_2'}{n_1\, v_1'}V_2'\Big)\dots\dots (2)$$

which in the case of mixtures of equal volumes becomes

$$V_1 + \frac{n_2}{n_1}\, V_2 = p\left(V'_1 + \frac{n_2}{n_1}V'_2\right),$$

$$\frac{a_1}{V_1} = \phi_1\,(V_1) \dots\dots\dots\dots\dots (3)$$

$$\frac{a_2}{V_2} = \phi_2\,(V_2) \dots\dots\dots\dots\dots (4)$$

I determined α_1 and α_2 from these equations by the following graphical process :—Equation (3) was employed by drawing, from experimental data, for simple solutions of electrolyte 1, a curve having values of the concentration of the ions (α/V) as abscissæ and corresponding values of the dilution (V) as ordinates. This curve was drawn once for all, and was used in all determinations. The curve embodying equation (4) had to be drawn anew, (or rather such portion of it as was necessary), for each mixture examined. In the case of a mixture of solutions containing n_1 and n_2 gramme-molecules per unit volume of electrolytes 1 and 2 respectively, the curve had as abscissæ the concentrations of ions of a series of simple solutions of electrolyte 2, and as ordinates, since Bender's mixtures were mixtures of equal volumes, n_2/n_1 times the corresponding values of the dilutions. Were the mixtures under consideration mixtures of unequal volumes, $n_2 v_2'/n_1 v_1'$ times the values of the dilutions would have to be used as the ordinates. Equations (1) and (2) were applied by finding, by inspection, two points, one on each of the above curves having a common abscissa $(\alpha_1/V_1 = \alpha_2/V_2)$ and having ordinates (V$_1$ and $\frac{n_2}{n_1}$ V$_2$ respectively) of such magni-

tude as to have a sum equal to p times the sum of the ordinates of the points on the curves determined by the dilutions (V_1' and V_2' respectively) before mixing. The value of the abscissa common to the two points thus determined, gives the concentrations of ions of both constituents in the mixture. The corresponding ordinate of the first curve, and that of the second curve multiplied by n_1/n_2, give the dilutions (V_1 and V_2) of the constituents in the mixture. The products of the common value of α/V into V_1 and V_2 are the required values of α_1 and α_2 respectively.

The above process will be more readily understood by reference to the accompanying diagram. A B is the curve whose abscissæ are the values of α/V and whose ordinates are the corresponding values of V for a series of solutions of electrolyte 1. If we are to determine the concentration of ions in a mixture of equal volumes of solutions of electrolytes 1 and 2 respectively, we draw the curve C D whose abscissæ are the values of α/V and whose ordinates are n_2/n_1 times the corresponding values of V, for a sufficiently extended series of solutions of electrolyte 2. Let O F and F E represent the concentration of ions and the dilution (V_1') of the solution of electrolyte 1 which is to be mixed with an equal volume of a solution of electrolyte 2, and let O H and H G represent the concentration of ions and

n_2/n_1 times the dilution (V'_2) of the latter solution. Then, since

$$V_1' = \frac{v_1'}{n_1 \, v_1'} = \frac{1}{n_1}, \text{ and } V'_2 = \frac{v_2'}{n_2 \, v_2'} = \frac{1}{n_2},$$

we have

$$V_1' = \frac{n_2}{n_1} V_2'.$$

Hence F E and H G are equal. In order to determine the concentration of ions after mixing, we must find two points J, K, on the curves A B and C D respectively, having according to equation 1, a common abscissa O L, and having according to equation 2, ordinates L K and L J which together are equal to p times the sum of F E and H G. If p is equal to unity (*i. e.*, if the change of volume on mixing is negligible), the line J K joining the points J and K, when properly selected, will obviously be bisected by the line E G. The points J and K may thus be easily found by inspection. If p is not equal to unity, we must cut off from F E and H G or from these lines produced, portions F N and H P, equal to p. F E and p. H G respectively. Then, as before, the proper points Q, R will be so situated that the line Q R will be bisected by the line N P. Thus in this case also the points Q, R may readily be found by inspection. The points J, K (or Q, R) being thus found, O L (or O S) will represent the common concentration of ions in the mixture, and L K and L J (or S R and S Q) will represent the dilution of electrolyte 1, and n_2/n_1 times the dilution of electrolyte 2, respectively, in the mixture.

