(112) *Test Analysis, Group III.*—The following mixture was made up and analyzed by the method described under the above head. 0.5 gram were taken for analysis.

1.0 gram potassium bitartrate
1.0 gram calcium tartrate
0.5 gram alum
1.0 gram phosphate tartar substitute

This mixture contains 32.9 per cent. tartaric acid.
Amount found : 33.4 per cent. tartaric acid.

UNIVERSITY OF MANITOBA, } June, 1902.
UNIVERSITY OF TORONTO, }

[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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Received August 1, 1902.

I. PURPOSE OF THE INVESTIGATION.

IN calculating the degree of dissociation of a weak acid from its conductivity, it is first necessary to determine in some indirect way the value of its molar conductivity that corresponds to complete dissociation. This has been commonly done by adding to the molar conductivity of its sodium salt at extreme dilution the difference between that of hydrochloric acid and that of sodium chloride. The results so obtained may, however, be in error by a considerable amount, by reason of the fact that impurities in the water make it impossible to determine accurately the conductivity of hydrochloric acid (or any other strong acid) at a dilution where the dissociation is substantially complete. The values ordinarily employed have been obtained, therefore, by estimating, with the help of the change in the observed conductivity with the dilution, the probable effect of the impurities, and by making allowance for this effect.

A second, independent method that might be applied to the calculation of the molar conductivity of completely dissociated hydrochloric acid is to divide the equivalent conductivity of the chlorine ion by the transference number of moderately dilute hydrochloric acid. The former of these two values is already known with a fair degree of accuracy and certainty as a result of many transference and conductivity investigations on sodium and potassium chlorides. The latter has also been determined by Hittorf, Bein, Hopfgartner, and Jahn and Bogdan in connection with other transference experiments; but its importance in furnishing a reliable basis for the calculation of the dissociation-constants of acids has seemed to us to make it worthy of a more thorough investigation, especially as we had reason to expect that by employing the method previously described in this Journal[1] accurate results could be attained. It is the purpose of this article to present the results of such an investigation carried out with hydrochloric acid, mainly of 1/60 normal concentration and at the three temperatures of 10°, 20°, and 30°. To assist in the interpretation of the results, new determinations of the conductivity of the acid at these temperatures are also communicated.

II. PREPARATION AND STANDARDIZATION OF SOLUTIONS.

To insure their purity, all of the hydrochloric acid solutions submitted to electrolysis, except those numbered 1 and 2 for which chemically pure commercial acid was used, were made by diluting especially prepared concentrated solutions with water which had been distilled from alkaline permanganate. The concentrated acid used in the preparation of the solutions numbered 6, 7, 8, and 9 was made by generating hydrochloric acid gas by the action of pure concentrated sulphuric acid upon sodium chloride purified by previous precipitation with hydrochloric acid gas, conducting it through a wash-bottle containing a little water, and then absorbing it in pure water. For preparing solutions 3, 4, and 5, hydrochloric acid gas was generated by dropping concentrated sulphuric acid into pure concentrated hydrochloric acid solution; the gas was then washed and absorbed as before, and the resulting solution was appropriately diluted. The water used for all of the solutions employed in this investigation had at 25° a specific conductivity of less than 1.5×10^{-6} reciprocal ohms.

The hydrochloric acid solutions were standardized by precipitating 150-gram portions with silver nitrate with the addition of 2 cc. of strong nitric acid, heating half an hour to just below boil-

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[1] Noyes: This Journal, **23**, 39.

ing, collecting the precipitates, after washing them by decantation with cold water, in platinum Gooch crucibles, and drying them at 135° for twelve hours or more till the weight was constant to 0.1 milligram.

An approximately 0.1 normal barium hydroxide solution was prepared from the recrystallized commercial product, and was preserved in a bottle so arranged with a soda-lime tube and a delivery tube that portions could be drawn from it without introducing carbon dioxide from the air. It was proved to be entirely free from chloride by evaporating 100 cc. with nitric acid and testing with silver nitrate.

This barium hydroxide solution was standardized in terms of the hydrochloric acid solutions by titrating it with the help of phenolphthalein against 150-gram portions of the acid. Throughout these experiments all measurements of solutions were made by weight, and not by volume. The barium hydroxide solution was delivered from a long cylindrical 120-cc. drop-funnel, fitted with a perforated rubber stopper with a soda-lime tube, and having its delivery tube drawn to a point 10 cm. below the stop-cock. The drop funnel was filled by connecting the end of the delivery tube with the tube leading into the barium hydroxide bottle, and drawing the solution into the funnel by applying suction at the top, thus preventing the solution from coming into contact with the air. The end of the delivery tube was capped with a small test-tube during the weighings.

III. DESCRIPTION OF THE METHOD.

The apparatus used was that designed for the transference work previously done in this laboratory.[1] It consists of two large U-tubes of a bore of 3.5 cm. and a height of 40 cm., each of which has the top of one of its arms bent at right angles and has a small upright tube sealed into this bend so that the stem of a pipette can be introduced through it to the bottom of the U-tube. During the electrolysis the bent ends of the two tubes were joined by a piece of soft rubber tubing, and the tubes were clamped in a suitable support. The cathode was a spiral of platinum wire. The anode was a round plate of silver, 2 mm. thick, just large enough to enter the tube; it was riveted to a stout silver wire, which was

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[1] Noyes: This Journal, **23**, 42 (1901).

connected with a platinum wire sealed in a glass tube that passed through a rubber stopper fitting the mouth of the U-tube. The silver anode has, over the cadmium or zinc anode which has been hitherto employed, the advantage that no foreign substance is introduced by it into the solution, since only insoluble silver chloride is formed at its surface. This makes it possible to increase the proportion of the acid transferred.

Given in outline, the method of carrying out the transference experiments consisted in passing a suitable current for three hours through the standardized hydrochloric acid solutions in the apparatus just described, determining the quantity of electricity by means of silver voltameters placed in series with it, dividing the electrolyzed solution into a cathode, an anode, and three middle portions, titrating each of these except the anode portion with barium hydroxide to determine the concentration-changes of the hydrogen ion, and precipitating all five of them with silver nitrate and weighing the precipitates to determine the concentration-changes of the chlorine ion. From the analyses of the cathode and anode portions three separate values of the transference-number were obtained, and by the analysis of the middle portions it was made certain that no error arose through convection. In a few of the experiments, those first made, the acidimetric titrations were omitted, however.

The details of the procedure were as follows: Before filling the tubes with the solution each was weighed separately, the anode tube containing its electrode. They were then joined with a piece of tight-fitting soft rubber tubing, which was wired on and completely covered with vaseline to prevent danger of leakage. The anode tube was first filled with the acid solution up to 5 or 6 cm. of the top, and then corked tightly, the electrode being adjusted so as to be about 6 to 7 cm. below the surface of the liquid. The cathode tube was then charged with the solution until it half filled the outer arm; then the stopper with the electrode was tightly inserted, and the middle part of the apparatus completely filled through the small upright tubes, which were then stoppered. It was necessary to fill the anode tube to the higher level so as to lengthen that portion; for otherwise the changes in concentration would extend too far beyond the bend, up into the inner arm of ne tube.

