[Contribution from the Chemistry Department of Yale University]

Thermodynamics of Concentrated Aqueous Solutions of Hydrochloric Acid

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Introduction

For the calculation of arbitrary equilibria in saturated solutions of highly soluble, strong electrolytes, the approximate method suggested by one of us depends upon the use of data for the activity coefficient of some reference electrolyte in concentrated solutions. The only data available which could be used for this purpose were those of Randall and Young[1] for hydrochloric acid at 25°. However, since an extension of the solubility studies to other temperatures and also a checking of their data were highly desirable, the electromotive force of the cell H_2/HCl m/AgCl/Ag has been measured at round acid concentrations from 3 to 16 molal over the temperature range 0 to 50° in steps of ten degrees. The present study also represents a direct continuation of the measurements of Harned and Ehlers[2] for more dilute acid solutions.

Experimental Procedure

The solubility of silver chloride in hydrochloric acid solutions increases rapidly with the acid concentration. Already in 3 molal solutions a hydrogen electrode present in the neighborhood of a silver–silver chloride electrode becomes coated rapidly with a deposit of metallic silver which causes a very erratic behavior of its electromotive force. Therefore the cell employed, shown in Fig. 1, was designed to eliminate, as far as possible, the diffusion of silver to the hydrogen electrode by providing a long path normally closed by a stopcock near the silver–silver chloride electrode and opened only during the actual reading of the electromotive force of the cell. To prevent erratic behavior of the silver–silver chloride electrode due to complete exhaustion of silver chloride on its surface, its cell compartment was made relatively small.

The vapor pressure of some of the solutions employed reached or exceeded at the higher measuring temperatures half an atmosphere. The saturators employed were, however, of fully sufficient capacity to maintain saturation of the vapor from the solution. This is evidenced by the fact that identical readings could be obtained when the cells were returned to the initial temperature at the completion of a run. All cells were carefully freed from pinholes in the glass found by evacuating and checking with a vacuum leak tester. Before each run all stopcocks were cleaned, dried and regreased.

The hydrogen electrodes were prepared in the usual manner by depositing platinum black from a strongly acidified solution of platinum chloride on platinum foil of about 2 sq. cm. surface using 0.5 ampere for thirty seconds. After each run these electrodes were treated with hot, dilute nitric acid, washed and burned clean in an oxygen flame. Silver–silver chloride electrodes were obtained, also as usual, by coating small platinum spirals with silver oxide, heating to 450° and electrolyzing in hydrochloric acid. In the case of electrodes for the lower acid concentrations the current used was 10 milliamperes for one hour while those for very concentrated solutions were plated employing 20 milliamperes for two hours.

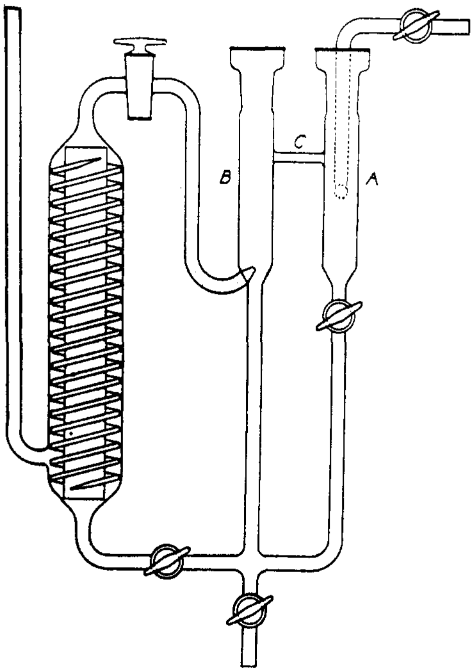

Fig. 1.—Apparatus.

The electromotive force of the cells was measured with an Eppley–Feussner type potentiometer thermostated in oil at the same temperature as that used by the Bureau of Standards for its calibration. The working standard cells were also thermostated and at frequent intervals checked against the laboratory standard set certified by the Bureau of Standards and permanently kept immersed in oil at 30.00 ± 0.01°. Connection between the cells to be measured and the potentiometer was obtained by a heavily insulated cable and a number of individual, completely enclosed mercury switches.

The temperature of the cell thermostat was controlled by a mercury regulator having a sensitivity of about 0.01°. The thermometer employed was calibrated against a Bureau of Standards certified platinum resistance thermometer using a Mueller resistance bridge. After it had

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(*) This paper contains material from a Dissertation presented to the Graduate School of Yale University by John W. Teare in partial fulfilment of the requirements of the Degree of Doctor of Philosophy, June, 1937.

(1) Randall and Young, This Journal, **50**, 989 (1928).

(2) Harned and Ehlers, *ibid.*, **55**, 2179 (1933).

been used for some time the readings of the thermometer were rechecked, but visible changes could not be detected.

Since the electromotive force of the electrodes employed is sensitive to traces of oxygen present, all stock solutions except the 16 molal acid were swept, before they were analyzed, over a period of three to four days with a steady stream of hydrogen. The stock solutions were stored in tightly stoppered five gallon (20 liter) Pyrex bottles provided with in and outlet for hydrogen and outlet for the solution. Small mercury manometers were inserted in the hydrogen outlet tube since a slight, constant excess gas pressure was advisable. The solution outlets from the various bottles were brought together in a single line along a straight rod directly above the balance used in making up the solutions to be measured. The balance was mounted on a rolling platform guided by a track. By moving the platform, the inlet of a flask suspended from the outer end of one of the balance arms could be brought directly under any one of the outlets from the solution bottles. To avoid absorption of air in the solutions during the weighing procedure a separate inlet was provided for a slow stream of nitrogen which filled the flask at the beginning of the weighing and maintained an atmosphere of nitrogen throughout the operation. The clearance between the gas and solution delivery tubes and the inner walls of the inlets of the weighing flasks was about one-sixteenth of an inch (1.6 mm.) which was sufficient to permit the free movement of the balance. Before entering the solution flask the nitrogen passed over copper heated to about 700° in a quartz tube to remove traces of oxygen and then through a large solution saturator. In view of the fact that nitrogen and air have practically the same density, the differences in the vacuum corrections are negligible. The tube furnace for the purification of the nitrogen was mounted on the balance platform and shielded by a heavy panel of transite.

The sensitivity of the balance employed was about 0.02 g. In the calculation of the gravimetric analyses of the stock solutions and for all weighings of solutions, the proper vacuum corrections were applied and the International atomic weights of 1936 were used. The transfer of the finished solutions from the weighing flask, which was equipped with a delivery tube, was accomplished by first evacuating the cells, then washing the cells three times with the solution and finally filling completely. After placing the cells in the thermostat and adjusting the hydrogen flow, they were allowed to come to equilibrium for a period of ten hours before the first electromotive force readings were taken. Cells having erratic readings or those showing a drift of more than a tenth of a millivolt were discarded and a new solution was made up and measured. All cells were run in duplicate or in triplicate and measurements were taken at ten degree intervals from 0 to 50°.

Since the increase in the solubility of silver chloride with the acid concentration may have some influence on the electromotive force measured, a number of solubility determinations were carried out at 25°. Silver chloride, precipitated with hydrochloric acid, washed and dried at 150° for two days, was used as solid phase. About 200 cc. of the acid of the desired concentration was made up in small Pyrex bottles fitted with carefully ground stoppers. The bottles were rotated at a speed of about 10 r. p. m. over a period of twenty hours in a water thermostat regulated at 25° with a precision of 0.02° and controlled with the same accuracy. The samples withdrawn weighed about 150 g. and they were evaporated down to dryness in small Erlenmeyer flasks provided with ground stoppers. The residue of pure silver chloride was faintly yellow in color.

The hydrochloric acid used for our measurements was an especially high grade analytical reagent and further purification was not attempted. Water was obtained from a Barnstead conductivity still. Tank hydrogen was purified by passing it over copper heated in a quartz tube to 750°. Silver oxide, prepared by precipitating from a hot solution of analytical reagent silver nitrate with the equivalent amount of sodium hydroxide, was washed until free of all impurities.

