

and when applied show an average error of 0.2%. If averages be found between these two sets of values, the new set would describe both the alcohols and the chlorides with an average error of 0.3% when applied to the chlorides.

The constitutive effect is strikingly brought out by comparing homologs. The maximum CH<sub>2</sub> value from methylethylhexylchloromethane to ethylpropylpropylchloromethane would be 14.8 units or 45% higher than the minimum value in comparing propylpropylpropylchloromethane and methylmethylhexylchloromethane.

### Summary

1. The densities, surface tensions and parachors of sixteen tertiary chlorides have been determined.

2. The parachors show a decrease with tem-

perature of approximately 0.2% per 10° rise in temperature.

3. The effect of substitution in trimethylchloromethane has been found to be of the same order as that with trimethylcarbinol.

4. Values for the individual CH<sub>2</sub> groups in the tertiary chlorides have been determined and found to be of approximately the same value as those obtained for the corresponding CH<sub>2</sub> groups in the tertiary carbinols.

5. The similarity of the values obtained for the chlorides and alcohols indicates that association is not an important factor in the parachor values of the alcohol series.

6. The values for the tertiary branching give closer agreement between the calculated and observed values than the values previously used.

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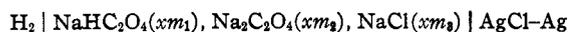
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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

## The Second Ionization Constant of Oxalic Acid from 0 to 50°

BY HERBERT S. HARNED AND LESLIE D. FALLON

From the electromotive forces of the cells



the ionization constant of HC<sub>2</sub>O<sub>4</sub><sup>-</sup> has been determined at 5° intervals from 0 to 50°.

The observed electromotive forces are given in Table I. The concentrations of the most concentrated solution,  $m_1$ ,  $m_2$  and  $m_3$ , are given. The concentrations of all other solutions are given by  $xm_1$ ,  $xm_2$  and  $xm_3$  where  $x$  is less than unity. The concentrations were known with an accuracy greater than 0.1%. The reproducibility of the measurements was of the order of  $\pm 0.05$  mv.

### The Determination of the Ionization Constant.

—By applying the method of Harned and Ehlers<sup>1</sup> in the manner used by Nims<sup>2</sup> for the second ionization constant of phosphoric acid, the electromotive force of the cell may be expressed by

$$\frac{(E - E_0)F}{RT} + \log \frac{m_{\text{Cl}} m_{\text{HC}_2\text{O}_4}}{m_{\text{C}_2\text{O}_4}} + \frac{2\mu \sqrt{\mu}}{1 + A \sqrt{2\mu}} = -\log K_2 + f(\mu) = -\log K_2' \quad (1)$$

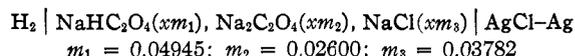
where the symbols have their usual significance. This differs from the equation of Nims by including the Debye and Hückel factor containing  $A$  which allows for the effect of the mean distance of

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

(2) Nims, *ibid.*, **55**, 1946 (1933).

TABLE I

### ELECTROMOTIVE FORCES OF THE CELLS



$t$	$x \dots 1$	0.8546	0.7263	0.5617
0	0.51317	0.51736	0.52217	0.52939
5	.51595	.52029	.52510	.53245
10	.51860	.52319	.52806	.53551
15	.52147	.52609	.53110	.53869
20	.52410	.52903	.53416	.54135
25	.52723	.53207	.53724	.54510
30	.53014	.53511	.54035	.54840
35	.53302	.53814	.54353	.55162
40	.53594	.54126	.54664	.55486
45	.53909	.54446	.54999	.55833
50	.54201	.54753	.55330	.56159
$t$	$x \dots 0.4684$	0.4050	0.3210	0.1737
0	0.53459	0.53851	0.54465	0.56180
5	.53767	.54187	.54823	.56570
10	.54096	.54504	.55167	.56935
15	.54416	.54836	.55504	.57308
20	.54739	.55172	.55849	.57691
25	.55073	.55509	.56206	.58066
30	.55412	.55856	.56570	.58461
35	.55741	.56202	.56925	.58850
40	.56090	.56554	.57285	.59244
45	.56431	.56915	.57662	.59654
50		.57275	.58016	.60054

approach of the ions. In order to determine the ionization constant,  $K_2$ , it is necessary to evaluate

the left side of this equation and extrapolate to zero ionic strength. The ionization constant is of the order of  $5 \times 10^{-5}$  and this is great enough to require a small correction to the ratio of  $m_{\text{HC}_2\text{O}_4}$  to  $m_{\text{C}_2\text{O}_4}$  in the term containing these quantities. This correction was made by arithmetical approximation using the expression for the thermodynamic ionization constant and the Debye and Hückel equation for the activity coefficient. At the lowest concentration the correction amounts to 0.007 in  $-\log K_2$  and at the higher concentrations it is negligible. In Fig. 1, various extrapolations are shown. The upper plots represent the

