2. From these and other suitable data, the values of α_1 and α_2 defined by equation (1) have been computed for a number of halide acid–halide mixtures.

3. It has been shown that the empirical rules of Åkerlöf and Thomas that (1) B is a constant and does not vary with the concentration, (2) α_1 and α_2 are not functions of m, are not valid. Neither B, α_1 or α_2 can be regarded as constants characteristic of a given pair of electrolytes.

4. The results have been discussed in relation to the original and extended theory of specific ionic interaction.

NEW HAVEN, CONN. RECEIVED JUNE 18, 1935

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

The Thermodynamics of Ionized Water in Sodium Chloride Solutions

BY HERBERT S. HARNED AND GEORGE E. MANNWEILER[1]

From measurements of the cells

$$H_2 \mid MOH(m_0), MX(m) \mid AgX \mid Ag, \text{ and} \qquad (A)$$

$$H_2 \mid HX(m_0), MX(m) \mid AgX \mid Ag \qquad (B)$$

$$M = Li, Na, K \quad X = Cl^-, Br^-$$

the thermodynamic properties of the ions of water in potassium and lithium chloride solutions, and potassium and sodium bromide solutions, have been studied over wide temperature and concentration ranges.[2] The only determination of the activity coefficient and dissociation of water in sodium chloride solutions is contained in the contribution by Harned where the method of determining these quantities from cells without liquid junction was first developed.[3] Since these results were obtained from scattered data at 25° only, they have been redetermined from measurements of the above cells by employing a consistent and more accurate technique. Further, the results have been extended to cover a temperature range from 0 to 60°. From these results we have computed: (1) the ionization constant of water; (2) the ionic activity coefficient product of water in sodium chloride solutions; (3) the ionization of water in sodium chloride solutions; and (4) the heat of ionization of water and the partial molal heat of ionization of water in sodium chloride solutions.

Experimental Results

The electromotive forces of cells of types (A) and (B) may be expressed as functions of the temperature by means of the quadratic equations

$$E_A = E_{A(25)} + c\,(t - 25) + d\,(t - 25)^2 \qquad (1)$$

$$E_B = E_{B(25)} + a\,(t - 25) + b\,(t - 25)^2 \qquad (2)$$

The values of $E_{B(25)}$, a, and b are given in Table I of an earlier investigation[4] and the values of $E_{A(25)}$, c, and d are contained in Table I of this communication. Measurements were made by a technique similar to that employed by Harned and Hamer[2] and Harned and Copson.[2] The experimental results were the mean of three cells which were measured at the concentrations specified from 0 to 60° at 5° intervals. The deviations from the mean were ±0.04 mv. and the experimental results smoothed to round concentrations agree with those computed by equation (2) to within approximately this limit.

TABLE I

$E_{A(25)}$ AND CONSTANTS OF EQUATION (1), $m_0 = 0.01$

μ	$E_{A(25)}$	$c \times 10^6$	$d \times 10^6$
0.02	1.05027	167.4	0.28
.03	1.03244	109.25	.25
.05	1.00887	34.65	.13
.11	0.99098	− 27.40	.12
.21	.97303	− 87.45	.11
.51	.94905	−162.00	.0
1.01	.93055	−225.35	− .07
2.01	.91132	−279.5	− .35
3.01	.89950	−309.1	− .62

The Ionization Constant of Water, the Ionic Activity Coefficient and Dissociation of Water in Sodium Chloride Solutions.—The ionization constant of water was determined from these results by the two methods developed by Harned and Hamer. The equation for the cells of type A may be written in the form

$$E_A - E_0 + \frac{RT}{NF}\ln\frac{m}{m_0} = \frac{RT}{NF}\ln\frac{\gamma_H\gamma_{OH}}{a_{H_2O}} - \frac{RT}{NF}\ln\gamma_H\gamma_{Cl} - \frac{RT}{NF}\ln K \qquad (3)$$

which corresponds to equation (4) of Harned and Hamer. By employing the values of molal po-

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[1] The present communication contains material from a thesis presented by George E. Mannweiler to the Graduate School of Yale University in partial fulfilment of the requirements for the degree of Master of Science, June, 1934.

