[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

The Heat of Dilution of Aqueous Hydrochloric Acid at 25°

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In connection with some projected calorimetric experiments with amino acids and proteins, it became necessary to have reliable values for the integral heats of dilution of aqueous hydrogen chloride. Since very considerable discrepancies exist between the calorimetric heats available in the literature and those calculated from electromotive force measurements, it seemed advisable to redetermine these quantities.

Experimental Part

The calorimeter used in these measurements will be described elsewhere. Because of the limited size of the dilution cup, three different types of dilution were made:

Type 1. Varying amounts of the stock solution of hydrochloric acid were diluted with water.

Type 2. The stock solution of hydrochloric acid was diluted with less concentrated acid. The heat effect in an experiment of this type is due to diluting the stock solution to the final concentration and concentrating the weaker solution to this concentration.

Type 3. A solution composed of appropriate quantities of stock solution and water was diluted with water.

The hydrochloric acid used was a J. T. Baker analyzed product. The stock solution was analyzed gravimetrically at the start and finish of the measurements, and its concentration is considered to be known within ±0.05%. All weighings were corrected for the buoyancy of the air.

The thermometer used to measure the temperature of the oil thermostat was calibrated against a platinum resistance thermometer certified by the Bureau of Standards. The standard cell used in the measurement of electrical energy input into the calorimeter was checked against the laboratory standard set of six calibrated cells. All timing was done with a synchronous clock furnishing audible signals and driven by a precision tuning fork. The over-all sensitivity of the thermometric system was 0.05 joule per mm. on the galvanometer scale.

TABLE I

INTEGRAL HEATS OF DILUTION OF HYDROCHLORIC ACID SOLUTIONS AT 25°

Square root of concentration (moles per 1000 g. $H_2O)^{1/2}$ Initial	Final	Diluent	Heat of dilution, $-\Delta H$ joules (int.) per mole
1.8267	0.4463	0	3039
1.8267	.1919	0	3448
1.8267	.2676	0	3317
1.8267	.3272	0	3179
1.8267	.5377	0.3050	2899
1.8267	.6128	.4214	2781
1.8267	.7604	.6264	2529
1.8267	.8623	.7651	2357
1.8267	.9695	.8917	2165
1.8267	.1339	0	3533
1.8267	.3367	0	3212
1.8267	.1132	0	3566
1.8267	.3454	0	3194
1.8267		Dilution cup leaked	
1.8267	.2230	0	3397
1.8267	.2332	0	3369
1.8267	.3349	0	3227
1.8267	.3836	0	3140
1.8267	.0678	0	3605
1.8267	.0943	0	3617
1.8267	.9628	0.8345	2175
1.8267	1.0647	0.9800	1976
1.8267	1.2179	1.1470	1654
1.8267	0.4748	0	2997
1.8267	.5434	0	2882
1.7783	.4528	0	2889
1.7214	.4757	0	2664
1.4840	.4229	0	2069
1.2513	.3541	0	1617

Experimental Results.—The observed heats of dilution are summarized in Table I. The first and second columns in this table give the initial and final molalities, respectively. In the third column are listed, for dilutions of Type 2, the molalities of the diluting solutions. In the fourth column are the heats of dilution, expressed in international joules per mole of hydrogen chloride. In the case of dilutions of Type 2 these values are calculated according to the formula

$$\Delta H = \frac{\Delta q + a_2\,\Delta H_1}{a_1 + a_2} \qquad (1)$$

where Δq is the observed heat absorption in joules, a_1, a_2 are the number of moles of hydrogen chloride in the dilution cup and in the calorimeter before the dilution, and ΔH_1 is the heat of the dilution, per mole of solute, of the stock solution to the molality of the solution originally present in the calorimeter. This latter quantity was obtained by graphical interpolation in the results of the previous runs, a method of successive approximations being employed if necessary. The heats of dilution have been corrected to 25.00° using the following temperature coefficient which is based on the data of Rossini[1] for the apparent molal heat capacity of the solute

$$d(\Delta H)/dt = 30.1(m_2^{1/2} - m_1^{1/2}) \qquad (2)$$

where m_1, m_2 are the initial and final molalities, respectively. Since the heat capacity used to evaluate the energy change during the dilution was that of the products plus the calorimeter, the observed heat of dilution corresponds to the initial temperature of the experiment. The initial temperatures deviated on the average about ±0.1° from 25°.

