solutions has been calculated relative to its value in 0.01 M hydrobromic acid solution. These results have been expressed in a brief form by recording in Table V the constants of the equation

$$\overline{H} - \overline{H}_{0.01} = (\overline{H} - \overline{H}_{0.01})_0 + \alpha t + \beta t^2 \qquad (15)$$

$(\overline{H} - \overline{H}_{0.01})_0$, α and β are functions of E''_{25}, a'' and b'' of equation (2).

The range of validity of equation (15) is from 0 to 40°. In the intermediate range of temperatures, 5 to 35° inclusive, the accuracy is of the order of ±30 cal.

Summary

1. Measurements of the cells

$$H_2 \mid LiOH\ (0.01),\ LiBr\ (m) \mid AgBr - Ag$$
$$H_2 \mid HBr\ (0.01),\ LiBr\ (m) \mid AgBr - Ag$$

have been made at 5° intervals from 0 to 50° inclusive.

2. From these results, the ionization constant of water, the standard electromotive force of the silver–silver bromide electrode, the activity coefficient, the relative partial molal heat content of hydrobromic acid in lithium bromide solutions, the ionic activity coefficient product and heat of ionization of water in lithium bromide solutions have been computed.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

The Ionization of Acetic Acid in Aqueous Sodium Chloride Solutions from 0 to 40°

BY HERBERT S. HARNED AND F. C. HICKEY, O.P.[1]

Harned and Robinson[2] and Harned and Owen[3] have shown that the ionization constant and the actual ionization of an acid in a salt solution may be determined from electromotive force measurements of unbuffered cells without liquid junctions of the type

$$H_2 \mid HAc\ (M),\ MCl\ (m) \mid AgCl - Ag - AgCl \mid HCl\ (0.01) \mid H_2 \qquad (1)$$

Harned and Owen[3] developed the thermodynamic theory of these cells, the details of the computation, and applied the method to measurements at 25° of acetic acid in sodium chloride solutions, and of formic acid in potassium and sodium chloride solutions. Likewise, Harned and Murphy[4] investigated the ionization of acetic acid in sodium and potassium chloride solutions at 15, 25 and 35°.

Although these cells are the best for the determination of the ionization of the acid in salt solutions, they are not so suitable for the determination of ionization constants as the buffered type

$$H_2 \mid HAc\ (M),\ MAc\ (m),\ MCl\ (m) \mid AgCl - Ag \qquad (2)$$

From electromotive forces of the latter type, Harned and Ehlers[5,6] obtained accurate values of the ionization constant of acetic acid at temperatures from 0 to 60°. Since these values were at our disposal, we decided to make a more thorough and accurate investigation of aqueous acetic acid solutions containing sodium chloride. To this end, measurements of unbuffered cells were made with an improved technique from 0 to 40°, inclusive, at 5° intervals. The concentration of acetic acid was varied from 0.1 to 0.5 M and the salt concentration from 0.05 to 3 M. From these results, the ionization and activity coefficient of the acid in the salt solutions were determined, and the temperature variation of ionization at all salt concentrations investigated. Further, the heat of ionization of acetic acid and its variation as a function of salt concentration has been computed for the first time.

Experimental Results

Since the experimental procedure was essentially the same as that previously used by others,[5] a brief summary is sufficient. (1) A vacuum technique was employed which served to free all cell solutions from dissolved gases. The previous work with unbuffered cells was carried out with solutions containing some dissolved air. (2) All chemicals were purified carefully. (3) The acetic acid content of the solutions was known with an accuracy of ±0.1%. The sodium chloride content was known with considerably greater accuracy. (4) The hydrogen electrodes were of platinum foil type. The silver–silver

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(1) This contribution contains material from a dissertation presented by Frederick C. Hickey to the Graduate School of Yale University in partial fulfilment of the requirements for the Degree of Doctor of Philosophy, June, 1937.

(2) Harned and Robinson, THIS JOURNAL, **50**, 3157 (1928).

(3) Harned and Owen, *ibid.*, **52**, 5079 (1930).