Experimental Results

The mean values of the electromotive force data corrected to one atmosphere partial hydrogen pressure are given in Table I. Table II contains the vapor pressures of the acid solutions

TABLE I

AVERAGE CORRECTED ELECTROMOTIVE FORCE IN VOLTS OF THE CELL

Pt/H_2/HCl m/AgCl/Ag

HCl, m	0°	10°	20°	30°	40°	50°
3.000	0.16795	0.16217	0.15598	0.14937	0.14240	0.13505
4.000	.13925	.13305	.12635	.11941	.11217	.10451
5.000	.11274	.10614	.09918	.09211	.08462	.07695
6.000	.08786	.08111	.07399	.06676	.05927	.05146
7.000	.06437	.05751	.05022	.04298	.03542	.02766
8.000	.04200	.03504	.02777	.02043	.01295	.00522
9.000	.02112	.01410	.00672	− .00055	− .00813	− .01578
10.000	.00150	− .00554	− .01305	− .02025	− .02767	− .03534
11.000	− .01734	− .02438	− .03142	− .03890	− .04616	− .05379
12.000	− .03448	− .04159	− .04898	− .05610	− .06336	− .07079
13.000	− .05087	− .05805	− .06506	− .07245	− .07930	− .08582
14.000	− .06665	− .07354	− .08052	− .08735	− .09391	− .10113
15.000	− .08124	− .08818	− .09463	− .10135	− .10769	− .11466
15.878	− .09327	− .09979	− .10632	− .11220	− .11957	

TABLE II

INTERPOLATED VALUES FOR THE TOTAL VAPOR PRESSURE OF HYDROCHLORIC ACID IN MM. CORRECTED TO 0°

HCl, *m*	0°	10°	20°	30°	40°	50°
3	4	8	15	27	46	79
4	4	7	14	25	43	74
5	3	7	13	23	40	69
6	3	6	12	21	37	64
7	3	5	11	19	34	59
8	2	5	10	18	32	56
9	2	5	9	18	32	57
10	2	5	10	18	35	62
11	3	6	12	23	43	78
12	4	9	18	35	64	116
13	7	15	30	55	98	179
14	12	24	51	91	160	277
15	25	49	90	158	271	460
15.88	38	74	133	232	398	677

used in correcting the electromotive force data, as interpolated from the values given in "International Critical Tables," Vol. III, p. 301. According to the accompanying note, these values have in the temperature range employed an accuracy of about 2% for solutions of 5 to 12 molal hydrochloric acid and of 5 to 15% for lower and higher concentrations. To calculate the activity coefficient of the acid from the experimental data in Table I according to the equation $E = E_0 - 2k \log \gamma m$, the observed E_0 values of Harned and Ehlers were used. The first part of Table III gives the E_0 values as well as all other constants needed.

For computations at odd temperatures the following formulas may be used for the values of the constants:

$$
\begin{aligned}
B &= 0.11180 - 0.000310t \\
C &= 0.009190 - 0.0000558t \\
D &= -0.0007611 + 0.00000467t \\
E &= 0.00001716 - 0.000000137t \\
u &= 1.8143 \cdot 10^6 \cdot (\epsilon T)^{-3/2} \\
\log \epsilon &= 1.9051 - 0.00205t
\end{aligned}
$$

where ϵ is the dielectric constant of the solvent.

An estimate of the error that may appear in the observed values for the logarithm of the activity coefficient shows that an error of 0.2 millivolt causes a deviation of about 0.0010. Weighing and temperature errors are practically negligible, but the error that may be caused by the increasing solubility of silver chloride with the acid concentration needs careful consideration, as to whether it would be sufficiently large to cause an appreciable distortion. A summary of a number of solubility determinations at 25° is given in Table IV.

As shown in the last column of this table, the silver chloride solubility amounts even at the highest acid concentration only to a small fraction of the same and should, therefore, have a negligible influence on the electromotive force of the cells measured. However, the influence must be even less than might be indicated by the results of the solubility determinations because the solution around the hydrogen electrode could have contained only very faint traces of silver chlo-

TABLE III, PART I

CONSTANTS USED FOR CALCULATING "OBSERVED" VALUES OF THE ACTIVITY COEFFICIENT OF HYDROCHLORIC ACID

	0°	10°	20°	30°	40°	50°
E_0	0.23634	0.23126	0.22551	0.21912	0.21200	0.20437
k	0.05421	0.05619	0.05818	0.06016	0.06215	0.06413

$R = 8.3156$ $F = 96{,}500$ $T = 273.1 + t$

TABLE III, PART II

CONSTANTS USED FOR COMPUTING "CALCULATED" VALUES OF THE ACTIVITY COEFFICIENT OF HYDROCHLORIC ACID

t	*u*	*B*	*C*	*D*	*E*
0°	0.487	0.11180	0.009190	−0.0007611	0.00001716
10	.494	.10870	.008632	.0007144	.00001579
20	.502	.10560	.008074	.0006677	.00001442
30	.511	.10250	.007516	.0006210	.00001305
40	.522	.09940	.006958	.0005743	.00001168
50	.534	.09630	.006400	.0005276	.00001031

TABLE IV

THE SOLUBILITY OF SILVER CHLORIDE IN CONCENTRATED AQUEOUS SOLUTIONS OF HYDROCHLORIC ACID AT 25°

HCl, m_1	AgCl, m_2	m_2 as % of m_1
4	0.0011	0.03
5	.0030	.06
6	.0051	.08
7	.0076	.11
8	.0112	.14
9	.0156	.17
10	.0215	.22
11	.0264	.24
12	.0312	.26
13	.0353	.27
14	.0390	.28
15	.0424	.28
15.88	.0447	.28

ride since diffusion into its compartment was eliminated by the stopcock placed immediately below that of the silver–silver chloride electrode. The liquid junction potential caused by the presence of silver chloride in the solution around the latter would also be negligible since the amount present was very small as compared to the acid concentration. At temperatures higher or lower than 25° we should expect to find silver chloride solubilities of the same order of magnitude as at this temperature. In Fig. 2 is shown the solubility curve for silver chloride according to the data in Table IV. As a comparison three points from the recalculated data of Forbes and Cole[3] are given and indicated by round dots.

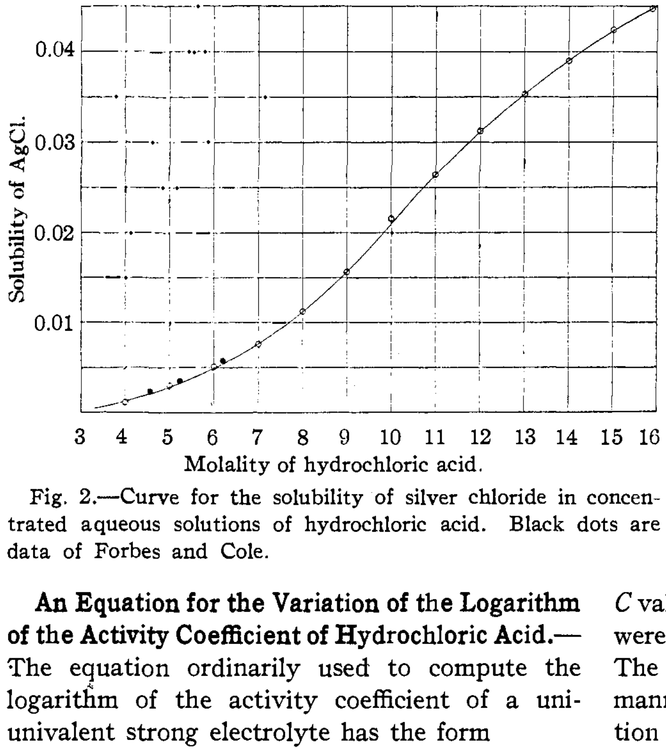

Fig. 2.—Curve for the solubility of silver chloride in concentrated aqueous solutions of hydrochloric acid. Black dots are data of Forbes and Cole.

