sponds to no gross discontinuity in the curve of activity *vs.* concentration

Obviously the present data give no information as to the way in which the water held by curd fibers is arranged except to confirm the conclusion of McBain and Ford[5] that in dilute curds the water held mechanically exists in capillary spaces filled to such a level that the effective diameter is about 10^{-4} cm.

This discussion has omitted reference to the fact that moist soap curds are electrolytically conducting systems[19] and to the effects of electrolytic charges on hydration such as are considered, for example, by von Nitsch.[20]

Summary

1. The activity of water in soap curd has been

determined by two independent methods: namely, measurement of the vapor pressure at constant temperature, and of the amount of ice formed at various temperatures, both as functions of total composition.

2. Sodium palmitate and sodium oleate can contain up to nearly one mole of combined water per mole of soap. Fibers crystallizing from more dilute systems contain more water than this (30–40% for NaP, 15–60% for NaOl) depending on the criterion for "bound" water.

3. Water in excess of 40% for sodium palmitate or 60% for sodium oleate is not chemically combined or sorbed, although its activity is slightly and progressively lowered by confinement in capillary spaces of the order of magnitude of 10^{-4} cm. in diameter.

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(19) M. E. Laing McBain, *Trans. Faraday Soc.*, **31**, 153 (1935).
(20) W. von Nitsch, *Kolloid-Z.*, **93**, 114 (1940).

The Ionization Constants of Oxalic Acid at 25° from Conductance Measurements

BY LAWRENCE S. DARKEN[1]

The success of the conductance method in determining the ionization constants of monobasic acids, together with the various general tendencies learned from the work on these, led the author to believe that the ionization constants of certain dibasic acids could be determined by a similar method, due account being taken of the rather small increment in conductance occasioned by the second ionization.

The ionization of oxalic acid in aqueous solution may be represented as

$$H_2Ox \rightleftharpoons H^+ + HOx^-$$
$$HOx^- \rightleftharpoons H^+ + Ox^-$$
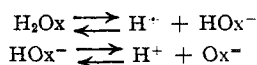
The ionization constant for the first dissociation cannot be determined by the method used for the ionization constant of a monobasic acid for two reasons: first, the measured conductance includes the contributions of both the first and the second ionizations; second, the equivalent conductance of the theoretical strong acid dissociating according to the first of the above equations only, Λ_e, defined by the equation

$$\Lambda_e = l_{H^+} + l_{HOx^-}$$

(where the l's are the equivalent ionic conductances), cannot be obtained in the customary manner from data on the sodium salt since the sodium salt undergoes secondary ionization to a marked extent.

The latter difficulty can be overcome by use of the empirical rule, developed in previous work,[2] that the plot of the logarithm of the ionization constant versus the concentration of un-ionized acid is linear; Λ_0 is selected so that the plot is linear. Successful application of this method to the measured conductances of a dibasic acid requires first a correction for the second ionization. If C is the concentration of the oxalic acid, α the degree of dissociation for the first step, and Δ the concentration of the Ox^- ion, then

$$C_{H_2Ox} = C(1 - \alpha); \quad C_{H^+} = C\alpha + \Delta; \quad C_{HOx^-} = C\alpha - \Delta; \quad C_{Ox^-} = \Delta$$

$$k_1 = \frac{C_{H^+} C_{HOx^-}}{C_{H_2Ox}} = \frac{C\alpha^2}{1 - \alpha} - \frac{\Delta^2}{C(1 - \alpha)}$$

$$K_1 = \frac{C\alpha^2 \gamma_1^2}{1 - \alpha} - \frac{\Delta^2 \gamma_1^2}{C(1 - \alpha)}$$

$$k_2 = \frac{C_{H^+} C_{Ox^-}}{C_{HOx^-}} = \frac{(C\alpha + \Delta)\Delta}{C\alpha - \Delta} \doteq \Delta$$

$$K_2 = \frac{(C\alpha + \Delta)\Delta \gamma_+ \gamma_-}{(C\alpha - \Delta)\gamma_-}$$

(1) Present address: Research Laboratory, United States Steel Corporation, Kearny, New Jersey.

(2) Saxton and Darken, THIS JOURNAL, **62**, 846 (1940).

