[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

The Dissociation Constant of Chloroacetic Acid from 0 to 40°[1]

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The two potentiometric methods recently devised in this Laboratory[2] for the precise determination of the dissociation constants of organic acids make use, in their original form, of the hydrogen electrode, in cells without liquid junctions. To treat acids for which this electrode is unsuitable, such as volatile acids and those which are reduced by hydrogen in the presence of platinum black, other electrodes reversible to hydrogen ions must be employed, of which the most important are the glass electrode and the quinhydrone electrode. The present study is an application of the latter to the determination of the dissociation constant of chloroacetic acid from 0 to 40°.[3] It has been found[4] that this halogenated acid is typical of the second class above mentioned in that it is reduced at an ordinary platinum foil hydrogen electrode.

Outline of the Method

The dissociation constant is determined, following the general method of Harned and Owen,[2] from measurements of the electromotive force of the cells

$$\text{Pt/Quinhydrone, } CH_2ClCOOH\ (M),\ NaCl\ (m)/AgCl/Ag \qquad (I)$$

$$\text{Pt/Quinhydrone, } HCl\ (0.01\ M)/AgCl/Ag \qquad (II)$$

The values of M and m, the number of moles of acid and salt, respectively, per thousand grams of water, must be such that the hydrogen-ion concentration is below 0.02 or, preferably, 0.01 M.

The "apparent hydrogen-ion concentration," m'_{H}, is here defined by the equation

$$-\log m'_{\mathrm{H}} = \frac{F}{2.3026RT} E_1 - A(t) + \log m + 2 \log \gamma^{\circ}_{\mathrm{HCl}} \qquad (1)$$

Its relation to the real hydrogen-ion concentration, m_{H}, is given by

$$\log m'_{\mathrm{H}} = \log m_{\mathrm{H}} + 2 \log \frac{\gamma_{\mathrm{HCl}}}{\gamma^{\circ}_{\mathrm{HCl}}} + \frac{1}{2} \log \frac{a_{\mathrm{Hq}} a_{\mathrm{Q}'}}{a_{\mathrm{Q}} a_{\mathrm{Hq}'}} \qquad (2)$$

E_1 is the electromotive force of cell I. $A(t)$ is defined as

$$A(t) = \frac{F}{2.3026RT} E_2 + 2 \log (\gamma_{0.01})(0.01) \qquad (3)$$

where E_2 represents the electromotive force of cell II and $(\gamma_{0.01})(0.01)$ the activity of hydrochloric acid in that cell. The last term in equation (2) represents the difference between the activities of quinone and hydroquinone in cell I (primed) and cell II (unprimed), the so-called "salt effect" of the quinhydrone electrode, which becomes negligible in the extrapolation to infinite dilution. γ_{HCl} and $\gamma^{\circ}_{\mathrm{HCl}}$ are used in the same sense employed by Harned and Owen, and our extrapolation function $(\log k' - 2a\sqrt{\mu'})$, differs from theirs only by the inclusion of exact values for a, the Debye–Hückel limiting slope.

Measurements of Cell I

The general operative procedure for cell I was the same as that for cell II, which has been fully discussed in a previous contribution.[5] The chloroacetic acid–sodium chloride solutions were prepared as follows.

High grade analyzed sodium chloride was further purified by filtering a saturated solution, evaporating to one-third volume, and drying the crystals which separated at 130° for twenty-four hours.

Chloroacetic acid, from the Dow Chemical Company and the Eastman Kodak Company (No. 68), was purified by fractional distillation under reduced pressure, and kept preserved against moisture. Its purity was determined from time to time by titration with carbonate-free base, all samples coming within 0.1 mole per cent. of the theoretical equivalent. The acid was therefore considered 100% pure for purposes of calculation. It could be weighed out accurately except on extremely humid days.

The cell solutions contained sodium chloride at molality m and chloroacetic acid at molality M. Hydrolysis made it impossible to employ a stock solution of the acid but labor was saved by the use of stock solutions of sodium chloride of approximately the strengths desired. They were prepared air-free and kept under nitrogen. To make up a cell solution, solid chloroacetic acid was weighed directly into a liter flask and the

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(1) This paper forms a part of the dissertation presented by Donald D. Wright to the faculty of the Graduate School of Yale University in June, 1933, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

(2) Harned and Owen, THIS JOURNAL, **52**, 5079 (1930); Harned and Ehlers, *ibid.*, **54**, 1350 (1932).

(3) For an example of the application of the glass electrode, see MacInnes and Belcher, *ibid.*, **55**, 2630 (1933).

(4) B. B. Owen, Thesis, Yale University, 1930.

(5) Harned and Wright, THIS JOURNAL, **55**, 4849 (1933).

proper quantity of salt solution added. A relatively short boiling under reduced pressure, which was generally carried out at room temperature, then sufficed to remove any air absorbed during the weighing process without causing much risk of hydrolysis. These solutions were backed with nitrogen during the filling of the cells.

