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THE CONDUCTANCE OF AQUEOUS SOLUTIONS OF IODIC ACID AND THE LIMITING VALUE OF THE EQUIVALENT CONDUCTANCE OF THE HYDROGEN ION

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Introduction

While the conductance of aqueous solutions of the salts has been extensively investigated and we now have fairly reliable data for these substances to concentrations as low as $10^{-4} N$ or even lower, the corresponding data for the strong acids and bases in aqueous solutions remain very uncertain. Obviously, the limiting values of the equivalent conductance for the acids and bases are even less certain. This lack of accurate data for the acids and bases is largely due to the fact that at low concentrations conductance measurements with these substances are attended with difficulties inherent in the nature of the solutions in question. In measuring the conductance of a dilute solution it is necessary, on the one hand, that all the electrolyte present shall be in a known state and, on the other, that the specific conductance due to this electrolyte shall be determinable. Except in the case of salts of weak acids and bases, where hydrolysis intervenes, impurities present in the water have little influence on the state of the salt in solution. At the same time, any impurities present are not measurably influenced by the presence of the salt, and accordingly the conductance due to these impurities may be corrected for by measuring the conductance of the water from which these solutions are made up. With solutions of the acids and bases, this is not the case. In view of the fact that the present investigation is limited to an acid, it is unnecessary to discuss the case of solutions of bases further than to state that the behavior of these substances is similar to that of the acids. If the impurity present in the water from which an acid solution is made up contains a base, or the salt of a weak acid, then the concentration of the acid will be influenced by the presence of this material; furthermore, the correction to be applied for the conductance due to the impurity cannot be determined by measuring the conductance of the original solvent. This difficulty was met with at a very early date. It was found that the equivalent conductance of an acid, instead of approaching a limiting value asymptotically as the concentration is decreased, passes through a maximum after which it decreases the more, the lower the concentration.¹ It has been suggested that this result is due to the presence of a base or a salt of a

¹ Arrhenius, Bihang Schwed. Akad., 8, Nos. 13 and 14 (1884). Kohlrausch, Ann. Physik, 26, 161 (1885). Ostwald, J. prakt. Chem., 31, 433 (1885). Compare also Kohlrausch and Holborn, "Leitvermögen der Elektrolyte," Teubner, Leipzig, 1898, p. 92.

weak acid in the solvent, as a result of which a certain amount of the hydrogen ion disappears on reaction with the base and the equivalent conductance is accordingly decreased.² This decrease will, of course, be relatively the greater, the lower the concentration of the acid. Thus far, however, no measurements have been carried out in which this source of error has been eliminated.

Indeed, the error in the case of the acids may be traced to two sources: first, impurities present in the water used in making up the solution; and second, impurities dissolved from the containing vessels. The first of these sources of error has been recognized as mentioned above, but the second source of error appears not to have been considered heretofore. It is well known, however, that even the best of glass is appreciably soluble in acids and it is accordingly to be expected that experiments carried out in glass cells will be measurably affected at low concentrations owing to the solubility of the glass. In order to overcome these difficulties, therefore, it is necessary to carry out measurements with water which has been freed from all impurities and in cells which are resistant to the action of acids. In the present investigation, pure water has been prepared by a method previously developed in this Laboratory³ and measurements have been carried out in a quartz cell.

In selecting an acid for the purpose of this investigation, it appeared desirable, if possible, that the acid should be relatively strong in order to reduce the errors due to extrapolation and that it should be readily manipulated for the purpose of making up the solutions. For this reason iodic acid was chosen, since it is readily prepared in a pure state as a solid, in which condition it may be weighed and transferred to the cell, while at the same time it is but little weaker than hydrochloric acid.

Preparation of Materials

Iodic Acid.—The iodic acid employed in this investigation was prepared from the best quality of iodic acid obtainable on the market. This acid was purified by repeated recrystallization. Considerable difficulty was at first experienced in the process of recrystallization owing to the fact that, on evaporating an aqueous solution, the acid forms a supersaturated solution which is brought to crystallization with difficulty, even on inoculation. It was found, however, that when a small amount of nitric acid is added to the water solution and the water is extracted slowly in a desiccator, beautiful crystals of the acid are formed. A beaker containing sodium hydroxide was placed in a desiccator with sulfuric acid, together with the solution of iodic acid. The purpose of the sodium hydroxide was to prevent the concentration of the nitric acid from reaching too high a value. After precipitation, the crystals of iodic acid were washed with very dilute nitric acid and then dried over a solution of potassium hydroxide. This was for the purpose of removing any possible remaining traces of nitric acid. The last traces of moisture were removed over sulfuric acid. The final process of desiccation was carried

² Whetham and Paine, Proc. Roy. Soc., 81A, 58 (1908). Paine and Evans, Proc. Cambridge Phil. Soc., 18, 1 (1914).

⁸ Dexter, Dissertation, Clark University, 1917. This JOURNAL, 44, 2468 (1922).

out shortly before the iodic acid was to be used, since otherwise, as was found, a certain amount of the anhydride, I_2O_5 , is liable to be formed. The process of recrystallization above described was carried out 4 times.

The purity of the acid was tested by various methods. First, the acidity was determined by comparison with a solution of hydrochloric acid which had been standardized against silver by weighing as silver chloride. The average of three determinations gave for the normality of the acid the value $0.10273 \pm 3 N$. The sodiumhy droxide solution used compared with this standard acid, in two titrations, gave the factor 0.099193 ± 11 , weight burets being employed. On titrating the iodic acid against this solution of sodium hydroxide, the results given in Table I were obtained.

	1 A.	BLE I	
	DETERMINATION OF	ACIDITY OF IODIC ACI	ID
HIO₃ taken	NaOH	HIO3 found	Error
G.	G.	G.	%
0.74285	42.581	0.74307	+0.03
0.51119	39.318	0.51162	+0.08
0.85278	48.9185	0.85367	+0.016

The acidity was likewise determined by a new method which consists in precipitating the iodate with silver as silver iodate and weighing. Since silver iodate is somewhat soluble, the filtrate is saved and analyzed, iodine being liberated with potassium iodide and sulfuric acid and titrated against standard thiosulfate solutions. The results of this method are given in Table II.

