mize the amount of dust which might be blown against and adhere to the sides of the bulb. These ignitions were continued until no further loss of weight was observed. In making the calculations the atomic weight of chlorine was assumed to be 35.46. The temperature of the balance and the barometric reading were recorded in the case of the individual weights and these numbers were used in applying the vacuum corrections. In the calculation the density of tantalum chloride was taken as 3.68 and that of the weights as 8.4. As mentioned previously, no vacuum correction was applied in the case of the tantalum oxide, since this correction, which was smaller than the error in weighing, affected the fifth decimal only. The following table includes the results of all determinations made which were carried to completion without accident.

Series.	Bulb.	Wt. of $TaCl_5$ (vac.).	Wt. of Ta_2O_5 (vac.).	100 parts of $TaCl_5$ = parts of Ta_2O_5.	At. wt. of Ta.
II	3	12.99680	8.02326	61.733	181.49
II	5	9.24957	5.71104	61.744	181.60
II	4	10.17456	6.28133	61.736	181.52
II	1	17.99542	11.11014	61.739	181.55
II	2	11.70558	7.22693	61.739	181.55
III	4	6.24767	3.85658	61.728	181.46
III	3	7.26375	4.48398	61.731	181.48
I	2	15.88270	9.80465	61.732	181.49
				Mean,	181.52

Summary.

In eight experiments 91.51605 grams of tantalum chloride gave 56.49791 grams of tantalum oxide, corresponding in round numbers to 181.5 as the atomic weight of tantalum, a number one-half a unit higher than that now given in the international table. In conclusion, it may be as well to state that further work upon the value of this constant is in progress.

URBANA, ILL.

[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY. NO. 57.]

THE IONIZATION RELATIONS OF SULPHURIC ACID.

BY A. A. NOYES AND M. A. STEWART.

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CONTENTS.

INTRODUCTION.—OUTLINE OF THE INVESTIGATION AND REVIEW OF PREVIOUS WORK.

It is commonly assumed that sulphuric acid in aqueous solution ionizes in two stages according to the reactions

$$H_2SO_4 = H^+ + HSO_4^- \quad \text{and} \quad HSO_4^- = H^+ + SO_4^{=},$$

but no investigation, except that of Noyes and Eastman,[1] which was begun after this one, has furnished valuable evidence as to the proportion of the intermediate hydrosulphate ion (HSO_4^-) present, or indeed as to its existence in the solution. This research was therefore undertaken with the hope of furnishing more definite knowledge in regard to the ionization relations of this important acid.

The separate determination of the ionization constants for the two hydrogens is attended with much greater difficulty in the case of this acid than in the case of almost any of the organic dibasic acids or of such inorganic acids as sulphurous or phosphoric acid. This is true for the reasons, first, that the first hydrogen, and probably also the second hydrogen, of sulphuric acid is so largely ionized that the mass-action law cannot be employed in the study of its equilibrium relations; and second, that the difference between the degrees of ionization of the two hydrogens of sulphuric acid is much smaller than in the case of the other acids referred to, thus causing both stages of its ionization to be superposed, and preventing, among other things, a direct determination of the conductance of the intermediate hydrosulphate ion, a knowledge of which is of great importance in interpreting the conductance and transference data. In consequence of these difficulties many of the commonly applied methods fail to give, in this case, reliable results.

Thus it might be thought that the transference experiments which have previously been made by several investigators would throw much

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[1] *Carnegie Institution Publications*, 63, 239–81 (1907).

light upon the question of the intermediate ion; but the following simple calculation shows that the transference number would not be greatly different whether the acid be completely ionized in the one way or the other, provided a certain probable value be assumed for the conductance of the hydrosulphate ion. The number of chemical equivalents of sulphate ion transferred for each faraday of electricity passed would evidently be given in the two cases by the expressions:

$$\frac{\Lambda_{SO_4}}{\Lambda_H + \Lambda_{SO_4}} \text{ and } \frac{2\Lambda_{HSO_4}}{\Lambda_H + \Lambda_{HSO_4}}$$

respectively, where the Λ's represent the equivalent conductances of the ions indicated by the subscripts. At 18° the value of the first expression is $68/(68 + 315) = 0.178$; and, assuming that hydrosulphate ion has the same conductance as acetate ion,[1] the value of the second expression would be $70/(315 + 35) = 0.200$, provided in both cases it be assumed that Λ_H has the value (315) which it has at zero concentration. The matter is, however, complicated by the uncertainty as to the value of Λ_H that should be used in calculating the transference number at higher concentrations. Thus, if we put $\Lambda_H = 330$ in accordance with the transference results of Noyes and Sammet and of Noyes and Kato[2] with 0.006–0.018 normal acids, the transference number for complete ionization into hydrogen ion and sulphate ion becomes 0.171, and for that into hydrogen ion and hydrosulphate ion becomes 0.192. Experimentally the transference number for sulphuric acid at 18° in 0.01 to 0.05 formal[3] solution has been found by Tower and by Jahn and Hugbrechts to be 0.176, within a limit of error that can hardly exceed 0.002. These considerations indicate that a not very large proportion of hydrosulphate ion is present; but they also show that, on account of the errors involved in the measurement and interpretation of the transference number, it does not furnish a satisfactory means of calculating the concentration of that ion. It will be shown below, however, that the transference data do furnish valuable evidence as to the equivalent conductance of the hydrosulphate ion, and that, assuming that ion is really present in considerable proportion, they confirm the approximate validity of Noyes and Eastman's assumption in regard to it.

The existing freezing-point determinations, made by a great number of different investigators,[4] show that hydrosulphate ion is at 0° largely

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[1] This assumption was made in all their computations by Noyes and Eastman, but without other basis than the apparently similar molecular complexity of the two ions.

[2] See *Carnegie Institution Publications*, **63**, 326 (1907).

[3] In accordance with the practice now followed in this laboratory, the term "formal" is here used to express a solution containing one formula weight (in this case of H_2SO_4) per liter of solution.

[4] For references see the following section.

dissociated. Thus, in 0.05 formal solution, the value of the mol number i (representing the mols from one formula weight) has been found to be about 2.22, while in 0.01 formal solution values between 2.42 and 2.56 have been obtained. Complete ionization into H^+ and HSO_4^- would, of course, require the value 2.00, and into $2H^+$ and $SO_4^=$ the value 3.00. Moreover, it will be shown below that the quantity $(i - 1)$ is equal to the number of equivalents of hydrogen ion resulting from one formula weight of sulphuric acid (that is, $i - 1 = C_H/C$, where C is the formal concentration of the sulphuric acid), and that therefore freezing-point values furnish a quantitative measure of the concentration of this constituent.

The experiments on the relative catalytic influences of sulphuric acid and of hydrochloric acid upon the rate of hydrolysis of cane sugar and of ethyl acetate also furnish a means of determining the proportion of hydrogen ion in sulphuric acid solutions. The results will be considered more fully below. It may be mentioned here, however, that those of Ostwald on the sugar inversion indicate that at 25° in 0.05 formal solution 1.20 equivalents of hydrogen ion result from one formula weight of sulphuric acid; and that those of Kay on the ethyl acetate catalysis indicate that at 35° at the same concentration 1.16 equivalents result.

Noyes and Eastman,[1] upon the basis of certain probable assumptions, have derived from their conductance measurements with sulphuric acid and potassium hydrogen sulphate through a wide range of temperature definite estimates of the concentrations of sulphate ion and of hydrosulphate ion in solutions of both of these substances. Thus they estimate that in a 0.05 formal solution of sulphuric acid at 18° there are 6 per cent. H_2SO_4, 61 per cent. of HSO_4^-, and 33 per cent. of $SO_4^=$. This corresponds to 127 per cent. of hydrogen ion, which is in rough agreement with the results of the hydrolysis experiments just referred to. In view of the assumptions involved in their estimates, independent determinations of the concentrations of these constituents seem very desirable.

From the existing thermochemical data on the heat of neutralization of sulphuric acid, Noyes and Eastman have also calculated the heat of ionization of the hydrosulphate ion, and have found that it corresponds roughly with the heat value derived from the change of dissociation of that ion with the temperature.

The purpose of this article is to discuss critically the existing data relating to sulphuric acid and the conclusions to be drawn from them, and to present the results of some new work, which includes measurements of the conductance of sulphuric acid and sodium hydrogen sulphate, transference experiments with solutions of this salt, experiments upon the relative effect of sulphuric and hydrochloric acids upon the

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[1] *Carnegie Institution Publications*, **63**, 274–6 (1907).

ionization of picric acid, and determinations of the distribution of sulphuric acid between water and amyl alcohol.

PART I.—SOLUTIONS OF SULPHURIC ACID.

1. The Hydrogen-Ion Concentration Derived from Freezing-Point Measurements.

The equivalents of hydrogen ion resulting from one formula weight of the acid can be calculated from the value of the mol number i, as determined from the freezing-point lowering, by merely subtracting unity from it; that is, $C_H/C = i - 1$. For evidently:

$$i\,C = C_H + C_{H_2SO_4} + C_{HSO_4} + C_{SO_4}, \text{ and } C = C_{H_2SO_4} + C_{HSO_4} + C_{SO_4},$$

where C represents the formal concentration of the acid and the C's with subscripts the formal concentration of the constituents represented by those subscripts.

The freezing points of dilute sulphuric acid solutions have been determined by Pickering,[1] Loomis,[2] Jones,[3] Wildermann,[4] Ponsot,[5] Barnes,[6] Hausrath[7] and Bedford.[8] In order to determine the best values at a series of round concentrations and to form an estimate of their probable accuracy, the results of all these investigators (except the early ones of Pickering) have been correlated and combined by a method described by Noyes and Falk.[9] Only the values of $i - 1$ or C_H/C corresponding to the final values of i derived by them need therefore be reproduced here. It seems scarcely possible that any of these values at the concentrations 0.02 to 0.1 formal inclusive are in error by as much as 2 per cent., but those at 0.01 and 0.005 may well be in error by two or three times this amount.

TABLE I.—VALUES OF THE HYDROGEN-ION CONCENTRATION (C_H/C) AT 0° DERIVED FROM FREEZING-POINT MEASUREMENTS.