If the solutions to be mixed have unequal volumes (v_1' and v_2') we must draw the curve c d having as abscissæ the concentrations of ions, and as ordinates $\frac{n_2 \, v_2'}{n_1 \, v_1'}$ times the corresponding dilutions of a series of solutions of electrolyte 2. Let Oh and hg represent the concentration of ions, and the dilution (V_1') respectively, of the solution of electrolyte 1, which is to be mixed with a solution of electrolyte 2, and let Of and fe represent the concentration of ions, and $\frac{n_2 \, v_2'}{n_1 \, v_1'}$ times the dilution (V_2') of the latter solution, respectively.

From the equations

$$V_1' = \frac{1}{n_1}, \quad \text{and} \quad V_2' = \frac{1}{n_2},$$

it follows that

$$V_1' : \frac{n_2 \, v_2'}{n_1 \, v_1'} \, V_2' = v_1' : v_2'.$$

Hence $f\,e$ and $h\,g$ being proportional to the volumes of the solutions before mixing will be unequal. As before, we have to determine points j and k on curves $c\,d$ and A B respectively, having a common abscissa $O\,l$ and so situated that if p is equal to unity,

$$k\,l + j\,l = e\,f + g\,h,$$

and if p is not equal to unity,

$$k\,l + j\,l = p\,(e\,f + g\,h).$$

If, in cases in which p is equal to unity, the points j, k be properly selected, it is obvious that a line $i\,m$ drawn through i the point of bisection of $e\,g$, parallel to the axis of ionic concentrations, $O\,h$, will bisect $j\,k$. Hence the points j, k, will be easily determined by inspection. If p is not equal to unity, the points corresponding to j and k may be determined by proceeding in a manner similar to that used in the case of a mixture of equal volumes of the constituent solutions. To avoid complication the construction is not inserted in the diagram.

It will be obvious that the values of a_1 and a_2 for a solution containing two electrolytes with a common ion, may be determined in the above way, whether it has been formed by the mixing of two simple solutions or not. It may always be imagined to have been formed in this way, and in cases in which p is not negligible, if data are not available for its determination, special density measurements may be made.

DATA FOR THE CALCULATIONS.

Bender's paper contains all the data required for the calculation of the conductivities of mixtures of solutions of potassium and sodium chlorides, with the single exception of the specific

molecular conductivity of the simple solutions at infinite dilution. Owing to the want of this datum, I have drawn the curves $a/V = \phi(V)$ by means of data based on Kohlrausch and Grotrian's and Kohlrausch's *observations of the conductivity of solutions of these salts. They are as follows :—

NaCl SOLUTIONS.

Concentration Gramme-molecules per litre.	Specific molecular conductivity.	Dilution Litres per Gramme-molecule.	Concentration of Ions.
0.5	757	2	0.3682
0.884	710.42	1.1312	0.6109
1	695	1	0.6761
1.830	618.59	0.5465	1.1012
2.843	539.93	0.3517	1.4932
3	528	0.3333	1.5418
3.924	466.35	0.2548	1.7802
5	398	0.2	1.936
5.085	392.53	0.1967	1.9416
5.325	377.65	0.1878	1.9562
5.421	371.95	0.1845	1.9611

KCl SOLUTIONS.

Concentration Gramme-molecules per litre.	Specific molecular conductivity.	Dilution Litres per Gramme-molecule.	Concentration of Ions.
0.5	958	2	0.3939
0.691	933.43	1.4472	0.5304
1	919	1	0.7558
1.427	890.70	0.7008	1.0452
2.208	855.52	0.4529	1.5535
3	827	0.3333	2.0409
3.039	823.95	0.3291	2.0592
3.213	817.94	0.3112	2.1612

It will be seen that the above data are quite sufficient for drawing the curves representing a/V as $\phi(V)$ in the parts corresponding to small dilutions ; but that the data are few for the parts corresponding to the greater dilutions, where the curvature is more rapid. In order to draw these parts of the curves therefore, I obtained interpolation formulæ, expressing a/V

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*Wiedemann's Annalen, VI, p. 37 (1879) and XXVI, p. 195, (1885).

in the case of each salt in terms of reciprocals of powers of V. In obtaining these formulæ, I made use of Kohlrausch's data only, Kohlrausch and Grotrian's data not being at the time available to me. As the experimental data from which the formulæ were obtained, applied to a much greater range of dilution than that of the parts of the curves in the drawing of which these formulæ were used, I did not think it necessary to re-determine the formulæ when Kohlrausch and Grotrian's observations came into my hands. The following tables shew the accuracy with which the formulæ reproduced the experimental data on which they were founded :