TABLE II

DETERMINATION OF IODIC ACID AS SILVER IODATE					
AgIO3	HIO_3 in filtrate	Total HIO ₃ found	Error		
G.	G.	G.	%		
0.33721	0.0027	0.21247	+0.04		
0.24019	0.00226	0.15168	+0.07		
0.26617	0.00192	0.16750	-0.11		
	ETERMINATION AgIO3 G. 0.33721 0.24019 0.26617	AgIO3 HIO3 in filtrate G. G. 0.33721 0.0027 0.24019 0.00226 0.26617 0.00192	$\begin{array}{cccc} {\rm ETERMINATION \ OF \ IODIC \ ACID \ AS \ SILVER \ IODATE \\ {\rm AgIO}_3 & {\rm HIO}_3 \ in \ filtrate \ Total \ {\rm HIO}_3 \ found \\ {\rm G.} & {\rm G.} & {\rm G.} \\ 0.33721 & 0.0027 & 0.21247 \\ 0.24019 & 0.00226 & 0.15168 \\ 0.26617 & 0.00192 & 0.16750 \end{array}$		

The nitrate content was shown to be negligible by a colorimetric test, using phenolsulfonic acid, the iodate being precipitated with silver sulfate. This test showed roughly 6 parts of nitrogen as nitrate per million of iodate. An attempt was also made to determine the iodic acid by dehydrating to anhydride and weighing the difference, as well as by liberating the iodine by means of potassium iodide and estimating by means of standard thiosulfate solution. Neither of these latter tests proved entirely satisfactory, however, the former on account of the difficulty of perfect dehydration, and the latter owing to the large amount of iodine liberated. The former tests, however, in all cases fell within the limit of experimental error and were thus satisfactory from that point of view.

The best proof of the purity of the iodic acid, however, consists in the agreement of the values obtained with samples of iodic acid from the different crystallizations. The precision of the conductance measurements is far greater than that of any analytical method which is here applicable. The four runs in dilute solutions given below represent results with three different crystallizations of the acid; and, as may be seen, these agree very closely.

Water.—The water employed in this investigation was purified by the method developed in this Laboratory. Ordinary water was distilled from an alkaline permanganate solution under the usual conditions, the first fraction of the distillation being discarded. The product obtained was then again distilled from a dil. alkaline permanganate solution in a special still of the type mentioned above in which carbon dioxide was removed by fractional condensation. In order to avoid contamination due to the surrounding atmosphere, distillation was carried out under a slight pressure of air which had previously been purified, as will be described below. The water employed in



Fig. 1.—Construction of air purifying towers.

these measurements had a specific conductance varying between 0.09×10^{-6} and 0.5×10^{-6} . As will be seen below, with water having the higher value of the specific conductance, the influence of the impurities could be detected in the conductance values.

Purification of Air.—Pure air was necessary for the purpose of stirring the solution in the cell as well as for the preparation of the water as stated above. The air used for this purpose was purified by means of a special set of continuously acting towers, a sketch of which is shown in Fig. 1. The air enters through the tube A, carrying before it a column of the purifying solution which is raised to the top of the tower and there projected over the beads with which the tower is filled. The air then passes down among the beads over which the solution is continuously flowing. The chamber containing the beads has a length of approximately 50 cm. and a diameter of 3 cm. so that the rate of flow of the air through the purifying apparatus is relatively low. This method of purification was found very successful. In order to remove both ammonia and carbon dioxide, 3 towers were employed, the first of which was filled with a solution of sulfuric acid and the remaining 2 with solutions of sodium hydroxide. The necessary pressure for the air

was obtained by means of an aspirator.

Measuring Apparatus

Bridge.—A drum-wound, slide-wire bridge with extension coils was used in measuring the resistance of the solutions. The bridge wire was calibrated by the Kelvin method, and by means of the corrections obtained it was possible to check resistance readings to better than 0.01%. Air condensers were employed to balance out the effects of inductance and capacity in the circuit. The entire apparatus was carefully shielded, all connections being lead covered and grounded and all measuring instruments being kept within a lead-lined case.

Source of E.M.F.—A Vreeland oscillator was employed as a source of alternating current. The oscillator was fitted out with a variable air transformer by means of which it was possible to regulate the voltage, while the frequency of the oscillator was adjusted

by means of suitable capacities introduced in the oscillator circuit. In general, 4 combinations of capacities were employed and the frequencies corresponding to these were determined by means of an oscillograph. Prints of the records thus obtained are shown in Fig. 2. The horizontal dashes appearing in the figure are due to the timing device. It is seen that the oscillator gave a perfect sine wave. Since



Fig. 2.—Oscillogram of Vreeland oscillator.

the oscillograph had a frequency considerably above 10,000, any overtones which might have been present would unquestionably have appeared on the plate.⁴ The four fre-

⁴ This result would appear to contradict the statement of Eyster [J. Am. Inst. Elec. Eng., 39, 889 (1920)] to the effect that the Vreeland oscillator does not give a sine wave.

quencies thus determined were found to be 1747, 1217, 986.5 and 489.5 per second. It was found that in most cases a frequency of 1217 gave the most satisfactory result, both as regards the accuracy of the readings and the distinctness of the setting. This frequency was, therefore, used practically throughout this work.

Resistances.—The resistance boxes consisted of Curtis-wound coils, ranging from 10 to 10,000 ohms capacity. These were calibrated against resistance standards which had recently been calibrated at the Bureau of Standards. In the older measurements, which were carried out with solutions contained in glass cells, the resistances had not been calibrated, for which reason the measurements are not as accurate as those later obtained. These earlier results, however, have not been used for the purpose of determining the final conductance values. In the later measurements with quartz and Pyrex glass cells, which were begun in about September, 1919, and completed in June, 1920, calibration corrections were made. Two series of calibrations of the resistances were carried out, one in September, 1919, and another in May, 1921. All the coils below 10,000 ohms were found to be constant over this interval to better than 0.01%, but the 10,000 ohm coils showed a variation of 0.88%. Accordingly, in correcting the measurements, it was assumed that the resistance varied as a linear function of the time, and a correction applied which amounted to 0.044% per month. Four standard resistances of 10, 100, 1,000 and 10,000 ohms were employed. These were found to be mutually consistent. All calibrations were carried out with a direct current and galvanometer. With all corrections applied, it was found possible to obtain check measurements within 0.005%.