Formal concentration..	0.005	0.010	0.020	0.025	0.050	0.100
C_H/C	1.59	1.47	1.35	1.32	1.22	1.13

2. The Hydrogen-Ion Concentration Derived from Conductance and Transference Measurements.

Noyes and Eastman, as stated in the introduction to this article, derived from their conductance measurements alone, with the aid of certain

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[1] *J. Chem. Soc.*, **57**, 363 (1890). See also *Z. physik. Chem.*, **7**, 397 (1891).

[2] *Physic. Rev.*, **1**, 281 (1893).

[3] *Z. physik. Chem.*, **12**, 629 (1893).

[4] *Ibid.*, **15**, 350 (1894); **19**, 241 (1896).

[5] *Ann. chim. phys.*, [7] **10**, 109 (1897).

[6] *Trans. Royal Soc. Canada*, [2] **6**, III, 48 (1900). See also *Trans. N. S. Inst. of Science*, **10**, 222 (1900).

[7] *Drude's Ann.*, **9**, 547 (1902).

[8] *Proc. Roy. Soc., London A* **83**, 454 (1910).

[9] THIS JOURNAL, **32**, 1027 (1910).

assumptions, an estimate of the hydrogen-ion concentration in sulphuric acid solutions at various concentrations and temperatures. Making the assumption that the HSO_4^- ion has the same equivalent conductance as the acetate ion, they first showed that the hydrogen-ion concentration must lie between certain comparatively narrow limits. Then making the further assumption, based on the conductivity results at high temperatures, that sulphuric acid has with respect to its first hydrogen the same ionization tendency as hydrochloric acid, definite values of the concentrations of all the constituents in the solution were derived.

It may readily be shown that the first and most arbitrary of these two assumptions can be dispensed with by combining with the conductance values the results of transference experiments. Thus for the specific conductance L we have

$$1000\ L = C_H\Lambda_H + 2C_{SO_4}\Lambda_{SO_4} + C_{HSO_4}\Lambda_{HSO_4}, \qquad (1)$$

where the C's represent the formal concentrations and the Λ's the equivalent conductances of the various ions. And for the number of equivalents (N_{SO_4}) of SO_4 transferred per faraday of electricity, we have

$$N_{SO_4} = \frac{2C_{SO_4}\mathit{\Lambda}_{SO_4}}{1000\ L} + \frac{2C_{HSO_4}\mathit{\Lambda}_{HSO_4}}{1000\ L}. \qquad (2)$$

This follows from the principle that the quantity in equivalents of each ion transferred per faraday is equal to the ratio of its conductance to the whole conductance and from the fact that one electrical equivalent of HSO_4 ion yields two chemical or analytical equivalents of SO_4. Writing this equation in the form

$$\tfrac{1}{2} \times 1000\ L\ N_{SO_4} = C_{SO_4}\mathit{\Lambda}_{SO_4} + C_{HSO_4}\mathit{\Lambda}_{HSO_4}, \qquad (3)$$

subtracting it from equation (1), dividing both members by C, the formal concentration of the sulphuric acid, and putting $1000L/2C = \mathit{\Lambda}$, the equivalent conductance of the acid, we get

$$2\mathit{\Lambda}\ (1 - \tfrac{1}{2}N_{SO_4}) = \frac{C_H\mathit{\Lambda}_H}{C} + \frac{C_{SO_4}\mathit{\Lambda}_{SO_4}}{C}. \qquad (4)$$

The last term of this expression is relatively small and can vary only between the limits zero and $\frac{1}{2}(C_H/C)\mathit{\Lambda}_{SO_4}$, corresponding to the two limiting cases where HSO_4^-, and where $SO_4^=$, is the only anion present. Within corresponding limits the value of C_H/C can therefore be determined, and evidently without involving any assumption as to the value of $\mathit{\Lambda}_{HSO_4}$.

Let us now consider the transference and conductance data available for this calculation.

The transference number for sulphuric acid has been determined by many different investigators,[1] but only the determinations by Bein, by

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[1] Wiedmann, *Pogg. Ann.*, 99, 162 (1856); Hittorf. *Ibid.*, 106, 401 (1859); Bein, *Z. physik. Chem.*, 27, 52 (1898); Starck, *Ibid.*, 29, 394 (1899); Tower, THIS JOURNAL, 26,

Tower, and by Jahn and Hugbrechts, seem to have been made with precautions sufficient to warrant the consideration of the results. The following table contains the final values obtained by them for the transference number of the anion (N_{SO_4}) reduced to uniform temperatures by means of the temperature coefficient 0.0011[1], and in the case of Jahn and Hugbrecht's results interpolated for round concentrations.

TABLE II.—TRANSFERENCE NUMBER FOR THE SULPHATE ION.

Formal concen.	At 8°.		At 20°.		At 32°.		At 97°.
	Bein.	Tower.	Tower.	J. & H.	Tower.	J. & H.	Bein.
0.5000	...	...	0.188	...	...	...	...
0.250	...	...	0.187	...	...	...	...
0.125	...	...	...	0.170	...	...	...
0.100	...	...	0.181	...	...	...	...
0.050	...	0.164	0.176	0.177	0.192	...	...
0.025	0.172	0.164	0.179	0.177	0.192	0.194	0.304
0.010	...	0.168	0.181	0.178	0.191	0.189	...
0.004	...	...	...	0.158	...	0.164	...

From these results one is justified in concluding that the transference number is substantially constant between 0.01 and 0.05 formal, and that within this concentration interval it has the following values:

0°.	8°.	18°.	20°.	25°.	32°.
0.157[2]	0.165	0.176	0.178	0.184	0.192

At the higher concentrations 0.1 to 0.5 formal Tower's data are to be regarded as the best values, in view of the concordance of his results with the cathode and anode portions, and of the constancy in content of the middle portions.

Two entirely independent series of measurements of the conductance of sulphuric acid at 25° have recently been made in this laboratory, by Mr. G. W. Eastman[3] and by Mr. F. L. Hunt,[4] respectively, and a series at 0° with the same solutions has been made by the latter.[5] The

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1062 (1904): Jahn and Hugbrechts, *Z. physik. Chem.*, **58**, 651 (1907); Whetham and Paine, *Proc. Royal Soc.*, A81, 69 (1908).

[1] This is the value found by Tower for the temperature-coefficient ($\Delta N_{SO_4}/\Delta T$) between 8 and 32° for 0.01 to 0.05 formal solutions. The reduction was in no case for a greater interval than 3°.

[2] This value is extrapolated, but can in consequence hardly be in error by more than 0.001.

[3] *Carnegie Institution Publications*, **63**, 262 (1907).

[4] In connection with a research which is soon to be published in detail.

[5] Measurements with dilute sulphuric acid have been previously published at 18° by Kohlrausch (L.-B.-M. Tabellen, p. 746); at 0 and 18° by Barnes (*Proc. Royal Soc. Canada*, [2] **6**, III, 46 (1900)); at 0, 15, 25 and 35° by Jones and Douglas (*Am. Chem. J.*, **26**, 436 (1901)); see also Tower's "Conductivity of Liquids," p. 164); at 0 and 18° by Whetham (*Z. physik. Chem.*, **33**, 351 (1900); **55**, 205 (1906)); and at 18° to 306° by Noyes and Eastman (*Loc. cit.*).

results of these determinations are presented in the following table. The concentrations are expressed in formula weights per liter at the temperature of the measurement, and the equivalent conductance in reciprocal ohms:

TABLE III.—EQUIVALENT CONDUCTANCE OF SULPHURIC ACID AT 25° AND 0°.

Formal concen.	25°. N. & E.	25° F. L. H.	25°. Mean.	0°. F. L. H.
0.1000	...	234.7	234.7	165.4
0.0500	251.2	251.2	251.2	177.2
0.0250	273.0	273.1	273.0	191.5
0.0125	...	299.3	299.2	206.9
0.00625	327.5	...	327.5	...
0.00500	(337.0)	336.8	336.8	226.4
0.00100	390.8	...	390.8	...
0.00025	413.7	...	413.7	...
0.00010	418.5	...	418.5	...

Besides the transference and conductance data for the acid, the values of the equivalent conductances of hydrogen ion (Λ_H) and sulphate ion (Λ_{SO_4}) are needed for the computation of C_H/C. For Λ_H at zero concentration, Goodwin and Haskell[1] and also Kohlrausch[2] have derived the value 315 at 18°, which corresponds to 348 at 25° if the temperature coefficient ($d\Lambda/\Lambda_{18}dT = 0.0153$) given by Kohlrausch be employed. For Λ_{SO_4} the value given by Kohlrausch[2] at 18° is 68, which, using his temperature coefficient (0.0227), becomes 79 at 25°.

The values of Λ_H and Λ_{SO_4} at 0° at zero concentration we have found to be 224 and 43, respectively, by the following method of derivation. Noyes and Coolidge,[3] from their measurements at 0° of the conductance of potassium chloride (which are perfectly concordant with those of Whetham), obtained the value 81.4 for Λ_0 for that salt. Multiplying this by the transference number 0.496 (assumed to be the same as at 18°) we get $\Lambda_K = 40.3$ and $\Lambda_{Cl} = 41.1$. Furthermore, Λ_0 for HCl at 0° was found to be 265.4 by multiplying Λ_0 for HCl at 18° = 379.5 by the ratio of the Λ values for 0.01 normal HCl at 0° and 18°, which ratio has been found to be 0.700 by Barnes[4] and 0.6994 by Déguisne.[5] Subtracting $\Lambda_{Cl} = 41.1$, we then obtain $\Lambda_H = 224$.[6] Similarly, Λ_0 for K_2SO_4 at 0° was found to be 83.1 by multiplying Λ_0 for K_2SO_4 at 18° = 132.6 by the ratio of the Λ values for 0.001 normal K_2SO_4 at 0° and at 18°,

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[1] *Phys. Rev.*, **19**, 395 (1904).

[2] *Z. Elektrochem.*, **13**, 333 (1907).

[3] *Carnegie Institution Publications*, **63**, 47 (1907).

[4] *Trans. N. S. Inst. of Science*, **10**, 150 (1900).

