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THE TRANSPORT NUMBER OF SULPHURIC ACID.

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I. INTRODUCTION.

In general, the transport numbers of acids are difficult to determine accurately on account of the great speed of the H ion, as compared with that of the negative ion, with which it is associated. Recently, however, the transport number of hydrochloric acid has been determined with excellent results by Noyes and Sammet.[1] The dissociation of hydrochloric acid in dilute solutions cannot be other than very simple, that is, into the ions $\overset{+}{H}$ and $\overset{-}{Cl}$. It, therefore, seemed desirable to investigate with considerable care the transport number of a dibasic acid where the conditions may not be so simple. Sulphuric acid has been chosen for this purpose. In fairly strong solutions some molecules of this acid dissociate into the ions $\overset{+}{H}$ and $\overset{-}{HSO_4}$, and some into the ions $2\overset{+}{H}$ and $\overset{=}{SO_4}$. As the dilution increases the number of $H\overset{-}{S}O_4$ ions gradually becomes less, and finally practically all disappear. Since the nature of the anion is thus changing as the concentration of the acid becomes less, the transport number will probably also

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[1] This Journal, **24**, 944 (1902).

vary with the concentration more than in the case of a monobasic acid.

The transport number of sulphuric acid has been investigated by Wiedemann,[1] Hittorf,[2] Bein[3] and Starck.[4] Of these Starck's determinations are the most recent and the most numerous, but his results differ greatly from those of the other investigators. This, therefore, was an additional reason for a systematic redetermination of this quantity.

Some of the investigators just mentioned worked with a platinum anode and some with a cadmium anode; in some of the experiments, also, a diaphragm was used to separate the anode from the cathode portion of the solution. A summary of the results obtained is shown in Table I. The approximate concentration of the solution, expressed in normal terms, is indicated by m. The transport number n has been multiplied by 1000 in every case.

TABLE I.

Hittorf, H. (1859), Cd anode, with diaphragm, and Wiedemann, W. (1856), Pt anode.

m.	n.	Investigator.
3.0	174	H.
2.0	189	W.
0.8	177	H.
0.4	176	W.
0.2	212	H.
0.13	206	H.

Bein (1898), Cd anode.

m = 0.05. Temp.	n anode.	n cathode.
11°	174	172
11	175	180
9	...	176
	Mean, 175	
23	...	200

Starck (1899), Pt anode.

With diaphragm. 17°–20°.

m.	n anode	Number of determinations made.
3.0	195	5
2.0	199	2
1.0	175	1
0.5	163	1
0.11	145	5
0.06	135	1

Without diaphragm.

m.	Temp.	n anode.	n cathode.	n mean.
1.0	7°	191	190	191
1.0	16	201	194	198
0.1	31	208	199	204

II. METHOD.

The form of apparatus used for holding the solution is shown in the accompanying figure. It consists essentially of two U-tubes, provided with side apertures, so that they can be connected.

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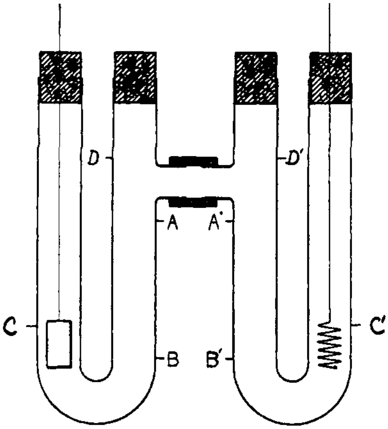
[1] Pogg. *Ann.*, **99**, 184 (1856).

[2] *Ibid.*, **106**, 400 (1859).

[3] *Ztschr. phys. Chem.*, **27**, 52 (1898).

[4] *Ibid.*, **29**, 385 (1899).



For the first experiments tubes were employed which were 40 cm. in length and 2 cm. in diameter. For the more recent experiments, which make up the larger number, tubes of the same length, but 3 cm. in diameter, were used. The anode was of cadmium, while the cathode was a platinum spiral. A platinum anode is apt to lead to errors in the analysis of the anode portion of the solution on account of the formation of hydrogen dioxide and of persulphuric acid. Some experiments were first made with a lead anode in the hope that with the weak current used the anion would react with the electrode forming lead sulphate. This, however, had to be abandoned, as only a small quantity of sulphate was formed, oxygen being liberated and some hydrogen dioxide and lead dioxide were produced. With a cadmium electrode the cadmium sulphate formed goes, of course, into solution, but since the Cd ion migrates much more slowly than the H ion, apparently no appreciable error was introduced.

The solution was introduced by the middle necks and was not allowed to rise higher in the outside limbs than *C C'*, while it stood at about *D D'* in the inside limbs. During electrolysis the liquid became heavier around the anode, and this adjustment tended to prevent convection currents. During an experiment this whole apparatus stood in a water-bath at the desired temperature, which was maintained constant within ±0.2°. The electrolysis was not begun until the solution had reached the temperature of the bath.

The current employed had a potential fall of 110 volts in the circuit and a current strength on the average of 0.07 ampere. The latter was somewhat greater when some of the more concentrated solutions were electrolyzed and somewhat less in all the experiments with twentieth- and fiftieth-normal acid. The current strength was regulated by means of appropriate resistances and remained practically constant throughout an experiment, as was proved by making frequent readings on a milliammeter which was in the circuit during some of the experiments. The electrolysis was continued for two or three hours, according to the conditions of the experiments, and the amount of electricity passed was determined by means of a silver voltameter. The silver anode of the voltameter was wrapped in filter-paper, and the rod leading to it was well insulated by passing through a glass tube, supported by a clamp, tipped with cork. There was, therefore, no chance for leakage around the voltameter.

After an experiment the solution was carefully drawn off from the tubes by means of a large pipette, provided with a stop-cock. The tip end of the pipette turned up, and its mouth was always kept just below the level of the liquid. A constant suction was maintained by using an aspirator. The first three portions were removed to tared flasks and their weight determined. First the middle portion down to about $A\ A'$ (see figure) was removed, then the portions from A to B and from A' and B'. The U-tubes were then disconnected, the electrodes removed and the portions $B\ C$ and $B'\ C'$ were weighed in the tubes, the tubes having been tared before filling. These five portions will be designated as follows: That about the anode by A, that next adjacent by A_1, the middle portion by M, that about the cathode by C, and that next adjacent to the cathode by C_1. The total anode portion is then $A + A_1$, and the total cathode portion $C + C_1$.

III. PREPARATION AND ANALYSIS OF SOLUTIONS.

Experiments have been made with sulphuric acid of six strengths, *viz.*, normal, half-normal, fifth-normal, tenth-normal, twentieth-normal and fiftieth-normal. These concentrations are only approximate, the exact strength being given in connection with each experiment. The temperature at which most of the experiments were made was 20° ; some were also made at 8° and at 32°. The acid from which the solutions were prepared was the so-called chemically pure; it was distilled just before use, only the middle fraction being retained. All of the water employed in making the solutions had a conductivity of less than 1.5×10^{-6} reciprocal ohms at 18°.

The strength of the solutions were determined by precipitating the acid as barium sulphate, the filtration and weighing being carried out in a Gooch crucible. The degree of accuracy attained can be seen from the results given in Table II. This table contains the results of the analyses of all the solutions used in the second or larger apparatus.

The data here given show the grams of H_2SO_4 in 1 kg. of solution derived from each solution from three separate determinations, the mean of these three results and the average deviation of the individual results from this mean.

TABLE II.

	Sol. No. 8.	Sol. No. 9.	Sol. No. 10.	Sol. No. 11.	Sol. No. 12.
	47.330	48.768	47.749	25.092	23.555
	47.305	48.765	47.775	25.181	23.546
	47.317	48.765	47.756	25.164	23.560
Mean,	47.318	48.766	47.760	25.146	23.554
a. d.,	0.009	0.0013	0.010	0.036	0.005
	Sol. No. 13.	Sol. No. 14.	Sol. No. 15.	Sol. No. 16.	Sol. No. 17.
	5.0230	4.9378	4.9272	4.9926	5.0623
	5.0109	4.9414	4.9225	4.9958	5.0587
	5.0161	4.9395	4.9325	4.9876	5.0646
Mean,	5.0167	4.9396	4.9274	4.9920	5.0619
a. d.,	0.0042	0.0012	0.0034	0.0029	0.0021
	Sol. No. 18.	Sol. No. 19.	Sol. No. 20.	Sol. No. 21.	Sol. No. 22.
	2.5603	2.5831	2.4613	2.4347	1.0320
	2.5627	2.5802	2.4625	2.4314	1.0353
	2.5589	2.5844	2.4587	2.4358	1.0337
Mean,	2.5606	2.5826	2.4608	2.4340	1.0337
a. d.,	0.0014	0.0016	0.0014	0.0017	0.0011
	Sol. No. 23.	Sol. No. 24.	Sol. No. 25.	Sol. No. 26.	
	1.0230	1.0745	0.99478	1.0120	
	1.0208	1.0728	0.99620	1.0135	
	1.0216	1.0723	0.99342	1.0141	
Mean,	1.0218	1.0732	0.99480	1.0132	
a. d.,	0.0008	0.0009	0.00093	0.0008	

The average of the average deviation of the individual results from the mean is a little less than 1 part in 1000, which is about the limit of accuracy in determining sulphuric acid as barium sulphate. The analytical results of the first seven solutions, which were used in the smaller apparatus, showed an average deviation no greater than the above. The strength of these solutions will be found in connection with the calculation of the transport numbers in Table IV.

