2. The heat of wetting of silica gel by water has been found to be positive between 0° and 4°.

3. The observed heats of wetting have been satisfactorily accounted for on the basis of surface energy changes.

BALTIMORE, MARYLAND.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN.]

THE TRANSFERENCE NUMBERS OF SULFURIC ACID BY THE CONCENTRATION CELL METHOD.

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The concentration cell method for the determination of transference numbers was shown, in this laboratory[1] to be more accurate in the case of uni-univalent electrolytes than the Hittorf method. In the present investigation it is found to apply equally well in the case of the uni-bivalent electrolyte H_2SO_4.

The determination involves the measurement of the potentials of a concentration cell without diffusion; a concentration cell with diffusion and reversible with respect to the cation; and a concentration cell with diffusion and reversible with respect to the anion.

The total potential of the concentration cell, reversible with respect to the cation, $Pt_H \mid H_2SO_4\ c_1 \mid H_2SO_4\ c_2 \mid Pt_H$, consists of the algebraic sum of the two electrode potentials and the potential at the boundary of the solutions. On the assumption that sulfuric acid dissociates into two hydrogen ions and one sulfate ion, the algebraic sum of the electrode potentials is expressed by the well-known formula

$$E_1 = \frac{RT}{F} ln \frac{c_1}{c_2}. \tag{1}$$

The potential at the liquid boundary is expressed by the formula

$$E_B = \frac{2U_c - U_a}{2(U_c + U_a)} \frac{RT}{F} \cdot ln \frac{c_1}{c_2}. \tag{2}$$

The hydrogen electrode in the concentrated solution is positive with respect to the hydrogen electrode in the dilute solution. At the boundary of the solutions, the sulfuric acid diffuses from the concentrated to the dilute side, and since the hydrogen ion moves faster than the sulfate ion, the dilute side is positively charged with respect to the concentrated. This means that the potential developed at the boundary opposes the potential of the hydrogen electrodes. The total potential of the hydrogen concentration cell is, therefore, expressed by the equation

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[1] A. L. Ferguson, *J. Phys. Chem.*, **20**, 326 (1916).

$$E_1 - E_B = E_3 = \frac{RT}{F} ln \frac{c_1}{c_2} - \frac{2U_c - U_a}{2(U_c + U_a)} \frac{RT}{F} ln \frac{c_1}{c_2}$$

$$= \left[1 - \frac{2U_c - U_a}{2(U_c + U_a)}\right] \frac{RT}{F} ln \frac{c_1}{c_2} = \frac{3}{2} \frac{U_a}{U_a + U_c} \frac{RT}{F} ln \frac{c_1}{c_2}.$$

By the substitution of the transference number of N_a, of the anion for $U_a/(U_a + U_c)$ the equation

$$E_H = \frac{3}{2} N_a \frac{RT}{F} ln \frac{c_1}{c_2} \quad (3)$$

is obtained.

The total potential of the concentration cell, reversible with respect to the anion, Hg | Hg_2SO_4, H_2SO_4 c_1 | H_2SO_4 c_2, Hg_2SO_4 | Hg, consists of the algebraic sum of the two electrode potentials and the potential at the boundary of the solutions. The algebraic sum of the electrode potentials is expressed by the formula

$$E_4 = \frac{RT}{2F} ln \frac{c_1}{c_2}. \quad (4)$$

The boundary potential is the same as in the hydrogen concentration cell, and is in the same direction. The algebraic sum of the sulfate electrode potentials is also in this direction. Therefore the total potential of the sulfate concentration cell is expressed by the equation

$$E_4 + E_B = E_{SO_4} = \frac{RT}{2F} ln \frac{c_1}{c_2} + \frac{2U_c - U_a}{2(U_c + U_a)} \frac{RT}{F} ln \frac{c_1}{c_2}$$

$$= \left[\frac{1}{2} + \frac{2U_c - U_a}{2(U_c + U_a)}\right] \frac{RT}{F} ln \frac{c_1}{c_2} = \frac{3}{2} \frac{U_c}{U_c + U_a} \frac{RT}{F} ln \frac{c_1}{c_2}.$$

By the substitution of the transference number, N_c, of the cation for the expression $U_c/(U_a + U_c)$ the equation becomes·

$$E_{SO_4} = \frac{3}{2} N_c \frac{RT}{F} ln \frac{c_1}{c_2}. \quad (5)$$

The potential of the concentration cell without diffusion, Pt_H | 0.1 M H_2SO_4, Hg_2SO_4, | Hg | Hg_2SO_4, 0.01 M H_2SO_4|Pt_H, is represented by the equation

$$E = \frac{3}{2} \frac{RT}{F} ln \frac{c_1}{c_2}. \quad (6)$$

The value E may be obtained experimentally from the difference between the potentials of the cells Pt_H | 0.1 M H_2SO_4, Hg_2SO_4 | Hg, and Pt_H | 0.01 M, H_2SO_4, Hg_2SO_4 | Hg.