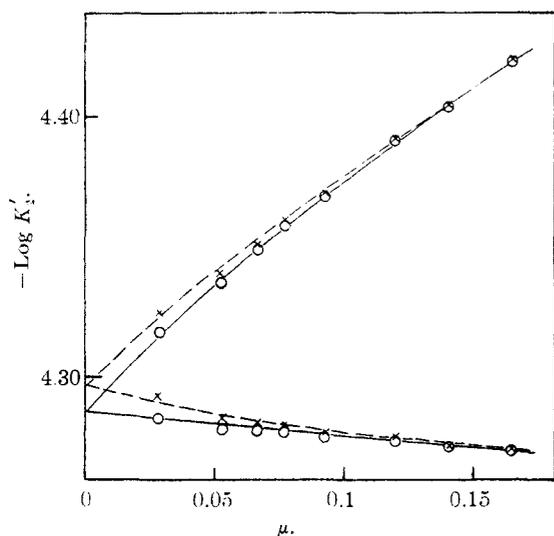


Fig. 1.—Extrapolation at 25°: crosses, uncorrected extrapolation function; circles, extrapolation function corrected for hydrogen ion concentration; upper plots, limiting law; lower plots, limiting equation with term for "mean distance of approach of ions"; diameter of circles equals 0.2 mv.

extrapolation when the Debye and Hückel term,  $2u\sqrt{\mu}$ , is employed. The lower plots represent the extrapolation when the complete Debye and Hückel expression is used.  $A$  was taken to be unity. From the character of these graphs, it is apparent that the latter function yields the better extrapolation. The crosses are the values of the left side of equation (1) uncorrected for hydrogen ion concentration, while the circles represent the values of this quantity when the ratio of  $m_{\text{HC}_2\text{O}_4}$  to  $m_{\text{C}_2\text{O}_4}$  has been corrected. The uncorrected function (dashed lines) leads to a higher value of  $-\log K_2$ . The corrected function (lowest plot) is a straight line and is easy to extrapolate. The uncertainty in the evaluation of  $-\log K_2$  is about 0.002.

Parton and Gibbons<sup>3</sup> and Parton and Nicholson<sup>4</sup> have used a similar cell in which the hydrogen electrode was replaced by the quinhydrone electrode for the determination of  $K_2$ . The plots of their results lie very close to ours. At 25°, they obtained 4.300 for  $-\log K_2$  at 25° but they did not make the hydrogen ion correction. The present results lead to a value of 4.297 under these circumstances which is excellent evidence of the experimental accuracy of both series of results. Our corrected value is 4.286 at 25°. The same remarks also apply to their results at 30 and 35°.

**Heat Content and Heat Capacity of the Ionization Reaction.**—Results have been obtained at a sufficient number of temperatures to permit the evaluation of the thermal data from the values of ( $-\log K_2$ ) given in Table II. The equation of

TABLE II  
THE IONIZATION CONSTANT,  $K_2$ , HEAT CONTENT AND HEAT CAPACITY OF THE REACTION  $\text{HC}_2\text{O}_4^- \rightleftharpoons \text{H}^+ + \text{C}_2\text{O}_4^{2-}$

$t$	$-\log K_2$ obsd.	$-\log K_2$ calcd.	$K_2 \times 10^5$	$-\Delta H$	$-\Delta C_p$
0	4.228	4.229	5.91	278	43
5	4.235	4.234	5.82	501	46
10	4.244	4.243	5.70	739	49
15	4.255	4.254	5.55	993	52
20	4.268	4.269	5.40	1264	56
25	4.286	4.286	5.18	1551	59
30	4.308	4.308	4.92	1856	63
35	4.331	4.331	4.67	2178	66
40	4.356	4.358	4.41	2519	70
45	4.388	4.387	4.09	2877	74
50	4.417	4.420	3.83	3256	77

Constants of equation (2):  $\log K_m = \bar{5}.774$ ;  $\theta = -6.8^\circ$ ;  $p = 6 \times 10^{-5}$ .

Harned and Embree<sup>5</sup>

$$\log K_2 = [\log K_m - p\theta^2] + 2p\theta t - pt^2 \quad (2)$$

was found to fit the data very accurately if  $p$  has the value of  $6 \times 10^{-5}$ . In this equation,  $K_m$  is the value of  $K_2$  at its maximum, and  $\theta$  is the temperature at which  $K_2$  is a maximum. In most cases of uni-univalent electrolytes, a value of  $5 \times 10^{-5}$  for  $p$  is suitable. In the present case, the higher value is somewhat better.  $K_m$  was found to be  $5.94 \times 10^{-5}$  at  $-6.8^\circ$ . Substitution of these values in equation (2) leads to the convenient numerical equation

$$\log K_2 = \bar{5}.771 - 0.000816t - 6 \times 10^{-5} t^2 \quad (3)$$

The agreement between the observed results and those calculated by this equation is shown in the

(3) Parton and Gibbons, *Trans. Faraday Soc.*, **35**, 542 (1939).