[2] Harned and Hamer, THIS JOURNAL, **55**, 2194 (1933); (b) **55**, 4496 (1933); Harned and Copson, *ibid.*, **55**, 2206 (1933).

[3] Harned, *ibid.*, **47**, 930 (1925).

[4] Harned, *ibid.*, **57**, 1865 (1935).

tential of the silver chloride electrode, E_0, determined by Harned and Ehlers,[5] the left side of this equation was evaluated. This quantity was plotted against μ and extrapolated to zero μ, at which point it is equal to $(-RT/NF \ln K)$. From these values K was computed at 5° temperature intervals from 0 to 60°. This extrapolation is unusually favorable for the evaluation of K since the plots are straight lines with small slopes.

As a check of this determination, we have also evaluated K from our measurements of both cells of types A and B. This procedure does not require the values of E_0 determined by others and consequently serves as a good test of the general accuracy of the data. From the equations of the cells and the limiting equation of the theory of Debye and Hückel to which a term linear with μ is added, the equation

$$E_A - E_B - \frac{RT}{NF}\ln\frac{m_0^2\,(m + m_0)}{m} + \frac{RT}{NF}\,\frac{5.908 \times 10^6}{D^{3/2}\,T^{3/2}}\,\sqrt{2\mu} = \beta\mu - \frac{RT}{NF}\ln K \qquad (4)$$

may be derived. This equation corresponds to equation (16) given by Harned and Hamer. The left-hand member of this equation was evaluated, plotted against μ, and from its value at $\mu = 0$, K was computed. This method is not as favorable for the determination of K as the one previously described since the plots possess a greater slope. However, a good extrapolation was possible and the results checked those obtained by the first method within the experimental error. The values of the ionization constant thus obtained are in close agreement with the results of Harned and Hamer with the exception of the value at 0° where the difference was 1%. At the temperatures of 20 to 50° inclusive, the agreement is 0.1% or better, at 5, 10, 15, 55 and 60°, the agreement is 0.3 to 0.4%. The results at the designated temperatures are given in Table II.

TABLE II

THE IONIC ACTIVITY COEFFICIENT PRODUCT OF WATER IN SODIUM CHLORIDE SOLUTIONS, $\gamma_H\gamma_{OH}/a_{H_2O}$

μ	0	10	20	25	30	40	50	60
0.02	0.761	0.763	0.760	0.759	0.759	0.752	0.751	0.751
.03	.723	.732	.726	.725	.725	.717	.715	710
.06	.680	.666	.664	.664	.663	.653	.649	.643
.11	.610	.613	.608	.607	.605	.595	.589	.583
.21	.560	.559	.557	.556	.553	.544	.538	.532
.51	.517	.520	.516	.514	.513	.502	.497	.488
1.01	.540	.542	.537	.535	.531	.517	.507	.495
2.01	.691	.699	.691	686	.681	.654	.629	.600
3.01	.971	.985	.972	.962	.948	.898	.855	.791
$K \times 10^{14}$	.1134	.2919	.681	1.007	1.470	2.914	5.482	9.651

By substitution of these values of K and the values of $\gamma_H\gamma_{Cl}$ in sodium chloride solutions computed from the electromotive forces of cells of type B in equation (3), the ionic activity coefficient product of water, $\gamma_H\gamma_{OH}/a_{H_2O}$, may be computed since the left side of this equation is known. The values of this quantity are given at convenient temperatures in Table II. Values at intermediate temperatures may be interpolated.

Because of the importance of this quantity for the study of ionic equilibria in aqueous solutions, we have given at convenient salt concentrations in Table III the values recently determined at 25° for cases of a number of uni-univalent salt solutions. Although on the whole the agreement with the results of Harned, Harned and Swindells, and Harned and James[6] is good when allowance is made for the differences in reference values, the recent results are the more accurate since a simpler method is used which permits better extrapolations.