DILUTION (V).	CONCENTRATION OF IONS (a/V) CALCULATED FROM	
	KOHLRAUSCH'S OBSERVATIONS.	FORMULA.
NaCl SOLUTIONS.		
10	0.08414	0.08413998
2	0.3682	0.3681999
1 .	0.6761	0.6760998
0.3	1.5418	1.541798
0.2	1.9360	1.936008
KCl SOLUTIONS.		
10	0.08610	0.086099
2	0.3939	0.393900
1 .	0.7558	0.755802
0.3	2.0409	2.04088

As the formulæ, owing to the narrow range of their applicability, are of no permanent value, they need not be given here. The consistency of the results of the calculations based on them, as given in the table below, would seem to show that they were sufficiently accurate for the purpose in hand.

As Bender measured the specific gravities of both his simple solutions and his mixtures, his paper affords the necessary data for determining the change of volume on mixing. Such change

will have a double effect on the calculated conductivity, (1) affecting the value of a as determined from the curves, and (2) introducing the factor p in the final computation. In the case of Bender's solutions, though in some cases they were nearly or quite saturated, the first effect was so small as to be much less. than the error incidental to the graphical process, and I did not. therefore take it into account. The second effect was also very small; but as in some cases it was nearly as great as Bender's. estimated error, I took it into account in all the calculations.

While Kohlrausch's solutions had at 18°C both the constitu-. tion and the conductivity specified in his tables, Bender's solutions: had at 15° the constitution, and at 18° the conductivity ascribed to them. I found that it did not appreciably affect the values. found for a_1 and a_2 to regard the concentrations at 15° as being the concentrations at 18°, but that this approximation was. inadmissible in calculating the conductivity, as in some cases it. made a difference of about the same magnitude as Bender's. estimated error. Hence in the calculations, I took as the values. of n_1 and n_2, Bender's values multiplied by the ratio of the volume of the solution at 15° to its volume at 18°. As Bender measured the thermal expansion of his solutions, his paper· furnishes the necessary data for this correction.

The conductivities given by Bender as the results of his. observations are the actual results of measurement, and are thus. affected by accidental errors, which in some cases are considerable. In order that his observations might be rendered comparable with the results of calculation, these accidental errors must as. far as possible be removed. I therefore plotted all his series of observations on co-ordinate paper, drew smooth curves through. them, and estimated as well as I could, in this way. the accidental errors of the single measurements. The corrections. thus determined are given in the table below in the column headed : Correction a.

Bender himself draws attention to certain differences between his observations of the conductivity of simple solutions of K Cl and Na Cl, and those for solutions of the same strength con-.

tained in Kohlrausch's tables of interpolated values, ascribing
them (1) to his own observations being the results of actual
measurements, and (2) to the different temperatures at which
their respective solutions had the specified strength.   These
differences are shewn in the following table :—

SALT IN SOLUTION.	CONDUCTIVITY.		DIFFERENCE.
	BENDER.	KOHLRAUSCH.	
Na Cl.	388	380	+ 8
K Cl.	478	471	+ 7
Na Cl.	702	698	+ 4
K Cl.	916	911	+ 5
Na Cl.	977	974	+ 3
Na Cl.	1217	1209	+ 8
K Cl.	1362	1328	+34
Na Cl.	1425	1412	+13
Na Cl.	1594	1584	+10
K Cl.	1741	1728	+13
Na Cl.	1745	1728	+17
Na Cl.	1845	1846	− 1
K Cl.	2106	2112	− 6
K Cl.	2484	2480	+ 4
K Cl.	2820	2822	− 2

It will be noticed that the differences are all of the same sign
up to conductivities of about 1800, and nearly all of the opposite
sign for higher conductivities ; also, that for any given conduc-
tivity the difference is of the same sign and of about the same
magnitude for solutions of both salts.   If they were due to the
first of the above causes, since Kohlrausch's interpolated values
agree well with his observations we should expect more alternation
of sign ; if to the second, there should be no change of sign ; if
to both, there should be greater and more irregular variation in
the magnitude.   The fact that the differences are practically the
same for both electrolytes at any given value of the conductivity
would seem to show that the cause of the differences, a defect in
the apparatus possibly, or in the distilled water, was operative
in the measurements of both sets of simple solutions, and there-
fore probably in the measurements of the mixtures.   Hence, to
render the results of calculations based on Kohlrausch's data for
the simple solutions, comparable with Bender's results for