The analysis of the five portions of the solution drawn off after electrolysis will now be considered. The first one of these, the anode portion *A*, contained much cadmium and was always analyzed by precipitating the sulphuric acid as barium sulphate, precisely as the original acid solutions were analyzed. The other four portions were analyzed by titration with a solution of potassium hydroxide, the strength of this solution varying according to the concentration of the acid solutions. For the strongest acid solutions, normal and half-normal, alkali solutions of approximately half these concentrations were employed; for the acid solutions, fifth-normal and tenth-normal, they were of about equal concentration; for the weakest solutions, twentieth-normal and fiftieth-normal, the alkali solutions were of about twice the concentration.

The alkali solutions were prepared by dissolving Schuchardt's *Kalium hydric. alc. dep.* in water, boiling with a small quantity of lime and filtering directly into the reservoir, from which the solution was to be drawn off for use. In this reservoin it was protected from the carbon dioxide of the atmosphere by means of tubes of soda-lime. Phenolphthaleïn was used as indicator. All titrations were carried out by weighing the solutions The strengths are, therefore, all expressed in parts by weight All weighings here, as well as elsewhere in the course of this work, have been reduced to weight *in vacuo*. The alkali solutions were standardized by titrating against the standard sulphuric acid solutions. To illustrate the accuracy with which the titrations were made, an example is given in Table III with each strength of acid used.

TABLE III.

	Grams alkali equivalent to 100 grams acid.					
	N/1 H_2SO_4. Sol. No. 8.	N/2 H_2SO_4. Sol. No. 11.	N/5 H_2SO_4. Sol. No. 4.	N/10 H_2SO_4. Sol. No. 15.	N/20 H_2SO_4. Sol. No. 18.	N/50 H_2SO_4. Sol. No. 26.
	222.33	204.88	139.46	108.80	49.81	50.17
	222.36	204.98	139.53	108.98	49.81	50.24
	222.54	204.90	139.68	108.93	49.83	50.17
	222.41	.....	139.41	109.01	49.82	50.15
Mean,	222.41	204.92	139.52	108.93	49.82	50.18
a. d.,	0.065	0.040	0.085	0.065	0.008	0.028

The average of the average deviation of the individual results from the mean is here about 1 part in 2000. This is a greater degree of accuracy than could be attained by precipitating the acid in these solutions as barium sulphate, and hence the reason for analyzing all the portions, where possible, in this manner. The portion A_1 contained traces of cadmium in the experiments with the twentieth-normal and fiftieth-normal solutions and in one or two other exceptional instances. On precipitating the cadmium, however, as cadmium sulphide, not more than a milligram was ever found, and this quantity was considered to be too slight to affect the titration of this portion.

IV. CALCULATION OF THE TRANSPORT NUMBERS.

The quantity of cadmium in the anode portion *A* was estimated from the weight of the silver precipitated in the voltameter. Experiment showed it to be slightly greater than this, as solution began as soon as the electrode was introduced into the acid and before the electrolysis was begun. The difference between the quantity found and that estimated was small—usually only a few milligrams—and since the solutions were weighed only to centigrams, the quantity, as estimated, was sufficiently accurate.

Let W^a be the weight of the anode portion, after electrolysis, minus the weight of the cadmium dissolved, X the unknown weight of the same portion before electrolysis, *n* the transport number of the anion, and *s* the weight of the silver deposited in the voltameter. Then, since $n.s.\frac{M(SO_4)}{M(2Ag)}$[1] is the amount of SO_4

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[1] The expression $\frac{M(SO_4)}{M(2Ag)}$ indicates the ratio of the molecular weight of the SO_4 group to twice the atomic weight of silver. Similar expressions are to be interpreted in the same manner.

which has migrated to the anode, and $(1-n).s.\frac{M(2H)}{M(2Ag)}$ is the amount of H which has migrated away from it, we have

$$W_a = X + n.s.\frac{M(SO_4)}{M(2Ag)} - (1-n).s.\frac{M(2H)}{M(2Ag)},$$

or

$$W_a = X + n.s.\frac{M(H_2SO_4)}{M(2Ag)} - s.\frac{M(2H)}{M(2Ag)}. \qquad (1)$$

The amount of acid a_1, which is present in the anode portion after electrolysis, is

$$a_1 = pX + n.s.\frac{M(H_2SO_4)}{M(2Ag)}, \qquad (2)$$

in which p is the amount of acid in 1 gram of the solution before electrolysis.

Combining (1) and (2) so as to eliminate X, we obtain the value of n from the change in concentration around the anode,

$$n = \frac{a_1 - pW_a - p.s.\frac{M(2H)}{M(2Ag)}}{(1-p).s.\frac{M(H_2SO_4)}{M(2Ag)}}. \qquad (3)$$

Making, for the sake of simplicity,

$$\frac{M(H_2SO_4)}{M(2Ag)} = \frac{1}{k},$$

and

$$\frac{M(2H)}{M(H_2SO_4)} + l,$$

(3) becomes

$$n = \frac{1}{1-p} \cdot \left(\frac{a_1 - pW_a}{s} k - pl.\right). \qquad (4)$$

Likewise, at the cathode, let W_c be the weight of the total cathode portion after electrolysis and Y its weight before electrolysis. Then there migrates away from the cathode an amount of SO_4 equal to $n.s.\frac{M(SO_4)}{M(2Ag)}$, and there migrates to it an amount of H equal to $(1-n).s.\frac{M(2H)}{M(2Ag)}$, while an amount of H equal to $s.\frac{M(2H)}{M(2Ag)}$ is set free. We therefore have

$$W_c = Y - n.s.\frac{M(SO_4)}{M(2Ag)} + (1-n).s.\frac{M(2H)}{M(2Ag)} - s.\frac{M(2H)}{M(2Ag)},$$

or

$$W_c = Y - n.s.\frac{M(H_2SO_4)}{M(2Ag)}. \tag{5}$$

The amount of acid a_2 at the cathode, after electrolysis, is

$$a_2 = pY - n.s.\frac{M(H_2SO_4)}{M(2Ag)}. \tag{6}$$

By eliminating Y in (5) and (6) we obtain

$$n = \frac{pW_c - a_2}{(1-p).s.\frac{M(H_2SO_4)}{M(2Ag)}}. \tag{7}$$

Substituting as in (3) this becomes

$$n = \frac{1}{1-p}.\frac{pW_c - a_2}{s}k. \tag{8}$$

Equations (4) and (8) have been used for calculating the transport numbers in the work which follows. The atomic weights used were those from the Report of the International Committee or 1903. The values of the constants, k and l, are, therefore,

$$k = 2.201,$$
$$l = 0.02055.$$

V. RESULTS OF THE EXPERIMENTS.

With the smaller apparatus, which was the first one used, six experiments were made with each one of the concentrations, normal, fifth-normal and tenth-normal, and four with the concentration, twentieth-normal. All these were made at 20°. Three of the experiments with normal acid, the first made, have been discarded on account of serious experimental errors. The results of the others are given in Table IV. The content of the different columns will be evident without much explanation. The symbols on parentheses at the heads of the columns refer to those of the formulas of the preceding section. The letters in the fifth column indicate the portion of the solution withdrawn after electrolysis, as explained at the end of section II. Column 10 contains the lgebraic sum of the numbers opposite A and A_1, and C and C_1, espectively, of column 9 (see foot-note at bottom of table). The tansport numbers, which have been multiplied by 1000, have been calculated from the numbers of column 10 by means of equations (4) and (8) of the preceding section.

TABLE IV.

Normal sulphuric acid at 20°.

Expt. number.	Solution number.	Milligrams of H_2SO_4 per gram (1000p).	Silver in voltameter (s).	Portion.	Weight of portion (W).	Initial content (pW).	Final content (a).	Change ($a-p$W).	Total change (a_1-pW$_a$) and (a_2-pW$_c$).	Transport number (1000n).
1	1	48.660	0.7361	A	92.94[1]	4.5226	4.5841	+0.0615	+0.0593	185.
				A_1	73.49	3.5752	3.5730	—0.0022		
				M	67.36	3.2778	3.2785	+0.0007		
				C_1	80.94	3.9386	3.9392	+0.0006		
				C	119.73	5.8262	5.7658	—0.0604	—0.0604[2]	189.
2	2	48.190	0.7411	A	119.83	5.7750	5.8403	+0.0653	+0.0618	191.
				A_1	64.69	3.1176	3.1141	—0.0035		
				M	74.72	3.6010	3.6008	—0.0002		
				C_1	74.13	3.5725	3.5723	—0.0002		
				C	101.94	4.9127	4.8505	—0.0622	—0.0622	194.
3	2	48.190	0.7550	A	104.57	5.0395	5.0995	+0.0600	+0.0600	182.
				A_1	71.38	3.4400	3.4408	+0.0008		
				M	68.04	3.2790	3.2784	—0.0006		
				C_1	78.35	3.7759	3.7763	+0.0004		
				C	119.34	5.7512	5.6916	—0.0596	—0.0596	182.

