This method has been in successful use in these laboratories for nearly a year. By its use it is possible to saponify esters by boiling with a 50 per cent. solution of potassium hydroxide (using a return condenser) or to boil concentrated sulphuric acid in a test-tube, without any bumping. Only two cases have been met with in which bumping persisted after the capillary was introduced. Both were reactions carried out with a return condenser. Although the bumping continued, it was so greatly lessened that the liquid was not thrown out of the upper end of the condenser and there was no danger of having the flask broken.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY,
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[CONTRIBUTIONS FROM THE LABORATORIES OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY.]

THE EQUIVALENT CONDUCTIVITY OF THE HYDROGEN ION DERIVED FROM TRANSFERENCE EXPERIMENTS WITH HYDROCHLORIC ACID.

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(SECOND PAPER.)

IN a previous communication[1] bearing the same title made by A. A. Noyes and G. V. Sammet three series of determinations of the transference-numbers for $^1/_{60}$ molar hydrochloric acid, at 10°, 20°, and 30°, respectively, were presented, from which by combination with the fairly accurately known values for the conductivity of the chlorine ion, the following ones for that of the hydrogen ion were obtained.

t.	10°.	18°.	20°.	25°.	30°.
Λ	288.7	329.8	340.0	364.9	389.1

These values are 4 to 6 per cent. higher than those derived by Ostwald and Kohlrausch through a consideration of the change of conductivity of strong acids with the dilution. It was not considered possible that this divergence could arise from experimental errors in the transference determinations; but it was suggested that it might be due, at any rate in part, to a difference in the transference-numbers of the acid at extreme dilution and at the investigated dilution of 60 liters. To test this possibility, a new series of determinations has been made at 20° with an approxi-

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

mately $^1/_{180}$ molar acid; and it is the purpose of this article to communicate the results. In this investigation I have been ably assisted by Mr. Raymond Haskell.

The method employed was substantially identical with that described in the previous article. The acid used was prepared from pure salt and sulphuric acid, washed with water, absorbed in a little pure water, and diluted with water having a conductivity of 1.5×10^{-6} reciprocal ohms. Three separate solutions, numbered 10, 11 and 12 in the table, were employed. These yielded respectively 0.7870, 0.7815, and 0.8240 milligram AgCl per gram of solution.

The data are given in detail in the following table, which is arranged like those previously published. The headings are for the most part self-explanatory. The content is always expressed in milligrams AgCl per gram of solution. The silver precipitated in the voltameters is also given in milligrams. The "transference-numbers" of the table are the actual values for the anion multiplied by 1000. The letters in the third column have the following significance : K = cathode portion ; A = anode portion ; M_K and M_A the middle portions adjoining these, respectively; M, the middle portion of all, lying between the last two.

$^1/_{180}$-MOLAR HCL AT 20°.

Expt. No.	Solution No.	Portion.	Weight of portion. Grams.	Initial content.	Final content.	Change in content.	Total change in content.	Silver in voltameters.	Transference number.
33	10	K	346.42	272.6	223.7	—48.9	—48.9	217.2	169.4
		M_K	210.26	165.4	165.2	— 0.2	.....	217.4	....
		M	177.44	139.6	138.1	— 1.5	.....	217.1	....
34	11	K	343.00	268.1	230.7	—37.4	—37.4	168.4	166.9
		M_K	142.68	111.5	111.7	+ 0.2	.....	168.7	....
		M	163.00	127.4	127.1	— 0.3	.....	168.7	....
35	11	K	340.56	266.2	229.3	—36.9	—36.9	167.1	166.3
		M_K	160.37	125.3	125.5	+ 0.2	.....	167.2	....
		M	168.81	131.9	130.8	— 1.1	.....	167.4	....
36	11	K	356.44	278.6	237.5	—41.1	—41.1	186.1	166.4
		M_K	160.64	125.5	125.5	± 0.0	.....	186.0	....
		M	183.78	143.6	140.9	— 2.7	.....	185.8	...
37	11	K	349.28	273.0	234.8	—38.2	—38.2	172.0	167.2
		M_K	160.89	125.7	125.5	— 0.2	.....	171.8	....
		M	187.42	146.5	142.5	— 4.0	.....	172.1	....
		A	487.95	381.4	424.1	+42.7	+38.7	....	169.3

