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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

The Thermodynamics of Aqueous Hydrochloric Acid Solutions from Electromotive Force Measurements

BY HERBERT S. HARNED AND RUSSELL W. EHLERS

In a previous communication[1] which was devoted to the accurate determination of the dissociation constant of acetic acid from 0 to 35° by measurements of suitable cells, it was necessary for us to determine the normal potential of the silver–silver chloride electrode throughout this temperature range from electromotive forces of the cell

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

More recently, these measurements have been extended to 60°, and throughout a very much greater concentration range. These results have been employed to compute activity coefficients, partial heat contents and partial specific heats. By virtue of the fact that the above cell has been shown[2] by many investigations to be one of the most accurately measurable and reproducible, it will serve particularly well to test to what extent the heat data may be determined from measurements of this kind.

Electromotive Forces of the Cells

$$H_2 \mid HCl(m) \mid AgCl \mid Ag$$

Since the materials, preparation of electrodes, accuracy of analysis and technique of the measurements were described in our earlier contribution, further comments are unnecessary. Suffice it to say that all solutions were air free and that a vacuum technique was employed. A given cell was never measured over the entire temperature range. Four series of results were made. The first was from 0 to 20°; the second from 15 to 35°; the third from 35 to 60°; and the fourth from 45 to 60°. As new solutions were prepared for measurements from 35 to 60°, the two series of results at 35° serve as an excellent means of checking the reproducibility of the method. The temperature control was within ±0.01°

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(1) Harned and Ehlers, THIS JOURNAL, **54**, 1350 (1932); **55**, 652 (1933).

(2) Ellis, *ibid.*, **38**, 737 (1916); Noyes and Ellis, *ibid.*, **39**, 2532 (1917); Linhart, *ibid.*, **39**, 2601 (1917); **41**, 1175 (1919); Scatchard, *ibid.*, **47**, 641 (1925); Nonhebel, *Phil. Mag.*, [7] **2**, 1085 (1926); Güntelberg, *Z. physik. Chem.*, **123**, 199 (1926); Randall and Young, THIS JOURNAL, **50**, 989 (1928); Carmody, *ibid.*, **54**, 183 (1932).

from 0 to 40°, and from 45 to 60° the variation was less than ±0.03°. All the electromotive forces are calculated for one atmosphere pressure of hydrogen.

The electromotive forces which we have employed for the computations are contained in three tables. The results from 0 to 35° at low acid concentrations are contained in the first table[3] of our earlier communication. The more recent measurements from 35 to 60° at lower acid concentrations are given in Table I, while those of higher acid concentrations from 0 to 60° are compiled in Table II.

TABLE I

ELECTROMOTIVE FORCE OF THE CELL

H_2 | HCl(m) | AgCl | Ag, FROM 35 TO 60°

m	E_{35}	E_{40}	E_{45}	E_{50}	E_{55}	E_{60}
0.004153		0.51219	0.51323			0.51557
.004931				0.50459	0.50526	.50585
.005022				.50315	.50421	.50471
.005146		.50047	.50139	.50218	.50283	.50338
.005734	0.49405		.49568			
.005829	.49321	.49416	.49496	.49572		
.005900	.49244	.49333	.49415	.49487	.49534	.49575
.006237	.48975	.49062	.49130	.49193	.49243	.49277
.006347	.48883	.48995	.49055	.49104		
.006748	.48546	.48622				
.006794			.48670		.48766	.48794
.006862	.48472	.48547	.48612	.48699	.48722	
.006864	.48487	.48559	.48628	.48684	.48725	.48749
.007072	.48323	.48400	.48464	.48518	.48562	.48578
.007242	.48209	.48282	.48343	.48391	.48429	.48454
.007302	.48144		.48281	.48324	.48368	
.007697	.47887	.47956	.48007	.48053	.48089	.48106
.007870	.47775	.47839	.47891	.47937	.47966	.47984
.008033		.47730	.47780	.47825	.47854	.47864
.008198	.47590	.47664	.47715	.47752	.47768	.47784
.008199	.47579	.47646	.47693	.47734	.47754	.47760
.008496	.47389	.47451	.47499	.47537	.47564	.47560
.008523			.47476		.47530	
.008948	.47125	.47182	.47228	.47261	.47281	.47286
.009143	.46998		.47102	.47133	.47158	.47166
.009379	.46878	.46934	.46970	.46996	.47011	.47014
.009626	.46762	.46814	.46859		.46991	.46912
.009744	.46696	.46747	.46790	.46812	.46829	.46825
.009754				.46805	.46819	.46819
.010043	.46540	.46589	.46621	.46643	.46651	.46650
.010387	.48381	.46428	.46453	.46475	.46477	.46478
.010448	.46344	.46388	.46430	.46441	.46448	.46452
.010524	.46303	.46348	.46378	.46399	.46408	.46490
.011247	.45963	.46002	.46030	.46044	.46046	.46036

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[3] The last result on the right side of this table at 0.05314 M is erroneous due to a typographical oversight on our part and should be eliminated.