At least half an hour before the electrolysis was started, the tubes were immersed in a large thermostat at the proper temperature to such a depth that the middle horizontal part of the apparatus was entirely covered. When the temperatures had equalized themselves, the electrodes were connected through a switch, a 16-candle-power 220-volt lamp, a Weston milliammeter, and two silver voltameters, with the terminals of a 110-volt circuit; and the current was turned on. The silver voltameters consisted of platinum dishes (which served as the cathodes) containing a 15 per cent. silver nitrate solution, just beneath the surface of which was placed a horizontal silver plate (to serve as anode) which was wrapped with filter-paper, and supported by a silver rod riveted through it. One of these voltameters was inserted at each end of the electrolytic apparatus. The milliammeter served only to indicate roughly the strength of the current.

The electrolysis was allowed to continue for three hours in all the experiments. The current was closely watched, and, if at any time it tended to diminish, the external resistance was changed, so as to keep the current approximately constant.

At the end of the electrolysis, the cathode was removed, shaking off any drops that adhered to it, and a rubber stopper was inserted in its place. The stoppers in the middle upright tubes were then removed, and three middle portions were withdrawn slowly by means of a pipette connected with a suction pump, the tip being lowered gradually so as to be always just beneath the surface of the liquid. These portions were transferred to tared flasks and weighed. The first portion extended to just below the bend in the middle horizontal part of the tubes; the other two portions reached in the inner arms to just above the level of the bends at the bottom of the tubes. The apparatus was next removed from the thermostat and separated at the rubber band: the tubes were wiped dry on the outside: the liquid adhering to the inside of the upper part of the middle arms was also removed: and the tubes were then weighed separately.

The cathode portion was now titrated in the tube by adding barium hydroxide solution from a weighed drop-funnel such as was described in Section 2 above. It was then transferred to a beaker and analyzed for its chlorine-content in the same manner as the solution had been previously standardized. The middle portions, also, were titrated with the alkali, and then analyzed for chlorine in the same way. The anode portion when titrated with barium hydroxide was found to give utterly discordant results, owing probably to the liberation of some oxygen at the electrode and the production of a corresponding quantity of acid. It was therefore not titrated in most of the experiments. Its chlorine-content was determined in the following manner. The main solution containing silver chloride in suspension was poured into a beaker from the U-tube, which was rinsed out with enough ammonia to dissolve all the precipitate. The electrode, which was incrusted with silver chloride, was treated for an hour with concentrated ammonia with frequent rubbing; and after decanting the solution into the main solution, the electrode and the deposit of loose silver from it were warmed with nitric acid, until the surface layer had dissolved off the electrode. The solution and any residue of silver chloride remaining were washed into the main solution, which had meanwhile been filtered to remove particles of silver. The solution was now made acid with nitric acid and treated with an excess of silver nitrate, the precipitate being collected and weighed as before.

The filtrate from the silver chloride precipitate was treated with sulphurous acid and allowed to stand on a hot plate over night, in order to test it for free chlorine or oxyacids of chlorine. In only one of the final determinations did a precipitate appear; this was filtered off, washed and weighed, and added to the main quantity of the silver chloride precipitated. In several preliminary determinations, however, it was found that the anode values were abnormally low, and that the filtrate from the silver chloride gave a considerable precipitate with sulphurous acid on standing ten to twelve hours. This difficulty was entirely removed by reducing the current density. It was found that when the current was less than 4.5 milliamperes per square centimeter no free chlorine was generated.

After the electrolysis had continued for an hour or so, it was occasionally observed that the current rapidly decreased, owing to an increase in the resistance at or near the anode. This arose either from its becoming too thickly coated with silver chloride or from the solution in its immediate neighborhood becoming nearly exhausted. The first of these effects was greatly diminished by reducing the current-strength; the second, by placing the anode 6 to 8 cm. below the surface of the liquid, so that the weakened solution would rise and cause a slow stirring in the neighborhood of the electrode, thus increasing the quantity of electrolyte available for electrolysis. Under these conditions, the current could be kept practically constant during the three hours of an experiment.

In every experiment, the silver chloride formed a cloud around the anode and then extended slowly down the tube to the bend, where it formed a perfectly sharp line at the level of the top of the bend. The formation and maintenance of this sharp line showed conclusively that there was no stirring taking place in the tubes.

IV. THE EXPERIMENTAL DATA AND RESULTS.

The first experiments were made with approximately 1/20 normal hydrochloric acid; but most of the work was done upon an acid three times more dilute, as this was about the limit to which the dilution could be carried without some sacrifice of experimental accuracy. The exact concentrations of the various solutions employed are given in the following table expressed in milligrams of silver chloride per gram of solution. Each value is the mean derived from a series of analyses, and its probable accuracy is indicated by the number of these and its average deviation (A. D.).[1]

Solution number.	Analyses made.	Concentration.	A. D. of the result.
1	3	7.3651	0.0001
2	3	7.7091	0.0007
3	3	6.7519	0.0013
4	3	7.3924	0.0017
5	3	2.4813	0.0011
6	3	2.4537	0.0007
7	4	2.5268	0.0008
8	5	2.4718	0.0003
9	4	2.4789	0.0001

Two different barium hydroxide solutions were employed. The first of these, approximately 1/6 normal, was standardized separately against acid solution No. 7 and another standard hydrochloric acid solution which was not used in the final experiments, and its concentration was found to correspond to 24.203 and

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[1] This is the average deviation (a. d.) of the separate values from the mean divided by the square root of the number of values and is equal to 1.18 times the "probable error."

24.191 milligrams silver chloride per gram solution, respectively, the divergence being therefore only 0.05 per cent. The second solution, roughly 1/12 normal, was standardized against solutions Nos. 8 and 9, and its concentration was found to correspond to 12.612 and 12.600 milligrams silver chloride per gram solution, respectively (divergence, 0.1 per cent.). Each barium hydroxide solution was used in titrating, after the electrolysis, the acid solutions against which it had been standardized.

The data of the experiments and the calculated transference values are given in the following tables. The *first* column contains the number of the experiment; the *second*, the number of the acid solution used; the *third*, letters representing the different portions submitted to analysis, K signifying the cathode solution, M_K the adjoining middle portion, M the next portion, M_A the portion adjoining the anode, and A the anode portion itself; the *fourth* gives the weight in grams of the portions analyzed; the *fifth* column, vacant in the case of the first fourteen experiments, contains the number of grams of barium hydroxide solution used in neutralizing the portions after the electrolysis; the *sixth* contains the initial content expressed in milligrams of silver chloride as calculated from the weight of the portion and the standardization value; the *seventh*, the final content determined by direct weighing of the silver chloride, and, on the line below, except in the first fourteen experiments, the value of it calculated from the barium hydroxide used; the *eighth*, the change in content of the separate portions; the *ninth*, the total change in content, which includes the changes in the portions adjoining the cathode and anode; the *tenth*, the milligrams of silver precipitated in the voltameters: and the *eleventh*, the calculated transference numbers multiplied by 1000.[1]

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[1] The way in which these were calculated may be illustrated with the help of the data obtained in the second experiment. The cathode portion submitted to analysis weighed 452.76 grams and was found to yield 3158.8 mg. of silver chloride. To determine the original content the weight of the portion is multiplied by the original concentration of the solution (7.3651 mg.), which gives 3334.6. The decrease in concentration at the cathode is, therefore, 175.8 mg. Adding to this the decrease in the adjoining middle portion (1.0 mg.) and dividing by the equivalent weight of silver chloride (143.38) and by the number of equivalents of silver (803.3/107.93) precipitated in the voltameter, the transference number is found to be 0.1656.