Equation 5 divided by Equation 6 gives $E_{SO_4}/E = N_c$, which expresses the transference number of the cation in terms of E_{SO_4} and E. In a similar way the expression $E_H/E = N_a$, is obtained, as $N_a + N_c = 1$, therefore $E_{SO_4}/E + E_H/E = 1$; and

$$E_{SO_4} + E_H = E. \quad (7)$$

It is evident from Equation 7 that the same value should be obtained by the sum of the potentials E_{SO_4} and E_H as by the difference of the potentials $E_{0.01}$ and $E_{0.1}$.

Since, to obtain the total potential, E_{SO_4}, the boundary potential is added to the electrode potentials, while for the total potential, E_H, it is subtracted, then, by a combination of these as shown below, a formula is obtained which expresses the boundary potential in terms of E_{SO_4} and E_H.

$$E_H = \frac{RT}{F} ln \frac{c_1}{c_2} - \frac{(2-3N_a)}{2}\frac{RT}{F} ln \frac{c_1}{c_2};\ E_{SO_4} = \frac{RT}{2F} ln \frac{c_1}{c_2} + \frac{(2-3N_a)}{2}\frac{RT}{F} ln \frac{c_1}{c_2};$$

$$2E_{SO_4} = \frac{RT}{F} ln \frac{c_1}{c_2} + \frac{2(2-3N_a)}{2}\frac{RT}{F} ln \frac{c_1}{c_2}$$

$$\frac{2\,E_{SO_4}-E_H}{3} = \frac{(2-3N_a)}{2}\frac{RT}{F} ln \frac{c_1}{c_2}. \qquad (8)$$

Therefore the value for the boundary potential may be obtained by the substitution of the measured potentials E_{SO_4} and E_H in the above equation.

Apparatus and Materials.

The potential measurements were made with an Otto Wolff 15,000-ohm potentiometer, using a certified Weston cell as a standard. The solutions were prepared from a commercial c. p. sulfuric acid of 1.84 sp. gr. and were standardized by means of sodium carbonate prepared by the fusion of c. p. sodium hydrogen carbonate in an atmosphere of carbon dioxide. The mercurous sulfate was electrolytically prepared by the Hulett[2] method. The hydrogen was obtained by the electrolysis of 5 *N* sodium hydroxide solution using a generator similar to that of Bodenstein and Pohl,[3] and the hydrogen electrodes were of the ordinary foil type. The mercury used was twice distilled. All measurements were made with the cells contained in an electrically heated and regulated oil thermostat maintained at a constant temperature of 25°.

The concentration cell method, as previously shown, requires the consecutive measurement of 4 distinct potentials which must be extremely constant and reproducible. Much experimental work was required before the satisfactory system of cells shown in Fig. 1 was developed. In this arrangement the connections, between the separate cells, are made by means of siphons (M, N, H and G). A method whereby they could be filled with the proper solutions before being connected with the arms of the containers was considered essential. In this way new boundaries could be introduced without disturbing the electrodes. Connections were made with the cells through the reservoirs (R_a, R_b, R_c, R_d, Fig. 1) on the arms of the containers.

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[2] Hulett, *Phys. Rev.*, **32,** 257 (1911).

[3] Bodenstein and Pohl, *Z. Elektrochem.*, **11,** 373 (1905).

Arrangement of Cells and Method of Procedure.

In Fig. 1, A and B are the mercurous sulfate electrodes; C and D are the hydrogen electrodes. A and C contain 0.1 *M* and B and D 0.01 *M* sulfuric acid. The electrodes A and C are connected by the siphon H, B and D by the siphon G. The two sulfate electrodes are connected by the siphon M; the two hydrogen electrodes by the siphon N.