TABLE I (*Concluded*)

m	E_{35}	E_{40}	E_{45}	E_{50}	E_{55}	E_{60}
0.012486		0.45480	0.45496	0.45498	0.45481	0.45472
.013605		.45033	.45041	.45038	.45026	.44999
.014924		.44542	.44551	.44543	.44525	.44488
.016169		.44144	.44139	.44124	.44098	.44059
.017456		.43754	.43741	.43720	.43684	.43644
.018139	.43552	.43554	.43544	.43526	.43476	.43421
.019506		.43171	.43161	.43127	.43091	.43030
.02558	.41822	.41798	.41765	.41717	.41653	.41574
.03524	.40219	.40171	.40107	.40036	.39949	.39847
.04902	.38577	.38506	.38415	.38320	.38194	.38065
.05254	.38232	.38153	.38063	.37752	.37843	.37711
.06569	.37132	.37025	.36922	.36793	.36652	
.07040				.36442	.36291	.36136
.07336		.36462	.36343	.36247		
.08092	.36080	.35971	.35849	.35716	.35551	.35382
.08967	.35582	.35461	.35328	.35187	.35012	.34847
.09828	.35118	.34994	.34859		.34526	.34350
.10909	.34582	.34446	.34303	.34150	.33956	.33773

Evaluation of the Normal Electrode Potential, E_0, of the Silver–Silver Chloride Electrode.—For the purpose of obtaining results at convenient concentrations, the following procedure was adopted. The equation for the cell may be written

$$E + 2k \log m = E_0 - 2k \log \gamma \qquad (1)$$

where E is the measured electromotive force of the cell at a molal concentration m, E_0 the normal potential, γ the activity coefficient of the acid at a concentration m, and k equals 2.3026 RT/NF. The left side of this equation was plotted against $m^{1/2}$, and from this very sensitive family of curves the electromotive forces from 35 to 60° were obtained at round concentrations. Those obtained by the same method from 0 to 35° inclusive are given in the second table of our earlier contribution.[4] Hitchcock's[5] method of extrapolation was employed. In dilute solutions, the equation

$$\log \gamma = -um^{1/2} + bm \qquad (2)$$

expresses accurately the variation of log γ with m at constant temperature. u is the constant of the Debye and Hückel theory. Combining equations (1) and (2), we obtain

$$E + 2k \log m - 2kum^{1/2} = E_0 - 2kbm \qquad (3)$$

The left side of this equation was then plotted against m. These graphs may be easily extrapolated to zero m, at which value the ordinate readings give E_0. Wyman's values of the dielectric constant of water calculated from the formula

$$D = 78.54[1 - 0.00460\,(t - 25) + 0.0000088\,(t - 25)^2] \qquad (4)$$

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[4] Harned and Ehlers, THIS JOURNAL, **54**, 1350 (1932).

[5] Hitchcock, *ibid.*, **50**, 2076 (1928).

TABLE II

ELECTROMOTIVE FORCES OF THE CELLS, H_2 | HCl (m) | AgCl | Ag, FROM 0–60° AT HIGHER CONCENTRATIONS

m	0°	5°	10°	15°	20°	25°	30°	35°	40°	45°	50°	55°	60°
0.10266	0.35400	0.35379	0.35336	0.35280	0.35211	0.35130							
.13096									0.33531	0.33391	0.33203	0.33015	0.32923
.13810					.33796	.33688	0.33564	0.33426	.33277	.33112	.32944	.32745	.32548
.20207									.31332	.31138	.30944	.30727	.30508
.20227					.31958	.31821	.31671	.31503	.31326	.31134	.30941	.30723	.30499
.20301	.32330	.32254	.32162	.32057	.31935	.31803							
.31887	.30239	.30131	.30002	.29862	.29714	.29545							
.32623									.28834	.28606	.28379	.28130	.27878
.33187					.29521	.29347	.29160	.28959	.28744	.28518	.28292	.28037	.27778
.39638					.28626	.28439	.28237	.28024	.27798	.27558	.27315	.27054	.26781
.41638									.27526	.27281	.27037	.26769	.26498
.48968	.28193	.28055	.27896	.27727	.27535	.27342							
.58757									.25631	.25364	.25098	.24808	.24512
.60585					.26422	.26204	.25968	.25728	.25476	.25210	.24944	.24648	.24320
.67023	.26616	.26454	.26270	.26076	.25867	.25644							
.79832	.25696	.25520	.25324	.25112	.24882	.24650							
.82882									.23640	.23352	.23061	.22750	.22431
.83640					.24627	.24387	.24130	.23865	.23585	.23295	.23005	.22688	.22369
.96991	.24623	.24429	.24218	.23998	.23756	.23513							
.98615					.23661	.23410	.23147	.22869	.22577	.22282	.21977	.21653	.21326
1.2045	.23362	.23148	.22924	.22691	.22432	.22174							
1.2310					.22295	.22031	.21754	.21436	.21157	.20851	.20535	.20202	.19858
1.3938					.21494	.21220	.20932	.20631	.20316	.20000	.19675	.19339	.18985
1.4407	.22253	.22029	.21787	.21536	.21265	.20992							
1.5553	.21752	.21522	.21274	.21014	.20741								
1.5872					.20604	.20328	.20033	.19721	.19399	.19072	.18741	.18389	.18016
1.7196	.21084	.20847	.20590	.20324	.20040								
1.7983					.19721	.19427	.19123	.18805	.18476	.18140	.17801	.17745	.17062
1.9753	.20096	.19846	.19582	.19303	.19012								
1.9789					.19015	.18716	.18405	.18082	.17746	.17401	.17057	.16686	.16284
2.3802	.18684	.18427	.18157	.17858	.17552	.17245							
2.9566	.16838	.16565	.16267	.15965	.15645	.15324							
4.0875	.13594	.13292	.12972	.12648	.12307	.11968							

which he used to represent his results from 0 to 100° were used. We have employed this series[6] of results both because of their consistency and since in an extended series of measurements of the dielectric constants of many solvents and their mixtures, Åkerlöf[7] has checked Wyman's results very closely. The values of u calculated therefrom are given in the second column of Table VII. The values of E_0 determined in this manner are given in the second column of Table III. They differ a few hundredths of a millivolt in some cases from 0 to 30° from our earlier values. This is due to the fact that we had previously used 0.5 for u throughout this temperature range in the former computation. The value at 35° has been recomputed.