The Measuring Cells.—In all, 5 cells were used in measuring the conductance of the acid, in addition to an auxiliary cell of the pipet form which was employed for the



Fig. 3.-Construction of various types of cells employed.

purpose of calibrating the measuring cells. Two of the measuring cells were constructed of soda-lime glass, and two of quartz, and a fifth cell was constructed of Pyrex glass. The cells are shown in outline in Fig. 3. In this figure, V A and V B represent front and side elevations, respectively, of the glass cell which was employed in measuring the conductance of the dilute solutions. The electrodes of this cell had an area of approximately 1.5 sq. cm. and were placed 4 cm. apart. The body of the cell was approximately 60 cm. long and 5 cm. in diameter and had a volume of approximately 1 liter. The glass cell used for measurements at higher concentrations had electrodes of the same cross section as Cell V which were placed at a distance of 17 cm. from each other. This cell is shown as VI A and VI B in the figure. The height of this cell was approximately 30 cm. and its volume approximately 200 cc. The electrodes in all cells were platinized according to the method of Kohlrausch, and were then heated in a blowpipe flame until gray.

In the same figure, II represents the large quartz cell employed in measurements with the more dilute solutions. This cell consisted of a Vitreosil flask having a volume a little over 3 liters. The electrodes had an area of 1.5 sq. cm. and were placed at a distance of 2.5 cm. from each other. The electrodes were provided with a brace underneath in order to guard against displacement. The electrode stems were constructed of glass, but the tube F, through which air was blown for the purpose of stirring the solution, was constructed of quartz. A rubber stopper D served to hold the electrodes in position in the cell. The cell was calibrated in order to determine the effect of the position of the electrodes, especially with reference to the level of the liquid. A curve of resistance readings for different heights of the liquid was made and the height corresponding to a minimum distance was chosen for the position of the electrodes. In this position a difference of 1.25 cm. in the level of the liquid was required to make a difference of 0.01% in the resistance. The quartz cell used for carrying out the measurements at higher concentrations is shown as IV A and IV B. Circular electrodes, having an area of approximately 1.5 sq. cm., were placed in a horizontal quartz tube of 30 cm. length and of 2 cm. diameter. The leads were introduced after the manner described by Kraus.⁵ The form of the cell as here shown was so designed that its contents could readily be mixed by shaking without removing it from the thermostat. The capacity of this cell was approximately 1.5 liters. The construction of the Pyrex glass cell was similar to that of Cell IV.

The Thermostat.—The thermostat employed in these measurements was kept at a constant temperature within 0.002° by means of a steel-contained mercury thermoregulator. In carrying out the measurements with the glass cells, the thermostat was filled with water, but in all the later measurements the thermostat was filled with kerosene. At very low concentrations, where the resistance of the cell is large, capacity effects apparently are introduced when a water-filled thermostat is employed, and it was for this reason that kerosene was later employed in place of water.

Balance.—The balance used for weighing out the acid was a standard analytical balance especially adjusted for a sensitivity of 0.02 mg. It was found possible to obtain check weighings to 0.01 mg. The weights used were calibrated against a set of assay weights which had been standardized by the Bureau of Standards.

Preliminary Measurements

Cell Constant.—The values of the cell constant throughout this investigation are based upon the measurements of Kohlrausch and Maltby⁶ with solutions of potassium chloride at 18°. The constant of the auxiliary cell, from which the constants of the other cells were determined by intercomparison, was determined at 18°, according to the method described in the preceding paper by the present authors.

The cell constants as determined with a series of independent solutions are given in Tables III and IV. In Table III are given values of the con-

⁶ Kohlrausch and Maltby, Wiss. Abh. Phys.-Tech. Reichsanst., 3, 157 (1900).

⁵ Kraus, U. S. pat., No. 1,093,997, 1914.

stant for the standard cell I as determined at different times during the course of the investigation.

		TABLE III	
	Cons	STANT OF STANDARD CELL	I
В	efore Run I	After Run V	After Run VI
	3.67125	3.67039	3.67041
	3.67113	3.67098	3.67037
	3.67108		
	3.67123		
Av.	3.67117	3.67068	3.67039

It will be seen that there is a slow drift of these values with the time. A sufficient check, however, was kept upon this variation so that the cell constant as determined for the measuring cells may be relied upon. In Table IV are given the constants of the large quartz cell II, the Pyrex glass cell III, the small quartz cell IV, the large lime glass cell V, and the small lime glass cell VI.

TABLE	IV
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CONSTANTS OF DIFFERENT CELLS USED IN MEASURING THE CONDUCTANCE OF IODIC

			ACID		
	Cell II				
	Before Run I	Before Run II	Before Runs III, IV,	After V Run V	
	0.28616	0.285436	0.284748	0.284697	8.26770
	0.28644	0.285379	0.284711	0.284796	8.26665
		0.285391	0.284741		
Av.	0.28630	0.285402	0.284733	0.284747	8.26717
		Cell IV		Cell V	Cell VI
	Run VI	Ru	n VII		
	6.98116	6.9	99346 ().715824	6.35052
	6.98186	6.9	99317 ().715403	6.35013
		6.9	99278		
	Av. 6.98151	6.9	99313	0.715613	6.35033

The constants of Cells III, IV and VI were determined at 25° , using the specific conductance given in the preceding article. The values of the constant of Cell II, which was used for the most accurate determinations in dilute solutions, are given as determined at different times. These determinations were made each time with a series of independent solutions made up in the cell and then intercompared with the standard Cell I. The resistance of the solution in Cell II was usually in the neighborhood of 400 ohms, although at one time the resistance of the solution was varied between 250 and 1300 ohms in order to determine, if possible, whether the cell constant varies as a function of the concentration. The measurements in the more dilute solutions, however, did not check well because

of various sources of error.⁷ The cell constants finally employed in this investigation are the mean values given at the bottom of Tables III and IV.

