

II.—ON THE CALCULATION OF THE CONDUCTIVITY OF AQUEOUS SOLUTIONS CONTAINING HYDROCHLORIC AND SULPHURIC ACIDS.—BY JAMES BARNES, B. A., *Dalhousie College, Halifax, N. S.*

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The prediction of the conductivity of dilute aqueous solutions containing two electrolytes, which have one ion in common, has been shown to be possible, according to the dissociation theory, when the electrolytes are salts, or a salt and a diatomic acid such as hydrochloric acid.¹ The experiments described in the present paper were made, at Prof. MacGregor's suggestion, in order to ascertain if it is possible to make the prediction in the case of solutions formed by mixing hydrochloric and sulphuric acid solutions.

The attempt to calculate the conductivity of a complex solution containing sulphuric acid as one constituent is of special interest because of the fact that it is supposed to have a mode of ionization which varies with the concentration of the solution, its molecules in dilute solutions dissociating into 2 H and SO₄, but in stronger solutions partly into H and H SO₄. It is of course impossible to calculate the conductivity of a complex solution, one of the constituents of which has a mixed mode of ionization. I have therefore assumed that the mode of ionization in the moderately dilute solutions which I examined would be the same as it is usually supposed to be at great dilution.

The conductivity of a mixture of two solutions of electrolytes 1 and 2, with a common ion and definite modes of ionization

¹ MacGregor: *Trans. N. S. Inst. Sci.*, 9, 101, 1895-6.
McIntosh: *Ibid.*, 9, 120, 1895-6.
Archibald: *Ibid.*, 9, pp. 291, 307, 1897-8.
McKay: *Ibid.*, 9, 321, 1897-8.
Barnes: *Ibid.*, 10, 49, 1898-9.

is given, according to the dissociation theory, by the equation :

$$k = \frac{1}{p(v_1 + v_2)} (a_1 v_1 n_1 \mu_{\infty 1} + a_2 v_2 n_2 \mu_{\infty 2}), \dots (A)$$

where v_1, v_2 are the volumes, and n_1, n_2 the concentrations of the solutions mixed, $\mu_{\infty 1}, \mu_{\infty 2}$ the specific molecular conductivities of simple solutions of the electrolytes at infinite dilution, a_1 and a_2 the ionization co-efficients of the respective electrolytes in the mixture, and p the ratio of the volume of the mixture to the sum of the volumes of the constituent solutions.

¹ Prof. MacGregor has shown that the ionization coefficients in a mixture of this kind may be found by the solution of four equations, and I have pointed out in a former paper² that by throwing these equations into other forms and applying a graphical method they may be solved with little trouble, even in cases in which but few observations of the conductivity of simple solutions of the electrolytes in the mixtures are available. The forms of the equations referred to are as follows :

$$\begin{aligned} k_1 &= \frac{\mu_{\infty 1}}{\mu_{\infty 2}} k_2, \\ \frac{N_1}{C_1} + \frac{N_2}{C_2} &= 1, \\ k_1 &= f_1(C_1), \\ k_2 &= f_2(C_2), \end{aligned}$$

where the k 's and C 's are the regional conductivities and regional concentrations, and the N 's the concentrations of the mixture, with respect to the electrolytes 1 and 2 respectively. By the regional conductivity and the regional concentration of an electrolyte in a mixture are meant the conductivity and concentration of the portion or region of the mixture which the one electrolyte may be supposed to occupy to the exclusion of the other. If there is no change of volume on mixing, they are the conductivities and concentrations of the isohydric constituents of the mixture.

¹ Trans. N. S. Inst. Sci., 10, 63, 1898-9.

² Trans. N. S. Inst. Sci., 10, 113, 1899-1900.

The method of obtaining the ionization coefficients by means of these equations is described in my former paper, the first stage in the process being the determination of the k 's and C 's. In the calculation of the conductivity, however, we save labour if instead of determining the ionization coefficients, we express the conductivity in terms of the k 's and C 's.

