determination of these quantities involves the first and second differential coefficients of the original results with the temperature. If our results agree with those determined by well conducted calorimetric measurements, we have reason to believe in the accuracy of the original electromotive forces as well as the calorimetric data. In matters of this sort, it is very important to obtain agreement by the use of entirely different experimental mechanisms.

Considering all the difficulties, both experimental and arithmetical, we regard the agreement so far obtained to be very encouraging, particularly in those cases when the amalgam electrode has been employed. This among other facts surely indicates that these measurements approach closely the cell mechanism which has been premised.

Summary

1. Measurements of the cells $H_2 | NaOH\ (m) | Na_xHg | NaOH\ (0.05) | H_2$ have been made from 0 to 35° at 5° intervals.

2. From these, activity coefficients, relative partial molal heat contents and heat capacities of sodium hydroxide from 0 to 35° have been computed. Good agreement has been obtained with calorimetric data.

3. A useful equation for the extrapolation of the partial molal heat content has been developed.

STERLING CHEMISTRY LABORATORY
NEW HAVEN, CONNECTICUT

RECEIVED AUGUST 17, 1933
PUBLISHED DECEMBER 14, 1933

[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

A Study of the Cell, Pt/Quinhydrone, HCl (0.01 *M*)/AgCl/Ag, and the Normal Electrode Potential of the Quinhydrone Electrode from 0 to 40°[1]

BY HERBERT S. HARNED AND DONALD D. WRIGHT

Since its introduction in 1921, the quinhydrone electrode has found wide use as a convenient substitute for the hydrogen electrode in determining the *P*H of acid solutions, particularly in cases where the substances under examination are reduced by hydrogen in the presence of platinum black. However, in relatively few instances has it been employed in cells without liquid junctions, for the precise evaluation of thermodynamic data. Therefore, preliminary to using such cells in a determination of the dissociation constants of chloroacetic and other substituted acids, we found it necessary to study carefully the cell

$$\text{Pt/Quinhydrone, HCl } (m)\text{/AgCl/Ag} \qquad \text{(I)}$$

---

(1) The material contained in this paper forms part of the dissertation presented to the Faculty of the Graduate School of Yale University by Donald D. Wright in June, 1933, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

in order to perfect a simple and reliable method of operation, employing vacuum technique, and to establish the limits of reproducibility. Our purpose also required that we obtain an accurate series of values of the electromotive force of this cell from 0 to 40°, when the molality of acid is 0.01 *M*. We shall combine these with data from the cell

$$H_2\ (1\ \text{atm.})/\text{HCl}\ (m)/\text{AgCl}/\text{Ag} \qquad \text{(II)}$$

which was investigated by Harned and Ehlers,[2] employing a technique similar to ours. This procedure will give the normal potential of cell I and new values of the normal potential of the important cell

$$\text{Pt/Quinhydrone, HCl}\ (m)/H_2\ (1\ \text{atm.}) \qquad \text{(III)}$$

which is the normal electrode potential of the quinhydrone electrode.

The fundamental equation for the calculations is

$$E = E_0 - \frac{2RT}{F} \ln \gamma\, m - \frac{RT}{2F} \ln \frac{a_{\text{Quinone}}}{a_{\text{Hydroquinone}}} \qquad (1)$$

which gives the electromotive force of cell I, corresponding to the cell reaction

$$\text{Hydroquinone} + 2\ \text{AgCl} = \text{Quinone} + 2\ \text{HCl} + 2\ \text{Ag}$$

The last term on the right side of this equation, which cannot be evaluated from the cell measurements alone, may be neglected in this case, as the solution is distinctly acidic and has a low ionic strength, and the quinhydrone employed is believed to have been free from an excess of either of its components.[3] Therefore, with the aid of activity coefficients of hydrochloric acid taken from the data of Harned and Ehlers, the measured values of E found at slightly varying molalities may be corrected to even molality, $m = 0.01$, and from the series of standard values so obtained, the normal potential, E_0, may be computed over the entire temperature range. Knowing the E_0 values for cell II, those for cell III follow by simple subtraction.

