and Richards.[1] Richards's paper is in the form of a lecture delivered before the German Chemical Society.

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THE EQUIVALENT CONDUCTANCE OF HYDROGEN-ION DERIVED FROM TRANSFERENCE EXPERIMENTS WITH NITRIC ACID.

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1. Outline of the Investigation.

In an article published four years ago by A. A. Noyes and G. V. Sammet[2] there were described some transference determinations made with 1/20, 1/60 and 1/80 normal hydrochloric acid at 10°, 20°, and 30°, which, when combined with the equivalent conductance of chloride-ion (using the value of Kohlrausch) yielded for hydrogen-ion a much higher equivalent conductance than that which had been derived from the conductivity of acids at high dilutions. Thus the value for hydrogen-ion at 18° derived from the transference experiments was 330, while that of Kohlrausch derived from conductivity was 318. This serious divergence appeared greater than the possible errors in the transference determinations;[3] and it seemed as if it must be due either (1) to an error in the extrapolated values of the equivalent conductance of acids at zero concentration, (2) to the formation of complex ions or some other abnormality of the hydrochloric acid, or (3) to a marked difference in the relative velocities of the hydrogen-ion and the anion, at moderate and at very low concentrations. To test the first of these possibilities, a study of the effect of the impurities in the water upon the conductance of very dilute hydrochloric and nitric acids was made in this laboratory by H. M. Goodwin and R. Haskell,[4] the results of which showed that, after eliminating the effect of impurities as far as possible, a value for the equivalent conductance of hydrogen-ion at extreme dilution (315 at 18°) even lower than that previously derived by Kohlrausch (318) was obtained.

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[1] Ber., 40, 2767.

[2] This Journal, 24, 944–968; 25, 165–168 (1902–3); Z. physik. Chem., 43, 49–74 (1903).

[3] The experimental results of Noyes and Sammet have recently been fully confirmed by those of Jahn, Joachim and Wolff (Z. physik. Chem., 58, 641 (1907)).

[4] Phys. Rev., 19, 369–396 (1904); Proc. Am. Acad., 40, 399–415 (1904) Reviewed in Z. physik. Chem., 52, 630 (1905).

In view of these results it did not seem possible that the divergence could be due to the first-mentioned cause. The present investigation was therefore undertaken, in order to test the second explanation, or that being excluded, to estabish the correctness of the third one. It was carried on with the help of a grant from the Carnegie Institution of Washington, and a description of it substantially identical with that here presented forms a part of Publication No. 63 of that Institution.

It was thought that independent transference experiments with another acid, if they yielded results concordant with those with hydrochloric acid, would serve both to exclude any specific error that might arise from complex ion formation or other individual peculiarity of that acid and to confirm the experimental accuracy of the transference data, and that they would thus establish the fact that a marked change in the relative migration velocity of the ions of acids takes place on passing to very low concentrations. Nitric acid was selected as the second acid, since it is of quite a different chemical character.[1] Another purpose of this investigation, bearing directly on the third suggestion mentioned above, was to extend the transference measurements with both acids to a dilution of about 0.002 normal.

2. Preparation and Standardization of the Solutions.

The chemically pure nitric acid of trade was freed from lower oxides of nitrogen by diluting it with two-thirds its volume of conductivity water and drawing a current of purified air through it. It was carefully tested (using 5–10 cc.) for chloride with silver nitrate, for sulphate by evaporation with barium chloride, for ammonia with Nessler reagent, and for nitrite by diluting and adding starch and potassium iodide. These impurities could not be detected at all, or were present only in entirely insignificant quantity. Dilute solutions (from 0.06 to .0.0006 normal) were made up with water having in all cases a specific conductance lying between 0.9 and 1.2×10^{-6} reciprocal ohms at 18°, and were titrated with the help of phenolphthalein against a 0.1 normal solution of carefully purified barium hydroxide. The strength of the barium hydroxide solution was determined gravimetrically both by precipitating with sulphuric acid after neutralizing with hydrochloric acid and by evaporating to dryness with pure nitric acid and weighing the residue of anhydrous barium nitrate after heating to 160°–180°. The two methods gave for the content of the solution in milli-equivalents per kilogram 110.60 and 110.72, respectively; the value adopted was 110.64. Afterwards two other solutions of barium hydroxide were prepared and titrated against nitric acid solutions which had been standardized against the

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[1] A single transference experiment has already been made with this acid at 25° at 0.05 normal concentration by Bein (Z. physik. Chem., **27**, 44 (1898)).

first barium hydroxide solution. Solution No. 2 contained 119.04, and solution No. 3 contained 58.59 milli-equivalents per kilogram of solution.

The five solutions of nitric acid varying from about 0.06 to 0.006 normal, which were standardized for use in this work against these barium hydroxide solutions, showed as a mean in each case of 5 or 6 closely concordant determinations a content in milli-equivalents per kilogram of solution as follows:

	No. 1.	No. 2.	No. 3.	No. 4.	No. 5.
Content.......	59.22	57.42	18.426	6.809	6.605

The very dilute solutions (approximately 0.002 normal) of nitric and hydrochloric acids employed could hardly be titrated with sufficient accuracy by this method. The concentrations both of the original solutions and of the portions after electrolysis were therefore determined by measuring their conductance by the usual Kohlrausch method in a cylindrical cell with horizontal electrodes, and dividing the corresponding specific conductance by the equivalent conductance of the acid in question at this concentration and temperature. Goodwin and Haskell[1] have recently determined the equivalent conductances at 18° in 0.002 normal solution to be 371.3 for HNO_3, and 375.0 for HCl at 18°, from which follows with the help of Déguisne's temperature-coefficients:[2] 383.4 for HNO_3 and 387.4 for HCl at 20°, which are the values we have used in calculating the original concentrations. The actual conductance measured in the conductivity vessel, the specific conductance, and the concentration in milli-equivalents per liter calculated therefrom were as follows:

	Nitric acid solution.		Hydrochloric acid solution.	
	No. 6.	No. 7.	No. 1.	No. 2.
Actual conductance $\times 10^6$....	2,142	2,094	1,975	2,136
Specific conductance $\times 10^6$...	847.3	828.4	781.3	845.0
Milli-equivalents per liter......	2.210	2.161	2.017	2.181

The conductance capacity of the conductivity vessel was 0.3956 for all the measurements presented in this article.[3] Hydrochloric acid solution No. 1 was made by diluting quantitatively by weight (with water of conductivity 0.9×10^{-6}) a 0.13737 normal solution which had been standardized by weighing the silver chloride obtainable from it; the concentration calculated from the dilution was 2.015, in close agreement with that derived from the conductivity (2.017). Solution No. 2 was prepared from the same stock solution, which was itself made by treating pure salt with pure sulphuric acid, redistilling the strong acid obtained,

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[1] Phys. Rev., **19**, 381, 383 (1904). These values like all of ours given below were not corrected for the conductance of the water.