$^1/_5$-Normal sulphuric acid at 20°.

Expt. number.	Solution number.	Milligrams of H_2SO_4 per gram (1000p).	Silver in voltameter (s).	Portion.	Weight of portion (W).	Initial content (pW).	Final content (a).	Change ($a-p$W).	Total change (a_1-pW$_a$) and (a_2-pW$_c$).	Transport number (1000n).
4	3	9.625	0.8566	A	99.78	0.9603	1.0325	+0.0722	+0.0689	178.
				A_1	64.31	0.6190	0.6157	—0.0033		
				M	56.85	0.5472	0.5466	—0.0006		
				C_1	70.02	0.6739	0.6739	0.0000		
				C	117.68	1.1326	1.0645	—0.0681	—0.0681	176.
5	3	9.625	0.8954	A	98.37	0.9468	1.0209	+0.0741	+0.0705	174.
				A_1	67.20	0.6468	0.6432	—0.0036		
				M	60.18	0.5792	0.5790	—0.0002		
				C_1	72.68	0.6995	0.6992	-0.0003		
				C	105.44	1.0148	0.9421	—0.0727	—0.0727	180.
6	3	9.625	0.8933	A	102.04	0.9821	1.0578	+0.0757	+0.0709	176.
				A_1	67.33	0.6480	0.6432	—0.0048		
				M	64.04	0.6164	0.6168	+0.0004		
				C_1	74.03	0.7125	0.7120	—0.0005		
				C	110.30	1.0616	0.9901	—0.0715	—0.0715	177

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[1] The cadmium dissolved has been subtracted from the weight of the portion A every case.

[2] Differences not exceeding 0.0009 in the preceding column are not taken into consi eration in calculating the total change, as they are practically within the limit of expe mental error.

Expt. number.	Solution number.	Milligrams of H_2SO_4 per gram ($1000p$).	Silver in voltameter (s).	Portion.	Weight of portion (W).	Initial content (pW).	Final content (a).	Change ($a-p$W).	Total change (a_1-pW_a) and (a_2-pW_c).	Transport number ($1000n$).
7	4	10.387	0.9603	*A*	106.40	1.1119	1.1930	+0.0811	+0.0781	180.7
				A_1	58.97	0.6125	0.6095	—0.0030		
				M	59.93	0.6225	0.6218	—0.0007		
				C_1	72.68	0.7550	0.7543	—0.0007		
				C	104.84	1.0890	1.0100	—0.0790	—0.0790	183.0
8	4	10.387	0.8693	*A*	109.67	1.1392	1.2159	+0.0767	+0.0713	182.2
				A_1	58.32	0.6058	0.6004	—0.0054		
				M	58.12	0.6037	0.6039	+0.0002		
				C_1	70.52	0.7325	0.7319	—0.0006		
				C	106.77	1.1087	1.0379	—0.0708	—0.0708	181.1
9	4	10.387	0.7850	*A*	108.23	1.1242	1.1914	+0.0672	+0.0656	185.6
				A_1	57.78	0.6002	0.5986	—0.0016		
				M	51.78	0.5379	0.5375	—0.0004		
				C_1	67.58	0.7020	0.7017	—0.0003		
				C	119.56	1.2419	1.1755	—0.0664	—0.0664	188.1
$^1/_{10}$-Normal sulphuric acid at 20°.										
10	5	4.885	0.7584	*A*	98.40	0.4807	0.5439	+0.0632	+0.0590	171.9
				A_1	54.15	0.2645	0.2603	—0.0042		
				M	72.70	0.3551	0.3547	—0.0004		
				C_1	72.21	0.3528	0.3537	+0.0003		
				C	119.55	0.5840	0.5242	—0.0598	—0.0598	174.3
11	5	4.885	0.7071	*A*	106.77	0.5216	0.5795	+0.0579	+0.0539	168.5
				A_1	60.94	0.2977	0.2937	—0.0040		
				M	69.24	0.3383	0.3376	—0.0007		
				C_1	68.78	0.3360	0.3366	+0.0006		
				C	109.52	0.5350	0.4807	—0.0543	—0.0543	169.8
12	5	4.885	0.7162	*A*	114.61	0.5599	0.6209	+0.0610	+0.0584	180.3
				A_1	62.26	0.3041	0.3015	—0.0026		
				M	72.88	0.3560	0.3559	—0.0001		
				C_1	68.81	0.3361	0.3362	+0.0001		
				C	102.79	0.5021	0.4439	—0.0582	—0.0582	179.7
13	6	4.887	0.6479	*A*	105.77	0.5169	0.5732	+0.0563	+0.0514	175.3
				A_1	60.95	0.2979	0.2930	—0.0049		
				M	57.80	0.2825	0.2828	+0.0003		
				C_1	65.48	0.3200	0.3200	0.0000		
				C	106.59	0.5209	0.4700	—0.0509	—0.0509	173.7
14	6	4.887	0.7288	*A*	109.49	0.5351	0.5978	+0.0627	+0.0578	175.2
				A_1	61.48	0.3005	0.2956	—0.0049		
				M	54.32	0.2655	0.2650	—0.0005		
				C_1	64.97	0.3175	0.3168	—0.0007		
				C	106.94	0.5226	0.4646	—0.0580	—0.0580	176.0

Expt. number.	Solution number.	Milligrams of H_2SO_4 per gram (1000p).	Silver in voltameter (s).	Portion.	Weight of portion (W).	Initial content (pW).	Final content (a)	Change (a—pW).	Total change (a_1—pW_A) and (a_2—pW_C).	Transport number (1000n).
15	6	4.887	0.7033	*A*	113.03	0.5524	0.6138	+0.0614	+0.0555	174.5
				A_1	58.84	0.2875	0.2816	—0.0059		
				M	55.36	0.2705	0.2698	—0.0007		
				C_1	63.36	0.3096	0.3093	—0.0003		
				C	104.78	0.5121	0.4565	—0.0556	—0.0556	174.9
$^1/_{20}$-Normal sulphuric acid at 20°.										
16	7	2.3600	0.3646	*A*	100.44	0.2370	0.2682	+0.0312	+0.0288	174.2
				A_1	61.15	0.1443	0.1419	—0.0024		
				M	49.90	0.1177	0.1175	—0.0002		
				C_1	65.77	0.1552	0.1544	—0.0008		
				C	116.19	0.2742	0.2445	—0.0297	—0.0297	179.7
17	7	2.3600	0.3019	*A*	111.57	0.2633	0.2902	+0.0269	+0.0245	179.0
				A_1	55.45	0.1308	0.1284	—0.0024		
				M	69.33	0.1636	0.1633	—0.0003		
				C_1	64.69	0.1524	0.1523	—0.0001		
				C	105.63	0.2492	0.2256	—0.0236	—0.0236	172.4
18	7	2.3600	0.3021	*A*	117.88	0.2782	0.3031	+0.0249	+0.0239	174.5
				A_1	48.74	0.1150	0.1140	—0.0010		
				M	57.91	0.1366	0.1360	—0.0006		
				C_1	56.47	0.1333	0.1327	—0.0006		
				C	106.84	0.2521	0.2276	—0.0245	—0.0245	178.9
19	7	2.3600	0.3113	*A*	105.84	0.2497	0.2755	+0.0258	+0.0247	175.0
				A_1	61.43	0.1450	0.1439	—0.0011		
				M	50.18	0.1184	0.1179	—0.0005		
				C_1	63.75	0.1504	0.1502	—0.0002		
				C	106.66	0.2517	0.2268	—0.0249	—0.0249	176.4

The more recent results obtained with the larger apparatus are given in Table V. The experiments with tenth-normal, twentieth-normal and fiftieth-normal acid were made at three temperatures, *viz.*, 8°, 20° and 32°. The results are arranged as in the preceding table.

TABLE V.

Normal sulphuric acid at 20°.

