disappearance of the iodate; bromate and chlorate may be determined in either sulfuric or hydrochloric acid by adding titanium to the solution until the final drop which marks complete reduction, is reached.

3. Ferricyanide also may thus be determined electrometrically with titanium as accurately as any other form of ferric iron.

GRINNELL, IOWA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF CLARK UNIVERSITY, I, 28]

THE CONDUCTANCE OF DILUTE AQUEOUS SOLUTIONS OF HYDROGEN CHLORIDE

BY HENRY C. PARKER[1]

Received June 4, 1923

Introduction

In a recent investigation,[2] Kraus and Parker determined the conductance of iodic acid, using water of various degrees of specific conductance and both glass and quartz cells. If it is assumed that the measurements made in quartz cells with water having a specific conductance of 0.09–0.12 $\times$ 10^{-6} are correct, the presence of an error was demonstrated in the measurements made with water of higher specific conductance and with glass cells. The use of glass cells was shown to influence the results to a somewhat greater extent than the impurities that are present in ordinary "conductivity water." The limiting value for the equivalent conductance of iodic acid, found from the measurements in the quartz cells, was about 0.9% higher than the value found from the measurements in glass cells.

It appeared of interest to confirm the results of Kraus and Parker by carrying out a series of measurements with a typical strong acid in a quartz cell. Hydrochloric acid was chosen, since the equivalent conductance of the chloride ion is known with considerable certainty, and since solutions of this acid may be made by weighing the constituents involved.

Preparation of Materials

The hydrochloric acid was prepared by means of the apparatus shown in Fig. 1.

In this figure, A is the generating flask; B is a wash bottle, containing "special" sulfuric acid, and C is a trap, introduced to prevent the water in the absorption flask from being drawn back into the generating flask. This trap is likewise filled with "special" sulfuric acid. The absorption flask E is constructed of clear quartz and has a capacity of approximately 1500 cc. D is the drying tube containing phosphorus pentoxide. With the exception of a short piece of rubber tubing, connecting the absorption flask to the drying tube, all connections are of glass. In order to avoid contamination,

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[1] National Research Fellow in Chemistry.

[2] Kraus and Parker, THIS JOURNAL, **44**, 2429 (1922).

no stopcock grease was used on any of the ground-glass joints. The entire apparatus was cleaned and dried, the absorption flask being cleaned with cleaning mixture, live steam, distilled water, and finally with purified air. After drying, the absorption flask was weighed; and after several rinsings about 1000 g. of special conductivity was collected. About 80 g. of a highly purified commercial sodium chloride, which had been purified from insoluble matter by filtration and evaporation of the solution to dryness,[3] was then introduced into the generating flask and the sulfuric acid was allowed to flow upon it. Toward the end of the reaction a small amount of heat was applied to the generating flask, but care was exercised to keep the reaction running smoothly. When the reaction in the flask was completed, the difference in the weight of the absorption flask amounted to about 45 g. and this weight, together with the weight of the water originally introduced into the flask, gave the data necessary for the purpose of calculating the strength of the acid, with the accuracy of a few thousandths of 1%. Both of these weights were reduced to a vacuum. In this reduction, allowance was made for the change in density of the solution, and thus the difference between these weights gave the weight of the hydrogen chloride reduced to a vacuum.

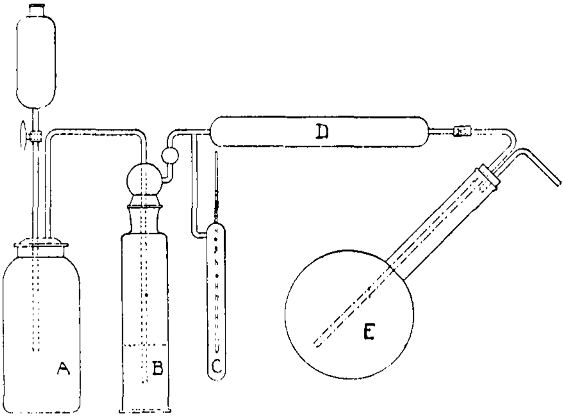

Fig. 1

The acid prepared in this manner had a concentration of approximately 1.4 *N*. About 150 g. of this concentrated solution was transferred by means of air pressure into a second quartz flask, which contained a weighed quantity (about 1000 g.) of the special conductivity water. The strength of this dilute solution (approximately 0.1 *N*) was still known to a few thousandths of 1%. This was the solution that was employed in making up the dilute solutions whose conductance was finally measured. The water employed in making up these solutions was prepared in the still described by Kraus and Dexter.[4] The method of purifying the air as well as other details of manipulation were the same as those previously employed with iodic acid and need not be further described here.

Measuring Apparatus

The apparatus employed in carrying out the electrical measurements was the same as that previously employed by Kraus and Parker. A fre-

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[3] This purification was carried out by Mr. G. F. Des Autels, to whom thanks are also due for checking several resistances and supervising the generation of the hydrogen chloride.

[4] Kraus and Dexter, This Journal, **44**, 2468 (1922).

quency of 1217 was used throughout this investigation at a potential of approximately 7 volts.

The dilute solution, mentioned above, was introduced into the large quartz cell from the weight pipet which is shown in Fig. 2.

All parts of this pipet that come in contact with the acid are constructed of quartz. The capacity is approximately 50 cc. The glass tube b serves the double purpose of centering the pipet over the hole in the stopper of the cell through which the solution was introduced, and of preventing evaporation when the weight of the pipet is being determined. The stopper h into which this glass tube is ground is made of de Khotinsky cement. The flow of the acid solution from this pipet is governed by the pinch clamp e.