$^1/_{20}$-MOLAR HCl AT 20°.

Expt. No. 1	Solution No. 2	Portion. 3	Weight of portion. 4	BaO_2H_2 solution used. 5	Initial content. 6	Final content. 7	Change in content. 8	Total change in content. 9	Silver in voltameters. 10	Transference numbers. 11
1	1	K	454.42	....	3346.9	3177.1	—169.8	—169.8	....	164.9
		M_K	142.03	....	1046.1	1046.2	+ 0.1	......	....	....
		M	191.04	....	1407.0	1407.2	+ 0.2	......	775.8	....
		M_A	125.84	....	926.9	924.7	— 2.2	......	....	....
		A	460.88	....	3394.5	3566.2	+171.7	—169.5	....	164.2
2	1	K	452.76	....	3334.6	3158.8	—175.8	—176.8	....	165.6
		M_K	147.35	....	1085.3	1084.3	— 1.0	.....	....	....
		M	177.29	....	1305.2	1304.9	— 0.3	......	803.3	....
		M_A	137.06	....	1009.5	1006.3	— 3.2	......	....	....
		A	468.79	....	3452.8	3631.2	+178.4	+175.2	....	164.2
3	1	K	450.38	....	3317.0	3150.8	—166.2	—166.7	....	165.9
		M_K	140.93	....	1038.0	1037.5	— 0.5	......	....	....
		M	182.69	....	1345.5	1345.3	— 0.2	......	756.6	....
		M_A	138.10	....	1017.1	1015.5	— 1.6	......	....	....
		A	474.20	....	3492.5	3662.9	+170.4	+168.8	....	167.9
4	1	K	446.61	....	3289.4	3110.4	—179.0	—179.5	....	166.3
		M_K	145.20	....	1069.4	1068.9	— 0.5	......		....
		M	181.60	....	1337.5	1337.8	+ 0.3	......	812.6 813.6	....
		M_A	121.14	....	892.2	891.2	— 1.0	......		....
		A	474.65	....	3496.0	3677.0	+181.0	+180.0	....	166.6
5	2	K	445.78	....	3436.5	3258.6	—177.9	—178.6	....	164.2
		M_K	149.21	....	1150.3	1149.6	— 0.7	......		....
		M	177.17	....	1365.8	1365.0	— 1.8	......	819.6 817.4	....
		M_A	136.20	....	1050.0	1044.3	— 5.7	......		...
		A	462.44	....	3565.0	3750.0	+185.0	+179.3	....	164.9
6	3	K	465.79	....	3144.2	2987.6	—156.6	—157.8	....	164.9
		M_K	131.02	....	884.4	883.2	— 1.2	......		....
		M	153.42	....	1035.6	1035.3	— 0.3	......	718.6 718.6	....
		M_A	141.65	....	956.1	950.8	— 5.3	......		....
		A	479.02	....	3233.5	3395.5	+162.0	+156.7	....	164.2
7	4	K	472.52	....	3493.0	3333.0	—160.0	—160.0	....	165.3
		M_K	125.31	....	926.3	926.4	+ 0.1	......		....
		M	192.57	....	1423.4	1422.5	— 0.9	......	729.1 728.0	...
		M_A	125.44	....	927.3	921.2	— 6.1	......		....
		A	469.99	....	3473.3	3640.2	+166.9	+160.8	....	166.1

Expt. No. 1	Solution No. 2	Portion. 3	Weight of portion. 4	BaO_2H_2 solution used. 5	Initial content 6	Final content. 7	Change in content. 8	Total change in content. 9	Silver in voltameters. 10	Transference numbers. 11
8	4	*K*	470.45	....	3477.8	3314.0	−163.8	−163.8	....	166.8
		M_K	136.10	....	1006.0	1005.9	− 0.1	......		....
		M	183.20	....	1354.1	1353.7	− 0.4	......	739.0 739.2	....
		M_A	132.97	....	983.0	978.8	− 4.2	......		....
		A	457.91	....	3385.0	3551.3	+167.3	+163.1	....	166.1
9	4	*K*	425.61	....	3146.2	2999.3	−146.9	−146.9	....	168.7
		M_K	142.24	....	1051.5	1051.5	± 0.0	......		....
		M	168.96	....	1249.0	1248.5	− 0.5	......	656.1 655.8	....
		M_A	136.19	....	1006.8	1002.2	− 4.6	......		....
		A	444.08	....	3282.8	3431.5	+148.7	+144.1	....	165.4

$^1/_{60}$-MOLAR HCl AT 20°.

Expt. No. 1	Solution No. 2	Portion. 3	Weight of portion. 4	BaO_2H_2 solution used. 5	Initial content 6	Final content. 7	Change in content. 8	Total change in content. 9	Silver in voltameters. 10	Transference numbers. 11
10	5	*K*	355.76	....	882.7	811.8	− 70.9	− 70.9	....	167.3
		M_K	96.06	....	238.3	238.3	± 0.0	......		....
		M	138.42	....	334.4	334.0	− 0.4	......	318.7 319.1	....
		M_A	128.67	....	319.1	318.0	− 1.4	......		....
		A	455.08	....	1129.2	1201.1	+ 71.9	+ 70.5	....	166.2
11	5	*K*	363.86	....	902.8	837.8	− 65.0	− 65.0	....	169.0
		M_K	96.28	....	238.8	238.7	− 0.1	......		....
		M	172.85	....	428.9	427.6	− 1.3	......	289.2 289.3	....
		M_A	113.91	....	282.6	282.0	− 0.6	......		....
		A	462.17	....	1146.7	1211.1	+ 65.6	+ 65.0	....	169.0
12	6	*K*	470.13	....	1154.0	1105.8	− 48.2	− 48.2	....	165.3
		M_K	139.06	....	341.3	341.6	+ 0.3	......		....
		M	198.19	....	486.5	486.6	+ 0.1	......	219.6 219.5	....
		M_A	150.33	....	369.0	367.9	− 1.1	......		....
		A	441.61	....	1084.0	1034.3	+ 49.7	+ 48.6	....	166.7
13	6	*K*	361.54	....	887.5	839.6	− 47.9	− 47.9	....	164.1
		M_K	94.13	....	231.0	231.3	+ 0.3	......		....
		M	147.26	....	361.5	361.6	+ 0.1	......	219.5 219.6	....
		M_A	187.43	....	460.2	460.3	+ 0.1	......		....
		A	420.39	....	1031.8	1080.7	+ 48.9	+ 48.9	....	167.9
14	6	*K*	483.59	....	1186.7	1123.1	− 63.6	− 63.6	....	166.3
		M_K	143.17	....	351.4	351.3	+ 0.1	......		....
		M	216.48	....	531.3	531.2	− 0.1	......	287.4 287.7	....
		M_A	106.86	....	262.3	261.1	− 1.2	......		....
		A	466.11	....	1143.8	1209.3	+ 65.5	+ 64.3	....	168.2