[5] See *Landolt-Börnstein-Meyerhoffer Tabellen*, p. 755.

[6] Attention may here be called to the fact that Johnston's rough estimate of Λ_H at 0° as 240 (THIS JOURNAL, **31**, 1015 (1909)) is much too high.

which ratio has the value 0.627 (0.628 according to Archibald[1] and 0.625 according to Déguisne). Subtracting $\Lambda_K = 40.3$, we get $\Lambda_{SO_4} = 42.8$.

It should be mentioned, however, that the transference experiments of Noyes and Sammet[2] and of Noyes and Kato[3] with hydrochloric and nitric acids have indicated that the equivalent conductance of hydrogen ion is about 5 per cent. greater in 0.005 to 0.02 normal solutions of these acids than it is at zero concentration. It seems reasonable to assume that this may be also the case in sulphuric acid solutions; and it seems therefore worth while to show in the subsequent calculations the effect of this assumption, according to which Λ_H would have the value 365 at 25° and 235 at 0°. At the same time it should be recognized that the employment of these particular values at higher concentrations than 0.02 normal has at present no experimental basis.

The values of C_H/C at 25° and at 0°, calculated from the foregoing data by means of equation (4) under the two limiting assumptions that C_{SO_4} is equal to zero and to $^1/_2 C_H$, respectively, and for the two values of Λ_H just referred to, are given in the following table. The first values given in each column are those corresponding to the assumption that SO_4 is the only anion present:

TABLE IV.—VALUES OF C_H/C AT 25° AND 0° DERIVED FROM CONDUCTANCE AND TRANSFERENCE MEASUREMENTS.

Formal concen.	C_H/C at 25° (for $\Lambda_H = 348$).	C_H/C at 25° (for $\Lambda_H = 365$).	C_H/C at 0° (for $\Lambda_H = 235$).	C_H/C at 0° (for $\Lambda_H = 224$).
0.100	1.10–1.22	1.05–1.16	1.19–1.29	1.24–1.36
0.050	1.18–1.31	1.13–1.24	1.27–1.39	1.33–1.46
0.025	1.28–1.42	1.23–1.35	1.38–1.49	1.44–1.57
0.0125	1.40–1.56	1.34–1.48	1.48–1.61	1.55–1.70
0.00625	1.53–1.71	1.46–1.62	....	....
0.00500	1.58–1.76	1.51–1.67	1.63–1.77	1.70–1.86

3. The Equivalent Conductance of Hydrosulphate Ion Derived from Conductance and Transference Measurements.

The value of the equivalent conductance of the hydrosulphate ion is of so much importance in the interpretation of transference and conductance results that it is worth while to consider just what conclusion in regard to it can be drawn from the existing data. For this purpose we may make use of equation (3), written in the form:

$$\Lambda N_{SO_4} = \Lambda_{SO_4}(C_{SO_4}/C) + \Lambda_{HSO_4}(C_{HSO_4}/C). \qquad (5)$$

In this equation N_{SO_4}, Λ, and Λ_{SO_4} are known; and between C_{SO_4}, C_{HSO_4}, and C_H (which last is known within comparatively narrow limits) there exists the following relation expressing the equality of the equivalent concentrations of the positive and negative ions:

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[1] *Trans. N. S. Inst. of Science*, **10**, 38 (1898).

[2] THIS JOURNAL, **24**, 958 (1902).

[3] *Ibid.*, **30**, 333 (1908).

$$C_{\mathrm{H}} = 2C_{\mathrm{SO_4}} + C_{\mathrm{HSO_4}}. \tag{6}$$

In order that $\Lambda_{\mathrm{HSO_4}}$ might be definitely determined by these equations, either $C_{\mathrm{SO_4}}$ or $C_{\mathrm{HSO_4}}$ would have to be known; but it is found by computation that the value involved is such that it can be determined within narrow limits, provided only the assumption is justified that the concentration $C_{\mathrm{HSO_4}}$ forms a reasonably large part (say as much as one-fourth) of the total ion concentration ($C_{\mathrm{HSO_4}} + 2C_{\mathrm{SO_4}}$). Thus the values of $\Lambda_{\mathrm{HSO_4}}$ calculated by (5) from the data given in Tables II, III and IV under the limiting assumption that $C_{\mathrm{HSO_4}} = C$ and under the assumption that $C_{\mathrm{HSO_4}} = \frac{1}{4}C_{\mathrm{A}}$, and with the values of C_{H}/C corresponding to the smaller and larger values of Λ_{H} are given in Table V.

TABLE V.—CALCULATED VALUES OF THE EQUIVALENT CONDUCTANCE OF HYDROSULPHATE ION AT 25° AND 0°.

	At 25°.				At 0°.			
	For $C_{\mathrm{HSO_4}}=C$.		For $C_{\mathrm{HSO_4}}=\frac{1}{4}C_{\mathrm{H}}$.		For $C_{\mathrm{HSO_4}}=C$.		For $C_{\mathrm{HSO_4}}=C$.	
Concentration.	$\Lambda_{\mathrm{H}}=348$.	$\Lambda_{\mathrm{H}}=365$.	$\Lambda_{\mathrm{H}}=348$.	$\Lambda_{\mathrm{H}}=365$.	$\Lambda_{\mathrm{H}}=224$.	$\Lambda_{\mathrm{H}}=235$.	$\Lambda_{\mathrm{H}}=224$.	$\Lambda_{\mathrm{H}}=235$.
0.100	36.0	38.4	37.0	44.0	18.9	20.2	13.8	17.6
0.050	35.1	37.5	34.0	41.0	18.8	20.1	14.1	17.6
0.025	35.3	37.7	34.5	41.0	18.8	20.2	14.5	18.3
0.0125	35.3	37.7	34.5	42.0	18.8	20.5	15.1	19.1
Mean.	35.4	37.8	35.0	42.0	18.8	20.2	14.4	18.1

It is evident from these calculations that at 25° the value of $\Lambda_{\mathrm{HSO_4}}$ is 35 ± 1 if $\Lambda_{\mathrm{H}} = 348$, or 40 ± 2 if $\Lambda_{\mathrm{H}} = 365$, and that at 0° the value is 16 ± 2 if $\Lambda_{\mathrm{H}} = 224$, or 19 ± 1 if $\Lambda_{\mathrm{H}} = 235$, it being always assumed that the $\mathrm{HSO_4^-}$ ion is present in sufficient proportion to make the calculated values significant. It will be noted that the value 40 at 25° or 19 at 0° for $\Lambda_{\mathrm{HSO_4}}$ is not far from one-half of that for $\Lambda_{\mathrm{SO_4}}$ (79 or 43), which would be the case if the frictional resistance to the motions of the two ions were nearly equal, since the electric force acting on the latter, owing to its double charge, is twice as great.

4. The Hydrogen-Ion Concentration Derived from Catalysis Experiments.

Since the catalytic influence of acids upon reactions of hydrolysis is nearly proportional to their hydrogen-ion concentration and is little influenced by other factors, the concentration of that ion in sulphuric acid solutions may be determined by comparing the effect of that acid on the reaction rate with that of an acid of known ionization, such as hydrochloric acid, at nearly the same ion concentration. The data that seem best adapted to this purpose are those of Ostwald[1] upon the sugar inversion and of Kay[2] on the ethyl acetate hydrolysis. Table VI contains the specific reaction rates as determined by these two investigators.

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[1] Ostwald, *J. prakt. Chem.*, [2] **31**, 313–4 (1885).

[2] Kay, *Proc. Royal Soc. Edinburgh*, **22**, 493–496 (1898–9).

TABLE VI.—RELATIVE CATALYTIC EFFECTS OF SULPHURIC AND HYDROCHLORIC ACIDS.

Acid.	Formal concen.	Sugar inversion at 25°.	Ethyl acetate hydrolysis at 35°.
HCl	0.5	20.5	...
	0.2	....	146.9
	0.1	3.34	71.8
	0.01	0.313	...
H_2SO_4	0.25	10.7	201.5
	0.05	2.08	44.1
	0.005	0.265	6.06

The best method of computation clearly seems to be to determine by interpolation the concentration (C_A) of a hydrochloric acid solution which has the same catalytic effect as each of the measured sulphuric acid solutions. This we have done (for the two most dilute solutions of the latter acid) by calculating first for the former acid the values of the ratio (k_A/C_A) of the specific reaction rate to the concentration, which values do not vary greatly with the dilution, interpolating for a concentration which is estimated to be nearly isohydric with the sulphuric acid solution in question, and then dividing the reaction rate for the latter acid by this ratio, the interpolation and division being once more repeated, if necessary. The concentration C_A of hydrochloric acid so obtained, when multiplied by the corresponding ionization (γ_A) as given by the conductance ratio (Λ/Λ_0), yields the hydrogen-ion concentration C_H in the solution of either acid, and this, when divided by the concentration of the sulphuric acid C_B, gives the mols of hydrogen ion resulting from one formula weight.

Two sets of values of the ionization γ_A were employed, these being obtained by dividing the values of Λ for hydrochloric acid at 18° found by Kohlrausch, Goodwin and Haskell, and Noyes and Cooper[1] in one case by $\Lambda_0 = 380$, and in the other case by $\Lambda_0 = 396$, corresponding respectively to the values of Λ_H at zero concentration (315), and at higher concentrations (331), as found by Noyes, Sammet, and Kato.

The data and results are given in Table VII:

TABLE VII.—VALUES OF HYDROGEN-ION CONCENTRATION AT 25° AND 35° DERIVED FROM CATALYSIS EXPERIMENTS.

C_B.	C_A at 25° (Ostwald).	C_A at 35° (Kay).	γ_A.	C_H/C_B. 25° (Ostwald).	C_H/C_B. 35° (Kay).
0.0500	0.0638	0.0619	0.940 or 0.902	1.20 or 1.15	1.16 or 1.11
0.0050	0.00847	0.00862	0.974 or 0.935	1.65 or 1.58	1.68 or 1.61

5. The Hydrogen-Ion Concentration Derived from the Relative Effects of Sulphuric and Hydrochloric Acids upon the Ionization of Picric Acid.

Experiments by M. A. STEWART.