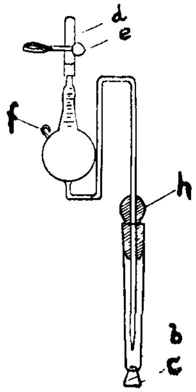

Fig. 2

The cell used in these measurements is the 3-liter Vitreosil flask called Cell II in the article by Kraus and Parker, a drawing of which is shown in Fig. 3 of that article. In the present investigation, however, the glass tubes, which were used to support the electrodes were replaced by quartz, the seals being made after the manner described by Kraus.[5] With these new electrodes it will be called Cell II_d. Owing to the difference in expansion between platinum and quartz, it was impossible to connect the brace across the lower ends of the electrodes to the upper part of the electrode stems, as was done with Cell II. The electrodes were held rigidly, however, by means of 2 heavy platinum wires, crossed nearly at right angles and welded to the small platinum tube leading from the quartz seal. This method gives sufficient rigidity for all purposes.

Intercomparison of Cell Constants

In a recent article,[6] Kraus and Parker showed the presence of an error in the data given by Kohlrausch and Holburn[7] which have been commonly used for the purpose of determining the cell constants in conductance investigations. They suggested the use of the data given by Kohlrausch and Maltby[8] for the specific conductance of potassium chloride, as a basis for this determination, and gave the necessary data for making up these solutions by weight methods. This was the procedure adopted in the present investigation. It was necessary, however, to use auxiliary cells of pipet form in order to calibrate Cell II_d. The constants for these auxiliary cells were determined at 18°, the data for which are found in Table I, while the intercomparison between these and Cell II_d was carried out at 25°.

[5] Kraus, U. S. pat. 1,093,997, **1914**.

[6] Kraus and Parker, THIS JOURNAL, **44**, 2422 (1922).

[7] Kohlrausch and Holburn, "Leitvermögen der Elektrolyte," Teubner, Leipzig, p. 76.

[8] Kohlrausch and Maltby. *Wiss. Abh. Phys.-Tech. Reichsanst.*, **3**, 180 (1900).

TABLE I

CONSTANTS OF STANDARD CELLS

	Cell A	Parallel-series combination	Cell D
Solution I	11.657_4	5.9478_0	3.1507_2
Solution II	11.657_4	5.9475_6	3.1507_7
Av.	11.657_4	5.9476_8	3.1507_4

The apparatus used in these intercomparison measurements is shown in Fig. 3 of a recent article by Parker.[9] In these measurements, unlike the measurements given in that article, the tube at *o*, the stopcock at *q*, and the pinch clamp at *p* were used in order to break the column of liquid through the tube *e*, just before resistance measurements were taken. This was accomplished by introducing a slight air pressure into the system at *a*, when the stopcock *q* was open.

In the present investigation, 4 pipet cells were intercompared with the Cell II_d. These 4 cells, called Cells *A*, *B*, *C* and *D*, were connected by means of T-tubes in the neighborhood of *d* (Fig. 3 mentioned above) and also at the upper part of the stem, where connections were made with the air line. In this manner the 4 cells acted simultaneously when the solution was being mixed. Resistance measurements were taken upon the 5 cells at each of a series of concentrations. Measurements were also made when the pipet cells were connected in series and parallel combina-

TABLE II

INTERCOMPARISON MEASUREMENTS OF CELL II_d

Before Run I

Resistance of Cell II_d Ohms	Cell constant from Cell *A*	Cell constant from parallel-series combination	Cell constant from Cell *D*
18.799	0.23163	0.23162	0.23161
41.006	.23121	.23120	.23119
96.922	.23088	.23085	.23086
209.71_2	$.23069_9$	$.23065_7$	$.23066_4$
601.73_8	$.23053_6$	$.23049_5$	$.23047_7$
1556.8_7	$.23058_5$	$.23049_4$	$.23050_9$
2629.5_5	$.23074_9$	$.23038_1$	$.23053_8$
3637.1_7	$.23116_7$	......	$.23059_2$
7394.4_1	......	$.23035_1$	$.23082_0$
$15586._6$	......	......	$.23861_1$
After Run I			
537.04_5	$.23057_6$	$.23055_9$	$.23055_0$
2442.0_7	$.23072_4$	$.23051_1$	$.23061_2$
After Run II			
242.37_6	$.23071_7$	......	$.23058_0$
331.39_5	$.23066_8$	$.23061_0$	$.23059_3$
1834.2_6	$.23080_4$	$.23060_0$	$.23066_0$

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[9] Parker, THIS JOURNAL, **45**, 1371 (1923).

tions. The results obtained with Cells II_d, *A* and *D*, and with the parellel-series combination (obtained when *B* and *C* are connected in parallel and in series with *D*) are given in Table II. Cells *A*, *B* and *C* have electrodes of 1 sq. cm. cross section, while Cell *D* has electrodes of twice this area. Cell *A* is about 15 cm. in length, while the others are half this length.

In the first column are given the resistances of Cell II_d obtained at each of a series of concentrations of potassium chloride. The data given in the second column have been obtained by dividing the resistance of Cell II_d by the resistance of Cell *A*, for the same concentration, and multiplying this by the constant of Cell *A* as found in Table I. The data found in the third and fourth columns have been obtained in a similar manner by making use of the resistances of the parallel-series combination and of Cell *D*, respectively. The values found in these columns, therefore, represent the apparent "cell constant" of Cell II_d for that particular concentration, when this is determined by intercomparison with the cell in question. These values are plotted against the resistance of Cell II_d in Fig. 3.