It should be noted that according to the work of Gucker and Schminke[2] the factor in equation (2) is about 21. However, the temperature correction amounts to only 0.1 to 0.2%, so that no serious uncertainties are introduced from this source.

Measurements of the heat capacity of the empty calorimeter, and of the calorimeter filled with water, were made. From these additional data the specific heat of the final solution in each run can be calculated. However, no attention was paid to keeping constant the amount of gold foil, vaseline and paraffin used to seal the dilution cup, so that the specific heats are not sufficiently precise to allow the calculation of the apparent molal heat capacities of the solute, since these quantities are very sensitive to errors in the specific heats for dilute solutions. The observed specific heats showed an average deviation of ±0.2% from those calculated from Rossini's values of Φ_C, and a slightly smaller deviation when Gucker and Schminke's values were used.

Treatment of Results.—The heats of dilution of the stock solution to molalities of 0.3 or lower were plotted against the square root of the molality on a large scale, and extrapolated to infinite dilution with the slope required by the limiting law of Debye and Hückel

$$\Phi_H - \Phi_H^0 = 1997\, m^{1/2} \qquad (3)$$

where $\Phi_H - \Phi_H^0$ is the apparent relative molal heat content of the hydrochloric acid. The slope was calculated according to the constants given by Harned and Ehlers.[3] The uncertainty in this extrapolation does not seem to exceed 10 joules per mole. The extrapolated value is the value of the apparent heat content of the stock solution. It is then a simple matter to evaluate this quantity for the solutions obtained by dilution. The values obtained are plotted against the square root of the molality in Fig. 1, the experimental points showing an average deviation from the smooth curve of ±5 joules per mole, corresponding to about ±0.15% of the observed dilution heats. Values read from the smooth curve at round values of $m^{1/2}$ are listed in the second column of Table II. These values are satisfac-

TABLE II

APPARENT AND PARTIAL RELATIVE MOLAL HEAT CONTENT OF SOLUTE AND PARTIAL RELATIVE MOLAL HEAT CONTENT OF SOLVENT IN HYDROCHLORIC ACID SOLUTIONS AT 25°

Square root of molality of hydrochloric acid	Heat content, joules (int.) per mole $\Phi_H - \Phi_H^0$	$\bar{L}_2$	$\bar{L}_1$
0.0000	0	0	0
.0500	97		
.1000	189	276	−0.0157
.1500	273		
.2000	354	515	−.116
.2500	434		
.3000	515	753	−.386
.3500	594		
.4000	672	985	−.902
.4500	749		
.5000	827	1223	−1.784
.5500	907		
.6000	988	1480	−3.191
.6500	1070		
.7000	1154	1737	−5.147
.7500	1237		
.8000	1320	2001	−7.852
.8500	1406		
.9000	1494	2307	−11.86
.9500	1587		
1.0000	1682	2647	−17.39
1.0500	1779		
1.1000	1880	3015	−24.74
1.1500	1986		
1.2000	2096	3432	−34.66
1.2500	2210		
1.3000	2326	3842	−46.16
1.3500	2442		
1.4000	2564	4314	−61.80
1.4500	2690		
1.5000	2819	4789	−79.86
1.5500	2952		
1.6000	3090	5348	−104.1
1.6500	3235		
1.7000	3384	5959	−134.1
1.7500	3538		
1.8000	3698	6631	−171.2
1.8267	3785		

[1] Rossini, *Bur. Standards J. Research*, **9**, 679 (1932).

[2] Gucker and Schminke, THIS JOURNAL, **54**, 1358 (1932).