K_2, and hence C_{Ox^-}, is of the order of 5×10^{-5}. At the lowest concentration used in this investigation the concentration of hydrogen ion is approximately 0.0023 (as $C \doteq 0.0024$ and $\alpha \doteq 0.96$), and the ratio of hydrogen ion contributed by the second ionization to the total hydrogen ion is $5 \times 10^{-5}/2.3 \times 10^{-3}$, or about 2%. At higher concentrations this ratio is much smaller. The percentage of the total conductance contributed by the second ionization is roughly the same as this hydrogen ion ratio (actually it is about 3% at the lowest concentration). Hence an accuracy of 1% or slightly better is sufficient in calculating the conductance correction made necessary by the second ionization. The contribution to the total conductance due to the second ionization is clearly the difference between that part of the conductance which the secondarily ionized HOx^- would have contributed had it not ionized and that part of the total conductance actually contributed by H^+ and $Ox^=$ resulting from the second ionization.[3]

This difference may be represented as

$$(l_{H^+} + 2\,l_{Ox^-} - l_{HOx^-})C_{Ox^-}$$

where the l's are the mobilities of the ions in the solution under consideration. Inserting

$$C_{Ox^-} \doteq k_2$$

(This expression contains no assumption as to the validity of the mass law as k_2 is calculated from K_2 and activity coefficients) and letting

$$\Lambda_\epsilon' = l_{H^+} + 2\,l_{Ox} - l_{HOx^-}$$

the above conductance difference becomes $k_2\Lambda_\epsilon'$. The specific conductance corrected for the second ionization may now be written

$$L_C = C\Lambda = L - k_2\Lambda_\epsilon'$$

L being the measured specific conductance, C the stoichiometic concentration; Λ, defined by the first equality, is the equivalent conductance as

(3) This statement is not exact, for the extent of second ionization does influence the extent of the first, as may be seen from the foregoing equation for K_1. However this influence is exceedingly small as may be shown by solving for α in the expression for k_1

$$\alpha = \frac{1}{2}\{[(k_1/C)^2 + 4(k_1/C + k_2^2/C^2)]^{1/2} - k_1/C\}$$

or expanding for reasonably low concentrations:

$$\alpha \doteq 1 - C/k_1 + \frac{k_2^2}{k_1 C}(1 - 2C/k_1)$$

Whereas α_u, the value of α obtained by ignoring the second ionization (*i. e.*, $K_2 = 0$), is clearly $\alpha_u = 1 - C/k_1$ whence $\alpha/\alpha_u \doteq 1 + k_2^2/k_1C$. The correction term k_2^2/k_1C amounts to less than 0.01% at all concentrations considered. Alternatively, it may be shown by substitution in the expression for k_1 that the second term involving $\Lambda^2 \doteq k_2^2$ is negligibly small over the concentration range investigated.

would be measured if no second ionization occurred. Using Λ_ϵ in its usual sense, *i. e.*, Λ/α, where α is the degree of the first ionization, we have

$$\alpha C = L/\Lambda_\epsilon - k_2\Lambda_\epsilon'/\Lambda_\epsilon$$

As the last term in the above equation is the correction term, it is assumed that $\Lambda_\epsilon'/\Lambda_\epsilon$ is a constant equal to the limiting value at infinite dilution; it is obvious from the fundamental conductance equation that the error due to this assumption is small.[4]

K_1, Λ_0 and K_2 may be found by a double series of successive approximations. The data are divided into two groups—high and low concentrations. The data at the higher concentrations where the effect of the secondary ionization is small are used to determine an approximate value of Λ_0 in this way. Various values of Λ_0 are substituted in Shedlovsky's modification of the Onsager conductance equation for a uniunivalent electrolyte

$$\Lambda_\epsilon = \Lambda_0 - (59.79 + 0.2274\Lambda_0)C_i^{1/2} + \beta C_i(1 - 0.2274C_i^{1/2})$$