Expt. number.	Solution number.	Milligrams of H_2SO_4 per gram (1000p).	Silver in voltameter (s).	Portion.	Weight of portion (W).	Initial content (pW).	Final content (a).	Change (a—pW).	Total change (a_1—pWa) and (a_2—pWc).	Transport number (1000n).
20	8	47.318	0.5655	A	206.76	9.7835	9.8360	+0.0525	+0.0487	197.8
				A_1	90.27	4.2713	4.2675	—0.0038		
				M	100.95	4.7767	4.7763	—0.0004		
				C_1	84.82	4.0135	4.0135	0.0000		
				C	187.04	8.8502	8.8014	—0.0488	—0.0488	199.4
21	8	47.318	0.7568	A	211.34	10.0000	10.0616	+0.0616	+0.0596	180.9
				A_1	94.94	4.4923	4.4903	—0.0020		
				M	68.93	3.2616	3.2610	—0.0006		
				C_1	98.52	4.6617	4.6625	+0.0008[1]		
				C	184.62	8.7356	8.6758	—0.0598	—0.0598	182.5
22	9	48.766	0.7600	A	207.47	10.1170	10.1810	+0.0640	+0.0610	184.4
				A_1	93.71	4.5698	4.5668	—0.0030		
				M	108.19	5.2760	5.2765	+0.0005		
				C_1	97.98	4.7780	4.7782	+0.0002		
				C	185.52	9.0470	8.9854	—0.0616	—0.0616	187.2
23	9	48.766	0.6447	A	215.07	10.4880	10.5450	+0.0570	+0.0554	197.4
				A_1	90.96	4.4357	4.4341	—0.0016		
				M	94.97	4.6313	4.6316	+0.0003		
				C_1	88.72	4.3264	4.3268	+0.0004		
				C	190.04	9.2672	9.2132	—0.0540	—0.0540	193.5
24	10	47.760	1.2088	A	221.75	10.5910	10.6820	+0.0910	+0.0965	183.4
				A_1	91.49	4.3695	4.3750	+0.0055		
				M	75.01	3.5824	3.5820	—0.0004		
				C_1	92.90	4.4369	4.4373	+0.0004		
				C	208.97	9.9805	9.8852	—0.0953	—0.0953	182.1
25	10	47.760	1.3778	A	203.33	9.7110	9.8134	+0.1024	+0.1089	181.6
				A_1	98.80	4.7187	4.7252	+0.0065		
				M	68.82	3.2868	3.2863	—0.0005		
				C_1	94.15	4.4965	4.4965	0.0000		
				C	201.12	9.6052	9.4968	—0.1084	—0.1084	181.8
½-Normal sulphuric acid at 20°.										
26	11	25.146	0.7617	A	212.67	5.3479	5.4160	+0.0681	+0.0636	188.0
				A_1	91.97	2.3128	2.3083	—0.0045		
				M	83.07	2.0889	2.0882	—0.0007		
				C_1	100.80	2.5347	2.5350	+0.0003		
				C	172.44	4.3362	4.2736	—0.0626	—0.0626	185.5

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[1] Differences in column 9 not exceeding 0.0009 with normal and ½-normal acid and not exceeding 0.0005 with 1/10-, 1/20-, and 1/50-normal acid have been neglected in calculating the numbers of column 10.

Expt. number.	Solution number.	Milligrams of H_2SO_4 per gram ($1000p$).	Silver in voltameter (s).	Portion.	Weight of portion (W).	Initial content (pW).	Final content (a).	Change ($a-pW$).	Total change (a_1-pW_a) and (a_2-pW_c).	Transport number ($1000n$).
27	11	25.146	0.7687	A	204.91	5.1526	5.2287	+0.0661	+0.0661	193.6
				A_1	98.75	2.4832	2.4836	+0.0004		
				M	105.45	2.6517	2.6523	+0.0006		
				C_1	100.90	2.5372	2.5369	—0.0003		
				C	188.84	4.7486	4.6831	—0.0655	—0.0655	192.4
28	11	25.146	0.8560	A	197.77	4.9731	5.0408	+0.0677	+0.0693	182.3
				A_1	96.93	2.4374	2.4390	+0.0016		
				M	99.43	2.5003	2.4997	—0.0006		
				C_1	91.52	2.3014	2.3014	0.0000		
				C	175.90	4.4232	4.3542	—0.0690	—0.0690	182.0
29	11	25.146	0.7200	A	175.24	4.4066	4.4678	+0.0612	+0.0612	191.5
				A_1	96.85	2.4354	2.4355	+0.0001		
				M	112.18	2.8184	2.8176	—0.0008		
				C_1	101.56	2.5538	2.5546	+0.0008		
				C	195.05	4.9048	4.8428	—0.0620	—0.0620	194.4
30	12	23.554	1.2893	A	213.95	5.0394	5.1516	+0.1122	+0.1062	185.5
				A_1	93.38	2.1995	2.1935	—0.0060		
				M	69.60	1.6394	1.6390	—0.0004		
				C_1	90.81	2.1390	2.1385	—0.0005		
				C	208.70	4.9158	4.8110	—0.1048	—0.1048	183.5
31	12	23.554	1.1628	A	216.99	5.1110	5.2058	+0.0948	+0.0938	181.7
				A_1	91.18	2.1477	2.1467	—0.0010		
				M	66.40	1.5640	1.5638	—0.0002		
				C_1	92.05	2.1682	2.1683	+0.0001		
				C	206.02	4.8527	4.7585	—0.0942	—0.0942	182.9

$^1/_{10}$-Normal sulphuric acid at 8°.

Expt. number.	Solution number.	Milligrams of H_2SO_4 per gram ($1000p$).	Silver in voltameter (s).	Portion.	Weight of portion (W).	Initial content (pW).	Final content (a).	Change ($a-pW$).	Total change (a_1-pW_a) and (a_2-pW_c).	Transport number ($1000n$).
32	13	5.0167	0.8048	A	210.17	1.0544	1.1216	+0.0672	+0.0583	160.2
				A_1	90.53	0.4542	0.4453	—0.0089		
				M	83.39	0.4183	0.4177	—0.0006		
				C_1	89.37	0.4483	0.4478	—0.0005		
				C	203.44	1.0206	0.9617	—0.0589	—0.0589	161.9
33	13	5.0167	0.7415	A	206.23	1.0346	1.0978	+0.0632	+0.0565	168.4
				A_1	89.40	0.4485	0.4418	—0.0067		
				M	73.61	0.3693	0.3688	—0.0005		
				C_1	90.86	0.4558	0.4559	+0.0001		
				C	197.62	0.9914	0.9371	—0.0543	—0.0543	162.0
34	13	5.0167	0.6925	A	198.82	0.9974	1.0516	+0.0542	+0.0514	164.1
				A_1	94.51	0.4741	0.4713	—0.0028		
				M	83.07	0.4167	0.4166	—0.0001		
				C_1	93.80	0.4706	0.4701	—0.0005		
				C	194.71	0.9768	0.9264	—0.0504	—0.0504	161.0

Expt. number.	Solution number.	Milligrams of H_2SO_4 per gram ($1000p$).	Silver in voltameter (s).	Portion.	Weight of portion (W).	Initial content (pW).	Final content (a).	Change ($a-p$W).	Total change $\{(a_1-pW_a)$ and (a_2-pW_c).	Transport number ($1000n$).
35	13	5.0167	0.6916	A	218.32	1.0953	1.1520	+0.0567	+0.0526	168.1
				A_1	79.94	0.4010	0.3969	—0.0041		
				M	94.31	0.4731	0.4737	+0.0006		
				C_1	88.87	0.4458	0.4461	+0.0003		
				C	196.93	0.9880	0.9360	—0.0520	—0.0520	166.3
36	13	5.0167	0.6154	A	195.57	0.9811	1.0321	+0.0510	+0.0470	168.8
				A_1	85.47	0.4288	0.4248	—0.0040		
				M	66.17	0.3320	0.3319	—0.0001		
				C_1	94.63	0.4747	0.4742	—0.0005		
				C	186.02	0.9332	0.8864	—0.0468	—0.0468	168.2
37	14	4.9396	0.6837	A	210.97	1.0421	1.0948	+0.0527	+0.0499	161.3
				A_1	82.36	0.4068	0.4040	—0.0028		
				M	73.30	0.3621	0.3618	—0.0003		
				C_1	95.45	0.4715	0.4711	—0.0004		
				C	190.09	0.9390	0.8888	—0.0502	—0.0502	162.4

$^1/_{10}$-Normal sulphuric acid at 20°.