Theory for the Variation

A theory to account for the variation in the apparent "cell constant" exhibited in the curves shown in Fig. 3 is outlined in a recent article by Parker.[10] This theory accounts for this variation by the presence of an adsorbed layer in proximity to the electrodes, which has a greater or less resistance than the body of the solution according as the electrolyte is adsorbed negatively or positively, in this layer. This theory appears to be supported by the present investigation. It appears probable that potassium chloride is negatively adsorbed at a platinum surface, while hydrochloric acid is positively adsorbed.[11]

Such an absorbed layer would be affected to a considerable extent by the conditions under which measurements were made. First, the resistance of this layer would have a relatively less effect upon the total resistance of the cell if the distance between the electrodes was great. Second, the resistance of such a layer would be inversely proportional to the cross section of the electrodes. Third, the adsorption occurring would be sensitive to factors such as traces of grease, dissolved gases, etc., which would lower the surface tension. Fourth, if we assume that the effect of the alternating current is to "spread out" this layer, it is evident that the "spreading" would be influenced by the voltage and frequency of the alternating current. The first of these phenomena has, in a previous communication,[12] been shown to occur. The occurrence of the second

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[10] Ref. 9, p. 1378.

[11] Pickles, *J. Chem. Soc.*, **119**, 1278 (1921). Schilow, *Z. physik. Chem.*, **100**, 425 (1922).

[12] Ref. 9, p. 1376.

will be demonstrated in a subsequent article. The third effect has been noted by the writer and was mentioned by Taylor and Acree.[13] The occurrence of the fourth was mentioned by Kraus and Parker,[14] in their measurements upon iodic acid, where it was found that an increase of voltage caused an apparent increase in the resistance of potassium chloride and a decrease with iodic acid solutions. (A decrease is likewise obtained with hydrochloric acid.) This difference in sign may be accounted for by the difference in sign of the adsorption.

If we have negative adsorption in the case of potassium chloride solution, then the resistance of the adsorbed layers in contact with the electrodes will be greater than that of the body of the solution. Hence the observed resistances in the more dilute solutions may be expected to be greater than the true resistances. Since the "cell constant" is proportional to the resistance of a given solution, such a cell as Cell II$_d$ would exhibit an increasing "cell constant" in the more dilute solutions when intercompared with a cell showing a *relatively* smaller correction, due to these adsorbed layers. In case the intercompared cell exhibited a relatively greater correction, then the apparent "constant" of Cell II$_d$ would decrease in the more dilute solutions. Both of these cases may be seen in Fig. 3, where the "constant" of Cell II$_d$ is shown as a function of the observed resistance. Its "constant" has been determined by intercomparison with 3 cells, 2 of which show a relatively smaller correction and the third a greater. Curves I and II, representing the former case, were plotted

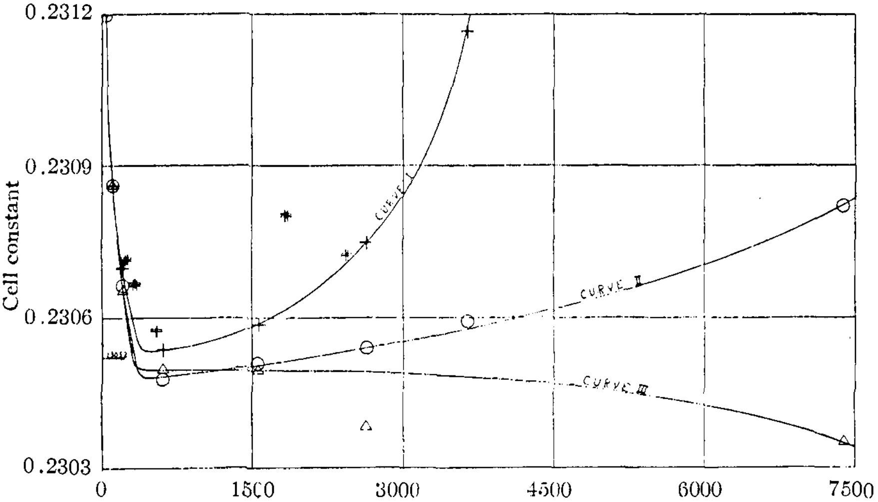

Fig. 3

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[13] Taylor and Acree, This Journal, 38, 2416 (1916).

[14] Ref. 2, p. 2438.

from the intercomparison data obtained with Cells A and D, respectively, while Curve III, representing the latter case, represents measurements with the parallel-series combination. The large effect obtained when cells are measured in series seems to be characteristic of these phenomena.

The independent and characteristic variation exhibited by the curves in Fig. 3 constitutes one of the strongest proofs that the effect is caused *in the cell.* It is evident that the measurements at the higher resistances are not at fault, or at least not to the same extent for each cell, since no single correction curve for the higher resistances could possibly be drawn which would reconcile these variations.

Selection of Cell Constant

The effect of such an adsorbed layer would probably become negligible in the more concentrated solutions. In order to determine the constant of a cell, therefore, this would make it advantageous to use as concentrated a solution as possible, providing the resistance is sufficiently high to avoid polarization effects. This condition has been fulfilled in all cases where the standard cells were calibrated directly against the standard potassium chloride solutions, so it is believed that the values given in Table I are accurate. With Cell II_d, however, it is impossible to utilize one of these standard solutions, on account of the presence of polarization at the low resistances which would be obtained. The electrodes of Cell II_d are about 2.3 cm. apart, so it is probable that there will be a considerable correction for the adsorbed layers, at the higher resistances, when potassium chloride solutions are used. It is evident that, if a cell could be found which would give nearly the same relative correction as Cell II_d at a given concentration but which could be calibrated with one of the standards in the more concentrated solutions, the corrections would cancel in the more dilute solutions, where the two cells could then be intercompared. Such a secondary cell is illustrated in the case of the parallel-series combination. It is evident from the curves of Fig. 3 that the Cell D has a somewhat greater correction than Cell II_d, while the parallel-series combination has only a slightly *smaller* correction. Curve III, therefore, is most suitable for the determination of the correct "constant" for Cell II_d.

