solutions studied mainly as the chloropalladite ion, $PdCl_4^=$.

3. For the half-cell reaction $Pd(s) + 4Cl^-(1\ f) = PdCl_4^= (1 - 4\,f\ HCl) + 2e^-$, the formal potential $E^{0'''}$ at 25° was found to be related to the ionic strength μ by the equation $E^{0'''} = -0.6290 + 0.0080\mu$, $1.0 < \mu < 4.0$, with a temperature coefficient of +0.00046 volt/degree. Related thermodynamic constants have been presented.

4. The potentials have also been measured in perchloric acid solution in the absence of chloride ion. For the half-cell reaction $Pd(s) = Pd^{II}$ $(4.00\ f\ HClO_4) + 2e^-$, the formal potential $E^{0''}$ has been calculated to have the value -0.987 volt at 25°. An approximate value of 6×10^{-14} has been obtained for the dissociation constant of the chloropalladite anion at 25°.

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[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

The Effect of Sodium Chloride upon the Ionization of Boric Acid at Various Temperatures[1]

BY BENTON BROOKS OWEN AND EDWARD J. KING[2]

The exact determination of the effects of neutral salts upon the ionization of weak electrolytes is important, but involves so much labor that only formic,[3] acetic[3,4] and lactic[5] acids have been investigated by the thermodynamic method proposed by Harned and Owen.[3,4] This method made use of unbuffered cells of the type

$$H_2 \mid HA\ (m_1),\ NaCl\ (m_2) \mid AgCl,\ Ag \qquad \text{I}$$

and required a difficult extrapolation. In the present study of boric acid, buffered solutions have been used to increase the accuracy, and the method has been radically altered so as to simplify the extrapolation. In describing the method and treating the experimental results, it will be convenient to employ sodium chloride solutions instead of pure water, in defining standard states. Thus the activity coefficient of any solute at infinite dilution in an M-molal sodium chloride solution is unity. This device will receive particular attention because it will expedite the calculations in future studies of this nature, and has already proved useful in elucidating the effect of pressure[6] upon ionic equilibria in salt solutions.

Outline of the Method.—The cell used in this investigation can be represented by

$$H_2 \mid HBO_2\ (m),\ NaBO_2\ (m),\ NaCl\ (M - m) \mid AgCl,\ Ag \qquad \text{II}$$

where m and M are concentrations in moles per kilogram of water. The stoichiometric ratio of boric acid to sodium metaborate is always unity. The total molality of the solutions used in a series of cells is kept constant (M), because variations in ionic strength may introduce considerable curvature[7] in the extrapolation. The electro-chemical equation for this cell will be written in the form

$$E_{II} = E^{0*} - k \log m_H m_{Cl} - k \log \overset{*}{\gamma}_H \overset{*}{\gamma}_{Cl} \qquad (1)$$

where the factor k equals $0.00019844\ T$, and *the asterisk indicates that the standard state is chosen so that the activity coefficients are unity at infinite dilution ($m = 0$) in a sodium chloride solution of concentration, M.* E^{0*} is therefore given by the limit

$$E^{0*} = [E_{II} + k \log m_H m_{Cl}]_{0,M} \qquad (2)$$

in which the double subscript (0, M) refers, in order, to the value of m and to the sodium chloride concentration.

According to this same convention, the ionization constant of boric acid in an M-molal salt solution is written

$$K^* = \frac{\overset{*}{\gamma}_H \overset{*}{\gamma}_{BO_2}}{\overset{*}{\gamma}_{HBO_2}} \frac{m_H m_{BO_2}}{m_{HBO_2}} = \left[\frac{m_H m_{BO_2}}{m_{HBO_2}}\right]_{0,M} \qquad (3)$$

Eliminating $\overset{*}{\gamma}_H m_H$ between equations (1) and (3) and rearranging terms, we obtain

$$[E_{II} - E^{0*} + k \log m_{Cl} + k \log \rho] = -k \log K^* - k \log \frac{\overset{*}{\gamma}_{Cl} \overset{*}{\gamma}_{HBO_2}}{\overset{*}{\gamma}_{BO_2}} \qquad (4)$$

where ρ is the buffer ratio, m_{HBO_2}/m_{BO_2}. K^* is readily evaluated by extrapolation, since

$$-k \log K^* = [E_{II} - E^{0*} + k \log m_{Cl} + k \log \rho]_{0,M} \qquad (5)$$

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(1) This communication contains material from a thesis presented by Edward J. King to the Graduate School of Yale University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1942.

(2) Allied Chemical and Dye Corporation Fellow 1941–1942.

(3) H. S. Harned and B. B. Owen, THIS JOURNAL, **52**, 5079 (1930).

(4) H. S. Harned and P. C. Hickey, *ibid.*, **59**, 1284 (1937).

(5) F. C. Hickey, *ibid.*, **62**, 2916 (1940).

(6) B. B. Owen and S. R. Brinkley, Jr., *Chem. Rev.*, **29**, 461 (1941).

(7) B. B. Owen and S. R. Brinkley, Jr., THIS JOURNAL, **64**, 2071 (1942); *cf.* p. 2074 *et seq*

Given the values of E^{0*} recorded in the next section, the determination of K^* in salt solutions is formally similar to the determination of K in pure water.[8] The most important difference concerns the practical details of performing the extrapolation. Thus in pure water as the standard reference medium

$$-k \log K = [E_{\mathrm{II}} - E^0 + k \log m_{\mathrm{Cl}} + k \log \rho]_{0,M} \quad (6)$$

and the limit is evaluated by extrapolation of values of the bracketed terms at various ionic strengths to the limit, $\mu = 0$, in a manner suggested by the Debye–Hückel equation. On the other hand, the limit in equation (5) corresponds to a finite ionic strength, $\mu = M$, and the extrapolation is performed against m at a constant value of M. This procedure is suggested by the behavior of certain electrolytes in mixtures as represented by equation (9). Figure 2 illustrates the extrapolation at constant M. All of the plots are practically linear below $m = 0.02$, regardless of the value of M.