Expt. number.	Solution number.	Milligrams of H_2SO_4 per gram ($1000p$).	Silver in voltameter (s).	Portion.	Weight of portion (W).	Initial content (pW).	Final content (a).	Change ($a-p$W).	Total change $\{(a_1-pW_a)$ and (a_2-pW_c).	Transport number ($1000n$).
38	14	4.9396	0.6855	A	209.26	1.0337	1.0937	+0.0600	+0.0549	177.0
				A_1	89.29	0.4410	0.4359	—0.0051		
				M	72.44	0.3578	0.3577	—0.0001		
				C_1	88.04	0.4349	0.4346	—0.0003		
				C	201.81	0.9969	0.9421	—0.0548	—0.0548	176.8
39	14	4.9396	0.7247	A	217.31	1.0734	1.1367	+0.0633	+0.0582	177.5
				A_1	87.61	0.4328	0.4277	—0.0051		
				M	71.93	0.3553	0.3551	—0.0002		
				C_1	93.75	0.4631	0.4627	—0.0004		
				C	200.46	0.9902	0.9319	—0.0583	—0.0583	177.9
40	14	4.9396	0.7275	A	215.31	1.0635	1.1269	+0.0634	+0.0580	176.2
				A_1	91.43	0.4516	0.4462	—0.0054		
				M	74.82	0.3696	0.3692	—0.0004		
				C_1	89.32	0.4412	0.4409	—0.0003		
				C	198.21	0.9791	0.9219	—0.0572	—0.0572	173.9
41	15	4.9274	0.7009	A	212.71	1.0481	1.1099	+0.0618	+0.0563	177.6
				A_1	88.50	0.4361	0.4306	—0.0055		
				M	83.95	0.4137	0.4137	0.0000		
				C_1	87.60	0.4316	0.4317	+0.0001		
				C	203.99	1.0051	0.9490	—0.0561	—0.0561	177.0
42	15	4.9274	0.7079	A	213.75	1.0532	1.1156	+0.0624	+0.0568	177.4
				A_1	89.97	0.4433	0.4377	—0.0056		
				M	68.75	0.3388	0.3385	—0.0003		
				C_1	84.92	0.4184	0.4185	+0.0001		
				C	205.81	1.0141	0.9575	—0.0566	—0.0566	176.9

Expt. number.	Solution number.	Milligrams of H_2SO_4 per gram ($1000p$).	Silver in voltameter (s).	Portion.	Weight of portion (W).	Initial content (pW).	Final content (a).	Change ($a-p$W).	Total change (a_1-pW_A) and (a_2-pW_C).	Transport number ($1000n$).
43	15	4.9274	0.7021	A	213.56	1.0523	1.1139	+0.0616	+0.0553	174.1
				A_1	90.19	0.4444	0.4381	—0.0063		
				M	63.64	0.3136	0.3133	—0.0003		
				C_1	90.49	0.4459	0.4458	—0.0001		
				C	201.40	0.9924	0.9370	—0.0554	—0.0554	174.5

$^1/_{10}$-Normal sulphuric acid at 32°.

Expt. number.	Solution number.	Milligrams of H_2SO_4 per gram ($1000p$).	Silver in voltameter (s).	Portion.	Weight of portion (W).	Initial content (pW).	Final content (a).	Change ($a-p$W).	Total change (a_1-pW_A) and (a_2-pW_C).	Transport number ($1000n$).
44	15	4.9274	0.6215	A	208.95	1.0296	1.0898	+0.0602	+0.0540	192.2
				A_1	87.21	0.4297	0.4835	—0.0062		
				M	64.54	0.3180	0.3175	—0.0005		
				C_1	90.78	0.4473	0.4469	—0.0004		
				C	197.22	0.9718	0.9179	—0.0539	—0.0539	191.7
45	16	4.9920	0.6110	A	210.53	1.0510	1.1095	+0.0585	+0.0532	192.5
				A_1	91.48	0.4567	0.4514	—0.0053		
				M	69.98	0.3493	0.3490	—0.0003		
				C_1	90.15	0.4500	0.4501	+0.0001		
				C	201.34	1.0051	0.9521	—0.0530	—0.0530	191.9
46	16	4.9920	0.6545	A	189.70	0.9470	1.0086	+0.0616	+0.0566	191.2
				A_1	91.64	0.4575	0.4525	—0.0050		
				M	59.78	0.2984	0.2984	0.0000		
				C_1	91.21	0.4553	0.4549	—0.0005		
				C	218.88	1.0927	1.0358	—0.0569	—0.0569	192.3
47	17	5.0619	0.6504	A	220.63	1.1168	1.1793	+0.0625	+0.0567	192.7
				A_1	85.56	0.4331	0.4273	—0.0058		
				M	63.55	0.3217	0.3214	—0.0003		
				C_1	88.88	0.4499	0.4497	—0.0002		
				C	205.86	1.0420	0.9856	—0.0564	—0.0564	191.8
48	17	5.0619	0.6294	A	203.53	1.0302	1.0903	+0.0601	+0.0544	191.1
				A_1	94.08	0.4762	0.4705	—0.0057		
				M	67.36	0.3410	0.3405	—0.0005		
				C_1	88.75	0.4492	0.4489	—0.0003		
				C	205.53	1.0404	0.9861	—0.0543	—0.0543	190.8
49	17	5.0619	0.6182	A	203.11	1.0281	1.0858	+0.0577	+0.0535	191.3
				A_1	90.08	0.4560	0.4518	—0.0042		
				M	61.58	0.3117	0.3116	—0.0001		
				C_1	91.00	0.4606	0.4604	—0.0002		
				C	201.78	1.0214	0.9682	—0.0532	—0.0532	190.4

$^1/_{20}$-Normal sulphuric acid at 8°.

Expt. number.	Solution number.	Milligrams of H_2SO_4 per gram ($1000p$).	Silver in voltameter (s).	Portion.	Weight of portion (W).	Initial content (pW).	Final content (a).	Change ($a-p$W).	Total change (a_1-pW_A) and (a_2-pW_C).	Transport number ($1000n$).
50	18	2.5606	0.4342	A	196.26	0.5025	0.5364	+0.0339	+0.0323	164.1
				A_1	104.25	0.2669	0.2653	—0.0016		
				M	78.55	0.2011	0.2007	—0.0004		
				C_1	96.84	0.2480	0.2478	—0.0002		
				C	186.73	0.4781	0.4456	—0.0325	—0.0325	165.2

Expt. number.	Solution number.	Milligrams of H_2SO_4 per gram (1000p).	Silver in voltameter (s).	Portion.	Weight of portion (W).	Initial content (pW).	Final content (a).	Change ($a-p$W).	Total change (a_1-pWa) and (a_2-pWc).	Transport number (1000n).
51	18	2.5606	0.4328	A	193.17	0.4946	0.5285	+0.0339	+0.0323	164.2
				A_1	95.88	0.2455	0.2439	—0.0016		
				M	87.43	0.2239	0.2234	—0.0005		
				C_1	100.74	0.2580	0.2579	—0.0001		
				C	185.80	0.4758	0.4438	—0.0320	—0.0320	163.1
52	18	2.5606	0.4442	A	216.12	0.5534	0.5877	+0.0343	+0.0329	163.4
				A_1	95.13	0.2436	0.2422	—0.0014		
				M	70.23	0.1798	0.1799	+0.0001		
				C_1	98.55	0.2523	0.2524	+0.0001		
				C	191.69	0.4908	0.4578	—0.0330	—0.0330	163.9
53	19	2.5826	0.4328	A	194.66	0.5027	0.5373	+0.0346	+0.0320	163.1
				A_1	96.40	0.2490	0.2464	—0.0026		
				M	78.66	0.2031	0.2028	—0.0003		
				C_1	104.31	0.2694	0.2693	—0.0001		
				C	180.85	0.4671	0.4350	—0.0321	—0.0321	163.7
54	19	2.5826	0.4390	A	209.24	0.5411	0.5753	+0.0342	+0.0325	163.3
				A_1	90.67	0.2342	0.2325	—0.0017		
				M	72.82	0.1881	0.1878	—0.0003		
				C_1	101.23	0.2614	0.2612	—0.0002		
				C	188.34	0.4864	0.4541	—0.0323	—0.0323	162.3
55	19	2.5826	0.4440	A	191.26	0.4939	0.5298	+0.0359	+0.0331	164.4
				A_1	103.81	0.2681	0.2653	—0.0028		
				M	86.80	0.2242	0.2244	+0.0002		
				C_1	106.09	0.2740	0.2736	—0.0004		
				C	183.75	0.4745	0.4411	—0.0334	—0.0334	166.0
$^1/_{20}$-Normal sulphuric acid at 20°.										
56	18	2.5606	0.5759	A	205.68	0.5267	0.5790	+0.0523	+0.0469	179.6
				A_1	83.09	0.2128	0.2074	—0.0054		
				M	93.79	0.2402	0.2399	—0.0003		
				C_1	91.26	0.2337	0.2332	—0.0005		
				C	181.95	0.4659	0.4192	—0.0467	—0.0467	178.9
57	18	2.2506	0.6157	A	217.64	0.5583	0.6139	+0.0556	+0.0500	179.1
				A_1	79.83	0.2044	0.1988	—0.0056		
				M	87.94	0.2252	0.2255	+0.0003		
				C_1	85.80	0.2197	0.2193	—0.0004		
				C	186.00	0.4763	0.4267	—0.0496	—0.0496	177.7
58	19	2.5826	0.4963	A	192.46	0.4971	0.5395	+0.0424	+0.0401	178.2
				A_1	99.16	0.2561	0.2538	—0.0023		
				M	83.03	0.2144	0.2141	—0.0003		
				C_1	107.34	0.2772	0.2770	—0.0002		
				C	179.89	0.4646	0.4241	—0.0405	—0.0405	180.1

