TABLE IV

PARAMETERS OF EQUATIONS (4) AND (7). $\overline{L}_2$ AND $(\overline{C}_p - \overline{C}_{p0})$ AT 25°

m	$(-\alpha)$	β	$\overline{L}_{2(25)}$	$(\overline{C}_p - \overline{C}_{p0})_{25}$
0.003	640	0.00923	180	5.5
.005	619	.01061	324	6.3
.007	630	.01154	395	6.9
.01	609	.01223	478	7.3
.02	651	.01408	600	8.4
.03	669	.01500	664	8.9
.05	703	.01638	753	9.8
.07	735	.01730	802	10.2
.1	754	.01823	866	10.9
.2	839	.02077	1007	12.4
.3	934	.02284	1096	13.6
.5	1179	.02723	1241	16.2
.7	1430	.03138	1359	18.7
1	1704	.03646	1536	21.7
1.5	1999	.04292	1815	25.6
2	2169	.04799	2095	28.6
3	2285	.05561	2657	33.1

Relative Partial Molal Heat Content and Heat Capacity.—The heat data have been computed by the method described by Harned and Thomas[7] and mentioned by us.[4] The relative partial molal heat content, $\overline{L}_2$, is expressed by

$$\overline{L}_2 = \alpha + \beta T^2 \qquad (4)$$

α and β are given by

$$\alpha = -23{,}074[(E_{25} - E'_{0(25)}) - 298.1(a - a_0) + 88{,}864(b - b_0)] \qquad (5)$$

$$\beta = 23{,}074(b - b_0) \qquad (6)$$

respectively. $\overline{L}_2$ is in calories. The relative partial molal heat capacity may be computed by the equation

$$(\overline{C}_p - \overline{C}_{p0}) = 2\beta T \qquad (7)$$

Table IV contains the parameters α and β, from which $\overline{L}_2$ may be computed at all temperatures from 0 to 50° with an accuracy of the order of ±30 cal. by equation (4), and $(\overline{C}_p - \overline{C}_{p_0})$ with an accuracy of the order of ±1 cal. by equation (7). Values of $\overline{L}_2$ and $(\overline{C}_p - \overline{C}_{p_0})$ at 25° are given in the fourth and fifth columns of the table, respectively.

Summary

1. The electromotive forces of the cells

H_2 | HCl (m), Dioxane (45%), H_2O (55%) | AgCl-Ag

have been measured at 5° intervals from 0 to 50°, and from 0.1 to 3 M acid concentrations with an accuracy of ±0.05 mv.

2. From these and the results of Harned and Morrison in the dilute concentration range (0.003 to 0.1 M) the activity coefficient, the relative partial molal heat content and the heat capacity of the acid have been computed throughout these ranges of temperature and pressure.

NEW HAVEN, CONN. RECEIVED JUNE 21, 1938

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[7] Harned and Thomas, THIS JOURNAL, **58**, 761 (1936).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

The Thermodynamics of Hydrochloric Acid in Dioxane–Water Mixtures from Electromotive Force Measurements. VI. Extrapolations in the 70% Dioxane Mixtures and Standard Potentials

BY HERBERT S. HARNED AND CALVIN CALMON[1]

In an earlier communication in this series,[2] it was shown that accurate evaluations of the standard potentials of the cell

H_2 | HCl (m), dioxane (X), H_2O (Y) | AgCl-Ag

in mixtures containing 20 and 45% dioxane could be made by employing the Gronwall, La Mer and Sandved extension of the Debye and Hückel theory. At the same time, an extrapolation was made with the results obtained in a mixture of 70% dioxane–30% water at 25°. Since experimental results below 0.003 M were not available, a slight uncertainty in the extrapolation was suspected, and further calculations discontinued for the moment. This communication contains an attempt to obtain results at still lower concentrations, and to determine the lower limit of concentration at which reliable results can be obtained with the technique available.

Experimental Results

The preparation of solutions and the cell technique was carried out with all the precautions and in the same manner as that described by

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[1] This communication contains material from a dissertation presented by Calvin Calmon to the Graduate School of Yale University in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1938.

[2] Harned, THIS JOURNAL, **60**, 336 (1938).