Expt. No. 1	Solution No. 2	Portion. 3	Weight of portion. 4	BaO_2H_2 solution used. 5	Initial content. 6	Final content. 7	Change in content. 8	Total change in content. 9	Silver in voltameters. 10	Transference numbers. 11
15	7	K'	332.94	....	841.2	764.5	— 76.7	— 76.7	....	166.9
			.....	31.59	....	764.3	— 76.9	— 77.4	....	168.3
		M_K	201.41	....	509.0	509.1	+ 0.1	......		....
			.....	21.02	....	508.5	— 0.5	......	346.1	....
		M	193.79	....	489.7	489.7	± 0.0	......	345.9	....
			.....	20.23	....	489.5	— 0.2	......	....	....
		M_A	179.29	....	453.1	452.3	— 0.8	......	....	....
			.....	18.68	....	452.1	— 1.0	......	....	....
		A	372.48	....	941.2	1015.3	+ 74.1	+ 73.3	....	159.3
16	7	K'	341.83	....	863.8	787.0	— 76.8	— 76.6	....	166.4
			.....	32.52	....	786.6	— 77.2	— 77.0	....	167.2
		M_K	196.70	....	497.0	497.2	+ 0.2	......	....	....
			.....	20.55	....	497.2	+ 0.2	......		....
		M	172.22	....	435.2	434.2	— 1.0	......	346.5	....
			.....	17.95	....	434.5	— 0.7	......	346.7	....
		M_A	190.13	....	480.4	478.9	— 1.5	......	....	....
			.....	19.76	....	478.0	— 2.4	......	....	....
		A	374.58	....	946.5	1024.0	+ 77.5	+ 76.0	....	165.4
17	8	K'	332.90	....	822.8	744.6	— 78.2	— 77.7	....	167.3
			.....	59.05	....	744.8	— 78.0	— 78.3	....	168.5
		M_K	197.43	....	488.0	488.5	+ 0.5	......	....	....
			.....	38.67	....	487.7	— 0.3	......	349.7	....
		M	193.65	....	478.6	478.0	— 0.6	......	349.5	....
			.....	37.91	....	478.1	— 0.5	......	....	....
		M_A	174.96	....	432.4	430.6	— 1.8	......	....	....
			.....	34.10	....	430.0	— 2.4	......	....	....
		A	360.70	....	891.6	970.8[1]	+ 79.2	+ 77.4	....	166.7
18	8	K'	323.45	....	799.4	730.2	— 69.2	— 69.2	....	166.7
			.....	57.90	....	730.2	— 69.2	— 69.5	....	167.4
		M_K	193.69	....	478.7	478.8	+ 0.1	......	....	....
			.....	37.94	....	478.4	— 0.3	......	312.4	....
		M	182.17	....	450.3	450.1	— 0.2	......	312.2	....
			.....	35.71	....	450.4	+ 0.1	......	....	....
		M_A	179.51	....	443.7	442.1	— 1.6	......	....	....
			.....	35.03	....	441.7	— 2.0	......	....	....
		A	390.81	....	965.9	1037.0	+ 71.1	+ 69.5	....	167.4

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[1] In the analysis of this portion some silver chloride was obtained on boiling the filtrate from the silver nitrate precipitate, with sulphurous acid. This silver chloride was filtered, washed, weighed, and added to the weight of the first silver chloride precipitate. It amounted to 3.4 mg.

Expt. No. 1	Solution No. 2	*Portion.* 3	Weight of portion. 4	BaO_2H_2 solution used. 5	Initial content. 6	Final content. 7	Change in content. 8	Total change in content. 9	Silver in voltameters. 10	Transference numbers. 11
19	9	*K*	313.08	....	776.2	701.5	− 74.7	− 74.7	....	166.8
			.....	55.66	....	701.2	− 75.0	− 75.0	....	167.5
		M_K	185.94	....	460.9	461.0	+ 0.1	......	....	....
			.....	36.60	....	461.0	+ 0.1	......	337.2	....
		M	206.43	....	511.8	511.8	± 0.0	......	337.1	....
			.....	40.61	....	511.7	− 0.1	......	....	....
		M_A	181.86	....	450.9	449.4	− 1.5	......	....	....
			.....	35.69	....	449.6	− 1.3	......	....	....
		A	415.00	....	1028.8	1104.0	+ 75.2	+ 74.7	....	166.8
20	9	*K*	315.55	....	782.3	704.9	− 77.4	− 77.2	....	168.2
			.....	55.97	....	705.1	− 77.2	− 77.2	....	168.2
		M_K	188.97	....	468.5	468.7	+ 0.2	......	....	....
			.....	36.42	....	468.6	+ 0.1	......	346.0	....
		M	202.38	....	501.7	501.6	− 0.1	......	345.9	....
			.....	39.81	....	501.6	− 0.1	......	....	....
		M_A	185.19	....	459.1	459.1	± 0.0	......	....	....
			.....	36.42	....	459.2	+ 0.1	......	....	....
		A	410.17	....	1016.9	1093.8	+ 76.9	+ 76.9	....	167.3

$^{1}/_{60}$-MOLAR HCl AT 10°.

21	8	*K*	309.08	....	764.0	693.9	− 70.1	− 69.8	....	158.3
			.....	lost	....	....	......	......	....	....
		M_K	197.73	....	488.7	489.0	+ 0.3	......	....	....
			.....	38.76	....	488.8	+ 0.1	......	331.9	....
		M	184.62	....	456.3	456.1	− 0.2	......	331.8	....
			.....	36.17	....	456.2	− 0.1	......	....	....
		M_A	191.34	....	473.0	473.4	+ 0.4	......	....	....
			.....	37.50	....	473.4	± 0.0	......	....	....
		A	409.12	....	1011.3	1080.2	+ 68.9	+ 69.3	....	157.1
22	8	*K*	333.89	....	825.3	755.9	− 69.4	− 69.4	....	158.9
			.....	59.98	....	756.5	− 68.8	− 68.9	....	157.8
		M_K	193.83	....	479.1	479.1	± 0.0	......	....	....
			.....	37.98	....	479.0	− 0.1	......	328.8	....
		M	150.23	....	371.3	371.3	± 0.0	......	328.6	....
			.....	29.44	....	371.3	± 0.0	......	....	....
		M_A	196.16	....	484.9	484.9	± 0.0	......	....	....
			.....	38.44	....	484.9	± 0.0	......	....	....
		A	426.77	....	1054.9	1124.4	+ 69.5	+ 69.5	....	159.1