Materials and Apparatus

Quinhydrone.—As already pointed out, the quinhydrone used in electrode work should be free from any excess of either quinone or hydroquinone. There is a great diversity of opinion as to the best method of obtaining such a product.[4] Biilmann[5] believes that the crude crystals made by precipitation from an aqueous hydroquinone solution with ferric alum are suitable after simple washing with cold water and subsequent drying at room temperature. The difficulty in further purification lies in finding

---

(2) Harned and Ehlers, THIS JOURNAL, **54**, 1350 (1932); **55**, 2179 (1933).

(3) The last term may be divided into two parts, the logarithm of a concentration ratio and the logarithm of a ratio of activity coefficients. Since $K_1 = 10^{-10}$ and $K_2 < K_1$ for the ionization of hydroquinone (see p. 406 in Clark, "The Determination of Hydrogen Ions," 3rd ed., 1928, Williams and Wilkins Co., Baltimore) the molalities of quinone and hydroquinone are practically equal, and the concentration factor vanishes in solutions more acid than P_H 7, provided that the quinhydrone is pure. According to Hückel's equation, the activity coefficient factor equals $B\mu$, where μ is the ionic strength. The proportionality constant is small in the present instance, so that the term becomes negligible when $\mu = 0.01$.

(4) See pp. 410–411 in Clark, "The Determination of Hydrogen Ions," 3rd ed., 1928, Williams and Wilkins Co., Baltimore.

(5) Biilmann, *Bull. soc. chim.*, [4] **41**, 213 (1927).

the proper solvent for recrystallization. In water and alkaline media there is danger of autoxidation of hydroquinone to quinone,[6] while the beautiful product obtained from acetic acid solution is always under suspicion of containing adsorbed acid. Because of the divergence of opinion, the following method was devised for this work, with a special view to avoiding autoxidation. Eastman product was recrystallized from boiled water at 70° in an atmosphere of nitrogen. The crystals which separated on cooling were filtered on a Büchner funnel, washed as far as possible in the absence of air, and dried at room temperature between filter papers. This product melted sharply at about 170°. It was stored in a brown glass-stoppered bottle. Certain investigators, such as Biilmann and Jensen,[7] have found it advisable to wash the quinhydrone just before use with some of the cell solution, in order to remove any excess hydroquinone left by slow evaporation of the quinone. This refinement was not adopted here, however, as being poorly suited to vacuum technique, but the dry quinhydrone was used directly from the bottle.

Hydrochloric Acid.—Stock solutions of approximately 0.01 *M* concentration were made from redistilled acid and analyzed gravimetrically. Their strengths were known to 0.3% or better.

Before the hydrochloric acid solution was run into the cells, it was boiled under reduced pressure to remove dissolved air, and then backed with nitrogen.[8] The loss in weight was assumed to be water. All weights were corrected to a vacuum basis.

Cell Technique.—The design and operation of a cell will be made clear by reference to Fig. 1. The quinhydrone electrode is represented by A, the silver–silver chloride electrode by B. Preliminary measurements had shown that because of diffusion of quinhydrone to the silver–silver chloride electrode, no equilibrium could be attained without complete separation of the two electrode compartments (D and E). Moreover, it was evident that there was no convenient means of washing solid quinhydrone with the cell solution when employing vacuum technique, while, on the other hand, washing was a necessity in the case of the silver–silver chloride electrode. Therefore, it was decided to interpose the 3 mm. stopcock, C, and 7 to 8 cm. of 3 mm. capillary tubing between the electrode compartments, D and E, and connect the outlets to air, vacuum and solution (F) and waste (I) all to the silver-silver chloride side of the cell, so that, first, the silver–silver chloride electrode could be rinsed completely without wetting the quinhydrone side, D, second, both D and E could then be evacuated and filled simultaneously, and, finally, the solution in compartment D could be separated from that in E except at the moment of reading the electromotive force. At point F, the upper tube divided into two branches, one through the stopcock G, leading to the solution flask and the other through the stopcock, H, leading to the vacuum and air lines. The cell was held in