A method which naturally suggests itself for the determination of the

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[1] *Carnegie Institution Publications*, 63, 138 (1907).

hydrogen-ion concentration is that based on the principle of isohydric solutions, which consists in finding the concentration which a solution of sulphuric acid must have in order that it may be mixed with a definite solution of hydrochloric acid with the production of a mixture whose specific conductance is the mean of that of the separate solutions. Theoretically this result occurs only when the hydrogen-ion concentrations of the two acids are equal. Both calculation and experiment clearly showed, however, that the sensitiveness of the method was so slight as to make it of no value.

A new method was therefore employed. This consists in principle in determining the relative concentrations of hydrochloric acid and of sulphuric acid which drive back the ionization of a third acid to the same extent. Picric acid was chosen as the third acid, and the condition of equal concentration of its un-ionized part in the solution was determined by shaking it with benzene, between which and water it distributes itself, as shown by the investigation of Rothmund and Drucker.[1]

The experiments were carried out in detail as follows: In one of two bottles of two-liter capacity were placed about 1300 cc. of the sulphuric acid solution to be investigated, and in the other the same volume of a hydrochloric acid solution (of a concentration estimated to be about isohydric); then to both were added an equal volume (about 70 cc.) of a nearly saturated solution of picric acid in benzene. These were rotated for four to five hours in a thermostat at 25°. The same volume (about 50 cc.) of the benzene phase was then removed from each, and, after the addition of a little water, each portion was titrated with about 0.3 normal barium hydroxide, using phenolphthalein as indicator. Then the experiment was repeated with a second solution of hydrochloric acid of somewhat different concentration from that first used, and the rate of change was computed of the concentration of the acid with the quantity of picric acid contained in the benzene phase,

$$\left(\frac{\Delta C_{HCl}}{C_{HCl}} \Big/ \frac{\Delta C_{HP}}{C_{HP}}\right);$$

and therefrom, under the assumption of proportionality, the concentration of hydrochloric acid which would have an effect just identical with that of the sulphuric acid was calculated.

The picric acid used was purified by crystallization from dilute hydrochloric acid, from benzene, from alcohol, and from water. The benzene used was the thiophene-free commercial product.

Preliminary experiments showed that no appreciable amount of either sulphuric acid or hydrochloric acid would go into the benzene. Normal sulphuric acid was shaken with 50 cc. of benzene; the benzene layer was separated, and to it were added a little water and phenolphthalein and

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[1] *Z. physik. Chem.*, 46, 827–53 (1903).

then 0.1 normal alkali. One drop of the alkali gave as strong a coloration as in the case of pure water to which phenolphthalein was added, showing that no appreciable amount of sulphuric acid could have gone into the benzene. A similar experiment with normal hydrochloric acid gave the same result.

The error due to the effect of the picric acid on the ionization of the sulphuric and hydrochloric acids is very small: first, because the amount of picric acid is relatively small, so that the hydrogen ion from it forms only a small part of the total hydrogen ion, and second, because the sulphuric and hydrochloric acids would be affected to nearly the same extent and in the same direction. Moreover, since the ion concentrations in the two acid solutions are nearly the same, an appreciable error can hardly arise through a variation in the distribution ratio for the picric acid between the two phases.

The experimental results, all of which are at 25°, are given in the following table. The fourth column shows the percentage difference in the concentrations of the picric acid in the two benzene solutions which had been shaken with the hydrochloric acid and with the sulphuric acid solutions. The values in heavy type in the rows below each group of experiments, show in the second and third columns the calculated concentrations of the two acids at which they have the same hydrogen-ion concen-

TABLE VIII.—VALUES OF HYDROGEN-ION CONCENTRATION AT 25° DERIVED FROM EXPERIMENTS WITH PICRIC ACID.

Expt. No.	Formal concentration C of H_2SO_4.	Formal concentration of HCl.	Percentage difference in picric acid concentrations.	Percentage ionization of HCl.	Hydrogen ion concentration C_H.	Ratio C_H/C.
1	0.4923	0.5547	—0.33	....	....	....
2	0.4923	0.5652	+0.03	....	....	....
	0.4923	**0.5645**	**±0.00**	**85.5**	**0.4826**	**0.98**
3	0.2500	0.3129	+2.59	....	....	....
4	0.2500	0.2535	—3.27	....	....	....
5	0.2500	0.3192	+2.99	....	....	....
6	0.2500	0.2825	—0.20	....	....	....
	0.2500	**0.2846**	**±0.00**	**88.8**	**0.2526**	**1.01**
7	0.09983	0.12022	+1.27	....	....	....
8	0.09983	0.11690	—0.23	....	....	....
	0.09983	**0.1174**	**±0.00**	**92.0**	**0.1080**	**1.08**
9	0.05000	0.05942	—1.19	....	....	....
10	0.05000	0.06089	—0.05	....	....	....
	0.05000	**0.06095**	**±0.00**	**94.1**	**0.0573**	**1.15**[1]
11	0.02506	0.03197	—0.42	....	....	....
12	0.02506	0.03253	—0.07	....	....	....
	0.02506	**0.03264**	**±0.00**	**95.8**	**0.03126**	**1.25**[2]

[1] Or 1.10, assuming Λ_0 = 396 and 100γ = 90.3.

[2] Or 1.20, assuming Λ_0 = 396 and 100γ = 92.0.

tration, and in the last three columns the corresponding values of the percentage ionization of the hydrochloric acid (as derived from its conductance ratio Λ/Λ_0, using Kohlrausch's data[1] at 18° and taking $\Lambda_0 = 380$), of the hydrogen-ion concentration C_H in either solution, and of the ratio C_H/C of that concentration to the formal concentration of the sulphuric acid. The calculated values of C_H and C_H/C would be 4 per cent. smaller than those gven in the table if in calculating the ionization Λ_0 be taken equal to 396. This may be justifiable for the two most dilute solutions, but any value assumed for the more concentrated solutions would be entirely arbitrary.

6. Comparison of the Hydrogen Ion Concentrations Derived by Various Methods.

The values of the hydrogen-ion concentration (C_H/C) derived by the methods already considered are brought together in Table IX. Excepting those derived from the freezing point, the values given are those calculated under the assumption that the equivalent conductance of hydrogen ion Λ_H is that derived from the conductance of acids at zero concentration. If it be assumed, in correspondence with the transference results of Noyes, Sammet, and Kato, that in acid solutions of medium concentrations Λ_H is 5 per cent. greater than at zero concentration, then all the values of C_H/C (except those derived from the freezing point) should be increased by 4 to 5 per cent.

TABLE IX.—VALUES OF THE HYDROGEN ION CONCENTRATION DERIVED BY VARIOUS METHODS.

Formal concentration.	Freezing point. 0°.	Conductance and transference. 0°.	Conductance and transference. 25°.	Sugar catalysis. 25°.	Picric acid expts. 25.	Ester catalysis. 35°.
0.050	1.22	1.33–1.46	1.18–1.31	1.20	1.15	1.16
0.025	1.32	1.44–1.57	1.28–1.42	....	1.25	....
0.005	1.59	1.64–1.79	1.58–1.76	1.65	....	1.68

It will be seen that at 0° the values derived from the freezing points are much less than even the lower limiting values derived from the conductivity and transference experiments, which values were obtained under the assumption that only H^+ and $SO_4^=$ ions exist in the solution. This discordance may well be due in part to error in the value of (Λ_H) employed, but it can not be wholly accounted for in this way.

It will also be noted that the conductance and transference data show that there is a large decrease in the hydrogen-ion concentration between 0° and 25°. It will also be observed that the values derived from the conductance are in accordance with those derived from the sugar catalysis; but that they are considerably higher at 0.05 and 0.025 formal than those derived by the picric acid method. It may be recalled that a change

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[1] As given in *Landolt-Börnstein-Meyerhoffer's Tabellen*, p. 746.

in the assumed value of Λ_H will not account for this divergence, since it would affect the latter values to nearly the same extent as those from the conductance.

7. Concentration of the Other Constituents.

Since the values of the hydrogen-ion concentration calculated from the conductance and transference data differ by about 10 per cent. in the two limiting cases, in one of which no hydrosulphate ion and the other of which no sulphate ion is assumed to be present, it might seem that the proportion of these two ions in the solution might be obtained by considering in connection with these limiting values that of the hydrogen-ion concentration derived by some of the other methods. The degree of inaccuracy of all the values is, however, great enough to make such a calculation of little, if any, value. Indeed, the values obtained by the picric acid distribution methods (like those at 0° obtained from the freezing point) are below the lower limit of those derived from the conductance, so that upon solving the appropriate equations mathematically a negative value of the hydrosulphate ion concentration results.

In order to determine the concentration of the other constituents ($SO_4^{=}$, HSO_4^{-}, and H_2SO_4), further information in regard to at least one of them is therefore essential. The others would then become determined in virtue of the condition equations,

$$C_H + C_{HSO_4} + 2C_{H_2SO_4} = 2C, \tag{7}$$

and

$$C_{SO_4} + C_{HSO_4} + C_{H_2SO_4} = C. \tag{8}$$

To find a method which will give such information in a conclusive way is difficult. The most promising line of attack would seem to be to determine the concentration of the sulphate ion through the measurement of some property closely related to it; and in the hope of doing this we have studied the effects of sodium sulphate, sodium hydrogen sulphate, and sulphuric acid on the solubility of thallous sulphate. But the results of these experiments, which will be described in another article, show, even in the case of sodium sulphate, such a wide divergence from the law of the solubility product that it seems impracticable to employ them for the purpose in question. Another method, simpler in principle, of determining the sulphate-ion concentration in sulphuric acid solutions is to measure the electromotive force of a concentration cell, such as is represented by the combination Hg, Hg_2SO_4, K_2SO_4Aq, H_2SO_4Aq, Hg_2SO_4, Hg. Experiments of this kind are to be undertaken in this laboratory.

In the absence of information as to the sulphate ion the conclusion of Noyes and Eastman that the ionization tendency of sulphuric acid with reference to its first hydrogen is the same as that of hydrochloric acid is the only principle that seems to be sufficiently well substantiated to warrant being made the basis of a provisional computation of the constitution of sulphuric acid solutions.