In order to have a standard series of values of E_0 to be used for further computation, we have resorted to the method of least squares as a means of obtaining the constants of the equation

$$E_0 = E_{0(25)} + a(t - 25) + b(t - 25)^2 + c(t - 25)^3 \qquad (5)$$

Usually an equation of this kind involving the first two constants is sufficient. In the present instance, we have employed both a three and a four constant equation for the purpose of comparing their accuracy in reproducing the observed values. As a result, the following two equations were obtained:

$$E_0 = 0.22237 - 639.64 \times 10^{-6}(t - 25) - 3.181 \times 10^{-6}(t - 25)^2 \qquad (6)$$

and

$$E_0 = 0.22239 - 645.52 \times 10^{-6}(t - 25) - 3.284 \times 10^{-6}(t - 25)^2 + 9.948 \times 10^{-9}(t - 25)^3 \qquad (7)$$

Table III contains the observed and calculated values of E_0. The third and fifth columns contain the values calculated by equations (6)

TABLE III

CALCULATED AND OBSERVED VALUES OF E_0

t, °C.	E_0 (obs.), volt	E_0 (calcd.), volt, Eq. 6	Δ (mv.), Eq. 6	E_0 (calcd.), volt, Eq. 7	Δ (mv.), Eq. 7
0	0.23634	0.23638	+0.04	0.23632	−0.02
5	.23392	.23389	− .03	.23391	− .01
10	.23126	.23124	− .02	.23130	+ .04
15	.22847	.22845	− .02	.22851	+ .04
20	.22551	.22549	− .02	.22554	+ .04
25	.22239	.22237	− .02	.22239	.00
30	.21912	.21909	+ .03	.21908	− .04
35	.21563	.21565	+ .02	.21561	− .02
40	.21200	.21206	+ .06	.21200	.00
45	.20821	.20831	+ .10	.20825	+ .04
50	.20437	.20440	+ .03	.20436	− .01
55	.20035	.20032	− .03	.20033	− .02
60	.19620	.19608	− .12	.19620	.00

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(6) Wyman, *Phys. Rev.*, **35**, 623 (1930).

(7) Åkerlöf, THIS JOURNAL, **54**, 4125 (1932).

and (7), respectively. The fourth and sixth columns contain the differences in millivolts between the calculated and observed values.

It is to be noted that the agreement is good in both cases and that the three-constant equation reproduces the results more accurately, particularly through the temperature range of from 40 to 60°.

The first step in the subsequent treatment of the results was to construct a table of electromotive forces at round concentrations from the very carefully drawn large-scale graphs of the function, $E + 2k \log m - 2kum^{1/2}$.

The next step was to express the results at these concentrations by the equation

$$E = E_{25} + a(t - 25) + b(t - 25)^2 \tag{8}$$

and also

$$E = E_{25} + a(t - 25) + b(t - 25)^2 + c(t - 25)^3 \tag{9}$$

Since results were available at thirteen temperatures, the method of least squares was employed to evaluate the constants. This we regard as more accurate than a graphical method such as the one employed by Harned and Nims.[8] The constants of these equations are given in Table IV. Both equations represent the smoothed electromotive forces at the concentrations given to within ±0.05 mv. from 0 to 40°. From 40 to 60° the three-constant equation is better and within this limit of accuracy.

TABLE IV

CONSTANTS OF EQUATIONS (8) AND (9)

	I. Equation (8)			II. Equation (9)			
m	E_{25}	$a \times 10^6$	$b \times 10^6$	E_{25}	$a \times 10^6$	$b \times 10^6$	$c \times 10^9$
0.0001	0.69620	950.8	−3.166	0.69622	945.53	−3.26	8.89
.0002	.66083	832.5	−3.174	.66084	827.11	−3.27	9.37
.0005	.61421	678.2	−3.146	.61422	672.16	−3.23	8.37
.001	.57912	560.1	−3.149	.57912	554.53	−3.23	9.33
.002	.54421	444.0	−3.159	.54423	438.44	−3.26	9.67
.005	.49841	291.8	−3.075	.49843	287.00	−3.16	8.45
.01	.46416	177.9	−3.041	.46418	173.84	−3.11	7.00
.02	.43022	66.69	−2.934	.43023	64.24	−2.98	4.25
.05	.38587	− 73.93	−2.946	.38588	− 77.42	−3.01	6.05
.1	.35239	−180.5	−2.885	.35240	−181.57	−2.90	1.79
.2	.31871	−280.4	−2.789	.31874	−283.61	−2.85	5.65
.5	.27229	−414.0	−2.764	.27230	−417.05	−2.82	5.25
1	.23328	−512.1	−2.541	.23328	−517.64	−2.64	9.61
1.5	.20719	−568.7	−2.362	.20719	−572.85	−2.44	7.15
2	.18634	−610.2	−2.335	.18634	−608.72	−2.31	−2.54
3	.15184	−656.9	−1.950	.15184	−660.00	−2.34	−1.08
4	.12214	−688.0	−1.757	.12215	−670.76	−3.81	2.46

At concentrations higher than 2 *M*, equations (6) and (7) are only reliable from 0 to 25° if the above constants are employed. The experimental results at these high concentrations and temperatures above 25° are not very reliable. The results at the four lowest concentrations are extrapolated.