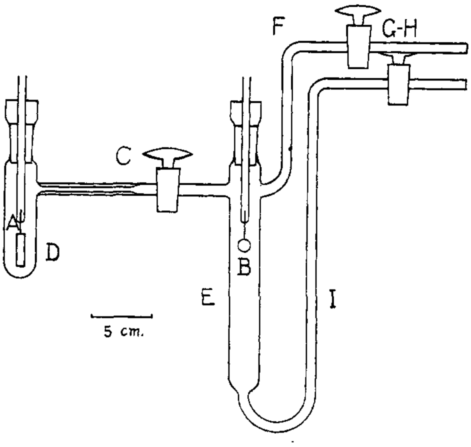

Fig. 1.—The cell.

---

(6) La Mer and Parsons, *J. Biol. Chem.*, **57**, 613 (1923); La Mer and Rideal, THIS JOURNAL, **46**, 223 (1924).

(7) Biilmann and Jensen, *Bull. soc. chim.*, [4] **41**, 151 (1927).

(8) Hydrogen is unsuitable for this purpose, as it quickly diffuses through the solution and causes measurable reduction of the quinhydrone. This is a possible source of error in the direct use of cell III.

place in the thermostat by a rack and connected to the solution flask and the air-vacuum-waste manifolds by short pieces of pressure tubing.

The operation of filling the cell proceeded as follows: the cell, previously rinsed with water, distilled water, and redistilled alcohol, and dried, was put in place in the thermostat, a quantity of quinhydrone was dropped to the bottom of compartment D sufficient to saturate the solution in that compartment, and the two electrodes, A and B, were inserted. Then stopcock C was closed and compartment E evacuated with the water pump and rinsed completely with the solution. The solution was sucked out through I into the waste flask, the necessary air being admitted through H. E was then re-evacuated and rinsed with solution to a level above that of the silver–silver chloride electrode. When this solution had been sucked out, stopcock C was opened and the whole cell evacuated and finally filled completely with solution for the run. It is recognized that the evacuation process is open to the theoretical objection that it might alter the composition of the quinhydrone by volatilization of some quinone, but it is difficult to see how this disadvantage can be dissociated from the vacuum technique which has been shown to be necessary with the silver–silver chloride electrode.[9]

Between runs the platinum foil electrodes (2.5 × 0.5 cm.) were kept immersed in a dichromate cleaning mixture, after the method of Morgan, Lammert and Campbell,[10] and before use they were thoroughly rinsed with water, distilled water, and redistilled alcohol, and dried in a current of clean, dry air. The silver–silver chloride electrodes were those described as Type 2, by Harned.[11] They were made one day in advance of use and kept in distilled water until needed. Rinsing them with the cell solution before inserting them in the cells was found to add little, if anything, to the reproducibility attained.

The temperature of the water thermostat, which was read from a calibrated thermometer, generally remained constant to ±0.02°, both with ice and with electric heating. The electromotive forces were read upon a Leeds and Northrup Type K potentiometer with a high sensitivity galvanometer. Owing to the high internal resistance of the cells, the fifth decimal place in volts could in most cases only be estimated by interpolation. However, since the estimate was generally good to two or three hundredths of a millivolt, and several readings were included in the reported average, the averaged readings could justifiably be expressed to hundredths of a millivolt.