(4) Harned and Murphy, *ibid.*, **53**, 8 (1931).

(5) Harned and Ehlers, *ibid.*, **54**, 1350 (1932).

(6) Harned and Ehlers, *ibid.*, **55**, 652 (1933).

chloride electrodes were prepared by baking silver oxide on platinum spirals. The silver chloride was formed on the silver thus produced by electrolysis. (5) Temperature control was ±0.02°. The thermometers employed were carefully calibrated against a standard resistance thermometer. (6) Three cells were measured at each concentration and temperature. (7) The electromotive forces were measured with an Eppley Feussner type potentiometer. Standard working cells were calibrated frequently against standard saturated Weston cells of Eppley manufacture.

At temperatures from 0 to 40°, inclusive, the reproducibility of the cell electromotive force was well within ±0.05 mv. Above 40°, a greater variation was observed and it was decided to let 40° terminate the temperature range. For purposes of brevity, we have expressed the great majority of the results by the equation

$$E = E_{20} + a(t - 20) + b(t - 20)^2 \qquad (3)$$

Values of E_{20}, a and b are given in Table I. Results in acetic acid solutions at 0.2 and 0.5 M, thus expressed, were determined at nine temperatures from 0 to 40°. In the last column of the table, $\Delta_{\text{ave.}}$ signifies the average magnitude of the deviations between the observed electromotive force and E calculated by equation (3). Since the maximum mean deviation is 0.025 mv., this equation is seen to represent the observed results adequately. In addition to these results, we have added to the table a brief series with 0.1 M acetic acid at 0 and 25°.

TABLE I

ELECTROMOTIVE FORCES OF CELLS

H_2 | HAc (M), NaCl (m) | AgCl − Ag

M	m	E_{20}	$a \times 10^6$	$b \times 10^6$	$\Delta_{\text{av.}}$, mv.
0.2007	0.05027	0.46432	203	−1.80	0.014
.2011	.10079	.44784	144	−1.60	.022
.2001	.20051	.43159	87	−1.50	.025
.2002	.30091	.42184	51	−1.66	.018
.2007	.50267	.40910	7.5	−1.57	.020
.2001	1.0022	.39054	− 63	−1.33	.020
.2002	2.0056	.36868	−144	−0.988	.012
.2011	3.0230	.35241	−199	− .820	.010
0.5222	0.05019	0.45110	158	−2.06	0.017
.5213	.10034	.43473	101	−1.80	.023
.5230	.20080	.41835	42.5	−1.90	.011
.5228	.30154	.40856	9.75	−1.61	.014
.5217	.50275	.39593	− 34.5	−1.57	.019
.5268	1.0445	.37612	−111.5	−1.45	.025
.5216	2.0055	.35545	−183	−0.90	.017
.5238	3.0119	.33943	−242	−1.15	.017
		E_0	E_{25}		
0.1004	0.10032	0.45297	0.45796		
.1004	.20073	.43768	.44121		
.1004	.30101	.42855	.43121		
.1003	.50152	.41684	.41832		

The electromotive force, E, of these cells is given by

$$E - E_r = \frac{RT}{F} \ln \frac{\gamma_r^2 m_r^2}{\gamma_H \gamma_{Cl} m_H m_{Cl}} \qquad (4)$$

where E_r is the electromotive force of the cell

$$H_2 \mid HCl\ (0.01) \mid AgCl - Ag$$

γ_r, m_r the activity coefficient and molality of the acid in the reference solution at 0.01 M, and γ_H, γ_{Cl}, m_H, m_{Cl} are the activity coefficients and molalities of the species denoted by subscripts in the solution containing acetic acid, sodium chloride and water. 8.314, 273.1 + t, and 96,500 were employed for R, T, and F, respectively. For E_r, 0.45780, 0.45943, 0.46084, 0.46207, 0.46319, 0.46419, 0.46499, 0.46565, and 0.46615 have been used at 0, 5, 10, 15, 20, 25, 30, 35 and 40°, respectively.[5,7] For γ_r, 0.903, 0.905, 0.905, 0.905, 0.904, 0.904, 0.904, 0.902, and 0.900 have been used at these temperatures.[8]

For the purpose of immediate discussion, employing the values of E_r and γ_r at 25° we shall write equation (4) in the following convenient form, in which the quantity, 2 log γ^0_{HCl}, has been added to both sides.

$$16.9062\,E - 3.7601 + \log m + 2 \log \gamma^0_{HCl} = -\log m_H - 2 \log \frac{\gamma_{HCl}}{\gamma^0_{HCl}} \qquad (5)$$

This is Harned and Owen's equation (2).