[2] Kohlrausch and Holborn, Leitvermögen der Elektrolyte (1898), p. 199.

[3] A 0.009,954 normal potassium chloride solution measured in it showed as an average of several determinations a conductance of 3111.3×10^{-6} reciprocal ohms.

and diluting it; it was proved to be free from non-volatile matter and from sulphuric acid.

3. Description of the Experiments.

The apparatus, consisting of two connecting U-tubes, was almost identical with that used by Noyes and Sammet, and the procedure followed in the transference experiments was nearly the same. Referring the reader therefore to this article[1] for the main features, we will here describe only the modifications adopted in our work. In order to avoid all danger from leakage, the two U-tubes were joined by drawing over their ends two thicknesses of light black tubing, tightly wiring this on, and entirely covering the joint with melted paraffin. The anode consisted of a circular platinum plate, convex downward, soldered with gold to a platinum wire. The cathode was a straight platinum wire which dipped into the solution always less than 1 cm., so that by having the current dense the reduction of the nitric acid was as far as possible prevented. Since the solution weakened around the cathode and concentrated around the anode, to avoid stirring, the cathode arm was filled with liquid nearly to the top, while the anode arm was filled only a few centimeters above the bend and the electrode was placed just below the surface. To keep the solution at this level the anode arm was fitted with a rubber stopper carrying a delivery tube which dipped into an outside vessel of water whose level could be varied.

Given in outline, the method of carrying out the transference experiments consisted in passing a suitable current for three hours and fifteen minutes (except when otherwise noted in the table) through the standard nitric or hydrochloric acid solutions in the apparatus just described, determining the quantity of electricity by means of two silver coulometers placed in series with it, one on either side, dividing the electrolyzed solution into a cathode, an anode, and three middle portions, and titrating each of these with barium hydroxide (or, in the case of the 0.002 normal solutions, measuring the conductance at 20°) to determine the concentration changes. From the analyses of the cathode and anode portions two 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.

The method of procedure at the end of electrolysis was to transfer by means of a pipette the three middle portions to tared wide-mouth Erlenmeyer flasks with rubber stoppers. Then the two U-tubes were separated from each other, stoppered, well cleaned and dried outside, and weighed. The solutions in them were then, after thorough mixing, poured as completely as practicable into tared flasks, again weighed,

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[1] This Journal, 24, 946 (1902).

and finally titrated, allowance being made in the calculation for the small portion that remained in the tubes, which were themselves cleaned, dried, and weighed empty. In the titration of all the portions, the quantity of barium hydroxide solution added was determined by again weighing the flasks containing them after exact neutralization with the base. In those cases where the titration was replaced by a measurement of the conductance, each portion was poured in succession into a cylindrical conductance cell with horizontal platinized electrodes 2.5 cm. apart and measured as accurately as possible, using three resistances in the rheostat.

The principal error to be feared was that which might arise in the analysis of the cathode portion through the reduction of some of the nitric acid by the electrolytic hydrogen. To reduce this to a minimum the cathode was, as already stated, made as small as possible. Since careful analytical tests[1] showed (except in one experiment, No. 2, where the cathode was known to be badly arranged) no nitrite or ammonia in the cathode portion or nitrous vapors in the hydrogen evolved, there is good reason to believe that the error from this source was not serious in most of the other experiments. The effect of this error, it may be noted, would be to cause an apparent *increase* in the transference number of the anion when calculated from the cathode change.

In case of the 0.002 normal hydrochloric acid solution investigated there was the possibility of an opposite error from the liberation of chlorine at the anode, which would have resulted in too small a transference number as calculated from the anode change. With so very dilute a solution and the low current density used, there was probably little danger of this; but to detect any such effect, two different forms of anodes were employed--a short platinum wire in Experiments 1--5 (see Table 1) and a platinum disc in Experiments 6, 7, 9, and 10. As the mean results (167.8 and 168.8) with the two electrodes with such different surface areas agreed almost completely, it seems hardly possible that there was a serious error from this source, especially in the latter experiments.[2]

In order to determine what error, if any, might arise in the very di-

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[1] These tests were made by adding to 10 cc. of the cathode portion after its neutralization a few drops of pure sulphuric acid and some starch solution containing potassium iodide; by adding to 10 cc. of the neutralized portion a few drops of Nessler reagent; and by conducting the hydrogen evolved at the cathode through a tube containing filter paper moistened with a solution of starch and potassium iodide. All these tests gave a slight positive indication in the one experiment mentioned above, but in no other case, though they were tried in most of them.

[2] The cathodes were also varied in form (since the cathode results were considerably higher than the anode results), though there seemed to be no possibility of an abnormal reaction. A platinum disc was used in Experiments 1–5, a spiral wire in 6–8, and a short straight wire in 9–10. The form of electrode had no influence, however. In Experiment 8 a silver anode was used.

lute solutions from contamination during the experiment, a "blank" experiment was made, in which the solution was treated in absolutely the same way as usual except that no current was passed. The stock solution of hydrochloric acid used (No. 2) had a conductance of 21372 and the portion withdrawn at the end of the experiment had conductances as follows: K,[1] 21336; M_K, 21355; M, 21349; M_A, 21349; A, 21356. There was on an average a decrease of 0.1 per cent. Although this would cause a not considerable divergence of the cathode and anode transference numbers, yet it would not appreciably affect their mean; therefore no correction was made for it (except that the use of 21360 as the initial value eliminated it in great measure in the experiments with this solution).