Cell II_d was thrice intercompared with Cells A, B, C and D. The results that were obtained after Run I with hydrochloric acid and at the conclusion of Run II indicated a constant about 0.02% greater than that found in the first series of measurements. This is shown by the points above Curve I, Fig. 3, where the results obtained after Run I are indicated as double crosses and those after Run II as triple crosses. The difference was so small, however, that the same "constant" for Cell II_d was assumed for the two runs, the results of the two intercomparisons being averaged. If we select Curve III to determine the "constant" of Cell II_d, it is evident from the preceding discussion that the position upon this curve the most likely to give the correct value would be in concentrated solutions, just before the commencement of polarization. When this value was determined from Curve III, a correction of 0.01% was added, on account of the higher value found in the two later intercomparisons. The final value thus selected was 0.23052, which is indicated in Fig. 3. If Curves I or II had been chosen, instead of Curve III, this value would be changed to the extent of about ±0.015%.

It is probable that hydrochloric acid is positively adsorbed from the solution in contact with the electrodes. Whether the actual resistance should be greater or less than the observed will depend on two factors. First, the resistance of the adsorbed layer would be less than that of the body of the solution, and if the alternating current is assumed to cause considerable "spreading" of this adsorbed material, the resistance observed might be less than the true resistance. Second, if this adsorption takes place to such an extent that the concentration in the body of the solution is reduced, the observed might be greater than the true resistance. The large volume of the solution (3 liters) surrounding the electrodes of Cell II_d would reduce an error of the latter nature, but in any case it is probable that these factors both are small and partly compensate each other, so it is evident that no correction should be applied to this "constant" when measuring acid solutions. The assumption will be made then that this value remains fixed at 0.23052, for these solutions.

Density of Hydrochloric Acid

The densities of the solutions of hydrochloric acid which were used in these calculations were taken from the data of Cameron and Robinson.[15] These data are plotted in Fig. 4. It is seen that the points at 0.005 and 0.01 *N* do not coincide with the curve, which is drawn straight down to the density of water at 25°, in the more dilute solutions. These points appear to be somewhat in error, although the other points agree with the results of Reyher[16] for more concentrated solutions, so it is thought that the remaining points are sufficiently reliable. In any case, the corrections for the change of density upon the dilute solutions used in this investigation are almost negligible. The densities were read from the smooth curve shown in Fig. 4.

Experimental Procedure and Results

The experimental procedure was very similar to that employed in the investigation with iodic acid, the principle changes being due to the use of a solution of hydrogen chloride, instead of a solid in order to make up the solutions whose conductance was examined. The water in which the

[15] Cameron and Robinson. *J. Phys. Chem.*, **14**, 1 (1910).

[16] Reyher, *Z. physik. Chem.*, **2**, 548 (1888).

hydrogen chloride was absorbed and that u for diluting the concentrated solution was drawn from the cell as it was being filled with the conductivity water, and consequently was the best obtainable. The diluted standard hydrochloric acid solution, added to the cell, was allowed to stand in the quartz pipet for an hour before the latter was refilled and weighed. The pipet was handled with great care in order that the weighings should be accurate. The smallest amount of acid solution weighed was 0.6 g., while the weighings were reproducible to better than 0.1 mg. In all, 50 cc. of the dilute acid solution was added to the cell. The neck of the quartz flask serving as a cell was large enough so that this amount of liquid made a difference in the height of the solution of about 25 mm. It was experimentally determined that the addition of this amount of solution did not change the "cell constant" appreciably.

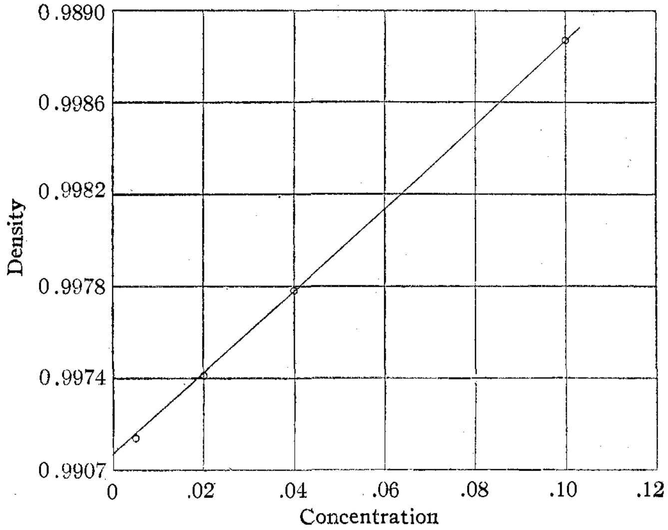

Fig. 4.—Density of HCl at 25°. Cameron and Robinson

The data obtained in these measurements are given in Table III, where are shown the values of the equivalent conductance and the concentration, the latter of which is expressed in millimoles per liter. The molecular weight assumed for the hydrochloric acid is 36.468. At the bottom are given the weight of water in the cell, the specific conductance of the water, the cell constant, resistance of the leads and the strength of the acid solution that was added to the cell. The latter is expressed as grams of hydrogen chloride (reduced to a vacuum) per gram of solution (weighed in air). The other weights are reduced to a vacuum.