Experimental Results with the Cell, Pt/Quinhydrone, HCl (0.01)/AgCl/Ag.—Since our measurements were made with a somewhat different technique than hitherto employed with the quinhydrone and silver–silver chloride electrodes, it was thought necessary to make a sufficient number of runs to show definitely the reproducibility of the cell, and the limits of time during which equilibrium could be considered as established. Although, under some conditions, the quinhydrone electrode reaches equilibrium almost immediately[5] and is extremely reproducible,[10,12] this could not necessarily be expected to hold in our case. The reproducibility was studied by running each day four cells filled with the same solution. They were started at a definite temperature and the electromotive force was read until equilibrium apparently had been reached. Then the temperature was raised and the process repeated several times. When the

---

(9) Güntelberg, *Z. physik. Chem.*, **123**, 199 (1926).

(10) Morgan, Lammert and Campbell, THIS JOURNAL, **53**, 454 (1931).

(11) Harned, *ibid.*, **51**, 416 (1929).

(12) Morgan and Lammert, *ibid.*, **53**, 2154 (1931); Lammert and Morgan, *ibid.*, **54**, 910 (1932).

readings finally began to drift noticeably, the run was stopped. Enough runs were made so that at least one was started fresh at each temperature reported.

Careful scrutiny of all the cell measurements first leads to the following conclusions. (1) In the particular type of cell employed, the time required to reach equilibrium varies from three hours at 0° to thirty to forty-five minutes at 25° and higher temperatures. (2) At low temperatures the cell is very difficult to read, both because of its high internal resistance and because of polarization of the quinhydrone electrode. (3) For unknown reasons, some cells do not reach equilibrium within a reasonable time. (4) While at low temperatures the electromotive force first decreases with the time, in nearly all cases it eventually begins to rise.[13] The rate of this rise varies with the individual cell, but it always increases with temperature and becomes quite pronounced above 25°. Consideration of equation (1) shows that this drift corresponds to an increase in the activity of hydroquinone or a decrease in the activity of quinone or of hydrochloric acid. It has long been known that quinone and concentrated hydrochloric acid react to form chlorohydroquinone,[14] and it therefore seems justifiable to ascribe the cause of the drift to this reaction, even at the low concentration of hydrochloric acid present in our cells.

In view of these conclusions, it was deemed best to report as the final value of the electromotive force, E_m, for a single run, the mean of all the readings for the four cells, excluding those values in which equilibrium had not yet been reached and completely excluding those cells which showed too rapid a drift in voltage and those which differed consistently from the others in their set by several tenths of a millivolt. About 8% of the cells were rejected. The deviations from the mean were calculated and used as a test of reproducibility, bearing in mind the number of readings excluded, if any.

The data thus obtained are given in Table I. This table contains, first, the mean values of the electromotive force of cell I at different temperatures and molalities, each run being reported separately, and, next, data on the reproducibility of this cell. The maximum and average deviations are deviations from the mean of those readings included in it. In column 8 are found values of $E_{0.01}$, the electromotive force at even molality $m = 0.01$, which were computed from E_m with the aid of equation (1). The runs are arranged in the table, at each temperature, according to the length of the time interval between filling the cell and commencing the readings, the run in which this time was shortest being placed first. No readings were made until thirty minutes had elapsed; in some cases they were reported up to ten hours. It is evident that the maximum and average deviations are not functions of the time, but rather of the tempera-

---

[13] This rise may also be observed in the data of Biilmann, *Ann. chim.*, [9] **15**, 109 (1921).

[14] Wöhler, *Ann.*, **51**, 155 (1844).

TABLE I

ELECTROMOTIVE FORCES OF CELL I FROM 0 TO 40°, WITH DATA ON ITS REPRODUCIBILITY AND VALUES OF THE ELECTROMOTIVE FORCE CORRECTED TO 0.01 M CONCENTRATION