The containers were fastened in their proper position and filled with the electrode materials. The siphons H and G were put in place and filled by suction. The stopcocks J and O, P and K were then closed. The hydrogen was admitted to C and D through the inlets S and S′ and bubbled through the solutions. It escaped through the outlets W and W′ into chambers (not shown) of about 10 cc. capacity. When the hydrogen electrodes became constant, the stopcock O was opened long enough to measure the potential $E_{0.1}$ between the sulfate and hydrogen electrodes in 0.1 *M* sulfuric acid solution. In a similar way the measurement $E_{0.01}$ was made for the sulfate and hydrogen electrodes in 0.01 *M* sulfuric acid. By the proper manipulation of the stopcocks, the solutions in those halves of siphons H and G connected to the sulfate electrodes were emptied. The arms of the siphons M and N with the rubber stoppers attached were immersed in 2 beakers which contained 0.1 *M* and 0.01 *M* sulfuric acid. The solutions were drawn into the arms of the siphons and formed the boundary within the stopcocks t and q. These siphons were then placed

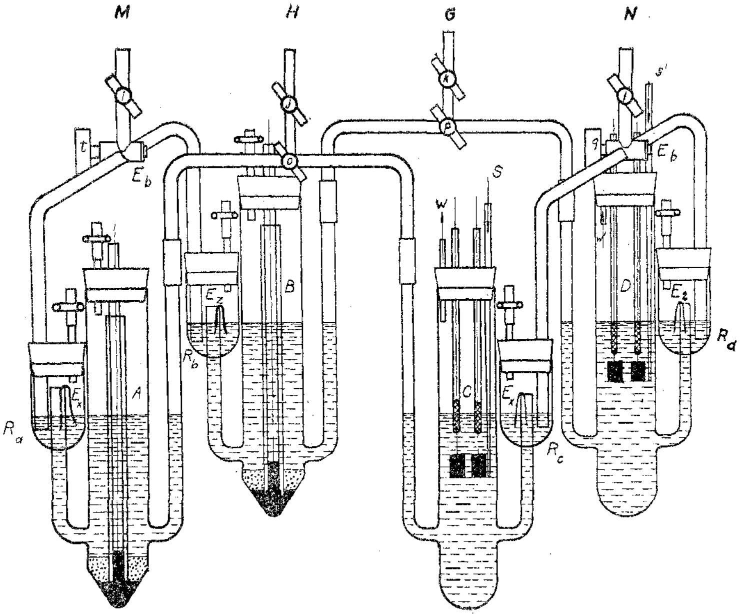

Fig. 1.—Arrangement of cells as used.

in their proper positions connecting the cells.[4] The stopcock q was opened and the potential E_H of the hydrogen concentration cell measured. In a similar way the potential of the sulfate concentration cell (E_{SO_4}) was measured.

The leads from the electrodes were permanently connected to a switchboard so the potentials between any two electrodes could be measured by the manipulation of a switch connected to the potentiometer.

In the first part of the work the measurements showed considerable fluctuation, which was traced to the leakage of current from the high potential electrical circuits in connection with the thermostat. The difficulty was overcome by the replacement of the water by kerosene.

During the development of this work some information was obtained which may be of assistance to others concerned with similar investigations. It was found that the length of time required for the mercurous sulfate electrodes to reach a condition of equilibrium could be greatly reduced by vigorously shaking the sulfuric acid and mercurous sulfate in a mechanical shaker before using in the cells. The first cells constructed contained the hydrogen electrodes in the same chamber as the mercurous sulfate electrode and the potentials were found to vary greatly. This was believed to be due to the catalytic effect of the platinum black which was loosened by the action of the hydrogen on the electrode and fell on to the mercurous sulfate. The difficulty was eliminated by the use of separate chambers for the electrodes.

The final measurements were made and are given in four tables of which I and II are examples.

In the following tables Col. E_H contains the potentials of the hydrogen concentration cell with diffusion, $Pt_H \mid 0.1\ M\ H_2SO_4 \mid 0.01\ M\ H_2SO_4 \mid Pt_H$;

TABLE I.