TABLE III

THE VALUES OF [LOG $(\gamma_H\gamma_{OH}/a_{H_2O})$ + 1] OF UNI-UNIVALENT HALIDE SOLUTIONS AT 25°

$\mu^{1/2}$	CsCl[a]	KCl[b]	NaCl	LiCl[c]	KBr[d]	NaBr[d]	LiBr[e]
0.04	0.962	0.962	0.962	0.962	0.962	0.962	0.962
.07	.935	.935	.935	.935	.935	.935	.935
.1	.912	.912	.912	.912	.912	.912	.912
.2	.848	.847	.845	.839	.847	.845	.839
.3	.810	.802	.797	.777	.804	.797	.777
.4	.783	.771	.760	.728	.773	.761	.728
.5	.761	.747	.735	.690	.749	.738	.690
.6	.746	.732	.719	.662	.733	.723	.662
.7	.741	.727	.711	.640	.726	.716	.641
.8	.748	.735	.710	.624	.732	.715	.626
.9	.763	.750	.716	.611	.747	.721	.614
1.0	.785	.769	.728	.602	.766	.734	.606
1.2	..	.819	.772	.598	.811	.779	.610
1.4	..	.891	.838	.612	.874	.842	..
1.7	..	1.010	.966	.664	.980	.953	..
2.0	..	..	..	.746	..	..	..

[a] Harned and Schupp, Jr., THIS JOURNAL, **52**, 3892 (1930). [b] Harned and Hamer, *ibid.*, **55**, 2194 (1933). [c] Harned and Copson, *ibid.*, **55**, 2206 (1933). [d] Harned and Hamer, *ibid.*, **55**, 4496 (1933). [e] Vance, *ibid.*, **55**, 4518 (1933).

There is one result characteristic of this quantity which is of interest. In Fig. 1, we have plotted [log $(\gamma_H\gamma_{OH}/a_{H_2O})$ + 1] against the quantity $\Sigma(1/a)$, or $(1/a_+ + 1/a_-)$ at concentrations of $\mu^{1/2}$ equal to 0.5 and 1. The ionic radii employed were taken from the values derived by Pauling[7] from crystallographic data for all ions except hydrogen ion. In the latter case, Bragg's[8]

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(5) Harned and Ehlers, THIS JOURNAL, **55**, 2179 (1933).

(6) Harned, *ibid.*, **47**, 930 (1925); Harned and Swindells, *ibid.*, **48**, 126 (1926); Harned and James, *J. Phys. Chem.*, **30**, 1060 (1926).

(7) Pauling, THIS JOURNAL, **49**, 765 (1927).

(8) Bragg, *Phil. Mag.*, [6] **40**, 169 (1920).

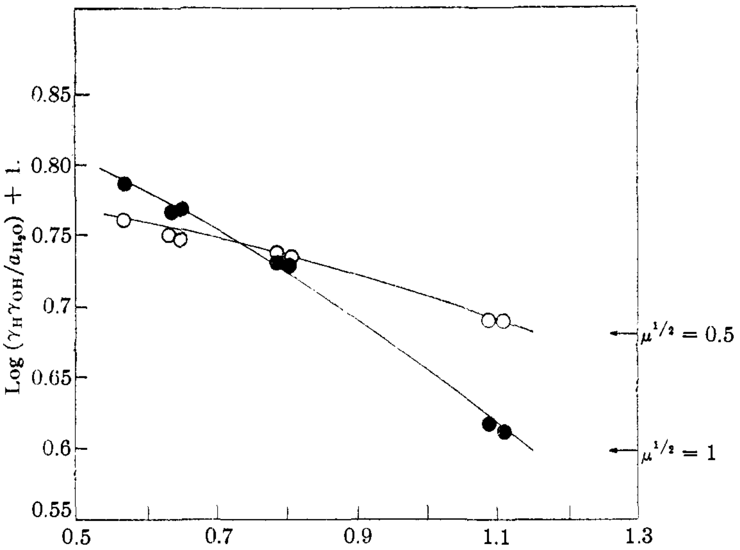

Fig. 1.—Plots of [log $(\gamma_H\gamma_{OH}/a_{H_2O}) + 1$] against $\Sigma 1/a_i$ at constant molality.