(β is taken equal to the coefficient of $C_i^{1/2}$ as has been found for monobasic acids[2]). The values of Λ_ϵ so obtained are used to determine values of K_1 according to the equation

$$K_1 = \frac{\alpha^2}{1-\alpha}C\gamma_i^2 = \frac{(\Lambda/\Lambda_\epsilon)^2}{1-\Lambda/\Lambda_\epsilon}C\gamma_i^2$$

until those corresponding to a certain Λ_0 make the plot of $\log K_1$ *vs.* C_u linear. The ionic activity coefficients, γ_i's, are calculated from the Debye–Hückel law. Values of Λ_ϵ calculated from the above equation using the selected value for Λ_0 and the corresponding values of α for the low concentration data are substituted in the right hand side of the equation:

$$k_2\Lambda_\epsilon'/\Lambda_\epsilon = L/\Lambda_\epsilon - \alpha C$$

to give values of $k_2\Lambda_\epsilon'/\Lambda_\epsilon$, which are multiplied by $\gamma_+\gamma_-/\gamma_-$ (evaluated for each concentration) to give $K_2\Lambda_\epsilon'/\Lambda_\epsilon$. This quantity divided by the proper values of $\gamma_+\gamma_-/\gamma_-$, is then applied as a correction term to the measured specific conductances at the higher concentrations, using

(4) The general theory of the conductance of mixed electrolytes at low concentrations has been developed by Onsager and Fuoss [*J. Phys. Chem.*, **36**, 2689 (1932)]. The special case of the conductance theory for 3 ionic species in solution where one species is at low concentration compared to the other two was developed previously by Bennevitz, Wagner and Küchler [*Physik. Z.*, **30**, 623 (1929)]. Using the equations developed by them it is found that in the present case

$$\Lambda_\epsilon'/\Lambda_\epsilon \doteq 1.18 - 0.30\sqrt{C}$$

The error involved in taking $\Lambda_\epsilon'/\Lambda_\epsilon$ as the constant 1.18 is about 0.01% of the measured conductance over the entire range.

the same equation, and Λ_0 and K_1 are redetermined. Then a new value of $K_2\Lambda'_e/\Lambda_e$ is obtained. This process is repeated until further repetition does not change Λ_0, K_1^0 or $K_2\Lambda'_e/\Lambda_e$. It will be noted that the method forces a constant value for Λ_0 and K_1^0 in so far as a value for Λ_0 can always be found which makes the plot of log K_1 vs. C_u sensibly linear and this line must extrapolate to some value for K_1^0. Since there is nothing inherent in the method to force a constant value for K_2, the fact that it is found experimentally to be constant (within the experimental error) lends support to the data and method.

The treatment of the data on sodium oxalate was suggested by the findings of Shedlovsky and Brown.[5]

Apparatus and Materials.—The apparatus has been described previously.[6,7] Bright electrodes were used.

Oxalic Acid.—Baker oxalic acid was recrystallized four times from conductivity water. The dihydrate thus formed was partially dried on a Buchner funnel and then placed in a vacuum desiccator over anhydrous oxalic acid and allowed to stand for about a week. The product from which the stock solutions were prepared analyzed 100.05% (indicating that due to temperature gradient it was slightly dehydrated) by titration against sodium hydroxide solution which had been standardized against Bureau of Standards potassium acid phthalate and benzoic acid. The stock solutions were titrated against this same base (precision: 1 part in 10,000).

Sodium Oxalate.—Bureau of Standards sodium oxalate was used. The stock solution was made up by weight. The factor was checked after the experiment by evaporation to dryness; no change was found.

Results and Discussion

Sodium Oxalate.—The data on sodium oxalate are presented in Table I. The concentrations are expressed in gram moles per 1000 cc. of solution.

Shedlovsky and Brown[5] found that the conductance of uni-bivalent electrolytes may be expressed by the equation