No.	Date.	Time.	Bar. Mm.	E_H.	E_{SO_4}.	$E_{0.1}$.	$E_{0.01}$.	E by $E_H + E_{SO_4}$.	E by $E_{0.01} - E_{0.1}$.
1	10/13	3:00 P.M.	741.6	....	....	0.74202	0.80260	....	....
2	10/13	4:00	741.6	....	....	0.74200	0.80260	....	....
3	10/13	7:30	740.4	0.01137	0.04933	0.74205	0.80275	0.06070	0.06070
4	10/13	9:00	740.0	0.01139	0.04930	0.74210	0.80274	0.06069	0.06064
5	10/13	10:30	740.0	0.01139	0.04929	0.74212	0.80276	0.06068	0.06064
6	10/13	11:30	739.5	0.01141	0.04928	0.74212	0.80279	0.06069	0.06067
7	10/14	10:00 A.M.	736.0	0.01136	0.04900	0.74203	0.80249	0.06036	0.06036
8	10/14	1:30 P.M.	734.5	0.01133	0.04913	0.74201	0.80246	0.06046	0.06035
9	10/14	3:30	734.5	0.01130	0.04918	0.74203	0.80245	0.06048	0.06042
		Av.		0.01136	0.04922	0.74207	0.80263	0.06058	0.06056

The cell was set up at 9:00 A.M. on October 13, 1919.

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[4] In the measurement for the transference numbers of H_2SO_4 the reservoirs (R_a, R_b, R_c, R_d,) were filled above the openings of the side arms. In the later work when gelatin was used they were filled as shown in the diagram.

TABLE II.

1	10/15	10:00 A.M.	739.3	....	....	0.74166	0.80192	....	....
2	10/15	1:30 P.M.	.....	....	....	0.74209	0.80263	....	....
3	10/15	5:45	.....	....	....	0.74200	0.80268	....	....
4	10/15	7:15	.....	....	....	0.74205	0.80269	....	....
5	10/15	10:00	737.3	0.01136	0.04922	0.74195	0.80256	0.06058	0.06061
6	10/15	12:00	737.0	0.01127	0.04921	0.74212	0.80257	0.06048	0.06045
7	10/16	9:00 A.M.	736.3	0.01120	0.04927	0.74209	0.80253	0.06047	0.06044
8	10/16	10:30	736.5	0.01121	0.04923	0.74210	0.80247	0.06044	0.06037
			Av.	0.01126	0.04923	0.74206	0.80253	0.06049	0.06047

The cell was set up at 11 P.M. on October 14, 1919.

Col. E_{SO_4} those of the sulfate concentration cell with diffusion, Hg | Hg_2SO_4 0.01 M H_2SO_4 | 0.1 M H_2SO_4, Hg_2SO_4 | Hg; Col. $E_{0\cdot 1}$ the potentials of the cell, Pt_H | 0.1 M H_2SO_4, Hg_2SO_4 | Hg; and Col. $E_{0\cdot 01}$ the potentials of the cell, Pt_H | 0.01 M H_2SO_4, Hg_2SO_4 | Hg. The column headed "E by $E_H + E_{SO_4}$" contains the sums of the values recorded in Cols. E_H and E_{SO_4}. The column "E by $E_{0\cdot 01} - E_{0\cdot 1}$" contains the differences between the values recorded in $E_{0\cdot 01}$ and $E_{0\cdot 1}$.

The 0.1 M and 0.01 M cells were prepared and placed in the thermostat where they remained for about 12 hours to come to equilibrium before the boundaries were introduced. This accounts for the blank spaces in the tables.

As pointed out in the theoretical discussion the values recorded in column $E_H + E_{SO_4}$ should be equal to those recorded in column $E_{0\cdot 01} - E_{0\cdot 1}$. The close agreement of these values indicates the accuracy of the potential measurements. The differences between the successive values in each column indicates the degree of constancy of the cells. The differences in columns $E_{0\cdot 01}$ and $E_{0\cdot 1}$ may be attributed, in part, to changes in barometric pressure, for which corrections have not been applied, as such corrections are unnecessary for the calculations in which the measurements are used.

The remarkable agreement between the averages in the different tables indicates the reproducibility of the work.

In the theoretical treatment formulas were given by means of which the values of E, E_H, E_{SO_4} and E_B can be calculated. Table III contains a summary of such calculated values together with the measured values.

TABLE III.—COMPARISON BETWEEN CALCULATED AND MEASURED POTENTIALS.

