of only 0.02% water, if the source of the difference is attributed entirely to moisture. Our solutions stood for a few days in well-stoppered, ordinary glass bottles which had been used for acetic acid solutions for several months previously. They were protected by beakers sealed with paraffin.

The measurements were made on apparatus[3] of the a. c. bridge type consisting of the following parts: a 1000-cycle microphone hummer, a Kohlrausch slide wire (Leeds and Northrup Co.), non-inductive type resistance (Leeds and Northrup Co.), accurate to 0.05%, a variable air condenser across the resistance box to balance the capacity of the cell, and a two-stage audio amplifier with headphones matched to the frequency of the oscillator. The center of the bridge is grounded and all leads are shielded. The conductivity cell is placed in a thermostat which is constant to 0.005°.

Conclusions

1. A conductivity method is described for the precise determination of small quantities of sulfuric acid when dissolved in anhydrous acetic acid.
2. The specific conductances of the complete range of acetic acid–water mixtures have been determined.
3. The molal conductances of solutions of 0.005 to 0.10 *M* sulfuric acid in anhydrous acetic acid were determined. The data agree very well with the recent measurements of Hall and Voge.

(3) Kindly loaned to us by Professor J. J. Beaver of this Department.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

The Ionization Constant of Monochloroacetic Acid, at 25°, from Conductance Measurements[1]

BY BLAIR SAXTON AND THEODORE W. LANGER

In sufficiently dilute aqueous solution the thermodynamic ionization constant of a weak acid, HA, is given by the equation

$$K = \gamma^2 C_i^2/(C - C_i) = \gamma^2 K' \tag{1}$$

where γ is the geometrical mean activity coefficient, C_i is the concentration of the ionized portion, and C is the total concentration of the acid. K' is the usual concentration (or dilution) constant. Evaluating γ by means of the limiting law of Debye and Hückel,[2] taking the dielectric constant for water at 25° as 78.56 (the mean of the results of Drake, Pierce and Dow[3] and Wyman),[4] we may write

$$\log K = \log K' - 1.013 \sqrt{C_i} \tag{2}$$

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[1] This paper contains material which represents part of the dissertation submitted by Theodore W. Langer to the Graduate School of Yale University in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1931. The authors wish to acknowledge their indebtedness to Lawrence S. Darken and Harry F. Meier, who contributed the measurements on hydrochloric acid and its sodium salt.

[2] Debye and Hückel, *Physik. Z.*, **24**, 185 (1923).

[3] Drake, Pierce and Dow, *Phys. Rev.*, **35**, 613 (1930).

[4] Wyman, *ibid.*, **35**, 623 (1930).

When C_i has been determined from conductance measurements, this equation has been verified by MacInnes and Shedlovsky[5] for acetic acid, Davies[6] for mandelic acid, and by our own results.

The ionic concentration can be determined from conductance data by means of the relation

$$C_i = \alpha C = \Lambda/\Lambda_{(\mathrm{H^+ + A^-})}\, C = 1000\, k\, (L/\Lambda_{(\mathrm{H^+ + A^-})}) \tag{3}$$

where k is the cell constant and α, L, Λ and $\Lambda_{(\mathrm{H^+} + \mathrm{A^-})}$ are the degree of ionization, the cell conductance, the equivalent conductance and the sum of the equivalent conductances of the ions of the weak acid, respectively. For a given value of C_i, the denominator can be determined by the relation

$$\Lambda_{(\mathrm{H^+ + A^-})} = \Lambda_{(\mathrm{HCl})} - \Lambda_{(\mathrm{NaCl})} + \Lambda_{(\mathrm{Na\,A})} \tag{4}$$

For very dilute aqueous solutions Λ for each of the strong electrolytes can be expressed as a function of C_i by means of the Debye–Hückel–Onsager[7] equation

$$\Lambda = \Lambda_0 - (0.2276\, \Lambda_0 + 59.88)\sqrt{C_i} \tag{5}$$

Shedlovsky[8] has empirically extended this to more concentrated solutions, obtaining the equation

$$\Lambda_0 = \frac{\Lambda + 59.88\sqrt{C_i}}{1 - 0.2276\sqrt{C_i}} - BC_i = \Lambda_0' - BC_i \tag{6a}$$

$$\Lambda = \Lambda_0 - (0.2276\, \Lambda_0 + 59.88)\sqrt{C_i} + BC_i(1 - 0.2276\sqrt{C_i}) \tag{6b}$$

in which B is an arbitrary constant. Using this equation for each strong electrolyte an equation of the type of (6b) for $\Lambda_{(\mathrm{H^+} + \mathrm{A^-})}$ results through substitution in equation (4). Values of C_i, K' and K can then be computed from equations (3), (1) and (2), respectively. This method has been used successfully by MacInnes and Shedlovsky[9] in their work on acetic acid. Since the conductance data for each of our strong electrolytes is represented by equation (6b), we have also used this method.