An Equation for the Variation of the Logarithm of the Activity Coefficient of Hydrochloric Acid.—The equation ordinarily used to compute the logarithm of the activity coefficient of a uni-univalent strong electrolyte has the form

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

where u is a universal and A and B are empirical constants. As is well known, this equation has been applied successfully to the experimental data for aqueous solutions of a large number of uni-univalent electrolytes up to concentrations of 3 or 4 molal. It cannot, however, be used in the present case where the lowest concentration dealt with lies near the limit of its applicability. Apparently the simplest method of simultaneously obtaining agreement with the already existing data at lower concentrations and with those obtained in this study would be accomplished by adding terms representing higher powers of the concentration. Thus it was found necessary to give the equation the form

$$\log \gamma = -\frac{u\sqrt{m}}{1 + \sqrt{2m}} + Bm + Cm^2 + Dm^3 + Em^4 \tag{2}$$

where B, C, D and E are empirical constants. Since the constants employed in this equation have no particular theoretical significance, the A constant of equation (1) was taken as equal to unity and independent of temperature. This procedure agrees closely with the results of Harned and Ehlers, who found A values differing about 2% from unity. It was also far more convenient to operate with molalities rather than molarities which vary with temperature.

The following method of determining the empirical constants was employed. Using the observed values for the logarithm of the activity coefficient, four simultaneous equations representing the data for 3, 7, 11 and 15.88 molal acid were set up for each experimental temperature and solved for B after first evaluating in order E, D and C. The B values were then plotted against temperature and found to vary linearly. After interpolation and introduction in equation (2), C was obtained from two sets of simultaneous equations at each temperature. The C values also varied linearly with temperature and were interpolated and introduced as the B values. The D constant was then evaluated in the same manner as the C constant and again a linear variation with temperature was found. The E term of equation (2) is very small until very high concentrations are reached and values of the E constant were therefore obtained by the use of data for acid concentrations above 8 molal. Even the E constant varied linearly with the temperature and thus all the empirical constants employed in equation (2) have this property in common. In part II of Table III is given a summary of the constants obtained and their temperature coefficients. Table V contains the calculated values for the logarithm of the activity of hydrochloric acid. A comparison has been made between these and the observed values and it was found

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(3) Forbes and Cole, THIS JOURNAL, **43**, 2492 (1921); *cf.* also Forbes, *ibid.*, **33**, 1937 (1911).

that the average difference over the entire concentration and temperature ranges employed was ±0.0010. The largest differences were found in the case of the 15.88 molal acid but it should be remembered that the vapor pressure correction was very large and may be in error to the extent of 15%. In Fig. 3 are shown the isotherms for the logarithm of the activity coefficient. The dotted lines represent the curves calculated for 60, 70 and 80°. In contrast to the behavior of the activity coefficient of a number of other uni-univalent electrolytes like sodium or potassium chloride that of hydrochloric acid has a comparatively very large temperature coefficient.

Comparison with Earlier Data.—Randall and Young made a survey of all older experimental data that could be used to compute the activity coefficient of hydrochloric acid and obtained from these and their own electromotive force measurements a table of values representing the concentration range 0 to 16 molal at 25°. In Table VI is given a comparison between their values and those obtained from equation (2) using the constants in Table III. The E_0 value employed by Randall and Young differed by only 0.2 millivolt from the one found by Harned and Ehlers and therefore a recalculation to conform with the latter was considered unnecessary. The agreement between the two sets of data is reasonably good and does not reveal any differences larger than those that might be expected from ordinary experimental errors. In Table VI is also included a comparison between our values and those of Harned and Ehlers for 3 and 4 molal acid solutions from 0 to 25°. The latter values show a constant difference from ours of about 0.008 which may be due either to differences in the vapor pressure correction applied to the hydrogen electrode or experimental errors caused by silver deposits on the same.

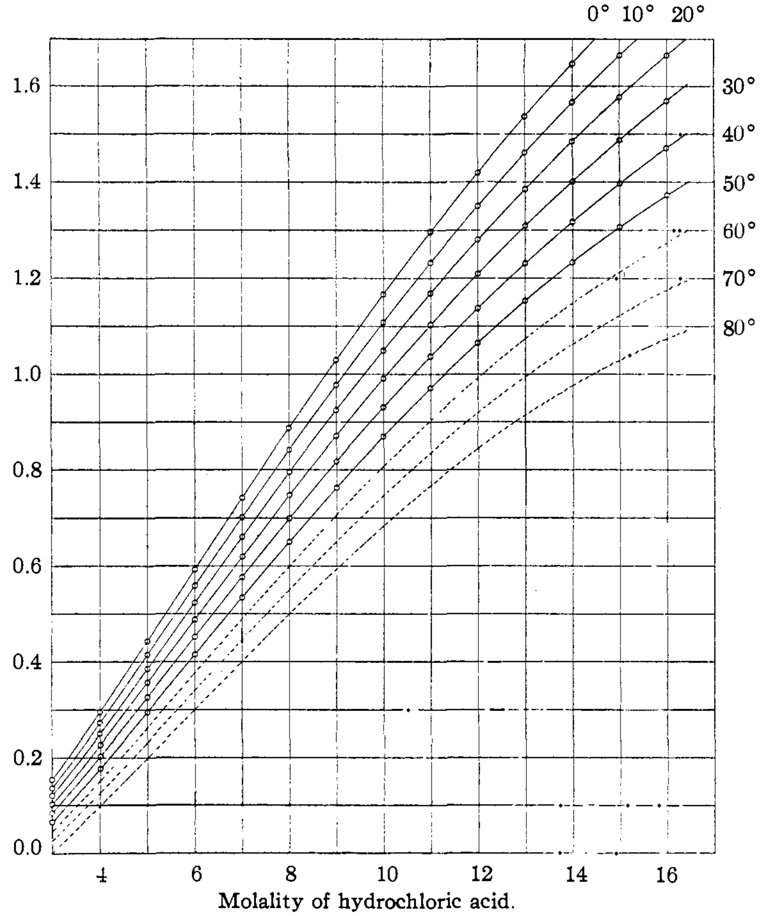

Fig. 3.—Isotherms for the logarithm of the activity coefficient of hydrochloric acid in concentrated solutions. Dotted lines represent the curves calculated for 60, 70 and 80°.

TABLE V

CALCULATED VALUES FOR THE LOGARITHM OF THE ACTIVITY COEFFICIENT OF HYDROCHLORIC ACID IN CONCENTRATED AQUEOUS SOLUTIONS

HCl, m	0°	10°	20°	30°	40°	50°
3	0.1544	0.1377	0.1205	0.1028	0.0841	0.0650
4	.2955	.2732	.2503	.2269	.2025	.1775
5	.4427	.4145	.3857	.3564	.3260	.2951
6	.5922	.5581	.5233	.4879	.4516	.4146
7	.7413	.7011	.6603	.6190	.5765	.5335
8	.8877	.8415	.7948	.7475	.6990	.6500
9	1.0297	.9776	.9250	.8718	.8175	.7625
10	1.1661	1.1082	1.0498	.9908	.9306	.8699
11	1.2962	1.2326	1.1684	1.1036	1.0377	.9712
12	1.4196	1.3503	1.2803	1.2097	1.1380	1.0657
13	1.5366	1.4613	1.3855	1.3090	1.2314	1.1531
14	1.6476	1.5662	1.4841	1.4016	1.3178	1.2334
15	1.7536	1.6656	1.5770	1.4878	1.3975	1.3065
16	1.8559	1.7608	1.6650	1.5687	1.4711	1.3730

The Activity of the Solvent.—According to the Gibbs–Duhem equation

$$d \log a_1 = -N_2/N_1 \, d \log a_2 \qquad (3)$$

where a_1 and a_2 are the activities and N_1 and N_2

TABLE VI

COMPARISON BETWEEN (1) THE 25° ISOTHERM CALCULATED FROM EQUATION (2) AND THE DATA OF RANDALL AND YOUNG, (2) THE CALCULATED VALUES FOR 3 AND 4 MOLAL ACID SOLUTIONS FROM 0 TO 25° AND THE CORRESPONDING DATA OF HARNED AND EHLERS