Method of Calculation of the Ionization, k_A

Harned and Owen[3] have developed in detail the method for the determination of the ionization of an acid in a salt solution from cells of type (1). γ^0_{HCl} is the activity coefficient of hydrochloric acid at zero molality in an aqueous salt solution of concentration m. γ_{HCl} is this quantity in a salt solution containing acetic acid at concentration M. γ^0_{HCl} may be obtained from the data of Mannweiler.[8] γ_{HCl} is not known but can be evaluated as described below. If we define an apparent hydrogen ion concentration, m'_H, by $m'_H = m_H \gamma^2_{HCl}/\gamma^{0\,2}_{HCl}$, then equation (5) becomes

$$16.9062\,E - 3.7601 + \log m + 2 \log \gamma^0_{HCl} = -\log m'_H \qquad (6)$$

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

[8] Mannweiler, Thesis, Yale University, 1934. The values of E used for computing this quantity are contained in the communication by Harned, THIS JOURNAL, **57**, 1865 (1935).

from which it is obvious that m'_H may be determined directly from the electromotive forces when γ^0_{HCl} is known. The thermodynamic ionization constant of the acid K_A, or $a_H a_{Ac}/a_{HAc}$, is related to other important quantities of the definitional equations by

$$K_A = \gamma^2_A k_A = \gamma'^2_A k'_A = \gamma^{02}_A k^0_A \tag{7}$$

in which k_A equals $m^2_H/M - m_H$, $k'_A = m'^2_H/M - m'_H$, $\gamma^2_A = \gamma_H\gamma_{Ac}/\gamma_{HAc}$ and $\gamma'^2_A = \gamma'_H\gamma'_{Ac}/\gamma'_{HAc}$. The reference value is such that $K_A = k_A = k^0_A$ when $M = 0$, and $m = 0$, or when $\gamma_A = \gamma^0_A = 1$. From the cell measurement, m'_H and subsequently k'_A are determined directly. If M is maintained constant, k'_A will not equal K_A but will equal k^0_A at zero salt concentration. At a given salt concentration, k'_A will equal k_A when $M = 0$. These matters have been discussed carefully by Harned and Owen.

These cells are most useful for determining k_A. By extrapolating to zero acetic acid at a given salt concentration we may determine the value of the ionization $m^2_H/M - m_H$ of the acid in the salt solution. By extrapolating to zero acetic acid and zero salt, the ionization constant, K_A, can be evaluated but not so well as by means of the buffered cell. The medium effect of acetic acid molecules upon the activity coefficient of hydrochloric acid relative to its value in pure water also may be evaluated.

For purposes of extrapolating to zero salt concentration, we have employed the equation of Debye and Hückel, which includes the apparent ionic diameter, a refinement of the procedure of Harned and Owen. Following the method by which Harned and Owen derived their equation (13), we obtain

$$\log k'_A - \frac{2u\sqrt{\mu'}}{1 + A\sqrt{2\mu'}} = \left(\log k^0_A + 2\log\gamma^0_A + 2\log\frac{\gamma_A}{\gamma'_A}\right) - 2B\mu' \tag{8}$$

As the apparent ionic strength μ' approaches zero, γ_A approaches unity, γ'_A approaches γ^0_A, and therefore the expression on the left of the equation equals $\log k^0_A$ at zero ionic strength. A plot of the left side of this equation against μ' will lead to the evaluation of all the important quantities derivable from these cell measurements when combined with the values of the ionization constant, K_A, determined by Harned and Ehlers.[5,6]

