

good agreement with those for cinnamic acid and 1,3-dichloropropane. The discrepancy in the case of the nitroanilines is, however, larger than would be expected.

### Summary

The solubilities in water of sixteen slightly soluble organic substances have been determined by means of an analytical method employing an interferometer.

DURHAM, NORTH CAROLINA

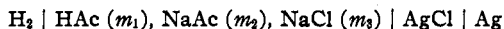
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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

## The Dissociation Constant of Acetic Acid from 0 to 60° Centigrade<sup>1</sup>

BY HERBERT S. HARNED AND RUSSELL W. EHLERS

In a recent communication,<sup>2</sup> we showed that it was possible to determine the dissociation constant of a weak acid with very high accuracy from electromotive force measurements of the cells



Values of the dissociation constants were determined from 0 to 35° inclusive at 5° intervals. More recently, we have obtained data from which this important constant may be obtained from 0 to 60° at 5° intervals. This determination involves values of the normal potential of the silver-silver chloride electrode through this temperature range. The values of this quantity which we shall employ have been revised slightly by us between 0 and 35° and determined between 35 and 60°.<sup>3</sup>

The method of calculation of  $K$  is described fully in our earlier contribution and was adhered to in all its detail. The equation for the electromotive force,  $E$ , of the cell is

$$E - E_0 + \frac{RT}{F} \ln \frac{m_{\text{HAc}} m_{\text{Cl}}}{m_{\text{Ac}}} = - \frac{RT}{F} \ln \frac{\gamma_{\text{H}} \gamma_{\text{Cl}} \gamma_{\text{HAc}}}{\gamma_{\text{H}} \gamma_{\text{Ac}}} - \frac{RT}{F} \ln K \quad (1)$$

$E_0$  is the normal potential of the cell,  $K$ , the dissociation constant, and the "m's" and "γ's" are the molalities and activity coefficients of the species denoted by subscripts.  $m_{\text{HAc}}$  and  $m_{\text{Ac}}$  were evaluated as previously described. As before, we let the right side of the equation equal  $-RT/F \ln K'$ , and then plot this quantity against  $\mu$ . At zero  $\mu$ ,  $K'$  equals  $K$ . The extrapolation is easily carried out accurately as indicated by Fig. 1 of the former investigation. The value of  $K$  at 35° was redetermined and the

(1) This contribution contains material which constituted a part of a Thesis presented to the Graduate School by Russell W. Ehlers in partial fulfillment of the requirements of the degree of Doctor of Philosophy, June, 1932.

(2) Harned and Ehlers, THIS JOURNAL, 54, 1350 (1932).

(3) The considerations and new data which have led to the review of the normal electrode potential,  $E_0$ , will be published in another contribution.

result agreed with the revised result of the earlier data. In Table I are given the electromotive forces of the cells. In the present instance  $m_1$ ,  $m_2$  and  $m_3$  were all at the same concentration. In the second part of the table are the values of  $K'$  and of  $K$  determined by extrapolation. The values of  $E_0$  employed are given at the bottom of the table.

TABLE I

ELECTROMOTIVE FORCES OF THE CELLS: $\text{H}_2 \mid \text{HAc} (m_1), \text{NaAc} (m_2), \text{NaCl} (m_3) \mid \text{AgCl} \mid \text{Ag}$						
$m_1 = m_2 = m_3$	$E_{35}$	$E_{40}$	$E_{45}$	$E_{50}$	$E_{55}$	$E_{60}$
0.006313	0.64143	0.64511	0.64887	0.65247	0.65623	0.65980
.012869	.62267	.62594	.62936			.63943
.021015	.60965	.61281	.61596	.61898	.62215	.62534
.047973	.58775	.59049	.59331	.59594	.59873	.60146
.07613	.57553	.57802	.58067	.58316	.58569	.58821
.10031	.56837	.57083	.57316	.57561	.57799	.58039
.008419	.63386	.63738	.64091	.64447	.64796	.65149
.010131	.62895	.63239		.63939	.64279	.64624
.011845	.62474	.62815	.63155	.63493	.63829	.64165
.014868	.61875	.62201	.62533	.62858	.63184	.63509