Expt. number.	Solution number.	Milligrams of H_2SO_4 per gram (1000p).	Silver in voltameter (s).	Portion.	Weight of portion (W).	Initial content (pW).	Final content (a).	Change ($a-p$W).	Total change (a_1-pWa) and (a_2-pWc).	Transport number (1000n).
59	19	2.5826	0.4790	A	193.16	0.4989	0.5401	+0.0412	+0.0378	174.1
				A_1	103.88	0.2683	0.2649	—0.0034		
				M	66.12	0.1708	0.1709	+0.0001		
				C_1	101.58	0.2623	0.2623	0.0000		
				C	180.56	0.4664	0.4284	—0.0380	—0.0380	175.0
60	19	2.5826	0.4585	A	213.24	0.5507	0.5905	+0.0398	+0.0372	179.0
				A_1	89.25	0.2305	0.2279	—0.0026		
				M	63.32	0.1635	0.1633	—0.0002		
				C_1	101.12	0.2612	0.2613	+0.0001		
				C	197.12	0.5091	0.4716	—0.0375	—0.0375	180.5
61	21	2.4340	0.2882	A	194.49	0.4734	0.4965	+0.0231	+0.0231	176.8
				A_1	95.32	0.2320	0.2317	—0.0003		
				M	64.68	0.1574	0.1575	+0.0001		
				C_1	89.56	0.2180	0.2178	—0.0002		
				C	192.49	0.4685	0.4449	—0.0236	—0.0236	180.7
$^1/_{20}$-Normal sulphuric acid at 32°.										
62	20	2.4608	0.5068	A	215.58	0.5305	0.5794	+0.0489	+0.0444	193.2
				A_1	84.54	0.2080	0.2035	—0.0045		
				M	55.47	0.1365	0.1361	—0.0004		
				C_1	88.32	0.2173	0.2169	—0.0004		
				C	202.67	0.4987	0.4547	—0.0440	—0.0440	191.6
63	20	2.4608	0.5441	A	210.72	0.5185	0.5718	+0.0533	+0.0473	191.8
				A_1	87.04	0.2142	0.2082	—0.0060		
				M	61.21	0.1506	0.1503	—0.0003		
				C_1	87.06	0.2142	0.2142	0.0000		
				C	198.35	0.4881	0.4412	—0.0469	—0.0469	190.2
64	20	2.4608	0.5165	A	213.09	0.5244	0.5728	+0.0484	+0.0445	190.0
				A_1	87.60	0.2156	0.2117	—0.0039		
				M	57.61	0.1418	0.1417	—0.0001		
				C_1	88.26	0.2172	0.2169	—0.0003		
				C	204.49	0.5032	0.4584	—0.0448	—0.0448	191.4
65	20	2.4608	0.5301	A	202.33	0.4979	0.5496	+0.0517	+0.0459	191.0
				A_1	88.21	0.2171	0.2113	—0.0058		
				M	76.46	0.1881	0.1879	—0.0002		
				C_1	90.45	0.2226	0.2223	—0.0003		
				C	196.88	0.4845	0.4386	—0.0459	—0.0459	191.1
66	20	2.4608	0.4771	A	211.82	0.5212	0.5655	+0.0443	+0.0414	191.4
				A_1	88.01	0.2166	0.2137	—0.0029		
				M	58.09	0.1429	0.1427	—0.0002		
				C_1	89.14	0.2194	0.2189	—0.0005		
				C	197.49	0.4860	0.4450	—0.0410	—0.0410	190.5

Expt. number.	Solution number.	Milligrams of H_2SO_4 per gram (1000p).	Silver in voltameter (s).	Portion.	Weight of portion (W).	Initial content (pW).	Final content (a).	Change (a—pW).	Total change (a_1—pW$_a$) and (a_2—pW$_c$).	Transport number (1000n).
67	21	2.4340	0.5109	A	216.44	0.5268	0.5752	+0.0484	+0.0447	193.0
				A_1	89.21	0.2171	0.2134	—0.0037		
				M	67.09	0.1633	0.1636	+0.0003		
				C_1	89.31	0.2174	0.2169	—0.0005		
				C	194.82	0.4742	0.4294	—0.0448	—0.0448	193.5

$^1/_{50}$-Normal sulphuric acid at 8°.

Expt. number.	Solution number.	Milligrams of H_2SO_4 per gram (1000p).	Silver in voltameter (s).	Portion.	Weight of portion (W).	Initial content (pW).	Final content (a).	Change (a—pW).	Total change (a_1—pW$_a$) and (a_2—pW$_c$).	Transport number (1000n).
68	22	1.0337	0.2178	A	195.08	0.2016	0.2202	+0.0186	+0.0165	166.9
				A_1	99.96	0.1033	0.1012	—0.0021		
				M	47.66	0.0493	0.0491	—0.0002		
				C_1	105.31	0.1089	0.1087	—0.0002		
				C	185.03	0.1913	0.1748	—0.0165	—0.0165	166.9
69	22	1.0337	0.2060	A	230.21	0.2380	0.2555	+0.0175	+0.0160	171.1
				A_1	74.07	0.0766	0.0751	—0.0015		
				M	79.31	0.0820	0.0818	—0.0002		
				C_1	88.57	0.0916	0.0912	—0.0004		
				C	202.28	0.2091	0.1934	—0.0157	—0.0157	167.9
70	23	1.0218	0.2067	A	203.49	0.2079	0.2261	+0.0182	+0.0159	169.1
				A_1	91.76	0.0938	0.0915	—0.0023		
				M	85.44	0.0873	0.0870	—0.0003		
				C_1	99.69	0.1019	0.1016	—0.0003		
				C	179.48	0.1834	0.1676	—0.0158	—0.0158	168.0
71	23	1.0218	0.2112	A	189.27	0.1934	0.2113	+0.0179	+0.0162	169.0
				A_1	93.50	0.0955	0.0938	—0.0017		
				M	92.03	0.0940	0.0942	+0.0002		
				C_1	96.70	0.0988	0.0986	—0.0002		
				C	183.50	0.1875	0.1714	—0.0161	—0.0161	168.0
72	24	1.0218	0.2022	A	204.91	0.2094	0.2262	+0.0168	+0.0155	168.9
				A_1	91.83	0.0938	0.0925	—0.0013		
				M	63.47	0.0649	0.0645	—0.0004		
				C_1	90.09	0.0921	0.0922	+0.0001		
				C	201.35	0.2057	0.1903	—0.0154	—0.0154	167.8
73	24	1.0732	0.2050	A	204.27	0.2192	0.2365	+0.0173	+0.0156	167.7
				A_1	95.88	0.1029	0.1012	—0.0017		
				M	75.28	0.0808	0.0805	—0.0003		
				C_1	89.82	0.0964	0.0962	—0.0002		
				C	204.00	0.2189	0.2032	—0.0157	—0.0157	168.7

$^1/_{50}$-Normal sulphuric acid at 20°.

Expt. number.	Solution number.	Milligrams of H_2SO_4 per gram (1000p).	Silver in voltameter (s).	Portion.	Weight of portion (W).	Initial content (pW).	Final content (a).	Change (a—pW).	Total change (a_1—pW$_a$) and (a_2—pW$_c$).	Transport number (1000n).
74	22	1.0337	0.2330	A	192.61	0.1991	0.2202	+0.0211	+0.0190	179.7
				A_1	105.38	0.1089	0.1068	—0.0021		
				M	64.52	0.0667	0.0666	—0.0001		
				C_1	104.28	0.1078	0.1077	—0.0001		
				C	173.80	0.1797	0.1605	—0.0192	—0.0192	181.5