That conclusion, it may be recalled, was based: (1) on the fact that at the temperature of 156° the formal conductance of potassium hydrogen sulphate (435) in 0.1 formal solution has become even less than that of potassium chloride (490), showing that the former salt can dissociate to an important extent only into K^+ and HSO_4^-, that therefore the ion HSO_4^- is only very slightly dissociated; (2) on the conclusion that this ion must *a fortiori* be very slightly dissociated in fairly concentrated solutions of sulphuric acid itself at 156° and above; (3) on the fact that the conductance of such solutions when interpreted under this assumption shows that the ionization of the acid is substantially equal to that of hydrochloric acid of the same concentration at 156, 218, and 306°; and (4) on the assumption that this equality of ionization holds true also at lower temperatures, such as 18°, inasmuch as differences in ionization of largely ionized substances are as a rule less pronounced at lower than at higher temperatures.

Upon the basis of this conclusion in regard to the un-ionized H_2SO_4, the concentration of the constituents may be calculated by equations (7) and (8) by using separately each of the values of C_H/C, given in Table IX. It has seemed worth while, however, to make such calculations only with the values at 0° derived from the freezing point and with the mean of the values at 25° derived from the sugar catalysis experiments and the picric acid experiments. We have, in addition, calculated the concentrations of the various constituents by the method described by Noyes and Eastman[1] from the conductance and transference data at 0° and 25°, so that the results may be compared on the one hand with those at 0° obtained from the freezing-point data, and on the other hand with those at 25° obtained by the catalysis and picric acid experiments. The results are given in Table X.

TABLE X.—CONCENTRATIONS OF THE CONSTITUENTS IN SULPHURIC ACID SOLUTIONS.

Formal concen.	C_H/C.	$C_{H_2SO_4}/C$.	C_{HSO_4}/C.	C_{SO_4}/C.	C_H/C.	$C_{H_2SO_4}/C$.	C_{HSO_4}/C.	C_{SO_4}/C.
	From conductance data at 0°.				From freezing-point data at 0°.			
0.050	1.38	0.06	0.50	0.44	1.22	0.06	0.66	0.28
0.025	1.48	0.05	0.42	0.53	1.32	0.05	0.58	0.37
0.005	1.67	0.02	0.29	0.69	1.59	0.02	0.37	0.61
	From conductance data at 25°.				From isohydric data at 25°.			
0.050	1.25	0.06	0.63	0.31	1.17	0.06	0.71	0.23
0.025	1.33	0.05	0.57	0.38	1.25	0.05	0.65	0.30
0.005	1.62	0.02	0.34	0.64	1.65	0.02	0.31	0.67

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[1] *Loc. cit.*, p. 273.

8. Relative Concentrations of Un-ionized Sulphuric Acid Derived from Distribution Experiments.

Experiments by M. A. STEWART.

In the hope of furnishing further evidence as to the proportion of un-ionized H_2SO_4 in the sulphuric acid solutions, an attempt was made to find an organic solvent between which and water the acid would distribute itself to an appreciable extent. In this way at least the relative concentrations of H_2SO_4 in different solutions might be determined. Though the experiments made in this direction do not lead to very definite conclusions, yet they seem worthy of record.

Amyl alcohol was the only solvent that was found to take up from water a considerable quantity of sulphuric acid, and the commercial product did this in much less degree after it had been thoroughly washed with cold dilute sulphuric acid (one volume of the concentrated acid and two of water), with alkali, and with water, and distilled. It was, however, the so-purified alcohol that was used for the following experiments.

The methods of measurement and of computation were as follows: The sulphuric acid solutions and amyl alcohol were shaken from four to six hours at 25°, in bottles which had previously been well steamed out in an inverted position and then quickly dried by a current of air. After settling clear, a certain volume of the alcohol phase was removed and shaken in a dry bottle with a certain volume of water which had been saturated with amyl alcohol at 25°. This second water phase was then separated and its specific conductance measured. The specific conductances of the first water phase (*i. e.*, the sulphuric acid solutions after they were shaken with the amyl alcohol) were also measured. The concentration of sulphuric acid in the first water phase and also its concentration in the amyl alcohol phase (derived from its concentration in the water with which that phase was shaken) were obtained from a plot of the cube root of the specific conductance against the ratio of the specific conductance to the concentration (L/C).

This method of determining the concentration of the sulphuric acid in the amyl alcohol was used because the concentrations were so small that by ordinary chemical methods of determination large errors would be likely to be introduced. The concentration of sulphuric acid in the first water phase had to be determined after the shaking because some of the water went into the amyl alcohol and some amyl alcohol went into it, thereby changing its concentration. The specific conductance of ordinary solutions of the acid in water could not be used in this case, for it was found that the amyl alcohol which went into the water phase decreased its specific conductance. Three experiments, made to determine the magnitude of the necessary correction, showed that the decrease of specific conductance due to saturation with amyl alcohol was

5 per cent. at 0.1897 formal, 7.2 per cent. at 0.0471 formal, and 7.6 per cent. at 0.0059 formal.

The specific conductance of a 0.0016 normal solution of sulphuric acid in amyl alcohol (obtained by shaking amyl alcohol with 0.094 normal aqueous sulphuric acid) was found to be less than 9×10^{-6}, which showed that the ionization of the sulphuric acid in the amyl alcohol was negligible.

The following tables contain the results. Under C_W is given the formal concentration of the sulphuric acid present after shaking in the aqueous phase, and under C_A/C_W the ratio to this concentration of that (C_A) in the amyl alcohol phase. An *s* attached to the experiment number shows the equilibrium was approached from the side of supersaturation, namely, by first shaking the amyl alcohol with a stronger sulphuric acid solution than that with which it was finally brought into equilibrium. All the experiments were made at 25°.

TABLE XI.—DATA RELATING TO THE DISTRIBUTION BETWEEN WATER AND AMYL ALCOHOL.

Expt. No.	C_W.	$10^3 C_A/C_W$.
1	0.1752	8.996
2	0.1749	8.825
3*s*	0.1844	9.183
4*s*	0.1849	9.207
5	0.08340	7.142
6	0.08131	7.183
7*s*	0.09034	7.271
8*s*	0.09154	7.384
9	0.04484	6.093
10	0.04447	6.138
11*s*	0.04695	6.140
12*s*	0.04695	6.257
13	0.02216	5.347
14	0.02234	5.294
15*s*	0.02160	5.355
16*s*	0.02162	5.232

TABLE XII.—MEAN VALUES OF THE DISTRIBUTION RATIO.

C_W.	C_A/C_W.
0.0220	0.00531
0.0460	0.00617
0.0870	0.00725
0.1800	0.00906

It will be seen that the concentration (C_A) of the acid in the alcohol increases more rapidly than its concentration (C_W) in the water, corresponding to the increase in the proportion of un-ionized acid in the more concentrated aqueous solutions. The fact that the rate of that increase is so small—smaller even than in the case of hydrochloric acid at corresponding concentrations—is apparently significant, for it indicates that the un-ionized H_2SO_4 is formed out of two ions (H^+ and HSO_4^-) in analogy with diionic substances, instead of directly out of three ions (H^+, H^+, and $SO_4^=$), in analogy with triionic substances.[1]

PART II.—SOLUTIONS OF SODIUM HYDROGEN SULPHATE.

9. Transference Measurements.

BY M. A. STEWART.

Transference experiments with sodium hydrogen sulphate should throw much light on the extent to which hydrosulphate ion ionizes into hydrogen ion and sulphate ion. Such experiments were therefore made with an approximately 0.1 formal solution of this salt at 25°.

a. Preparation and Analysis of the Solutions.—A solution of sulphuric acid approximately 1-formal was made up and titrated against ignited sodium carbonate. About 500 cc. of this acid solution were weighed out, and enough sodium carbonate was added to it to neutralize it to within 0.5 per cent. This solution was boiled to expel the carbon dioxide and the neutralization completed with sodium hydroxide, with methyl orange as indicator. (Sodium hydroxide was not used for the entire neutralization for the reason that it is not readily obtained so pure as the carbonate.) To this solution was then added a second portion of the original sulphuric acid solution, of the same weight as the first portion, and the mixture made up to ten liters. A second solution (No. 2) was afterwards prepared in the same way.

The solutions were analyzed: (1) by determining the sodium by evaporating, igniting, and weighing as Na_2SO_4; (2) by determining the sulphate as barium sulphate; and (3) by determining the hydrogen by titrating (by weight) with a standardized, approximately 0.2 formal, sodium hydroxide solution.

The mean results of the analyses of the sodium hydrogen sulphate solutions are as follows, the content being referred to 1000 grams of the solution:

	Mols. SO_4.	Mols. H.	Mols. Na.	Density at 25°/4°.
Solution No. 1..........	0.09889	0.09905	0.09886	1.0063
Solution No. 2..........	0.10090	0.10096	0.10083	1.0065

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[1] The results of a distribution experiment made by shaking a 0.1015 formal solution of sodium hydrogen sulphate with amyl alcohol are also worth recording. It was found in this case that the value of C_A was 0.000299. Correcting the $NaHSO_4$ concentration to just 0.1000 formal, we get for C_A the value 0.000294; and interpolation of the data obtained for the acid itself shows that the sulphuric acid solution which would be in equilibrium with this same amyl-alcohol phase, and which would therefore contain un-ionized sulphuric acid at the same concentration as the 0.1000 formal sodium hydrosulphate is 0.0474 formal.

b. Description of the Apparatus and Method.—The apparatus used in these experiments was of the same form as that used earlier by Noyes.[1] It consisted of two glass U-tubes, each with one arm bent at right angles, joined together by a double band of rubber tubing. The inside diameter of the tubes used at first was about 3.5 cm. and the height about 37 cm. Smaller tubes, 2.5 cm. in diameter, with the other dimensions the same as before, were used later. The positive electrode was a polished platinum disk which would just fit loosely in the tube, and the negative electrode was a platinum spiral. A disk was used as anode, in order to give a large surface, so as to reduce the current density and prevent as far as possible the formation of decomposition products of sulphuric acid. The surface of the liquid at the cathode was kept at about two-thirds of the height of the tube, and the surface at the anode about 5 cm. above the top of the lower bend, with the anode about 1 cm. below the surface. The surface of the liquid in the anode limb was kept at this low position because the liquid around the anode tends to become heavier (due to the migration of sulphuric acid into it), so that to fill up that limb much above the bend would unnecessarily increase the quantity of solution. This position was maintained by connecting the anode arm with a small tube dipping beneath a column of water. All the openings were closed with rubber stoppers, but the liquid in the cathode arm was open to the outside air through a glass tube passing through the stopper. The middle portions of the solutions were removed through the small upright tubes on the middle arms. In order to make the joint between the U-tubes as tight as possible, a coating of vaseline was put over the rubber band and each side wound around with wire. The apparatus was immersed in a thermostat at 25° ± 0.02°, so that the horizontal middle part was covered by at least 3 cm. of water. Two silver coulometers were used, one on each side of the transference apparatus, in order to make sure that there was no leakage of the electric current.