The actual measurements on iodic acid, and most of the measurements on the cell constants, were carried out at a temperature of 24.958° instead of 25° . All data have been converted to the corrected temperature by factors which were determined by measurements made at the two temperatures with a series of solutions. These factors are as follows: to convert the resistance of the potassium chloride solution from 24.958° to 25° , multiply by 0.999202; to convert the resistance of iodic acid solutions from 24.958° to 25° , multiply by 0.999434. In determining these factors, the solutions were carried back and forth between the temperatures in question several times. The readings agreed to better than 0.01%. The values given are the averages of all the readings taken.

Temperature.—The temperatures of 18° and 25° were established by means of 2 Beckmann thermometers which had been calibrated against a platinum resistance thermometer.⁸ A series of comparisons were made over a range of temperatures in the neighborhood of the temperatures in question and the results were plotted in order to determine the readings at 18° and 25° . The temperature interval from 18° to 25° , which had been used previous to this calibration, was found to be correct to 0.01° . The final calibration was found to agree exactly with the reading of a mercury thermometer which had been calibrated by the Reichsanstalt in 1910.

Density Measurements.—In order to reduce the concentrations to a volume normal basis, it was necessary to determine the density of iodic acid solutions. The results of these measurements are given in Table V and are shown graphically in Fig. 4. The results of Heydweiller and Groschuff, made at 18° and 0° , respectively, and reduced to 25° , are also shown on the figure. In correcting these results to 25° , it was assumed that the density change of the solution between the temperatures in question is the same as that of pure water between the same temperatures. As may be seen from the figure, the three series of measurements check closely up to a concentration of about 0.5 N. It is probable that above

⁷ A further investigation, in order to determine whether or not the cell constant varies as a function of the concentration, has been carried out by one of the present authors (Parker) using a very accurate method of intercomparison. This investigation showed that the constant of this cell and, in fact, the constant of every cell investigated, varies appreciably with the concentration. The results will appear shortly in a publication from this Laboratory.

⁸ The thermometer in question is one which was in use in the Research Laboratory of Physical Chemistry of the Massachusetts Institute of Technology and which had been carefully calibrated by Dr. James A. Beattie. We wish to express our indebtedness to Dr. Beattie for his assistance in connection with the calibration and also to Dr. Frederick G. Keyes, Director of the Research Laboratory. this concentration the assumption made for the reduction of the results of Heydweiller and Groschuff to 25° does not hold. For the measure-



ments at 0.08373 N and 0.68879 N a pycnometer was used, while at the other concentrations given in the table the results were obtained by means of a Mohr's balance. The final values employed were read from the smooth curve shown in the figure.

TABLE V DENSITY OF IODIC ACID SOLUTIONS AT 25° ₫4²⁵ d₄25 Conc. Conc. 0.08373 1.00902 0.664271.094670.144854 1.018780.688791.09768 0.318609 1.04379 0.911111.129571.05675 0.40788.

Resistance of Leads.—The resistance of the leads to the cells was in each case determined by filling the cell with mercury and measuring the resistance against a series of low resistances, using direct current and a galvanometer. The resistance of the wires leading from the bridge to the resistance box had to be taken into consideration. In view of the fact that readings were carried out with the bridge setting near the middle of the bridge, sufficient precision was obtained by subtracting from the total calculated resistance the difference between the resistance of the leads in the cell and the remaining leads in the bridge set-up. The values of these differences as determined were as follows: Cell I, 0.047 ohms; Cell II, 0.032 ohms; Cell III, 0.092 ohms.

Variation of Cell Resistance with Frequency and Potential.-Taylor and Acree⁹, in their investigation, found a variation of the cell resistance with the frequency of the current and also with the value of the impressed voltage. These effects were also observed in the present investigation. It was always found possible to eliminate the change of resistance with the frequency by sufficient platinization of the electrodes so that the difference in resistance between 500 and 1700 cycles was as low as 0.01%. In measurements with the quartz cell, no readings were made with resistances below 300 ohms, since the above-mentioned effect was found to increase greatly at low resistances. The change of resistance with the voltage was more difficult to eliminate. It was suggested by Taylor and Acree that this change is due to contamination of the solution in the cell, but it is difficult to believe that this is the sole reason for this behavior, since the effect was observed in the quartz cell after one or two bucketsscrupulously clean-had been dropped into conductivity water of a specific conductance of only 0.09×10^{-6} . A voltage change from 0.2 to 7 volts usually produced a change in the apparent resistance of about 0.02%. In the case of the iodic acid solutions, it was noticed that the higher voltage gave the lower resistance, while in that of potassium chloride solutions the effect was in the opposite direction and of about the same order of magnitude. This effect was also observed when film resistances were employed in place of the Curtis coils, thus showing that the phenomenon is localized in the cell itself. It was not found possible to locate the cause of this effect in the limited time available and, since it was necessary to use a higher voltage in order to obtain reliable bridge readings at the higher resistances, it was decided to employ the higher voltage throughout the measurements. With low resistances, the higher voltage caused some difficulty as a result of thermal effects but this was eliminated by rapid readings.

Experimental Procedure and Results

Manipulation.—The method of carrying out a series of conductance measurements was as follows. The iodic acid was weighed in small quartz buckets which were hung on a platinum wire in a desiccator. These buckets were all weighed and checked shortly before making a run. In the case of the runs carried out with the quartz cells, the buckets were provided with a small bulb at the top which served to float them, thus keeping them out of the way of the electrodes and also providing a quick and convenient method of obtaining concentration equilibrium in the solution. At the bottom, the buckets were provided with a small opening through which the solution flowed out as rapidly as formed. With the use of these buckets, it was usually possible to obtain concentration equilibrium at the end of a period of 10 minutes. The buckets were cleaned

⁹ Taylor and Acree, THIS JOURNAL, 38, 2415 (1916).

by treating with cleaning mixture, boiling water, and finally by steaming and drying over an electric hot plate. The cells were cleaned inside and out with hot cleaning mixture, after which hot water was allowed to run through them for an hour. They were then steamed, with frequent rinsing, and finally they were attached to the still. In the case of the quartz cells, a slight pressure of purified air was applied in filling in order to prevent