		E'.	E''.	E.	E_H.	E_{SO_4}.	E_B.
Calc. from	Cond.	0.10511	0.06693	0.07883	0.014716	0.06407	0.03781
	Fz. Pt.	0.08072	....	0.06054	0.011301	0.04918	0.02908
Measured		....	....	0.06054	0.011310	0.04925	0.02906

These calculations involve the ratio $\alpha_1 C_1/\alpha_2 C_2$. It has been customary to use conductivity values in its calculation. Since the work of Jones is probably the most reliable on the conductivity of sulfuric acid, his results were used in these calculations. This ratio may also be obtained from freezing-point data. The values obtained from these two sources are decidedly at variance. No freezing-point data are available for the degree of dissociation of 0.1 M sulfuric acid. However, a complete table is given by Lewis and Linhart[5] for concentrations between 10^{-2} and 10^{-6} molar. The degree of dissociation given by Lewis and Linhart for 0.01 M sulfuric acid was substituted in the equation for E together with the measured potential (0.06054), and the equation solved for the degree of dissociation for 0.1 M sulfuric acid. In the curve of Fig. 2 the abscissas are the molar concentrations and the ordinates the degrees of dissociation. The portion indicated by the solid line was obtained from the freezing-point data and the broken portion is an extension to include the value calculated from the potential measurements. Since this is a smooth curve, the indication is that the point obtained from the potential measurements is approximately the same as would have been obtained from the freezing-point determination. In every instance the results obtained when the freezing-point values are used in the ratio α_1C_1/α_2C_2 show better agreement with the measured potentials than when the conductivity values are used. The latter results are in all cases higher than the measured. It should be noticed, however, that the exact agreement between the measured and calculated values for E is to be expected, since it was from this measured value of E that C_2 was calculated. The close agreement between the measured and calculated values of E_{H}, $E_{\mathrm{SO_4}}$ and E_{B} is a true indication of the correctness of the value 0.2973 for the degree of dissociation of 0.1 M sulfuric acid.

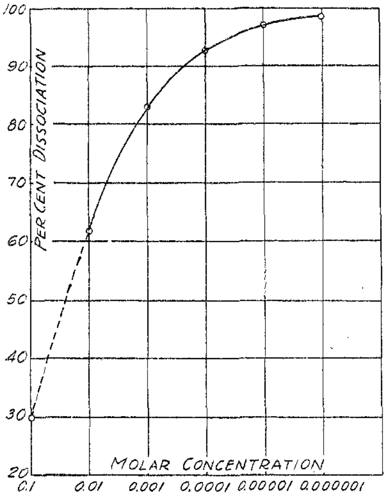

Fig. 2.—Dissociation-concentration curve.

It is important to note that all of the values thus far calculated are based on the assumption that sulfuric acid dissociates entirely into two hydrogen ions and one sulfate ion. Column E' shows the values for E calculated on the assumption that the sulfuric acid dissociates into one hydrogen ion and one hydrogen sulfate ion. The fact that the measured potentials agree so well with those calculated on the first assumption and do not agree with those calculated on the second assumption is a strong indication that

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[5] Lewis and Linhart, This Journal, 41, 1959 (1919).

the sulfuric acid dissociates almost entirely into 3 ions at these concentrations.

It has been noticed by others that the calculated values for potential measurements are always higher than the measured values when conductivity dissociation ratios are used. Ferguson[1] in his work on hydrochloric acid attributed the difference to the fact that the formula assumes the complete dissociation of the acid. As the acid is not completely dissociated the formula does not exactly represent the facts and must be corrected so as to include the undissociated acid. Such a correction was made for hydrochloric acid and, when applied to the formulas involving conductivity ratios, gave values which agreed more closely with those measured. A similar correction can be developed for the sulfuric acid concentration cell.

When two faradays of electricity pass through a sulfuric acid concentration double cell, one mol of acid is transferred from one concentration to the other. The electrical work which accompanies this change is represented by $W = 2\ EF$. The osmotic work required to effect this same change is usually represented by $W = 3\ RT\ ln\ c_1/c_2$. This assumes that the acid is completely dissociated into 3 ions. Since it is not completely dissociated what actually happens is (1) the transference of an amount of hydrogen ion equal to twice the concentration times the dissociation of the acid; (2) the transference of an amount of sulfate ion equal to the concentration times the dissociation of the acid; (3) the transference of an amount of undissociated acid equal to the concentration of the undissociated acid. The general expression which represents the sum of the osmotic work in (1) and (2) is $W_1 = \alpha 3RT\ ln\ \frac{c_1}{c_2}$.