Harned and Morrison.[3,4] The only difference which need be mentioned is the preparation and behavior of the silver–silver chloride electrodes. Electrodes of this type prepared electrolytically as described by Harned and Morrison[3] are reproducible to within ±0.1 mv. in solutions containing acid at 0.003 *M* or higher. Below this concentration, they fail to function satisfactorily. After proving this fact, electrodes made by mixing nine parts of silver oxide with one part of silver chlorate were employed. This mixture was spread on a platinum wire spiral and heated at a temperature of 450° for ten minutes as described by Rule and La Mer.[5,6] In solutions containing hydrochloric acid of concentrations 0.002 and 0.003 *M*, these electrodes behaved very satisfactorily. Equilibrium was attained in twelve hours and the electromotive forces agreed very closely at 0.003 *M* with those obtained by the electrolytically prepared electrodes of Harned and Morrison. Further, after measurements at different temperatures, the cells could be brought back to the initial temperature after a period of ten to twenty hours and the original electromotive force reproduced. In more dilute solutions, however, a longer period of time, from forty-eight to sixty hours, was required for equilibration. Also, at concentrations near 0.001 *M*, the reproducibility was found to be considerably less than at 0.002 *M*. Within the limit of ±0.5 mv., these electrodes would operate satisfactorily over periods of forty-eight hours, and after the temperature changes had been made.

Our experience may be summarized by the statement that an accuracy of ±0.1 mv. may be obtained at concentrations of 0.002 *M* and higher; that the reproducibility decreases with concentration decrease, and becomes approximately ±0.5 mv. at 0.001 *M*. These estimates will suffice to show the present experimental status of this subject.

The cells were run in triplicate. For each concentration, two series of measurements were made. Each series was begun at 25° and readings were taken at 5° intervals to 50° and finally at 25° again. The second series was also started at 25°, then readings were taken at 0° and at 5° intervals until 25° was reached. If at the end of each run the difference in readings at 25° was greater than 0.3 mv., the results were discarded. The vapor pressure data of Hovorka, Schaeffer and Dreisbach[7] were employed in making the usual correction for hydrogen pressure. Table I contains the electromotive forces.

TABLE I

ELECTROMOTIVE FORCES OF THE CELLS

H_2 | HCl (*m*), dioxane (*X*)–H_2O (*Y*) | AgCl–Ag

X = 70% by weight

	m				
t	0.003292	0.002366	0.001043	0.001001	0.0008146
0	0.40050	0.41283	0.4463	0.4467	0.4556
5	.39822	.41078	.4430	.4443	.4540
10	.39580	.40860	......	.4427	.4519
15	.39325	.40626	.4395	.4405	.4501
20	.39059	.40376	.4373	.4388	.4480
25	.38780	.40112	.4348	.4364	.4453
30	.38485	.39830	.4321	.4346	.4421
35	.38176	.39535	.4295	.4313	.4402
40	.37855	.39226	.4270	.4286	.4386
45	.37520	.38903	.4245	.4253	.4366
50	.37170	.38568	.4221	.4214	.4319
Reproducibility (mv.)	±0.1	±0.1	±0.5	±0.5	±0.5

Extrapolations and Evaluation of the Standard Electrode Potential.—The extrapolation was carried out in the manner described by Harned[2] by employing the function E', defined by the equation

$$E' = E + 2k \log m - \frac{2ku\sqrt{c}}{1 + A\sqrt{2c}} - 2k \log (1 + 0.002\, G_0 m) = E_0' + f(m) \quad (1)$$

E is the observed potential of the cell, k equals 2.3026 RT/F, u is the universal constant of the Debye and Hückel theory, A is the parameter which involves the mean distance of approach of the ions, a, G_0 is the mean molecular weight of the solvent (ref. 4, eq. (6)), and E_0' is the standard potential of the cell. m is the concentration of the acid in moles per 1000 grams of solvent, and c is its concentration in moles per liter of solution. The use of the Gronwall, La Mer and Sandved extension of the theory makes possible a more certain evaluation of E_0'. Arithmetical approximations showed that a value of "a" of 5.6 Å. at all temperatures gave satisfactory extrapolations. Thus, the values of $E' - E_{Ex}$, where E_{Ex} represents the contribution of the extended terms to the electromotive force, was very constant at concentrations between 0.002 and 0.02 *M*. At concentrations between 0.0008 and 0.002 *M*, the results are not as consistent, but in general indicate that the method is good.

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[3] Harned and Morrison, *Am. J. Sci.*, **33**, 161 (1937).

[4] THIS JOURNAL, **58**, 1908 (1936).

[5] Rule and La Mer, *ibid.*, **58**, 2339 (1936).

[6] Keston, *ibid.*, **57**, 1671 (1935).

[7] Hovorka, Schaeffer and Dreisbach, *ibid.*, **58**, 2264 (1936).