value was employed. $\Sigma 1/a$ was found to be 1.09, 1.11, 0.78, 0.80, 0.63, 0.65 and 0.57 for lithium bromide and chloride, sodium bromide and chloride, potassium bromide and chloride, and cesium chloride, respectively. The values are in the order $\Sigma 1/a$. Since the curves drawn through the points show only a slight curvature and since this result must be regarded as a rough approximation, we may represent it by a linear equation. Thus

$$\log \frac{\gamma_H\gamma_{OH}}{a_{H_2O}} = \log \frac{K}{m_H m_{OH}} = A - B\Sigma \frac{1}{a}; \quad [\mu = \text{constant}] \quad (5)$$

where K is the thermodynamic ionization constant, m_H and m_{OH} the molalities of the ions, and A and B are positive constants. Consequently

$$\log m_H m_{OH} = C + B\Sigma 1/a \quad (6)$$

where C is a constant. Thus, the smaller the value of $\Sigma 1/a$ for the ions of the salt, the greater the ionization of the solvent. This result is in the expected direction. The value of $B/\mu^{1/2}$ is a function of μ.

The Total Heat of Ionization of Water in Sodium Chloride Solutions

As shown by Harned and Hamer,[2b] the total heat of ionization of water may be computed from these results by the equation

$$\Delta H = -F(E_B - E_A)_{25} + FT(A) + F[(A) - 2T(B)]\,(t - 25) + F(B)\,(t - 25)^2 \quad (7)$$

where $(E_B - E_A)_{25}$ are the differences in electromotive forces of the cells at 25° and at a given concentration, t is °C., (A) equals $(c-a)$, and (B) equals $(d-b)$. a, b, c, and d are the constants of equations (1) and (2). The results may be expressed within the experimental error, estimated to be of the order of ±50 cal. or ±0.4%, by the equation

$$\Delta H = \Delta H_i + \omega\mu^{1/2} \quad (8)$$

The values of ΔH_i obtained by extrapolation agreed with those of Harned and Hamer to within this limit from 25 to 60°. At the lower temperatures the values obtained were about 80 cal. greater than those given by Harned and Hamer. The average value of ΔH_i is well represented by the equation

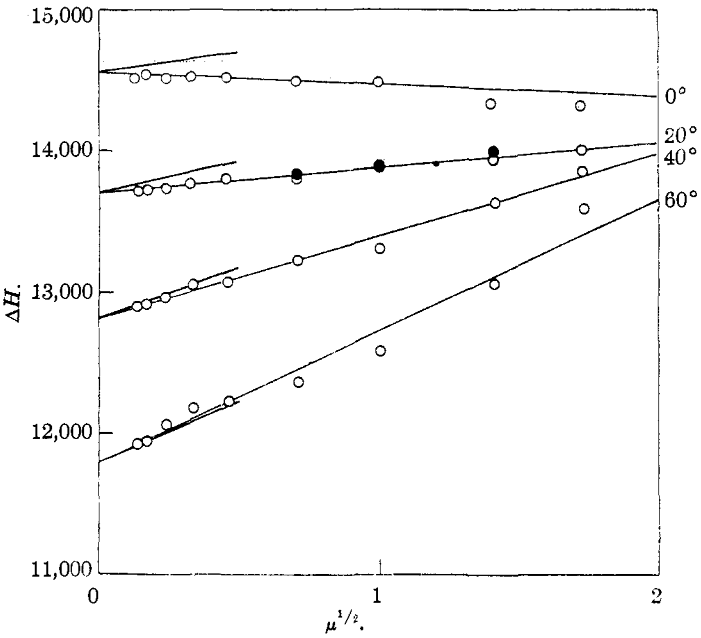

Fig. 2.—Plots of the total heat of ionization of water in sodium chloride solutions against $\mu^{1/2}$.

$$\Delta H_i = 20{,}182 + 0.026117T - 0.078067T^2 + 0.0000079127T^3 \quad (9)$$

In Table IV, the values of ω obtained from plots of ΔH *versus* $\mu^{1/2}$ are given at the temperatures designated.