Similarly the osmotic work in (3) is $W = (1-\alpha)RT\ ln\ \frac{c_1}{c_2}$. In the application to sulfuric acid (c_1) in (W_1) becomes $2c_1H^+ = 2\ c_1\alpha' = c_1SO_4^{--}$; and c_2 becomes $2c_2H^+ = 2c_2\ \alpha'' = c_2SO_4^{--}$.

Similarly c_1 in W_2 becomes $c_1H_2SO_4 = c_1\ (1-\alpha')$; and c_2 becomes $c_2H_2SO_4 = c_2(1-\alpha'')$; and, as the total electrical work is equal to the total osmotic work,

$$W = 2EF = \alpha 3RT\ ln \frac{c_1\alpha'}{c_2\alpha''} + (1-\alpha)\ RT\ ln \frac{c_1(1-\alpha')}{c_2(1-\alpha'')}$$

$$E = \alpha \frac{3}{2} \frac{RT}{F} ln \frac{c_1\alpha'}{c_2\alpha''} + \frac{(1-\alpha)}{2} \frac{RT}{F} ln \frac{c_1(1-\alpha')}{c_2(1-\alpha'')}.$$

This formula cannot be taken as absolutely correct since it assumes that the dissociation is the same in both concentrations, which is not true. The most reliable value that can be used for α is $\frac{\alpha'+\alpha''}{2}$, in which α' is the degree of dissociation in c_1 and α'' is the degree of dissociation in c_2.

Col. E'' Table III shows the result of the application of this correction. It is evident that the correction is an improvement since the difference (0.00639) between the measured value and that calculated from the corrected formula is much less than the difference (0.01829) between the measured value and that calculated from the usual formula.

In the theoretical part of this work it was shown that the boundary potential can be calculated from the formula $E_B = \frac{2-3\,N_a}{2}\,\frac{RT}{F}\,ln\,\frac{c_1}{c_2}$; also that $E_B = \frac{2E_{SO_4} - E_H}{3}$. Column E_B contains the results from the calculation by the first formula. Again the close agreement between the measured and calculated values in the case of the freezing-point ratio and lack of agreement in the case of the conductivity ratio are evident.

MacInnes[6] has developed a formula for boundary potentials of uni-univalent electrolytes which involves the transference number of the cation and the potentials of the cells with and without diffusion. He states that it "contains no asssumption regarding the concentration of the ions of the solutions." In the following development the same reasoning is applied to the uni-bivalent acid, sulfuric acid, on the asssumption that it dissociates into two hydrogen ions and one sulfate ion.

When two faradays of electricity pass through the cell the net result is the transference of one mol of sulfuric acid from the concentrated to the dilute side. The current is carried across the boundary between the two solutions by the transference of 2 N_c gram ions of hydrogen ions in one direction and $1-N_c$ gram ions of sulfate ions in the opposite. The osmotic work at the boundary is proportional to the algebraic sum of the number of gram ions that have passed through it. Therefore the osmotic work W is proportional to $3N_c - 1$. The electrical work which accompanies the transference of one mol of sulfuric acid from the concentrated to the dilute side is equal to the product of the electromotive force of the cell and the number of faradays required to effect the transference. Since this is so, the following relation holds.

$$2EF : 2E_BF :: 3 : 3N_c - 1$$

and $E_B = E(3N_c - 1)/3$; for E, $\frac{E_{SO_4}}{N_c}$ may be substituted, since it has been shown that $N_c = \frac{E_{SO_4}}{E}$. The formula then becomes

$$E_B = E_{SO_4}\,(3N_c - 1)\,/3N_c.$$

Substituting the correct values for N_c and E_{SO_4} as measured, the value 0.02904 is obtained. This is in almost perfect agreement with the measured value 0.02906 and proves the validity of the formula.

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[6] MacInnes, THIS JOURNAL, **37,** 2301 (1915).