Temp., °C.	m	Mean E_m	E. m. f. values Included in mean	E. m. f. values Excluded from mean	Max. dev., mv.	Av. dev., mv.	$E_{0.01}$ (obs.)	$E_{0.01}$ (calcd.)	ΔE, mv.
0.18	0.01003	−0.26007	18	6	0.18	0.09	−0.25993	−0.25992	−0.01
10.00	.01003	− .24998	16	0	.10	.03	− .24983	− .24982	− .01
	.01003	− .24997	12	0	.15	.10	− .24982		.00
15.00	.01003	− .24495	11	2	.06	.03	− .24480	− .24490	+ .10
	.00986	− .24421	4	0	.11	.08	− .24487		+ .03
15.04	.01003	− .24502	8	0	.16	.08	− .24487	− .24486	− .01
20.00	.01003	− .24022	10	2	.12	.07	− .24007	− .24012	+ .05
	.00986	− .23950	13^a	0^a	.15	.09	− .24017		− .05
	.00986	− .23956	8	0	.10	.05	− .24023		− .11
	.01003	− .24028	8	0	.06	.04	− .24013		− .01
25.00	.01009	− .23598	14^a	1^a	.10	.03	− .23554	− .23549	− .05
	.01009	− .23602	6^b	0^b	.07	.03	− .23558		− .09
	.01003	− .23546	8	0	.07	.04	− .23530		+ .19
	.00986	− .23484	9^a	0^a	.06	.03	− .23552		− .03
	.01009	− .23604	12	0	.11	.05	− .23560		− .11
	.01003	− .23555	7	1	.06	.04	− .23539		+ .10
	.00986	− .23477	4	0	.11	.06	− .23545		+ .04
30.00	.01010	− .23153	15	0	.11	.05	− .23103	− .23101	− .02
	.01009	− .23141	15^b	0^b	.16	.05	− .23096		+ .05
	.01009	− .23138	12^a	0^a	.07	.03	(− .23093)		(+ .08)
	.00986	− .23024	6^a	0^a	.07	.04	(− .23093)		(+ .08)
	.01003	− .23088	8	0	.09	.04	(− .23072)		(+ .29)
	.01003	− .23104	8	0	.14	.09	(− .23088)		(+ .13)
35.00	.01009	− .22721	7^a	3^a	.06	.04	− .22675	− .22667	− .08
	.01010	− .22708	8	0	.09	.04	(− .22657)		(+ .10)
	.01009	− .22691	6^c	0^c	.08	.03	(− .22645)		(+ .22)
39.94	.01009	− .22291	6^a	0^a	.05	.03	− .22245	− .22253	+ .08
40.00	.01011	− .22309	20	7	.15	.06	− .22252	− .22248	− .04
	.01010	− .22275	12	0	.12	.05	(− .22223)		(+ .25)

[a] Values from three cells only. One cell completely excluded. [b] Values from three cells only. [c] Values from two cells only. Two cells completely excluded.

ture, being least in the middle range from 25 to 35°. The mean values of $E_{0.01}$, however, show a consistent rise with time at 30, 35 and 40°, as would be expected from the previous discussion. At 40° the readings generally become unreliable within three hours, and we consider that temperature to be the upper limit for precise work of this nature.

In order to find an analytic expression for $E_{0.01}$ as a function of temperature, taking into account this drift, all values were assigned equal weight except the bracketed ones, which were given no weight at all, and the method of least squares applied, assuming an equation of the form, $E = a + b(t - 25) + c(t - 25)^2$. The solution was

$$E_{0.01} = -0.23549_0 + 0.0009112_3(t - 25) - 2.939_1 \times 10^{-6}(t - 25)^2 \qquad (2)$$

Values of $E_{0.01}$ calculated by means of this equation are given in the next to the last column of Table I, with the residual, or deviation between calculated and observed values, given in the last column.

We believe that the variations represented by the maximum and average deviations are inherent in this cell, and that an attempt to reduce them would render the technique too involved for general use. On the other hand, the discrepancies between the various runs, represented by ΔE, could doubtless be reduced by more precise analytical work and more uniform manipulation. We consider the present values from equation (2) accurate to within 0.1 mv. from 0 to 25° and to 0.15 mv. from 30 to 40°.