HCl, m	log γ eq. (2)	R. and Y.	HCl 3 m	log γ eq. (2)	H. and E.
3	0.1120	0.1205	0°	0.1544	0.1620
4	.2389	.2460	10	.1377	.1464
5	.3714	.3757	20	.1205	.1287
6	.5059	.5078	25	.1120	.1193
7	.6400	.6403			
8	.7714	.7705	HCl 4 m		
9	.8988	.9000			
10	1.0208	1.0189	0°	.2955	.3023
12	1.2457	1.2367	10	.2732	.2813
14	1.4436	1.4368	20	.2503	.2582
16	1.6179	1.6276	25	.2389	.2453

TABLE VII

CALCULATED VALUES FOR THE LOGARITHM OF THE ACTIVITY OF THE SOLVENT IN CONCENTRATED AQUEOUS SOLUTIONS OF HYDROCHLORIC ACID

HCl, m	0°	10°	20°	30°	40°	50°
3	−0.0565	−0.0556	−0.0546	−0.0536	−0.0525	−0.0514
4	.0892	.0876	.0859	.0841	.0823	.0805
5	.1282	.1256	.1225	.1202	.1174	.1146
6	.1730	.1692	.1653	.1614	.1574	.1534
7	.2231	.2179	.2126	.2073	.2018	.1964
8	.2779	.2711	.2642	.2572	.2501	.2431
9	.3367	.3281	.3193	.3106	.3017	.2928
10	.3987	.3881	.3774	.3666	.3558	.3448
11	.4632	.4505	.4376	.4246	.4116	.3984
12	.5297	.5147	.4993	.4839	.4688	.4529
13	.5977	.5801	.5620	.5440	.5259	.5076
14	.6670	.6466	.6254	.6046	.5833	.5620
15	.7377	.7140	.6893	.6648	.6404	.6155
16	.8102	.7827	.7539	.7255	.6969	.6679

the mole fractions of solvent and solute, respectively. Adding to both sides of equation (3) the quantity $2m$ d log $m/55.51$ and integrating we thus obtain

$$\log a_1 = -\frac{2m}{55.51\cdot 2.3026} - \frac{2}{55.51}\int_0^m m \, \mathrm{d} \log \gamma \quad (4)$$

Differentiating equation (2) and multiplying by m gives for m d log γ

$$m \, \mathrm{d} \log \gamma = -\frac{u\sqrt{m}}{2(1+\sqrt{2m})^2}\,\mathrm{d}m + Bm\mathrm{d}m + 2Cm^2\mathrm{d}m + 3Dm^3\mathrm{d}m + 4Em^4\mathrm{d}m \quad (5)$$

Integration of this expression gives the second term on the right side of equation (4)

$$-\frac{2}{55.51}\int_0^m m \, \mathrm{d} \log \gamma = \frac{u}{55.51\sqrt{2}}\left[(1+\sqrt{2m}) - 2 \log (1+\sqrt{2m}) - \frac{1}{(1+\sqrt{2m})}\right] - \frac{2}{55.51}\,[Bm^2/2 + 2Cm^3/3 + 3Dm^4/4 + 4Em^5/5] \quad (6)$$

Table VII contains the values of the logarithm of the activity of the solvent as calculated from equations (4) and (6). The values obtained by Randall and Young at 25° by graphical integration are from 2 to 8% lower than ours at the same temperature. In Fig. 4 the variation of log a_1 with the acid concentration is shown graphically. The curves seem to straighten out rapidly with increasing concentration and temperature.

The Relative Partial Molal Heat Content of the Solute.—According to definition this quantity $\overline{L}_2$ is given by the equation

$$\frac{\mathrm{d} \ln a_2}{\mathrm{d}T} = -\frac{\overline{H}_2 - \overline{H}_2^0}{RT^2} = -\frac{\overline{L}_2}{RT^2} \quad (7)$$

Differentiation of equation (2) and substitution in equation (7) gives

$$\overline{L}_2 = -6.9078RT\left[\frac{u\sqrt{m}}{1+\sqrt{2m}}\,(1 - bT)\right] - 4.6052RT^2Z \quad (8)$$

where Z is the term $[m\mathrm{d}B/\mathrm{d}T + m^2\mathrm{d}C/\mathrm{d}T + m^3\mathrm{d}D/\mathrm{d}T + m^4\mathrm{d}E/\mathrm{d}T]$ and b is the constant of Åkerlöf[4] used for expressing the temperature variation of the dielectric constant ϵ of the solvent according to the relation

$$T/\epsilon \times \mathrm{d}\epsilon/\mathrm{d}T = -bT = 2.3026 \times 0.00205 \quad (9)$$

The values of the heat content of hydrochloric acid computed from equation (8) are presented in Table VIII. They should have a considerable accuracy and they are in excellent agreement with the results of Harned and Ehlers as shown by the following comparison of the data for an acid concentration of 3 molal.

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[4] Åkerlöf, THIS JOURNAL, 54, 4125 (1932).

Temp., °C.	Harned and Ehlers $\bar{L}_2$, cal.	This study
0°	1175	1159
10	1303	1284
20	1436	1418
30	1577	1561
40	1723	1713
50	1876	1875

Also the values obtained by Rossini[5] for $\bar{L}_2$ at 25° agree very well with ours calculated for the same temperature. In Fig. 5 are shown the isotherms of $\bar{L}_2$ as plotted against the acid concentration. They are practically linear in appearance and it is only at the lowest concentrations that a more pronounced curvature is visible.

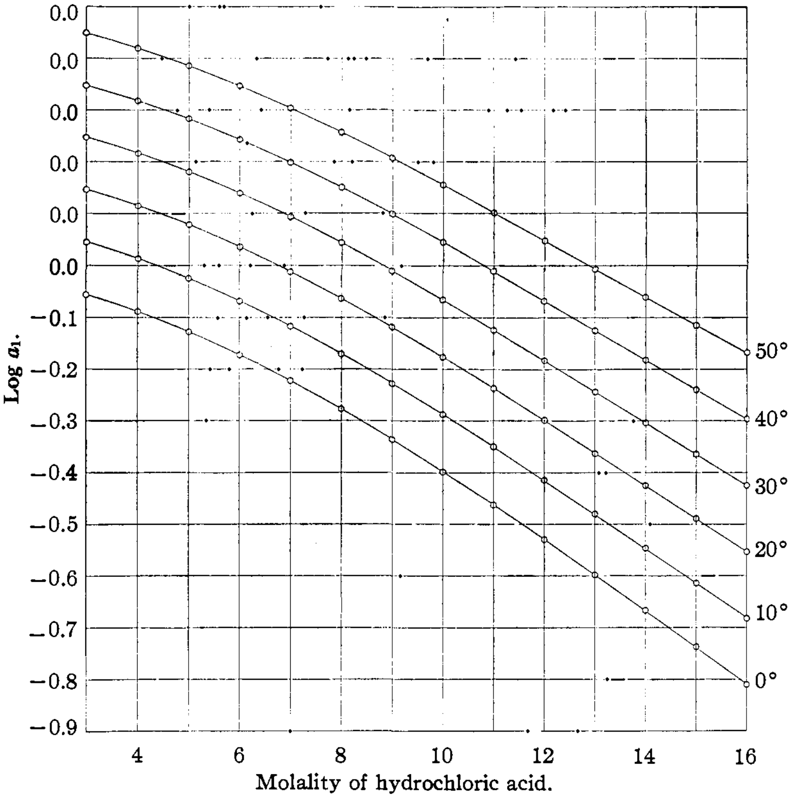

Fig. 4.—Isotherms for the logarithm of the activity of the solvent in concentrated aqueous solutions of hydrochloric acid. Ordinates shifted successively for the different curves.