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[8] Harned and Nims, THIS JOURNAL, **54**, 423 (1932).

The calculated and observed results for E_0 shown in Table III illustrate this point and are typical of all the calculations.

For the determination of the temperature coefficient of electromotive force equation (9) is too sensitive at temperatures from 0 to 10°, and 50 to 60°. This is evident upon differentiation of (9), which gives the term $3c(t - 25)^2$. Thus, when t equals 60°, any error in c is multiplied by 3675. The results are not sufficiently accurate to stand such a test. On the other hand, both equations (8) and (9) give upon differentiation closely agreeing values of dE/dT through the temperature range from 10 to 45°, inclusive. At 0, 5, 50, 55 and 60°, the equation (8) yields more consistent results.

In the subsequent treatment, it will be necessary to know c, the concentration in moles per liter of solution. From the molalities and densities[9] of the solutions, the ratio c/m was computed and found to be linear with m. Thus

$$\frac{c}{m} = a_1 - b_1 m \qquad (10)$$

In Table V, the constants a and b of this equation are given at each of the temperatures in question.

TABLE V

CONSTANTS OF EQUATION (10)

Temp., °C.	a_1	b_1	Temp., °C.	a_1	b_1
0	0.9998	0.01707	35	0.9941	0.01825
5	1.0000	.01742	40	.9922	.01825
10	.9995	.01760	45	.9901	.01815
15	.9990	.01782	50	.9879	.01815
20	.9982	.01805	55	.9855	.01805
25	.9972	.01817	60	.9832	.01805
30	.9958	.01822			

The Activity Coefficient of Hydrochloric Acid in Aqueous Solutions.— Preliminary computations were made by evaluation of the activity coefficients from the normal potentials given by equation (7) and the electromotive forces at the round concentrations given by equation (9) and the constants in Table IV. In order to evaluate the apparent ionic diameter "a" of the ions, the approximate equation of Hückel[10]

$$\log \gamma = -\frac{u\sqrt{c}}{1 + A\sqrt{2c}} + Bc - \log(1 + 0.036\, m) \qquad (11)$$

was first employed. The constants A and B were then evaluated at each temperature by substituting the observed activity coefficients at 0.1 M and 1 M and the values of c in equation (11) and then by solving the two equations formed in this manner for A and B. The apparent ionic di-

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[9] "International Critical Constant Tables," McGraw-Hill Book Co., Inc., New York, 1928, Vol. III, p. 54.

[10] Hückel, *Physik. Z.*, **26**, 93 (1925).

ameter, "a," in Ångström units was obtained from these values of A by the equation

$$A = K'a \tag{12}$$

The values of K' were computed from the theoretical equations and Wyman's values of the dielectric constant and are given in Table VII.

A striking result was immediately obtained. From this first approximation, the values of "a" actually found were, 4.00, 4.10, 4.20, 4.23, 4.23, 4.22, 4.21, 4.21, 4.20, 4.22, 4.26, 4.31, 4.40, Ångström units at 0, 5, 10, 15, 20, 25, 30, 35, 40, 50, 55 and 60°, respectively. We have considerable confidence in this result and can unquestionably regard "a" as constant over this range of temperature.

By equation (11) the activity coefficient could be computed to within ±1.5 in the third decimal place from 0 to 1 M. At lower concentrations, however, a definite trend was noticed in the deviations between the calculated and observed results which could be accounted for by the Gronwall, La Mer and Sandved[11] extension of the Debye and Hückel theory. Consequently, in the subsequent computation the extended terms have been employed as well as a constant value of "a" of 4.30 Å. which takes into account the slight modification of "a" due to the extended terms.

Consequently, in order to compute the activity coefficient from 0 to 60° and from 0 to 4 M, we have employed the equation

$$\log \gamma = -\frac{u\sqrt{c}}{1 + A\sqrt{2c}} + C\left(\frac{1}{a}\right)^3 10^3\left[\frac{1}{2}X_3(x) - 2Y_3(x)\right] + K\left(\frac{1}{a}\right)^5 10^5\left[\frac{1}{2}X_5(x) - 4Y_5(x)\right] - \log(1 + 0.036\, m) + Bc + Dc^2 \tag{13}$$

The second and third terms on the right represent the terms of the Gronwall, La Mer and Sandved extension of the theory. C equals $\left(\frac{\epsilon^2}{kTD}\right)^3 \frac{1}{2.3026}$, K equals $\left(\frac{\epsilon^2}{kTD}\right)^5 \frac{1}{2.3026}$ and "a" is in Ångströms. The values of C and K computed from Wyman's dielectric constants are given in Table VII. The bracketed terms were obtained from Table V in the contribution of Gronwall, La Mer and Sandved in which x equals $A\sqrt{2c}$ and "a" = 4.30 Å. The values of the extended terms at 0, 25 and 60° are given in Table VI.