An alternate evaluation of log K^* is based upon the determination of

$$-k \log K' \equiv -k \log K^* - [k \log \gamma_{\mathrm{H}}\gamma_{\mathrm{Cl}}]_{0,M} = [E_{\mathrm{II}} - E^0 + k \log m_{\mathrm{Cl}} + k \log \rho]_{0,M} \quad (6a)$$

by extrapolation. Combination of this expression with equations (5) and (8) leads to

$$\log K^* = \log K' - [\log \gamma_{\mathrm{H}}\gamma_{\mathrm{Cl}}]_{0,M} \quad (6b)$$

Thus log K^* can be obtained from the values of E^0 and $[\log \gamma_{\mathrm{H}}\gamma_{\mathrm{Cl}}]_{0,M}$ instead of E^{0*}. Log K' may be smoothed graphically against M, and if the value in pure water is not known, it may be obtained very simply by extrapolation to $M = 0$. This would often be an important practical consideration, but since the ionization constant of boric acid has been directly measured in pure water,[8] no extrapolation to $M = 0$ is necessary in the present research.

For purposes of exposition we have chosen to evaluate log K^* directly by equation (5) to emphasize the analogy with equation (6), and to focus attention upon the new standard state at the very beginning. This will bring out some interesting thermodynamic relationships, and indicate the general utility of the new standard states.

Evaluation of E^{0*}.—If the electromotive force of cell II is expressed in the conventional manner in terms of activity coefficients referred to unity at infinite dilution in pure water, we obtain

$$E^0 = [E_{\mathrm{II}} + k \log m_{\mathrm{H}} m_{\mathrm{Cl}} + k \log \gamma_{\mathrm{H}}\gamma_{\mathrm{Cl}}]_{0,M} \quad (7)$$

in the limit when $m \rightarrow 0$. Subtraction of this relation from equation (2) yields

$$E^{0*} = E^0 - [k \log \gamma_{\mathrm{H}}\gamma_{\mathrm{Cl}}]_{0,M} \quad (8)$$

Since E^0 is known[9] over the range 0 to 60°, the evaluation of E^{0*} reduces to the determination of $[k \log \gamma_{\mathrm{H}}\gamma_{\mathrm{Cl}}]_{0,M}$.

For this purpose we use the cell

$$\mathrm{H_2} \mid \mathrm{HCl}\ (m_1),\ \mathrm{NaCl}\ (M - m_1) \mid \mathrm{AgCl,\ Ag} \quad \mathrm{III}$$

Mannweiler[10] investigated cells of this type in which m_1 was 0.01, and $M - m_1$ varied from 0.01 to 3 molal. The temperature range was 0 to 60°. It has been shown repeatedly[11,12] that if M is kept constant

$$[\log \gamma_{\mathrm{H}}\gamma_{\mathrm{Cl}}]_{0,M} = [\log \gamma_{\mathrm{H}}\gamma_{\mathrm{Cl}}]_{m_1,(M-m_1)} - 2m_1\alpha_1 \quad (9)$$

where α_1 is a function of M and T, but not of m_1. If all of the activity coefficients in this equation are now referred to unity in an M-molal sodium chloride solution, the left-hand member becomes zero, and the equation reduces to

$$[\log \overset{*}{\gamma}_{\mathrm{H}}\overset{*}{\gamma}_{\mathrm{Cl}}]_{m_1,(M-m_1)} = 2m_1\alpha_1 \quad (10)$$

Combination of equation (10) with the expression

$$E_{\mathrm{III}} = E^{0*} - k \log m_1 M - k \log \overset{*}{\gamma}_{\mathrm{H}}\overset{*}{\gamma}_{\mathrm{Cl}} \quad (11)$$

for the e. m. f. of cell III, in terms of the new standard state, leads to the relation

$$E^{0*} = E_{\mathrm{III}} + k \log m_1 M + 2km_1\alpha_1 \quad (12)$$

which we employ to evaluate E^{0*}. Harned[13] has estimated α_1 from the measurements of Mannweiler[10] and Ehlers[9] within the range 0 to 40°, and 0.1 to 3 molal. We have completed the calculations at other temperatures. In estimating α_1 at values of M below 0.10, where experimental data are lacking, we used an extrapolation of log α_1 against log M which is practically linear in dilute solutions.[14]

The "experimental" values of E^{0*}, calculated from equation (12), can be expressed as a quadratic function of the temperature at each value of M. Thus

$$E^{0*} = E^{0*}_{25} + a^{0*}(t - 25) + b^{0*}(t - 25)^2 \quad (13)$$

The similar equations

$$E^0 = E^{\,0}_{25} + a^0(t - 25) + b^0(t - 25)^2 \quad (14)$$

$$E_{\mathrm{III}} = E_{\mathrm{III}(25)} + a_{\mathrm{III}}(t - 25) + b_{\mathrm{III}}(t - 25)^2 \quad (15)$$

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(8) B. B. Owen, THIS JOURNAL, **56**, 1695 (1934).

(9) H. S. Harned and R. W. Ehlers, *ibid.*, **55**, 2179 (1933).

(10) G. E. Mannweiler, Dissertation, Yale University, 1934.

(11) E. Güntelberg, *Z. physik. Chem.*, **123**, 199 (1926).

(12) H. S. Harned, THIS JOURNAL, **48**, 326 (1926); see ref. 13 for bibliography.

(13) H. S. Harned, *ibid.*, **57**, 1865 (1935).

(14) Whether this plot should become parallel to the log M axis within the range $0.1 \geq M \geq 0.01$ need not concern us at this point, as the maximum uncertainty that this could produce in the estimation of $2km_1\alpha_1$ is of the order of 0.02 mv. when $M = 0.02$.

have been used[9,13] to express E^0 and E_{III} over the same temperature range. The values of E^{0*}_{25}, a^{0*} and b^{0*} recorded in Table I have been smoothed against M as explained below.

