zinc nitrate–water from 0 to 82% concentration and from 10 to 60° are given. This includes vapor pressures for unsaturated, saturated and supersaturated solutions and for eutectic mixtures of crystals.

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[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

The Ionization Constant of α-Crotonic Acid at 25° from Conductance Measurements[1]

BY BLAIR SAXTON[2] AND GEORGE W. WATERS

A general outline of the experimental technique and method of calculation employed in this study can be found in previous communications[3,4] from this Laboratory. Measurements of the conductance of α-crotonic acid ($CH_3CH{=}CHCOOH$) at concentrations above 0.002 demal, and of its sodium salt at all concentrations, were made in a cell of Type B described by Saxton and Langer.[3] The cell constant was 3.7261 estimated on the basis of a 0.1 demal potassium chloride solution according to Jones and Bradshaw.[5] Measurements on the acid at concentrations below 0.002 demal were performed in a silica cell similar to that of Saxton and Meier,[4] and of cell constant, 1.0830 based upon the 0.01 demal solution of Jones and Bradshaw.[5] The bridge was built by Leeds and Northrup according to the description of Dike,[6] and the source of power was a Leeds and Northrup Audio Frequency Oscillator No. 9842 operating at 1000 cycles.

Preparation of Materials

The α-crotonic acid was a commercial product subjected to five recrystallizations from carefully purified petroleum ether, and slowly sublimed. The white crystalline product was almost odorless, and melted between 71.5 and 71.7° according to measurements made in a simple Thiele tube with a recently calibrated thermometer. The value 71.4° was previously obtained in this Laboratory[7] from cooling curves with acid from the same source. The acid was stored in a vacuum desiccator over calcium chloride and suffered no appreciable change in melting point during the course of the conductance measurements.

The sodium salt was prepared from sodium carbonate (*ex* bicarbonate) and α-crotonic acid in sufficient excess to bring the resulting solutions to a *p*H of 6.7 to 7.0 on the basis of Lamotte standard buffers and brom thymol blue. Conductivities of these solutions were corrected[8] for the effect of the excess acid.

The experimental results, $\Lambda_{(\text{obsd.})}$, for sodium α-crotonate are recorded in Table I along with values derived from the semi-empirical equation[9]

$$\Lambda_{(C_4H_5O_2Na)} = 83.30 - 78.84\sqrt{c} + 97.27c(1 - 0.2276\sqrt{c}) \qquad (1)$$

TABLE I

SODIUM α-CROTONATE

$c \times 10^3$	$\Lambda_{(\text{obsd.})}$	$\Lambda_{(\text{Eq. 1})}$
0.18773	82.13	82.24
.75176	81.19	81.21
1.6436	80.23	80.29
2.6083	79.45	79.52
2.8315	79.38	79.38
3.9861	78.68	78.71
4.5069	78.48	78.44
5.6194	77.95	77.93
7.2425	77.31	77.28
9.8864	76.46	76.40
14.735	75.19	75.12
20.222	74.04	73.99
23.334	73.49	73.45
29.457	72.48	72.52
32.616	72.08	72.10

The parameters of this equation were adjusted to fit the data by the method of least squares. Assuming the validity of the Kohlrausch principle, equation (1) may be combined with the expressions

$$\Lambda_{HCl} = 426.28 - 156.84\sqrt{c} + 169.7c(1 - 0.2276\sqrt{c}) \qquad (2)$$

$$\Lambda_{NaCl} = 126.47 - 88.65\sqrt{c} + 94.8c(1 - 0.2276\sqrt{c}) \qquad (3)$$

previously obtained in this Laboratory[10] to yield the relation

$$\Lambda_{C_4H_5O_2H} = 383.11 - 147.03\sqrt{c_i} + 172.2c_i(1 - 0.2276\sqrt{c_i}) \qquad (4)$$

for the hypothetical completely dissociated α-crotonic acid at an ion concentration c_i.

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[1] This communication embodies part of the experimental material to be presented by George W. Waters to the Graduate School of Yale University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] After Professor Saxton's death, June 16, 1936, this work was continued under the direction of Professor Benton B. Owen.

[3] Saxton and Langer, THIS JOURNAL, **55**, 3638 (1933).

[4] Saxton and Meier, *ibid.*, **56**, 1918 (1934).

[5] Jones and Bradshaw, *ibid.*, **55**, 1780 (1933).

[6] Dike, *Rev. Sci. Instruments*, **2**, 379 (1931).

[7] Saxton and Skau, THIS JOURNAL, **52**, 335 (1930).

[8] MacInnes and Shedlovsky, *ibid.*, **54**, 1429 (1932).