mixtures, we must determine what the conductivities of Bender's mixtures would have been if Kohlrausch had prepared and measured them. To find this out as nearly as possible, I plotted the data of the above table with Bender's conductivities as abscissæ, and the differences between them and Kohlrausch's corresponding values as ordinates, and drew a smooth curve through the points. By the aid of this curve I determined the correction b of the table given below. This correction is of course a more or less doubtful one; for it is not certain that the observations on mixtures suffered from the same unknown source of error as the observations on simple solutions. It seems probable however that they did; and the results of the table given below would appear to render it almost certain.

It may be well in one case to give an example of the mode of calculation. We may take for this purpose the mixture of solutions containing each 1 gramme-molecule of salt. It is found by the graphical process that the value of a/V for this mixture is 0.718 gramme-molecules per litre and that the dilutions in the mixture are 0.937 and 1.063 litres per gramme-molecule for the Na Cl and K Cl respectively. The densities of the constituent solutions were 1.0444 and 1.0401 respectively, and that of the mixture 1.0422. The expansions per unit volume between $15°$ and $20°$ were 0.0013569 and 0.0012489 respectively. The values of the conductivity at infinite dilution, I took to be 1028 and 1216 respectively, according to Kohlrausch's observations. Hence the conductivity of the mixture

$$k = \tfrac{1}{2} \frac{2 \times 1.0422}{2.0845} \left(\frac{1 \times 0.718 \times 0.937 \times 1028}{1 + 0.6 \times 0.00136} + \frac{1 \times 0.718 \times 1.063 \times 1216}{1 + 0.6 \times 0.00125} \right) = 809.2$$

Bender's observed value (he used the same standard as Kohlrausch) was 814. To this a correction of about -3 must be applied to make the observation agree with the others of the same series (correction a) and a correction of about -3 to make it comparable with a calculated value based on Kohlrausch's data (correction b). Bender's reduced value is thus 808, which differs from the calculated value by 1.2, or 0.15 per cent.

RESULTS OF THE CALCULATIONS.

The following table gives the results of the calculations, the 2nd and 3rd columns containing the numbers of gramme-molecules per litre in the simple solutions at 15°C, the 4th column Bender's observed values of the conductivities of the mixtures, the 5th and 6th, corrections a and b referred to above, the 7th, Bender's reduced values, the 8th, the calculated values, and the 9th, the excess of the calculated values over those observed, expressed as per-centages of the latter :—

NUMBER.	Constituent solutions;—grm.-molecules per litre.		Conductivity of Mixture.					Diff., per cent.
	Na Cl.	K Cl.	Bender observed.	Corrections,		Bender reduced.	Calculated.	
				a.	b.			
1	0.5	0.1875	291	0	....	291	289.5	− 0.52
2	″	0.375	377	0	− 7	370	373.1	+ 0.84
3	″	0.5	436	0	− 6	430	426.1	− 0.90
4	″	0.75	545	0	− 5	540	537.6	− 0.44
5	″	1.5	866	0	− 3	863	858.3	− 0.54
6	1.0	0.1875	442	+ 23	− 6	459	461.4	+ 0.52
7	″	0.375	546	0	− 5	541	540.6	− 0.07
8	″	0.75	707	0	− 4	703	701.1	− 0.27
9	″	1.0	814	− 3	− 3	808	809.2	+ 0.15
10	″	1.5	1014	+ 6	− 5	1015	1015.2	+ 0.02
11	″	2.0	1224	− 6	− 9	1209	1200.6	− 0.69
12	2.0	0.1875	776	0	− 3	773	773.9	+ 0.12
13	″	1.0	1085	0	− 6	1079	1086.3	+ 0.68
14	″	2.0	1458	0	− 13	1445	1458	+ 0.90
15	″	3.0	1832	− 9	0	1823	1808.6	− 0.79
16	3.0	1.0	1332	0	− 11	1321	1324	+ 0.23
17	″	2.0	1674	0	− 10	1664	1660	− 0.24
18	″	3.0	2003	0	+ 4	2007	1988.7	− 0.91
19	4.0	0.375	1367	− 10	− 12	1345	1350.4	+ 0.40
20	″	2.0	1857	0	+ 1	1858	1849.3	− 0.47
21	″	3.5	2300	0	+ 3	2303	2239.2	− 2.77
22	″	4.0	2428	+ 6	− 2	2432	2345.3	− 3.56

It will be seen that in the case of the more dilute solutions Nos. 1-17 and 19, the differences, which are in all cases less than

1 per cent., and for the most part considerably less, are one half positive and one half negative, and that whether the solutions are arranged in the order of conductivity, or in the order of mean concentration, they exhibit quite a sufficient alternation of sign to warrant the conclusion that they are due chiefly at least, to errors in the observations and in the graphical portion of the calculations.