TABLE I

PARAMETERS OF EQUATION (13)

M	E^{0*}_{25}	$-a^{0*} \times 10^4$	$-b^{0*} \times 10^6$
0	0.22239	6.40	3.18
0.02	.22928	6.09	2.96
.07	.23331	5.86	2.85
.16	.23624	5.69	2.79
.25	.23759	5.61	2.75
.36	.23839	5.56	2.71
.50	.23869	5.52	2.67
.725	.23829	5.49	2.60
1.00	.23701	5.47	2.50
1.25	.23542	5.46	2.38
1.50	.23355	5.46	2.26
2.00	.22925	5.47	2.01
2.50	.22446	5.48	1.75
3.00	.21929	5.50	1.50

The "experimental" values of E^{0*}_{25} were represented by the equation

$$E^{0*}_{25} = 0.22239 + \frac{0.05984\sqrt{M}}{1 + 1.35\sqrt{M}} - 0.01242M - 0.000240M^2 + 0.1183 \log (1 + 0.036M) \quad (16)$$

which conforms to the requirements of equation (8). The agreement between experimental values and those calculated by equation (16) is ±0.04 mv. on the average, with a maximum difference of 0.11 mv. at $M = 0.02$.

The values of a^{0*} and b^{0*} in Table I were read from large-scale plots of the values derived from equation (13) against $\sqrt{M}$. These plots are illustrated in Fig. 1. The intercepts are the values[9] of a^0 and b^0, because equation (13) reduces to equation (14) when $M = 0$. The limiting slopes for $a^{0*} - a^0$ and $b^{0*} - b^0$ were calculated from the Debye–Hückel theory, and are represented by broken lines in the figures. Thus, by equating the values of $\partial(E^{0*} - E^0)/\partial T$ derived from equations (13), (14) and (8), at 25° we obtain

$$a^{0*} - a^0 = -\frac{\partial[k \log \gamma_{\mathrm{H}}\gamma_{\mathrm{Cl}}]_{0.M}}{\partial T} = \frac{\bar{S}^{0*} - \bar{S}^0}{\mathbf{F}} \quad (17)$$

Similarly the second derivative $\partial^2(E^{0*} - E^0)/\partial T^2$ yields

$$b^{0*} - b^0 = -\frac{\partial^2[k \log \gamma_{\mathrm{H}}\gamma_{\mathrm{Cl}}]_{0.M}}{\partial T^2} = \frac{\bar{C}_p^{0*} - \bar{C}_p^0}{2\mathbf{F}T} \quad (18)$$

These last two equations show that $a^{0*} - a^0$ and $b^{0*} - b^0$ are proportional to ΔS and ΔC_p for the transfer of one mole of hydrochloric acid from infinite dilution in pure water to infinite dilution in an M-molal sodium chloride solution.

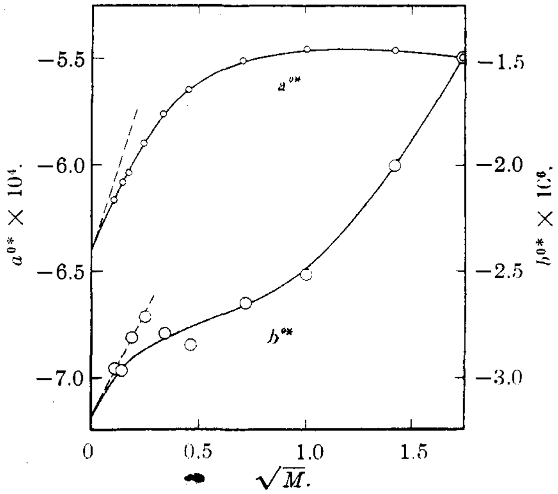

Fig. 1.—Graphical smoothing of the parameters a^{0*} and b^{0*}.

Equation (18) and the relation[15]

$$b^{0*} = b_{\mathrm{III}} + m_1 \frac{\partial^2(k\alpha_1)}{\partial T^2} \quad (19)$$

which is derived from equations (12), (13) and (15), served as a guide in determining the proper shape of the b^{0*} curve in Fig. 1 at the lower values of M. Although the smoothing of b^{0*} was drastic, it has a negligible effect upon the agreement between the "experimental" values of E^{0*} and those calculated by equation (13). Comparisons made at each temperature and experimental concentration showed an average discrepancy of ±0.03 mv., and a maximum of 0.25 mv. Discrepancies greater than 0.1 mv. were observed in less than 2% of the comparisons. The parameters in Table I therefore yield a self-consistent series of values of E^{0*} which are almost comparable in accuracy to the values of E^0 upon which they are based.[9]

Experimental

All solutions were made up on a (vac.) weight basis from distilled water and purified borax and sodium chloride. The borax was stored over a saturated solution of sucrose and sodium chloride[16,17] so that it could be weighed as the decahydrate. The sodium chloride was heated over-

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[15] The second derivative of $k\alpha_1$ is independent of T when $M > 0.1$, but appears to vary with T at lower values of M. This variation, if real, indicates an incompatibility between equations (13) and (15), but this point cannot be decided by the data at hand because the factor m_1 ($\leq M$) renders the term negligible compared to b_{III} when $0.1 \geq M$.

[16] H. Menzel, *Z. anorg. allgem. Chem.*, **224**, 1 (1935).

[17] F. H. Hurley, *Ind. Eng. Chem., Anal. Ed.*, **9**, 237 (1937).