TABLE VI

VALUES OF EXTENDED TERMS OF THE DEBYE-HÜCKEL THEORY, a = 4.3 Å.

m	0°	25°	60°	m	0°	25°	60°
0.001	−0.00009	−0.00010	−0.00011	0.2	−0.00067	−0.00072	−0.00085
.002	− .00015	− .00018	− .00019	.5	− .00045	− .00049	− .00057
.005	− .00027	− .00030	− .00036	1	− .00027	− .00028	− .00032
.01	− .00041	− .00045	− .00053	1.5	− .00017	− .00019	− .00020
.02	− .00055	− .00061	− .00072	2	− .00012	− .00013	− .00015
.05	− .00071	− .00077	− .00091	3	− .00007	− .00007	− .00008
.1	− .00075	− .00080	− .00094	4	− .00004	− .00005	− .00006

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(11) Gronwall, La Mer and Sandved, *Physik. Z.*, **29**, 358 (1928).

Values at the other temperatures may be obtained from these by interpolation.

Since the equation for the cell is

$$\frac{(E - E_0)N\mathbf{F}}{4.6052RT} + \log m + \log \gamma = 0 \tag{14}$$

we may substitute for log γ its value given by equation (13) and obtain

$$\left[\frac{(E - E_0)N\mathbf{F}}{4.6052RT} + \log m - \frac{u\sqrt{c}}{1 + A\sqrt{2c}} + Z - \log(1 + 0.036\,m)\right] = -Bc - Dc^2 \tag{15}$$

where Z represents the total contribution of the extended terms. The left side of this equation was evaluated from the electromotive forces and standard potentials, and by taking "a" to be 4.3 Å. This function was then plotted against c and was found to be not quite linear so that the extra term Dc^2 was added. From the plots at the thirteen temperatures, B and D were evaluated, and it was found that these constants were given by the linear equations

$$B = 0.1390 - 0.000392t \tag{16}$$

$$D = 0.0070 - 0.000033t \tag{17}$$

Upon substitution of these values of B and D in equation (13), values of γ may be obtained very accurately throughout the entire temperature range, and from 0 to 4 M concentration at the lower temperatures and from 0 to 2 M at temperatures from 30 to 60°. The probable error is estimated to be less than ±5 in the fourth decimal place of activity coefficient.

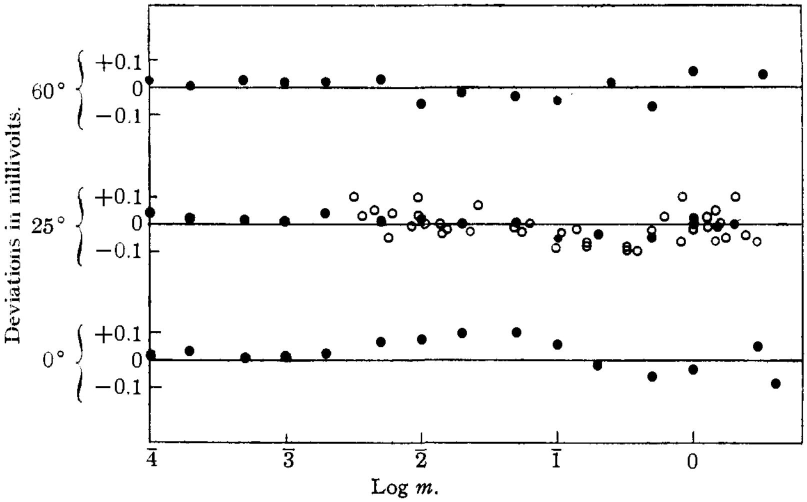

Fig. 1.—Deviations of observed electromotive forces from those calculated by equations (13), (16) and (17).

In Fig. 1 we have illustrated the deviations of the experimental results from those obtained from our equations (13), (16) and (17), by calculating for each E the value of the normal potential, E_0. Only deviations at 0, 25 and 60° are shown. At 25° the circles represent the deviations computed from the original electromotive forces in Tables I and II. The inked in circles represent deviations obtained from the electromotive forces computed by equation (9). The results at 25 and 60° are typical of the results at all temperatures from 10 to 60°, inclusive. The results at 0 and 5° indicate a slightly greater deviation in the concentration range of 0.005 to 0.1 *M;* 90% of the values derived from the electromotive forces obtainable from equation (9) show deviations of less than ±0.04 mv.

TABLE VII

CONSTANTS REQUIRED FOR CALCULATIONS

t, °C.	u	K'	C	K	U'	W
0	0.487	0.2295	0.1434	0.0685	433	9.6
5	.490	.2300	.1452	.0700	479	10.4
10	.494	.2305	.1474	.0717	537	11.2
15	.498	.2311	.1498	.0737	594	11.9
20	.502	.2317	.1523	.0757	654	12.7
25	.506	.2324	.1551	.0781	717	13.4
30	.511	.2332	.1581	.0806	785	14.0
35	.516	.2340	.1613	.0834	856	14.7
40	.522	.2348	.1649	.0864	931	15.4
45	.528	.2357	.1685	.0897	1009	16.0
50	.534	.2366	.1725	.0934	1090	16.7
55	.540	.2375	.1766	.0969	1171	17.2
60	.547	.2386	.1812	.1011	1261	17.8