TABLE VI			
COND	UCTANCE OF IODI	C ACID IN QUARTZ CE	LLS
Run 1, Cell II,	K = 0.28630,	$\mu = 0.5 \times 10^{-6}$	W = 3127.70
Cone. \times 10 ³	Λ	Cone. $ imes$ 10 ³	Λ
0.0762746	386.308	0.247254	387.218
0.148601	386.875	0.426920	387.061
Run 2, Cell II,	K = 0.285402,	$\mu = 0.115 \times 10^{-6}$,	W = 3187.98
0.0537214	388.673	0.410722	387.496
0.131132	388.799	0.681964	386.035
0.232533	388.295	1.10967	384.076
Run 3, Cell III.	K = 0.284733,	$\mu = 0.0976 \times 10^{-6}$,	W = 3169.38
0.0664405	389.046	0.439514	387.207
0.142177	388.535	0.703408	385.963
0.251694	388,192	1.10330	384.217
Run 4, Cell II,	K = 0.284733,	$\mu = 0.095 \times 10^{-6},$	W = 3206.57
0.0685165	389.018	0.648686	386.117
0.144572	388.940	0.986010	384.543
0.233308	388.311	1.49429	382.36 0
0.399158	387.462	2.11108	380.059
Run 5, Cell II,	K = 0.284733,	$\mu = 0.0989 imes 10^{-6}$,	W = 3226.16
0.0962906	389.022	0.710642	385.764
0.168284	388.616	1.02335	384.310
0.286320	388.036	1.52809	382.259
0.465172	386.999	2.10323	380.092
Run 6, Cell IV,	K = 6.98151,	$\mu = 0.46 \times 10^{-6}$,	W = 993.332
0.623489	384.974	9.03267	362.151
1.73067	380.918	16.1179	349.421
3.07736	376.582	30.5179	330.179
5.38453	370.333		
Run 7, Cell IV,	K = 6.99313,	$\mu = 0.38 \times 10^{-6}$,	W = 951.129
0.00143615	382.195	0.0183879	345.876
0.00304044	376.774	0.0349757	325.852
0.00547988	370.130	0.0673634	298.053
0.00969682	360.794	0.193258	244.359

contamination from the external atmosphere. In collecting the water in the cell, steam was first allowed to blow through the cells for a time, during which, also, they were thoroughly rinsed with water very nearly at its boiling point. Finally, the condensed water was cooled by means of a suitable cooler and the cell was repeatedly rinsed out by filling and siphoning off the water. Throughout these operations, the resistance of the water in the cell was measured and when water of a desired quality was obtained the cell was filled.

After filling, the cell was removed from the still, weighed, and placed in a thermostat where it was left for 3 hours to come to temperature, this being the longest time necessary in order to insure equilibrium, according to a series of measurements. When temperature equilibrium was established, the first quartz bucket was introduced and resistance measurements were made every 15 minutes. In the case of the first

TABLE VII			
Conductance of Iodic Acid in Lime Glass Cells			
Run 8, Cell V, J	K = 0.715613,	$\mu = 0.8 \times 10^{-6},$	W = 917.867
Conc. \times 10 ³	Δ	Conc. \times 10 ³	Δ
0.17619	376.313	1.4305	381.416
0.36624	380.412	2.8999	376.974
0.54857	382.745	4.3311	373.094
0.70948	382.775	5.7854	369.541
1.0938	382.316		
Run 9, Cell V, A	X = 0.715613,	$\mu = 0.24 \times 10^{-6}$,	W = 892.875
0.096707	373.45	1.3786	381.634
0.241261	381.879	2.0890	379.363
0.37173	383.475	2.7931	377.244
0.58002	383.684	4.2595	373.107
0.83381	383.362	8.5392	363.322
1.1043	382.413		
Run 10, Cell VI,	K = 6.35033,	$\mu = 1.05 \times 10^{-6}$,	W = 103.504
0.0041409	373.509	0.066075	298.911
0.019662	344.082	0.087229	285.669
0.025734	335.869	0.12811	266.024
0.036047	324.093	0.25030	229.872
0.046199	314.358	0.49329	191.609

bucket, with Cell II, it was found necessary to assume that the minimum resistance observed was the correct one, since there was a gradual change with the time extending over a period of several hours, due to the solution of glass from the leads carrying the electrodes. When the resistance began thus to increase the second bucket was introduced, and from then on resistance measurements were continued at each point until no drift was apparent in the readings. The effect in question was negligible in all cases in which the contents of the bucket dissolved promptly.

Conductance Data.—The results obtained in this investigation are given in Tables VI, VII and VIII. At the head of each sub-table is given a number indicating the cell used, the constant of the cell K, the specific conductance of the water employed, μ , and the total weight, W, of the water employed in making up the solution.

All weights given are reduced to a vacuum. The value of the molecular weight of iodic acid was assumed to be 175.928.

TABLE VIII

 CONDUCTANCE OF IODIC ACID IN PYREX GLASS CELL

 Run 11, Cell III, K = 8.26717, $\mu = 0.53 \times 10^{-6}$, W = 367.578

 Conc. × 10³

 1. 63835

 381.261

 3.62966

The results are shown graphically in Figs. 5 and 6. In Fig. 5, values of Λ are plotted against values of the logarithm of the concentration, while in Fig. 6 values of $1/\Lambda$ are plotted against values of the specific conductance.



From an examination of Fig. 6, it will be seen that in Run 1 the curve exhibits a minimum point at a concentration of approximately 1.3×10^{-4} N, after which it rises sharply as the concentration decreases. This aberration of the curve is unquestionably due to the presence of impurities in the water, as a result of which a portion of the acid is neutralized. As purer water is employed, this effect becomes less pronounced and ultimately disappears entirely. In Run 2, the point at the lowest concentration still shows the effect to a slight extent. In this run, resistance measurements were taken over a period of 3 hours after the first addition of acid. These data showed a steady increase in resistance. The resistance was plotted as a function of the time and the curve was extrapolated to zero time. The resistance at the end of 3 hours was 13668.6, while the extrapolated resistance read 13623.5. In order to correct the rest of the run for this effect, the weight of acid added was multiplied by

the ratio of these resistances. This run has been corrected throughout in this manner, otherwise the second and third points would rise somewhat above the positions as indicated on the plot. The fourth point, however, would not be measurably affected. The remaining runs in quartz at low concentrations were all carried out with water of a high degree of purity and no corrections were applied.