[3] Harned and Ehlers, THIS JOURNAL, **55**, 2179 (1933).

torily represented at concentrations up to $m^{1/2}$ = 1.2 by the expression

$$\Phi_H - \Phi_H^0 = \frac{1997m^{1/2}}{1 + 1.123m^{1/2}} + 747m \qquad (4)$$

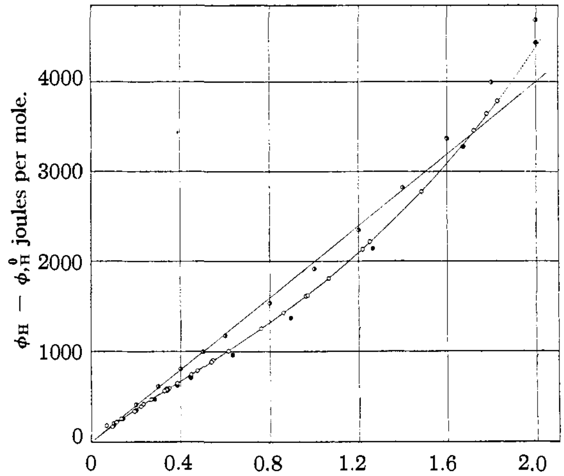

Fig. 1.—Relative apparent molal heat content of hydrochloric acid. The straight line is the Debye–Hückel limiting law. Open circles, this research; half-inked circles, Rossini; inked circles, Harned and Ehlers.

Values of $\bar{L}_2$, the partial relative molal heat content of the solute, were calculated according to the equation

$$\bar{L}_2 = \Phi_H - \Phi_H^0 + {}^1/_2 m^{1/2} \frac{d(\Phi_H - \Phi_H^0)}{dm^{1/2}} \qquad (5)$$

the necessary slopes being read from the large-scale plot of the original heat data. These quantities are listed in the third column of Table II, and are plotted in Fig. 2. An idea of the accuracy of the reading of the slopes is given by the closeness with which the calculated values fall on a smooth curve, the average deviation being of the order of ±5 joules per mole.

The relative partial molal heat content of the solvent is readily calculated from the relation

$$\Phi_H - \Phi_H^0 = \bar{L}_2 + \frac{55.506}{m} \bar{L}_1 \qquad (6)$$

The last column of Table II gives the values obtained in this way.

Estimate of Accuracy.—As mentioned above, all due care has been taken in the calibration of the instruments used in this research. It is therefore considered, since no sources of systematic error are believed to have been overlooked, that a reasonable estimate of the reliability of the results can be based on their internal consistency and the reliability of the extrapolation to infinite dilution.

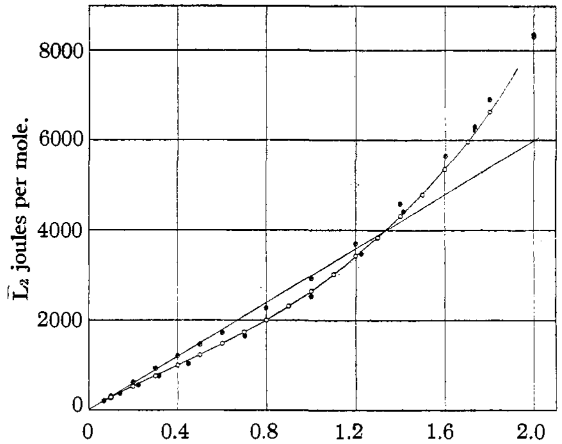

Fig. 2.—Relative partial molal heat content of hydrochloric acid. The straight line is the Debye–Hückel limiting law. Open circles, this research; half-inked circles, Åkerlöf and Teare ($m^{1/2}$ = 1.732 and 2.0 only); three-quarters-inked circles, Rossini; full-inked circles, Harned and Ehlers. In the plot, Rossini's points at $m^{1/2}$ = 0.1 and 2.0 are obscured by those of Harned and Ehlers.

On this basis it is concluded that the smoothed values of the apparent molal heat content should be reliable to about ±20 joules per mole, with considerably smaller limits of error associated with differences between these quantities. Since the values of the partial molal heat content involve slopes read from a graph, they are subject to somewhat larger uncertainties.