Normal Potentials.—From the values of $E_{0.01}$ computed at different temperatures by means of equation (2), the normal potential of cell I may be found by substituting in equation (1). It is important to note, however, that the values of E_0 obtained for this cell, cell II, and all other cells in which the electrolytes take part in the cell reactions, and the values of the activity coefficients of these electrolytes, are directly dependent on the choice of numerical values for the factor $k = 2.3026\ RT/F$, and for the Debye–Hückel limiting slope also, if we use Hitchcock's extrapolation.[15] We have therefore carried our calculations through in two ways: (a) using the values $k = 0.00019844T$ and $T = t + 273.1$;[16] in conformity with the choice of Harned and Ehlers,[17] and (b) employing the more recent values of Birge,[18] according to which $k = 0.00019848_5T$ and $T = t + 273.18$.

For method (a), E_0 for cell II is given by the least square equation of Harned and Ehlers

$$E_0 = 0.22239 - 645.52 \times 10^{-6}(t - 25) - 3.284 \times 10^{-6}(t - 25)^2 + 9.948 \times 10^{-9}(t - 24)^3 \quad (3a)$$

To obtain this quantity for method (b), it was necessary to perform a new extrapolation from the original electromotive force data of Harned and Ehlers. This was done from 0 to 40°, starting with their electromotive forces at round concentrations and using Hitchcock's method of extrapolation,[19] with Birge's values of the fundamental constants and Wyman's dielectric constants. The results, which are presented in the second column of Table II, are reproduced over the temperature range 0 to 40° by the least square equation

$$E_0 = 0.22223_1 - 644.80 \times 10^{-6}(t - 25) - 3.300 \times 10^{-6}(t - 25)^2 \quad (3b)$$

with a maximum deviation of 0.03 mv.

Then E_0 for cell I was calculated, first by method (a), using the activity coefficients evaluated by Harned and Ehlers from equation (3a) and their equation (9), and then by method (b), with activity coefficients found from equation (3b) and their equation (9). The observed values are set forth in

---

(15) This choice has virtually no effect on the correction of E_m to $E_{0.01}$. The activity coefficients employed in this calculation were those mentioned below under method (a).

(16) Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York, 1923.

(17) Harned and Ehlers, THIS JOURNAL, **55**, 2179 (1933). The values of the Debye–Hückel constant given by these authors were calculated from "International Critical Tables" data and the dielectric constants of Wyman, *Phys. Rev.*, **35**, 623 (1930).

(18) Birge, *Phys. Rev. Supplement*, **1**, 1 (1929).

(19) Hitchcock, THIS JOURNAL, **50**, 2076 (1928).

TABLE II

NORMAL POTENTIALS OF CELLS I, II AND III FROM 0 TO 40°

t	E_0 − IIb (obs.)	E_0 − Ia (obs.)	E_0 − Ib (obs.)	E_0 − IIIb (Eq. 5b)
0	0.23627	−0.48156	−0.48160	−0.71790
5	.23384	− .48038	− .48048	− .71429
10	.23116	− .47936	− .47952	− .71066
15	.22833	− .47851	− .47867	− .70702
18				− .70482
20	.22537	− .47780	− .47799	− .70336
25	.22223	− .47728	− .47744	− .69969
30	.21894	− .47691	− .47707	− .69600
35	.21544	− .47668	− .47684	− .69230
40	.21182	− .47660	− .47678	− .68858

the third and fourth columns, respectively, of Table II. The two sets were least squared to give the equations

$$E_0 = -0.47727_5 + 91.83 \times 10^{-6}(t - 25) - 3.174 \times 10^{-6}(t - 25)^2 \qquad (4a)$$

$$E_0 = -0.47745_6 + 91.02 \times 10^{-6}(t - 25) - 3.008 \times 10^{-6}(t - 25)^2 \qquad (4b)$$

which fit all the data with a maximum deviation of 0.02 mv.