For this purpose we have :

$$a_1 = \frac{k_1}{C_1 \mu_{\infty 1}},$$

and

$$a_2 = \frac{k_2}{C_2 \mu_{\infty 2}}.$$

Equation (A) thus becomes :

$$k = \frac{1}{p(v_1 + v_2)} \left(\frac{k_1 n_1 v_1}{C_1} + \frac{k_2 n_2 v_2}{C_2} \right).$$

In my experiments p was found to be practically equal to unity, and the volumes of the solutions mixed were in all cases equal. Hence the above equation becomes :

$$k = \frac{1}{2} \left(\frac{k_1 n_1}{C_1} + \frac{k_2 n_2}{C_2} \right) \dots \dots \dots (B)$$

The work involved in finding k by means of equation (B), included the following:—(1) The preparation and analysis of series of simple solutions of both acids, and the preparation of the mixtures; (2) observations on the specific gravity of the simple constituent solutions and their mixtures; (3) the measurement of the conductivity of series of simple solutions; (4) the measurement of the conductivity of mixtures of solutions; (5) the determination of the regional conductivity and regional concentration of the electrolytes in the mixtures; (6) the calculation by the aid of these data, of the conductivity of the mixtures.

The observations were carried out in the Physical and Chemical Laboratories of Dalhousie College, Halifax, during the spring and autumn of 1899.

Experimental Methods.

The hydrochloric acid was obtained from Eimer & Amend, and the sulphuric from Merck & Co. Both were guaranteed chemically pure. The redistilled water used in the preparation of the solutions was obtained by the method described in a former ¹paper, and it had a conductivity ranging from 0.95×10^{-6} to 1.01×10^{-6} expressed in ²Kohlrausch's new unit ($\text{ohm}^{-1} \text{ cm.}^{-1}$).

The amount of hydrochloric or sulphuric acid in a solution was determined volumetrically by means of aqueous solutions of potassium hydroxide, the strength of these being determined daily by titration with known quantities of dry oxalic acid. Phenol-phthalein was the indicator used. The potassium hydroxide solutions were kept in bottles with stoppers, each containing a soda lime tube. The pipettes, burettes and flasks were calibrated and used as described in the paper referred to above. The specific gravity at 18°C. was determined for many of the simple solutions with a pycnometer of the Ostwald-Sprengel form. The comparison of the values thus obtained with the values as given by Kohlrausch, acted as a check upon the concentration as determined above.

Kohlrausch's method with the alternating current and telephone was employed in the measurement of the conductivity.

The bath used to obtain a constancy of temperature, for a time sufficient to make the determination of the resistance in, contained tap water kept continually stirred by a mechanical stirrer driven by one of Henrici's small hot air motors. This motor worked without noise and on this account was found more serviceable than the hydraulic motor formerly employed. The thermometer used could be read to a hundredth of a degree, and had been tested at the Physikalisch-Technische Reichsanstalt, Berlin.

The resistance of the solutions was measured in a U-shaped cell having electrodes of stout platinum foil connected by thick

¹Trans. N. S. Inst. Sci., 10, 49, 1898-9.

²Kohlrausch u. Holborn: Leitvermögen der Elektrolyte, 1898, p. 1.

platinum wires to the ebonite covers. These electrodes were platinized in the solution proposed by ¹Lummer and Kurlbaum. The reduction factor by which the conductivities obtained in this cell are reduced to the standard employed by Kohlrausch, was obtained by comparing the value of the conductivities of two solutions of pure potassium chloride, twice recrystallized, of different concentrations, with values given by ²Kohlrausch for the same concentrations of the same salt. The ratio of Kohlrausch's value to the observed value gives the reduction factor. It was always determined before and after a series of observations, and was found to be the same in value at both times.

Solutions of different concentrations of each acid were prepared and carefully analysed. Fifty cubic centimetres of one of these solutions was placed in the electrolytic cell at a time, and two successive dilutions prepared in the cell by the addition of known volumes of water at 18°C. Then the other prepared solutions were introduced in order, and the same process of dilution repeated till a sufficient number of conductivity values had been obtained. In the case of mixtures, equal volumes (fifty cubic centimetres) of the constituent solutions were mixed at 18° C., and the mixture was then placed in the cell.

For a more detailed description of some of the above instruments and methods, see my former paper on conductivity.

Results of the Conductivity Observations on Simple Solutions.

It is necessary for the determination of the regional conductivities (k) and the regional concentrations (C) in the mixture (see my former paper),³ to draw curves showing the relation of conductivity to the concentration for each acid. In the case of one of the electrolytes, (hydrochloric acid was selected), the values of the conductivity must be multiplied by a constant before plotting, this constant being the ratio of the specific molecular conductivities at infinite dilution for the two

¹Wied. Ann., 66, 315, 1897.