4. The Experimental Data.

The data of the experiments and the calculated transference values for the 0.06–0.007 normal nitric acid solutions are given in Tables 1–3. 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, the weight in grams of the separate portions; the fifth contains the number of grams of barium hydroxide solution used in neutralizing the portions after the electrolysis; the sixth, the initial content, expressed in equivalents and multiplied by 10^6, as calculated from the weight of the portion and the standardization value;[2] the seventh, the final content 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;[3] the tenth, the milligrams of silver precipitated in the coulometers; and the eleventh, the calculated transference numbers for the anion multiplied by 1000.[4]

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[1] For the meaning of these letters see the next paragraph.

[2] See Section 3. BaO_2H_2 solution No. 1 was used in Experiments 1 to 6; solution No. 2 in Experiments 7 to 26; and solution No. 3 in Experiments 27 to 32.

[3] Except where the change in the adjoining portion was opposite in sign to that in the electrode portion.

[4] The way in which these were calculated may be illustrated with the help of the data obtained in the first experiment. The cathode portion submitted to analysis weighed 214.08 grams and was found to require 107.72 grams of the BaO_2H_2 solution containing 0.11064 milli-equivalent per gram, so that the final content of the portion was the product of these last two quantities or 11.918 milli-equivalents. To determine the original content the weight of the portion is multiplied by the original concentration of the solution (0.05922 milli-equivalent per gram), which gives 12.678 milli-equivalents. The decrease in content in the cathode portion is, therefore, 0.760 milli-equivalent. Adding to this the decrease in the adjoining middle portion (0.005) and dividing by the number of milli-equivalents of silver (523.0/107.93) precipitated

TABLE 1.—TRANSFERENCE DATA FOR 0.058 OR $^1/_{17}$ NORMAL NITRIC ACID AT 20°.

Experiment 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	Ag in coulometers. 10	Transference number $\times 10^3$. 11
1	1	K	214.08	107.72	12,678	11,918	— 760	— 765	523.2	157.9
		MK	74.55	39.86	4,415	4,410	— 5	...	...	...
		M	212.29	113.50	12,575	12,558	— 17	...	...	...
		MA	186.16	99.67	11,025	11,028	+ 3	...	...	...
		A	303.87	169.51	17,995	18,755	+ 760	+ 763	522.9	157.4
2	1	K	224.01	107.59	13,266	11,904	—1,362	—1,375	919.5	161.4
		MK	186.40	99.65	11,039	11,026	— 13	...	...	...
		M	185.02	99.01	10,957	10,955	— 2	...	...	...
		MA	108.02	57.86	6,397	6,402	+ 5	...	...	...
		A	298.46	171.71	17,675	19,002	+1,327	+1,332	919.7	156.3
3	1	K	245.61	116.57	14,545	12,898	—1,647	—1,686	1,129.5	161.1
		MK	126.48	67.56	7,490	7,451	— 39	...	...	...
		M	163.15	87.31	9,662	9,660	— 2	...	...	...
		MA	137.35	73.59	8,134	8,142	+ 8	...	...	...
		A	268.43	158.32	15,897	17,517	+1,620	+1,628	1,129.3	155.6
4	1	K	304.16	147.75	18,012	16,348	—1,664	—1,664	1,118.6	160.6
		MK	109.63	58.62	6,492	6,501	+ 9	...	...	...
		M	182.99	97.86	10,837	10,828	— 9	...	...	...
		MA	155.70	83.48	9,221	9,231	+ 10	...	...	...
		A	273.97	161.19	16,224	17,834	+1,610	+1,620	1,118.8	156.3
5	1	K	281.68	137.57	16,681	15,221	—1,460	—1,460	1,019.9	154.5
		MK	134.58	72.08	7,970	7,975	+ 5	...	...	...
		M	134.20	71.83	7,947	7,947	± 0	...	...	...
		MA	139.90	75.01	8,285	8,299	+ 14	...	...	...
		A	221.38	131.64	13,110	14,565	+1,455	+1,469	1,020.1	155.4
6	1	K	304.32	149.65	18,022	16,558	—1,464	—1,464	1,012.8	156.0
		MK	127.83	68.43	7,570	7,572	+ 2	...	...	...
		M	136.01	72.74	8,055	8,048	— 7	...	...	...
		MA	132.70	71.50	7,859	7,911	+ 52	...	...	...
		A	244.75	143.75	14,494	15,906	+1,412	+1,464	1,012.9	156.0
7	2	K	267.30	122.93	15,349	13,601	—1,748	—1,755	1,201.3	157.7
		MK	128.27	66.50	7,365	7,358	— 7	...	...	...
		M	140.92	73.07	8,091	8,085	— 6	...	...	...
		MA	131.81	68.51	7,568	7,580	+ 12	...	...	...
		A	236.68	138.33	13,590	15,305	+1,715	+1,727	1,201.2	155.2
8	2	K	256.11	120.13	14,705	13,292	—1,413	—1,429	988.3	156.0
		MK	148.68	77.01	8,537	8,521	— 16	...	..	...
		M	141.13	73.15	8,103	8,094	— 9	...	...	...
		MA	132.89	69.05	7,630	7,640	+ 10	...	...	...
		A	274.66	155.27	15,770	17,180	+1,410	+1,420	989.4	155.0

in the coulometer, the transference number is found to be 0.1579. The small correction for the change in weight of the electrode portions by the electrolysis and transference is applied later.

TABLE I (*Continued*).