In the case of the stronger solutions, Nos. 16-18 and 19-22, the alternation of sign has disappeared. In the weakest solutions of these two series, the differences are positive and small; but as the concentration increases, the differences become negative and take increasing negative values, the negative difference having its greatest value in No. 22, which is a mixture of a strong solution of Na Cl with a saturated solution of K Cl. The tendency towards a negative difference as the concentration increases, may be recognised also in Nos. 11 and 15; and it is perhaps worth noting that while the mean value of the positive differences is slightly greater than that of the negative differences up to a concentration of 1 gramme-molecule of salt per litre, the mean negative difference is the greater for higher concentrations.

It is manifest from these results that for solutions of these chlorides containing less than say 2 gramme-molecules per litre, it is possible to calculate the conductivity very exactly, but that for stronger solutions the calculated value is less than the observed.

The excess of the observed over the calculated conductivities, shews one or more of the assumptions implied in the mode of calculation to be erroneous. It would seem to be probable that the error is at any rate largely due to the assumption that the molecular conductivity of an electrolyte at infinite dilution is the same whether it exists in a simple solution or in a mixture, and that the discrepancy is thus due to the effect of mixing on the velocities of the ions. The mode of calculation assumes that in the mixture the constituents are not really mixed, but lie side by side, so that the ions of each electrolyte in their passage from electrode to electrode travel through the solution to which they

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belong only.   They must rather be regarded however as passing in rapid alternation, now through a region occupied by one solution, and now through a region occupied by the other.   The actual mean velocities of the ions in the mixture will therefore probably differ from their values in a solution of their own electrolyte only.   In the case of dilute solutions the difference will be small, in sufficiently dilute solutions inappreciable, but in the case of the stronger solutions it may account in large part for the discrepancy observed above.   We have however, so far as I am aware, no data for calculating the effect of mixture on the ionic velocities or the extent to which the discrepancy is due to this effect.

To obtain some rough conception of its magnitude, I have calculated the conductivity of the mixture No. 18, on two assumptions which seemed more or less probable, viz., (1) that the velocities of the ions of each electrolyte in the mixture are the same as they would be in a simple solution of their own electrolyte of a concentration (in gramme-molecules per litre) equal to the mean concentration of the mixture, and (2) that the velocities of the ions of each electrolyte, when passing through a region occupied by the other electrolyte, are the same as they would be in a simple solution of the former of a dilution equal to that of the latter.   The expression used for the conductivity wa

$$k = \frac{1}{2\,p} \left(a_1\ n_1\ \mu_{\infty 1} \frac{u_1{}'}{u_1} +\ a_2\ n_2\ \mu_{\infty 2} \frac{u_2{}'}{u_2} \right),$$

where u_1 and u_2 are the sums of the velocities of the ions of electrolytes 1 and 2 respectively in simple solutions of the dilutions which they have in the mixture, while $u_1{}'$ and $u_2{}'$ are the values these ionic velocities would have according to the particular assumption employed, the velocities in all cases being those corresponding to the same potential gradient.   As the graphical process above gave the dilution of each electrolyte in the mixture, the values of u and u' were readily determined by the aid of Kohlrausch's table of ionic velocities.*   I found that

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*Wiedemann's Annalen, L, p. 385, (1893).

according to assumption (1) the conductivity would be greater than Bender's reduced value by 1.6 per cent. and that according to assumption (2) it would be greater by 1.3 per cent. Similar calculations could not be carried out with solutions stronger than No. 18, owing to lack of data. If the above assumptions be regarded as representing even roughly the effect of mixing on the ionic velocities, the calculations based on them shew that the error introduced by neglecting the effect of mixing would be of the same sign and order of magnitude as the differences between the calculated and observed values of the above table. While, therefore, such calculations are of little value, they strengthen the suspicion that the discrepancies of the above table are due to the impossibility of taking into account the effect of mixing on the velocities of the ions.