$$\Lambda_0 = \Lambda'_0 - aC - bC \log C$$

where as usual

$$\Lambda'_0 = \frac{\Lambda + AC^{1/2}}{1 - BC^{1/2}}$$

In the case of the uni-bivalent electrolyte A and B are functions of the transport number. The solution of these equations for Λ_0 must depend on a method of successive approximations, since Λ_0 must be known approximately to obtain a transport number. When the transport number had been found to a sufficient degree of precision, various values of a were assumed until one was found which made the plot of $\Lambda'_0 - ac$ against $C \log C$ linear. This method yields a precision in the determination of Λ_0 comparable to the precision of the experimental data. However, it is impossible to evaluate a and b precisely except in terms of each other. The final graph of the determination of Λ_0 is shown in Fig. 1. The points shown on the graph have been corrected for hydrolysis (maximum correction $< 0.1\%$).
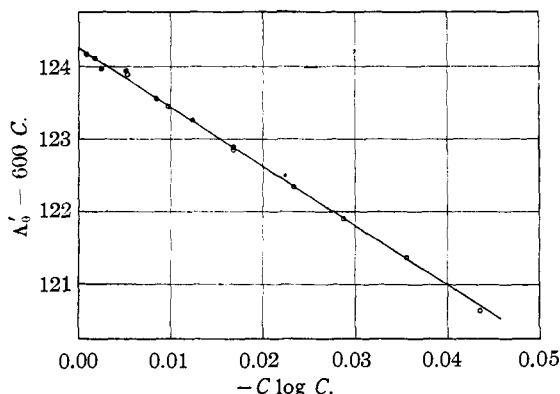

Fig. 1.—$\Lambda'_0 - 600C$ vs. $- C \log C$ for Na₂Ox.

The line of best fit is represented by the equation

$$124.25 = \Lambda'_0 - 600C - 81.7C \log C$$

where

$$\Lambda'_0 = (\Lambda + 155.3C^{1/2})/(1 - 0.756C^{1/2})$$

The precision of the value 124.25 for Λ_0 is probably ± 0.05.

Oxalic Acid.—The data on oxalic acid are presented in Table II. The density, determined in the usual manner in an approximately 10 cc. pycnometer, is expressed by the equation

$$\rho = 0.99704 + 0.0451C$$

TABLE I
SODIUM OXALATE

Series	A	B	A	A
$C \times 10^3$	0.22943	0.61611	0.80747	1.9089
Λ	120.53	118.29	117.36	114.16
Series	B	A	B	A
$C \times 10^3$	1.9589	3.4989	4.0974	5.5177
Λ	114.01	110.85	109.86	107.92
Series	B	A	A	A
$C \times 10^3$	7.9547	8.0432	10.182	11.674
Λ	105.14	105.13	103.22	102.11
Series	B	B	B	B
$C \times 10^3$	12.252	15.996	21.243	27.971
Λ	101.62	99.27	96.66	94.03

(5) Shedlovsky and Brown, THIS JOURNAL, **56**, 1066 (1934).
(6) Saxton and Langer, ibid., **55**, 3638 (1933).
(7) Saxton and Meier, ibid., **56**, 1918 (1934).

In this table the specific conductance is given instead of the equivalent conductance since the latter is rather meaningless on account of the second ionization.

TABLE II
OXALIC ACID

Series	I	II	II	I
$C \times 10^3$	2.38806	2.8225	5.2036	5.3939
$L \times 10^3$	0.90754	1.06107	1.86660	1.92832
$K_2 \times 10^5$	5.20	5.36	5.41	5.31

Series	I	II	I	II
$C \times 10^3$	7.2036	7.9151	9.4687	10.3471
$L \times 10^3$	2.5070	2.7290	3.2014	3.4635
$K_2 \times 10^5$	5.33	5.38	5.23	5.4

Series	II	I	II	II
$C \times 10^3$	12.6555	14.4429	14.9457	19.7437
$L \times 10^3$	4.1320	4.6325	4.7717	6.0467
$K_2 \times 10^5$	5.3	5.7	5.1	5.3380
				$(K_1 \times 10^2)$

Series	I	II	I	II
$C \times 10^3$	24.897	27.433	34.196	34.294
$L \times 10^3$	7.3375	7.9479	9.5044	9.5271
$K_1 \times 10^2$	5.3315	5.3292	5.3116	5.3139

Series	II	I	II	I
$C \times 10^3$	41.509	42.151	49.356	50.183
$L \times 10^3$	11.0942	11.2295	12.7093	12.8755
$K_1 \times 10^2$	5.2969	5.2960	5.2799	5.2771

Series	II	I	I	II
$C \times 10^3$	54.131	58.225	65.919	66.153
$L \times 10^3$	13.6551	14.4437	15.8819	15.9220
$K_1 \times 10^2$	5.2675	5.2569	5.2400	5.2345