TABLE IV

VALUES OF THE CONSTANT OF EQUATION (8)

t	ω	t	ω	t	ω
0	−40	25	290	50	700
5	0	30	370	55	780
10	50	35	460	60	860
15	130	40	550		
20	210	45	640		

In Fig. 2, we have plotted ΔH against $\mu^{1/2}$ at 0, 20, 40 and 60°. We have also indicated the limiting slope of the Debye and Hückel theory for the relative partial molal heat content of the ions of water. Our results should approach these slopes in very dilute solution ($m = 0.001$ or less). Since they cannot be extended to low dilutions with a high accuracy, no attempt has been made to employ the limiting laws for the purpose of extrapolation. As a confirmation of the correct character of the results at higher concentrations, we may compare our data with values of the same quantity determined from calorimetric measurements of the heat of neutralization of hydrochloric acid and sodium hydroxide by Richards and Rowe[9] at 20°. Their results are represented by the dots in Fig. 2. The agreement is within the limit of 40 cal.

Summary

1. Measurements of the cells

H_2 | NaOH (0.01), NaCl (m) | AgCl | Ag
H_2 | HCl (0.01), NaCl (m) | AgCl | Ag

in aqueous solution from 0 to 60° have been made.

2. From these the value of the ionic activity coefficient product of water in sodium chloride solutions has been computed.

3. It is shown that the logarithm of the ionization in alkaline halide solutious, $\log m_{H}m_{OH}$, at a given concentration varies nearly linearly with the sum of the reciprocal of the ionic radii. This is only a rough approximation but serves to show that ions of smaller radii cause the greater dissociation of the solvent.

4. The total heat content of the ionization of water and the relative partial molal heat content of the hydrogen and hydroxyl ions in sodium chloride solutions has been determined from 0 to 60°. Good agreement with the calorimetric heat of neutralization is found at 20°.

NEW HAVEN, CONNECTICUT RECEIVED JUNE 18, 1935

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(9) Richards and Rowe, THIS JOURNAL, **44**, 684 (1922).

[CONTRIBUTION FROM THE DEPARTMENT OF BIOLOGICAL CHEMISTRY, COLUMBIA UNIVERSITY]

Studies of Crystalline Vitamin B_1. XII. The Sulfur-Containing Moiety

BY H. T. CLARKE AND S. GURIN

The chemical investigation of vitamin B_1 was undertaken in this Laboratory on the invitation of Mr. R. R. Williams, who acquainted us with the sulfite cleavage reaction[1] and kindly furnished a supply of the crystalline vitamin and its basic cleavage product. Early in the course of our work we were able to suggest the presence of a thiazole nucleus in vitamin B_1, and this suggestion was incorporated by Williams in his tentative formula.[2]

In view of the presence of sulfur in the vitamin molecule,[3] our attention was primarily directed toward elucidation of the manner in which this element is combined, by the use of methods recently developed[4] for the study of sulfur in proteins. In the preliminary stages of this investigation, the recognition of the vitamin and its basic cleavage product as derivatives of thiazole was greatly aided by a study of their behavior toward alkaline plumbite and toward bromine water. Striking contrasts were observed between the two compounds with both reagents. When heated with the lead reagent, the vitamin yields lead sulfide relatively rapidly, while the thiazole base gives a visible precipitate only after several hours. Conversely, on treatment with bromine the base is largely oxidized to sulfuric acid under conditions in which the vitamin remains almost entirely unchanged and suffers little or no loss of physiological activity. On the basis of considerations discussed elsewhere,[4] the conclusion was almost inescapable that the sulfur atom in the base is linked to two carbon atoms in a structure of which the carbon groupings are more susceptible to oxidative attack than is the sulfur.

While this study was in progress, it was re-

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(1) Williams, Waterman, Keresztesy and Buchman, THIS JOURNAL, **57**, 536 (1935).

(2) Williams, *ibid.*, **57**, 229 (1935).

(3) Windaus, Tschesche, Ruhkopf, Laquer and Schultz, *Z. physiol. Chem.*, **204**, 123 (1932).

(4) Blumenthal and Clarke, *J. Biol. Chem.*, **110**, 343 (1935).