TABLE II

PARAMETERS OF EQUATION (20)

$m \times 10^3$	$a_{II} \times 10^5$	$b_{11} \times 10^7$	$E_{II(25)}$	$a_{11} \times 10^5$	$b_{11} \times 10^7$	$E_{11(25)}$	$a_{11} \times Z0^5$	$b_{II} \times 10^7$	$E_{II(25)}$
		$M = 3$			$M = 2$			$M = 1.25$	
5	59.83	−10.21	0.71293	64.38	−8.08	0.73170	68.24	−9.44	0.75023
7.5	59.83	− 9.97	.71310	64.80	−9.04	.73178	68.40[h]	−9.20[h]	.75050[h]
10	60.03	− 9.78	.71322	64.23	−6.96	.73193	68.06	−8.81	.75056
15	59.94	− 9.21	.71342	64.57	−9.90	.73229	68.53	−6.78	.75093
20	59.91	− 8.61	.71364	64.20	−6.73	.73244	68.47	−6.36	.75125
30	58.98	− 8.57	.71422	63.99	−8.16	.73306	67.85	−4.95	.75193
		$M = 0.725$			$M = 0.36$			$M = 0.07$	
5	72.63	− 7.27	0.76920	78.93	−5.21	0.79095	92.78	−1.76	0.83793
7.5	73.14	− 6.39	.76949	79.20	−3.20	.79129	93.12	−0.84	.83910
10	73.32	− 4.84	.76966	79.33	−2.22	.79157	94.02	−0.59	.84023
15	73.16[h]	− 3.20[h]	.77001[h]	79.52	−1.79	.79216	94.35	+0.55	.84272
20	72.89	− 2.46	.77036	79.39	−0.36	.79267	94.90	+1.02	.84534
30	72.50	− 2.15	.77122	78.70	+1.97	.79391	96.26	+2.98	.85156
		$M = 0.02$				$m \times 10^3$		$M = 0.02$	
1	98.40	−16.2	0.86907			5	105.4[l]	−0.5[l]	0.87643[l]
2	102.8[l]	0.0[l]	.87125[l]			7.5	107.28	+1.25	.88115
3.5	103.74	− 3.5	.87378			10	109.22	+1.48	.88704

[l] Low temperature series only (5 to 25°). [h] High temperature series only (25 to 55°).

night at 400° after preliminary drying below 140°. The purity of both salts was checked by comparing the electromotive forces of cells containing them, in turn, with those of duplicate cells containing more elaborately purified salts used in an earlier research.[8] The agreement was excellent (±0.01 mv.).

The hydrogen and silver–silver chloride electrodes were similar to those used previously[8] in both preparation and quality of materials. The manipulation of the cells and cell solutions insured exclusion of oxygen, and at concentrations above 1.25 molal diffusion of dissolved silver chloride to the hydrogen electrode was minimized by constricting the connection between the two electrode compartments. The thermometers were recently calibrated against a platinum resistance thermometer certified by the Bureau of Standards.

In correcting the electromotive forces to a hydrogen pressure of one atmosphere, the vapor pressures of M-molal sodium chloride solutions[18] were used. Borax was assumed to produce the same vapor pressure lowering per equivalent as sodium chloride. The small errors due to this simplification are eliminated by the extrapolation. Corrections of readings to exact, prescribed, temperatures and ionic strengths rarely exceeded 0.05 mv., and could not introduce appreciable errors. The average difference between the corrected readings of duplicate cells was about 0.04 mv.

The temperature range was covered by two independently prepared series of cells in the following orders: low temperature series, 25, 5, 10, 15, 20 and 25°; high temperature series, 25, 30, 35, 40, 45, 50, 55 and 25°. This return to the initial temperature (25°) brought out the fact that cells in which M exceeded unity were unreliable at high temperatures unless the connection between the two electrode compartments was constricted to prevent diffusion of the complex silver chloride ion. This constriction was used in the measurements at $M = 2$ and $M = 3$, and proved to be unnecessary at $M = 0.725$. Unfortunately the measurements at $M = 1.25$ were made before the need for a constriction was recognized, and the results at this concentration are probably 0.1, 0.2 and 0.3 mv. too low at 45, 50 and 55°. This circumstance has been taken into account in plotting ionization constants and derived quantities against M at 45 to 55°.

The observed electromotive forces[19] are too numerous to be recorded here, but at any given value of M they are satisfactorily represented by the equation

$$E_{II} = E_{11(25)} + a_{II}(t - 25) + b_{11}(t - 25)^2 \quad (20)$$

for which the parameters are given in Table II. The average discrepancy between observed electromotive forces and those given by equation

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(18) "International Critical Tables," McGraw-Hill Book Co., New York, N. Y., 1928, Vol. III, p. 370.

(19) See Dissertation, ref. 1.

TABLE III

OBSERVED VALUES OF $-\log K^*$ FOR BORIC ACID IN M-MOLAL SODIUM CHLORIDE SOLUTIONS

t	M = 0.00[a]	0.02	0.07	0.36	0.725	1.25	2.00	3.00
5	9.440	9.3188	9.2370	9.0888	9.0248	8.9856	8.9759	9.0056
10	9.3800	9.2601	9.1799	9.0326	8.9716	8.9329	8.9257	8.9556
15	9.3265	9.2065	9.1252	8.9808	8.9212	8.8842	8.8781	8.9080
20	9.2795	9.1583	9.0768	8.9329	8.8758	8.8388	8.8344	8.8633
25	9.2365	9.1149	9.0338	8.8901	8.8316	8.7977	8.7927	8.8213
30	9.1975	9.0744	8.9931	8.8504	8.7914	8.7578	8.7517	8.7786
35	9.164	9.0410	8.9572	8.8131	8.7554	8.7203	8.7140	8.7388
40	9.1320	9.0065	8.9240	8.7817	8.7212	8.6854	8.6774	8.7000
45	....	8.9774	8.8942	8.7500	8.6908	8.6532	8.6457	8.6642
50	9.080	8.9514	8.8679	8.7224	8.6622	8.6225	8.6153	8.6304
55	....	8.9290	8.8439	8.6982	8.6364	8.5942	8.5856	8.5972

[a] When the results in this column are expressed to five figures, they represent the average obtained in two independent series of measurements.[8]

(20) is 0.03_4 mv., and only 5.7% of them exceed 0.1 mv. In all calculations made in this paper the observed values are used exclusively.