The first ionization constant Λ_0 and $k_2\Lambda_e'/\Lambda_e$ were determined by the method of successive approximations as explained previously. From the value of Λ_0 for sodium oxalate the limiting value of Λ_e was found to be 458.8. The limiting value of Λ_e (which is Λ_0 for the first dissociation of oxalic acid) was found to be 390.0. These values were used to determine the K_2 values shown in Table II. The average value of K_2 is 5.3 ×
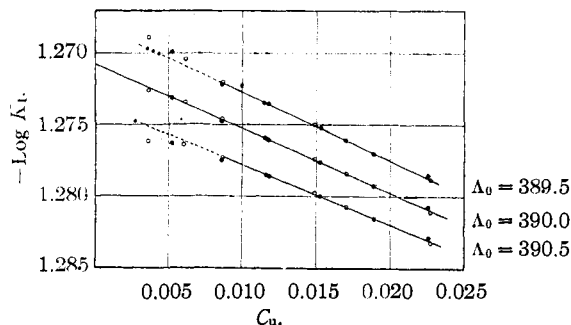

Fig. 2.—Log K_1 vs. C_u for oxalic acid.

10^{-5}. The limiting value of K_1 at infinite dilution was found to be 0.05360. The precision of this value for K_1 as measured by the deviation of the individual points of the straight line used for the extrapolation (see Fig. 2) is apparently 1 part in 4000. As mentioned before, the criterion used for the correct value of Λ_0 is that the plot of log K_1 versus C_u be linear; the experimental error in finding Λ_0 by this method seems to be a few tenths of a conductance unit as seen in Fig. 2, where it will be noticed that the curvature is pronounced if Λ_0 is taken 0.5 unit larger or smaller than the value selected. This uncertainty in the value of Λ_0 gives rise to an uncertainty of 1 part in 1000 in the value for K_1. The composite uncertainty of K_1 due to possible simultaneous fluctuation of K_2 and Λ_0 is but slightly larger. The over-all precision of the limiting value of K_1 from the measurements given in Table II is about 1 part in 1000.

The values obtained in this research are compared with that of Harned and Fallon[8] and those of Parton and Gibbons,[9] and Parton and Nicholson[10] and also of Gane and Ingold[11] in Table III.

TABLE III
IONIZATION CONSTANTS OF OXALIC ACID AT 25°

	K_1	$K_2 \times 10^5$
Gane and Ingold (electrometric titration)	0.059	6.40
Parton and Gibbons (e. m. f.)	.050	5.012
Parton and Nicholson (e. m. f.)	.0457	...
Harned and Fallon (e. m. f.)	....	5.18
Darken (conductance)	.0536	5.3

It is to be noted that Harned and Fallon point out that Parton, Gibbons and Nicholson failed to make certain corrections in the interpretation of their e. m. f.'s. The conductance method used in the research reported in this paper yields primarily a value of K_1; the value of K_2 is obtained only as a correction term; the e. m. f. method, on the other hand, yields primarily a value of K_2 and only an approximate value of K_1. Therefore, other things being equal, more reliance is to be placed on the e. m. f. values for K_2 and on the conductance value for K_1. The fact that the value of K_2 reported here checks so well with that obtained by e. m. f. methods would seem to lend added confidence to the values of K_1 and Λ_0 and appear to lead to the conclusion that the accu-

(8) Harned and Fallon, THIS JOURNAL, **61**, 3111 (1939).
(9) Parton and Gibbons, Trans. Faraday Soc., **35**, 542 (1939).
(10) Parton and Nicholson, ibid., **35**, 546 (1939).
(11) Gane and Ingold, J. Chem. Soc., 2156 (1931).

racy[12] of the values reported for these constants is of the same order of magnitude as the precision.

It is of interest to note that the slope d log K_1/

(12) The accuracy of the determination of K_1 and Λ_0, of course, depends on the function chosen for the final plot. This was discussed by Saxton and Darken[2] who pointed out that the plot of log K *versus* the concentration of undissociated acid seemed most suitable for extrapolation, where the activity coefficients included in K_1 are obtained from the formula log $\gamma_1 = 0.5063\ C_1{}^{1/2}$. The data on the acids considered in that paper seemed to indicate that the use of a denominator term in the above expression was undesirable. However, as oxalic acid is a stronger acid than any of those previously considered, it was thought that though the denominator term is negligibly small for the weaker acids it may not be so for oxalic. Hence the same method was applied using the expression log $\gamma_1 = 0.5063\ C_1{}^{1/2}/(1 + 0.200\ C_1{}^{1/2})$. It was found that the omission of the denominator term from the Debye–Hückel expression results in no significant change in K_1 or Λ_0 but yields a limiting value of K_1 which is about 0.5% lower than if the denominator term is used. If log K_1 be plotted against the total concentration instead of the concentration of undissociated acid, K_1 will be found about 1.5% higher (Λ_0 is found *to be 0.5* conductance unit lower).