To evaluate the left side of equation (8), it is first necessary to determine m'_H by equation (6). Since the cell contains both acetic acid and sodium chloride, γ^0_{HCl} is the activity coefficient of hydrochloric acid at a very low concentration (0.001 M) in sodium chloride solutions of a given concentration. Mannweiler[8] has determined the activity coefficient of this acid at 0.01 M in salt solutions of strengths from 0 to 3 M, and at the desired temperatures. These results have been corrected so that they apply to hydrochloric acid solutions of lower concentrations by subtracting 0.001 from the activity coefficient of the acid. This is in accord with the known behavior of these mixtures at constant total molality.[8,9] A large scale plot of these corrected values of log γ^0_{HCl} against μ was drawn. A preliminary value of m'_H led to an approximate value of μ' by which an approximate value of log γ^0_{HCl} was read from the plot. This value upon substitution in equation (6) led to a more accurate value of m'_H. By repeating, the correct value of m'_H was determined, usually in one or two trials. k'_A was then computed.

The constant A of equation (8) which is a function of the apparent ionic diameter, a, was determined by plotting the left of equation (8) with various assumed values of a from 4.0 to 4.6 Å., and the values of u and K' tabulated by Harned and Ehlers.[7] The value of 4.3 Å. gave a straight line extrapolation from 3 M to 0.

The plots of the negative of the left side of equation (8) at 0, 25, and 40° are shown in Fig. 1. First, we note that throughout the entire range of salt concentration, 0 to 3 M, the graphs are straight lines. Further, the graphs of the 0.2 and 0.5 M series are parallel at each temperature. The intercepts at zero μ' are the values of $-\log k^0_A$ (eq. 8) which refer to zero concentration of all ions but at designated concentrations of undissociated acetic acid molecules, $M - m_H$.

The values of $-\log k^0_A$ at a given temperature were plotted against the concentration of the undissociated acetic acid molecules. The point at zero $M - m_H$ is the negative of the logarithm of the ionization constant at that temperature. Our values of k^0_A have not been used to determine this constant but the graphs were drawn to values obtained from the buffered cells (2) by Harned and Ehlers.[6] These graphs were found to be linear, or nearly so. At the higher temperatures (20 to 40° inclusive), they were linear. At temperatures below 20°, an increasing cur-

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(9) Harned, THIS JOURNAL, **48**, 326 (1926).

vature was noted as the temperature decreased, with a maximum at 0°. Harned and Owen[3] found this linear variation at 25° and used as a measure of this medium effect the quantity, S, in the equation which expresses the variation of k^0_A, namely

$$2\,(M - m_H)\,S = \log k^0_A/K_A \qquad (9)$$

At 25°, our value of S is 0.053 which agrees well with the value of 0.047 obtained by Harned and Owen from data at higher acetic acid concentrations.

We may now compute k_A, the ionization of the acid at zero concentration in a salt solution of ionic strength, μ. From the plots in Fig. 1 (large scale), the slope of the parallel lines was determined at each temperature, and a parallel line (the dotted lines in Fig. 1) was drawn from the value of $-\log K_A$, as taken from Harned and Ehlers' ionization constants, at zero μ to 3.01 μ. These lines represent the values of $-\log k_A + 2u\sqrt{\mu}/(1 + A\sqrt{2\mu})$ which were read off the plots at convenient round concentrations of μ. From these, values of k_A were computed. We recall that $k_A = m^2_H/M - m_H$ at zero acetic acid concentration in a salt solution of the designated concentration. From equation (7)

$$K_A = \gamma^2_A\, k_A \qquad (7)$$

whence from our knowledge of K_A (Harned and Ehlers) and k_A, γ^2_A or $\gamma_H\gamma_{Ac}/\gamma_{HAc}$ may be calculated.

As previously pointed out, this method accomplishes the important task of separating ionization constants into two parts, one of which includes the actual molalities of the ionic species present and the other the activity coefficients which retain their usual practical and theoretical significance.