E_{Ex} is given by

$$E_{\mathrm{Ex}} = 2k\left[C\left(\frac{1}{a}\right)^3\left(10^3\left[\frac{1}{2}X_3(x) - 2Y_3(x)\right]\right) + K\left(\frac{1}{a}\right)^5\left(10^5\left[\frac{1}{2}X_5(x) - 4Y_5(x)\right]\right)\right] \qquad (2)$$

where

$$C10^3 = \frac{1}{2.3026}\left(\frac{\epsilon^2}{kTD}\right)^3 \qquad (3)$$

$$K10^5 = \frac{1}{2.3026}\left(\frac{\epsilon^2}{kTD}\right)^5 \qquad (4)$$

and

$$x = \kappa a = A\sqrt{2c} \qquad (5)$$

κ is the reciprocal radius of the ionic atmosphere. 4.774×10^{-10}, 1.371×10^{-16}, 6.06×10^{23}, and 273.1 were used for ϵ, k, N and T at 0°, respectively. The values of the dielectric constants of the mixtures were obtained from the data of Åkerlöf and Short[8] and the density data for the computation of c from m were those of Harned and Calmon.[9] Values of the quantities used in the computations are given in Table II. The values of the third and fifth approximations given in parentheses in equation (2) were obtained from Table V in Gronwall, La Mer and Sandved's contribution.

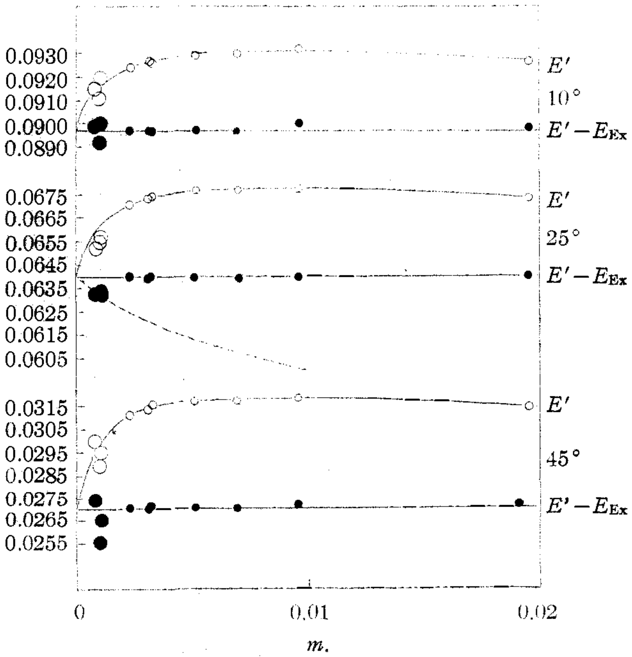

Fig. 1.—Extrapolation at 10, 25 and 45°.

TABLE II

VALUES OF D, u, C/a^3, K/a^5 AND A

a = 5.6 Å.

t	D	u	C/a^3	K/a^5	A
0	20.37	1.364	0.06584	0.01872	3.776
5	19.81	1.385	.06778	.01965	3.794
10	19.25	1.406	.07003	.02074	3.815
15	18.72	1.429	.07225	.02186	3.835
20	18.20	1.453	.07467	.02309	3.856
25	17.69	1.477	.07729	.02446	3.878
30	17.20	1.503	.07997	.02546	3.901
35	16.72	1.530	.08295	.02751	3.924
40	16.26	1.557	.08591	.02917	3.947
45	15.80	1.586	.08927	.03109	3.973
50	15.37	1.616	.09255	.03302	3.996

Values of E' and $E' - E_{\mathrm{Ex}}$ are plotted against the molal concentration in Fig. 1. The extrapolations at 10, 25 and 45° are given as typical. The plot at 10° is characteristic of the results at temperatures between 0 and 20°, inclusive, that at 25° is typical also of the results at 30, 35 and 40°, and that at 45° is similar to the result at 50°. The first thing to note is the characteristic "hump" in the plots of the Debye and Hückel function E' and the straight graphs for the functions, $E' - E_{\mathrm{x}}$. $E' - E_{\mathrm{x}}$ remains constant until a concentration of 0.02 M is reached which corresponds to a value of x or κa of the order of 0.7. The final values of E_0' have been computed from the more reproducible results at concentrations of 0.002 M or greater. With very few exceptions, the points computed from the results in the neighborhood of 0.001 M lie below the curves which indicates low values of the cell electromotive forces.

Values of the function $E' - E_{\mathrm{Ex}}$ at the temperatures shown in the graph are given in Table III. The bottom row of the table contains the extrapolated values of E_0'. The consistency of the results between 0.002 to 0.03 M is excellent. The values in parentheses at the lower concentrations indicate a much larger error and were not used in the final evaluation of the standard potential.