The stock solutions of sodium chloride were analyzed gravimetrically. The molality of the 0.2 *M* solution was found to within 0.1%. In the case of the other solutions, the analytical error may have been several times that amount, although the character of the extrapolations renders this improbable. Values of *M* were in general calculated from the amount of acid weighed out, but in some cases titrations against standard base were made as well, before assigning a final value.

The experimental results are given in the first three columns of Table I. Unless otherwise specified in the footnotes, all measurements were obtained at exactly even temperatures, with a maximum variation of ± 0.02°. Each electromotive force, the "Mean E_1," represents the average of the readings of two or, in most cases, three cells filled with the same solution, some few values which were not considered so reliable being listed as second class points. About 2% of the cells and 3% of the readings from the remaining cells were excluded in finding the reported electromotive forces. All the runs were made with fresh cells, except the 18 and 32° runs of the 0.02 and 0.2 *M* sodium chloride series, which were made with the same cells as the 10° and 25° runs, respectively. The general behavior of the cells

TABLE I

ELECTROMOTIVE FORCES OF THE CELL Pt/QUINHYDRONE, $CH_2ClCOOH$ (*M*), NaCl (*m*)/AgCl/Ag, WITH CORRESPONDING VALUES OF THE APPARENT HYDROGEN-ION CONCENTRATION

		0°				10°	
m	M	Mean E_1	m'_H	m	M	Mean E_1	m'_H
0.01892	0.02001	−0.25864[a,c]	0.00545	0.01894	0.02005	−0.24821	0.00541
.04836	.02006	− .27926[b]	.00563	.04827	.01982	− .26941	.00557
.09507	.01999	− .29378[b]	.00576	.10131	.02004	− .28608	.00576
.1903	.02008	− .30859[c]	.00586	.1902	.01998	− .29998	.00583
.01895	.04893	− .27038[c]	.00910	.01899	.05020	− .26070	.00914
.04835	.05018	− .29137[b]	.00950	.04826	.04997	− .28206	.00944
.09520	.05000	− .30611[b]	.00976	.10135	.05009	− .29888	.00977
.1903	.04963	− .32090[d]	.00990	.1904	.05001	− .31290	.00992
.01892	.1000	− .27950[e]	.01367	.01894	.1001	− .26975	.01351
.04837	.1002	− .30043[c]	.01410	.04827	.1000	− .29135	.01394
.09508	.1000	− .31510[g]	.01443	.10116	.0994	− .30805[h]	.01432
.1902	.0998	− .33005[b]	.01463	.1904	.1001	− .32234	.01463
.01892	.2004	− .28823[e]	.02025	.01895	.2002	− .27876	.01996
.04828	.2001	− .30928[c]	.02084	.04825	.1998	− .30050	.02057
.09511	.2001	− .32412[f]	.02132	.10118	.1998	− .31722[h]	.02100
.1902	.2000	− .33916[b]	.02160	.1904	.1998	− .33158	.02144
		18°				25°	
0.01894	0.02005	−0.23999	0.00533	0.01894	0.02007	−0.23299	0.00524
.04828	.02000	− .26191	.00554	.04804	.02000	− .25532	.00545
.10122	.01998	− .27896	.00571	.09509	.02000	− .27152	.00565
.1902	.01998	− .29330	.00581	.1906	.02004	− .28775	.00578
.01899	.05020	− .25286	.00902	.01892	.05005	− .24612	.00890
.04833	.04994	− .27488	.00936	.04805	.04977	− .26856	.00921
.10126	.05004	− .29202	.00965	.09523	.04998	− .28494	.00956
.1904	.05001	− .30653	.00985	.1906	.05009	− .30123	.00979
.01894	.1001	− .26215	.01333	.01894	.1003	− .25556	.01305
.04847	.1003	− .28450	.01383	.04802	.0999	− .27825	.01357
.10121	.1000	− .30166	.01425	.09500	.1000	− .29457	.01402
.1904	.1001	− .31623	.01454	.1905	.0995	− .31102	.01436
.01895	.2002	− .27139	.01969	.01894	.1999	− .26495	.01923
.04846	.2008	− .29386	.02037	.04803	.2000	− .28779	.01994
.10121	.1999	− .31105	.02087	.09499	.2000	− .30430[a]	.02063
.1904	.1998	− .32572	.02131	.1905	.1992	− .32078	.02109

TABLE I (*Concluded*)