E_0 for cell III may be found either by subtracting (3a) from (4a), or (3b) from (4b), or by subtracting Harned and Ehlers' equation (9)

$$E_{0.01} = 0.46418 + 173.84 \times 10^{-6}(t - 25) - 3.11 \times 10^{-6}(t - 25)^2 + 7.00 \times 10^{-9}(t - 25)^3$$

which gives the electromotive force of cell II at 0.01 M concentration, from our equation (2). Since the three resulting equations give almost identical values, we shall present only the second, namely

$$E_0 = -0.69968_7 + 735.82 \times 10^{-6}(t - 25) + 0.292 \times 10^{-6}(t - 25)^2 \qquad (5b)$$

Values calculated from it are found in the last column of Table II.

These figures may be compared with those from two other sources. Biilmann and Jensen[7] measured cell III directly at 0.01 N concentration of hydrochloric acid and obtained for E_0 the value −0.70479 ± 0.00002 volts at 18°, which is in very satisfactory agreement with our result. Biilmann and Krarup[20] measured the same cell at 0, 18, 25 and 37.5°, employing 0.1 N HCl, 0.1 N HCl + 0.09 N KCl, and a phosphate buffer as electrolytes. All their results could be reproduced by the equation, $E_0 = -0.7175 + 0.00074t$ to within 0.4 mv. Correcting from the measurements of Biilmann and Jensen at 18° for the difference between these cells and the 0.01 N HCl cell, we obtain

$$E_0 = -0.7181 + 0.00074t \qquad (6)$$

Values calculated from this equation agree with those of Table II to 0.2 mv. or less. While the normal electrode potential of the quinhydrone electrode can undoubtedly be found most accurately by the direct measurement of cell III, in view of the number and character of the present meas-

---

[20] Biilmann and Krarup, *J. Chem. Soc.*, **125**, 1954 (1924).

urements, we consider the values given in Table II to be the best available at this time.

Summary

1. A simple and reliable procedure has been described whereby the quinhydrone electrode may be used in cells without liquid junction, employing vacuum technique.

2. The reproducibility of the quinhydrone electrode in 0.01 *M* hydrochloric acid solution has been carefully studied, employing the cell Pt/quinhydrone, HCl (0.01 *M*)/AgCl/Ag. The electromotive force of this cell has been found to be reproducible to within a tenth of a millivolt from 0 to 40°, although side reactions destroy the equilibrium after a short time at temperatures above 30°.

3. Values have been obtained from 0 to 40° for the potential of the above cell and the normal potentials of that cell and the cell, Pt/quinhydrone, HCl/H_2, with an accuracy of ± 0.1 mv. from 0 to 25° and ± 0.15 mv. from 30 to 40°.

NEW HAVEN, CONNECTICUT

RECEIVED AUGUST 19, 1933
PUBLISHED DECEMBER 14, 1933

[CONTRIBUTION FROM THE PHYSICAL CHEMISTRY LABORATORY, STATE COLLEGE OF WASHINGTON]

The Activity Coefficients and Transference Numbers of Potassium Iodide[1]

BY RALPH W. GELBACH

Electromotive forces of concentration cells, with and without ion transfer, have been measured at 25 ± 0.02°. The following types of cells have been measured.

(A) KHg_x | KI m_1, AgI | Ag—Ag | AgI, KI m_2 | KHg_x
(B) KHg_x | KI m_1 | KI m_2 | KHg_x
(C) Ag | AgI, KI m_1 | KI m_2, AgI | Ag

Materials, Apparatus and Method.—Chemically pure potassium iodide was thrice recrystallized from distilled water and dried in an air-bath at about 80°. Solutions were made from weighed portions of the salt by adding a definite quantity of conductivity water and boiling for a definite time on an electric hot plate. The hot solutions were saturated with hydrogen by permitting the gas to bubble through them for several minutes, then finally cooled to room temperature under an atmosphere of hydrogen. By standardization of operations it was easily possible to control concentrations within 0.2%.

---

(1) A portion of the data was obtained by Helen Marburger Fredell as a partial fulfilment for the Master's Degree.