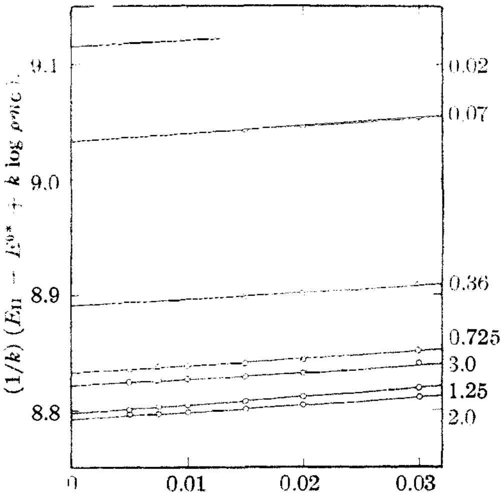

Fig. 2.—Evaluation of $-\log K^*$ for various values of M at 25°. Diameters of circles represent 0.3 mv.

Calculation of K^*.—The evaluation of K^*, according to equation (5), differs slightly from the procedure[8] by which K is determined in pure water. In the first place, the buffer ratio

$$\rho = (m + m_{OH})/(m - m_{OH}) \qquad (21)$$

requires the estimation of m_{OH} in various *salt solutions*. Neglecting activity coefficients where m_{OH} is small compared to m, m_{OH} is given with sufficient accuracy by

$$m_{OH} \simeq K_w^*/K^* \qquad (21a)$$

K^* is obtained by successive approximations.[8] Values of K_w^*, the ionization constant of water in an M-molal sodium chloride solution, can be calculated from the results of Harned and Mannweiler.[20] In the second place, the extrapolations for K^* illustrated in Figs. 2 and 3 are made at constant M, which in this case ensures practical constancy of the ionic strength.

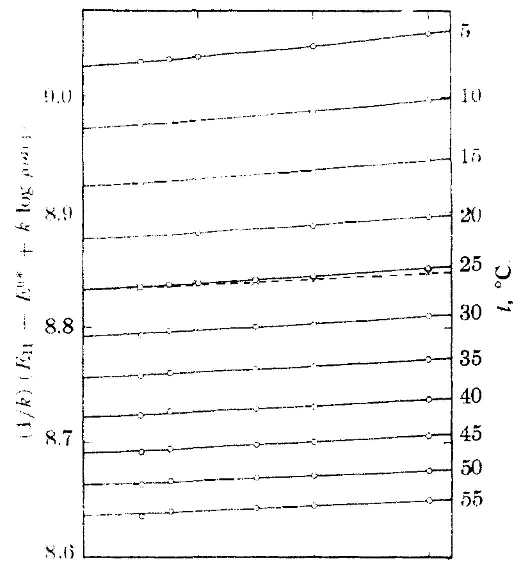

Fig. 3.—Evaluation of $-\log K^*$ for M = 0.725 at various temperatures. Diameters of circles represent 0.3 mv.

In Fig. 3, the lower curve at 25° (broken line and crosses) represents a series of measurements in which the sodium chloride concentration ($M - m$), rather than M, was kept constant. Both curves at 25° lead to practically the same intercept, and are very similar[21] in all respects, because activity coefficients vary very little when $\mu \simeq$

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[20] H. S. Harned and G. E. Mannweiler, THIS JOURNAL, **55**, 2194 (1933). K_w^* is the ratio of the values of K_w and $\gamma_H\gamma_{OH}/a_{H_2O}$ given in Table II of their paper. Compare equation (24).

[21] Although the difference is trivial in this case, it is usually more satisfactory to extrapolate at constant ionic strength than at constant sodium chloride concentration; see ref. 7.

0.725. It was the purpose of this series to show that, in electrochemical measurements, a sodium chloride solution could be formally treated as a mixed solvent in a manner very similar to that previously reserved for non-electrolytic solvents, such as dioxane–water mixtures. This treatment permits experimental simplifications in the study of ionic equilibria in sea water, which for certain thermodynamic purposes may be considered a sodium chloride solution of ionic strength, 0.725.

The extrapolated values of $-\log K^*$ are recorded in Table III. In order to smooth these results against M and T, and to obtain various derived quantities, such as ΔH^{0*}, etc., the equation

$$-\log K^* = -\log K - \frac{2S\sqrt{M}}{1 + A\sqrt{M}} + BM + CM^2 - \log(1 + 0.036M) \quad (22)$$

was used at constant T, and

$$-\log K^* = A^*/T + B^* + C^*T \quad (23)$$

was used at constant M. The form of equation (22) is suggested by the Debye–Hückel theory and the relation

$$K = K^*[\gamma_H\gamma_{BO_2}/\gamma_{HBO_2}]_{0,M} \quad (24)$$

derived from consideration of standard states. The theoretical limiting slopes, S, were calculated from constants given in the "International Critical Tables,"[22] and the dielectric constants of Wyman.[23] Equation (23) was recommended by Harned and Robinson,[24] and appears to be the most satisfactory equation proposed for the purpose. Preliminary values of the parameters of equation (23) were determined from the observed results (Table III) by the method of least squares. The values of $-\log K^*$ calculated[25] by equation (23) were then smoothed according to equation (22). The parameters of this equation are recorded in Table IV. Finally, the values calculated from equation (22) were fitted to equation (23) by the method of least squares to obtain the parameters given in Table V.

