Year.	Income.	Expense.	Surplus.	Deficit.	Excess of assets aver. liabilities.	Members.
1880	......	......	......	.....	......	288
1890	1,915.21	1,915.21	.....	.....	......	256
1900	10,190.87	9,943.95	246.92	None	5,155.81	1715
1905	16,532.37	15,353.76	1,178.61	None	7,027.51	2888
1906	23,106.67	20,494.44	2,612.23	None	13,875.74	3047
1907	33,275.25	27,248.89	6,026.36	None	17,490.06	3361
1908[a]	29,785.94	41,302.86	.....	11,516.92	5,171.53	3978
1909	55,985.65	51,175.20	4,810.45	None	14,316.09	4460
1910	61,760.91	52,483.64	9,277.27	None	19,659.17	5011
1915	109,377.71	101,286.41	8,091.30	None	34,820.06	7332
1916	136,557.65	123,375.77	13,181.88	None	51,038.25	8265
1917	196,210.57	173,195.10	23,015.47	None	87,407.37	10504
1918	203,483.32	165,158.92	38,324.40	None	126,601.27	12099
1919	232,935.53	227,731.94	5,203.59	None	150,068.24	13568
1920[b]	272,160.66	290,498.96	.....	18,338.30	131,729.94	15577

[a] Part of 1906 dues were credited to 1907 and there was no decrease in receipts in 1908.

[b] Estimate September 1, 1920.

[Contribution from the Chemical Laboratories of Columbia University, No. 343.]

THE DETERMINATION OF THE HYDROGEN-ION CONCENTRATION IN PURE WATER BY A METHOD FOR MEASURING THE ELECTROMOTIVE FORCE OF CONCENTRATION CELLS OF HIGH INTERNAL RESISTANCE.

By H. T. Beans and E. T. Oakes.

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The present investigation was undertaken for the purpose of developing a method of measuring the hydrogen-ion concentration of pure water as directly as possible. It was desired to carry out this work in such manner as to avoid, as much as possible, the use of data obtained from the investigation of various solutions of salts, acids or bases. The object was to make the primary measurements on pure water in such a way as to be translated into hydrogen-ion concentration through the use of only such data as are substantiated by such proof, both experimental and theoretical, as to make it readily acceptable to everyone.

The only investigation of this question so far carried out in which measurements were made on pure water was that of Kohlrausch and Heydweiller who measured the conductivity of pure water, but in order to calculate hydrogen-ion concentration use was made of the ionic mobilities as determined in solutions of acids, bases and salts. These mobilities may or may not hold true for pure water. A more complete discussion of the possible objections to be raised against this method as well as the additional objections to the various other methods will be given later.

Since it was desired to make the measurements on pure water the only other method that presented itself was that of determining the electromotive force of a cell such as Hg | HgCl KCl (saturated) | pure H_2O | H_2. Heretofore the main difficulty encountered in this measurement was that due to the extremely high resistance of pure water, making the use of the potentiometer, or any other instrument previously employed for such measurements, out of the question. The problem then became one of developing and applying a method of measuring potential differences in which the resistance of the circuit would not affect the accuracy of the results and which at the same time would not require an excessive amount of current for operation. This latter requirement is necessary in order not to change materially the concentrations in the cells during the process of measurement. In other words, the new method must have all the advantages of the potentiometer method with the additional advantage of being independent of the internal resistance of the cell. Such a method as this being accomplished, the measurement of the voltage of the cell Hg | HgCl KCl (saturated) | H_2O | H_2 becomes a comparatively simple operation. From these results the hydrogen-ion concentration of pure water may be readily calculated by making use of Nernst's formula ($E = 0.0002T \log C/K$), and the established value for the saturated calomel electrode.

It is also to be noted that the application of such a method would not be limited to the cell mentioned above. The same method could be applied to all concentration cells, finding its greatest use, however, in connection with the measurement of the electromotive force of cells having such a high internal resistance as to render them impossible of measurement so long as the potentiometer method is the only one available. The new method would also open up a procedure for the investigation of very dilute solutions. By this means experimental evidence could be brought to bear on many of the numerous assumptions regarding the applicability of the laws of moderately dilute solutions to those that are extremely dilute. In addition, as will be shown later, the method as developed makes an ideal arrangement for electrometric titrations.

Up to the present time there has been no measurement of the hydrogen-ion concentration of water based solely upon the results of an investigation of pure water. So far results have been based on (1) measurement of the electromotive force of concentration cells; (2) conductivity measurements; (3) hydrolytic dissociation of salts; (4) velocity of reaction; (5) by use of colored indicators.

In only one of these methods (2) have any measurements actually been made on pure water. Even in that method the ionic concentrations could be calculated only by means of data resulting from a number of other investigations in which not pure water but various solutions were employed.

The following table, giving the results of previous investigations, is a summary of what has been accomplished thus far.