Experiment 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	Ag in coulometers. 10	Transference number ×10³. 11
9	2	K	295.01	141.78	16,939	15,687	—1,252	—1,255	861.8	157.2
		M_K	105.16	54.54	6,038	6,035	— 3	...	...	...
		M	148.18	76.88	8,008	8,506	— 2	...	...	...
		M_A	147.77	76.75	8,485	8,492	+ 7	...	...	...
		A	281.13	157.05	16,144	17,376	+1,232	+1,239	861.4	155.2
10	2	K	258.40	124.30	14,837	13,753	—1,084	—1,085	758.2	154.5
		M_K	135.90	70.51	7,803	7,802	— 1	...	...	...
		M	143.28	74.35	8,227	8,227	± 0	...	...	...
		M_A	139.93	72.63	8,034	8,036	+ 2	...	...	...
		A	253.26	141.29	14,542	15,633	+1,091	+1,093	757.6	155.7
11	2	K	343.52	167.97	19,725	18,584	—1,141	—1,147	783.3	158.1
		M_K	148.88	77.20	8,548	8,542	— 6	...	...	...
		M	162.04	84.05	9,304	9,300	— 4	...	...	...
		M_A	139.38	72.33	8,003	8,003	± 0	...	...	...
		A	256.25	143.14	14,713	15,838	+1,125	+1,125	783.0	155.0
12	2	K	275.18	133.84	15,801	14,808	— 993	— 996	687.1	156.5
		M_K	154.33	80.06	8,861	8,858	— 3	...	...	...
		M	150.66	78.12	8,650	8,644	— 6	...	...	...
		M_A	132.84	68.94	7,627	7,628	+ 1	...	...	...
		A	304.76	167.07	17,499	18,485	+ 986	+ 987	686.8	155.1

TABLE 2.—TRANSFERENCE DATA FOR 0.0184 OR $^1/_{54}$ NORMAL NITRIC ACID AT 20°.

Experiment 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	Ag in coulometers. 10	Transference number ×10³. 11
13	3	K	288.64	40.98	5,319	4,879	—440	—443	300.7	159.0
		M_K	142.34	22.01	2,623	2,620	— 3	..	..	..
		M	180.71	27.93	3,329	3,325	— 4	..	..	..
		M_A	150.21	23.24	2,767	2,767	+ 0	..	..	..
		A	321.64	53.39	5,927	6,370	+443	+443	300.8	159.0
14	3	K	305.45	42.31	5,628	5,037	—591	—591	402.0	158.7
		M_K	151.88	23.51	2,799	2,799	— 0	..	..	..
		M	..	...	...	...	..	..	..	..
		M_A	129.16	20.01	2,380	2,382	+ 2	..	..	..
		A	308.11	52.70	5,677	6,273	+596	+598	401.8	160.6
15	3	K	334.04	46.44	6,155	5,529	—626	—630	420.8	161.6
		M_K	157.46	24.34	2,901	2,897	— 4	..	..	..
		M	164.29	25.42	3,027	3,026	— 1	..	..	..
		M_A	133.13	20.62	2,453	2,455	+ 2	..	..	..
		A	363.95	61.59	6,706	7,332	+626	+628	421.0	161.0
16	3	K	353.27	49.64	6,509	5,909	—600	—601	400.5	162.0
		M_K	161.93	25.06	2,984	2,983	— 1	..	..	..
		M	175.48	27.13	3,233	3,230	± 0	..	..	..
		M_A	136.96	21.23	2,524	2,527	+ 3	..	..	..
		A	299.07	51.23	5,511	6,099	+588	+591	400.5	159.2
17	3	K	342.27	46.04	6,307	5,481	—826	—833	564.6	159.2
		M_K	154.70	23.89	2,851	2,844	— 7	..	..	..

TABLE 2 (*Continued*).

Experiment 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	Ag in coulometers. 10	Transference number × 10³. 11
		M	171.63	26.57	3,162	3,163	+ 1	..	..	..
		MA	145.82	22.60	2,687	2,690	+ 3	..	..	..
		A	347.01	60.64	6,394	7,219	+825	+828	564.7	158.3
18	3	K	280.38	36.50	5,166	4,345	—821	—822	552.8	160.5
		MK	145.40	22.50	2,679	2,678	— 1	..	..	..
		M	159.65	24.70	2,941	2,940	— 1	..	..	..
		MA	135.00	20.97	2,487	2,496	+ 9	..	..	..
		A	307.95	54.44	5,674	6,480	+806	+815	553.0	159.1
19	3	K	340.61	45.45	6,276	5,410	—866	—870	588.7	159.5
		MK	127.96	19.77	2,358	2,354	— 4	..	..	..
		M	159.91	24.74	2,947	2,945	— 2	..	..	..
		MA	152.38	23.65	2,808	2,815	+ 7	..	..	..
		A	355.91	62.33	6,358	7,419	+861	+868	588.8	159.1
20	3	K	287.80	39.08	5,303	4,653	—650	—656	441.8	160.3
		MK	102.36	15.79	1,886	1,880	— 6	..	..	..
		M	111.64	17.26	2,057	2,055	— 2	..	..	..
		MA	131.39	20.30	2,421	2,417	— 4	..	..	..
		A	423.23	70.95	7,799	8,446	+647	+647	441.7	158.1

TABLE 3.—TRANSFERENCE DATA FOR 0.0067 OR $^1/_{150}$ NORMAL NITRIC ACID AT 20°.

21	4	K	..	...	...	...	..	..	636.4	..
		MK	129.36	7.02	881	836	— 45	..	..	..
		M	159.75	8.84	1,087	1,052	— 35	..	..	..
		MA	132.01	7.65	899	911	+ 12	..	..	..
		A	372.55	29.12	2,537	3,467	+930	+942	636.5	159.8
22	4	K	370.41	14.24	2,522	1,696	—827	—850	578.4	158.6
		MK	135.75	7.57	924	901	— 23	..	..	..
		M	162.43	9.14	1,106	1,088	— 18	..	..	..
		MA	124.36	7.20	847	857	+ 10	..	..	..
		A	379.59	28.75	2,584	3,422	+838	+848	578.5	158.2
23	4	K	383.23	17.51	2,609	2,085	—524	—531	352.9	160.3
		MK	123.40	7.00	840	833	— 7	..	..	..
		M	142.82	8.09	972	963	— 9	..	..	..
		MA	113.52	6.54	771	778	+ 7	..	..	..
		A	406.87	27.60	2,770	3,285	+515	+522	352.7	159.5
24	4	K	339.32	15.20	2,311	1,810	—501	—507	337.3	162.2
		MK	123.67	7.02	842	836	— 6	..	..	..
		M	162.28	9.26	1,105	1,102	— 3	..	..	..
		MA	111.23	6.38	757	759	+ 2	..	..	..
		A	376.62	25.71	2,564	3,061	+497	+499	337.4	159.6
25	4	K	352.55	16.62	2,401	1,978	—423	—429	281.7	164.3
		MK	133.83	7.60	911	905	— 6	..	..	..
		M	140.73	8.00	958	952	— 6	..	..	..
		MA	127.78	7.33	870	873	+ 3	..	..	..
		A	359.34	24.03	2,447	2,860	+413	+416	282.0	159.3

TABLE 3 (*Continued*).