d $C_u = -0.45$ is in good agreement with the relationship found by Saxton and Darken[2] between the values of this slope and the molecular weights of monobasic acids. (The predicted value would be about -0.38.)

Summary

The conductance method has been adapted to the determination of the ionization constants of oxalic acid. Application of this modified method to conductance data on oxalic acid and sodium oxalate in aqueous solution at 25° leads to the values $K_1 = 5.36_0 \times 10^{-2}$ and $K_2 = 5.3 \times 10^{-5}$. The limiting equivalent conductance of sodium oxalate was found to be 124.25 and that corresponding to the primary ionization of oxalic acid was found to be 390.0.

The Activity Coefficients of Lithium, Sodium and Potassium Sulfate and Sodium Thiosulfate at 25° from Isopiestic Vapor Pressure Measurements

By R. A. Robinson,[1] Jean M. Wilson and R. H. Stokes

The activity coefficients of lithium, sodium and potassium sulfate have been determined at 25° by Åkerlöf[2] from measurements on cells with amalgam electrodes and in the case of sodium sulfate Harned and Hecker[3] have extended the measurements over the temperature range 0 to 40°. We have now made measurements on these three alkali metal sulfates at 25° by the isopiestic vapor pressure method,[4] extending the concentration range to 3 M for lithium sulfate and to 4 M for the sodium salt. In addition, we have made measurements on sodium thiosulfate up to 3.5 M which lead to the first determination of the activity coefficient of this salt.

The four salts were recrystallized several times from water and their purity checked by analysis. Solutions of each of the salts were brought into equilibrium with solutions of potassium chloride by the isopiestic method with the results given in Table I. Platinum dishes were used to contain the thiosulfate solutions.

(1) Sterling Fellow, Yale University, 1940.
(2) G. Åkerlöf, This Journal, **48**, 1160 (1926); H. S. Harned and G. Åkerlöf, *Physik. Z.*, **27**, 411 (1926).
(3) H. S. Harned and J. C. Hecker, This Journal, **56**, 650 (1934).
(4) R. A. Robinson and D. A. Sinclair, *ibid.*, **56**, 1830 (1934).

Table I

Molalities of Solutions of Lithium, Sodium and Potassium Sulfate and Sodium Thiosulfate, Isopiestic with Solutions of Potassium Chloride at 25°

Lithium Sulfate

mKCl	mLi$_2$SO$_4$	mKCl	mLi$_2$SO$_4$	mKCl	mLi$_2$SO$_4$
0.09835	0.07310	1.114	0.8549	3.246	2.282
.1155	.08635	1.241	.9472	3.423	2.382
.1561	.1178	1.360	1.034	3.642	2.504
.1819	.1381	1.677	1.259	3.751	2.572
.3161	.2424	1.894	1.409	3.821	2.612
.3556	.2733	1.990	1.475	4.131	2.786
.5195	.4006	2.295	1.676	4.580	3.037
.5487	.4235	2.473	1.799	4.671	3.080
.7407	.5728	2.543	1.841	4.810	3.158
.8420	.6497	2.880	2.052	4.810	3.165
		3.107	2.194		

Sodium Sulfate

	mNa$_2$SO$_4$		mNa$_2$SO$_4$		mNa$_2$SO$_4$
0.1270	0.09830	1.031	0.9600	1.821	1.778
.1705	.1345	1.339	1.273	2.221	2.178
.1800	.1419	1.385	1.325	2.497	2.429
.3820	.3186	1.391	1.335	2.527	2.456
.5836	.5081	1.571	1.514	3.097	2.945
.6772	.5930	1.641	1.594	3.577	3.334
.8270	.7460	1.765	1.725	4.220	3.784
.9472	.8690			4.810	4.185