²Kohl. u. Holb., *loc. cit.*, p. 159, tab. 2.

³Trans. N. S. Inst. Sci., 10, 113, 1899-1900.

acids. Kohlrausch's latest determinations¹ of the values of the specific molecular conductivity at infinite dilution at 18° C. for the two acids were used, viz.: for hydrochloric acid, 3774, and for sulphuric acid, 3955, both expressed in terms of 10^{-4} times Kohlrausch's new unit ($\text{ohm}^{-1} \text{cm.}^{-1}$). Therefore, the ratio is 1.048.

Table I gives the data, obtained from the conductivity observations, for the drawing of these curves. The concentrations are expressed in terms of gramme equivalent per litre at 18°C. The atomic weights used are relative to Oxygen (16.00), and the same as employed by ²Kohlrausch. The specific conductivities are those at 18°C, expressed in terms of 10^{-4} times Kohlrausch's new unit ($\text{ohm}^{-1} \text{cm.}^{-1}$).

TABLE I.

H Cl. (36.46.)			$\frac{1}{2}$ H ₂ SO ₄ . (49.04.)	
Concentration (n_1).	Specific Conductivity (k_1).	$\frac{\mu_{\infty 2}}{\mu_{\infty 1}} k_1$	Concentration (n_2).	Specific Conductivity (k_2).
2.66	6018.	6305.	4.11	6158.
2.13	5281.	5534.	2.95	4948.
1.74	4627.	4848.	2.20	3947.
1.42	3994.	4185.	1.74	3255.
1.02	3055.	3201.	1.28	2472.
.716	2268.	2376.	.890	1779.
.502	1640.	1718.	.523	1070.
.344	1148.	1203.	.452	932.5
.265	898.3	941.2	.304	637.4
.188	645.3	676.2	.197	421.8
.126	439.7	460.8	.108	241.5
.0951	334.9	350.9	.0967	218.8
.0810	287.9	301.6	.0603	148.4
.0559	201.0	210.6	.0352	93.77
.0356	129.3	135.5
.0262	94.67	99.20

¹ Wied. Ann., 50, 385, 1893.² Kohl. u. Holb., *loc. cit.*, p. 205, tab. 14.

Determination of p.

When equal volumes of simple solutions are mixed the ratio expressed by p is equal to the ratio of the specific gravity of the mixture to the mean specific gravity of the constituent solutions. Table II shows that the ratio is practically equal to unity for the most concentrated solutions examined.

TABLE II.

SIMPLE SOLUTIONS.					Mean Sp. Gr.	Sp. Gr. of Mixture at 18°C.
Concentration.		Specific Gravity at 18°C.				
H Cl.	$\frac{1}{2}$ H ₂ SO ₄ .	H Cl.	$\frac{1}{2}$ H ₂ SO ₄ .			
3.05	2.95	1.0525	1.0912	1.0719	1.0720	
2.13	1.74	1.0371	1.0549	1.0460	1.0462	
1.02	“	1.0182	“	1.0366	1.0365	
.502	“	1.0091	“	1.0320	1.0319	

Results of the Observations and Calculations of the Conductivity of Mixtures.

Table III contains the results of the observations and the calculations, by means of the data given therein, of the conductivity of mixtures of the acids under consideration. The regional concentration k_1 of the hydrochloric acid may be obtained from the value k_2 by means of the expression

$$k_1 = \frac{\mu_{\infty 1}}{\mu_{\infty 2}} k_2,$$

where k_2 is the regional concentration of the sulphuric acid. The specific molecular conductivities at infinite dilution have the values given above. In this table the conductivities and concentrations are expressed as in Table I. The differences between the calculated and observed values of the conductivity are given as percentages of observed values.

TABLE III.