Date.	Investigator.	Method used.	Hydrogen-ion concentration.	Temp. ° C.
1893	Arrhenius[a]	Hydrolytic dissociation of 0.1 M sodium acetate solution. Taking Shields' values of 0.008% hydrolyzed at 25°	1.125×10^{-7}	25
1893	Arrhenius[b]	Calculated the e. m. f. of $H_2 \mid M\ HCl \mid M\ NaCl \mid M\ NaOH \mid H_2$ to be 0.806 volts neglecting contact-potential difference and assuming α HCl = 0.854 α NaOH = 0.776	1.125×10^{-7}	25
1893	Bredig[c]	Conductivity of aqueous solutions containing aniline	6.2×10^{-7}	25
1893	Ostwald[d]	E. m. f. $H_2 \mid M$ acid $\mid M$ base $\mid H_2$ Neglecting contact difference potential and assuming 100% ionization of both acid and base	9×10^{-7}	Room temp.
1893	Wijs[e]	Velocity of saponification of methyl acetate in water	1.4×10^{-7}	25
1894	Kohlrausch and Heydweiller[f]	Specific conductivity of pure water. Mobilities of ions at 26° taken as: H ion = 325, OH ion = 189; or at 18° H ion = 289, OH ion = 165.	1.10×10^{-7}	26
1894	Nernst[g]	Recalculated hydrogen-ion concentration from the average e. m. f. obtained by Ostwald and LeBlanc[h] correcting for contact potential difference, using mobilities as found by LeBlanc. Na ion = 32, Cl ion = 54, H ion = 272, OH ion = 143.	0.8×10^{-7}	18
1896	Lowenherz[i]	E. m. f. $H_2 \mid 0.1\ M\ HCl \mid 0.1\ M\ LiCl \mid 0.1\ M\ NaOH \mid H_2$, also 0.1 M KOH correcting for contact potential differences using ionic mobilities. H ion = 325, OH ion = 167, Cl ion = 70.2, Na ion = 49.2, Li ion = 39.8.	NaOH cell 1.19×10^{-7} KOH cell 1.13×10^{-7}	26
1907	Lunden[j]	Measured dissociation constant and degree of hydrolysis of *p*-nitrophenol and trimethylpyridine	1.05×10^{-7}	25

[a] Arrhenius, *Z. physik. Chem.*, **11**, 805 (1893).

[b] Arrhenius, *ibid.*, **11**, 808 (1893).

[c] Bredig, *ibid.*, **11**, 830 (1893).

[d] Ostwald, *ibid.*, **11**, 521 (1893).

[e] Wijs, *ibid.*, **12**, 514 (1893).

[f] Kohlrausch and Heydweiller, *ibid.*, **14**, 330 (1894).

[g] Nernst, *ibid.*, **14**, 155 (1894).

[h] LeBlanc, *ibid.*, **8**, 299 (1891).

[i] Lowenherz, *Z. physik. Chem.*, **20**, 283 (1896).

[j] Luden, *J. chim. phys.*, **5**, 574 (1907).

Date.	Investigator.	Method used.	Hydrogen-ion concentration.	Temp. °C.
1907	Kanolt[a]	Hydrolytic dissociation of ammonium salt of diketo-tetrahydro-thiazole	0.91×10^{-7}	
1907	Noyes[b]	Conductivity measurements of various aqueous solutions	0.91×10^{-7}	
1909	Lorenz[c] Böhi	E. m. f. $H_2 \mid 0.1\ M\ HCl \mid 0.1\ M\ KCl \mid 0.1\ M\ KOH \mid H_2$, correcting for contact potential differences, using ionic mobilities of Kohlrausch. K ion = 74.5, H ion = 352.1, Cl ion = 75.3, OH ion = 195.9, at 25°	1.1×10^{-7}	25
1915	Fales[d] Nelson	Indicator method similar to Sorenson[e] Using *p*-nitrophenol as an indicator and comparing to mixtures of citrate solutions and 0.1 *M* sodium hydroxide	15.8×10^{-7}	25
1915	Sherman[f] Thomas	Confirmed Fales and Nelson results by the same method	15.8×10^{-7}	25

[a] Kanolt, THIS JOURNAL, **29**, 1492 (1907).

[b] Noyes, *Carnegie Inst. Pub.*, **1907**.

[c] Lorenz and Bohi, *Z. physik. Chem.*, **66**, 733 (1909).

[d] Fales and Nelson, THIS JOURNAL, **37**, 2769 (1915).

[e] Sorensen, *Biochem. Z.*, **21**, 131 (1909).

[f] Sherman and Thomas. THIS JOURNAL, **37**, 623 (1915).

No attempt will be made to give the complete theory of each of the above methods, since they are readily accessible in the original works and in all standard texts on physical chemistry. The mere mention of the method employed serves to recall the numerous assumptions surrounding the calculation of the results from the experimental data. The most interesting and remarkable feature of these results is that data from such entirely different sources furnishes values for the hydrogen-ion concentration of water so comparable to each other. However, upon examination of the original data represented above we find that without exception the accuracy of each of the individual results is seriously affected either by the method employed or its execution or both, and each makes use of a multiplicity of assumptions which may or may not be justified.