These data are shown in Fig. 5, where $1/\Lambda$ is plotted against $C\Lambda$. The consistency of this work with hydrochloric acid is seen to be nearly as great as that of the results with iodic acid. The impurities in the water are

Table III

Conductance of Hydrochloric Acid

Run I		Run II	
Concn. × 10³	Λ	Λ	Concn. × 10³
0.037653_3	424.32_8	0.036012_6	424.42_8
$.098305_3$	424.95_7	$.079849_8$	425.06_3
$.14387_8$	425.05_1	$.11434_5$	425.52_5
$.23408_4$	424.73_0	$.18285_7$	424.97_1
$.36600_4$	424.26_4	$.32813_8$	424.42_0
$.76350_6$	422.58_8	$.53297_4$	423.55_9
1.3697_9	422.24_0	1.2123_0	421.58_3
2.9041_4	418.66_0	2.6494_0	418.92_5

	Wt. H_2O in vacuum	Sp. cond. H_2O	Wt. HCl (vac.) per g. of soln. added	Cell const.	Resist. of leads
Run I	3249.00	0.15×10^{-6}	0.0072783_6	0.23052	0.507
Run II	3265.89	$.09 \times 10^{-6}$	$.0066616_9$	0.23052	0.507

shown to influence the results to a somewhat greater degree than in the case of iodic acid. A possible explanation is that the dilute acid solution becomes slightly contaminated when it is being introduced into the cell. The first two points in each run will have to be neglected, when extrapolating

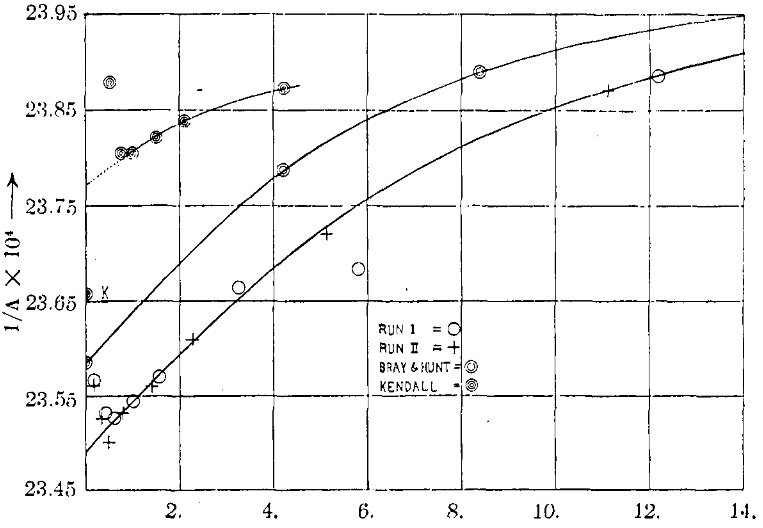

Fig. 5

to infinite dilution, for this reason. The seventh point of Run I is also in error for some unknown reason.

Conductance Data at Round Concentrations

The data given in Table III were plotted on a large scale in order to interpolate the values at round concentrations. $\Lambda_0 - \Lambda$ was plotted against

C. The first two points of each run were neglected, and Runs I and II were weighted as 1:2, which is about the relative precision of two runs carried out in succession in this manner. The values for the concentration expressed in millimoles per liter, the values for the specific conductance, for γ, for K, and for the equivalent conductance, Λ, which were obtained by means of this plot are given in Table V. In the last column are given the average deviations of the experimental points from the interpolated curve, when these points have been weighted as above.

TABLE IV

HYDROCHLORIC ACID AT ROUND CONCENTRATIONS

Concn. $C \times 10^3$	Spec. cond. $L \times 10^3$	γ	$K = \frac{\gamma^2 C}{1-\gamma}$	Equiv. cond., Λ	Av. dev. %
0.0	0	1.0		425.69	
0.05	0.021274_4	0.999_{53}	0.10_5	425.48_9	
.1	1.042528_6	$.999_{05}$	$.10_5$	425.28_6	0.025
.2	$.08497_{66}$	$.9981_0$	.105	424.88_3	..
.3	$.12734_4$	$.9971_6$	.105	424.48_1	.008
.4	$.16963_3$	$.9962_2$	$.105_0$	424.08_2	..
.5	$.21184_2$	$.9952_8$	$.105_1$	423.68_3	.002
.6	$.25398_1$	$.9943_9$	$.105_6$	423.30_2	..
.7	$.29605_2$	$.9935_1$	$.106_4$	422.93_1	.016
.8	$.33808_0$	$.9927_4$	.1085	422.60_0	..
.9	$.38004_2$	$.9920_1$	.1108	422.29_1	..
1.0	$.4219_{97}$	$.9913_2$	.1131	421.99_7	.085
2.0	$.8397_{35}$	$.9863_2$	.1421	419.86_7	..
3.0	1.255_{63}	$.983_{21}$	$.172_6$	418.54	.005

In Table VI are found the values at round concentrations for iodic acid, from the work of Kraus and Parker.[17] For this interpolation the values of $\Lambda_0 - \Lambda$ were plotted against C, for the more dilute solutions, while Λ was plotted directly against C in the more concentrated. Run 1 was neglected, and Runs 2, 3, 4 and 5 were weighted in proportion to the numbers 1:2:3:4 which is, again, about the relative precision of a series of measurements carried out in this manner. Runs 6 and 7 were weighted as 1:2, over the part of the concentration range covered by these runs. The first two points in Runs 6 and 7 were neglected for reasons given in that article. The data given in Table VII (Kraus and Parker, Run 10) obtained in glass cells, are used for the interpolation below 0.01 N, where the concentration is high enough so that the impurities in the water and alkali from the glass do not measurably affect the results.