The Ionization, k_A, and its Variation with Temperature in Sodium Chloride Solutions.—Harned and Embree[10] have shown that the ionization constants of weak uniunivalent electrolytes in aqueous solution may be expressed, as functions of temperature, by the equation

$$\log K - \log K_m = -p(t - \theta)^2 \qquad (10)$$

in which K_m is the maximum value of K at a temperature θ, and p is a constant equal to 5×10^{-5} deg.$^{-2}$. They[11] showed that this relation was also valid for the ionization constant of acetic acid in 10 and 20% methyl alcohol solutions. Further, Harned and Kazanjian[12] have proved the validity of equation (10) for the ionization constant of acetic acid in 20, 45, and 70% dioxane-water mixtures. The present values of k_A are sufficient to show that the relation is adequate to express the variation of the ionization of acetic acid in sodium chloride solutions.

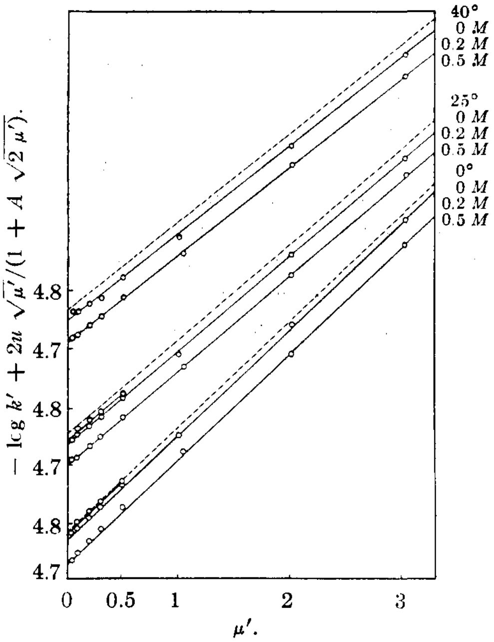

Fig. 1.—Plots of negative of left side of eq. 8 *vs.* μ'.

Values of $k_{A(m)}$ and θ, evaluated by the graphical method described by Harned and Embree,[10] are given in Table II. In the last column the average deviations between observed values of $\log k_A$ and those calculated are given. From the magnitude of these deviations, it is clear that the results are represented adequately by the equation. We note that the temperature of the maximum of

TABLE II

CONSTANTS OF THE EQUATION

$\log k_A - \log k_{A(m)} = -p(t - \theta)^2$; $p = 5 \times 10^{-5}$ [a]

μ	$-\log k_{A(m)}$	θ	$\Delta_{av.}$
0.00	4.7544	22.6	0.0009
.02	4.6388	25.1	.0007
.03	4.6189	25.6	.0007
.06	4.5798	26.4	.0007
.11	4.5432	27.6	.0009
.21	4.5061	29.2	.0011
.51	4.4752	32.3	.0009
1.01	4.4957	35.7	.0012
2.01	4.5875	45.0	.0029
3.01	4.7132	50.9	.0038

[a] Since $k_A = K$ when $\mu = 0$, this equation equals equation (10) when $\mu = 0$.

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(10) Harned and Embree, THIS JOURNAL, **56**, 1050 (1934).

(11) Harned and Embree, *ibid.*, **57**, 1669 (1935).

(12) Harned and Kazanjian, *ibid.*, **58**, 1924 (1936).

the ionization, θ, increases with salt concentration, a fact which we shall show is linked with the behavior of the relative partial molal heat content of the ions.

Since both K_A and k_A from 0 to 40°, inclusive, may be computed by the equation, and since $K_A = \gamma_A^2 k_A$, γ_A may be computed when desired. This is a brief and convenient way of expressing all the results. Since the values of k_A involve the combined errors of our measurements and those of the activity coefficients of hydrochloric acid in salt solutions derived from the measurements of Mannweiler, as well as the approximation introduced by the use of the equation of Harned and Embree, it is difficult to estimate their accuracy. An approximate estimate indicates that k_A is given with an error less than $\pm 0.5\%$ and, therefore, log k_A is known within ± 0.002.