A second method of extrapolation which will be described in a future communication dealing with 82% dioxane–water mixtures depends on a previous knowledge of the ionization constant of hydrochloric acid in the mixture. In Fig. 1, the dashed line represents a suitable function computed from the electromotive forces and a value of 0.0077 for the ionization constant of the acid, determined by Owen and Waters in this Laboratory. This extrapolates to the value previously obtained. Our experience indicates that the first method is the more satisfactory in these

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[8] Åkerlöf and Short, THIS JOURNAL, **58**, 1241 (1936).

[9] Harned and Calmon, *ibid.*, **60**, 334 (1938).

TABLE III

VALUES OF THE EXTRAPOLATION FUNCTION, $E' - E_{Ex}$ AT 10, 25, 45°

m	t....10°	25°	45°
0.03203	0.08961	0.06372	0.02720
.01927	.08984	.06400	.02746
.009612	.09003	.06399	.02727
.006950	.08972	.06391	.02704
.005188	.08970	.06389	.02708
.003292	.08965	.06393	.02718
.003164	.08970	.06390	.02699
.002366	.08970	.06400	.02709
.001043	(.0900)	(.0634)	(.0265)
.001001	(.0892)	(.0632)	(.0255)
.000815	(.0899)	(.0632)	(.0274)
E_0' (m = 0)	.08970	.06395	.02705

solutions where D equals approximately 20 and where the actual ionization in dilute solutions is high ($\alpha > 0.9$). In media of dielectric constant of 10 (82% dioxane), the second method seems to be more suitable than the one which employs the extended term theory since values of the ionization constant are known, and since the electrolyte is considerably weaker ($K \sim 0.0002$). Also in these solutions values of "a" computed by Bjerrum's theory are more reliable than in those of high dielectric constant.

In Table IV, the standard potentials at all temperatures are given. These results may be expressed by the equation

$$E_0' = 0.06395 - 17.67 \times 10^{-4}(t - 25) - 3.70 \times 10^{-6}(t - 25)^2 \quad (6)$$

The deviations between the observed values and those computed by this equation are given in parentheses immediately following the result. They are in hundredths millivolt and are positive when the calculated is greater than the observed value.

TABLE IV

STANDARD POTENTIAL OF THE CELL

H_2 | HCl (m), DIOXANE (70%), H_2O | AgCl–Ag

t	E_0'	t	E_0'
0	0.10584 (−3)	30	0.05500 (+3)
5	.09784 (−3)	35	.04587 (+4)
10	.08970 (−8)	40	.03661 (+1)
15	.08123 (+2)	45	.02705 (+8)
20	.07267 (+2)	50	.01746 (+1)
25	.06395 (+0)		

Summary

1. Electromotive forces of the cells

H_2 | HCl (m), dioxane (70%), H_2O | AgCl – Ag

have been obtained at 0.0008, 0.001, 0.002 and 0.003 M from 0 to 50° at 5° intervals.

2. From these and Harned and Morrison's results from 0.003 to 0.02 M, the standard potential of the cell has been evaluated.

NEW HAVEN, CONN. RECEIVED JUNE 21, 1938

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

The Thermodynamics of Hydrochloric Acid in Dioxane–Water Mixtures from Electromotive Force Measurements. VII. Properties of the 70% Dioxane Mixtures

BY HERBERT S. HARNED, JOHN G. DONELSON AND CALVIN CALMON

Two earlier communications[1,2] contain electromotive forces of the cells

H_2 | HCl (m), dioxane (70%), H_2O | AgCl–Ag

at fourteen concentrations between 0.0008 and 0.2 M, and at temperatures from 0 to 50°. From these, the standard potentials of the cells have been computed throughout this temperature range.[2] To complete this study, measurements have been made at seven concentrations between 0.1 and 1.5 M. From the combined data, the activity coefficient, the relative partial molal heat content, and heat capacity of the acid have been computed. This completes the first comprehensive study of these properties of an electrolyte in a medium of dielectric constant of approximately 20.

Experimental Results

The results obtained from 0 to 50° at 5° intervals have been expressed by the equation

$$E = E_{25} + a(t - 25) + b(t - 25)^2 \quad (1)$$

The values of E_{25}, and the constants a and b are given in Table I. The fifth column of the table gives the maximum deviations in millivolts of the observed results from those calculated, and the last column contains the mean deviations.

These data were combined with those of Harned and Morrison[1] and Harned and Calmon[2] and

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[1] Harned and Morrison, THIS JOURNAL, **58**, 1908 (1936).

[2] Harned and Calmon, *ibid.*, **60**, 2130 (1938).