The average deviations of the experimental points from the interpolated curve are again given in the last column when weighted as above. If the different runs are not weighted, these deviations will, of course, be

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[17] Ref. 2, pp. 2439–40. In Table VI, p. 2439 the data given for the concentrations of Run 7 are expressed in moles per liter instead of millimoles, as indicated at the top of this table.

increased, but the values given in this column are very close to the values which would be found by using the more precise of the runs and neglecting the others. For that reason these values represent the true precision of the interpolated results more nearly than the values obtained by giving

Table V

Iodic Acid at Round Concentrations

Concn. $C \times 10^3$	Spec. cond. $L \times 10^3$	γ	$K = \frac{\gamma^2 C}{1-\gamma}$	Equiv. cond., Λ	Av. dev. %
0	....	1.0	....	389.55	....
.01	0.003894_{96}	$.999_{85}$	0.07_{17}	389.49_{6}	....
.02	$.007788_{84}$	$.999_{71}$	$.07_{17}$	389.44_{2}	....
.03	$.011681_{6}$	$.999_{57}$	$.07_{17}$	389.38_{7}	....
.04	$.015569_{3}$	$.999_{43}$	$.07_{17}$	389.23_{3}	....
.05	$.019463_{9}$	$.999_{29}$	$.07_{17}$	389.27_{9}	0.022
.06	$.023347_{5}$	$.999_{15}$	$.07_{17}$	389.22_{5}	....
.07	$.027242_{0}$	$.999_{02}$	$.071_{7}$	389.17_{1}	....
.08	$.031129_{3}$	$.998_{87}$	$.071_{7}$	389.11_{6}	....
.09	$.035015_{6}$	$.998_{73}$	$.071_{7}$	389.06_{2}	....
.1	$.038900_{8}$	$.9985_{9}$	$.071_{7}$	389.00_{8}	.018
.2	$.07769_{40}$	$.9972_{1}$	$.071_{7}$	388.47_{0}	....
.3	$.11638_{0}$	$.9958_{4}$	$.071_{7}$	387.93_{4}	.002
.4	$.15496_{0}$	$.9944_{7}$	$.071_{7}$	387.40_{1}	....
.5	$.19343_{0}$	$.9931_{4}$	.0719	386.87_{9}	.013
.6	$.23181_{7}$	$.9918_{0}$	$.0720_{9}$	386.36_{1}	....
.7	$.27010_{2}$	$.9905_{1}$	$.0725_{0}$	385.86_{0}	.009
.8	$.30830_{4}$	$.9892_{8}$	$.0731_{4}$	385.38_{0}	....
.9	$.34642_{6}$	$.9880_{9}$	$.0739_{0}$	384.91_{8}	.005
1.0	$.38448_{0}$	$.9869_{8}$	$.0748_{4}$	384.48_{0}	.003
2.0	$.7609_{20}$	$.9766_{7}$	$.0817_{5}$	380.46_{0}	....
3.0	1.1311_{5}	$.9679_{2}$	$.0876_{0}$	377.05_{2}	.019
4.0	1.4962_{8}	$.9602_{6}$	$.0928_{2}$	374.07_{0}	....
5.0	1.8568_{3}	$.9533_{2}$	$.0973_{5}$	371.36_{6}	.027
6.0	2.2130_{7}	$.9468_{2}$	$.1012_{0}$	368.84_{5}	....
7.0	2.5653_{0}	$.9407_{6}$	$.1045_{7}$	366.47_{2}	.008
8.0	2.9141_{2}	$.9350_{9}$	$.1077_{7}$	364.26_{5}	....
9.0	3.2596_{5}	$.9297_{5}$	$.1108_{6}$	362.18_{4}	.004
10.0	3.6018_{4}	$.9246_{2}$	$.1134_{1}$	360.18_{4}	.006
20	6.870_{4}	$.8818_{4}$	$.1316_{2}$	343.52	....
30	9.966_{3}	$.8528_{0}$	$.1482_{3}$	332.21	.043
40	12.805	$.8218_{2}$	$.1516_{2}$	320.14	....
50	15.554	$.7985_{9}$	$.1583_{2}$	311.09	.005
60	18.192	$.7783_{3}$	$.1639_{8}$	303.20	....
70	20.735	$.7604_{2}$	$.1689_{4}$	296.22	.007
80	23.190	$.7441_{4}$	$.1731_{4}$	289.88	....
90	25.567	$.7292_{5}$	$.1767_{8}$	284.08	.01
100	27.873	$.7155_{2}$	$.1799_{7}$	278.73	.01
200	48.50_{4}	$.622_{56}$	$.205_{38}$	242.5_{2}	....
300	65.95_{5}	$.564_{34}$	$.219_{33}$	219.8_{5}	.03
400	81.76	$.524_{4}$	$.231_{6}$	204.4	....
500	95.85	$.492_{1}$	$.238_{4}$	191.7	.15

equal weight to the different runs. It may be mentioned that these interpolated results agree, in the more concentrated solutions, with the work of Ostwald[18] and Groschuff[19] upon iodic acid, well within the limits of their experimental error. This fact gives a check upon the values of the cell constants used in these measurements.

Discussion

The experimental values of $1/\Lambda$ and $C\Lambda$ obtained in the two runs with hydrochloric acid are plotted in Fig. 5. In comparison with the similar curve for iodic acid, given by Kraus and Parker,[20] it is seen that the form of the curve is very similar in the two cases. The slope of the curve for hydrochloric acid is less steep, showing the latter to be the more highly ionized, but the concentration range over which the measurements approximate a straight line, within the experimental error, is nearly identical. This type of curve may thus be considered the general form holding for solutions of strong acids. It is evident that such acids obey the mass-action law to a much closer approximation in the very dilute solutions than is the case with the inorganic binary salts.