[9] Shedlovsky, *ibid.*, **54**, 1405 (1932).

[10] The values of the characteristic parameters determined by Saxton and Langer (ref. 3) have been altered slightly to conform to present cell constants: *cf.* ref. 5.

The experimental equivalent conductances, Λ_c, of α-crotonic acid solutions are recorded in Table II. The ion concentrations,[11] c_i, and the values of the dilution constants are also included. Multiplication of K'

$$K' = c_i^2/(c - c_i) \qquad (5)$$

by the activity coefficient ratio, y_i^2/y_u, should yield the thermodynamic ionization constant, K, but because of the approximations introduced in the calculation of K', and our use of[11]

$$\log (y_i^2/y_u) = -1.013\sqrt{c_i} \qquad (6)$$

for estimating the unknown activity coefficients, the values of K recorded in the last column of Table II are not independent of the concentration. Fortunately the variation in log K is linear in $c_u (= c - c_i)$, which readily permits evaluation of the true thermodynamic constant by the extrapolation[12] illustrated in Fig. 1.

TABLE II

α-CROTONIC ACID

$c \times 10^3$	Λ_c	$c_i \times 10^3$	$K' \times 10^5$	$K \times 10^5$
0.95825	51.632	0.12970	2.0303	1.9771
1.7050	39.473	.17655	2.0394	1.9771
1.8047	38.343	.18154	2.0304	1.9676
3.2327	29.083	.24686	2.0410	1.9675
4.0138	26.249	.27675	2.0495	1.9715
4.9736	23.677	.30942	2.0527	1.9702
4.9974	23.602	.30992	2.0491	1.9667
5.8329	21.926	.33614	2.0556	1.9695
7.1422	19.861	.37297	2.0550	1.9645
10.259	16.652	.44946	2.0592	1.9598
14.511	14.053	.53691	2.0629	1.9544
17.779	12.716	.59554	2.0641	1.9499
22.512	11.318	.67150	2.0647	1.9437
27.730	10.200	.74587	2.0617	1.9340
33.246	9.3166	.81715	2.0591	1.9258
39.342	8.5629	.88915	2.0560	1.9178
49.149	7.6506	.99305	2.0478	1.9027

The intercept on this plot corresponds to $K = 1.97_5 \times 10^{-5}$. The same value was derived from the familiar extrapolation[8] of log K' vs. $\sqrt{c_i}$, but with less precision.

The value 2.03×10^{-5} previously obtained by Ives, Linstead and Riley[13] differs from ours by about ten times the discrepancy to be expected from experimental errors alone, but is readily accounted for by differences in primary standards. The limiting conductances of the hydrogen and sodium ions which they employ[14] would tend to make their K about 1% larger than ours, and their cell constants are based upon data[15] which are higher than the generally accepted standard[5] by amounts ranging from a few tenths to several per cent., depending upon the concentration. In the light of these considerations there is little doubt that the present determination is the more reliable.

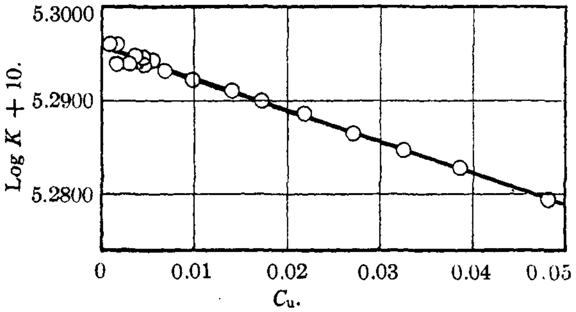

Fig. 1.

Summary

The equivalent conductances of α-crotonic acid and its sodium salt have been measured in dilute solution at 25°. The limiting equivalent conductance of sodium α-crotonate was found to be 83.30.

From these results, and data available in the literature, the value $K = 1.97_5 \times 10^{-5}$ was obtained for the thermodynamic ionization constant of α-crotonic acid at 25°.

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[11] *Cf.* Refs. 3 or 8 for details of calculations.

[12] An extended discussion of the extrapolation of dilution constants will appear in a communication by Saxton and Darken.

[13] Ives, Linstead and Riley, *J. Chem. Soc.*, 561 (1933).

[14] Ferguson and Vogel, *Phil. Mag.*, [4] **233**, 300 (1927); *cf.* MacInnes, Shedlovsky and Longworth, THIS JOURNAL, **54**, 2758 (1932) and ref. 3.

[15] Unpublished data of A. C. Melcher, Mass. Inst. Tech., 1912, quoted by Noyes and Falk, THIS JOURNAL, **34**, 454 (1912).