Considering first only the determinations from electromotive-force measurements, it is to be noted that while all these electromotive-force measurements give values for the concentration of the hydrogen ion in water between 9×10^{-7} and 1.2×10^{-7} none of the measurements was made on pure water and in the computations data were selected from a wide range, no two investigators selecting the same data for the same purpose. Furthermore, the conditions which were accepted for comparatively concentrated solutions were assumed to hold for pure water itself.

With the exception of the conductivity determinations by Kohlrausch and Heydweiller, the other methods outlined can at best serve only as corroborative evidence of the validity of values obtained by the electromotive-force method, for these contain so many more assumptions. It is interesting to note that Kanolt, who claims no additional accuracy for his own work, in 1907, after discussing the previous attempts, concludes thus, "Although these entirely different measurements have all given for the ionization of water values of the same order of magnitude and have thereby furnished one of the most striking evidences of the ionic theory, yet for none of these values can any considerable percentage of accuracy be claimed."

Considering now the conductivity measurements of Kohlrausch and Heydweiller, a number of questions might properly be raised: (*a*) Do the hydrogen and hydroxyl ions have the same mobilities in pure water as in solutions, and what is the ionizing effect of the electric field of force from the current? (*b*) Is the surface effect on the electrode negligible? (*c*) Do the ions carry the entire current? (*d*) Is the secondary ionization of hydroxyl into oxygen and hydrogen ions negligible in pure water? (*e*) Is it not possible that this secondary ionization takes place to a rather great extent at the surface of the electrode?

According to theory, in order that the alternating current be carried, a minute quantity of ion must be discharged and then recharged. In the case of the hydroxyl ion this would have to ionize further into oxygen and hydrogen ions before the oxygen could be discharged. The resultant of these effects depends upon their relative magnitude.

These factors, while supposedly negligible, may or may not be without considerable effect and are especially alluded to because they apply to the only work so far accomplished on this subject in which the measurements were carried out on pure water. In the works of Taylor and Acree,[1] in 1916, and of Newbery,[2] in 1918, this question has been attacked from 2 different angles. These investigators have shown that the above factors are not without effect on the results.

The main difficulty connected with the use of the potentiometer for measuring the electromotive force developed by cells of the type Hg | HgCl KCl | X | H_2, where X is a poor conductor, results from the lack of sufficient amperage to allow of accurate galvanometer readings. The problem then developed into devising a method whereby such a quantity of electricity as would accurately actuate the galvanometer, could be withdrawn from the cell, stored up, and instantaneously discharged through a ballistic galvanometer.

From a consideration of the relations of quantities of electricity and current strength and of current strength, voltage and resistance the solution to the above problem becomes apparent. Where the resistance is

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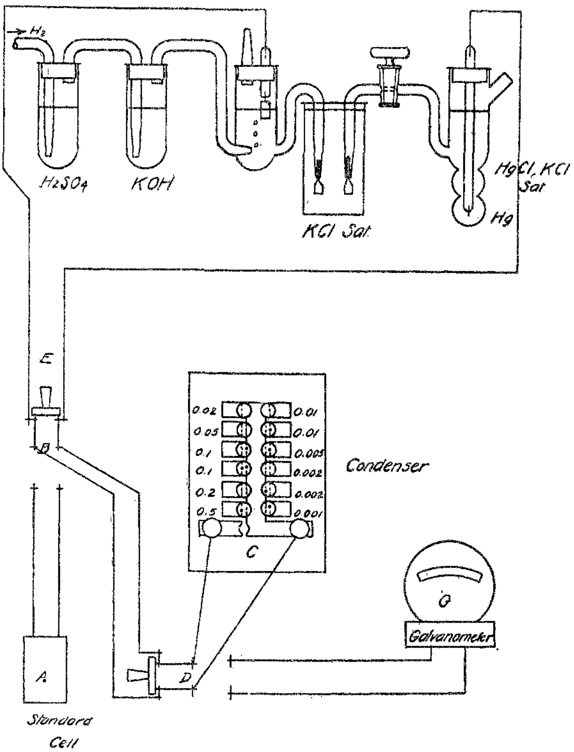
[1] Taylor and Acree, THIS JOURNAL, 38, 2396 (1916).

[2] Newbery, *J. Chem. Soc.* (*London*), **113**, 701 (1918).