32°				40°			
m	M	Mean E_1	m'_H	m	M	Mean E_1	m'_H
0.01894	0.02007	−0.22615	0.00515	0.01893	0.02002	−0.21852[a]	0.00501
.04806	.02001	− .24892	.00535	.04817	.02007	− .24221	.00528
.09509	.01998	− .26552	.00555	.09508	.02000	− .25892	.00543
.09509	.02000	− .26555	.00556				
.1906	.02004	− .28212	.00569	.1907	.02003	− .27597	.00557
.01892	.05005	− .23947	.00870				
.04803	.04994	− .26236	.00900	.04812	.05015	− .25587[i]	.00884
				.04816	.05018	− .25608[a]	.00891
.09513	.04998	− .27916	.00937	.09513	.04998	− .27288	.00916
.09523	.04998	− .27921[a]	.00938				
.1906	.05009	− .29587	.00962	.1906	.05002	− .29015	.00946
.01894	.1003	− .24917	.01279	.01895	.1003	− .24215	.01245
.04801	.1000	− .27241	.01332	.04823	.1005	− .26588[a]	.01292
				.04812	.1003	− .26591[i]	.01295
.09509	.0999	− .28923	.01383	.09519	.1001	− .28313	.01345
.1905	.0995	− .30587	.01412	.1910	.0997	− .30025	.01376
.01894	.1999	− .25872	.01881	.01895	.2006	− .25216[a]	.01845
.04802	.1999	− .28221	.01961	.04811	.1999	− .27588	.01901
.09499	.2000	− .29890	.02015	.09522	.2001	− .29317	.01965
.09517	.2000	− .29899	.02017	.09517	.2000	− .29301	.01954
.1905	.1992	− .31584	.02070	.1904	.2000	− .31054[a]	.02028

[a] Second class point. [b] Exact temperature = 0.11°. [c] 0.13°. [d] 0.14°. [e] 0.15°. [f] 0.18°. [g] 0.19°. [h] 10.02°. [i] 39.97°.

was similar to that of cell II.[5] A record of deviations shows that the values of E_1 are generally accurate to within ± 0.1 mv., with some few cases in which the accuracy is between 0.1 and 0.2 mv.

Determination of K

The fourth column of Table I contains the values of m'_H corresponding to each value of E_1. They were calculated from equation (1) by a process of successive approximation. For γ°_{HCl} we have employed activity coefficients of 0.01 M hydrochloric acid in sodium chloride solutions, calculated from unpublished electromotive forces obtained in this Laboratory by Dr. Leslie F. Nims and activity coefficients in pure 0.01 M hydrochloric acid as found by Harned and Ehlers.[6] Their use gives correct results for all our cells within the experimental error of one in the third decimal place of log γ. The function $A(t)$ was calculated from these same activity coefficients and the previously published electromotive forces of cell II.[5]

The two extrapolations necessary to determine log K were carried out from these data. First, the extrapolation function (log $k' - 2a\sqrt{\mu'}$), was calculated from m'_H. Then, to obtain log k°, each of the groups of values of (log $k' - 2a\sqrt{\mu'}$) which correspond to different values of M were plotted separately against μ', on a large scale. The resulting curves were nearly straight and nearly parallel and fitted the experimental points with maximum deviations of 0.002 for the four lower temperatures, 0.0045 at 32°, and, at 40°, 0.004 for the first class points and 0.0075 for the second class points. Correction of all the results to exactly even temperature and molality, M, was found to make no appreciable change.

Two independent extrapolations were made for log K. In the first of these, log k° was plotted against M; in the second, log k° was plotted against ($M - m^*_H$). m^*_H is the value which m'_H assumes in a salt-free acid solution of total acid molality M, which is the lowest point on the (log $k' - 2a\sqrt{\mu'}$) curve that may be attained experimentally. The procedure of Harned and Owen[2] was followed and a straight line relationship assumed between log k° and M, or ($M - m^*_H$), the lines being drawn so as to give the slopes a regular progression with temperature. The deviations from the curves are distributed quite at random and all amount to less than five in the third decimal place.

The final values of log K are given in the second and third columns of Table II, both methods of

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(6) Harned and Ehlers, THIS JOURNAL, **55**, 2179 (1933). Throughout the calculations, we have used the values $2.3026RT/F = 0.000198485_5T$ and $T = t + 273.18$, which are those of Birge, *Phys. Rev., Supplement*, **1**, 1 (1929).