Experiment 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	Ag in coulometers. 10	Transference number $\times 10^3$. 11
26	5	K	348.65	14.68	2,303	1,747	−556	−559	377.5	159.7
		M_K	139.89	7.73	924	921	− 3	..	..	..
		M	139.52	7.67	922	913	− 9	..	..	..
		M_A	115.36	6.43	762	766	+ 4	..	..	..
		A	393.06	26.49	2,596	3,153	+557	+561	378.0	160.3
27	5	K	391.96	35.02	2,589	2,051	−538	−546	353.7	166.7
		M_K	133.43	14.90	881	873	− 8	..	..	..
		M	167.47	18.77	1,106	1,100	− 6	..	..	..
		M_A	132.85	14.99	877	878	+ 1	..	..	..
		A	419.49	56.11	2,771	3,288	+517	+518	353.5	158.1
28	5	K	369.56	31.75	2,444	1,861	−583	−593	397.3	161.1
		M_K	136.30	15.19	900	890	− 10	..	..	..
		M	148.75	16.68	983	978	− 5	..	..	..
		M_A	116.62	13.27	770	777	+ 7	..	..	..
		A	394.42	54.39	2,605	3,187	+582	+589	397.5	160.0
29	5	K	407.05	36.61	2,688	2,145	−543	−550	371.2	159.9
		M_K	128.28	14.34	847	840	− 7	..	..	..
		M	148.07	16.62	978	974	− 4	..	..	..
		M_A	129.11	14.64	853	858	+ 5	..	..	..
		A	416.34	56.22	2,750	3,294	+544	+549	371.2	159.6
30[1]	5	K	407.80	39.75	2,693	2,329	−364	−368	236.2	168.2
		M_K	112.65	12.64	744	740	− 4	..	..	..
		M	160.22	18.07	1,058	1,059	+ 1	..	..	..
		M_A	119.82	13.49	791	791	+ 0	..	..	..
		A	412.34	52.52	2,724	3,078	+354	+354	236.2	161.8
31[2]	5	K	286.25	36.52	2,551	2,140	−411	−417	275.6	163.3
		M_K	143.83	16.11	950	944	− 6	..	..	..
		M	148.08	16.59	978	972	− 6	..	..	..
		M_A	107.04	12.07	707	707	+ 0	..	..	..
		A	382.47	49.94	2,526	2,926	+400	+400	275.8	156.6
32[2]	5	K	409.57	34.24	2,705	2,006	−699	−703	472.0	160.7
		M_K	119.64	13.41	790	786	− 4	..	..	..
		M	164.62	18.49	1,087	1,083	− 4	..	..	..
		M_A	131.90	14.96	871	877	+ 6	..	..	..
		A	410.17	58.11	2,709	3,404	+695	+701	472.1	160.3

Tables 4 and 5 present the results obtained with the more dilute solutions, where the concentration was determined by conductance measurements. The first four columns are the same as in the preceding tables.

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[1] In this experiment (No. 30) the period during which the solution was electrolyzed was greater than the usual time (3½ hours), namely, 6 hours.

[2] In these experiments (Nos. 31 and 32) the solution was electrolyzed 4½ hours and 6 hours, respectively.

TABLE 4.—TRANSFERENCE DATA FOR 0.0022 NORMAL NITRIC ACID AT 20°.

Experiment No. 1	Solution No. 2	Portion. 3	Weight of portion. 4	Actual conductance × 10⁶. 5	Change in conductance × 10⁶. 6	Change in content. 7	Total change in content. 8	Ag in coulometers. 9	Transference number × 10⁴. 10
33[1]	6	K	349.79	1,498	—644	—2,336	—2,345	154.5	163.8
		M_K	97.13	2,133	— 9	— 9	...	...	...
		M	151.75	2,139	— 3	— 5	...	...	...
		M_A	118.86	2,156	+ 14	+ 17	...	...	...
		A	389.53	2,707	+565	+2,282	+2,299	154.5	160.6
34	7	K	349.70	1,813	—281	—1,019	—1,021	66.8	165.1
		M_K	119.33	2,092	— 2	— 2	...	...	...
		M	..	2,086	— 8	...	...	...	...
		M_A	123.57	2,095	+ 1	+ 1	...	...	...
		A	359.49	2,358	+264	+ 984	+ 985	66.7	159.3
35	7	K	359.94	1,562	—532	—1,986	—1,988	131.3	...
		M_K	106.04	2,092	— 2	— 2	...	...	...
		M	134.48	2,089	— 5	— 7	...	...	...
		M_A	113.76	2,104	+ 10	+ 12	...	...	...
		A	393.43	2,571	+477	+1,946	+1,958	131.2	161.0
36	7	K	350.57	1,528	—566	—2,058	—2,073	135.5	165.1
		M_K	104.87	2,080	— 14	— 15	...	...	...
		M	132.59	2,090	— 4	— 5	...	...	...
		M_A	115.59	2,105	+ 11	+ 13	...	...	...
		A	386.20	2,603	+509	+2,039	+2,052	135.5	163.4
37	7	K	..	...	...	...	...	134.6	...
		M_K	125.23	2,086	— 8	— 10	...	...	...
		M	134.42	2,095	+ 1	+ 1	...	...	...
		M_A	139.43	2,104	+ 10	+ 14	...	...	...
		A	376.86	2,606	+512	+2,001	+2,015	134.6	161.6

TABLE 5.—TRANSFERENCE DATA FOR 0.0021 NORMAL HYDROCHLORIC ACID AT 20°.