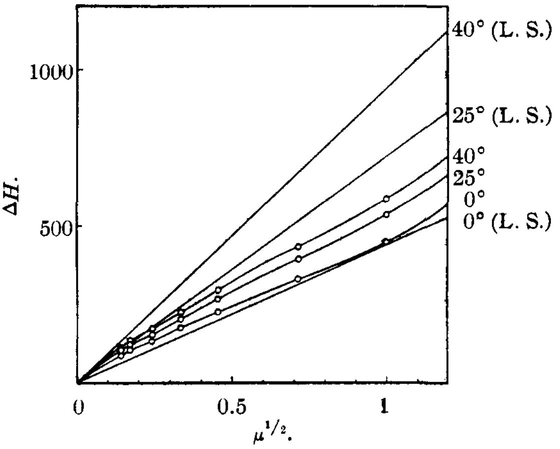

Fig. 2.—Plots of $\Delta\overline{H}$ *vs.* $\mu^{1/2}$.

An Estimate of the Heat of Ionization of Acetic Acid in Sodium Chloride Solutions.—Upon substitution of the expression for log K given by equation (10) in

$$\partial \ln K/\partial T = \Delta H/RT^2 \qquad (11)$$

we obtain

$$\Delta H = -4575 \times 10^{-4}T^2(t - \theta) \qquad (12)$$

for the heat content of ionization of acetic acid. This quantity is made up of two parts, ΔH_i, the usual heat content of ionization at zero ionic strength, and $\Delta\overline{H}$, the sum of the relative partial molal heat contents of the hydrogen and acetate ions in the salt solutions. Thus

$$\Delta H = \Delta H_i + \Delta\overline{H} \qquad (13)$$

Since these quantities may be computed easily by means of equation (12) and the values of θ in Table II, no table of the results is given. However, in Fig. 2, $\Delta\overline{H}$ is plotted *versus* $\mu^{1/2}$ at 0, 25, 40°. The actual values of ΔH_i are 771, −97, and −780 cal. at these temperatures, respectively. The straight lines (designated L. S.) in the figure are the plots of the limiting law for the variation of the relative partial molal heat content, $\Delta\overline{H}_i$, of the ions, derived from the theory of Debye and Hückel. The actual results are similar to those obtained in the cases of relative heat content of hydrochloric or hydrobromic acids in their corresponding halide solutions.

It is well known that the estimation of ΔH from equilibrium data is subject to large errors. From equation (12), it follows that an error in the estimation of θ of 1° causes an error in ΔH of 34 cal. at 0° and 45 cal. at 40°. In the intermediate range of temperature (10 to 30°) where the values are probably the more accurate, the error should not be greater than ± 50 cal. in the estimation of ΔH and probably less than this in the estimation of $\Delta\overline{H}$. Only a rough estimate of the specific heat is possible. ΔC_p of the ionization reaction derived from the values of ΔH_i is found to be 31, 41, and 47 cal. at 0, 25 and 40°, respectively. The relative partial molal heat capacity of the hydrogen and acetate ions is found to be 4 cal. at 1 M sodium chloride concentration, which seems of the right order of magnitude, since acids like hydrochloric or hydrobromic have values of this quantity of the order of 6–8 cal. at this concentration.

Summary

1. Accurate measurements of the electromotive forces of the cells

$$H_2 \mid HAc\ (M),\ NaCl\ (m) \mid AgCl - Ag$$

at 0.2 and 0.5 M acetic acid, at salt concentrations varying from 0.05 to 3 M, and from 0 to 40° at 5° temperature intervals have been made.

2. By using a modification of the method of extrapolation of Harned and Owen,[3] values of the ionization of acetic acid, k_A or $m_H^2/M - m_H$, in the salt solutions have been computed as well as values of the activity coefficient $\gamma_H\gamma_{Ac}/\gamma_{HAc}$.

3. The ionization, k_A, possesses a maximum at a certain temperature and its variation with temperature conforms with the equation of Harned and Embree.[10]

4. Reasonable values for the total heat of ionization of acetic acid and the relative partial molal heat content of its ions in salt solutions were obtained.

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