Concentrations, Constituent Solutions.		Regional Conductivity of $\frac{1}{2}$ H ₂ SO ₄ (<i>k</i> ₂).	Regional Concentrations.		Specific Conductivity of Mixture.		Difference Per Cent.
H Cl. (<i>n</i> ₁).	$\frac{1}{2}$ H ₂ SO ₄ (<i>n</i> ₂).		H Cl. (<i>C</i> ₁).	$\frac{1}{2}$ H ₂ SO ₄ (<i>C</i> ₂).	Calculated Value.	Observed Value.	
3.80	2.95	6522.	2.83	4.50	6324.	6252.	+ 1.15
3.05	"	6013.	2.44	3.95	5840.	5784.	+ .97
1.74	"	4905.	1.77	2.92	4786.	4763.	+ .48
.0810	"	2948.	.925	1.55	2938.	2918.	+ .70
.804	.917	2240.	.669	1.15	2178.	2169.	+ .41
.328	"	1495.	.432	.739	1469.	1464.	+ .34
.0521	"	1036.	.292	.503	1033.	1035.	- .19
1.64	.291	2910.	.907	1.53	2788.	2779.	+ .32
1.02	"	2018.	.596	1.02	1936.	1934.	+ .10
.804	"	1638.	.487	.831	1606.	1607.	- .06
.328	"	886.0	.249	.429	857.3	856.7	+ .07
.0810	"	459.1	.125	.215	452.7	454.7	- .44
1.74	.0552	2832.	.880	1.48	2705.	2704.	+ .04
.502	"	927.8	.261	.450	888.0	889.6	- .18
.0951	"	219.2	.0581	.0967	211.1	211.8	- .33
.0810	"	194.7	.0515	.0823	187.8	188.3	- .27
.0521	"	143.1	.0376	.0575	138.4	138.5	- .08
.0264	"	96.65	.0256	.0363	94.43	94.54	- .12

In this table it will be noticed in the first series of observations, where the concentration of the constituent solution of sulphuric acid is constant, while the constituent solution of hydrochloric acid has a variable concentration, that the calculated values are all greater than the observed, and that the differences gradually increase as the concentration of the hydrochloric acid increases. This is also true for the second and third series, except in the case of the weaker hydrochloric acid solutions where the calculated is now less than the observed value. Prof. MacGregor has shown in a note to my former ¹paper, in which I drew attention to a regular progression similar to the above for series of solutions of potassium chloride and potassium sulphate, which were for the most part of moderate concentration, that the regular progression observed may be due to two sources of error. The second source, namely, the impossibility of drawing with perfect accuracy the dilution-ionic-concentration curves, has, I think, been considerably reduced, for in place of drawing these curves, which for moderate concentration curve quite rapidly, concentration-specific-conductivity curves were employed, these curves having but slight curvature and being thus easily interpolated. The other source of error, namely, the using for the value of the ionization coefficient the quotient of the specific molecular conductivity by the specific molecular conductivity at infinite dilution, still remains. In the above fourth series where the first two mixtures are of moderate concentration and the other four may be called dilute solutions, this regular progression has disappeared and the differences are all negative, except in the first mixture. The disappearance of the progression is consistent with its being due to the above sources of error; for in dilute solutions they both produce a very small effect upon the result. Two reasons may be assigned for the signs being all negative in the fourth series:—(1) The use of the above values of the specific molecular conductivity at infinite dilution; for if either of the values used should not be correct then it would clearly produce an error of the same sign

¹ *Loc. cit.*

in all the calculated values of the conductivity. There is also (2) the possibility referred to above, of the sulphuric acid breaking up not only into ions of 2H and SO_4 , but also into H and H SO_4 .

It is also possible by plotting the above series to obtain series of mixtures having a constant concentration for the constituent hydrochloric acid solutions and variable concentrations for the sulphuric acid constituent solutions; and it will be found in series of this kind that the same regular progression is exhibited as in the above. It may be well to note that in the last three series of the above Table where the sign of the difference changes, this change happens for all when the average concentration of the mixture is about 0.6 gramme-equivalents.

Finally, since my experiments are estimated as affected by an error which may amount to about ± 0.3 per cent., it is seen in the table that as the differences for the three last series are all within or in a few cases but little beyond this error, it may be concluded that the conductivity of mixtures of dilute solutions of hydrochloric and sulphuric acid can be calculated within the limit of my experimental error, by the expression of the dissociation theory and on the assumption that the sulphuric acid dissociates into 2H and SO_4 as ions, up to an average concentration of about 0.5 in cases in which the concentration with respect to sulphuric acid is relatively large, and up to an average concentration of about 0.9 in cases in which the concentration with respect to this acid is relatively small.