The points which are most likely to be in error in this work are those at the lowest concentration, where the weight of acid is small and the errors due to weighing have an appreciable influence, while the effect of impurities in the water is relatively great.

At high concentrations, polarization effects may make their appearance. With the exception of the last point in Run 10, using a glass cell, no resistance was measured below 250 ohms. The last mentioned effect may therefore be considered negligible. During Run 6, it was found that a slight crack had developed in one of the electrode lead tubes, which permitted a trace of acid to act on the mercury. This is unquestionably the cause for the displacement of the points obtained in this run. In Run 7, the crack had been partially mended and the results, as may be observed, were considerably improved, but the error is still appreciable. The cause of the error was so obvious and the effect was so small at the higher concentrations that it was thought unnecessary to repeat the entire series of measurements. With the exception of the measurements just mentioned, the conductance data in quartz cells are consistent within nearly 0.01%.

Relative Values of the Specific Conductance of 0.01 N Potassium Iodate and Iodic Acid at 18° and 25°.—In order to derive the value for the conductance of the hydrogen ion at 25°, the limiting value of the equivalent conductance of the iodate ion at that temperature must be known; while, to derive that at 18°, the limiting value of the equivalent conductance of iodic acid at that temperature must be known. The equivalent conductance of the iodate ion at 18° has been derived by Noyes and Falk¹⁰ from the conductance measurements of Kohlrausch,¹¹ with potassium iodate. They assign to it the value 34.0, basing this on the Λ_0 value 98.5 for potassium iodate and the value 0.496 for the transference number of the potassium ion in potassium chloride at 18°.

The conductance of the iodate ion at 25° has not been determined. For the purpose of determining the limiting value of the conductance of this ion at 25° , the specific conductance of potassium iodate was measured at a concentration of 0.00149105 N. This concentration is based on the density values 0.99733 and 0.99888, at 25° and 18° , respectively.¹² The concentrations and corresponding values of Λ as measured are given in the following table.

Table IX

CONDUCTANCE OF	DILUTE POTASSIUM IODATE	Solutions at 18° and 25°
Temperature ° C.	Concentration	Λ
25	0.00149105	110.855
18	0.00149337	95.4318

Correcting the measured specific conductance at 18° for the change in concentration due to temperature change, for the ratio of the specific conductances at 25° and 18° the value 1.16158 is obtained.

In order to check this value, a smooth curve was drawn through Kohlrausch's values at 18° and a conductance value for the concentration 0.00149105 was interpolated and found to be 95.487. Dividing this by the observed value of the equivalent conductance given in the table above for 25°, we have for the ratio of the conductances at the two temperatures the value 1.16095, which agrees with the above-determined value within 0.054%. Multiplying 98.5, the value of Λ_0 for potassium iodate at 18°, as determined by Noyes and Falk, by the ratio 1.16158, we obtain 114.42 for the value of Λ_0 for potassium iodate at 25°.

The specific conductance of iodic acid at a concentration of 0.001 N was determined at 18° and 25° in Cells II and III. The conductance at 18° was corrected for the concentration change due to the temperature change from 25° to 18°. The ratio of the conductances at the same

¹⁶ Noyes and Falk, THIS JOURNAL, **34,** 454 (1912).

¹¹ Kohlrausch, Sitzb. köngl. preuss. akad. Wiss., 1900, p. 1002.

¹² Sullivan, Z. physik. Chem., 28, 525 (1899).

concentration in the 2 cells was found to be 1.11432 and 1.11410, or, in the mean, 1.11421.

Discussion

The Influence of Impurities on the Conductance of Dilute Acid Solutions.—Reference has already been made in an earlier section of this paper to the influence of impurities on the conductance of dilute acid solution. The influence of impurities is to reduce the observed conductance below the true value. As a consequence, the conductance values of dilute acid solutions pass through a maximum value, instead of approaching a definite limit. The weaker the acid and the lower the concentration, the more pronounced is this effect.

The influence of impurities in the water and of the alkali due to glass cells is illustrated in Fig. 5, in which values of the equivalent conductance Λ are plotted as ordinates and values of the logarithms of the concentration as abscissas. Curve I represents the results obtained with the quartz cells II and IV, Runs 4, 5, 6 and 7 being plotted. Runs 2 and 3 lie on the same curve but have been omitted for the sake of clearness in the figure. Curve II represents the results obtained with the quartz cell II, with water having a specific conductance of 0.5×10^{-6} . Curve III represents the results of Runs 9 and 10, with the soda-lime glass cells V and VI, the water in the case of the dilute solutions having a specific conductance of 0.24 \times 10⁻⁶. Curve IV represents the results of Runs 8 and 10 with the same soda-lime glass cells, with water having a specific conductance of 0.8 \times 10⁻⁶. It is seen that, with the quartz cells and water having a specific conductance of 0.115×10^{-6} , or lower, a maximum does not appear in the conductance curve down to the lowest concentrations measured. Curve II, however, the measurements for which were carried out with water having a specific conductance of 0.5×10^{-6} , exhibits a slight maximum. The difference between Curves I and II is, therefore, due to the influence of impurities present in the water. The pronounced maximum in Curve III is largely due to the influence of the alkali in the glass, since in this case the water had a specific conductance of 0.24×10^{-6} . This curve lies much below Curve II, in which case the water had a specific conductance of 0.5×10^{-6} . The difference between Curve III and Curve IV is due to the water, since the measurements were carried out under otherwise comparable conditions. It will be observed that the shift in the curves due to a change in the specific conductance of the water from 0.24 to 0.8 is markedly lower than that due to substitution of glass for quartz, which is represented approximately by Curves I and III. With the water used in these measurements, the influence of the alkali derived from the cell is, therefore, markedly greater than that of the impurities in water having a specific conductance of 0.8×10^{-6} .