Apparatus

The Bridges.—Two bridges were used. The first was a modified Jones and Josephs[10] type constructed from apparatus at hand in the laboratory. The Wagner ground consisted of a Kohlrausch slide wire and a General Radio type 219 G condenser. The ratio arms were a Leeds and Northrup Kohlrausch slide wire of the older, marble drum type. An a. c.–d. c. calibration showed that the a. c. error was very small for readings near the center of the bridge. The standard resistances were a Curtis coil and a bifilarly wound decade box, both from Leeds and Northrup, which were calibrated against similar boxes certified by the Bureau of Standards. An air condenser and a General Radio type 219 G condenser, shunted across the standard resistance, produced the correct phase relations. Current from the bridge was led through a transformer, thence to a two-stage amplifier

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

(6) Davies, *ibid.*, **54**, 1698 (1932).

(7) Debye and Hückel, *Physik. Z.*, **24**, 305 (1923); Onsager, *ibid.*, **27**, 388 (1926); **28**, 277 (1927); *Trans. Faraday Soc.*, **23**, 341 (1927); *J. Phys. Chem.*, **36**, 2689 (1932).

(8) Shedlovsky, THIS JOURNAL, **54**, 1405 (1932).

(9) MacInnes and Shedlovsky, *ibid.*, **54**, 1429 (1932).

(10) Jones and Josephs, *ibid.*, **50**, 1049 (1928).

and telephone. At all concentrations absolute silence was obtained. All measurements with cell A, the weak acid and its sodium salt, were taken with this bridge.

All measurements with cell B, hydrochloric acid and its sodium salt, were made with the new Leeds and Northrup bridge which has been described by Dike.[11] The ratio arms and all resistances were carefully calibrated against standard resistances certified by the Bureau of Standards. The condensers built into the bridge were sufficient to produce the correct phase relations.

Cells.—Two cells were used: cell A for the weak acid and its sodium salt, and cell B for hydrochloric acid and its sodium salt. A diagram of cell A, drawn approximately to scale, is shown in Fig. 1 (A). It is made entirely of Pyrex. The flask is two liters in capacity. The electrodes are heavy platinum disks, 3.8 cm. in diameter, and are sealed through the glass by means of platinum tipped tungsten rods. The opening at the top of the cell is ground to fit the collar of a weight buret. Cell B is made of Jena "Geräteglas." Figure 1 (B), giving the lower section of this cell, shows the other essential difference in the construction of the two cells. The electrodes are 2.5 cm. in diameter and are supported by thin-walled platinum tubing. A tube, provided with a stopcock, is sealed into the bottom of the electrode compartment. Through this tube air, freed from carbon dioxide and ammonia, was blown through the water at the beginning of a run until the conductance remained sensibly constant. Both cells were well annealed and sufficiently aged. The electrodes in both cells are unplatinized in order to facilitate the transfer from one concentration or electrolyte to another and to avoid any possible effect on the weak acids. Our results indicate that accurate conductance measurements can be made with such unplatinized electrodes. That there is no serious capacitance to earth is shown by the fact that no change was noticed when the quantity of solution in the cell was varied from the amount necessary to barely fill the electrode compartment to an amount which filled the flask more than half full. With cell B, the capacitance correction given in equation (7) was negligible in the range of concentrations of hydrochloric acid and sodium chloride used.

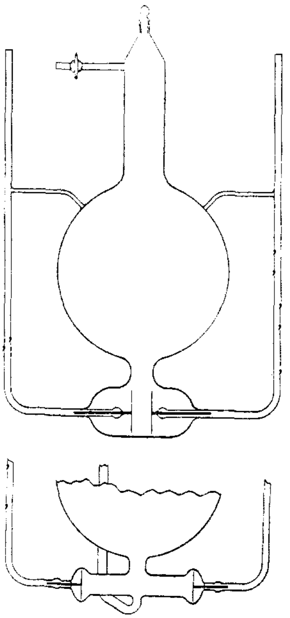

Fig. 1.—A, above; B, below.

Source of Power.—All recorded determinations were made at 1000 cycles generated by a shielded Vreeland oscillator situated about thirty feet from the bridge in another room. The low voltage secondary was connected to a potential divider, a manganin wire a meter long and of sixteen ohms resistance. By tapping about a millimeter from one binding post, a very low voltage was led directly to the first bridge. A somewhat greater voltage was sent through an intervening transformer to the second bridge.

Thermoregulation.—A rectangular porcelain thermostat, containing forty-five gallons of transformer oil, maintained a constant temperature. The bath was adjusted and its variation observed by a Beckmann thermometer which had recently been standardized against a platinum resistance thermometer. The temperature was 25.000 ± 0.005°.

Preparation of Materials

Conductivity Water.—For the measurements on the weak acid and its sodium salt, the water was obtained from a Barnstead automatic water still, electrically heated. The

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

cooling water was so regulated that less than one-half of the steam condensed. The first four liters after starting were discarded. The water was distilled directly into the vessel in which it was to be used. With care, the specific conductance was 10^{-6} mhos. Except for some of the most dilute solutions, the water conductance was less than 1% of the total conductance.