TABLE IV

PARAMETERS OF EQUATION (22)

t°	$-\log K$	$2S$	A	$B \times 10^4$	$C \times 10^5$
5	9.4382	0.9804	1.019	463	844
10	9.3805	.9875	1.077	488	782
15	9.3278	.9950	1.100	511	717
20	9.2799	1.0029	1.122	533	639
25	9.2365	1.0115	1.136	553	579
30	9.1975	1.0206	1.150	572	515
35	9.1626	1.0301	1.156	589	429
40	9.1316	1.0401	1.161	605	350
45	9.1043	1.0508	1.164	620	268
50	9.0806	1.0618	1.157	633	183
55	9.0603	1.0735	1.149	645	96

$A \times 10^3 = 1136 + 2.78(t - 25) - 0.078(t - 25)^2$

$B \times 10^4 = 553.3 + 3.91(t - 25) - 0.0285(t - 25)^2$

$C \times 10^5 = 579 - 14.4(t - 25) - 0.057(t - 25)^2$

TABLE V

PARAMETERS OF THE EQUATION (23) FOR VARIOUS CONCENTRATIONS (M) OF SODIUM CHLORIDE

M	A^*	B^*	C^*
0.00	2291.9	−3.6865	0.017560
.02	2221.1	−3.2837	.016595
.07	2136.4	−2.7805	.015590
.36	1881.8	−1.2322	.012782
.725	1695.2	−0.0750	.010799
1.25	1496.2	1.1962	.008662
2.00	1264.9	2.7439	.006053
3.00	984.7	4.7340	.002626

These parameters, obtained by successive smoothing against T, M and T, were used to calculate the thermochemical quantities discussed in the next section, and yield the final values of $-\log K^*$ recorded in Table VI. Comparison of the results in Tables VI and III shows that the average difference between the calculated and observed values of $-\log K^*$ is 0.00083, and the maximum difference is 0.0043 for $M = 1.25$ at 55°. The exceptionally large differences for $M = 1.25$ at high temperatures were purposely introduced[25] for experimental reasons discussed in the preceding section.

Although we regard equation (23) as the more trustworthy source of derived thermochemical quantities, it will be interesting to consider the result of fitting the equation[26]

$$\log K^* = \log K^*_\vartheta - p(t - \vartheta)^2 \quad (25)$$

to the results in Tables III and VI. By this equation, the ionization constant attains a maximum value, K^*_ϑ, at the centigrade temperature, ϑ. For most weak acids in pure water,[27] in salt solutions,[4,5] and in some mixtures of water, and non-aqueous solvents,[28,29] the parameter p is 5×10^{-5}, or very close to this value. Boric acid

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(22) Ref. 18, pp. 17–18.

(23) J. Wyman, Jr., *Phys. Rev.*, [2] **35**, 623 (1930).

(24) H. S. Harned and R. A. Robinson, *Trans. Faraday Soc.*, **36**, 473 (1940).

(25) The least square calculation accentuated the experimental inconsistency (due to diffusion of AgCl) in the series at $M = 1.25$, by giving the best fit at the higher temperatures. For this reason the observed results at $M = 1.25$ were used in the smoothing against M at all temperatures.

(26) H. S. Harned and N. D. Embree, THIS JOURNAL, **56**, 1050 (1934).

(27) H. S. Harned and B. B. Owen, *Chem. Rev.*, **25**, 31 (1939).

(28) H. S. Harned and N. D. Embree, THIS JOURNAL, **57**, 1669 (1935).

(29) H. S. Harned and G. L. Kazanjian, *ibid.*, **58**, 1912 (1936).

TABLE VI

SMOOTHED VALUES OF $-\log K^*$ FOR BORIC ACID IN M-MOLAL SODIUM CHLORIDE SOLUTIONS

t°	M = 0.00	0.02	0.07	0.36	0.725	1.25	2.00	3.00
5	9.438	9.318	9.237	9.089	9.024	8.985	8.976	9.005
10	9.380	9.260	9.180	9.034	8.970	8.934	8.926	8.956
15	9.328	9.207	9.127	8.982	8.920	8.885	8.878	8.908
20	9.280	9.158	9.078	8.934	8.874	8.840	8.834	8.863
25	9.237	9.114	9.034	8.891	8.831	8.798	8.791	8.820
30	9.198	9.074	8.994	8.850	8.791	8.758	8.752	8.779
35	9.163	9.038	8.957	8.814	8.754	8.721	8.714	8.739
40	9.132	9.006	8.924	8.780	8.720	8.687	8.679	8.701
45	9.104	8.978	8.895	8.750	8.689	8.655	8.646	8.665
50	9.081	8.952	8.869	8.722	8.661	8.626	8.614	8.630
55	9.060	8.931	8.846	8.697	8.635	8.598	8.585	8.597

TABLE VII

PARAMETERS OF EQUATION (25) AND $-\log K^*_\vartheta$ AND FROM EQUATION (23)

	From observed K^*			From smoothed K^*			From Equation (23)	
M	$-\log K^*_\vartheta$	ϑ	$p \times 10^6$	$-\log K^*_\vartheta$	ϑ	$p \times 10^6$	$-\log K^*_\vartheta$	ϑ
0.00	9.025	76.7	8.0	9.022	76.9	8.0	9.002	88.2
.02	8.880	80.3	7.7	8.884	79.5	7.8	8.858	92.7
.07	8.791	81.9	7.5	8.793	81.5	7.6	8.762	97.1
.36	8.632	86.2	6.9	8.627	87.4	6.8	8.577	110.6
.725	8.548	92.7	6.2	8.550	91.9	6.3	8.482	123.1
1.25	8.468	104.6	5.2	8.485	101.8	5.4	8.396	142.5
2.00	8.448	107.8	5.0	8.445	108.2	5.0	8.298	184.0
3.00	8.338	137.6	3.8	8.331	138.4	3.8	7.950	339.3

is exceptional in this respect, as p has the value 8×10^{-5} for this acid in pure water,[8] and the present results show that, in sodium chloride solutions, p depends to a marked degree upon the value of M. The results in Table VII illustrate this point, and also show that the same variation in p results from the use of either the observed values of K^* or those smoothed against T by equation (23). The results in the last two columns were obtained by solving equation (23) for the maximum value of $\log K^*$ and the temperature of the maximum, T_ϑ. The wide discrepancies between values of T_ϑ obtained from equations (23) and (25) show how sensitive these values are to the form of empirical equation employed, and almost eliminate the physical significance of values of T_ϑ, far removed from the experimental temperature range.