very great it is only necessary to connect the cell to a condenser of sufficient capacity and allow it to run until the required number of coulombs is delivered, and then to discharge the condenser through the galvanometer in one pulse. Accordingly, the arrangement represented by the figure was tried. (In the actual work a charge and discharge key was used.) With the switches B and D, as indicated, the concentration cell E is charging the condenser C with a quantity of electricity equal to the product of the voltage of the cell times the capacity of the condenser, or $Q = E\,C$. By reversing Switch D this quantity of electricity is discharged through the ballistic galvanometer G and the deflection noted as d_1. By reversing Switch B with D in its original position the standard cell charges the condenser with a known quantity of electricity which may then be discharged through the galvanometer and the deflection noted as d_2. Since these deflections are proportional to the quantities of electricity passing through the instrument which in turn equals the product of the capacity of the condenser and the voltage of the cell we have $E_1\,C/E_2\,C = d_1/d_2$ or $E_1/E_2 = d_1/d_2$, where E_1 and E_2 are the voltages of the concentration cell and the standard cell, respectively, and d_1 and d_2 are the galvanometer deflections resulting from the discharge of the quantities of electricity $E_1\,C$ and $E_2\,C$. Substituting the known value of E_2 and the observed values of d_1 and d_2 we can readily solve for E_1. In practise it is much easier to calibrate the galvanometer over the particular range of deflections to be observed, calculating the electromotive force of the unknown cell from the micro-coulomb sensitivity so determined or reading it from a chart constructed from these values. The former method was the one employed in this work, and the results were checked at frequent ntervals by using condensers of different capacities so as to get the same



deflection of the galvanometer with the standard cell and the unknown cell. This, of course, eliminated any slight variations due to imperfections of the scale divisions or to errors in estimating fractions of divisions. The re ults were then calculated directly from the formula $E_1C_1 = E_2C_2$, where E_1 and E_2 are the voltages of the unknown and standard cells, respectively, and C_1 and C_2 are the capacities of the condensers used in connection with the cells. Throughout this work no differences were obtained by using the two methods so that the second method, which is slightly longer, need be resorted to only when there are special reasons for checking the results obtained by the first method.

From a consideration of the equation $E_1/E_2 = d_1/d_2$ it is seen that the capacity of the condenser need not appear as a factor in the calculations. This makes it possible to use a single unit condenser of unknown capacity, calibrating the galvanometer for various voltages by means of a standard cell and such a condenser, using the necessary shunts in parallel with the galvanometer in order to secure deflections throughout the scale range. Such an arrangement would naturally result in a very material reduction in the cost of the apparatus. The very moderate cost of the apparatus thus modified as compared to that of the potentiometer equipment furnishes an additional argument for its use.

A Leeds and Northrup low sensitivity galvanometer was used for this work. The same standard cell and condensers were used in its calibration as were used in the investigation. A much more sensitive galvanometer is to be preferred. Although, as will be shown later, the galvanometer used gave results accurate to one millivolt, it required an undue amount of effort not needed if a more sensitive instrument were employed or if greater magnification of deflections of the scale were secured. With the scale at 0.5 meter from the galvanometer the following calibration was effected by discharging a standard Leeds and Northrup Weston cell through various capacities. This cell was checked against 2 other standard cells of the same make and found to develop an electromotive force of 1.01823 volt.

The condenser was manufactured by Jas. G. Biddle. The calibration certificate furnished with the instrument was checked in the Ernest Kempton Adams physical laboratory of Columbia University and found to be correct. The condenser was made up of units from 0.001 microfarad to 0.5 microfarad, the sum totaling 1.000 microfarad, so that capacities from 0.001 to 1.000 microfarad could be obtained.

All glassware was of the Non-sol brand and all bottles, flasks, beakers, etc., were subjected to the action of live steam for 3 hours before using, and twice thoroughly rinsed with the solution to be contained in them before introducing the main portion of the solution.

Condenser capacity. Microfarads.	Deflection, millimeters.	
	Left.	Right.
1.00	50.0	50.0
	50.0	....
	49.8	50.0
	50.0	....
0.50	25.0	25.0
	25.0	25.0
	25.0	25.0
0.40	20.0	20.0
	20.0	20.0
	20.0	20.0
0.30	15.0	15.0
	15.0	15.0
	15.0	15.0
0.20	10.0	10.0
	10.0	10.0
	10.0	10.0
0.10	5.0	5.0
	5.0	5.0
	5.0	5.0

The water used in this work for making up the calomel cell and for one series of hydrogen electrodes was obtained by twice distilling ordinary distilled water from an alkaline permanganate solution through a block-tin condenser which condensed only about $^1/_3$ of the steam. For another series the ordinary distilled water was distilled once from an alkaline permanganate solution and then from a solution containing a small amount of phosphoric acid.

The mercury used in the preparation of the calomel cells and for contacts in the electrodes was purified by first dropping through a 1.5 meter tower of nitric acid according to the method of Hildebrand,[1] filtering through a dry cloth and then distilling under reduced pressure in a current of air as described by Hulett.[2]

The hydrochloric acid was prepared by distilling from a resistance glass flask through a quartz condenser and collecting the middle fraction in a quartz receiver, transferring it to a Non-sol bottle after it had cooled. This was then used in the preparation of the calomel and the standard 0.1 *M* hydrochloric acid solution. This latter was standardized by titration against sodium carbonate solution, using methyl orange as the indicator and was found to be 0.09996 *M*.

The calomel was prepared by the electrolytic method of Ellis.[3] After thoroughly washing it with pure water and then with saturated

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[1] Hildebrand, This Journal, 31, 933 (1907); 35, 847 (1913).

[2] Hulett, *Z. physik. Chem.*, 33, 611 (1900).