Expt. number.	Solution number.	Miligrams of H_2SO_4 per gram (1000p).	Silver in voltameter (s).	Portion.	Weight of portion (W).	Initial content (pW).	Final content (a).	Change (a—pW).	Total change (a_1-pW_a) and (a_2-pW_c).	Transport number (1000n).
75	22	1.0537	0.2158	A	204.98	0.2119	0.2315	+0.0196	+0.0178	181.7
				A_1	92.29	0.0954	0.0936	—0.0018		
				M	82.04	0.0848	0.0845	—0.0003		
				C_1	94.16	0.0973	0.0970	—0.0003		
				C	198.79	0.2055	0.1878	—0.0177	—0.0177	180.7
76	23	1.0218	0.2408	A	198.29	0.2026	0.2252	+0.0226	+0.0201	183.9
				A_1	93.30	0.0953	0.0928	—0.0025		
				M	72.07	0.0736	0.0737	+0.0001		
				C_1	97.43	0.0996	0.0995	—0.0001		
				C	193.80	0.1980	0.1782	—0.0198	—0.0198	181.0
77	23	1.0218	0.2312	A	201.68	0.2061	0.2281	+0.0220	+0.0191	182.0
				A_1	92.27	0.0943	0.0914	—0.0029		
				M	78.03	0.0797	0.0797	0.0000		
				C_1	94.35	0.0964	0.0964	0.0000		
				C	190.70	0.1949	0.1758	—0.0191	—0.0191	182.0
78	24	1.0732	0.2514	A	218.09	0.2341	0.2573	+0.0232	+0.0206	180.5
				A_1	82.79	0.0889	0.0863	—0.0026		
				M	67.68	0.0726	0.0722	—0.0004		
				C_1	89.82	0.0964	0.0962	—0.0002		
				C	202.45	0.2173	0.1967	—0.0206	—0.0206	180.5
79	24	1.0732	0.2445	A	217.95	0.2339	0.2567	+0.0228	+0.0196	176.6
				A_1	82.73	0.0888	0.0856	—0.0032		
				M	71.19	0.0764	0.0765	+0.0001		
				C_1	86.66	0.0930	0.0927	—0.0005		
				C	201.47	0.2162	0.1961	—0.0201	—0.0201	181.1
$^1/_{50}$-Normal sulphuric acid at 32°.										
80	25	0.9948	0.2636	A	217.93	0.2168	0.2424	+0.0256	+0.0228	190.6
				A_1	88.15	0.0877	0.0849	—0.0028		
				M	62.47	0.0621	0.0622	+0.0001		
				C_1	87.73	0.0873	0.0870	—0.0003		
				C	196.87	0.1959	0.1730	—0.0229	—0.0229	191.4
81	25	0.9948	0.2714	A	208.64	0.2076	0.2351	+0.0275	+0.0238	193.2
				A_1	88.74	0.0883	0.0846	—0.0037		
				M	74.69	0.0743	0.0746	+0.0003		
				C_1	86.63	0.0862	0.0860	—0.0002		
				C	200.13	0.1991	0.1755	—0.0236	—0.0236	191.6
82	25	0.2262	0.2262	A	210.60	0.2095	0.2312	+0.0217	+0.0200	194.8
				A_1	87.12	0.0867	0.0850	—0.0017		
				M	69.63	0.0693	0.0688	—0.0005		
				C_1	83.98	0.0835	0.0838	+0.0003		
				C	208.05	0.2070	0.1874	—0.0196	—0.0196	190.9

Expt. number.	Solution number.	Milligrams of H_2SO_4 per gram ($1000p$).	Silver in voltameter (s).	Portion.	Weight of portion (W).	Initial content (pW).	Final content (a).	Change ($a-p$W).	Total change (a_1-pW$_a$) and (a_2-pW$_c$).	Transport number ($1000n$).
83	25	0.2262	0.2353	A	206.72	0.2056	0.2293	+0.0237	+0.0203	190.1
				A_1	87.19	0.0867	0.0833	−0.0034		
				M	55.73	0.0554	0.0552	−0.0002		
				C_1	81.19	0.0808	0.0805	−0.0003		
				C	204.50	0.2034	0.1829	−0.0205	−0.0205	191.9
84	26	1.0132	0.2434	A	212.52	0.2153	0.2401	+0.0248	+0.0211	191.0
				A_1	85.64	0.0868	0.0831	−0.0037		
				M	65.55	0.0664	0.0660	−0.0004		
				C_1	88.50	0.0897	0.0896	−0.0001		
				C	203.23	0.2059	0.1851	−0.0208	−0.0208	188.3
85	26	1.0132	0.2455	A	208.33	0.2111	0.2366	+0.0255	+0.0214	192.0
				A_1	88.54	0.0897	0.0856	−0.0041		
				M	61.66	0.0625	0.0623	−0.0002		
				C_1	85.66	0.0868	0.0866	−0.0002		
				C	204.33	0.2070	0.1860	−0.0210	−0.0210	188.5

In general, it may be said that the current was passed from two and a half to three hours in all the experiments at 8° and at 20°, while in those at 32° the time was somewhat less than this on account of the more rapid electrolytic action. In experiment 61, however, the current was passed only one and three-fourth hours. In experiments 24 and 25, and 30 and 31 a current was used of about twice the strength of that employed in the other experiments at the same concentrations. It will be observed that no experiments were made at other than 20° with acid of the concentrations, normal, half-normal and fifth-normal.

If the numbers in column 7 represented the exact initial content of the different portions, the factors $\frac{a_1-p\text{W}_a}{s}k$ of formula (4) and $\frac{p\text{W}_c-a_2}{s}k$ of formula (8), would at once give the value of the transport number. But the numbers of column 7 are calculated from those of column 6, and in this column the weight of the respective portions, after electrolysis, is given, which is manifestly different from the weight of these portions before electrolysis. Hence the need of the other factors in formulas (4) and (8), which are to be looked upon as corrections applied on account of our ignorance of the true weight of the several portions prior to electrolysis. These corrections are the subtraction of pl in formula (4) and then multiplying by the factor $\frac{1}{1-p}$ in both formulas. These corrections become smaller as the concentration becomes less. With fiftieth-normal sulphuric acid pl has become so small that it has no appreciable effect on the value of the transport number. The factor $\frac{1}{1-p}$ at this concentration affects the transport number by 1 or 2 units in the first decimal place, and has not, therefore, been neglected in the calculation.

A summary of the transport numbers is given in Table VI. Both the actual and the percentage average deviation of the individual numbers from the mean are shown.

TABLE VI.

	Normal H_2SO_4, 20°.		N/2 H_2SO_4, 20°.		N/5 H_2SO_4, 20° (S.A.).[1]	
	Anode.	Cathode.	Anode.	Cathode.	Anode.	Cathode.
	185.3[1]	189.8[1]	188.0	185.5	178.5	176.9
	191.7[1]	194.0[1]	193.6	192.4	174.8	180.4
	182.7[1]	182.4[1]	182.3	182.0	176.2	177.9
	197.8	199.4	191.5	194.4	180.7	183.0
	180.9	182.5	185.5	183.5	182.2	181.1
	184.4	187.2	181.7	182.9	185.6	188.1
	197.4	193.5				
	183.4	182.1				
	181.6	181.8				
Mean,	187.2	188.1	187.1	186.8	179.7	181.2
Mean of both,	187.7		186.9		180.5	
a.d.,	5.45		4.2		3.0	
Percentage a.d.,	2.9		2.2		1.7	

	N/10 H_2SO_4, 8°.		N/10 H_2SO_4, 20° (S.A.).[1]		N/10 H_2SO_4, 20°.		N/10 H_2SO_4, 32°.	
	Anode.	Cathode.	Anode.	Cathode.	Anode.	Cathode.	Anode.	Cathode.
	160.2	161.9	171.9	174.3	177.0	176.8	192.2	191.7
	168.4	162.0	168.5	169.8	177.5	177.9	192.5	191.9
	164.1	161.0	180.3	179.7	176.2	173.9	191.2	192.3
	168.1	166.3	175.3	173.7	177.6	177.0	192.7	191.8
	168.8	168.2	175.2	176.0	177.4	176.9	191.1	190.8
	161.3	162.4	174.5	174.9	174.1	174.5	191.3	190.4
Mean,	165.2	163.6	174.3	174.7	176.6	176.2	191.8	191.5
Me'n of b'th,	164.4		174.5		176.4		191.7	
a.d.,	3.0		2.4		1.1		0.6	
P'rc't'ge, a.d.,	1.8		1.4		0.6		0.3	

[1] This indicates the numbers obtained with the smaller apparatus. They are taken from Table IV.

TABLE VI—(*Continued*).

	N/20 H_2SO_4, 8°.		N/20 H_2SO_4, 20° (S.A.).[1]		N/20 H_2SO_4, 20°.		N/20 H_2SO_4, 32°.	
	Anode.	Cathode.	Anode.	Cathode.	Anode.	Cathode.	Anode.	Cathode.
	164.1	165.2	174.2	179.7	179.6	178.9	193.2	191.6
	164.2	163.1	179.0	172.4	179.1	177.7	191.8	190.2
	163.4	163.9	174.5	178.8	178.2	180.1	190.0	191.4
	163.1	163.7	175.0	176.4	174.1[1]	175.0[1]	191.0	191.1
	163.3	162.3			179.0	180.5	191.4	190.5
	164.4	166.0			176.8	180.7	193.0	193.5
Mean,	163.4	164.0	175.7	176.8	178.5	179.6	191.7	191.4
Me'n of b'th,	163.7		176.3		179.1		191.6	
a.d.,	0.7		2.2		0.9		0.9	
P'rc't'ge, a.d.,	0.4		1.3		0.5		0.5	

	N/50 H_2SO_4, 8°.		N/50 H_2SO_4, 20°.		N/50 H_2SO_4, 32°.	
	Anode.	Cathode.	Anode.	Cathode.	Anode.	Cathode.
	166.9	166.9	179.7	181.5	190.6	191.4
	171.1	167.9	181.7	180.7	193.2	191.6
	169.1	168.0	183.9	181.0	194.8	190.9
	169.0	168.0	182.0	182.0	190.1	191.9
	168.9	167.8	180.5	180.5	191.0	188.3
	167.7	168.7	176.6	181.1	192.0	188.5
Mean,	168.8	167.9	180.7	181.1	192.0	190.4
Mean of both,	168.1		180.9		191.2	
a.d.,	0.8		1.1		1.3	
Percentage, a.d.,	0.5		0.6		0.7	

The results obtained with normal sulphuric acid, both in the smaller apparatus and in the larger one, have been averaged together. The average deviation from the mean is considerable in either case, and there is no reason for assuming one set any more trustworthy than the other. With the more dilute solutions, *viz.*, tenth- and twentieth-normal, the case is somewhat different, for the average deviation from the mean of the numbers obtained with the smaller apparatus is more than twice as great as that of those obtained with the larger apparatus.