Experiment No. 1	Solution No. 2	Portion. 3	Weight of portion. 4	Actual conductance × 10⁶. 5	Change in conductance × 10⁶. 6	Change in content. 7	Total change in content. 8	Ag in coulometers. 9	Transference number × 10⁴. 10
1	1	K	384.26	1,250	—725	—2,862	—2,883	178.6	174.2
		M_K	125.64	1,959	— 16	— 21	...	...	...
		M	135.42	1,971	— 4	— 5	...	...	...
		M_A	126.10	2,000	+ 25	+ 32	...	...	...
		A	389.93	2,658	+683	+2,736	+2,768	178.9	167.1
2	1	K	313.49	1,360	—615	—1,980	—1,988	123.9	173.3
		M_K	132.60	1,969	— 6	— 8	...	...	...
		M	131.29	1,973	— 2	— 3	...	...	...
		M_A	112.29	1,989	+ 14	+ 16	...	...	...
		A	385.67	2,455	+480	+1,902	+1,918	123.9	167.2
3	1	K	372.66	1,466	—509	—1,949	—1,955	120.2	175.8
		M_K	121.26	1,970	— 5	— 6	...	...	...
		M	135.37	1,970	— 5	— 7	...	...	...
		M_A	130.33	1,985	+ 10	+ 13	...	119.8	...

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[1] In this experiment (No. 33) the electrolysis was continued for 4⅓ hours instead of for 3¼ hours as usual.

TABLE 5 (*Continued*).

Experiment No. 1	Solution No. 2	Portion. 3	Weight of portion. 4	Actual conductance × 10^6. 5	Change in conductance × 10^6. 6	Change in content. 7	Total change in content. 8	Ag in coulometers. 9	Transference number × 10^3. 10
4	1	K	385.12	1,295	—680	—2,690	—2,738	171.0	173.0
		M_K	115.65	1,935	— 40	— 48	...	...	...
		M	143.10	1,959	— 16	— 23	...	...	...
		M_A	126.67	1,995	+ 20	+ 26	...	...	...
		A	430.37	2,577	+602	+2,661	+2,687	170.9	169.7
5[1]	1	K	388.28	1,497	—478	—1,906	—1,917	115.0	180.1
		M_K	122.78	1,966	— 9	— 11	...	...	...
		M	138.55	1,970	— 5	— 7	...	...	...
		M_A	122.73	1,975	+ 0	+ 0	...	...	...
		A	424.00	2,383	+408	+1,777	+1,777	114.8	167.0
6	2	K	420.70	1,546	—590	—2,549	—2,574	161.0	172.5
		M_K	121.58	2,116	— 20	— 25	...	...	...
		M	148.97	2,127	— 9	— 14	...	...	...
		M_A	102.76	2,163	+ 27	+ 28	...	...	...
		A	458.17	2,664	+528	+2,485	+2,513	161.1	168.5
7[1]	2	K	443.00	1,761	—375	—1,706	—1,710	105.8	174.4
		M_K	122.55	2,133	— 3	— 4	...	...	...
		M	143.52	2,136	+ 0	± 0	...	...	...
		M_A	127.24	2,141	+ 5	+ 7	...	...	...
		A	476.09	2,473	+337	+1,648	+1,655	105.8	168.8
8[1]	2	K	436.04	1,862	—274	—1,227	—1,238	78.0	171.6
		M_K	107.32	2,126	— 10	— 11	...	...	...
		M	142.92	2,129	— 7	— 10	...	...	...
		M_A	118.21	2,078	— 58	— 70	...	77.7	...
9	2	K	458.82	1,819	—317	—1,494	—1,495	92.7	174.1
		M_K	107.75	2,135	— 1	— 1	...	...	...
		M	160.12	2,133	— 3	— 5	...	...	...
		M_A	104.29	2,142	+ 6	+ 6	...	...	...
		A	478.33	2,430	+294	+1,444	+1,450	92.8	168.8
10	2	K	438.20	1,835	—301	—1,355	—1,361	85.0	173.0
		M_K	114.76	2,131	— 5	— 6	...	...	...
		M	143.57	2,132	— 4	— 6	...	...	...
		M_A	104.46	2,136	+ 0	+ 0	...	...	...
		A	471.81	2,411	+275	+1,333	+1,333	84.9	169.3

The fifth contains the actual conductance × 10^6; the sixth, the difference between this value and the initial conductance × 10^6 as given at the end of Section 2;[2] the seventh, the corresponding change in content of the whole portion, expressed in 10^{-7} equivalents, obtained by multiplying this difference by the conductance capacity of the vessel (0.3956), dividing by the equivalent conductance values 382.1 for HNO_3 and 385.8 for

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[1] In Experiments 5, 7 and 8 the electrolysis was continued for only 2¾ hours.

[2] These initial values are: 2142 for HNO_3 solution No. 6; 2094 for HNO_3 solution No. 7; 1975 for HCl solution No. 1; and 2136 for HCl solution No. 2.

HCl,[1] and multiplying by the volume of the portion (obtained from its weight by multiplying it by 1.0018); and the eighth, the total change of content or the sum of the changes in the electrode portion and the adjoining portion. The ninth column contains the milligrams of silver deposited in the coulometers; and the tenth, the transference number for the anion × 10^3.

5. Summary of the Transference Numbers.

The following table contains a summary of the transference numbers derived from the preceding experiments together with the means derived therefrom. In finding the separate means of the cathode and anode values a few abnormally high or low values (designated by an asterisk) have been omitted.[2] To these means in the case of the two most concentrated solutions a correction has been applied to remove a small error introduced by the method used for the calculation of the separate values,[3]

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[1] These values are those of $d\text{L}/d\text{C}$ at 0.002 normal, where L represents the specific conductance and C the equivalent concentration. We derived them through a careful consideration of all the results obtained by Goodwin and Haskell with both acids at 18° between the concentrations of 0.001 and 0.005 normal. The values were first derived at 18° and were found to be 370.0 for HNO_3 and 373.5 for HCl, and these were then increased with the help of Déguisne's coefficients so as to make them correspond to 20°. It is scarcely possible that the errors in these values exceed 0.3 per cent.

[2] The high cathode values in Experiments 2, 3 and 4 were probably due to reduction by the electrolytic hydrogen, which was proved to have taken place in Experiment 2. The cathode value in Experiment 22 was omitted since the middle portion showed a large change in content.