(4) Parton and Nicholson, *ibid.*, **35**, 546 (1939).

(5) Harned and Embree, *This Journal*, **66**, 1050 (1934).

second and third columns of Table II. The maximum deviation is 0.003 at 50° and the average deviation is only 0.001.

The changes in heat content and heat capacity accompanying the ionization reaction are given by the equations

$$\Delta H = -5.69 \times 10^{-4} T^2(t - \theta) \quad (4)$$

$$\Delta C_p = -5.49 \times 10^{-4} T(T + 2(t - \theta)) \quad (5)$$

which are derived by differentiation of equation (1). Values of these quantities are contained in the last two columns of Table II.

### Summary

1. By means of suitable cells without liquid junction, the second ionization constant of oxalic acid,  $K_2$ , has been determined at 5° intervals from 0 to 50°.

2. The equation  $\log K_2 = \bar{5}.771 - 0.000816t - 6 \times 10^{-5} t^2$  expresses the observed values of  $\log K_2$  with an average accuracy of  $\pm 0.001$ .

3. Values of the heat content and heat capacity of the ionization reaction have been tabulated.

NEW HAVEN, CONN.

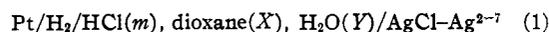
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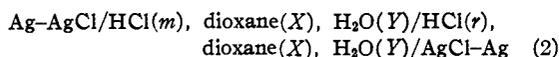
## Properties of Electrolytes in Mixtures of Water and Organic Solvents. IV. Transference Numbers of Hydrochloric Acid in Water and Dioxane-Water Mixtures from 0 to 50°

BY HERBERT S. HARNED AND EDWIN C. DREBY<sup>1</sup>

In conjunction with the extensive study of the thermodynamic properties of hydrochloric acid in water and in media covering a wide range of the dielectric constant by measurements of the electromotive force of cells of the type



it was considered appropriate to investigate the phenomenon of transference for this acid in the same media by means of the cells with transference of the type



Very extensive measurements were made which covered the acid concentration range from 0.005 to 3 *M*, a temperature range from 0 to 50° in solvents consisting of 0, 20, 45 and 70% dioxane-water mixtures. Results of less accuracy were also obtained in 82% dioxane-water mixtures ( $D \sim 10$ ).

The transference number which has been calculated is that defined by the well-known thermodynamic relation

$$T^+ = dE_t/dE \quad (3)$$

(1) This communication contains material from a dissertation presented by Edwin C. Dreby to the Graduate School of Yale University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1939.

(2) Harned and Donelson, *THIS JOURNAL*, **60**, 339 (1938).

(3) Harned and Ehlers, *ibid.*, **55**, 2179 (1933).

(4) Harned and Morrison, *ibid.*, **58**, 1908 (1936); *Am. J. Sci.*, **33**, 161 (1937).

(5) Harned and Donelson, *THIS JOURNAL*, **60**, 2128 (1938).

(6) Harned and Walker, *ibid.*, **61**, 48 (1939).

(7) Harned, Donelson and Calmon, *ibid.*, **60**, 2133 (1938).

where the transference number,  $T^+$ , at any particular concentration is the slope at the corresponding point on the plot of  $E_t$ , the electromotive force of the cell with transference, versus  $E$  the electromotive force of the cell without transference.

This is by far the most extensive study of the transference number of an electrolyte as a function of its concentration, the temperature and solvent composition. It is well known that this method is not so accurate as the moving boundary method, but it is reliable, rapid and therefore suitable for an extensive survey of the subject.

### Experimental Procedure

A diagram of the cell used is shown in Fig. 1. It consisted of two half-cells connected by means of a stopcock at

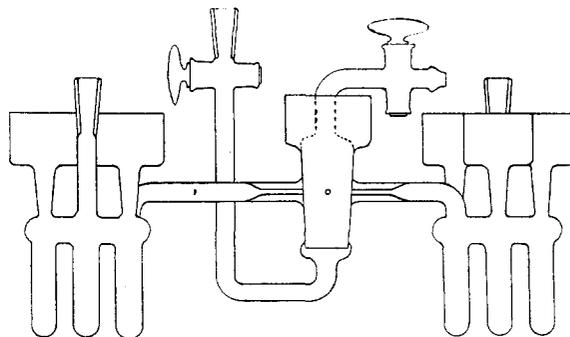


Fig. 1.—Transference cell.

which the liquid junction was formed. Each half-cell contained three legs into which the silver-silver chloride electrodes were inserted. Interchangeable ground glass joints were used between cell and electrode to give air-tight