Expt. No.	Solution No.	Portion.	Weight of portion.	BaO_2H_2 solution used.	Initial content.	Final content.	Change in content.	Total change in content.	Silver in voltameters.	Transference numbers.
1	2	3	4	5	6	7	8	9	10	11
23	8	*K*	321.79	....	795.3	726.8	— 68.5	— 68.5	....	158.8
			.....	57.66	....	727.2	— 68.1	— 68.4	....	158.6
		M_K	195.70	....	483.7	483.8	+ 0.1	......	....	....
			.....	38.42	....	483.4	— 0.3	......	324.7	....
		M	167.45	....	413.9	413.8	— 0.1	......	324.7	....
			.....	32.82	....	413.8	— 0.1	......	....	....
		M_A	194.57	....	480.9	480.8	— 0.1	......	....	....
			.....	38.11	....	480.6	+ 0.3	......	....	....
		A	406.20	....	1004.2	1073.0	+ 68.8	+ 68.8	....	159.4
24	9	*K*	305.05	....	756.2	689.6	— 66.6	— 66.6	....	159.2
			.....	54.74	....	689.6	— 66.6	— 66.6	....	159.2
		M_K	184.30	....	456.9	456.8	— 0.1	......	....	....
			.....	36.25	....	456.8	— 0.1	......	315.1	....
		M	194.00	....	480.9	480.6	— 0.3	......	315.0	....
			.....	38.16	....	480.8	— 0.1	......	....	....
		M_A	176.45	....	437.4	437.1	— 0.3	......	....	....
			.....	34.70	....	437.1	— 0.3	......	....	....
		A	405.62	....	1005.6	1072.0	+ 66.4	+ 66.1	....	158.0
25	9	*K*	307.11	....	761.4	693.6	— 67.8	— 67.8	....	157.4
			.....	55.04	....	693.3	— 68.1	— 68.1	....	158.0
		M_K	192.27	....	476.6	476.5	— 0.1	......	....	....
			.....	37.83	....	476.6	± 0.0	......	324.4	....
		M	199.80	....	495.3	495.4	+ 0.1	......	324.2	....
			.....	39.31	....	495.2	— 0.1	......	....	....
		M_A	186.63	....	462.7	462.7	± 0.0	......	....	....
			.....	36.71	....	462.6	— 0.1	......	....	....
		A	407.20	....	1009.5	1073.0	+ 63.5	+ 63.5	...	147.4
26	9	*K*	311.78	....	773.0	707.7	— 65.3	— 65.3	....	159.6
			.....	56.26	....	708.7	— 64.3	— 64.3	....	157.1
		M_K	187.16	....	464.0	464.1	+ 0.1	......	....	....
			.....	36.84	....	464.1	+ 0.1	......	307.9	....
		M	192.71	....	477.7	477.8	+ 0.1	......	308.0	....
			.....	37.93	....	477.8	+ 0.1	......	....	....
		M_A	196.10	....	486.1	486.0	— 0.1	......	....	....
			.....	38.58	....	486.0	— 0.1	......	...	....
		A	410.84	...	1018.5	1083.5	+ 65.0	+ 65.0	....	158.9

$^1/_{60}$-MOLAR HCl AT 30°.

Expt. No. 1	Solution No. 2	Portion. 3	Weight of portion. 4	BaO_2H_2 solution used. 5	Initial content. 6	Final content. 7	Change in content. 8	Total change in content. 9	Silver in voltameters. 10	Transference numbers. 11
27	7	*K*	321.75	....	813.2	730.3	— 82.9	— 84.4	....	176.1
			.....	30.18	....	729.9	— 83.3	— 84.8	....	176.8
		M_K	186.21	....	470.6	469.1	— 1.5	......	....	....
			.....	19.39	....	469.1	— 1.5	......	361.3	....
		M	152.06	....	384.2	384.1	— 0.1	......	361.4	....
			.....	15.84	....	383.3	— 0.9	......	....	....
		M_A	206.28	....	521.2	518.6	— 2.6	......	....	....
			.....	21.41	....	518.1	- 3.1	......	....	....
		A	384.70	....	972.1	1059.8	+ 87.7	+ 85.1	....	177.4
28	7	*K*	308.08	....	778.5	701.0	— 77.5	— 78.7	....	177.6
			.....	28.99	....	701.3	— 77.2	— 78.4	....	176.9
		M_K	198.08	....	500.5	499.3	— 1.2	......	....	....
			.....	20.64	....	499.3	— 1.2	......	333.4	....
		M	178.00	....	449.7	449.4	— 0.3	......	333.6	....
			.....	18.58	....	449.5	— 0.2	......	....	....
		M_A	195.76	....	494.7	492.7	— 2.0	......	....	....
			.....	20.38	....	493.0	— 1.7	......	....	....
		A	388.75	....	982.3	1063.1	+ 80.8	+ 78.8	....	177.9
29	7	*K*	314.65	....	795.1	741.1	— 54.0	— 54.1	....	177.3
			.....	30.64	....	741.1	— 54.0	— 54.0	....	177.0
		M_K	200.42	....	506.4	506.3	— 0.1	......	....	....
			.....	20.94	....	506.4	± 0.0	......	229.5	....
		M	166.17	....	420.0	420.1	+ 0.1	......	229.8	....
			.....	17.36	....	420.0	± 0.0	......	....	....
		M_A	214.62	....	542.4	542.2	— 0.2	......	....	....
			.....	22.42	....	541.9	— 0.5	......	....	....
		A	369.04	....	932.5	987.0	+ 54.5	+ 54.3	....	177.9
30	7	*K*	313.30	....	791.7	709.6	— 82.1	— 83.5	....	177.5
			.....	29.34	....	709.7	— 82.0	— 83.4	....	177.3
		M_K	193.66	....	489.3	487.9	— 1.4	......	....	....
			.....	20.17	....	487.9	— 1.4	......	354.0	....
		M	163.43	....	413.0	412.9	— 0.1	......	354.1	....
			.....	17.03	....	412.3	— 0.7	......	....	...
		M_A	185.48	....	468.7	467.4	— 1.3	......	....	....
			.....	19.31	....	467.0	— 1.7	......	....	....
		A	397.80	....	1005.3	1090.3	+ 85.0	+ 83.7	....	177.9

Expt. No. 1	Solution No. 2	Portion. 3	Weight of portion. 4	BaO_2H_2 solution used. 5	Initial content. 6	Final content. 7	Change in content. 8	Total change in content. 9	Silver in voltameters. 10	Transference numbers. 11
31	7	K	325.45	....	822.4	753.0	− 69.4	− 67.6	....	165.9
			.....	31.08	....	751.7	− 70.7	− 72.2	....	177.2
		M_K	197.36	....	498.8	499.6	+ 0.8	......	....	....
			.....	20.56	....	497.3	− 1.5	......	306.5	....
		M	200.17	....	505.8	505.8	± 0.0	......	306.8	....
			.....	20.90	....	505.3	− 0.5	......	....	....
		M_A	188.13	....	475.4	474.0	− 1.4	......	....	....
			.....	19.60	....	473.7	− 1.7	......	....	....
		A	367.01	....	927.4	1001.3	+ 73.9	+ 72.5	....	177.9
32	7	K	336.86	....	851.3	764.7	− 86.6	− 87.8	....	177.3
			.....	31.61	....	764.7	− 86.6	− 87.6	....	176.9
		M_K	190.35	....	481.0	479.8	− 1.2	......	....	....
			.....	19.84	....	480.0	− 1.0	......	372.7	....
		M	196.66	....	496.9	496.6	− 0.3	......	372.8	....
			.....	20.54	....	496.2	− 0.7	......	....	....
		M_A	181.63	....	459.0	458.5	− 0.5	......	....	....
			.....	18.90	....	457.3	− 1.7	......	....	....
		A	364.89	....	922.0	1009.8	+ 87.8	+ 87.3	....	176.3

V. SUMMARY OF THE TRANSFERENCE VALUES.

All the values of the transference numbers derived from the experiments recorded are summarized in the following tables:

$^1/_{20}$-MOLAR HCl AT 20°.