Expt. No	Solution No.	Portion.	Weight of portion. Grams.	Initial content.	Final content.	Change in content.	Total change in content.	Silver in voltameters.	Transference number.
38	12	K	319.12	263.0	221.8	—41.2	--41.2	185.0	167.7
		M_K	162.63	134.0	133.7	— 0.3	.....	185.0	....
		M	177.87	146.6	142.2	— 4.4	.....	185.1	....
		A	451.47	372.0	417.4	+45.4	+41.0	....	166.8
39	12	K	323.36	266.5	232.4	—34.1	—34.1	155.8	164.6
		M_K	136.82	112.7	112.6	— 0.1	.....	156.0	....
		M	169.80	139.9	138.3	— 1.6	.....	156.0	....
		A	451.46	372.0	410.9	+38.9	+37.3	....	180.0
40	12	K	305.85	252.0	210.1	—41.9	—41.9	188.0	167.7
		M_K	156.41	128.9	128.6	— 0.3	.....	188.3	....
		M	181.01	149.2	143.3	— 5.9	.....	188.1	....
		A	431.19	355.3	403.3	+48.0	+42.1	....	168.5
41	12	K	306.64	252.7	216.9	—35.8	—35.8	167.9	160.5
		M_K	156.91	129.3	129.5	+ 0.2	.....	168.0	....
		M	177.42	146.2	143.4	— 2.8	.....	167.9	....
		A	445.75	367.3	407.1	+39.8	+37.0	....	165.9
42	12	K	309.99	255.4	219.2	—36.2	—36.2	163.4	166.4
		M_K	162.39	133.8	133.6	— 0.2	.....	163.9	....
		M	172.73	142.3	139.3	— 3.0	.....	163.8	....
		A	453.88	374.0	414.2	+40.2	+37.2	...	170.9

The transference numbers are summarized in the following table. The values marked with an asterisk were omitted in the calculation of the mean.

$^1/_{180}$-MOLAR HCL AT 20°.

Expt. No.	Cathode.	Anode.
33	169.4	....
34	166.9	....
35	166.3	....
36	166.4	....
37	167.2	169.3
38	167.7	166.8
39	164.6	180.0*
40	167.7	168.5
41	160.5*	165.9
42	166.4	170.9
Mean,	167.0	168.3
a.d.,	0.9	1.5
A.D.,	0.3	0.7

Final mean, 167.1

A.D., 0.3

The agreement of the cathode values among themselves is nearly as close as it was with the $^1/_{60}$ molar solution (where the a.d. was 0.8). The change in content of the adjoining portion M_K is also very small, mostly 0.2 mg. or less, and has opposite signs in different experiments. Even if this were added to the change in the cathode portion, it would increase the mean of the transference values by only 0.2 per cent. The anode values are much more discordant than the cathode values, owing to the more difficult manipulation involved in the preparation of the anode portion for analysis.[1] Nevertheless, the agreement of their mean with that of the cathode values within 0.8 per cent. is a confirmation of the substantial accuracy of the latter.

The final mean derived from the earlier determinations at 20° with $^1/_{60}$ molar solutions was 167.43 (A.D., 0.25). This agrees with the final mean of the present determinations (167.1: A.D., 0.3) at 20° with $^1/_{180}$ molar solutions within 0.25 per cent. (and within the limits of the sum of the A.D.'s). Hence it is justifiable to conclude that the transference-number of hydrochloric acid does not change appreciably with increase of the dilution after that of 60 liters is reached. The equivalent conductivities of the hydrogen ion derived in the previous article and summarized at the beginning of this one were therefore not vitiated by this assumption, which was made in their deduction.

The deviation between these values and those derived by extrapolation from the conductivities of acids still requires explanation. Whether it can be due to error in the estimate of the effect of the impurities of the water on the conductivities at great dilution could probably be determined through an investigation of that effect. Such an investigation will be undertaken in these laboratories.

BOSTON, November, 1902.

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[1] In the first four experiments the anode results had to be rejected, owing to the use in the process of a large and indefinite amount of ammonium hydroxide, which was afterwards found to contain an appreciable quantity of chloride. In the later experiments a smaller and definite quantity of ammonia was used, and its chlorine-content determined and subtracted.