[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

The Hydrolysis of the Acetate Ion in Sodium Chloride Solutions[1]

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

The thermodynamic equilibrium constant, K_h, for the hydrolysis of an anion

$$Ac^- + H_2O \rightleftharpoons HAc + OH^-$$

is defined by the equation

$$K_h = \frac{a_{HAc}a_{OH}}{a_{Ac}a_{H_2O}} = \frac{\gamma_{HAc}\gamma_{OH}}{\gamma_{Ac}a_{H_2O}} \frac{m_{HAc}m_{OH}}{m_{Ac}} \qquad (1)$$

where a, γ, and m are the activities, activity coefficients and molalities of the species denoted by subscripts. This constant can be defined by the equation

$$K_h = K_W/K_A \qquad (2)$$

where K_W and K_A are the ionization constants of water and the acid, respectively.

Recent determinations of K_W[2–4] and K_A[5] make possible the accurate evaluation of K_h from 0 to 40°. Further information concerning this hydrolytic reaction in salt solutions may be obtained by combining two other series of results. The ionization constant of water at a given temperature in a salt solution is given by the equation

$$K_W = \frac{\gamma_H\gamma_{OH}}{a_{H_2O}} m_H m_{OH} = \gamma_W^2 k_W \qquad (3)$$

in which γ_W represents the ionic activity coefficient of water, and k_W the ionization. Harned and Mannweiler,[3] from measurements of cells without liquid junction, have obtained γ_W, K_W and, consequently, k_W in sodium chloride solutions from 0 to 60°. Another series of investigations[6–8] has culminated in the determination of γ_A and k_A of acetic acid in sodium chloride solutions from 0 to 40°,[8] defined by the equation.

$$K_A = \frac{\gamma_H\gamma_{Ac}}{\gamma_{HAc}} \frac{m_H m_{Ac}}{m_{HAc}} = \gamma_A^2 k_A \qquad (4)$$

Dividing equation (3) by equation (4), equation (1) is obtained in a form which shows the relationship of the quantities defined by equations (3) and (4), namely

$$K_h = \frac{\gamma_{HAc}\gamma_{OH}}{\gamma_{Ac}a_{H_2O}} \frac{m_{HAc}m_{OH}}{m_{Ac}} = \frac{\gamma_W^2 k_W}{\gamma_A^2 k_A} = \gamma_h^2 k_h \qquad (5)$$

It is apparent that the previous knowledge of the ionizations, k_W and k_A, permit the separation of the activity coefficient and concentration terms of the hydrolytic reaction. In other words, since both k_W and k_A are known separately, γ_h and k_h are known separately.

It is important to note that k_A is the ionization, $m_H^2/M - m_H$,[8] of the acid at zero concentration in a given salt solution, or in the pure aqueous salt solution. Similarly, k_W is the ionization of water, $m_H m_{OH}$, in the pure salt solution. The ratio of these two quantities, k_h, is therefore the concentration term of the hydrolytic reaction in a salt solution containing zero concentration of the acetate ion.

Results of the Salt Effect on the Hydrolytic Reaction.—The values of K_h and k_h according to equation (5) have been calculated from the values of k_W determined by Harned and Mannweiler,[3] and the values of k_A determined in our first communication[8] are given in Table I. Since γ_h may be computed readily from these results, its values have not been included.

TABLE I

VALUES OF THE CONCENTRATION TERM OF THE HYDROLYTIC REACTION

$$k_h \times 10^9 = \frac{m_{HAc}m_{OH}}{m_{Ac}} \times 10^9 = \frac{k_W}{k_A} \times 10^9$$

$$(= K_h \times 10^9;\ (\mu = 0))$$

μ	0°	10°	20°	25°	30°	40°
0.00	0.0684	0.1688	0.388	0.574	0.840	1.711
.02	.0697	.1706	.392	.579	.845	1.729
.03	.0704	.1701	.392	.579	.845	1.729
.06	.0706	.1714	.393	.579	.844	1.731
.11	.0708	.1720	.395	.582	.850	1.739
.21	.0719	.1741	.398	.584	.854	1.736
.51	.0738	.1770	.403	.591	.857	1.744
1.01	.0761	.1820	.409	.596	.865	1.768
2.01	.0801	.1864	.411	.593	.854	1.748
3.01	.0818	.1858	.402	.574	.827	1.705
Δ[a]	17.5	9.9	5.6	3.8	2.9	3.6

[a] Total deviation from mass action law in per cent., computed from the middle value of k_h.

The results in the table show the variation of k_h, or $m_{OH}m_{HAc}/m_{Ac}$ with salt concentration. Since, according to the classic mass action law, k_h should be constant, these deviations from constancy indicate the departure from the mass action law due to salt effect. The bottom row

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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 Hamer, THIS JOURNAL, **55**, 2194 (1933).