The Relative Partial Molal Heat Content of the Solvent.—This quantity $\bar{L}_1$ may be calculated from the equation

$$\bar{L}_1 = -\frac{1}{55.51}\int_0^m m\,d\bar{L}_2 \qquad (10)$$

Differentiation of (8), multiplication with m, integration and substitution in (10) gives for $\bar{L}_1$

$$\bar{L}_1 = \frac{6.9078RTu\,(1-bT)}{55.51\cdot 2\sqrt{2}}\left[(1+\sqrt{2m}) - 2\log(1+\sqrt{2m}) - \frac{1}{(1+\sqrt{2m})}\right] + \frac{4.6052RT^2}{55.51}\left[\frac{m^2}{2}\cdot\frac{dB}{dT} + \frac{2m^3}{3}\cdot\frac{dC}{dT} + \frac{3m^4}{4}\cdot\frac{dD}{dT} + \frac{4m^5}{5}\cdot\frac{dE}{dT}\right] \qquad (11)$$

Table IX summarizes the values computed for $\bar{L}_1$ and in Fig. 6 the isotherms are plotted against

TABLE VIII

RELATIVE PARTIAL MOLAL HEAT CONTENT OF THE SOLUTE $\bar{L}_2$ IN CONCENTRATED AQUEOUS SOLUTIONS OF HYDROCHLORIC ACID

HCl, m	0°	10°	20°	30°	40°	50°
3	1159	1284	1418	1561	1713	1875
4	1566	1723	1889	2066	2255	2454
5	1969	2158	2357	2568	2791	3027
6	2371	2590	2822	3066	3323	3596
7	2771	3021	3285	3562	3853	4161
8	3170	3452	3747	4056	4381	4723
9	3570	3881	4207	4550	4909	5285
10	3969	4310	4668	5042	5435	5847
11	4368	4738	5127	5534	5961	6407
12	4765	5167	5587	6026	6485	6966
13	5163	5594	6046	6517	7009	7525
14	5561	6022	6504	7008	7533	8084
15	5958	6449	6962	7498	8057	8642
16	6355	6876	7420	7988	8581	9199

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[5] Rossini, *Bur. Standards J. Research*, **9**, 679 (1932); *cf.* also *ibid.*, **6**, 791 (1931); **7**, 47 (1931).

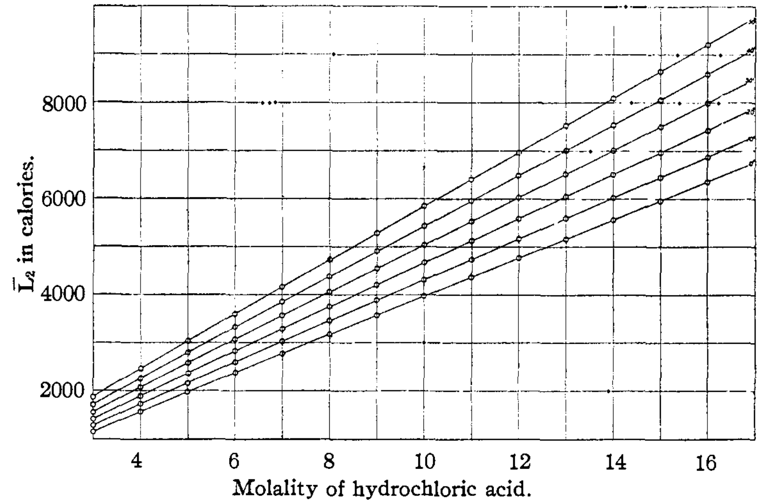

Fig. 5.—Isotherms for the relative partial molal heat content of the solute in concentrated aqueous solutions of hydrochloric acid.

the acid concentration. In contrast to the curves for $\overline{L}_2$ those for $\overline{L}_1$ are very strongly curved. However, if $\overline{L}_1$ is plotted against m^2 the curves obtained are practically straight lines and pronounced deviations appear only at the very highest acid concentrations as shown in Fig. 7. The values of Rossini for $\overline{L}_1$ at 25° agree very well with ours for the same temperature.

Relative Partial Molal Heat Capacity of the Solute.—According to definition $\overline{C}_{p_2} - \overline{C}^0_{p_2}$, is given by the equation

$$\overline{C}_{p_2} - \overline{C}^0_{p_2} = d\overline{L}_2/dT \qquad (12)$$

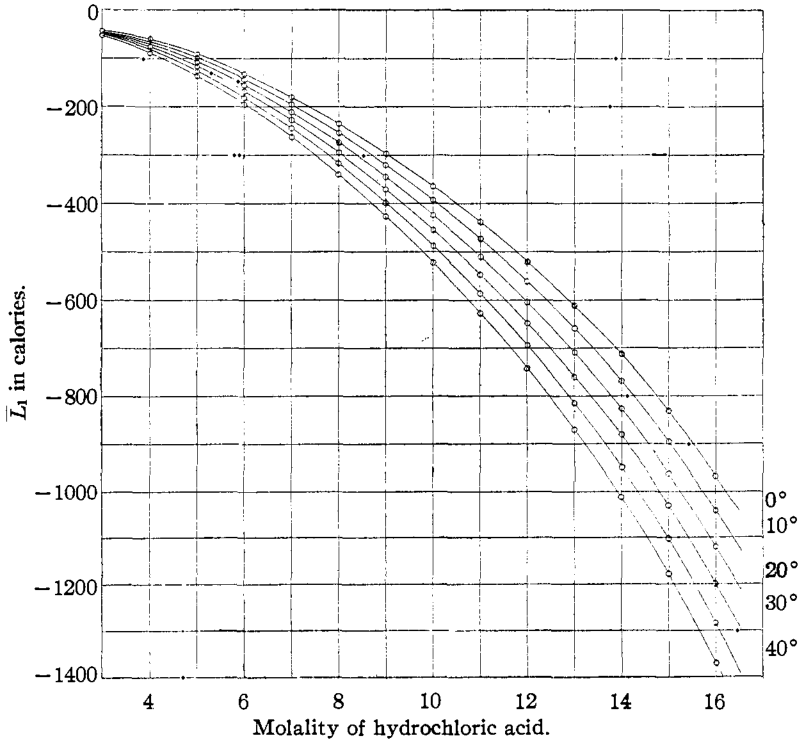

Fig. 6.—Isotherms for the relative partial molal heat content of the solvent in concentrated aqueous solutions of hydrochloric acid as plotted against the acid concentration.

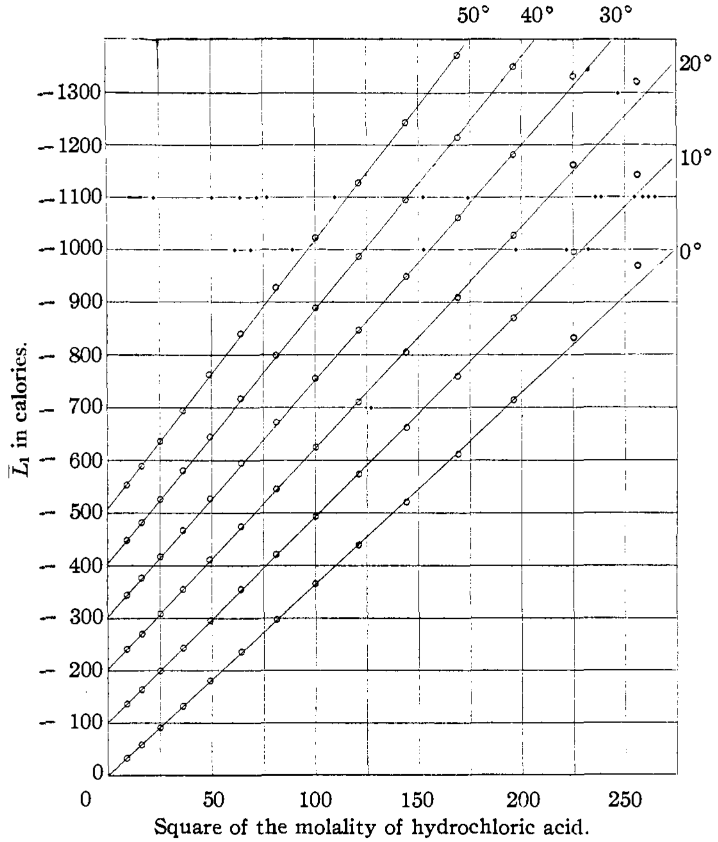

Fig. 7.—Isotherms for the relative partial molal heat content of the solvent in concentrated aqueous solutions of hydrochloric acid as plotted against the square of the acid concentration. Ordinates shifted successively for the different curves.