[3] Ellis, This Journal, 38, 737 (1916).

potassium chloride solution it was stored in a 500-cc. Non-sol bottle containing 400 cc. of the saturated potassium chloride solution. From these bottles it could then be transferred directly to the electrode.

The potassium chloride was purified by twice recrystallizing from distilled water Baker's analyzed potassium chloride and then fusing in platinum.

Compressed hydrogen was used, after it was passed through a solution of sodium hydroxide to insure the absence of carbon dioxide. The fact that the voltage of the cell did not change during long periods of use indicates that the hydrogen contained nothing to affect the cell.

The hydrogen electrodes were of platinum, platinized with platinum black. They were of plate form 2 × 1 × 0.025 cm.

All measurements were made at a temperature of 25° ± 0.01°.

In order to compare the accuracy of the condenser method with that of the potentiometer a cell was arranged as follows and the electromotive force measured by both methods,

$$\text{Hg} \mid \text{HgCl KCl (saturated)} \mid \text{KCl (saturated)} \mid 0.1\ M\ \text{HCl} \mid H_2.$$

The electromotive force of this cell was measured after the hydrogen had been bubbling through the hydrogen electrode for 5 hours and gave a voltage on the potentiometer of 0.3203 volt.

When measured by the condenser method, the cell 0.1 *M* HCl | calomel and the standard cell gave at 1.000 and 0.315 m. f., respectively, the galvanometer deflection 15.5, and at 0.500 and 0.157 m. f. the deflection 7.8, by 3 or more successive readings.

These results give a value of 0.3207 volt for the electromotive force of the above combination. Potentiometer measurements gave 0.3203 volt after 5 hours. Condenser measurements gave 0.3207 volt after 5 hours, 10 minutes. Potentiometer measurement gave 0.3200 volt after 5 hours, 20 minutes. Hence the condenser method with the set-up employed gives the voltage correct to ±0.0005 volt.

Since the voltage of the cell at the time these measurements were taken was undergoing a slow change the values recorded above are not to be taken as the true values for this cell, but were made for the sole purpose of indicating the accuracy of the condenser method.[1]

[1] Using a galvanometer of very much greater sensitivity the electromotive force of the cell Hg | HgCl 1.0 *M* KCl | Sat. KCl | 0.1 *M* HCl | H_2 where a capacity of 1.5 m. f. gave a deflection of 88.8 mm. as against a deflection of 87.2 mm. for a standard cell of 1.01844 volts through 0.5 m. f., a voltage of 0.3457 to 0.3461 was obtained where a potentiometer gave 0.3460 to 0.3462 volt. While this voltage is not the true one for this cell it serves to show the order of accuracy of the method. A reading of this same cell after it had come to equilibrium gave a voltage of 0.3471 on the potentiometer, thus checking the value 0.3470 ± 0.0002 volt obtained by Fales and Vosburgh (THIS JOURNAL, **40**, 1293, (1918)), and published in 1918. This preliminary work was done in November, 1916.

Having fully demonstrated the applicability of the method for measuring the electromotive force of cells of this type where the internal resistance is not great, it remained to be determined whether the same method would apply to cells of high internal resistance such as Hg | HgCl.-KCl | KCl | H_2O (pure) | H_2. Accordingly a quantity of ordinary distilled water was twice distilled from alkaline permanganate solutions and the cell Hg | HgCl.KCl (satd.) | KCl (satd.) | H_2O | H_2 prepared. The hydrogen was admitted into the electrode chamber and allowed to flow over the electrode half immersed in the water. The actual progress of the determination of the electromotive force of a single cell is given in Table I. In this table the third column gives the time in minutes required by the cell to reach equilibrium. The second column indicates the length of time required by the cell to charge the condenser fully. Both of these factors must be determined by repeated tests, as it is obvious that constant readings cannot be secured until both of these conditions are satisfied. The low reading recorded after the cell had reached equilibrium when only one minute was allowed for charging the condenser indicates that this time was not sufficient to completely charge the condenser.

Table I.—Electromotive Force of a Single Cell.

Condenser capacity. Microfarads.	Time for charging condenser. Min.	Time of hydrogen flow. Min.	Galvanometer deflections. Mm.	
			Right.	Left.
1.000	2	14	24.8	....
.....	5	19	24.8	....
.....	5	25	24.8	....
0.802	6	38	20.0	....
.....	5	45	20.0	....
1.000	6	59	24.9	....
.....	5	64	25.0	....
.....	2	66	25.0	....
		Reversed cell.		
.....	2	70	....	25.0
.....	1	71	....	24.0
.....	9	80	....	25.0
0.800	5	86	....	20.0
0.600	2	88	....	15.0
		Reversed cell.		
0.600	2	92	15.0	....
.....	3	95	15.0	....

Maximum voltage reached in 64 minutes = 0.5091 volt.
Hydrogen-ion concentration = $10^{-44.4}$.

The average deflection for this cell after reaching maximum voltage is 25.0 mm. for one microfarad capacity. Since the standard cell of 1.01823 volts gives a deflection of 50.0 mm. when used with a capacity of one microfarad, the voltage of this cell is 25.0/50.0 of 1.01823 volts or 0.5091 volt.