Expt. No.	Anode.	Cathode.
1	164.2	164.9
2	164.2	165.6
3	167.9	165.9
4	166.6	166.3
5	164.9	164.2
6	164.2	164.9
7	166.1	165.3
8	166.1	166.8
9	165.4	168.7
Mean,	165.51	165.84
a.d.,	1.03	0.96
A.D.,	0.34	0.32

Final mean, 165.69

A.D., 0.12

$^1/_{60}$-MOLAR HCl AT 20°.

Expt. No.	Anode.	Cathode from AgCl.	Cathode from BaO_2H_2.
10	166.2	167.3	....
11	169.0	169.0	....
12	166.7	165.3	....
13	167.9	164.1*	....
14	168.2	166.3	....
15	159.3*	166.9	168.3
16	165.4	166.4	167.2
17	166.7	167.3	168.5
18	167.4	166.7	167.4
19	166.8	166.8	167.5
20	167.3	168.2	168.2
Mean,	167.16	167.02	167.85
a.d.,	0.80	0.74	0.48
A.D.,	0.25	0.23	0.19

Final mean, 167.43

A.D., 0.25

$^1/_{60}$-MOLAR HCl AT 10°.

Expt. No.	Anode.	Cathode from AgCl.	Cathode from BaO_2H_2
21	157.1*	158.3	lost
22	159.1	158.9	157.8
23	159.4	158.8	158.6
24	158.0	159.2	159.2
25	147.4*	157.4	158.0
26	158.9	159.6	157.1
Mean,	158.85	158.70	158.14
a.d.,	0.42	0.57	0.61
A.D.,	0.21	0.23	0.27

Final mean, 158.62
A.D., 0.15

$^1/_{60}$-MOLAR HCl AT 30°.

Expt. No.	Anode.	Cathode from AgCl.	Cathode from BaO_2H_2.
27	177.4	176.1*	176.8
28	177.9	177.6	176.9
29	177.9	177.3	177.0
30	177.9	177.5	177.3
31	177.9	165.9*	177.2
32	176.3*	177.3	176.9
Mean,	177.80	177.42	177.01
a.d.,	0.16	0.12	0.15
A.D.,	0.08	0.06	0.06

Final mean, 177.34
A.D., 0.16

In obtaining the means of the values by each different method, those values designated by an asterisk in the tables were omitted. These values all deviate from the mean calculated without them by more than four times the average deviation of the other values from the mean. This average deviation is represented in the tables by a.d. By dividing this by the square-root of the number of observations, the "average deviation of the mean" represented by A.D. was calculated. The "final means" were obtained by combining the separate means, assigning to each a weight inversely proportional to the square of its A.D.

VI. PROBABLE ACCURACY OF THE RESULTS.

The probable degree of accuracy of the results both with respect to accidental and systematic errors may first be considered. In this connection it should be stated that all the determinations are recorded which were carried to completion after the method was perfected.

The four things that might affect the accuracy of the results are impurities in the acid solution electrolyzed, inaccuracy or variation in the temperature, errors in the voltameter measurements, and errors in the electrolysis or analysis of the solutions.

The purity of the samples of acid used is perhaps sufficiently demonstrated by their methods of preparation, and that of the water by its slight conductivity. That the acid solutions contained no impurity that could affect the results is further proved by the agreement of the transference values obtained with the acid from three different sources,[1] of the electrical conductivity (in the case of solution 9) with that found by other investigators (see below), and of the transference numbers calculated from the H˙ concentrations with those calculated from the Cl′ concentrations, thus proving that no other ions participated in the transference.

The temperatures were determined with a thermometer which was corrected by comparison with the standard of the Physical Department of this Institute. They were kept constant during the experiments within 0.02°, which is entirely sufficient as the temperature-coefficient of the transference-number is 0.6 per cent. per degree.

The voltameter measurements were made in accordance with the legal specifications, and were checked in almost all the experiments by inserting in the circuit two voltameters, one on each side of the electrolysis apparatus, thus preventing any error from leakage of electricity. The two values will be seen to check within 0.1 per cent. in all cases.[2]

Of the errors in the electrolysis and analysis of the solution the results themselves furnish a criterion in four different ways: namely, through a consideration of (1) the changes in concentration of the middle portions; (2) the agreement of the similarly determined transference-numbers in the different experiments; (3) the agreement of those calculated from concentration-changes at the two different electrodes in the same experiment; and (4) the agreement of those calculated from the concentration-changes of the two different ions. These four considerations will be taken up in the order named.

(1) It will be seen that the change in the middle portion of all is in only a very few cases more than 0.05 per cent and therefore no greater than the analytical error, and that the changes in the two adjoining middle portions are very small, showing that the changes at the electrodes were caused only by the transference and were

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[1] Thus experiments 1-5 were made with solutions prepared from chemically-pure commercial acid, experiments 12-32 with solutions made from hydrochloric acid gas generated from sodium chloride, and experiments 6-11 with solutions made from hydrochloric acid gas liberated from the commercial acid.

[2] We have not thought it necessary to correct our results for the deviation shown to exist by Richards, Collins, and Heimrod (*Proc. Am. Acad.*, **35**, 123) between the results of the legal silver voltameter and the requirements of Faraday's law; for this deviation amounts to less than 0.1 per cent.

not at all affected by convection currents. That there was no convection on the anode side was also shown, as was stated above, by the sharp line formed by the finely suspended silver chloride in the bend of the tube. No error was possible, of course, from the participation in the transference of foreign ions produced by the electrolysis; for the materials of the electrodes precluded this.

(2) The percentage average deviations (100 a.d./mean) of the separate values from the mean are nearly identical for the gravimetric cathode and anode values in each of the four series of experiments, and amount to 0.59, 0.44, 0.13, 0.09 with 1/20 molar HCl at 20°, and 1/60 molar at 20°, at 10°, and at 30°, respectively. The corresponding percentage "average deviations of the mean" (100 A.D./mean) are 0.19, 0.14, 0.14 and 0.04, respectively. These last values may be regarded as measures of the precision of the separate means, as far as the effect of accidental errors is concerned.

(3) It will be seen from the summary of the transference-values that the means calculated from the anode-portion analyses do not differ from those from the cathode-portion analyses by more than 1/4 per cent. in any one of the four series of experiments. Moreover, the average deviations of these means are nearly identical, thus showing that the more complicated procedure in the case of the anode portion did not introduce any error. This agreement not only eliminates to a greater extent the effect of accidental errors, but proves the absence of certain imaginable systematic errors of a greater magnitude than this, in the analysis of the solution; for, since at the cathode there is a decrease and at the anode an increase in the chlorine-content, the results would be affected by such errors in opposite directions; thus, this is true of errors in the determination of the original-content of the solution and of errors from loss of silver chloride or particles of asbestos from the crucibles in the final analyses.

(4) The mean transference-numbers calculated from the acidimetric titrations differ from those derived from the silver-chloride weighings by 0.33-0.39 per cent. in the three different cases. Within these limits, therefore, the agreement of the results by the two independent methods of analysis gives a further confirmation

of the accuracy of the analytical work. It shows, also, as stated above, that no ions other than those coming from the hydrochloric acid took part in the transference.