After the electrolysis the solution was divided into an anode, a cathode, and a middle portion (represented by A, C, and M in the tables below), except that in the first experiment the middle portion was divided into three parts (M_A, M, and M_C).

The middle portion was titrated with a solution of sodium hydroxide containing 0.19816 equivalent NaOH per 1000 grams of solution, the content having been determined by titration against a standard sulphuric acid solution. The cathode and anode portions were also titrated with this sodium hydroxide solution; and, in addition, their contents in sulphate and in sodium were determined in the same way as was done with

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[1] THIS JOURNAL, **23**, 42 (1901).

the original solution, the former by precipitating and weighing as barium sulphate and the latter by evaporating, igniting, and weighing as sodium sulphate. The determination of the sulphate was made in the portion of the solution that had already been titrated with sodium hydroxide.

c. Data of the Experiments.—Ten transference experiments were made, but in four of them the change in the middle portion was so large that the experiments were not completed. The results of the other six experiments are given in the following tables.

The headings of the columns are for the most part self-explanatory. The figures in columns II, IV, and V represent grams; those in VI, VII, VIII, and IX, milli-equivalents. In the case of Experiment No. 1, column VIII*a* contains the sum of the changes in the anode (A) and anode middle (M_A) portions or in the cathode (C) and cathode middle (M_C) portions:

TABLE XIII.—DATA OF THE TRANSFERENCE EXPERIMENTS.

Experiment No. 1.

Concentration of $NaHSO_4$: 0.09889 mol per 1000 grams. Time = 3.2 hours. Current = 0.060 ampere. Silver in coulometer: 758.5 mg.

I	II.	III.	IV.	V.	VI.	VII.	VIII.	VIIIa.	IX.
					Content of whole portion.				
Portion.	Weight of whole portion.	Constituent determined.	Weight of portion analyzed.	Weight of NaOH solution, of $BaSO_4$, and of Na_2SO_4.	Before electrolysis.	After electrolysis.	Change.	Total change.	Change per faraday.
A	208.09	H	85.39	49.50	20.542	23.830	+3.288	+3.334	+474.4
		SO_4	85.39	2.0905	41.141	43.578	+2.437	+2.449	+348.4
		Na	117.99	0.7960	20.564	19.750	—0.814	—0.848	—120.7
		Na+H —SO_4	....	....	—0.035	+0.002			
M_A	161.15	H	161.15	80.79	15.914	15.960	+0.046		
		SO_4	161.15	3.7270	31.872	31.884	+0.012		
		Na	....	....	....	....	—0.034[1]		
M	165.89	H	165.89	82.93	16.382	16.383	+0.001		
M_C	181.74	H	181.74	90.76	17.947	17.930	—0.017		
		SO_4	181.74	4.2042	35.944	35.967	+0.023		
		Na	....	....	....	....	—0.040[1]		
C	334.78	H	122.82	55.07	33.066	29.654	—3.412	—3.429	—487.9
		SO_4	122.82	2.7337	66.226	63.753	—2.473	—2.450	—348.6
		Na	164.62	1.1925	33.103	34.117	+1.014	+1.054	+150.0
		Na+H —SO_4	....	....	—0.057	+0.018			

[1] Obtained by difference.

TABLE XIII—(*Continued*).

Experiment No. 2.

Concentration of $NaHSO_4$: 0.09889 mol per 1000 grams. Time = 3 hours. Current = 0.059 ampere. Silver in coulometer: 721.5 mg.

I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.
					Content of whole portion.			
Portion.	Weight of whole portion.	Constituent determined.	Weight of portion analyzed.	Weight of NaOH solution, of $BaSO_4$ and of Na_2SO_4.	Before electrolysis.	After electrolysis.	Change.	Change per faraday.
A	291.74	H	125.49	69.56	28.803	31.94	+3.14	+469.7
		SO_4	125.49	3.0164	57.688	59.99	+2.30	+344.1
		Na	154.54	1.0533	28.840	27.98	—0.86	—128.7
		$Na+H-SO_4$	....	....	—0.045	—0.07		
M	124.38	H	124.38	62.17	12.283	12.282	—0.001	
C	424.68	H	103.92	47.95	41.944	38.71	—3.23	—483.2
		SO_4	103.92	2.3334	84.070	81.58	—2.49	—372.5
		Na	157.85	1.1327	41.990	42.87	+0.88	+131.6
		$Na+H-SO_4$	....	....	0.136	0.00		

Experiment No. 3.

Concentration of $NaHSO_4$: 0.10090 mol per 1000 grams. Time = 4.5 hours. Current = 0.045 ampere. Silver in coulometer: 824.5 mg.

A	326.58	H	116.89	66.04	32.961	36.563	+3.602	471.5
		SO_4	116.89	2.8635	65.850	68.438	+2.588	338.8
		Na	174.82	1.2147	32.925	31.924	—1.001	131.0
		$Na+H-SO_4$	....	....	0.036	0.049		
M	123.57	H	123.57	62.99	12.474	12.482	+0.008	
C	388.33	H	131.93	60.86	39.209	35.499	—3.710	485.7
		SO_4	131.93	3.0040	78.333	75.652	—2.681	351.0
		Na	184.62	1.3583	39.166	40.195	+1.029	134.7
		$Na+H-SO_4$	....	....	0.042	0.042		

Experiment No. 4.

Concentration of $NaHSO_4$: 0.10090 mol per 1000 grams. Time = 4 hours. Current = 0.034 ampere. Silver in coulometer: 568.5 mg.

A	176.28	H	81.86	47.46	17.791	20.253	+2.462	+467.4
		SO_4	81.86	2.0236	35.543	37.276	+1.733	+329.0
		Na	86.49	0.5944	17.771	17.044	—0.727	—138.0
		$Na+H-SO_4$	....	....	0.019	0.021		
M	121.89	H	121.89	62.09	12.305	12.304	0.01	
C	215.12	H	94.46	42.38	21.722	19.125	—2.597	—493.0
		SO_4	94.46	2.1264	43.398	41.434	—1.964	—372.9
		Na	117.28	0.8684	21.699	22.409	+0.710	+134.8
		$Na+H-SO_4$	....	....	0.023	0.100		

TABLE XIII—(*Continued*).

Experiment No. 5.

Concentration of $NaHSO_4$: 0.10090 mol per 1000 grams. Time = 3 hours. Current = 0.050 ampere. Silver in coulometer: 607.4.

I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.
					Content of whole portion.			
Portion.	Weight of whole portion.	Constituent determined.	Weight of portion analyzed.	Weight of NaOH solution, of $BaSO_4$ and of Na_2SO_4.	Before electrolysis.	After electrolysis.	Change.	Change per faraday.
A	182.45	H	75.31	43.84	18.413	21.047	+2.634	468.0
		SO_4	75.31	1.8680	36.785	38.712	+1.927	342.4
		Na	101.32	0.6962	18.393	17.638	—0.755	134.2
		$Na+H-SO_4$	....	....	0.021	0.027		
M	100.35	H	100.35	51.16	10.130	10.138	+0.008	
C	230.77	H	100.11	44.99	23.302	20.551	—2.751	488.8
		SO_4	100.11	2.2580	46.553	44.534	—2.019	358.8
		Na	125.26	0.9269	23.276	24.024	+0.748	132.9
		$Na+H-SO_4$	....	....	0.025	0.041		

Experiment No. 6.

Concentration of $NaHSO_4$: 0.10090 mol per 1000 grams. Time = 2 hours. Current = 0.060 ampere. Silver in coulometer: 534.4 mg.

A	181.84	H	66.20	37.94	18.352	20.651	+2.299	464.3
		SO_4	66.20	1.6283	36.665	38.260	+1.595	322.1
		Na	110.30	0.7631	18.332	17.699	—0.633	127.8
		$Na+H-SO_4$	....	....	+0.019	0.090		
M	118.14	H	118.14	60.15	11.926	11.920	—0.05	
C	215.80	H	89.38	40.40	21.790	19.329	—2.461	497.0
		SO_4	89.38	2.0208	43.532	41.745	—1.787	360.9
		Na	101.06	0.7473	21.766	22.450	+0.684	138.1
		$Na+H-SO_4$	....	....	+0.024	+0.034		

10. Summary of the Transference Results.

The results of the preceding experiments are summarized in the following table. The figures show the increase in the number of milli-equivalents of the three constituents named in the heading in the anode and cathode portions when one faraday of electricity is passed at 25° through a solution containing approximately 0.1 formula weight of sodium hydrogen sulphate per liter. The "weighted mean" is derived from the means of the anode and cathode values by assigning to each a weight inversely proportional to the square of its average deviation ("A. D."). The "final values" are derived from the three weighted means upon the basis of the principle[1] that the increment of the equiva-

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[1] This principle can be shown to be a consequence of the facts that one equivalent of hydrogen is produced at the anode by the electrolysis; that the only ions in

lents of hydrogen must equal the difference of the increments of the equivalents of sulphate and of sodium ($\Delta H = \Delta(\frac{1}{2}SO_4) - \Delta Na$), by distributing the deviation from this principle upon the three separate values in inverse proportion to the square of their average deviations.

TABLE XIV.—SUMMARY OF THE TRANSFERENCE DATA.