The value for the equivalent conductance at infinite dilution obtained from this curve is 425.69. If the value for Λ_0 for the chloride ion at 25° is assumed to be 75.8, as found by Noyes and Falk,[21] this will give a value of 349.89 for the limiting value of the hydrogen ion at 25°. The corresponding value obtained with the iodic acid was 349.93. It is evident that this check is even better than could be reasonably expected, although these numbers are based, in reality, upon the relative values of Noyes and Falk for the Λ_0 of the iodate ion at 18° and the chloride ion at 25°,[22] and thus these measurements constitute a check upon these relative values. The greater chance for a discrepancy between the work with iodic acid and hydrochloric acid, however, consisted in the determination of the cell constants, in the two cases. When the cell constants were determined in the investigation with iodic acid, it was not recognized that these quantities varied with the concentration in the case of some electrolytes, and it was more by accident than intention that the determination of this quantity was made in the neighborhood of the minimum of the cell constant curve for Cell II, when intercompared with the standard cell. The accurate method of intercomparison used in the present investigation had not then been devised and, since the measurements in the more dilute

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[18] Ostwald, *J. prakt. Chem.*, [2] **32**, 300 (1885).

[19] Groschuff, *Z. anorg. Chem.*, **47**, 331 (1905).

[20] Ref. 2, p. 2442.

[21] Noyes and Falk, THIS JOURNAL, **34**, 454 (1912).

[22] Thus, in the work with iodic acid the value for Λ_0 of the iodate ion, at 25°, was *experimentally* determined with considerable precision, in terms of the value given by Noyes and Falk, for 18°.

solutions were inconsistent, there was no other choice than to accept the measurements made in the neighborhood of this minimum point. The degree of precision obtained in these two investigations, which is indicated by the values for the average deviations from the interpolated curve, would indicate, of course, that a check of this order of magnitude might be expected.

The value of the mass-action constant, corresponding to the straight line drawn in the more dilute solutions of Fig. 5 is 0.105, while the corresponding value for iodic acid was found to be 0.0717. Whatever other significance these values may have, it is probable that at least they measure the relative "strength" of these acids.

Work of Other Investigators.—Hydrochloric acid has been the subject of several important investigations, although no two of the investigations show agreement at infinite dilution. Most of the investigations have been carried out at 18°, but these may be compared with the measurements at 25°, with the aid of a few assumptions. Thus, the difference in the Λ_0 values for the hydrogen ion at 18° and 25° was found experimentally by Kraus and Parker to be 34.31; while the difference between the corresponding values for the chloride ion given by Noyes and Falk, is 10.3, giving a total of 44.6 to be added to the value of Λ_0 for the hydrochloric acid at 18° in order to transform this value to that for 25°.[23] When this quantity is added to the values of Λ_0 at 18°, the following values are obtained at 25°, for the two most accurate investigations: Goodwin and Haskell,[24] —424.7; Noyes and Cooper,[25] —423.6. The values obtained in the investigations made at a temperature of 25° are as follows: Bray and Hunt,[26] —424; Kendall,[27] —422.7. The values obtained are seen to vary between 422.7 and 424.7. for the Λ_0 of hydrochloric acid at 25°. All of these investigations were made with glass cells and conductivity water of only a fair degree of purity. In none of these investigations were the solutions made up by weight methods, a procedure that has been accomplished in the present investigation.

Conclusion

The results of Kraus and Parker with iodic acid in glass and quartz cells and with water of various degrees of purity would indicate that, except for experimental error, the investigations mentioned in the pre-

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[23] It is believed that this value of 44.6 is relatively accurate, since the relative values of Λ_0 at 18° and 25° are known to a greater degree of precision than the absolute values. Thus, if the value given by Bates [This Journal, **35**, 534 (1913)] or by Washburn [This Journal, **40**, 158 (1918)] had been chosen for the Λ_0 of the iodate ion at 18°, instead of that of Noyes and Falk, the Λ_0 values of the hydrogen ion, determined by Kraus and Parker at 18° and 25° would both have been increased to the extent of 0.1 or 0.2, respectively, while the difference between these values at 18° and 25° would have remained unchanged. Similarly, the difference in the values of Λ_0 for the chloride ion at 18° and 25°, as found by the extrapolation method used by Bates and Washburn, would agree closely with the value 10.3 obtained by Noyes and Falk.

[24] Goodwin and Haskell, *Phys. Rev.*, **19**, 369 (1904).

[25] Noyes and Cooper, *Carnegie Inst. Pub.*, **63**, 137 (1907).

[26] Bray and Hunt, This Journal, **33**, 787 (1911).

[27] Kendall, *ibid.*, **39**, 13 (1917).

ceding paragraph should give a value of Λ_0 approximately 0.9% low.[28] This should vary, however, with the circumstances surrounding the investigations. Thus Goodwin and Haskell used a cell of which the greater part was of platinum, and employed two different methods of correcting for the impurities in the water, so it is evident that their determination should be but slightly lower than the value found in the present investigation. Bray and Hunt, whose calculated values are indicated in Fig. 5, used the results of Goodwin and Haskell for extrapolation, so these results should likewise, be, close. Both of these conditions are fulfilled. The results of Noyes and Cooper and of Kendall, of which the latter are shown in Fig. 5, are 0.5% and 0.7% lower, respectively, than the results obtained in the present investigation. The value of Λ_0 given by Kendall, however, is not obtained by extrapolation but by adding the limiting value for the chloride ion to a value of the hydrogen ion previously obtained. The value 422.7, obtained in this manner, is indicated in Fig. 5 at a point considerably below his experimental results and marked "*K*." An extrapolation such as indicated by the dotted line would give a result of 420.7, showing difference of 1.2% from the results obtained in the present investigation. The value for the mass-action constant, determined from this extrapolation, would be about 0.08 higher than that obtained in the present investigation. Thus, it is indicated that the results of other investigators confirm the conclusions reached by Kraus and Parker regarding the effect of (1) the impurities in the water and (2) the use of glass cells upon the conductance of an acid solution.