As the final means were obtained by a combination of the results of the three series of independent analyses, and as it is not possible that there was any considerable error except in connection with the electrolyzed solution, the average deviations of the final means are a measure of their probable accuracy with respect to errors from all sources. These average deviations lie between 0.10 and 0.15 per cent. in the case of the four series of experiments. It seems certain that the actual error cannot in any case exceed three times the larger of these deviations or 0.45 per cent. The probable and possible percentage errors would, of course, be only about one-fifth as great if the results were calculated for the cathion (instead of for the anion), as has been done by some investigators.

VII. COMPARISON WITH THE RESULTS OF PREVIOUS INVESTIGATIONS.

Transference numbers for hydrochloric acid were first published by Hittorf in his original memoirs on the general subject. As the values in the dilute solutions deviate greatly from all those more recently obtained, and as their accuracy was doubted by that investigator himself, they do not need to be considered here. Within the last four years, however, three other series of determinations have been communicated, namely by Hopfgartner,[1] Bein,[2] and Jahn and Bogdan.[3] We have reduced their determinations, which were made between 9° and 19°, to 20° by means of the temperature-coefficient which we found between 10° and 20°, which is identical, moreover, with that given by Bein. We recall that our values at 20° are 165.69 (A.D. = 0.12, 9 experiments, 18 values) for the 1/20 molar solution, and 167.43 (A.D. = 0.25. 11 experiments, 26 values) for the 1/60 molar solution. Hopfgartner's results with 1/10 and 1/5 molar solutions lead to 168.0 (A.D. = 1.6; 9 values); Bein's with 1/7 to 1/70 molar to 172.4

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[1] *Ztschr. phys. Chem.*, **25**, 135 (1898).

[2] *Ibid.*, **27**, 32, 49 (1898).

[3] *Ibid.*, **37**, 679 (1901).

(A.D. = 1.7; 5 values[1]; Jahn and Bogdan's, with 1/32 to 1/80 molar, to 176.0 (A.D. = 0.85; 11 values).

In view of the large average deviations of these results, their wide divergence from one another, and the facts that, except in the case of Bein's, they were not controlled by analyses of the portions at both electrodes and that in the cases of all of them the middle portions exhibited considerable changes, it seems probable that our values are nearer the true ones than any that might be obtained by combining them with these earlier results. The greater errors in these probably arose from two causes: first, the changes in concentrations in the portions around the electrode were small, amounting only to from 2 to 6 per cent. of the total salt-content; and secondly, a considerable proportion of the changes in concentration that did occur was in the middle portion, this proportion amounting to from 3 to 8 per cent. in most of Bein's experiments; in Jahn and Bogdan's experiments the percentage changes in concentration indicate that it was considerable, but the proportion of the total change cannot be stated since they failed to give the weights of the middle portion. In our experiments the changes in concentration were from 10-15 per cent. of the total salt content, and the changes in the middle portions were only from 0.1 to 0.3 per cent. of the total change.

VIII. CHANGE OF THE TRANSFERENCE-NUMBERS WITH THE CONCENTRATION.

It will be seen that at 20° the transference-number increases by just about 1 per cent. in passing from the dilution of 20 to that of 60 liters. It is not impossible that this apparent change arises wholly from experimental errors, as the 1/20 molar solution was the one first investigated, the average deviation of the separate values from the mean is greater than in any other case, and the results were not checked by an acidimetric titration. Still it is not probable that this is the case; for it would be necessary to assume errors of about three times the A.D's in the final means of both the 1/20 and 1/60 molar solutions, and that these lay in opposite directions. Even assuming that the whole change is real, it is still small enough to indicate that the value at infinite dilution cannot differ much from that at 1/60 molar. This is made still

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[1] The two experiments to which a weight of ½ is assigned are here considered as one. The three to which a weight of ¼ is given are left entirely out of consideration.

more probable by the consideration that the undissociated portion of the acid at that dilution amounts to only 6 per cent., and especially by the results of Jahn and Bogdan, which show no systematic change whatever in the transference-number between the dilutions of 32 and 110 liters. Still it must be admitted, that, though not probable, yet it is possible that an error of 1 to 2 per cent. would be made by assuming no further change in the transference number after 1/60 molar is reached.

IX. MEASUREMENTS OF THE CONDUCTIVITY OF HYDROCHLORIC ACID.

To assist in the discussion of the results it was desirable to know the temperature-coefficient of the conductivity of the hydrochloric acid between the temperatures in question. The conductivity of the acid was therefore measured by the usual Kohlrausch method at 10°, 20°, and 30° and at two dilutions. The results are given in the following table. The first column gives the temperature; the second, the volume in true liters[1] containing 1 mol; the third, the measured conductance in reciprocal ohms; the fourth, the molar conductivity calculated therefrom[2], and referred to the cubic centimeter as the unit of volume; the fifth, the values of it calculated from Kohlrausch's data[3] at 18° and Déguisne's temperature-coefficients[4]; and the sixth, the changes in conductivity for each interval of 10°.

Temperature.	Dilution.	Conductance.	Molar conductivity.		Change in conductivity.	
			N. and S.	K. and D.	N. and S.	K. and D.
10°	57.84	0.01994	316.4	319.1	61.2	60.8
20°	57.95	0.02375	377.6	379.9	60.0	59.6
30°	58.07	0.02747	437.6	439.5		
10°	251.8	0.004662	322.1	324.5	62.3	61.8
20°	252.3	0.005553	384.4	386.3	61.3	60.6
30°	252.8	0.006426	445.7	446.9		

It will be seen that our values of the conductivity and those of Kohlrausch and Déguisne agree within 1 per cent., and that the

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[1] The same solution was always measured at the three temperatures, the volume being corrected by means of the expansion-coefficient of water.

[2] The conductance at 20° of the resistance-cell when filled with 1/50 molar potassium chloride prepared as directed in Kohlrausch and Holborn's "Leitvermögen der Elektrolyte," page 77, was 0.009116 and 0.009114 respectively before and after the hydrochloric acid measurements. This value was divided into the constant 0.002501 given on page 204, yielding 0.2744 as the cell constant.

[3] Wied. *Ann. Phys.*, **66**, 811 (1898).

[4] Kohlrausch and Holborn's "Leitvermögen der Elektrolyte," pp. 11, 199.

changes of conductivity with the temperature agree almost completely. The temperature-coefficient is, moreover, almost exactly the same at the two dilutions when expressed in percentage of the value at 20°; namely, between 10° and 30°, it is, according to our determinations, 1.605 per degree at 1/58 molar, and 1.607 at 1/252 molar.

X. THE EQUIVALENT CONDUCTIVITY OF DISSOCIATED HYDROCHLORIC ACID AND OF THE HYDROGEN ION.

The equivalent conductivity of the chlorine ion at 18° and its temperature-coefficient between 2° and 34° has been calculated by Kohlrausch[1] on the basis of the exact conductivity determinations of Kohlrausch and Maltby on potassium chloride, the temperature-coefficients of Déguisne, and the value 0.503 for the transference number of the anion in potassium chloride. The conductivity values extrapolated for infinite dilution were made the subject of a careful study, and that adopted for potassium chloride is undoubtedly the best that can be obtained. It seems to us desirable, however, to review briefly here the recent determinations of the transference-numbers of potassium chloride, in order to arrive at the best possible value and to form an estimate of its accuracy; especially since new determinations have been published since Kohlrausch's calculations were made. All the recent results (multiplied by 1000) are summarized in the following table.