Expt. No.	Hydrogen (ΔH).		Sulphate $\Delta(\frac{1}{2}SO_4)$.		Sodium (ΔNa).	
	Anode.	Cathode.	Anode.	Cathode.	Anode.	Cathode.
1	+474.4	—487.9	+348.4	—348.6	—120.7[1]	+150.0[1]
2	469.7	483.2	344.1	372.5	128.7	131.6
3	471.5	485.7	338.8	351.0	131.0	134.7
4	467.4	493.0	329.0	372.9	138.0	134.8
5	468.0	488.8	342.4	358.8	134.2	132.9
6	464.3	497.0	322.1[1]	360.9	127.8	138.1[1]
Mean	469.2	489.3	340.5	360.8	131.9	133.5
a. d.	2.6	2.9	5.3	8.0	3.3	1.3
A. D.	1.1	1.2	2.4	3.3	1.5	0.7
Weighted mean	478.4		347.5		133.2	
Final value	478.8		345.8		133.0	

11. Conductance Measurements.

Before discussing further the transference values, the results of some conductance measurements with sodium hydrogen sulphate will be presented. These measurements were made in a U-shaped conductance vessel with electrodes which were mechanically roughened, but not platinized.

The results are given in the following table, in which the "dilution" signifies the liters of solution in which one formula weight of $NaHSO_4$ was contained.

TABLE XV.—FORMAL CONDUCTANCE OF SODIUM HYDROGEN SULPHATE AT 25°.

Dilution.	Series 1.	Series 2.	Mean.	Barth.
10	261.60	261.73	261.67	...
20	297.00	.....	297.00	...
40	337.78	337.68	337.73	336.8
80	381.42	....	381.42	380.7
160	424.94	424.58	424.76	423.0
320	463.48	463.10	463.30	463.0
640	494.40	494.60	494.50	497.0
1280	516.60	516.89	516.75	519.0
2560	530.74	531.20	530.97	...

the solution are H^+, Na^+, HSO_4^-, and $SO_4^{=}$; that the transference of each constituent is determined by that of these separate ions, as expressed by these equations:

$$\Delta H = 1 + HSO_4^- - H^+,\quad \Delta Na = -Na^+, \text{ and } \Delta SO_4 = HSO_4^- + SO_4^{=};$$

and that the sum of all the equivalents of all the ions transferred must be unity:

$$H^+ + Na^+ + HSO_4^- + 2SO_4^{=} = 1.$$

From these equations there results by combination:

$$\Delta H = 2\,\Delta SO_4 - \Delta Na = \Delta(\tfrac{1}{2}SO_4) - \Delta Na.$$

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[1] Omitted in the calculation, since their deviations are greater than 3 A. D.

Measurements of the conductance of this salt at 25° had previously been made by Barth.[1] His values, reduced from Siemens' units to reciprocal ohms and interpolated graphically (from a plot of Λ against log v) for the dilutions at which our measurements were made, are given in the last column of the table.

12. Concentrations of the Sodium Ion and Hydrogen Ion Derived from the Transference and Conductance Data.

A simple interpretation of the transference results is obtained through the following considerations. Let C_{H}, C_{Na}, $C_{\mathrm{SO_4}}$, and $C_{\mathrm{HSO_4}}$ represent the formal concentrations in the sodium hydrogen sulphate solution of the ions denoted by the subscripts; let Λ_{H}, Λ_{Na}, $\Lambda_{\mathrm{SO_4}}$, and $\Lambda_{\mathrm{HSO_4}}$ represent the equivalent conductances of those ions, and $\mathrm{N_H}$, $\mathrm{N_{Na}}$, and $\mathrm{N_{SO_4}}$ the equivalents of hydrogen, sodium, and sulphate transferred for each faraday of electricity passed; and let L represent the specific conductance of the solution. Then, since the number of equivalents of any ion transferred is equal to the ratio of the actual conductance of that ion to that of the solution, and since hydrogen is transferred in the two forms, H^+ and HSO_4^-, and sulphate in the two forms HSO_4^- and $SO_4^=$, we have the relations

$$\mathrm{N_{Na}} = \frac{C_{\mathrm{Na}}\Lambda_{\mathrm{Na}}}{10^3\,\mathrm{L}} \quad (9); \qquad \mathrm{N_H} = \frac{C_{\mathrm{H}}\Lambda_{\mathrm{H}} - C_{\mathrm{HSO_4}}\Lambda_{\mathrm{HSO_4}}}{10^3\,\mathrm{L}} \quad (10);$$

and

$$\mathrm{N_{SO_4}} = \frac{2C_{\mathrm{SO_4}}\Lambda_{\mathrm{SO_4}} + 2C_{\mathrm{HSO_4}}\Lambda_{\mathrm{HSO_4}}}{10^3\,\mathrm{L}}. \quad (11)$$

In these equations we may substitute $C\Lambda$ for 10^3L, introduce the values $\mathrm{N_{Na}} = 0.133$, $\mathrm{N_H} = 0.521$, $\mathrm{N_{SO_4}} = 0.346$, $\Lambda = 261.7$, $\Lambda_{\mathrm{Na}} = 51$, $\Lambda_{\mathrm{SO_4}} = 79$, $\Lambda_{\mathrm{H}} = 365$ or 348 (see Section 2), and $\Lambda_{\mathrm{HSO_4}} = 39.5$,[2] and solve for the ratios C_{Na}/C, C_{H}/C, etc. We thus obtain from equations (9) and (11),

$$\frac{C_{\mathrm{Na}}}{C} = 0.68, \text{ and } \frac{2C_{\mathrm{SO_4}}}{C} + \frac{C_{\mathrm{HSO_4}}}{C} = 1.15.$$

Since the sums of the equivalent concentrations of all the positive and negative ions must be equal, we have $C_{\mathrm{Na}} + C_{\mathrm{H}} = 2C_{\mathrm{SO_4}} + C_{\mathrm{HSO_4}}$, and therefore also

$$\frac{C_{\mathrm{Na}}}{C} + \frac{C_{\mathrm{H}}}{C} = 1.15, \text{ and } \frac{C_{\mathrm{H}}}{C} = 0.47.$$

A value of C_{H}/C lying between certain not very wide limits can be ob-

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[1] *Z. physik. Chem.*, 9, 182 (1892).

[2] In Section 3 $\Lambda_{\mathrm{HSO_4}}$ was found to be about 40 when Λ_{H} was taken as 365, and about 35 when Λ_{H} was taken as 348. We have assumed in these calculations $\Lambda_{\mathrm{HSO_4}} = \frac{1}{2}\Lambda_{\mathrm{SO_4}} = 39.5$, since equation (11) can then be solved directly for $2C_{\mathrm{SO_4}} + C_{\mathrm{HSO_4}}$. The error arising from this uncertainty is almost surely less than that arising from the errors in the transference data.

tained from equation (10) also, since the second term in its last member is a much smaller quantity than the first term which contains C_H/C. Placing C_{HSO_4}/C equal to zero as one limit and equal to 0.5 as the other (which last is the largest value, consistent with that of C_H/C, which it can have), one obtains

$$\frac{C_H}{C} = \begin{Bmatrix} 0.37 \text{ for } \Lambda_H = 365 \text{ and } C_{HSO_4}/C = 0.0 \\ 0.43 \text{ for } \Lambda_H = 365 \text{ and } C_{HSO_4}/C = 0.5 \end{Bmatrix}$$

or
$$\frac{C_H}{C} = \begin{Bmatrix} 0.39 \text{ for } \Lambda_H = 348 \text{ and } C_{HSO_4}/C = 0.0 \\ 0.45 \text{ for } \Lambda_H = 348 \text{ and } C_{HSO_4}/C = 0.5 \end{Bmatrix}.$$

Taking the mean (0.41) of these four values and combining it with the value (0.47) obtained from equation (11), we get as the final value

$$C_H/C = 0.44.$$

Although C_{HSO_4}/C can be definitely calculated by equation (10), by substituting in it the value of C_H/C derived from equation (11), yet the result (0.85 for $\Lambda_H = 365$ or 0.65 for $\Lambda_H = 348$) has no significance, since it is seriously affected by the accumulated error resulting from the two successive subtractions of terms much larger than that containing C_{HSO_4}/C.

It is therefore only the values of C_H/C and C_{Na}/C that can be derived with a fair degree of accuracy from the transference and conductance data, unless some additional assumption be made. It is of some interest to compare the values of these quantities obtained above with the results of Noyes and Eastman[1] for 0.1 formal potassium hydrogen sulphate at 18°, which were derived from conductance data alone with the help of estimates as to the concentrations of the un-ionized substances (K_2SO_4, H_2SO_4, and $KHSO_4$) in the solution, based upon analogies with other substances of these same types. Their values are $C_H/C = 0.51$ and $C_{Na}/C = 0.63$, while ours are $C_H/C = 0.44$ and $C_{Na}/C = 0.68$.

13. The Hydrogen-Ion Concentration Derived from Catalysis Experiments.

A value of the hydrogen-ion concentration may also be derived from the catalysis experiments made at 35° by Kay.[2] He found that the specific reaction rate of the hydrolysis of ethyl acetate under the influence of 0.1 formal sodium hydrogen sulphate is 32.4. This becomes 31.0 when corrected in accordance with his experiments for the influence of the neutral-salt ions (the Na^+ and $SO_4^=$) upon the rate. Dividing this value by the specific reaction rate per equivalent of hydrochloric acid (708) at the corresponding concentration, as determined by him, we get 0.0448 as the concentration of the hydrochloric acid solution which has the same catalytic effect as the 0.1 formal sodium hydrogen sulphate.[3]

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[1] *Carnegie Institution Publications*, **63**, 276 (1907).

[2] *Proc. Royal Soc. Edinburgh*, **22**, 491 (1898).

[3] Kay found the effect of $LiHSO_4$ to be nearly identical with that of $NaHSO_4$, and that of $KHSO_4$ to be about 2 per cent. smaller.

Taking the ionization of the acid as 95 per cent., we find *0.416* to be the value of C_H/C in the sulphate solution at 35°. The value derived from the transference and conductance measurements was 0.44 at 25°. The agreement is seen to be fairly close, especially in view of the fact that C_H/C decreases rapidly with rising temperature.