Discussion of Results

Several previous calorimetric determinations of the heat of dilution of aqueous hydrochloric acid have been made at various temperatures. These data have been summarized and calculated to 25° by Rossini,[1] who used the Debye–Hückel theory to extrapolate them to infinite dilution, and tabulated values of the apparent and partial relative molal heat contents at round values of the square root of the molality. The values given by Rossini are plotted in Figs. 1 and 2. Part of the relatively large discrepancy between these values and the ones found in the present research is due to the fact that the older values scatter rather badly below $m^{1/2}$ = 0.5, so that the extrapolation to infinite dilution is somewhat arbitrary. Thus, if the values given by Rossini for $\Phi_H - \Phi_H^0$ are brought into coincidence with the present values at $m^{1/2}$ = 0.5, the differences between the values thus obtained and the present ones gradually increase to a value of 130 joules per mole at $m^{1/2}$ =

1.8, as compared with a difference of 300 joules per mole before making this change.

A small part of the discrepancy is due to the fact that the limiting Debye–Hückel slope used by Rossini is a little larger than the correct one, because of omission of the term involving the change of density with temperature. This fact can account for about 30 joules per mole difference.

One source of systematic error in calorimetric observations on hydrochloric acid might be corrosion of the various metallic parts of the calorimeter. It is believed that errors from this source are eliminated in the present research since the calorimeter is composed of tantalum, platinum–iridium, and pure gold solder, while the dilution cup is closed by pure gold foil. Whether corrosion is a cause of the remaining differences between the older work and the present work cannot, of course, be definitely established. Some of the discrepancy to be accounted for may arise in the fact that most of the older work was done at temperatures other than 25°, so that corrections based on the heat capacities of hydrochloric acid solutions are involved.

Doehlemann and Lange[4] have measured the heat of dilution of hydrochloric acid in concentrations up to 0.09 molal. It seems impossible to reconcile their data below 0.0025 molal with the requirements of the Debye–Hückel theory, since these data lie on a curve which is apparently approaching an infinite slope at infinite dilution. Their data from 0.0025 to 0.02 molal fall on a straight line having the limiting Debye–Hückel slope; the intercept of this line gives values of the relative apparent molal heat content which are 20 to 30 joules per mole above the values found in the present research. Also the present values indicate definite divergence from the limiting slope at concentrations below 0.01 molal, while the values of Doehlemann and Lange follow this slope to 0.02 molal, except at the very lowest concentrations, as mentioned above.

Values of the relative partial molal heat content have been calculated by Harned and Ehlers, and by Åkerlöf and Teare,[5] from their measurements of the temperature coefficient of the electromotive force of the cell

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

Harned and Ehlers measured this cell in the concentration range up to 4 molal, and reported values of $\bar{L}_2$ from infinite dilution up to this concentration. By graphical integration (counting squares, and checking the result with a planimeter) values of the apparent heat content have been calculated from their values of $\bar{L}_2$. These quantities are plotted in Fig. 1, and are seen to agree more closely with the present calorimetric values than do the earlier calorimetric data. This agreement is especially satisfactory when it is considered that an error of 1 microvolt per degree in the temperature coefficient of electromotive force causes an error of about 30 joules per mole in $\bar{L}_2$.

Harned and Ehler's values of $\bar{L}_2$ are compared with the present ones in Fig. 2. They show a maximum deviation, at 3 molal, of about 130 joules per mole, which is within the estimated accuracy of the e. m. f. measurements. It should be noted that the value obtained by Åkerlöf and Teare at this concentration shows a deviation of only about 60 joules per mole. Further comparison with their values is impossible since this is the lowest concentration at which they worked.

Summary

The heat of dilution of aqueous solutions of hydrogen chloride at 25° has been measured up to a concentration of 3.3 molal. From these data have been calculated the apparent and partial relative molal heat content of the solute, and the partial relative molal heat content of the solvent.

NEW HAVEN, CONN. RECEIVED DECEMBER 28, 1939

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[4] Doehlemann and Lange, "Landolt-Börnstein Tabellen," 5th edition, Ergänzungsband IIIc, p. 2800.

[5] Åkerlöf and Teare, THIS JOURNAL, **59**, 1855 (1937).