The Relative Partial Molal Heat Content.—The relative partial free energy is given by

$$\overline{F} - \overline{F}_0 = 2RT \ln \gamma + 2RT \ln m \tag{18}$$

By substituting the value of ln γ derivable from equation (13) in the Gibbs–Helmholtz equation and performing the differentiation, we obtain for the relative partial molal heat content of a univalent electrolyte

$$\overline{H} - \overline{H}_0 = -\frac{3}{2}\frac{c^{1/2}}{D^{3/2}\,T^{1/2}}\frac{\omega}{1 + A\sqrt{2c}}\left[1 + \frac{T\mathrm{d}D}{D\mathrm{d}T} - \frac{1}{3}\frac{T}{c}\frac{\mathrm{d}c}{\mathrm{d}T}\right] - \frac{\omega}{(1 + A\sqrt{2c})^2}$$
$$\frac{\sqrt{2}\,T^{1/2}}{D^{3/2}}\left[c\frac{\mathrm{d}A}{\mathrm{d}T} + \frac{A}{2}\frac{\mathrm{d}c}{\mathrm{d}T}\right] - 4.6052 \times RT^2\left[(B + 2Dc)\frac{\mathrm{d}c}{\mathrm{d}T} + c\left(\frac{\mathrm{d}B}{\mathrm{d}T} + c\frac{\mathrm{d}D}{\mathrm{d}T}\right)\right] \tag{19}$$

if we neglect the term containing the temperature coefficient of Z, which for a univalent electrolyte in water causes a maximum contribution to $\overline{H} - \overline{H}_0$ (at 0.1 M and 60°) of 3 cal. if "a" is 4.3 Å. ω is given by

$$\omega = 2\left(\frac{\pi^{1/2}\,\epsilon^3\,N^{3/2}\,2^{1/2}}{k^{1/2}1000^{1/2}}\right) \tag{20}$$

The first member on the right of equation (19) reduces to

$$\overline{H} - \overline{H}_0 = \frac{U'\sqrt{c}}{1 + A\sqrt{2c}} \tag{21}$$

at constant temperature, where U' represents the slope of the Debye and Hückel limiting law. From Wyman's dielectric constants, and the values 4.774×10^{-10}, 6.061×10^{23}, 1.372×10^{-16} for ϵ, N and k, respectively, the values of U' given in the sixth column of Table VII were obtained. This includes the third term in the bracket involving d ln c/d ln T which was shown by Scatchard and Gatty to contribute to the limiting slope.[12]

The first term on the right of equation (19) is always positive, while the contribution due to the second term is negative in the present instance since $c\frac{\mathrm{d}A}{\mathrm{d}T} > \frac{A}{2}\frac{\mathrm{d}c}{\mathrm{d}T}$ and $\frac{\mathrm{d}A}{\mathrm{d}T}$ is positive. The contribution of the third term to $\overline{H} - \overline{H}_0$ is positive in the case of hydrochloric acid since $\mathrm{d}B/\mathrm{d}T$ and $\mathrm{d}D/\mathrm{d}T$ are both negative and $\mathrm{d}c/\mathrm{d}T$ is negative except at 0 and 5° at lower concentrations. This is opposite to the behavior of many electrolytes such as potassium chloride, sodium chloride and hydroxide in which it is known that $\mathrm{d}B/\mathrm{d}T$ and $\mathrm{d}D/\mathrm{d}T$ are positive. It is interesting to note that the third term contributes many times the amount of the other terms in concentrated solutions. Thus at 25° and 4 M, the first, second and third terms contribute 371, −84 and 1674 cal. to $\overline{H} - \overline{H}_0$, respectively. When $\mathrm{d}B/\mathrm{d}T$ and $\mathrm{d}D/\mathrm{d}T$ are positive, $\overline{H} - \overline{H}_0$ is known to pass through a maximum which is the case for both sodium chloride and hydroxide solutions at many temperatures.

By employing equation (19), $\overline{H} - \overline{H}_0$ was evaluated at concentrations from 0.005 to 3 M. For the sake of brevity, a table of these results is not given but instead we have expressed $\overline{H} - \overline{H}_0$ as a function of the temperature at constant concentration by the power series

$$\overline{H} - \overline{H}_0 = (\overline{H} - \overline{H}_0)_0 + \alpha t + \beta t^2 \qquad (22)$$

Values of $(\overline{H} - \overline{H}_0)_0$, α and β at the designated concentrations are given in Table VIII. These express within ±5 calories the values obtained by equation (19). The result at 4 M cannot be relied on to the extent of the others since it was obtained from fewer experimental observations and represents an extrapolation at the higher temperatures.

TABLE VIII

CONSTANTS OF EQUATION (22)

m	$(\overline{H} - \overline{H}_0)_0$	α	β	m	$(\overline{H} - \overline{H}_0)_0$	α	β
0.005	28	0.70	0.003	0.5	272	4.70	0.011
.01	39	1.00	.003	1	427	6.80	.015
.02	52	1.30	.004	1.5	615	8.20	.019
.05	82	1.85	.006	2	791	10.00	.023
.1	113	2.50	.008	3	1175	12.45	.031
.2	159	3.20	.009	4	1604	14.70	.040

In Fig. 2 we have represented by circles the values of $\overline{H} - \overline{H}_0$ at 0, 25, and 60° computed in the above manner. As a check of this calcu-

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(12) Scatchard, THIS JOURNAL, **53**, 2037 (1931); Gatty, *Phil. Mag.*, [7] **11**, 1082 (1931); see also Bjerrum, *Z. physik. Chem.*, **119**, 145 (1926); Rossini, *Bur. of Standards J. of Research*, **6**, No. 305 (1931).