This cell, using pure water in the hydrogen electrode element, reached a maximum voltage of 0.5091 volt in one hour, and this voltage had not changed in another half-hour. However, the same hydrogen electrode was used in this cell as was used in the 0.1 *M* hydrochloric acid cell and it was thought that some slight amount of acid might have been retained in the electrode even though it had been carefully washed several times with pure water. Accordingly the electrode was thoroughly washed again, this time in 3 lots of boiling water and a cell made up of pure water from the same lot as was used in the previous cell. This time the following results were obtained.

TABLE II.—CELL WITH WASHED ELECTRODE.

Condenser capacity. Microfarads.	Time for charging condenser. Min.	Time of hydrogen flow. Min.	Galvanometer deflections. Mm.
0.600	3	16	16.0
.....	4	20	17.3
.....	4	25	17.4
.....	7	32	17.6
.....	8	40	18.0
.....	4	51	18.0
1.000	2	66	28.0
.....	7	73	30.0
.....	37	110	30.0
0.800	4	126	24.0
.....	7	142	24.0

Maximum voltage reached in 40 minutes.
Average deflection for one m. f. after reaching maximum voltage 30.0 mm.
Electromotive force = 0.6109 volt.
Hydrogen-ion concentration = $10^{-6.24}$.

Following this a large number of cells were made up from water redistilled from alkaline permanganate solutions and from alkaline permanganate solutions followed by distillation from dilute solutions of phosphoric acid. The following table gives the results of a number of these experiments and indicates the futility of trying to secure water free from acid fumes under ordinary laboratory conditions even though a constant flow of uncondensed steam surrounds the mouth of the receiving vessel during the entire distillation.[1]

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[1] In order to check up again on the apparatus and calomel electrode the following combination was made up:

$$\text{Hg} \mid \text{HgCl.KCl (satd.)} \mid \text{KCl (satd.)} \mid 0.1\ M\ \text{HCl} \mid \text{H}_2.$$

After 6 hours this cell was measured by both the potentiometer and the condenser methods with the following results:

Potentiometer, 0.3115 volt. Condenser, 0.3116 volt.

After 7 hours this cell developed an electromotive force of 0.3113 volt and after 15.5 hours 0.3111 volt. This value (0.3111 volt) was then taken as the true voltage of the cell.

TABLE III.—CELLS MADE UP WITH WATER REDISTILLED FROM ALKALINE PERMANGANATE AND PHOSPHORIC ACID.

Number of alkaline permanganate distillations.	Time to reach max. voltage. Min.	Deflections at max voltage. using 1.0 m. f. Mm.	E. m. f. of cell. Volts.	Hydrogen-ion concentration.
1	35	28.2	0.5742	$10^{-5.58}$
1	50	28.2	0.5742	$10^{-5.58}$
2	35	28.0	0.5702	$10^{-5.52}$
2	30	27.8	0.5661	$10^{-5.45}$
2	60	28.5	0.5804	$10^{-5.69}$
1	40	28.2	0.5742	$10^{-5.58}$
1	30	28.5	0.5804	$10^{-5.69}$
1	30	28.5	0.5804	$10^{-5.69}$
1	40	29.2	0.5946	$10^{-5.92}$
2	40	29.2	0.5946	$10^{-5.92}$
2	60	29.4	0.5987	$10^{-5.99}$
One alk. permanganate followed by one acid distillation	70	28.2	0.5742	$10^{-5.58}$
Duplicate on last sample	40	25.1	0.5111	$10^{-4.52}$

The last cell recorded above was made up from the same sample of water as the cell recorded next above it. However, while the cell was being washed out a beaker of conc. hydrochloric acid was accidentally brought within about 2 feet of the unstoppered small-necked bottle containing the water. As soon as the odor of the fumes gave warning of the presence of the acid the bottle was stoppered and the cell taken to another room free from fumes. Here the cell was carefully washed out several times and filled from the bottle which had been exposed to the acid fumes for perhaps one-half minute. The electromotive force of this cell dropped to 0.5111 volt, a difference of 0.063 volt, due to the acid fumes, or in terms of hydrogen-ion concentration the change was from $10^{-5.58}$ moles per liter to $10^{-4.52}$ moles per liter. It is to be noted that the constant flow of hydrogen through the water in the cell and the maintaining of an atmosphere of hydrogen above the water should result in the complete removal of such gases as carbon dioxide and ammonia. This was observed to be true in the case of carbon dioxide, although it required days for the complete removal of very small quantities of this gas.

A large number of samples of water were prepared by distilling in a room where only ordinary precautions were taken against fumes. It was found impossible to duplicate results from water distilled under these conditions.[1,2] The distilling apparatus was therefore removed to a room free from all acid fumes when little difficulty was experienced in securing samples of water that gave the same electromotive force values. There

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[1] Kendall, THIS JOURNAL, **38**, 1480 (1916).