TABLE II

THE DISSOCIATION CONSTANT AND HEAT OF DISSOCIATION OF CHLOROACETIC ACID

t	log K (A)	log K (B)	log K (Eq. 4)	$K \times 10^3$	ΔH (Eq. 5)	ΔC_p (Eq. 6)
0	7.1836	7.1848	7.1840	1.528	− 149	−46.83
10	7.1720	7.1730	7.1735	1.491	− 593	−42.04
18	7.1581	7.1586	7.1574	1.437	− 914	−38.21
25	7.1402	7.1390	7.1391	1.378	−1170	−34.86
32	7.1163	7.1167	7.1174	1.310	−1402	−31.51
40	7.0897	7.0903	7.0896	1.229	−1639	−27.68

extrapolation, that against M, (A), and that against $(M - m^*_{\mathrm{H}})$, (B), being considered equally valid in the present instance. An analytic expression for log K as a function of temperature was found in the usual manner by the method of least squares. Equations for ΔH, the heat of dissociation, and ΔC_p, the difference in the molal heat capacities of the ions and undissociated acid, were found by differentiation. The following three equations were obtained for log K, ΔH and ΔC_p, respectively.

$$\log K = -6669.53/T - 89.40736 \log T + 0.0523310\, T + 225.1390_7 \quad (4)$$

$$\Delta H = 30505.9 - 177.6015\, T + 0.239358\, T^2 \text{ (cal.)} \quad (5)$$

$$\Delta C_p = -177.6015 + 0.478716\, T \text{ (cal.)} \quad (6)$$

Values of log K, K, ΔH and ΔC_p calculated from these equations are listed in Table II. The decrease of K with increasing temperature, shown in this table, contrasts markedly with the behavior observed in the case of water,[7] where K rises with temperature, and acetic,[8] propionic[9] and phosphoric acids,[10] where K passes through a maximum.

Consideration of the method of extrapolation will show that it is very sensitive to errors in the original experimental quantities of equation (1) and that the estimated errors in E_1 and log γ^0_{HCl} are thus more than sufficient to account for the random deviations observed in the extrapolation plots. We believe that these two observational errors have been almost eliminated by the double extrapolation and least squaring process and that equation (4) gives a consistent series of values of log K with an accuracy of one or two in the third decimal place.[11] However, errors in the terms $A(t)$ and log m, of equation (1), would affect all the measurements and would not be eliminated in the calculations. The maximum error from this source is estimated to be 0.0045 in log K or 1.1% in K from 0 to 25°, and 0.0064 in log K or 1.5% in K from 30 to 40°.

The "International Critical Tables" gives for K, from conductance data, $1.58 \cdot 10^{-3}$ at 14.1° and $1.52 \cdot 10^{-3}$ at 25°. Both of these values deviate widely from our results, as might be expected from the age of the data and the method of calculation used. Randall and Failey[12] have recalculated the constant from conductance measurements of Ostwald[13] using the method of Sherrill and Noyes.[14] The value which they obtain, $K = 1.39 \cdot 10^{-3}$ at 25°, agrees with ours within the estimated maximum error. This is, however, not true of the value of Larsson and Adell, $1.49 \cdot 10^{-3}$ at 18°,[15] which was found from measurements of cells with liquid junctions, nor that of Saxton and Langer, $1.396 \cdot 10^{-3}$ at 25°,[16] both of which are higher than our figures at the corresponding temperatures.[17]

The author wishes to express his appreciation to Professor Herbert S. Harned for suggesting this problem and for the guidance which he has given in its solution.

Summary

1. It has been shown that the method of Harned and Owen for determining the thermodynamic properties of weak acids from electromotive force measurements of cells without liquid junctions can be applied to halogenated acids by use of the quinhydrone electrode.

2. From electromotive force measurements of cells containing chloroacetic acid at 0.02, 0.05, 0.1, 0.2 M and sodium chloride at 0.02, 0.05, 0.1, 0.2 M concentration, the apparent hydrogen-ion concentration in these solutions and the dissociation constant of chloroacetic acid have been calculated at 0, 10, 18, 25, 32 and 40°.

3. By the method of least squares, equations have been obtained for log K, ΔH, the heat of dissociation and ΔC_p as functions of temperature, over the range 0 to 40°.

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[7] Harned and Hamer, THIS JOURNAL, **55**, 2194 (1933).

[8] Harned and Ehlers, *ibid.*, **55**, 652 (1933).

[9] Harned and Ehlers, *ibid.*, **55**, 2379 (1933).

[10] Nims, *ibid.*, **55**, 1946 (1933).

[11] It may be noted that, because of the size of the coefficients of equation (4), T and log T must be expressed to five and seven figures, respectively, to obtain accuracy in the third decimal of log K.

[12] Randall and Failey, *Chem. Rev.*, **4**, 291 (1927).

[13] Ostwald, *Z. physik. Chem.*, **3**, 170 (1889).

[14] Sherrill and Noyes, THIS JOURNAL, **48**, 1861 (1926).

[15] Larsson and Adell, *Z. physik. Chem.*, **A157**, 342 (1931).

[16] Saxton and Langer, THIS JOURNAL, **55**, 3638 (1933).

[17] Since this work was completed, MacInnes, Shedlovsky and Longworth, *Chem. Rev.*, **13**, 29 (1933), have reported the value $1.397 \cdot 10^{-3}$ at 25°.