Neglecting the results obtained with the smaller apparatus with the concentrations tenth- and twentieth-normal, the accuracy seems to increase as the concentration decreases to twentieth-normal, and

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[1] Omitted in calculating the mean, as the deviation of these from the mean is more than twice that of any of the other numbers.

then become less at fiftieth-normal. This was to be expected under the existing conditions for the following reasons: At the higher concentrations the change in concentration of the anode and cathode portions is small, compared with the total amount of acid in these portions, and the analytical errors have, therefore, a relatively large effect on the value of the transport number. This source of error becomes less with increasing dilution. However, when the concentration becomes small, fiftieth-normal for instance, disturbances caused by manipulation of the solution and by the flow of the current, begin to make themselves apparent and consequently decrease the accuracy of the experiment.

Table VII gives a list of the transport numbers for the different concentrations and temperatures, which, according to these experiments, seem to be the most trustworthy.

TABLE VII.

Concentration.	Temp. 8°.	20°.	32°.
Normal	....	187.7	....
$^1/_2$-Normal	....	186.9	....
$^1/_5$-Normal	....	180.5	....
$^1/_{10}$-Normal	164.4	176.4	191.7
$^1/_{20}$-Normal	163.7	179.1	191.6
$^1/_{50}$-Normal	168.1	180.9	191.2

The complete set of numbers at 20° seems to show that the transport number first decreases with the concentration and then increases. Most of this increase lies between the concentrations tenth- and twentieth-normal. There is no such increase noticed between the same concentrations at 8° and 32°, although there is an increase shown at 8° at the next concentration, *viz.*, fiftieth-normal. It, therefore, seems probable that the number 176.4 is for some unaccountable reason too low. On the whole, the transport numbers found at the different temperatures with the three most dilute solutions are sufficiently constant to indicate the existence of no HSO_4 ions beyond the concentration tenth-normal, or to indicate that some compensation has taken place in the dissociation of ions, possibly even more complex than HSO_4.

Since the number 176.4, found at 20° with tenth-normal acid, is as trustworthy experimentally as the numbers found with twentieth- and fiftieth-normal acid, the average of all three of the numbers, *viz.*, 178.8, is taken as the most probable value of the transport number of sulphuric acid in dilute solution at 20°.

The temperature coefficients calculated from the numbers in Table VII vary from 0.9 to 1.3, the average being 1.1, or when the transport numbers are not multiplied by 1000, 0.0011. In dilute solutions, therefore,

$$n_t = 0.1788 + 0.0011(t-20°).$$

VI. COMPARISON WITH RESULTS OF PREVIOUS INVESTIGATIONS.

A table containing most of the results of previous investigations on the transport number of sulphuric acid has already been given (Table I). My results agree perhaps best with those of Bein, although his results are somewhat higher at corresponding temperatures. Starck's results, with and without a diaphragm, are widely divergent from each other. The numbers obtained by him at small concentrations with a diaphragm are undoubtedly very much too low.

The results here reported with sulphuric acid can lay no such claim to exactness as those of Noyes and Sammet with hydrochloric acid. The average deviation from the mean of their results with sixtieth-normal HCl[1] is about one-half that of mine with twentieth-normal H_2SO_4. Some reasons for the greater trustworthiness of their results are: Hydrochloric acid can be determined as silver chloride more accurately than sulphuric acid as barium sulphate. Noyes and Sammet employed a silver anode; no secondary products thus went into solution around this pole to change the nature of the medium; the capacity of their apparatus was greater than that of mine. However, the results here reported with sulphuric acid are, without doubt, the most trustworthy of any yet obained with this acid.

VII. THE EQUIVALENT CONDUCTIVITY OF DISSOCIATED SULPHURIC ACID.

The most recent work on the conductivity of dilute solutions of sulphuric acid is by Jones and Douglas.[2] Their results are expressed as molecular conductivity in reciprocal Siemens units. When recalculated to equivalent conductivity in reciprocal ohms they find, for Λ_∞ at 15°, 346.5 and at 25°, 380.0. These numbers are the practically constant values obtained from the conductivity at the dilutions 2048, 4096 and 8192 liters, after subtracting the conductivity of the water employed in preparing the solutions. They are undoubtedly much too low for the following reasons:

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[1] This Journal, **24**, 958 (1902).

[2] *Am. Chem. J.*, **26**, 436 (1901).

In determining the conductivity of a weak solution of an acid or of a base the subtraction of the conductivity of the water used in the preparation of the solutions is now generally recognized as leading to erroneous results. If one plots in a curve the results of Jones and Douglas at the dilutions just preceding those mentioned, the form of the curve shows that the maximum value is by no means so near at hand. Interpolating from the values of Λ_∞ at 15° and 25°, Λ_∞ at 18° would be approximately 356.5, while Kohlrausch[1] has found $\Lambda = 368$ at 18° at a dilution of 2000 liters.

The conductivity of an acid at infinite dilution is much more difficult to estimate than that of a neutral salt. Even the strong monobasic acids, as hydrochloric and nitric acids, yield no definite value for this quantity as far as can be estimated from the conductivity alone. It is, therefore, scarcely to be expected that Λ_∞ of sulphuric acid can ever be accurately determined in this manner. We shall, therefore, proceed to estimate this quantity indirectly.

The most trustworthy determinations we possess of the transport numbers of sulphates are those by Noyes[2] with potassium sulphate and those by Steele and Denison[3] with calcium sulphate. A little less trustworthy, perhaps, are those of Jahn and Metelka[4] with copper sulphate. The transport numbers of these electrolytes, together with the migration numbers, calculated by their aid, are given in Table VIII. They are for a temperature of 18°. In the second column are the most probable values for Λ_∞ of these electrolytes. The migration numbers of the anion and cation are shown under l_a and l_c, respectively.

TABLE VIII.

Electrolyte.	Λ_∞.	n.	l_a.	l_c.
K_2SO_4	135.5	0.504	68.3	67.2
$CaSO_4$	122.0	0.559	68.2	53.8
$CuSO_4$	118.0	0.625	73.7	44.3

The values of the migration number of the SO_4 ion, obtained from the first two electrolytes, agree excellently, but the one from $CuSO_4$ is much higher. It may be said, however, that the migration number of the K ion, derived from potassium sulphate, is somewhat higher than the most probable value of this number

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[1] See Kohlrausch and Holborn : "Leitvermögen der Elektrolyte," p. 160.

[2] This Journal, **23**, 55 (1901).

[3] *Ibid.*, **81**, 466 (1902).

[4] *Ztschr. phys. Chem.*, **37**, 710 and 711 (1901).

(about 64.5), derived from the more trustworthy experiments with potassium chloride. This seems to indicate that the migration number of the SO_4 ion, derived from potassium sulphate, is too low, and the number found with copper sulphate is not, therefore, to be discarded. Consequently it will be assumed that the mean of the three numbers in the above table is the most probable value of this quantity. This is 70, which is also the value adopted by Kohlrausch in 1898.

Although in the case of a dibasic acid the calculation of the equivalent conductivity or migration number of the H ion can lead to no final results, nevertheless, it will be interesting to compare the number obtained with sulphuric acid with that obtained from other sources. At 18° the transport number of sulphuric acid, according to the above formula, is $0.1788 - 0.0022 = 0.1766$. Combining this with 70, the migration number just given for the SO_4 ion, we obtain 396 for V_∞ of H_2SO_4 at 18° and 326 as the migration number of the H ion at the same temperature. Noyes and Sammet have derived the value 330 for the latter quantity from transference experiments with hydrochloric acid. In 1898 Kohlrausch considered the most probable value to be 318.

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THE HYDRATION OF MILK-SUGAR IN SOLUTION.[1]

By C. S. HUDSON.

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CONTENTS.

I. THE ANHYDROUS AND HYDRATED FORMS OF MILK-SUGAR.

In a recent publication[2] I have shown the existence in aqueous

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[1] Read at the Providence meeting of the American Chemical Society.

[2] *Ztschr. phys. Chem.*, 44, 487-494 (1903).