[3] Namely, in calculating the original content the total weight of the electrode portion was simply multiplied by the initial content per gram. That weight had, however, been increased, over what it would have been originally, at the anode by the weight of the transferred nitric acid and had been decreased by the electrolysis out of it of the water corresponding to the hydrogen and oxygen evolved; and at the cathode it had been decreased by the weight of the transferred nitric acid.

By considering the effect of this on the result, it will readily be seen that when any acid of equivalent weight A, transference number n, and original content C in equivalents per gram of solution is electrolyzed as in this case with the production of hydrogen and oxygen, and the calculation is made as above (multiplying the total weight of the portion by C) then the anode transference-number should be increased by the fractional amount $(\text{A}n-9)\text{C}/n$ and the cathode transference number should be increased by the fractional amount AC. In this case, with the strongest (0.058) normal solution, the corrections, applied (since $\text{A} = 63$, $n = 0.156$, and $\text{C} = 0.000058$) are +0.03 per cent. on the anode value and +0.36 per cent. on the cathode value. With the 0.0184 normal solutions the corrections are one-third of these percentages.

The corresponding correction was not applied by Noyes and Sammet to their results with hydrochloric acid. It would have the effect of increasing their final value at 0.05 normal (165.69) by just 0.17 per cent. (to 165.06), while at the lower concentrations the correction would be scarcely appreciable.

A more simple way of calculating transference numbers from the experimental data is to refer the initial content to the weight of water present instead of to that of the whole solution, and to calculate correspondingly the weight of water in the portion and the results are designated "corrected means." These cathode and anode means have then been combined in the case of the three stronger nitric acid solutions under the assumption that each has a weight inversely proportional to the square of its average deviation (A. D.). Since the cathode values show in all three cases much greater variations, this procedure gives to the anode values a much greater weight, which would be *a priori* desirable since they are not subject to the possible error arising from the reduction of the nitric acid around the cathode. It is in fact very probable that both the larger variations and the greater magnitude of the cathode values are due to this cause. In spite of this source of error, it is to be noted that the mean cathode value exceeds the mean anode value by only 0.9, 0.6, and 1.1 per cent., respectively, in the case of the three more concentrated solutions. Taking into account the fact that almost all other errors affect the two results in opposite directions, we believe the final A. D. values give a fair measure of the probable precision of the final results, which is from 0.2 to 0.3 per cent. for the 0.06 to 0.007 normal nitric acid solutions.

In the case of the 0.002 normal solutions of both acids the divergence of the cathode and anode mean values is much greater, and it seemed best to assign an equal weight to each without reference to the value of

TABLE 6.—SUMMARY OF THE TRANSFERENCE VALUES.

0.058 normal HNO_3 at 20°.			0.0184 normal HNO_3 at 20°.			0.0067 normal HNO_3 at 20°.		
Experiment No.	Cathode.	Anode.	Experiment No.	Cathode.	Anode.	Experiment No.	Cathode.	Anode.
1	157.9	*157.4	13	159.0	159.0	21	...	159.8
2	*161.4	156.3	14	158.7	160.6	22	*158.6	158.2
3	*161.1	155.6	15	161.6	161.0	23	160.3	159.5
4	*160.6	156.3	16	162.0	159.2	24	162.2	159.6
5	154.5	155.4	17	159.2	158.3	25	164.3	159.3
6	156.0	156.0	18	160.5	159.1	26	159.7	160.3
7	157.7	155.2	19	159.5	159.1	27	*166.7	158.1
8	156.0	155.0	20	160.3	158.1	28	161.1	160.0
9	157.2	155.2	Mean	160.10	159.30	29	159.9	159.6
10	154.5	155.7				30	*168.2	161.8
11	158.1	155.0	Corrected mean	160.29	159.32	31	163.3	*156.6
12	156.5	155.1				32	160.7	160.3
Mean	156.49	155.53	a. d.	1.00	0.71	Mean	161.44	159.68
			A. D.	0.35	0.25	a. d.	1.36	0.69
Corrected mean	157.05	155.58	Final mean	159.64		A. D.	0.48	0.21
a. d.	1.10	0.41	Final A.D.	0.34		Final mean	149.96	
A. D.	0.36	0.12				Final A. D.	0.44	
Final mean	155.73							
Final A. D.	0.27							

after the electrolysis by subtracting from its total weight the weight of solute found in it; but even then a correction must be applied to the anode portion for the water electrolyzed out of it. The present basis of all such transference determinations is of course the assumption that the water itself does not migrate.

TABLE 6 (*Continued*).

0.0022 Normal HNO_3 at 20°.

Experiment No.	Cathode.	Anode.
33..........	163.8	160.6
34..........	165.1	159.3
35..........	163.5	161.0
36..........	165.1	163.3
37..........	...	161.6
Mean........	164.4	161.2
a. d.........	0.7	1.0
A. D........	0.4	0.5
Final mean..	162.8	
Final A. D...	1.2	

0.0021 Normal HCl at 20°.

Experiment No.	Cathode.	Anode.
1..........	174.2	*167.1
2..........	173.3	*167.2
3..........	175.8	..
4..........	173.0	*169.7
5..........	*180.1	*167.0
6..........	172.5	168.5
7..........	174.4	168.8
8..........	171.6	..
9..........	174.1	168.8
10..........	173.0	169.3
Mean.......	173.5	168.8[1]
A. D........	0.3	0.1
Final mean..	171.1	
Final A. D...	1.7	

its average deviation; for the divergence probably arises in the main from a slight contamination of these very dilute solutions during the experiment, which would affect the cathode and anode values oppositely and about equally. The final A. D. values, which expressed as percentages are 0.7 per cent. for the nitric acid and 1.0 per cent. for the hydrochloric acid, are again a fair measure of the maximum error of which there is any reasonable probability.