lation, we have also computed $\overline{H} - \overline{H}_0$ from the electromotive forces given by equation (8) upon substituting the values of a and b given in Table IV. To this end we first computed the partial molal heat content relative to the 0.005 M solution by the Gibbs–Helmholtz equation in the form

$$\overline{H} - \overline{H}_{0.005} = \overline{F} - \overline{F}_{0.005} - NFT\frac{\mathrm{d}(E - E_{0.005})}{\mathrm{d}T} \qquad (23)$$

Then from the values of $\overline{H}_{0.005} - \overline{H}_0$ determined by the first method $\overline{H} - \overline{H}_0$ was computed. This affords a comparison of the results from 0.005 M to 4 M. The inked circles in Fig. 2 represent the values determined by this method. The maximum deviations in the results obtained

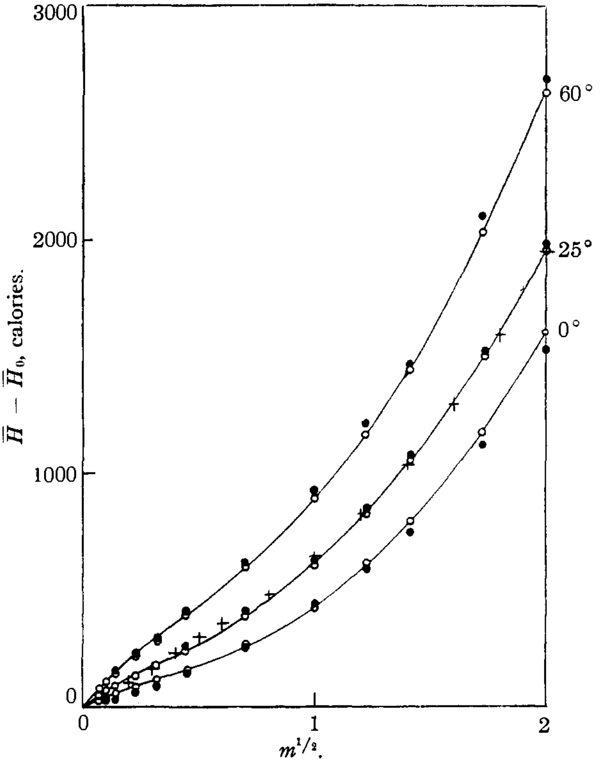

Fig. 2.—The relative partial molal heat content of hydrochloric acid in aqueous solution.

by the two methods is 50 calories. Below 2 M, where the greater accuracy is to be expected, the maximum discrepancy between the values obtained by the two methods is 30 cal. We consider this as good agreement since 0.001 mv. error in the temperature coefficient of electromotive force causes an error of 7 calories. We consider the values obtained by equation (19) to be the better throughout the entire temperature range. At temperatures in the middle range (15 to 45°), both methods of calculation of $\overline{H} - \overline{H}_0$ are good.

The best calculation of $\overline{H} - \overline{H}_0$ of hydrochloric acid at 25° from calorimetric data has recently been made by Rossini.[13] If we take our value at $m^{1/2}$ equals 0.3 as correct and change Rossini's values to meet this requirement, the crosses shown in Fig. 2 are obtained. Very close agreement is to be found throughout the entire concentration range of from $m^{1/2}$ equals 0.2 to 2. The maximum deviation occurs at $m^{1/2}$ of 0.5 and 0.6 and amounts to 30 calories. The only discrepancy occurs at 0.01 *M* and this is at a region of concentration where our method of determining this quantity should be very powerful.

The Relative Partial Molal Specific Heat.—We have not resorted to the very laborious differentiation of equation (19) with respect to temperature in order to evaluate the relative partial molal specific heat, $\overline{C}_p - \overline{C}_{p_0}$. The simple differentiation of equation (22) was used. On the other hand, the first term on the right of (19) omitting $(1 + A\sqrt{2c})$ was completely differentiated and the limiting slope of the Debye and Hückel theory given by

$$\overline{C}_p - \overline{C}_{p_0} = W\sqrt{c} \tag{24}$$

was evaluated from 0 to 60° at 5° intervals. The results are compiled in the last column of Table VII. Equation (4) was used to calculate the dielectric constant and its first and second derivations.

Differentiation of equation (22) obviously gives

$$\frac{\mathrm{d}(\overline{H} - \overline{H}_0)}{\mathrm{d}T} = \overline{C}_p - \overline{C}_{p_0} = \alpha + 2\beta t \tag{25}$$

and

$$\frac{\mathrm{d}(\overline{C}_p - \overline{C}_{p_0})}{\mathrm{d}T} = 2\beta \tag{26}$$

from which $\overline{C}_p - \overline{C}_{p_0}$ can be obtained readily by employing the constants in Table VIII.

Values of $\overline{C}_p - \overline{C}_{p_0}$ computed by equation (25) at 0, 25, and 60° are plotted against $m^{1/2}$ in Fig. 3. The straight lines represent the limiting slopes of the theory. The crosses represent recent values obtained by Gucker and Schminke,[14] which in the region of concentration of 0.25 to 2 *M* fall within a few tenths of a calorie of our results. Rossini[13] gives greater weight to results at higher concentrations and by employing a straight line function of $c^{1/2}$ obtains 10.8 for its slope. If we use our values at 1 *M* and 4 *M*, the slope of the straight line drawn through them is 9.2. Since values of $\overline{C}_p - \overline{C}_{p_0}$ are derived from the second derivative of our original electromotive forces, we consider the present agreement excellent.