Noyes and Eastman have already pointed out that their value of C_H/C at 100° (0.31 at 0.01 formal) agrees well with that (0.315) derived by Trevor[1] from sugar inversion experiments at 100°.

14. Concentrations of the Other Constituents.

Although unfortunately, on account of lack of accuracy, it was not possible to calculate the relative concentrations of sulphate ion and hydrosulphate ion from the transference and conductance data alone, yet we are in a better position to estimate these concentrations than were Noyes and Eastman, for there is now available not only a more directly determined value of C_H/C, but also, in addition, a fairly reliable value of C_{Na}/C. From the latter (0.68) one can at once conclude that the sum of the concentrations of the un-ionized salts ($2C_{Na_2SO_4} + C_{NaHSO_4}$) is 0.32, and no considerable error can result if we distribute this value between the two salts in the proportion $C_{Na_2SO_4} : 2C_{SO_4} = C_{NaHSO_4} : C_{HSO_4}$, in accordance with the principle that in a mixture with a common ion the un-ionized fraction of a unibivalent salt is approximately twice as large as that of a uni-univalent salt. (In making this distribution any probable value may be assigned provisionally to C_{SO_4}/C and C_{HSO_4}/C, such as 0.44 and 0.22, and the operation can then be repeated with the more accurate values of the latter quantities subsequently obtained.) If further we make the assumption, substantiated by Noyes and Eastman (see Section 7), that sulphuric acid with respect to its first hydrogen and hydrochloric acid are equally ionized under corresponding conditions, we can estimate the un-ionized H_2SO_4 present in the solution and finally obtain by subtraction the concentrations of the HSO_4^- and $SO_4^=$ ions. The results of such a calculation are given in the following table:

TABLE XVI.—CONCENTRATIONS OF THE CONSTITUENTS IN 0.1 FORMAL SODIUM HYDROGEN SULPHATE SOLUTION AT 25°.

C_{Na}/C	0.68	C_{NaHSO_4}/C	0.08
C_H/C	0.44	$C_{Na_2SO_4}/C$	0.12
C_{HSO_4}/C	0.44	$C_{H_2SO_4}/C$	0.02
C_{SO_4}/C	0.34		

It is of interest to calculate from these data and also from the corresponding data given in Table X for sulphuric acid the values of the product $C_H C_{SO_4}/C_{HSO_4}$, which, if the mass-action law held, would be the ionization constant for the second hydrogen of sulphuric acid. The values of this product at 25° are found to be 0.034, 0.031, and 0.022,

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[1] *Z. physik. Chem.*, **10**, 342 (1892).

using the data for 0.1 formal $NaHSO_4$, 0.05 formal H_2SO_4, and 0.025 formal H_2SO_4, respectively.[1] The "ionization constant" at these concentrations (0.025 — 0.1 formal) may therefore be taken in round numbers at 3×10^{-2}. The rough agreement of the values derived from the independent and widely different data for sulphuric acid and its acid salt is welcome evidence of the approximate correctness of the computed concentrations of the sulphate ion and hydrosulphate ion in the solutions, the computation of which was based in both cases, it must be remembered, upon the only indirectly substantiated principle that the hydrogen of hydrochloric acid and the first hydrogen of sulphuric acid are equally ionized under corresponding conditions.

SUMMARY.

It has been shown in Section 1 of this article that in the case of a dibasic acid like sulphuric acid the hydrogen-ion concentration (C_H) can be derived from the freezing-point lowering, or from any other property which gives the value of the mol number i, by the relation $C_H/C = i - 1$, where C represents the formal concentration of the acid (that is, the number of formula weights of H_2SO_4 per liter of solution). The values of C_H/C at 0° so derived from the existing freezing-point data have been presented.

Noyes and Eastman have previously shown that there can be derived from conductance data alone not very widely divergent maximum and minimum values of the hydrogen-ion concentration in sulphuric acid, corresponding to the two limiting cases where the only negative ion present is $SO_4^=$ and where it is HSO_4^-. In their calculations it was, however, necessary to assume a value for Λ_{HSO_4}, the equivalent conductance of hydrosulphate ion, the assumption made being that its conductance is equal to that of acetate ion, which has a similar molecular complexity. It has been shown that any such assumption can be dispensed with, if with the conductance data there be combined the transference data for the acid. In this way, using the existing transference data and the conductance data at 25° and 0° determined in this laboratory and presented in Section 2, limiting values of C_H/C at these temperatures have been calculated.

Incidentally, there have been derived through a consideration of the existing conductance data at 0° the best values to adopt for the equivalent conductance at 0° of certain ions. These values are $\Lambda_K = 40.3$, $\Lambda_{Cl} = 41.1$, $\Lambda_{SO_4} = 42.8$, and $\Lambda_H = 224$. The last value is much lower than that (240) estimated by Johnston.[2]

It has been shown in Section 3 that the transference and conductance data enable the value of Λ_{HSO_4} at 25° and 0° to be approximately calculated, provided it be true that the hydrosulphate-ion is present in the

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[1] The values at 0° are 0.061 for 0.05 formal H_2SO_4 and 0.042 for 0.025 formal H_2SO_4.

[2] THIS JOURNAL, 31, 1015 (1909).

sulphuric acid solution in considerable quantity, so that its conductance may enter as a factor. The values obtained (35 to 40 at 25°) are not far from one-half of that of Λ_{SO_4} (79 at 25°).

From a consideration of the relative catalytic effects of sulphuric and hydrochloric acids on the hydrolysis of cane sugar at 25°, as determined by Ostwald, and on that of ethyl acetate at 35° as determined by Kay, values of the hydrogen-ion concentration (C_H/C) have also been calculated (see Section 4).

A new isohydric method of determining the hydrogen-ion concentration has been described in Section 5. It consists in determining by experiment the relative concentrations of hydrochloric acid and of sulphuric acid which drive back the ionization of picric acid to the same extent, the condition of equal ionization of the picric acid being ascertained by shaking the aqueous solution with benzene, into which the un-ionized picric acid distributes itself.

The values of C_H/C at various concentrations at 0° and 25°, obtained by these various methods, will be found in Table IX on page 1146.

To derive the concentrations of the other constituents from these values of the hydrogen-ion concentration, the latter must be combined with some further knowledge or data relating to those constituents. Noyes and Eastman, through a study of the conductance of sulphuric acid and potassium hydrogen sulphate through a wide range of temperature, have made it highly probable that under corresponding conditions the first hydrogen of sulphuric acid is equally dissociated with that of hydrochloric acid. Upon the basis of this principle the concentration of the un-ionized H_2SO_4 was estimated by Noyes and Eastman, and, from this concentration and that of the hydrogen ion the concentrations of the other two constituents, the sulphate ion and hydrosulphate ion, were obtained by them by subtraction. We have made similar calculations, using the values of the hydrogen-ion concentration derived in this paper. The results, which will be found in Table X on page 1148, show that sulphate ion and hydrosulphate ion are both present in large proportions at medium concentrations, that the latter is present in much larger quantity at 0.05 formal and the former at 0.005 formal, and that at 0.05 formal the ratio C_{HSO_4}/C_{SO_4} increases greatly between 0° and 25°. It will also be seen that the hydrogen-ion concentration decreases markedly within the same temperature interval.

Experiments have been described in Section 8 upon the distribution of sulphuric acid between water and amyl alcohol. The ratio C_A/C_W of the concentration of the acid in the alcohol to that in the water was found to increase from 0.0053 for $C_W = 0.022$ to 0.0091 for $C_W = 0.180$, corresponding to an increase in the proportion of un-ionized sulphuric acid in the aqueous solution. The rate of this increase is somewhat smaller even than in the case of hydrochloric acid, indicating that the unionized H_2SO_4 is formed out of two ions (H^+ and HSO_4^-), in analogy with di-ionic substances, instead of directly out of three ions (H^+, H^+, and $SO_4^=$) in analogy with tri-ionic salts.

Determinations were also made of the transference of sodium, of hydrogen, and of sulphate occurring during the electrolysis of a 0.1 formal solution of sodium hydrogen sulphate at 25°. The results are summarized in Table XIV, on page 1156. Measurements were also made upon the conductance of this salt at various concentrations at 25°. By combining the transference and conductance data the concentrations of the sodium ion and hydrogen ion in the 0.1 formal solution were calculated (in Section 12). The values so obtained are $C_{Na}/C = 0.68$, and $C_H/C = 0.44$.

It has also been shown (in Section 13) that the experiments of Kay on the catalysis of ethyl acetate by 0.1 formal sodium hydrogen sulphate at 35° furnish an independent means of determining the hydrogen-ion concentration, and that the value of C_H/C derived therefrom is 0.416, which agrees well with that (0.44) derived from the transference experiments.

From the values of C_H/C and C_H/C_{Na} derived from the transference and conductance data the concentrations of the other constituents in the 0.1 formal $NaHSO_4$ were computed (in Section 14) with the help of the principle above referred to in regard to the ionization of the first hydrogen of sulphuric acid. In this way C_{HSO_4}/C was found to be 0.44 and C_{SO_4}/C to be 0.34 (see Table XVI).

From these data and also from the corresponding ones for 0.05 formal H_2SO_4 the values of the product $C_HC_{SO_4}/C_{HSO_4}$, the ionization constant of the second hydrogen of sulphuric acid, were calculated to be 0.034 and 0.031, respectively, or in round numbers 3×10^{-2} at concentrations 0.025 to 0.1 formal.

BOSTON, July, 1910.

ON SURFACE ENERGY AND SURFACE TENSION.

BY J. E. MILLS AND DUNCAN MACRAE.

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In an article by Whittaker[1] "On the Theory of Capillarity," it was shown that the following empirical relation was apparently true: "*The surface energy of a liquid in contact with its own vapor at any temperature is proportional to the product of the internal latent heat and the (absolute) temperature.*"

The proposed relation and further related applications and inferences have since been discussed by Kleeman in a number of papers.[2]

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[1] *Proc. Roy. Soc.*, 81, 21 (1908).

[2] *Phil. Mag.*, 18, 39, 491, 901 (1909); 19, 783 (1910)