[3] Harned and Mannweiler, *ibid.*, **57**, 1873 (1935).

[4] Harned and Copson, *ibid.*, **55**, 2206 (1933).

[5] Harned and Ehlers, *ibid.*, **55**, 652 (1933).

[6] Harned and Robinson, *ibid.*, **50**, 3156 (1928).

[7] Harned and Owen, *ibid.*, **52**, 5079 (1930).

[8] Harned and Hickey, *ibid.*, **59**, 1284 (1937).

in the table gives the maximum variation in per cent. of this deviation at each temperature. This is a maximum at 0° and reaches a minimum of only 3% at about 30°. Further, k_h at each temperature from 10 to 40° is a maximum at some salt concentration.

Summary

1. From measurements of the cells without liquid junction,

$$H_2 \mid NaOH\ (m_0),\ NaCl\ (m) \mid AgCl - Ag$$
$$H_2 \mid HAc\ (M),\ NaCl\ (m) \mid AgCl - Ag$$

the thermodynamics of the hydrolytic reaction

$$Ac^- + H_2O \rightleftharpoons HAc + OH^-$$

has been studied from 0 to 40° and from 0 to 3 *M* sodium chloride concentration.

2. Of the quantities in the equation of equilibrium

$$K_h = \frac{\gamma_{OH}\gamma_{HAc}}{\gamma_{Ac}a_{H_2O}}\frac{m_{OH}m_{HAc}}{m_{Ac}} = \gamma^2_h k_h$$

K_h, γ_h and k_h have been evaluated. By this method the concentration term, k_h, has been separated from the activity coefficient term, γ_h.

3. Our results show that from 25 to 40°, inclusive, and from 0 to 3 *M* salt concentration, the total deviation from the mass action law is not greater than 4%.

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The Thermodynamics of Aqueous Potassium Chloride Solutions from Electromotive Force Measurements

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The electromotive forces of the cells

$$Ag\text{-}AgCl \mid KCl\ (m) \mid K_xHg \mid KCl\ (m_0) \mid AgCl\text{-}Ag \quad (1)$$

have been measured at 25° by MacInnes and Parker[1] and Harned[2] and at 0° by Smith.[3] These measurements have been extended by us to cover the ranges of temperature and concentration from 0 to 40° and 0.05 to 4 *M*, respectively. From these data, the activity coefficient, relative partial molal heat content and the relative partial molal heat capacity of potassium chloride in aqueous solutions have been computed.

Experimental Results

The cell technique was essentially the same as that employed by Harned[2] and Smith.[3] The electromotive force at each concentration was measured at 5° intervals from 0 to 40°, inclusive. The results have been expressed by the equation

$$E = E_{25} + a(t - 25) + b(t - 25)^2 \quad (2)$$

Values of E_{25}, *a* and *b* are given in Table I. *b'* in the fifth column are smoothed values of *b* which may be used for the calculation of the relative partial molal heat capacity. In the last column of the table, the average value in millivolts of the deviation, Δ, of the observed electromotive forces from those calculated by equation (2) are given.

TABLE I

ELECTROMOTIVE FORCES OF THE CELLS

$Ag\text{-}AgCl \mid KCl(m) \mid K_xHg \mid KCl(0.05) \mid AgCl\text{-}Ag$

AT 25° AND CONSTANTS OF EQUATION (2). VALID FROM 0 TO 40°

m	E_{25}	$a \times 10^6$	$-b \times 10^6$	$-b' \times 10^6$	Δ, mv.
0.1	0.03263	114	0.29	0.30	0.07
.2	.06478	224	.49	.50	.06
.3	.08332	284	.70	.66	.07
.5	.10677	372	.90	.87	.05
.7	.12220	440	1.02	1.00	.12
1.0	.13866	498	1.20	1.20	.06
1.5	.15768	574	1.48	1.50	.05
2.0	.17165	634	1.75	1.70	.06
2.5	.18274	682	1.85	1.86	.07
3.0	.19203	710	2.00	2.02	.07
3.5	.20030	745	2.20	2.18	.09
4.0	.20759	784	2.31	2.30	.05

For purposes of theoretical calculation, it is necessary to know the concentrations in formula weights per liter of solution, *c*. These may be obtained with an accuracy of ±0.04% by the equation

$$c/m = d_0 + Am \quad (3)$$

TABLE II

CONSTANTS OF EQUATION (3)

t	d_0	$-A$
0	0.9999	0.0263
5	1.0000	.0265
10	0.9997	.0266
15	.9991	.0267
20	.9982	.0270
25	.9970	.0272
30	.9957	.0273
35	.9940	.0274
40	.9922	.0276

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[1] MacInnes and Parker, THIS JOURNAL, **37**, 1445 (1915).

[2] Harned, *ibid.*, **51**, 416 (1929).

[3] Smith, *ibid.*, **55**, 3279 (1933).