Water having a specific conductance of 0.8×10^{-6} is what would be ordinarily termed "conductivity water." It is evident that, with water

of this degree of purity in glass cells, it is not possible to obtain reliable conductance measurements at concentrations below $3 \times 10^{-3} N$. With water of a high degree of purity in glass cells, the conductance measurements might be extended to $10^{-3} N$. With water of a specific conductance 0.5×10^{-6} in quartz cells, the influence of the impurities in the water becomes felt at a concentration of about $5 \times 10^{-4} N$. The influence of impurities on the conductance of dilute solutions of acids is brought out more distinctly in plotting the reciprocal of the equivalent conductance against the specific conductance, as in Fig. 6. An inspection of this figure shows that the points of Run 1 lie on a curve which exhibits a pronounced minimum in the neighborhood of $1.3 \times 10^{-4} N$. But even the results of Run 2, which do not exhibit a maximum, diverge markedly at the lowest concentrations. It is evident that, if the measurements had been carried to lower concentrations in this case, a minimum would have been found.

Some further evidence may be given relative to the influence of glass cells on the results obtained with dilute acids. Even in the case of the Pyrex glass cell III, the conductance as measured in Run 11, with water having a specific conductance of 0.53×10^{-6} , is markedly lower than in Run 1 with the quartz cell, with water having approximately the same specific conductance. The results with the Pyrex glass cell are indicated in Fig. 5 by combined cross and circle. In order to test out this effect further, the cell constant of this cell was checked out against the large quartz cell II immediately after Run 11. First, a solution of potassium chloride was made up in the large quartz cell and its resistance measured, after which the solution was transferred to the Pyrex cell and its resistance again measured. The value obtained for the constant of the Pyrex cell in this case was 8.26792, which checks closely with the value 8.26717 as determined directly by means of 0.1 N standard potassium chloride solution. Then an acid solution, having a concentration of approximately 0.001 N, whose resistance was approximately the same as that of the potassium chloride solution, was also made up in the quartz cell, and its resistance in this cell compared with that in the Pyrex cell. The cell constant obtained with the acid was found to be 8.28604, a difference of 0.2%, by direct check at the same resistance. This effect is evidently due to the action of the alkali of the glass cell. The relative magnitude of this effect will naturally depend upon the conditions under which the experiments are carried out, as well as upon the dimensions of the cell, etc. The effect of the glass is most clearly shown by introducing an acid solution of a concentration in the neighborhood of $2 \times 10^{-8} N$ into a glass cell and thereafter measuring the resistance as a function of the time. When left in Cell V for a period of 30 minutes, it was found that the resistance increased by approximately 0.04%. On shaking the solution, however, a further increase in resistance took place of the same order of magnitude. This effect is unquestionably due to the fact that the concentration of the impurities arising from the glass is greater in the immediate neighborhood of the cell walls than in the vicinity of the electrodes. On mixing the contents of the cell, these impurities are distributed throughout the volume of the solution with a consequent decrease of the observed resistance. It may be noted that, when the original measurements were carried out in the glass cell, this effect was not observed and did not lead to irregularities in the measured values, for the reason that the conductance of the solutions was measured at each concentration after the same interval of time (45 minutes).

In the case of solutions of weaker acids, a maximum in the conductance values at concentrations down to 2×10^{-4} N has not been observed. This is due to the fact that the maximum cannot appear until the decrease of conductance, due to the influence of impurities, overbalances the increase due to the increased ionization of the acids as the concentration is decreased. The weaker the acid, the greater the relative conductance change for a given concentration change. Consequently, it is only in the case of the strong acids that this effect is observed at higher concentrations. This doubtless accounts for the absence of such an effect in the measurements of Kendall.¹³ Nevertheless, in the case of the weak acids, the effects due to impurities are present and influence the observed conductance values, and consequently also the values of Λ_0 obtained from such measurements by extrapolation.

Many instances of this effect may be found in the literature, although, apparently, in few cases has this effect been studied closely, while in other cases it has not been correctly interpreted. Noyes and Kato,¹⁴ in their transference experiments with nitric and hydrochloric acids, found a decrease of the specific conductance of their 0.002 N acid solutions amounting to 0.1% on standing for 3 hours. This is one of the few cases in which this effect has been measured.

It is, of course, obvious that this effect will make itself felt, not only in the case of conductance measurements, but likewise in that of all other measurements which depend primarily upon the concentration of hydrogen ions. So, for example, Beans and Oakes¹⁵ have measured the concentration of the hydrogen ion in so-called pure water by means of concentration cells. Their water had a specific conductance of the order 0.9×10^{-6} and the value which they obtained for the concentration of the hydrogen ions was about 1/10 that determined by other methods. Since these measurements were carried out in glass cells, it is clear that the impurities in the water, as well as the alkali due to the glass cells, must have had a con-

¹³ Kendall, J. Chem. Soc., 101, 1375 (1912).

¹⁴ Noyes and Kato, This Journal., **30**, 323 (1908).

¹⁵ Beans and Oakes, *ibid.*, **42**, 2128 (1920).

siderable influence on the resulting value of the hydrogen-ion concentration as measured.

Nearly all determinations of hydrogen-ion concentrations have been carried out in glass cells with water which, at best, has a purity corresponding with that of what is commonly known as "conductivity water," which has a specific conductance of 1×10^{-6} . It is clear that all such measurements in which the acid concentration approaches $10^{-3} N$ must be measurably in error, while at concentrations below this value the errors reach correspondingly greater values. Without doubt, these effects had an influence on the electromotive-force determinations of Noyes and Ellis,¹⁶ which led them to state that "the plot indicates that the value of the electromotive force at 0.000999 N is affected by a considerable error." So, also, this effect undoubtedly underlies the observations of Linhart¹⁷ with the hydrogen electrode at 0.000136 N, which led to a decrease of 1.5% in the electromotive force on standing over a period of 126 hours, while in the case of the more concentrated solutions an increase of the electromotive force occurred under the same conditions.

It may be safely assumed that all electromotive-force measurements with the acids, carried out at concentrations approaching $10^{-3} N$, are in error by varying amounts depending upon the length of time during which the solution was left in contact with the glass surfaces, as well as upon other factors.