[2] Kendall, *ibid.*, **38**, 2460 (1916).

was no difference in the results obtained from water prepared by distilling ordinary distilled water once from an alkaline permanganate solution and from that distilled twice from an alkaline permanganate solution. Samples prepared by distilling ordinary distilled water once from an alkaline permanganate solution and once from a solution containing a few drops of phosphoric acid did not give such reliable results as those distilled from alkaline permanganate solution alone. The results given in the table below were obtained on samples of water from entirely different distillations. In every case the results on each sample were checked by measuring the voltage of a number of cells made up from the same sample of water. Such cells rarely exhibited a measurable difference in voltage. The cells requiring an excessive length of time to develop their maximum voltage were those in which fresh hydrogen electrodes were used. When the electrode was already thoroughly saturated with hydrogen the cells reached their maximum voltage in less than 40 minutes.

TABLE IV.—EFFECT OF DISTILLATION FROM ALKALINE PERMANGANATE SOLUTION.

Number of alkaline permanganate distillations.	Time to reach maximum voltage. Min.	Deflection at maximum voltage. Mm.	E. m. f. of cell. Volts.	Hydrogen-ion concentration.
2	300	35.1	0.7149	$10^{-7.94} = 1.15 \times 10^{-8}$
2	720	35.0	0.7129	$10^{-7.91} = 1.23 \times 10^{-8}$
1	20	35.0	0.7129	$10^{-7.91}$
1	10	35.0	0.7129	$10^{-7.91}$
1	60	35.0	0.7129	$10^{-7.91}$
2	40	35.0	0.7129	$10^{-7.91}$

Using a galvanometer having a ballistic period of 8 seconds and a sensitivity of 0.0003 micro-coulomb per mm. a sample of water having a specific conductivity of 0.9×10^{-6} reciprocal ohms was tested with the following results:

Capacity of condenser. M. f.	Deflection with standard cell. Mm.	Deflection with calomel pure water cell. Mm.	E. m. f. of cell. Volts.	Hydrogen-ion concentration.
0.1	164.1	.....	1.0187	....
...	164.0	.....	1.0187	....
...	164.1	.....	1.0187	....
0.2	328.0	.....	1.0187	....
0.2	.....	229.5	0.7128	$10^{-7.91}1.23 \times 10^{-8}$

In the above determinations of the e. m. f. of the pure water cell the following 9 readings were made over a period of 4 hours: 230.0, 229.7 229.3, 230.0, 230.2, 229.2, 229.5, 230.0, 229.0. Average, 229.5.

In this series the deviation from the mean is, therefore, about two parts per thousand.

The apparatus assembled by Leeds and Northrup as set forth in a recent catalogue is a direct result of our work. However, we recommend a galvanometer of a sensitivity of 0.0003 micro-coulomb per mm. such as was used in this more recent work.

Consider now the cell $\underbrace{\text{Hg} \mid \text{HgCl.KCl}}_{E_1}$ (satd.) | KCl (satd.) | (0.1 *M* $\underbrace{\text{HCl} \mid \text{H}_2}_{E_2}$, the voltage of which, as determined in this investigation is 0.3111 volt and 0.3094 volt as determined by Nelson and Beegle.[1] The contact potential difference at the juncture of the saturated potassium chloride and hydrochloric acid solutions is zero. This is evidenced by the work of Fales and Vosburgh.[2] When pure water is substituted for the hydrochloric acid solution this contact potential difference is still zero. This is evidenced by practically all of the results for the mobilities of the potassium and the chloride ions. While various investigators have obtained different results all agree in that the mobility of the potassium ion is sensibly equal to that of the chloride ion.

Since the contact potential difference at the juncture of solutions is due to a difference in the mobilities of the ions if these mobilities are equal the contact potential difference is zero.

It is evident then that the measured electromotive force of 0.3111 volt is the resultant of E_1–E_2. Fales and Vosburgh[3] have measured this voltage E_2 and found it to be 0.2179 volt. It is, therefore, evident that since $E_1 - 0.2179$ volt = 0.3111 volt, then $E_1 = 0.5290$ volt. Hence by subtracting 0.5290 volt from the observed voltage of the cell Hg | HgCl.KCl (satd.) | KCl (satd.) | H_2O | H_2 we obtain the voltage of the element H_2O | H_2. Substituting this value in the Nernst equation, $E = 0.0002T \log C_{H^+}/K$, where $T = 25°$, $C = 298°$ absolute, and $K = 10^{-4.820}$(4,5,6,7,8) we can solve for C_H. It was in this way that the concentrations of hydrogen ions were calculated from the voltages of the cells whose electromotive forces were measured in this work.

The value of $10^{-7.91}$ moles per liter for the hydrogen-ion concentration in water was obtained from the experiments in which water of the highest degree of purity was used. The other results recorded above are published merely to show the variations to be expected unless extreme care is exercised in all operations. For example, failure to boil out the hydrogen electrode thoroughly after using it in 0.1 *M* hydrochloric acid resulted in

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[1] Nelson and Beegle, THIS JOURNAL, 41, 559 (1919). (Private communication.)

[2] Fales and Vosburgh, *ibid.*, 40, 1293 (1918).