VALUES OF $K'$ AND EXTRAPOLATED VALUES OF THE DISSOCIATION CONSTANT $K$						
$\mu =$ $m_2 + m_3 + m_{\text{H}}$	$t = 35^\circ$	$40^\circ$	$K' \times 10^5$ $45^\circ$	$50^\circ$	$55^\circ$	$60^\circ$
0.01266	1.728	1.700	1.664	1.633	1.585	1.543
.02577	1.714	1.693	1.659			1.536
.04206	1.712	1.684	1.654	1.628	1.587	1.534
.09598	1.709	1.686	1.654	1.630	1.585	1.543
.14229	1.706	1.686	1.653	1.625	1.582	1.542
.20066	1.696		1.650	1.617	1.580	1.537
.01687	1.722	1.696	1.666	1.631	1.590	1.544
.02030	1.720	1.694		1.625	1.586	1.536
.02372	1.723	1.694	1.664	1.631	1.590	1.544
.02977	1.723	1.694	1.663	1.631	1.590	1.545
$E_0$ (obs.)	0.21563	0.21200	0.20821	0.20437	0.20035	0.19620
$K \times 10^5$	1.729	1.701	1.668	1.633	1.590	1.542

One further refinement has been carried out. By the method of least squares, we have computed  $E_0$  as a function of the temperature.<sup>3</sup> Its value is given by the equation

$$E_0 = 0.22239 - 645.52 \times 10^6 (t - 25) - 3.284 \times 10^{-6} (t - 25)^2 + 9.948 \times 10^{-9} (t - 25)^3 \quad (2)$$

If we employ the values computed by this equation which are given in column two of Table II, we obtain the values of  $K$  in the third column. These we regard as our final values. At  $25^\circ$  our result of  $1.754 \times 10^{-5}$  checks very closely that of  $1.753 \times 10^{-5}$  recently determined by MacInnes and Shedlovsky<sup>4</sup> from conductance measurements. We have no accurate values with which to compare our results at other temperatures. In Fig. 1 we have plotted  $K$  against the temperature. All points except that at  $30^\circ$

(4) MacInnes and Shedlovsky, THIS JOURNAL, 54, 1429 (1932).

fall on the smooth curve to within  $\pm 2$  in the third decimal place which corresponds to an error of  $\pm 0.03$  of a millivolt. It is apparent that  $K$  increases, reaches a maximum at about  $23^\circ$  and then decreases with increasing temperature.

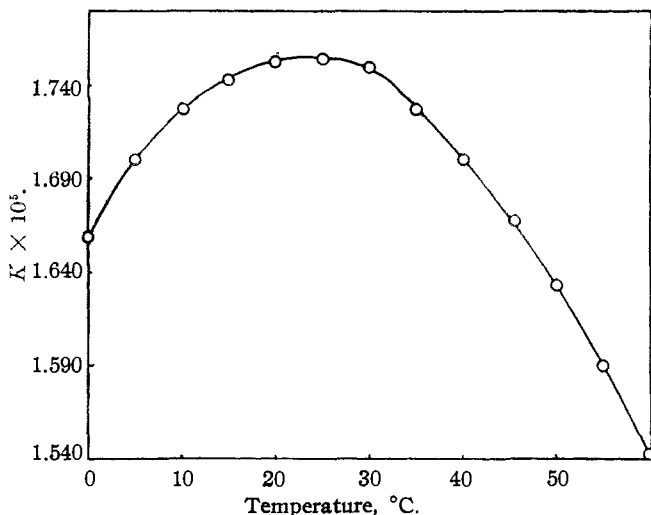


Fig. 1.—The dissociation constant of acetic acid as a function of the temperature.

To determine the heat content of ionization of the acid, we employed the equation

$$\frac{d \ln K}{dT} = \frac{\Delta H}{RT^2} \quad \text{or} \quad (3)$$

$$\frac{d \ln K}{d(1/T)} = -\Delta H \quad (4)$$

$\ln K$  was plotted against  $1/T$ , and  $\Delta H$  was evaluated from the slope. A plot of these values of  $\Delta H$  against  $T$  revealed that  $\Delta H$  varied approximately linearly with the temperature. This suggested that the problem could be treated in the usual way.  $\Delta H$  was taken to vary with the temperature according to

$$\Delta H = a + bT + cT^2 \quad (5)$$

Upon substituting this value of  $\Delta H$  in equation (3) and performing the integration

$$\log K = -\frac{a}{2.303 RT} + \frac{b}{R} \log T + \frac{c}{2.303 R} T + d \quad (6)$$

is obtained in which  $a$ ,  $b$ ,  $c$  and  $d$  are empirical constants. By substitution of the known values of  $K$  and  $T$  in equation (6), thirteen equations were obtained from which the constants were evaluated by the method of least squares. The equation with the empirical constants was

$$\log K = -\frac{1500.65}{T} - 6.50923 \log T - 0.0076792 T + 18.67257 \quad (7)$$

Values of  $K$  computed by this equation are given in the fourth column of Table II. The differences between the observed and calculated results are given in the fifth column. At the higher and lower temperatures the calculated values are slightly higher than the observed, while in the middle range of temperature they are somewhat lower. We have previously noted this behavior when dealing with a similar calculation and function,<sup>3</sup> and found that another term,  $dT^3$ , is necessary in equation (5) in order to represent the results within the experimental error throughout the entire concentration range. In the present treatment, we have not resorted to this refinement. On the whole the agreement is good. The mean deviation is  $\pm 0.003$ , which corresponds to about  $\pm 0.04$  millivolt.