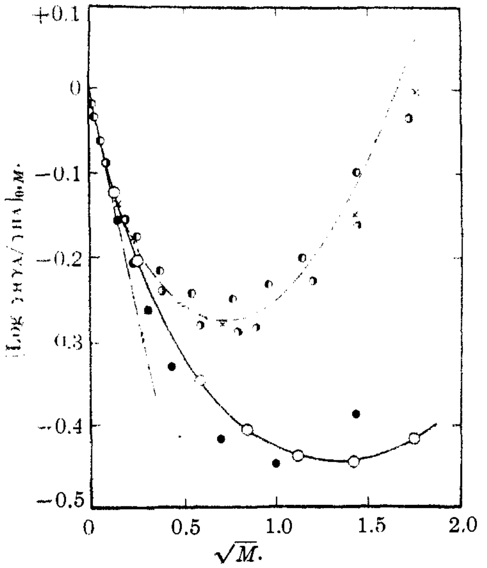

Fig. 4.—The activity coefficient function of various weak electrolytes at infinite dilution in M-molal sodium chloride solutions at 25°: ○, boric acid; ●, lactic acid; ◐, α-dinitrophenol; ×, acetic acid; ◑, water. The broken curve represents $\log \gamma_H\gamma_{Cl}$.

Other Thermodynamic Quantities.—The activity coefficient function $[\gamma_H\gamma_{BO_2}/\gamma_{HBO_2}]_{0,M}$ for boric acid at infinite dilution in salt solutions is calculable from equation (24) and Table VI, or from equation (22) and Table IV. Figure 4 compares the behavior of this function for boric acid with that of other weak electrolytes, and hydrochloric acid in the same salt solutions. Larsson and Adell[30] derived similar curves for a large number of weak organic acids from their measurements on cells with liquid junctions. All of their results for normal fatty acids fall between those for α-dinitrophenol[31] and water[20] in Fig. 4. Furthermore, the effect of a substituent group

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(30) E. Larsson and B. Adell, *Z. physik. Chem.*, **A157**, 342 (1931); **A156**, 381 (1931).

(31) H. v. Halban and G. Kortüm, *ibid.*, **A170**, 351 (1934).

(methyl, phenyl and hydroxyl) is slight,[32] unless it occupies the *alpha* position to the carboxyl carbon. The curve for boric acid roughly follows that for lactic acid, a typical α-hydroxy acid.

Associated with the ionization reaction

$$HBO_2 \longrightarrow H^+ + BO_2^-$$

at constant temperature and pressure at infinite dilution in various sodium chloride solutions, there are changes in free energy, heat content, heat capacity, and entropy which can be readily derived from equation (23) and the parameters given in Table V. Thus

$$\Delta F^{0*} = 2.303R[A^* + B^*T + C^*T^2] \quad (26)$$

$$\Delta H^{0*} = 2.303R[A^* - C^*T^2] \quad (27)$$

$$\Delta C_p^{0*} = -2.303R[2C^*T] \quad (28)$$

and

$$\Delta S^{0*} = -2.303R[B^* + 2C^*T] \quad (29)$$

Table VIII contains numerical values calculated from these equations at 25°. The variations of

TABLE VIII

THERMODYNAMIC CHANGES ACCOMPANYING THE IONIZATION OF BORIC ACID AT INFINITE DILUTION IN *M*-MOLAL SODIUM CHLORIDE SOLUTIONS AT 25°

M	ΔF^{0*}	ΔH^{0*}	$-\Delta C_p^{0*}$	$-\Delta S^{0*}$
0.00	12597	3346	47.9	31.04
.02	12430	3415	45.3	30.24
.07	12320	3436	42.5	29.80
.36	12125	3413	34.9	29.22
.725	12044	3365	29.5	29.12
1.25	11998	3323	23.6	29.10
2.00	11990	3326	16.5	29.06
3.00	12029	3438	7.2	28.82

the last three of these quantities with salt concentration is illustrated in Figs. 5 to 7. A noteworthy feature of these plots is the crowding of the curves at large values of M, which shows that the effect of temperature is least at the higher salt concentrations. The curves for ΔS^{0*} and ΔH^{0*} at various temperatures appear to intersect at $M \simeq 4$.

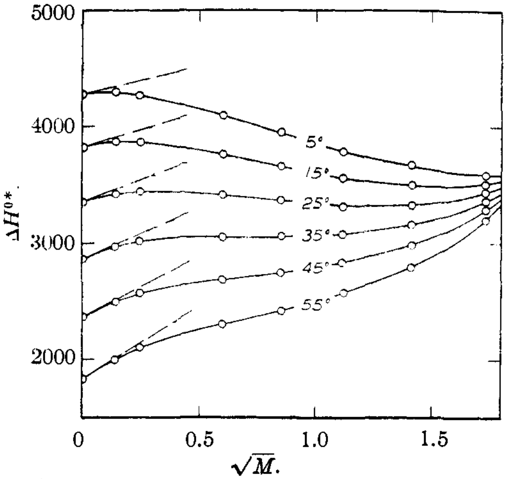

Fig. 5.—ΔH^{0*} for the ionization of boric acid at infinite dilution in M-molal sodium chloride solutions. Diameters of circles 50 cal. deg.$^{-1}$ mole^{-1}.

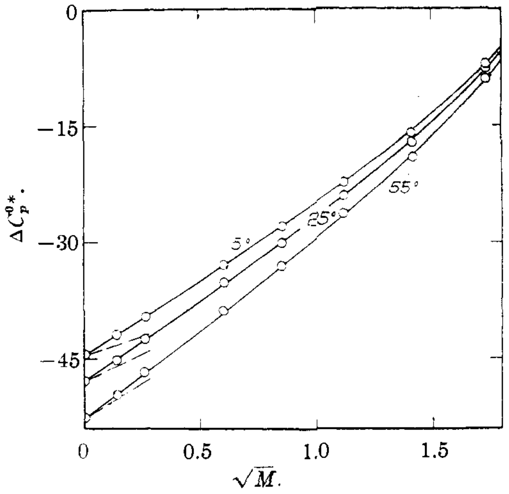

Fig. 6.—ΔCp^{0*} for the ionization of boric acid at infinite dilution in M-molal sodium chloride solutions. Diameters of circles 1 cal. deg.$^{-1}$ mole^{-1}.