Form of the Conductance Curve at Low Concentrations.---If the law of mass action is approached as a limiting form, then, as Kraus and Bray have pointed out,¹⁸ the curve in which values of $1/\Lambda$ are plotted against values of the specific conductance, becomes a straight line at low concentrations. The curve in Fig. 6 has been drawn to pass through the points within the limits of experimental error, and, where the deviation from a linear relation lies within the limit of the experimental error, the curve has been continued as a straight line. Whether or not the massaction law is approached as a limiting case in aqueous solutions of strong electrolytes, it will be admitted that the value of Λ_0 obtained by this linear extrapolation represents a minimum value. As may be seen from Fig. 6, at a concentration below $2 \times 10^{-4} N$, the points lie upon a straight line within the limits of the experimental error. In carrying out the extrapolation, somewhat greater weight has been given to the results of Runs 4 and 5 than on preceding runs, since in carrying out the later runs the details of manipulation had been worked out more minutely and the results themselves are mutually more consistent. The value of Λ_0 , as thus determined by extrapolation, was found to be 389.55. The true

¹⁶ Noyes and Ellis, THIS JOURNAL, **39**, **2**542 (1917).

¹⁸ Kraus and Bray, *ibid.*, **35**, 1337 (1913).

¹⁷ Linhart, *ibid.*, **4**1, 1178 (1919).

value of Λ_0 cannot differ greatly from this value, for, at higher concentrations, the curvature of the above curve diminishes as the concentration decreases. If, beginning at a concentration of $2 \times 10^{-4} N$, the curves were continued with the same curvature, the resulting value of Λ_0 obtained would differ from that found above by only a few tenths of a unit.

The value of the mass-action constant, corresponding to the straight line drawn in Fig. 6, is 0.0717. It is clear that the value of the ionization function for iodic acid at a given concentration is much greater than that of ordinary salts, such as potassium chloride, and that the limiting value approached, if such a limit exists, is much greater than that of salts.¹⁹ Comparing the ionization of iodic acid with that of the salts, this acid is to be classed as a strong electrolyte. At low concentrations, certainly, it does not differ greatly in strength from such strong acids as hydrochloric and nitric acids.

The Conductance of the Hydrogen Ion at 25° and 18°.—From the data given in the preceding section, the conductance of the hydrogen ion may be closely approximated at 25° and 18°. From the ratio of the conductance of 10^{-8} N potassium iodate solutions at 25° and 18° the value 114.42 was obtained for the limiting value of the equivalent conductance of potassium iodate. Subtracting the value of 74.8 for the conductance of the potassium ion at 25° ,²⁰ we obtain the value 39.62 for the conductance of the iodate ion at this temperature. This yields for the conductance of the hydrogen ion at 25° the value 349.93. One of the uncertainties underlying the value of the conductance of the iodate ion given above is due to the assumption that the ratio of the Λ_0 values for potassium iodate at 18° and 25° is equal to that of the conductance values of the same salt at a concentration in the neighborhood of 10^{-3} N. It is believed, however, that the error introduced in this way is small.

The value thus obtained for the equivalent conductance of the hydrogen ion is nearly 1% greater than that obtained by Kendall¹³ from the conductance of solutions of weak acids. Whatever other errors may have affected Kendall's results, it is certainly true that the influence of impurities in the water, as well as the influence of alkali from the cell walls, might be expected to lead to low values of the above order of magnitude.

In Section V, the ratio for the equivalent conductance of iodic acid at a concentration of $10^{-3} N$ at 25° and 18° was found to be 1.11421. Dividing 389.55, the value of Λ_0 for iodic acid at 25° , by this ratio, we obtain the value 349.62 for Λ_0 of this acid at 18° . Subtracting 34.0, the conductance of the iodate ion, as derived by Noyes and Falk, we obtain for

¹⁹ The maximum value which might be assigned to the limit approached by the mass action function in the case of KCl is 0.02 according to Washburn and Weiland [THIS JOURNAL, 40, 146 (1918)].

²⁰ This value is that derived by Noyes and Falk (Ref. 10), assuming the value 0.497 for the transference number of the potassium ion in potassium chloride at 25° .

the conductance of the hydrogen ion at 18° the value 315.62. This value is slightly higher than that derived by Noyes and Falk. It would appear, however, that this value would necessarily represent a lower limit in view of the method of extrapolation employed in determining the value of Λ_0 .

Summary

1. The apparatus employed and the precautions observed in carrying out conductance measurements with iodic acid at concentrations down to $5 \times 10^{-5} N$ are described. Measurements were carried out in glass and in quartz cells and with water of various degrees of purity in order to determine the influence of impurities on the conductance of acid solutions at low concentration.

2. It was found that the conductance curve exhibits a maximum due to impurities with water having a specific conductance above 0.1 to 0.2 $\times 10^{-6}$. The influence of alkali derived from glass cells is, if anything, greater than that of the impurities present in the water having a specific conductance of 0.8×10^{-6} . Conductance measurements with iodic acid in quartz cells with water having a specific conductance of 0.1×10^{-6} were carried to concentrations as low as $5 \times 10^{-5} N$ with a relative precision of a few hundredths of 1%. Extrapolating on the assumption that the mass-action law is approached as a limiting form at low concentrations, 389.55 is found for the value of Λ_0 of iodic acid at 25°, which may be accepted as a lower limit to the possible value of this constant. The massaction constant corresponding to the extrapolation has a value of 0.0717. Iodic acid is thus a much stronger electrolyte than potassium chloride.

3. The conductance of the iodate ion was evaluated at 25° on the assumption that the Λ_0 value between 18° and 25° changes in the same proportion as the conductance of a 0.0015 N solution of the acid. The value 39.62 was thus found for the conductance of the iodate ion. For the conductance of the hydrogen ion at 25° the value 349.93 results. Assuming that the limiting value of the equivalent conductance of iodic acid between 18° and 25° varies in the same ratio as that of a 0.001 N solution of the same acid, 349.62 is found for the value of Λ_0 of iodic acid at 18° . Assuming the value 34.0 for the equivalent conductance of the iodate ion at 18° , there is obtained the value 315.62 for the conductance of the hydrogen ion at 18° .

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