6. Summary and Discussion.

The final results of the transference experiments described in this article, as well as of those carried out by Noyes and Sammet[2] with 0.05–0.006 normal hydrochloric acid at 20°,[3] are brought together in Table 7. In this table are also given the values of the equivalent conductance of hydrogen-ion calculated from each transference number and from the most probable values for nitrate-ion and chloride-ion (64.6 and 68.5, respectively) at 20° and extreme dilution.[4] In the last row of the table are given the corresponding values for zero concentration as derived from Goodwin and Haskell's conductivity experiments.[5]

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[1] The mean of all the anode values is 168.3 but it seems best to omit the first four, in which experiments an anode of small surface was used, and which are somewhat lower perhaps owing to the evolution of a small quantity of chlorine.

[2] Z. physik. Chem., **43**, 63 (1903); This Journal, **24**, 958; **25**, 167 (1902–3).

[3] Corrected for the inaccuracy in their calculation as described in a preceding footnote.

[4] The value here given for the Cl is that derived by Noyes and Sammet from Kohlrausch's conductivity data and the existing transference data for potassium chloride. That for the NO_3 ion we have obtained by subtracting from that for the Cl the difference for these two ions at 20° given by Kohlrausch (*Sitzungsber. königl. preuss. Akad. der Wissensch.*, 1901, 1031). These values have then simply been multiplied by $(1 - n)/n$.

[5] These investigators found for Λ_0 at 18° 377.0 for HNO_3 and 380.1 for HCl. The corresponding values at 20° calculated with Déguisne's coefficients are 389.2 and 392.5 respectively. Subtracting from these the values for the NO_3 and Cl ions (64.6 and 68.5) one obtains the values for the hydrogen-ion given in the table.

TABLE 7.—FINAL VALUES OF THE TRANSFERENCE NUMBERS AND THE EQUIVALENT CONDUCTANCE OF HYDROGEN-ION.

Equivalent per liter.		Transference number × 10^3.		Equivalent conductance of hydrogen-ion from experiments with	
HNO_3.	HCl.	HNO_3.	HCl.	HNO_3.	HCl.
0.058	0.051	155.7	166.0	350.3	344.2
0.0184	0.017	159.6	167.5	340.2	340.5
0.0067	0.0056	160.0	167.1	339.1	341.4
0.0022	0.0021	162.8	171.1	332.2	331.8
0	0	166.0	174.5	324.6	324.0

It will be seen from Table 7 that, except at the highest concentration (0.055 normal), there is substantial agreement between the values of the equivalent conductance of hydrogen-ion derived from the independent transference experiments with the two different acids, and that the (nearly constant) value for the concentration interval between 0.018 and 0.006 normal is nearly 5 per cent. larger than that derived from conductivity measurements at extreme dilution. The reality of this divergence, first discovered by Noyes and Sammet, confirmed as it is on the conductivity side by the investigation of Goodwin and Haskell and on the transference side by the recent determinations of Jahn, Joachim, and Wolff, and by these new experiments with nitric acid, can, we believe, no longer reasonably be doubted. It must therefore be concluded that *the transference number of the anion of acids, and therefore the ratio of the velocity of the anions to that of the hydrogen-ion, is several per cent. larger at very small concentration* (0.001 normal and less) *than at moderate concentrations* (0.05 to 0.005 normal). Thus a change in the relative velocities takes place even after the concentration of the solute has become so small that as a medium the solution scarcely differs from the pure solvent. The fact that higher transference numbers were obtained with the 0.002 normal solutions than with the more concentrated solutions of both acids confirms the conclusion drawn from the comparison with the conductivity data. The values obtained at 0.002 normal show, moreover, that even at this very low concentration the velocities have not yet become identical with those at zero concentration.

This change of the transference number may, of course, arise either from an acceleration of the anion or from a retardation of the hydrogen-ion at very high dilution, or from both causes combined. The facts that salts do not as a rule show any change in their transference numbers after a moderate dilution is reached and that their ionization values calculated from freezing-point lowering and other molecular properties agree with those corresponding to the conductance ratio (Λ/Λ_0)[1] make it probable, however, that it is the fast-moving hydrogen-ion that is

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[1] See A. A. Noyes, Z. physik. Chem., 52, 634.

mainly, if not wholly, affected.[1] It is under this (possibly incorrect) assumption, namely, that neutral ions have the same velocity at moderate and at very low concentrations, that the values, given in Table 7, of the equivalent conductance of hydrogen-ion at various concentrations were derived.

The fact that the values of the equivalent conductance of hydrogen-ion are nearly constant for the interval of concentration 0.006–0.018 seems to indicate that these are the normal ones, and that the variations at lower concentrations arise from some secondary effect of a general character, determined perhaps by the smallness of the ion-concentration itself.

The results obtained at the highest concentration (0.05 to 0.06 normal) differ in the case of the two acids, which makes it seem probable that the variation in the stronger solution is due to some different cause, probably one of a specific chemical nature, from that which gives rise to the change at high dilutions.

As to the bearing of these results on the calculation of ionization values, it may be said that in the case of largely ionized acids at moderate concentrations it seems in the light of now existing knowledge most appropriate to divide the observed equivalent conductance of the acid by a Λ_0 value obtained by adding to the equivalent conductance of the anion that of the hydrogen-ion obtained by the transference experiments above described at the concentration in question. On the other hand, in the case of any acid solution in which the *ion* concentration is less than 0.001 normal the older value (324 at 20° or 315 at 18°) for hydrogen-ion is to be preferred.

It is of interest to compare the ionization of hydrochloric acid computed in the manner just stated with that of neutral salts of the same ionic type, like potassium and sodium chlorides. At the concentration 0.05 normal the ionization value derived from Kohlrausch's value (360) of the equivalent conductance of the acid at 18° is found to be 0.948, provided the equivalent conductance of hydrogen-ion is taken at 315 as derived from the conductivity of the acid at small concentrations; but it becomes 0.900 when the equivalent conductance of hydrogen ion is taken 6.2 per cent. larger than this, in accordance with the transference results. At this same concentration the ionization values for potassium chloride and sodium chloride, as derived from their equivalent conductances, are 0.891 and 0.878. The approximate agreement of these values with the new one for hydrochloric acid seems to justify the extension to largely ionized acids of the principle that salts of the same ionic type have at the same concentration roughly the same degree of ionization.

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[1] It is therefore probable that the decrease in the conductance of strong acids always observed at very high dilutions is not wholly due to impurities in the water.