Differentiation of (8) with respect to T gives immediately

$$\bar{C}_{p_2} - \bar{C}^0_{p_2} = 3.4539R\,[1 - 2(bT) + 3(bT)^2]\,\frac{u\sqrt{m}}{1 + \sqrt{2m}} - 9.2104RTZ \quad (13)$$

where Z is defined as above. It may be pointed out that since m does not vary with the temperature this also holds true for Z. Table X contains the values of $\bar{C}_{p_2} - \bar{C}^0_{p_2}$ as calculated according to equation (13). Figure 8 shows the

TABLE IX

RELATIVE PARTIAL MOLAL HEAT CONTENT OF THE SOLVENT $\bar{L}_1$ IN CONCENTRATED AQUEOUS SOLUTIONS OF HYDROCHLORIC ACID

HCl, m	0°	10°	20°	30°	40°	50°
3	−33.42	−36.85	−40.59	−44.57	−48.82	−53.34
4	58.17	63.71	69.54	75.71	82.24	89.14
5	91.11	99.24	107.8	116.8	126.2	136.2
6	131.9	143.2	155.1	167.5	180.5	194.1
7	180.1	195.2	210.9	227.3	244.4	262.4
8	235.3	254.5	274.6	295.5	317.4	340.2
9	296.9	320.8	345.8	371.8	398.9	427.2
10	364.8	393.9	424.2	455.8	488.6	522.8
11	439.2	474.0	510.1	547.8	586.9	627.6
12	521.0	562.0	604.6	648.9	694.9	742.8
13	611.8	659.6	709.4	761.0	814.7	870.4
14	713.9	769.5	827.2	881.6	949.3	1013.9
15	831.2	895.5	962.4	1031.8	1103.8	1178.5
16	968.1	1042.7	1120.3	1200.7	1284.2	1370.7

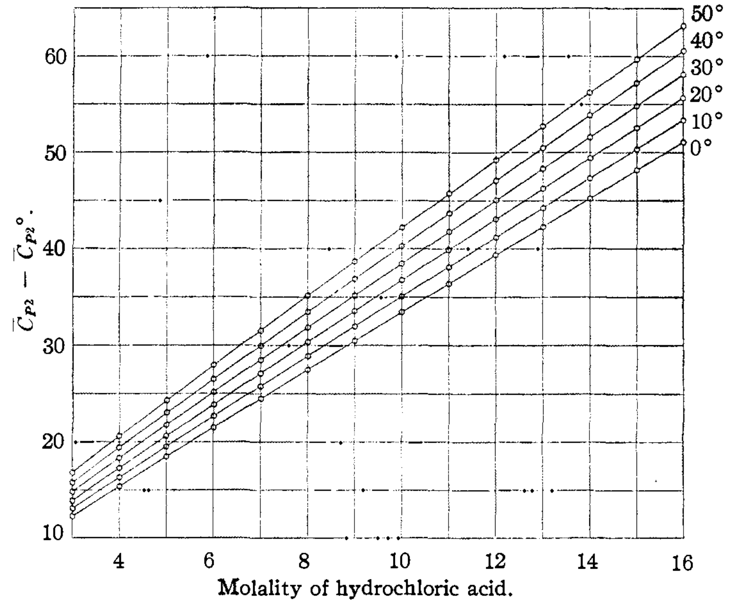

Fig. 8.—Isotherms for the relative partial molal heat capacity of the solute in concentrated aqueous solutions of hydrochloric acid.

isotherms as plotted against the acid concentration. As in the case of $\overline{L}_2$ they show a practically linear variation of the heat capacity.

Relative Partial Molal Heat Capacity of the Solvent.—Analogous to the calculation of $\overline{L}_1$ from $\overline{L}_2$ we obtain for $\overline{C}_{p_1} - \overline{C}_{p_1}^{\,0}$ the equation

$$\overline{C}_{p1} - \overline{C}_{p1}^{\,0} = -\frac{1}{55.51}\int_0^m m\,\mathrm{d}(\overline{C}_{p2} - \overline{C}_{p2}^{\,0}) \quad (14)$$

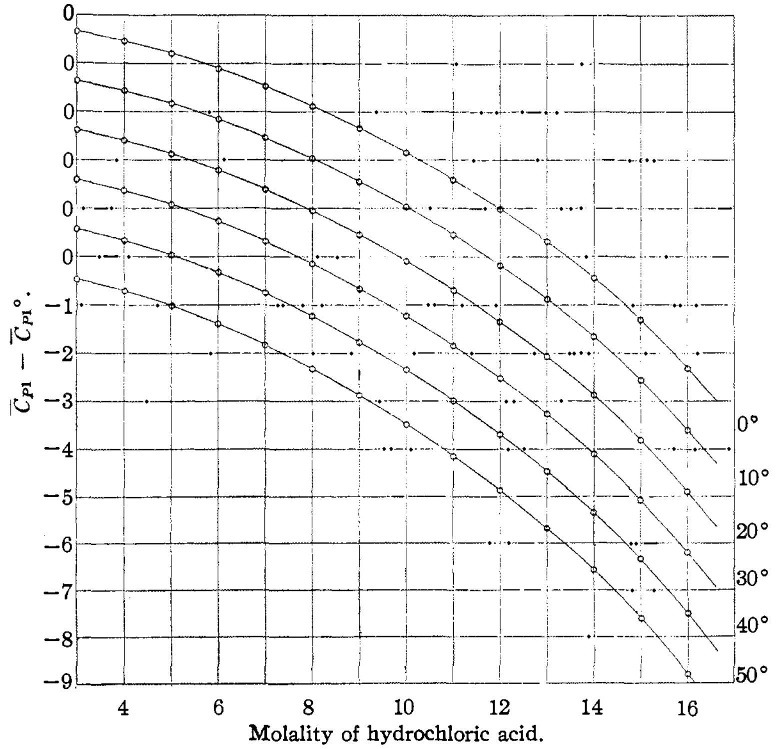

Fig. 9.—Isotherms for the relative partial molal heat capacity of the solvent in concentrated aqueous solutions of hydrochloric acid as plotted against the acid concentration. Ordinates shifted successively for the different curves.

TABLE X

RELATIVE PARTIAL MOLAL HEAT CAPACITY OF THE SOLUTE $\bar{C}_{p_2} - \bar{C}_{p_2}^0$ IN CONCENTRATED AQUEOUS SOLUTIONS OF HYDROCHLORIC ACID

HCl, m	0°	10°	20°	30°	40°	50°
3	12.27	13.06	13.89	14.79	15.76	16.80
4	15.39	16.31	17.28	18.31	19.42	20.59
5	18.46	19.50	20.60	21.76	22.99	24.29
6	21.49	22.64	23.86	25.13	26.49	27.92
7	24.49	25.77	27.11	28.50	29.98	31.53
8	27.48	28.88	30.33	31.84	33.44	35.11
9	30.44	31.95	33.52	35.14	36.86	38.65
10	33.41	35.03	36.71	38.45	40.28	42.18
11	36.37	38.10	39.89	41.75	43.68	45.70
12	39.32	41.15	43.06	45.02	47.07	49.20
13	42.26	44.21	46.22	48.30	50.46	52.70
14	45.19	47.26	49.39	51.57	53.85	56.20
15	48.13	50.30	52.54	54.84	57.22	59.69
16	51.06	53.35	55.69	58.10	60.59	63.17

Differentiation of (13), multiplication with m, integration and substitution in (14) gives for $\bar{C}_{p_1} - \bar{C}_{p_1}^0$

$$\bar{C}_{p_1} - \bar{C}_{p_1}^0 = \frac{3.4539\,Ru}{55.51 \times 2\sqrt{2}}\,[1 - 2(bT) + 3(bT)^2]\left[(1 + \sqrt{2m}) - 2\log(1 + \sqrt{2m}) - \frac{1}{(1 + \sqrt{2m})}\right] + \frac{9.2104\,RT}{55.51}\left[\frac{m^2}{2}\cdot\frac{dB}{dT} + \frac{2m^3}{3}\cdot\frac{dC}{dT} + \frac{3m^4}{4}\cdot\frac{dD}{dT} + \frac{4m^5}{5}\cdot\frac{dE}{dT}\right] \quad (15)$$

Table XI gives the computed values of $\bar{C}_{p_1} - \bar{C}_{p_1}^0$ and Figs. 9 and 10 show the isotherms plotted against m and m^2, respectively. As in the case of $\bar{L}_1$ the values of $\bar{C}_{p_1} - \bar{C}_{p_1}^0$ vary practically linearly with m^2 with small deviations only at very high concentrations.