That this expression $E_B = E_{SO_4}(3N_c - 1)/3N_c$ is but another form of the usual expression $E_B = \frac{2-3N_a}{2}\frac{RT}{F} ln \frac{c_1}{c_2}$ for boundary potential, can readily be shown, since

$$E_B = \frac{E_{SO_4}}{3N_c}(3N_c-1) \qquad (9)$$

and

$$E_{SO_4} = N_c \frac{3}{2}\frac{RT}{F} ln \frac{c_1}{c_2}.$$

Substituting in (9)

$$E_B = \frac{N_c\frac{3}{2}\frac{RT}{F} ln \frac{c_1}{c_2}}{3N_c}(3N_c-1) = \frac{RT}{F} ln \frac{c_2}{c_2}(3N_c-1)$$

is obtained; as $(3N_c - 1) = (2 - 3N_a)$

$$E_B = \frac{RT}{F} ln \frac{c_1}{c_2}(3N_c-1) = \frac{2-3N_a}{2}\frac{RT}{F} ln \frac{c_1}{c_2}.$$

Therefore

$$E_B = \frac{E_{SO_4}}{3N_c}(3N_c-1) = \frac{2-3N_a}{2}\frac{RT}{F} ln \frac{c_1}{c_2} = \frac{2E_{SO_4}-E_H}{3}.$$

A consideration of these formulas indicates the advantage of the formula $(2E_{SO_4}-E_H)/3$ since it contains no assumption regarding the concentration of the ions, nor does it require a knowledge of the transference numbers.

The averages of E_H, E_{SO_4}, and E from a few of the tables obtained are contained in Table IV, together with the transference numbers calculated from them.

TABLE IV.

SUMMARY OF POTENTIALS AND TRANSFERENCE NUMBERS.

Table.	E_H.	E_{SO_4}.	E or $E_{0.01} - E_{0.1}$.	N_a. E_H/E.	N_a. $1 - E_{SO_4}/E$
II	0.01136	0.04922	0.06056	0.1875	0.1875
III	0.01126	0.04923	0.06047	0.1862	0.1862
IV	0.01137	0.04929	0.06059	0.1875	0.1874
V	0.01126	0.04927	0.06053	0.1868	0.1868
Av.	0.01131	0.04925	0.06054	0.1868	0.1868

To facilitate the comparison of the value obtained in this investigation with those obtained in others, a summary of such values is contained in Table V.

Attention should be called to the fact that the values recorded in columns E_H/E and $1 - E_{SO_4}/E$ of Table IV are determined from separate and distinct potential measurements. The agreement between the successive values in each column and between the averages of the two columns demonstrates the reliability of the concentration cell method for the determination of the transference numbers of sulfuric acid.

TABLE V.

SUMMARY OF TRANSFERENCE NUMBERS OF SULFURIC ACID.

Investigator.[7]		Concentration.	Temp. °C.	N_a.	N_a corrected to 25°.
Bein	1898	0.24%	11	0.175±3	0.1804
McIntosh	1898	1.0–0.001 *M*	18	0.174±18	0.1817
Starck	1899	0.5–0.6%	17–20	0.145±7	......
Jahn and Huybrechts	1902	0.06–0.005 *M*	18	0.176±4	0.1837
Eisenstein	1902	0.124 *M*	18	0.168±3	0.1757
Eisenstein	1902	0.01 *M*	30	0.188±1	0.1825
Tower	1904	0.1 *M*	20	0.1805	0.1860
Tower	1904	0.01 *M*	20	0.1809	0.1864
Whetham and Paine	1908	0.05 *M*	18	0.184	0.1917
Ferguson and France	1920	0.1–0.01 *M*	25	0.1868	0.1868

Summary.

1. A method has been described for the determination of the transference numbers of a uni-bivalent electrolyte by the measurement of the potentials of concentration cells.
2. The transference number of the anion of sulfuric acid for concentrations between 0.1 *M* and 0.01 *M* has been measured and found to be 0.1868 ± 7 at 25°.
3. It has been shown that dissociation values determined from freezing-point data are more satisfactory for calculating the potentials of concentration cells than those obtained from conductivity data.
4. A correction to the formula for the potential of a concentration cell has been developed which takes into account the undissociated part of the acid.
5. It has been shown that the concentration-cell method is entirely satisfactory for the determination of the transference numbers of sulfuric acid.

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[7] The values and the limits of accuracy of the first six investigations are taken from MacBain's abstract of transference data (*J. Wash. Acad. Sci.*, **9**, 11 (1905)). In the first six investigations the analytical method was employed. According to MacBain the results of Jahn and Huybrechts and of Tower are probably the most reliable. Whetham and Paine employed the conductivity method. The values in the last column were obtained from the values in the preceding column by the application of the temperature coefficients given by Tower (THIS JOURNAL, **26**, 1038 (1904).