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(13) Rossini, *Bur. of Standards J. of Research*, **9**, 499 (1932).

(14) Gucker and Schminke, THIS JOURNAL, **54**, 1358 (1932).

One further point requires attention. According to equation (26), two times the constants β in Table VIII gives the temperature coefficient of the relative partial molal specific heat. Since these results are derived from the third derivative of our electromotive forces with respect to temperature, they cannot be expected to be of a high order of accuracy. On the other hand, we believe that they represent a real effect.

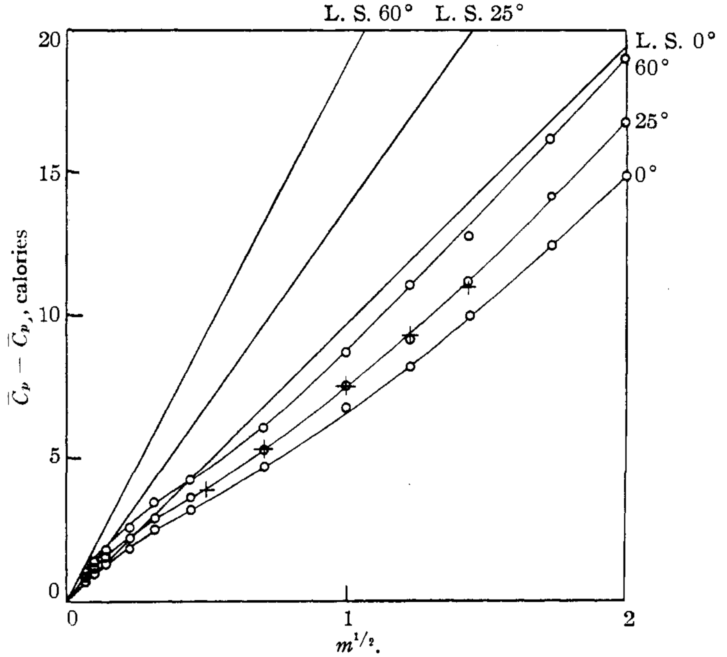

Fig. 3.—The relative partial molal specific heat of hydrochloric acid in aqueous solution.

Further evidence of this is obtained from the following consideration. Equation (8) gives the electromotive force at a concentration m as a function of t. We may readily obtain from this equation

$$E_m - E_{0.0001} = a'(t - 25) + b'(t - 25)^2 \qquad (27)$$

where a' equals $(a_m - a_{0.0001})$ and b' equals $(b_m - b_{0.0001})$. Now, the relative partial molal specific heat, $\bar{C}_p - \bar{C}_{p_0}$, is related to the free energy according to the equation

$$\bar{C}_p - \bar{C}_{p_0} = -T\,\frac{\partial^2(\bar{F} - \bar{F}_0)}{\partial T^2} \qquad (28)$$

By multiplying equation (27) by $N\mathbf{F}$, substituting in (28) and performing the differentiation, we readily obtain

$$\bar{C}_p - \bar{C}_{p_{0.0001}} = 2b'N\mathbf{F}T = 46{,}118b'T \qquad (29)$$

which upon differentiation gives

$$\frac{\mathrm{d}(C_p - C_{p_{0\cdot 0001}})}{\mathrm{d}T} = 46{,}118b' \qquad (30)$$

Thus, if it is necessary to employ a constant b in equation (8) in order to express the electromotive force as a function of the temperature, then the relative partial molal specific heat has a temperature coefficient. We know of no electromotive force data which can be expressed as a function of the temperature by the simple linear equation which omits a "b" term. The b' values as defined were first calculated from the b constants in Table IV and smoothed by plotting against $m^{1/2}$. The temperature coefficient of $(\overline{C}_{p_{0.0001}} - \overline{C}_{p_0})$ was determined from the values of the limiting slopes, W, in Table VII and found to be 0.0015. This was added to $46{,}118b'$ to give 0.005, 0.007, 0.009, 0.012, 0.014, 0.018, 0.023, 0.030, 0.037, 0.043, 0.055, 0.067, at 0.005, 0.01, 0.02, 0.05, 0.1, 0.2, 0.5, 1, 1.5, 2, 3 and 4 M, respectively. These values agree very well with those determined previously, or with 2β in Table VIII.

Summary

1. Accurate measurements of the cell $H_2 | HCl\ (m) | AgCl | Ag$ from 0 to 60 at 5° temperature intervals have been made.

2. The standard potential of the silver–silver chloride electrode from 0 to 60° has been evaluated.

3. Equations which give the electromotive forces as a function of the temperature have been obtained by the method of least squares.

4. An equation has been formed by means of which the activity coefficient of hydrochloric acid in water, γ, may be computed from 0 to 60° through the concentration range of 0 to 4 M with a very high accuracy.

5. By differentiation of this equation, the relative partial molal heat content of the acid was computed from 0 to 60° and from 0 to 4 M. Good agreement was obtained with calorimetric data.

6. From the heat content data, the relative partial molal specific heat has been computed through the wide concentration and temperature ranges under consideration. Good agreement is found with the calorimetric data.

7. The temperature coefficient of the relative partial molal specific heat has been roughly evaluated.

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