Relative Partial Molal Free Energy of Solute and Solvent.—In the case of the solute the quantity $\bar{F}_2 - \bar{F}_2^0$ may be calculated using the equation

$$\bar{F}_2 - \bar{F}_2^0 = 2\,RT \ln \gamma\, m \quad (16)$$

where the values of γ are those given in Table V. A summary of the values obtained for $\bar{F}_2 - \bar{F}_2^0$ is presented in Table XII. The relative partial molal free energy of the solvent $\bar{F}_1 - \bar{F}_1^0$ may be obtained from the equation

$$\bar{F}_1 - \bar{F}_1^0 = -\frac{1}{55.51}\int_0^m m\,d\,(\bar{F}_2 - \bar{F}_2^0) \quad (17)$$

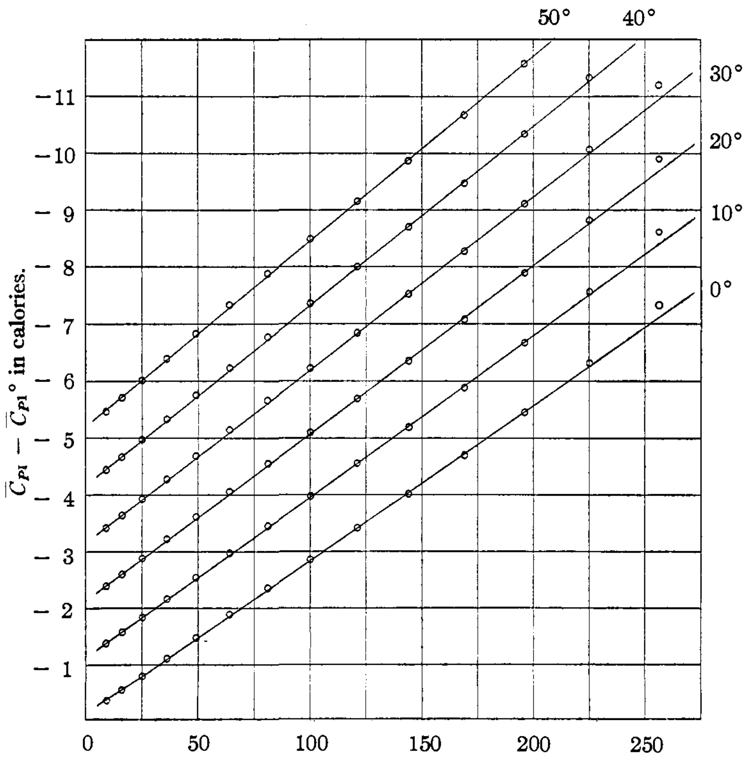

Fig. 10.—Isotherms for the relative partial molal heat capacity of the solvent in concentrated aqueous solutions of hydrochloric acid as plotted against the square of the acid concentration. Ordinates shifted successively for the different curves.

TABLE XI

RELATIVE PARTIAL MOLAL HEAT CAPACITY OF THE SOLVENT $\bar{C}_{p_1} - \bar{C}_{p_1}^0$ IN CONCENTRATED AQUEOUS SOLUTIONS OF HYDROCHLORIC ACID

HCl, *m*	0°	10°	20°	30°	40°	50°
3	−0.344	−0.366	−0.389	−0.413	−0.439	−0.460
4	.541	.571	.603	.637	.672	.710
5	.796	.837	.879	.924	.971	1.020
6	1.107	1.160	1.216	1.273	1.333	1.395
7	1.472	1.539	1.609	1.681	1.756	1.834
8	1.886	1.970	2.056	2.144	2.236	2.331
9	2.347	2.449	2.553	2.660	2.769	2.882
10	2.854	2.975	3.099	3.225	3.355	3.488
11	3.408	3.551	3.695	3.843	3.995	4.149
12	4.016	4.182	4.350	4.521	4.696	4.874
13	4.690	4.880	5.074	5.271	5.471	5.676
14	5.446	5.665	5.887	6.112	6.342	6.575
15	6.312	6.564	6.819	7.076	7.339	7.605
16	7.323	7.612	7.905	8.200	8.501	8.805

TABLE XII

RELATIVE PARTIAL MOLAL FREE ENERGY OF THE SOLUTE $\bar{F}_2 - \bar{F}_2^0$ IN CONCENTRATED AQUEOUS SOLUTIONS OF HYDROCHLORIC ACID

HCl, *m*	0°	10°	20°	30°	40°	50°
3	1579	1594	1604	1610	1609	1604
4	2245	2269	2288	2301	2307	2306
5	2855	2887	2911	2929	2939	2941
6	3427	3464	3493	3514	3526	3529
7	3967	4008	4040	4064	4076	4079
8	4479	4523	4557	4581	4593	4595
9	4962	5008	5044	5068	5080	5079
10	5417	5465	5502	5526	5535	5532
11	5846	5895	5931	5954	5961	5955
12	6249	6298	6333	6353	6357	6346
13	6629	6676	6708	6725	6725	6707
14	6987	7032	7060	7071	7065	7040
15	7327	7367	7389	7394	7379	7345
16	7653	7686	7700	7696	7670	7625

Differentiation of (16), multiplication with *m*, integration and substitution in (17) gives the equation

$$\bar{F}_1 - \bar{F}_1^0 = -\frac{2RT}{55.51}\left[m - \frac{2.3026\,u}{2\sqrt{2}}\left(1 + \sqrt{2m} - 2\log\left(1 + \sqrt{2m}\right) - \frac{1}{1 + \sqrt{2m}}\right) + 2.3026\left(m^2 B/2 + 2\,m^3 C/3 + 3\,m^4 D/4 + 4\,m^5 E/5\right)\right] \quad (18)$$

Table XIII contains the calculated values for $\bar{F}_1 - \bar{F}_1^0$.

Relative Partial Molal Entropy of Solute and Solvent.—These quantities $\bar{S}_2 - \bar{S}_2^0$ and $\bar{S}_1 - \bar{S}_1^0$, respectively, may now be obtained since both the corresponding free energy and heat content data are available

$$-(\bar{S}_2 - \bar{S}_2^0) = [(\bar{F}_2 - \bar{F}_2^0) - (\bar{H}_2 - \bar{H}_2^0)]/T \quad (19)$$

$$-(\bar{S}_1 - \bar{S}_1^0) = [(\bar{F}_1 - \bar{F}_1^0) - (\bar{H}_1 - \bar{H}_1^0)]/T \quad (20)$$

Tables XIV and XV give the values computed. A study of the data indicates that at a given concentration the entropy varies practically linearly with the temperature and the coefficient of this

TABLE XIII

RELATIVE PARTIAL MOLAL FREE ENERGY OF THE SOLVENT $\bar{F}_1 - \bar{F}_1^0$ IN CONCENTRATED AQUEOUS SOLUTIONS OF HYDROCHLORIC ACID

HCl, *m*	0°	10°	20°	30°	40°	50°
3	−70.71	−72.11	−73.21	−74.38	−75.35	−76.39
4	111.6	113.5	115.3	116.8	118.0	119.1
5	160.3	162.8	164.3	166.8	168.3	169.5
6	216.4	219.3	222.6	224.0	225.6	226.9
7	279.0	282.5	285.3	287.6	289.4	290.5
8	347.5	351.4	353.5	356.9	358.5	359.6
9	421.0	425.3	428.6	431.0	432.6	433.2
10	498.5	503.0	506.5	508.7	510.0	510.2
11	579.2	584.0	587.2	589.3	591.8	589.4
12	662.4	667.2	670.1	671.6	672.1	670.1
13	747.4	749.3	754.2	755.0	753.9	751.0
14	834.0	838.1	839.3	839.1	836.2	831.4
15	922.5	925.5	925.1	922.6	918.1	910.6
16	1013.0	1014.6	1011.7	1006.9	999.1	987.2