Investigator.	Temperature.	Dilution in liters.	Number of experiments.	Mean value.	A.D. of mean.
Bein[2]	9°–12°	12–90	3.5[5]	505.1	0.6
Jahn and Bogdan[3] .	18°–19°	30–120	11	503.2	0.5
Steele and Denison[4]	....	200–400	9	504.8	0.7
			Final mean,	504.4	0.5

As there is no indication that the transference number changes appreciably with the temperature or concentration, we adopt as the most probable value the mean result from these three series of experiments (504.4). We have then multiplied this by Kohlrausch's conductivity values for potassium choride at the three

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[1] *Sitzsungsber königl. preuss. Akad. der Wiss.*, (1900), p. 1002; (1901), p. 1031.

[2] *Ztschr. phys. Chem.*, **27**, 50 (1898).

[3] *Ibid.*, **37**, 684 (1901).

[4] *Ibid.*, **40**, 753; *Trans. Chem. Soc.*, **81**, 468 (1902).

[5] Bein attributes to two of his experiments a weight of 1/4 each.

temperatures. The values[1] so obtained for the chorine ion are:

Cl': 54.5 at 10°, 68.5 at 20°, 83.3 at 30°.

By combining these values with the final means of our transference experiments with the 1/60 molar hydrochloric acid solution, the following values of the equivalent conductivity, in reciprocal ohms, of completely dissociated hydrochloric acid are obtained:

$H^{\bullet} + Cl'$: 343.6 at 10°, 409.1 at 20°, 469.7 at 30°.

The accidental errors in these results can be equalized, and a further indication of their magnitude obtained, by calculating from each of the three values the other two by means of the temperature-coefficient of the conductivity of dilute hydrochloric acid. It has already been shown in Section IX that Deguisne's value of this coefficient is in close agreement with our own, and that the coefficient does not change appreciably with the dilution. Employing his value,[1] the following results are obtained, the one which forms the basis of the calculation being printed in italics.

10°.	20°.	30°.
343.6	409.0	473.0
343.7	*409.1*	473.2
341.2	406.1	*469.7*

We assign to the results based upon the 10° and 20° values twice as much weight as to that based upon the 30° value because of their agreement and its divergence, and especially because the transference numbers of potassium chloride were determined between 10° and 20°, and its molar conductivity at infinite dilution was accurately deduced for 18°, the values of these quantities at 30° being based upon the assumption of a temperature-coefficient of zero for the transference-number and upon one for the con-

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[1] The transference numbers of sodium chloride furnish an independent means of deriving these conductivities; but these numbers vary with the temperature, and the determinations of them are less numerous. The only ones that are of significance to us are those of Bein around 10°, from which is derived a value at 10°, of 614.9 (A.D. 2.0; 7 experiments) and those of Jahn and Bogdan at 18.5° from which is derived with the help of Bein's temperature-coefficient a value at 20° of 603.3 (A.D. 0.3; 12 experiments). By multiplying Bein's result by Kohlrausch's value of the conductivity at infinite dilution of sodium chloride (89.87) we get 55.3 at 10° for the chlorine ion; but, owing to the large A.D. of the former value, very little weight is to be attached to this result in comparison to that attached to the one from the potassium chloride experiments. From Jahn and Bogdan's transference value we get 68.7 at 20° for the chlorine ion in close agreement with that derived through potassium chloride.

[2] $L_t = L_{18}\,[1 + 0.0164\,(t - 18) - 0.000015\,(t - 18)^2]$.

ductivity derived from values less carefully determined than those at 18°. Taking the means under this assignment of weights, and interpolating with the help of Déguisne's temperature-coefficient for 18° and 25°, we get the following final values for the equivalent conductivity in reciprocal ohms of completely dissociated hydrochloric acid and of the hydrogen ion:

	10°.	18°.	20°.	25°.	30°.
$H^{\cdot} + Cl'$......	343.2	395.5	408.5	440.7	472.4
$H^{\cdot}$	288.7	329.8	340.0	364.9	389.1

XI. PROBABLE ACCURACY OF THE FINAL CONDUCTIVITY VALUES.

Aside from the uncertainty in the assumption that the transference-number of hydrochloric acid has the same value at extreme dilution as at one of 60 liters, a fair estimate can be formed of the probable accuracy of these final results through a consideration of the data upon which they are based. It will be recalled that the three factors involved are the molar conductivity and the transference-number of completely dissociated potassium chloride and the transference-number of 1/60 molar hydrochloric acid: (1) In regard to the first of these, Kohlrausch shows that the formula which he employs for expressing the change of conductivity with the dilution gives interpolated values between 0.1 and 0.0001 molar agreeing with the observed ones within 0.1 per cent. We may therefore estimate that the value extrapolated for zero concentration is probably in error by only a little greater amount, say by 0.2 per cent.; (2) The average deviation of the mean value of the transference-number for potassium chloride from the three series of independent determinations was seen above to be 0.1 per cent.: and as this transference-number shows no variation between 1/12 and 1/400 normal, there is probably no error in the assumption that it has the same value at infinite dilution; (3) The average deviation of the final means of the hydrochloric acid transference number was about 0.1 per cent. From this estimate and these deviations, we find the average deviation or probable error of the final values of the conductivity of $H^{\cdot} + Cl'$ and $H^{\cdot}$ to be 0.25 per cent. Assuming that the actual error in each of the three factors was twice its percentage average deviation, and that the effect of these errors all lay in the same direction, the error in the final result would be 0.8 per cent. This may be regarded as a limit which it is almost certain is not exceeded by the effect of the errors arising from all sources except the assumption that the hydrochloric acid transference value does not change with the dilution after 60 liters are reached. It is not probable that any considerable error arises through this assumption; but there is a possibility that the final conductivity values are 1 to 2 per cent. too high as a result of it (see Section VIII). The uncertainty can be removed only by transference-determinations at a greater dilution, which will be undertaken in this laboratory as soon as the opportunity offers.

XII. COMPARISON WITH PREVIOUSLY ADOPTED VALUES.

It is of interest to compare our final values with those that have been previously employed. Ostwald[1] estimated ten years ago upon the basis of the then existing conductivity values that the equivalent conductivity at 25° of the hydrogen ion was 345 when expressed in reciprocal ohms; and it is this value that has been used in almost all the calculations of the dissociation and the dissociation-constants of acids. The value to which this investigation has led is, however, 365, which is 5.8 per cent. higher than that commonly employed.

Kohlrausch[2] has very recently adopted 318 as the most probable value at 18°. Our value is 330, which is greater by 3.8 per cent.

In spite of the fact that a small degree of uncertainty attaches to our results for the reason stated in the preceding section, we believe that they rest upon a more satisfactory foundation than do the other ones, which were based upon an almost unguided extrapolation from the conductivity-values of acids.

BOSTON, MASS., July, 1902.

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[1] "Lehrbuch der allgemeinen Chemie." Vol. II, part 1, p. 675.

[2] *Sitzungsber. der königl. preuss. Akad. der. Wiss.*, (1902), p. 1031.