It is interesting to note that the impurities of the water in the investigation by Kendall are apparently of a different nature from those obtained in the present investigation. This is seen by the sharper minimum in his experimental results. The next experimental point in the more dilute solutions would come far above the plot. The slope of the line given by Bray and Hunt's calculated values is nearly identical with that obtained in the present investigation. This fact would tend to support the expedients employed by Goodwin and Haskell for the elimination of the effect of the impurities in the water. The actual experimental values obtained by Bray and Hunt are far above the plot and cannot be indicated. It appears, however, that their curve would coincide with the curve obtained in the present investigation, if these were extended to the more concentrated solutions.

The value of Λ_0 for the hydrogen ion obtained in this investigation is based upon a somewhat firmer foundation than the value obtained with

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[28] Upon extrapolating to infinite dilution the results for iodic acid in a glass cell, 386.04 is found for Λ_0, a value 0.9% lower than for the results in quartz cells. The corresponding value of the mass-action constant is 0.05 high.

iodic acid, due to the greater certainty in the determination of the cell constant. Heretofore, the values of Λ_0 for the other ions were known to a considerably greater degree of accuracy than was the case with the hydrogen ion. These two investigations upon iodic acid and hydrochloric acid seem to have reversed the situation. The extrapolation of the results with strong acids appears to be somewhat more safely accomplished, due to the fact of closer conformity to the mass-action law. Until the values for the chloride and iodate ions are known with a greater degree of accuracy, there is small purpose in giving the value for the hydrogen ion to more than one decimal place. However, if it is assumed that the value for the chloride ion at 25° is 75.8, the most probable value for the hydrogen ion appears to be 349.89 ± 0.05. This number will, of course, represent a lower limit to this value, due to the method of extrapolation.

Summary

1. The conductance of aqueous solutions of hydrochloric acid has been determined at 25° between the concentrations of 0.04 and 3.0 millimoles per liter. The solutions were made up by weight methods to an accuracy of a few hundredths of 1%. Water was used having a specific conductance of the order of 0.1×10^{-6}.

2. The values for the equivalent conductance show a slight maximum in the neighborhood of 0.1 millimoles per liter, due to the influence of the impurities in the water, which apparently cause a somewhat greater effect than in the case of iodic acid.

3. Comparison with the results of other investigators confirm the conclusions of Kraus and Parker regarding the considerable influence of the impurities in the water and of the alkali in glass cells upon the conductance o dilute acid solutions.

4. Values at round concentrations have been interpolated from the results upon hydrochloric and iodic solutions. The data for iodic acid are given from 0.05×10^{-3} *N* to 0.5 *N*.

5. The "cell constant" was determined by an intercomparison with 3 standard cells, over a considerable range of concentrations with potassium chloride as the electrolyte. The unusual results of this intercomparison may be explained by assuming the presence of an adsorbed layer (in contact with the electrodes) whose resistance is greater or less than that of the body of the solution, according to whether the electrolyte is negatively or positively adsorbed. One of the intercompared cells apparently has a greater correction for this "adsorbed layer" than the cell used in the measurements with the hydrochloric acid, while the other two have a smaller correction. On the supposition that hydrochloric acid will be positively adsorbed and will consequently have but slight correction for this effect, a value for the "constant" is selected at the minimum point of

the "cell constant" curve, which value is assumed to remain fixed in the measurements with the acid solutions.

6. Extrapolation of the results upon the assumption that the mass-action law is approached as a limiting form at infinite dilution, gives a value of Λ_0 for hydrochloric acid of 425.69. Assuming that the value of Λ_0 for the chloride ion at 25° is 75.8, a value of 349.89 for the hydrogen ion at that temperature is obtained. By comparing this with the value 349.93 obtained by Kraus and Parker for iodic acid, the value 349.89 ± 0.05 is deduced as the most probable value for the hydrogen ion at 25°—the basis for the "cell constant" being more firmly established in the measurements with hydrochloric acid. The mass-action constant corresponding to this extrapolation has a value of 0.105.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

GERMANIUM.[1] VI. METALLIC GERMANIUM. REDUCTION OF GERMANIUM DIOXIDE. PREPARATION OF FUSED GERMANIUM. PHYSICAL AND CHEMICAL PROPERTIES

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Received June 4, 1923

Material.—The germanium that was used in these investigations was prepared by the reduction of pure germanium dioxide that was practically free from other metals, including arsenic.[3]

Dehydration of Germanium Dioxide

Since it was desirable that germanium dioxide be thoroughly dehydrated before experiments were made upon its reduction, the lowest temperature at which complete dehydration resulted was ascertained by heating germanium dioxide that had been dried at about 100° to successively higher temperatures until constant weight was obtained. It was found that the dioxide is completely dehydrated when heated to a temperature of 950° for about 3 hours, and that there is no volatilization of germanium dioxide at a temperature of 1250°. The dehydration may be effected rapidly by heating the oxide over a gas-air blast flame, and the product that is formed is not hygroscopic.

[1] This article is based upon the theses presented to the Faculty of the Graduate School of Cornell University by Katharina M. Tressler and F. E. Hance in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] The experimental work of this investigation was carried on separately and not jointly by Miss Tressler and Mr. Hance.

[3] Dennis and Papish, THIS JOURNAL, **43**, 2131 (1921). Dennis and Johnson, *ibid.*, **45**, 1380 (1923).