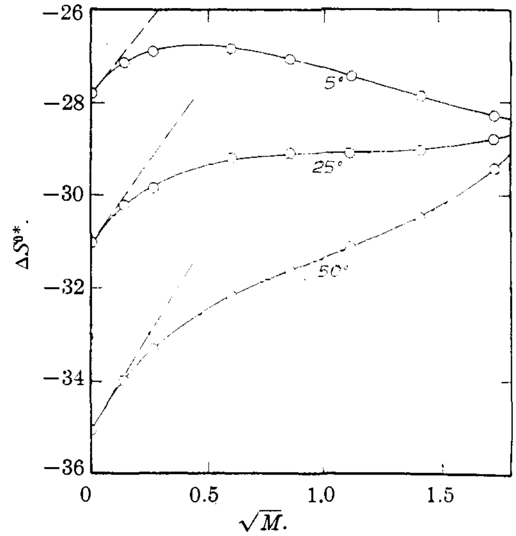

Fig. 7.—ΔS^{0*} for the ionization of boric acid at infinite dilution in M-molal sodium chloride solutions. Diameters of circles 0.2 cal. deg.$^{-1}$ mole^{-1}.

Within the experimental concentration range, ΔC_p^{0*} is proportional to T by equation (28). At high dilutions this proportionality is inconsistent with the results obtainable by differentiation of equation (22) and the parameters in Table IV, but this is of no practical importance. The second derivative of the difference between E_{II} measured in this research and E^{0*}, obtained

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[32] E. Güntelberg and E. Schiödt, *Z. physik. Chem.*, **135**, 393 (1928).

by combining two other series of measurements, can at best yield reasonable values of ΔC_p^{0*} within the experimental concentration range, and cannot be expected to prove or disprove the requirements of theory below this range. Furthermore, the values of ΔC_p^{0*} at the extremes of the temperature range are very sensitive to the form of the equation by which log K^* is expressed as a function of T. We have used equation (23) for this purpose for reasons of convenience and precedent,[24] and because it more accurately represents the observed temperature variation of log K^*, toward the limits of the range, than does equation (22).

Similar considerations led us to express the temperature variation of E^{0*} by equation (13) instead of by equation (16) with temperature dependent parameters. Equation (13) was more satisfactory on two counts. It gave a more accurate representation of the observed values of E^{0*}. Further, if E^{0*} is expressed by equation (16) at all temperatures (with the parameters smoothed against T by least squares) these new values of E^{0*} lead to values of log K^* which cannot be represented by equation (22) as accurately as those based upon values of E^{0*} from equation (13). We therefore feel justified in expressing the temperature dependence of our primary quantities, E^{0*} and log K^*, by the simplest equations, (13) and (23), which will represent them within the experimental errors. This should lead to reasonable values of the derived quantities, ΔH^{0*}, ΔS^{0*}, and ΔC_p^{0*}, in the middle third of the temperature range and within the experimental concentration range.

Summary

A method is described by which the ionization of a weak acid in salt solutions is determined by means of cells containing buffered solutions without liquid junctions. By a shift of standard state to conform with each salt concentration, the method is formally equivalent to that used in determining ionization constants in pure water, and in mixtures of water and non-aqueous solvents.

The necessary values of E^{0*} for the new standard states are given over a wide range of temperatures and salt concentrations.

The ionization constant, K^*, of boric acid is determined in sodium chloride solutions at seven concentrations between 0.02 and 3.0 molal, and at 5° intervals between 5 and 55°.

The derived thermodynamic quantities $[\gamma_{H} \cdot \gamma_{BO_2}/\gamma_{HBO_2}]_{0,M}$, ΔH^{0*}, ΔC_p^{0*}, and ΔS^{0*} are calculated, and their variations with temperature and salt concentration illustrated by plots and tables.

NEW HAVEN, CONNECTICUT

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[CONTRIBUTION FROM THE WILLIAM G. KERCKHOFF LABORATORIES OF THE BIOLOGICAL SCIENCES, CALIFORNIA INSTITUTE OF TECHNOLOGY]

Thermal Data. XVII. The Heat Capacity, Entropy, and Free Energy of Formation of Cyclohexane. A New Method of Heat Transfer in Low Temperature Calorimetry

BY ROBERT A. RUEHRWEIN AND HUGH M. HUFFMAN[1]

We have measured the heat capacity of cyclohexane over the temperature range 13 to 300° K. The results of our measurements differ from those reported by Aston, Szasz and Fink[2] by an amount greater than the claimed experimental errors of both laboratories. We are presenting our results and a description of our apparatus and methods so as to have them on record and because they may be of use in tracing the source of the discrepancy.

We have also calculated the entropy of cyclohexane and used this datum in conjunction with existing data to calculate the free energy of formation of cyclohexane.

The Cyclohexane.—The material used in this investigation was kindly furnished in a purified form by the Shell Development Company. An estimate of the liquid soluble-solid insoluble impurity was made by means of measurements of the temperature as a function of the fraction melted, and by observations on the premelting during the heat capacity measurements. The impurity was estimated by these means to be approximately 0.015 mole per cent.

The Cryostat and Calorimeter.—The cryostat is similar to that described by Blue and Hicks[3] except that a simpler

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[1] Present address, Bureau of Mines, Bartlesville, Okla.

[2] Aston, Szasz and Fink, THIS JOURNAL, **65**, 1135 (1943).

[3] Blue and Hicks, *ibid.*, **59**, 1962 (1937).