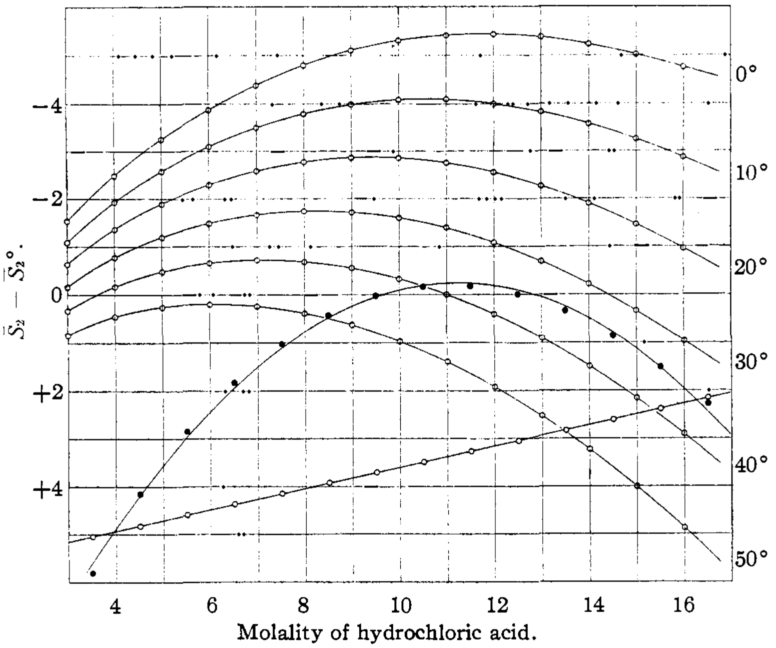

Fig. 11.—Isotherms for the relative partial molal entropy of the solute in concentrated aqueous solutions of hydrochloric acid. Straight line represents variation of temperature coefficient.

variation changes linearly with the acid concentration in the case of $\bar{S}_2 - \bar{S}_2^0$ as shown in Fig. 11. In the case of $\bar{S}_1 - \bar{S}_1^0$ the temperature coefficient varies approximately linearly with m^2. The entropy isotherms for $\bar{S}_2 - \bar{S}_2^0$ are fairly closely represented by symmetrical parabolas with average

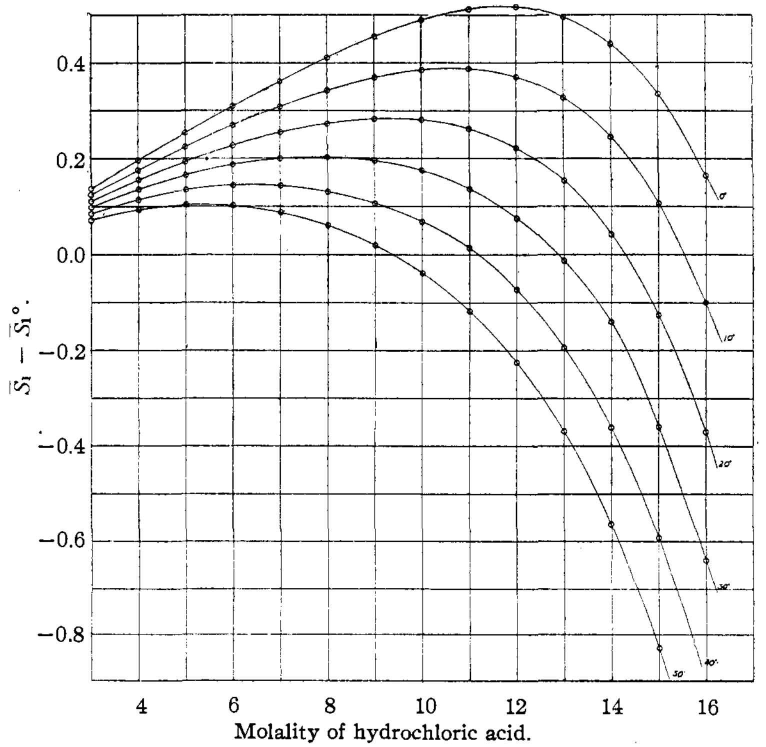

Fig. 12.—Isotherms for the relative partial molal entropy of the solvent in concentrated aqueous solutions of hydrochloric acid.

TABLE XIV

RELATIVE PARTIAL MOLAL ENTROPY OF THE SOLUTE—$(\overline{S}_2 - \overline{S}_2^0)$ IN CONCENTRATED AQUEOUS SOLUTIONS OF HYDROCHLORIC ACID

HCl, *m*	0°	10°	20°	30°	40°	50°
3	1.538	1.095	0.634	0.162	−0.332	−0.839
4	2.486	1.928	1.361	0.775	.166	− .458
5	3.244	2.575	1.890	1.191	.473	− .266
6	3.867	3.087	2.289	1.478	.648	− .207
7	4.379	3.486	2.576	1.656	.712	− .254
8	4.793	3.783	2.763	1.732	.677	− .396
9	5.097	3.981	2.856	1.709	.546	− .637
10	5.302	4.080	2.845	1.597	.319	− .975
11	5.412	4.087	2.743	1.386	.000	−1.399
12	5.434	3.995	2.545	1.079	− .409	−1.919
13	5.368	3.822	2.258	0.686	− .907	−2.532
14	5.221	3.568	1.897	.208	−1.495	−3.231
15	5.013	3.242	1.457	− .343	−2.165	−4.014
16	4.753	2.861	0.955	− .963	−2.909	−4.871

TABLE XV

RELATIVE PARTIAL MOLAL ENTROPY OF THE SOLVENT $\overline{S}_1 - \overline{S}_1^0$ IN CONCENTRATED AQUEOUS SOLUTIONS OF HYDROCHLORIC ACID

HCl, *m*	0°	10°	20°	30°	40°	50°
3	0.1366	0.1247	0.1112	0.0983	0.0846	0.0715
4	.1955	.1759	.1563	.1356	.1143	.0928
5	.2534	.2246	.1927	.1650	.1344	.1030
6	.3094	.2688	.2303	.1864	.1440	.1015
7	.3621	.3084	.2538	.1989	.1437	.0870
8	.4108	.3423	.2692	.2026	.1312	.0600
9	.4544	.3691	.2825	.1953	.1076	.0186
10	.4896	.3854	.2808	.1745	.0683	− .0390
11	.5126	.3885	.2631	.1369	.0156	− .1182
12	.5177	.3716	.2235	.0749	− .0728	− .2250
13	.4965	.3268	.1528	− .0198	− .1942	− .3695
14	.4398	.2458	.0413	− .1402	− .3612	− .5648
15	.3343	.1060	− .1273	− .3603	− .5931	− .8291
16	.1644	− .0993	− .3705	− .6394	− .9106	−1.1869

deviations of about 1%, as shown in Fig. 11 where the data for the 10° isotherm also have been plotted on double the scale for the ordinates to obtain a comparison with a calculated curve. The deviations are without much doubt real but it probably also is true that the accuracy of the data in Tables XIV and XV cannot be much better. The isotherms for $\overline{S}_1 - \overline{S}_1^0$ given in Fig. 12 do not fit a simple quadratic equation.

Summary

The electromotive force of the cell H_2 / HCl *m* / AgCl/Ag has been measured at even molalities of the acid from 3 to 16 and at ten-degree temperature intervals from 0 to 50°. Using the electromotive force data the logarithm of the activity coefficient of hydrochloric acid was found to be expressed adequately by the equation

$$\log \gamma = -\frac{u\sqrt{m}}{1 + \sqrt{2m}} + Bm + Cm^2 + Dm^3 + Em^4$$

where *u* is the universal constant of the Debye–Hückel limiting law, *m* the acid concentration in moles per 1000 grams of water, *B*, *C*, *D* and *E* empirical constants varying linearly with the temperature. The observed and calculated values for log γ showed an average difference of ± 0.0010.

Using the formula just given equations have been derived for the calculation of the activity of the solvent, the relative partial molal heat content, heat capacity, free energy and entropy of both solute and solvent. The computed values of these properties are given in a series of tables.

NEW HAVEN, CONN.

RECEIVED JUNE 21, 1937