The equation for the change in heat content of the dissociation of acetic acid derived from equation (7) is

$$\Delta H = 6871.0 - 12.9436T - 0.035161T^2 \quad (8)$$

Values of  $\Delta H$  computed by this equation are given in the sixth column of Table II. In column seven,  $\Delta C_p$ , the differences in specific heat of the ions and the undissociated molecule of acetic acid computed from the equation

$$\Delta C_p = -12.9436 - 0.070322T \quad (9)$$

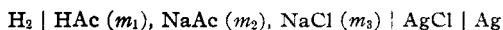
are compiled.

TABLE II  
DISSOCIATION CONSTANT AND HEAT OF IONIZATION OF ACETIC ACID

$t$ , °C.	$E_0$	$K \times 10^5$ (obs.)	$K \times 10^5$ (Equation 6)	$\Delta$	$\Delta H$	$\Delta C_p$
0	0.23632	1.657	1.667	+0.010	714	-32.15
5	.23391	1.700	1.702	+ .002	552	-32.50
10	.23130	1.729	1.728	+ .002	389	-32.85
15	.22851	1.745	1.745	.000	223	-33.20
20	.22554	1.753	1.752	- .001	57	-33.55
25	.22239	1.754	1.751	- .003	- 112	-33.91
30	.21908	1.750	1.741	- .009	- 282	-34.26
35	.21561	1.728	1.724	- .004	- 455	-34.61
40	.21200	1.703	1.700	- .003	- 628	-34.96
45	.20825	1.670	1.669	- .001	- 804	-35.31
50	.20436	1.633	1.633	.000	- 982	-35.66
55	.20033	1.589	1.592	+ .003	-1161	-36.02
60	.19620	1.542	1.547	+ .005	-1342	-36.37

### Summary

#### 1. Measurements of the cells



have been made from 35 to 60° at 5° intervals.

2. By a method previously described by us, the dissociation constant of acetic acid has been computed from 35 to 60° at 5° intervals from these results. Our earlier results from 0 to 35° have been recomputed by the use of more recently determined values of the normal potential of the silver-

silver chloride electrode. Final values of the dissociation constant of acetic acid from 0 to 60° at 5° intervals have been tabulated. Our value of  $1.754 \times 10^{-5}$  agrees excellently with the value,  $1.753 \times 10^{-5}$ , determined from the conductance measurements by MacInnes and Shedlovsky.

3. The dissociation constant is given by the equation

$$\log K = -\frac{1500.65}{T} - 6.50923 \log T - 0.0076792T^2 + 18.67257$$

4. The heat of dissociation is given by the equation

$$\Delta H = 6871.0 - 12.9436T - 0.035161T^2$$

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## Types of Chemical Reactions

BY WILLIAM ALBERT NOYES

A study of the interaction of nitrogen trichloride with nitric oxide and with nitrogen tetroxide has given results from which, in conjunction with other experimental evidence and with current electronic theories, it is possible to define accurately, with a high degree of probability, the electronic course of several types of reactions.

The discussion which follows applies, primarily, to elements with atomic weights of 40 or below. For elements of higher atomic weights the outer shell of valence electrons seems to be less sharply defined.

Three principles are used. (1) On account of their "spin" and for other reasons, the electrons of the valence shell of an atom are usually, not always, associated in pairs, octets or sextets. (2) Every atom must have the positive charge of its nucleus balanced by the electrons immediately associated with it, or it must be an ion or form part of a complex ion, which is held to or in the neighborhood of another ion of the opposite sign, by static attraction. (3) In balancing the positive charge of the nucleus of an atom the pair of electrons of a covalence is equivalent to a single unshared electron.

### 1. Formation of Ions

A. **Permanent ions**, formed with an outer shell of electrons (usually an octet) for some atom, in such a manner that the positive charge of the kernel or nucleus is overbalanced or underbalanced by the electrons surrounding it: (a) by the gain or loss of one or more electrons, as for sodium, calcium, chlorine or sulfur; (b) by the addition of a positive hydrogen or methyl ion to ammonia or to a tertiary amine, a positive hydroxyl group

to a tertiary amine,  $\text{CH}_3:\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{N}}}:\overset{+}{\text{H}}$  or a positive methyl to dimethyl