[3] Fales and Vosburgh, THIS JOURNAL, 40, 1293 (1918).

[4] Loomis and Acree, *Am. Chem. J.*, 46, 585 (1911).

[5] Ellis, THIS JOURNAL, 38, 737 (1916).

[6] Fales and Vosburgh, *ibid.*, 40, 1293 (1918).

[7] Wilsmore, *Z. physik. Chem.*, 36, 91 (1900).

[8] Nelson and Beegle, THIS JOURNAL, 41, 559 (1919).

an increase of the hydrogen-ion concentration of $10^{1.8}$, even though the electrode had been washed several times with pure water. Also less than one minute exposure of the water contained in a small-necked bottle to fumes from a beaker of conc. hydrochloric acid caused an increase of 10^1 in the hydrogen-ion concentration.

In order to test the applicability of this method for measuring the electromotive force developed in organic cells a cell was set up with ethyl bromide dissolved in dry ether. A platinum strip was used for one electrode and a magnesium rod for the other. Due to the high resistance of the ether solution of ethyl bromine a much longer time was required to charge the condenser than was the case with pure water. However, the measurements made proved that this method can be successfully used with cells of this type where the internal resistance is many times greater than that of a cell of pure water.

In using this method for electrometric titrations it is first necessary to calibrate the galvanometer. This may be done either by means of calibrated capacities and a single voltage or by means of an unknown capacity used in conjunction with the standard voltage and the proper galvanometer shunts. From the results obtained by either method a graph may be constructed whereby the voltage corresponding to any deflection may be read directly.

With regard to the effects of polarization on the results obtained by this method it need only be pointed out that if a condenser of one microfarad is used and the electromotive force of the cell is one volt, then one hundred billionth of an equivalent of ion is discharged. This is still less than the amount which would ordinarily be discharged during the adjustment of the instrument when a potentiometer is used. The fact that the voltage of the cell does not exhibit a measurable change over periods as great as 24 hours, during which frequent measurements are taken, indicates the reliability of the method and the lack of effects due to polarization.

Summary.

1. A new method of measuring the electromotive force of concentration cells has been applied with an accuracy of 0.5 millivolt.

2. The hydrogen ion concentration of pure water has been measured and found to be 1.23×10^{-8} or $10^{-7.91}$.

3. The time required by the cell Hg | HgCl.KCl | KCl | H_2O | H_2 to charge a condenser of one microfarad capacity is from 3 to 5 minutes.

4. For a cell of low internal resistance such as Hg | HgCl.KCl | KCl | HCl | H_2 only an instant is required to charge the condenser.

5. The cell Hg | HgCl.KCl sat. | KCl. sat. | H_2O | H_2 reaches its maximum voltage in from 40 minutes to one hour and then remains constant for at least 24 hours.

6. Without sacrificing accuracy the new method makes possible the use of a much less expensive equipment than is used in the potentiometer method.

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THE FORMATION OF ADDITION COMPOUNDS BETWEEN 100% SULFURIC ACID AND THE NEUTRAL SULFATES OF THE ALKALI METALS.

JAMES KENDALL AND MARY LOUISE LANDON.

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An extensive study of the freezing-point curves of various pairs of organic substances[1] and of water solutions of acids and bases[2] has gradually yielded increasing evidence in support of a general rule for compound formation—namely, that "the stability of an addition compound increases with the difference in character (*i. e.*, the positive or negative nature of the constituent groups) of its 2 components." In the application of this rule to compound formation in aqueous solutions, the complex nature of the question of salt hydration has been briefly treated,[3] and the difficulty of bringing it into line with other work discussed. The proposal was made to attack this question by first investigating the extent of compound formation in systems of the types HX–RX and ROH–RX. If the results of this work should lead to the formulation of any general rules for these cases, then it was suggested that a comparison of these results with those from a study of the systems $HX–H_2O$ and $ROH–H_2O$ might make possible the statement of general rules for the system $RX–H_2O$.

It was in initiation of this broad plan that the present work was undertaken, the type of system investigated being HX–RX. Because of its relatively high freezing point, 100% sulfuric acid was chosen as the acid component. As salts the anhydrous normal sulfates of sodium, potassium, lithium and ammonium were selected.

Previous Work.—The data available on the formation of addition compounds of the neutral sulfates of the alkali metals with sulfuric acid are very incomplete.[4] Most of the results are in the form of isolated observations which have been incidental in the study of other problems,

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[1] Kendall, THIS JOURNAL, 36, 1222, 1722 (1914); 38, 1309 (1916); Kendall and Carpenter, *ibid.*, 36, 2498 (1914); Kendall and Gibbons, *ibid.*, 37, 149 (1915); Kendall and Booge, *ibid.*, 38, 1712 (1916).

[2] Kendall, Booge and Andrews, *ibid.*, 39, 2303 (1917); Kendall and Booge, *ibid.*, 39, 2323 (1917).

[3] Kendall, Booge and Andrews, *loc. cit.*, p. 2304.

[4] References to previous work will be found later, under each particular system examined.