For the measurements on hydrochloric acid and its sodium salt the water was obtained by redistilling distilled water containing alkaline potassium permanganate in a Barnstead "Conductivity Water Still" which is a modified form of that described by Kraus and Dexter.[12] In general it was distilled directly into the vessels in which it was used, but for storage a properly protected 15-liter "Vitreosil" retort was used. The specific conductance of the water so stored was 3×10^{-7} mhos, while that of water collected directly in cell B and subsequently treated with air freed from carbon dioxide and ammonia was $1-2 \times 10^{-7}$ mhos.

Acids.—Baker C. P. Analyzed special arsenic free hydrochloric acid was distilled twice from an all Pyrex glass still by trapping the hydrogen chloride gas which was driven off in water whose volume was one-third that of the acid introduced into the flask. Eastman's No. 68 monochloroacetic acid was distilled twice under diminished pressure. The product was a white solid melting at 62°. The cold solution showed no immediate turbidity with silver nitrate.

Salts.—For the cell constant determinations, Kahlbaum "Kaliumchlorid zur Analyse" was recrystallized four times from water. After drying for a day at 110°, it was fused in a platinum dish, then it was ground to a fine powder in an agate mortar. It was stored in a weighing bottle kept in a desiccator. A saturated solution of Baker C. P. Analyzed sodium chloride was dropped slowly into ethyl alcohol which had been distilled from lime. The precipitate was dissolved in water and the solution evaporated partially to reprecipitate sufficient salt. All the crystals were semi-dried by pressing and aspirating dust-free air over them. To prepare sodium monochloroacetate, the required amount of sodium carbonate was added slowly and with constant shaking to a known amount of the acid. The solution was neutral to litmus. The sodium carbonate was made from Merck C. P. sodium bicarbonate according to the directions in Treadwell–Hall.[13]

After being made alkaline with sodium carbonate and acidified with nitric acid, all solutions remained perfectly clear on addition of barium chloride, and all, except the chlorides, remained perfectly clear on addition of silver nitrate. The acids left no detectable residue when evaporated in platinum.

Experimental Procedure

The Conductance Measurements.—All measurements were in concentration series. A weighed amount of conductivity water was introduced into the cell, brought to the temperature of the thermostat and its conductance measured. Successive samples of analyzed stock solution were added with a weight buret, the solution thoroughly mixed, and after reaching the temperature of the thermostat, the conductance of the solution was determined. In each measurement the cell and standard resistance were reversed and the ratio again taken. With the first bridge, the ratio arms were kept as nearly as possible equal to unity, with the second bridge

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(12) Kraus and Dexter, THIS JOURNAL, **44**, 2469 (1922).

(13) Treadwell–Hall, "Analytical Chemistry," John Wiley and Sons, New York, 1924, Vol. II, p. 475.

the ratio arms were always equal. The equivalent series resistance, R_4, of the cell was calculated from the equation[14]

$$R_4 = \frac{R_2}{R_1}\,\frac{R_3}{1 + R_3^2\,\omega^2\,C_3^2 + R_3\omega C_3\theta_3} \tag{7}$$

where R_1 and R_2 are the resistances of the ratio arms of the bridge, R_3 is the standard resistance, C_3 is the capacity of the condenser shunting R_3, and ω is 2π times the frequency. The last term in the denominator including θ_3, the phase difference in the condenser, is negligible except in the case of a few of the more concentrated solutions when measured in cell A. No change in the value of R_4, calculated from this equation, resulted when the frequency was changed from 1000 to 500. The whole water conductance was subtracted for the salts and neglected for the acids. The cell constants were determined with one hundredth demal potassium chloride prepared according to the directions of Parker and Parker.[15] Taking their value of 0.0014078_9 as the specific conductance, the cell constants are 0.07308 and 3.8503 for cells A and B, respectively.[16]

Determination of Concentrations.—The analyses of the stock solutions were calculated as the true weight of electrolyte per gram of solution weighed in air. Chlorides were weighed as silver chloride. In the case of sodium chloride this was checked against the value determined by synthesis. Monochloroacetic acid was titrated against sodium carbonate with sodium alizarin sulfonate as indicator. From the amounts used in preparation, the concentration of sodium monochloroacetate was calculated. Estimating the densities by interpolation, the concentration, in moles per liter of solution, was calculated.

Results

The measured equivalent conductances of the necessary strong electrolytes are expressed in equations (8), (9) and (11), and from these expressions equations (10) and (12) are derived.

$H^+ + Cl^-$;[17] $\Lambda = 426.01 - 156.84\sqrt{C_i} + 169.7\,C_i(1 - 0.2276\sqrt{C_i})$ (8)

$Na^+ + Cl^-$;[17] $\Lambda = 126.39 - 88.65\sqrt{C_i} + 94.8\,C_i(1 - 0.2276\sqrt{C_i})$ (9)

$H^+ - Na^+$; $\Lambda = 299.62 - 68.19\sqrt{C_i} + 74.9\,C_i(1 - 0.2276\sqrt{C_i})$ (10)

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[14] This relation, easily derived from the theory of the alternating current bridge on the assumption that R_1, R_2 and R_3 are reactance free, is essentially the same as equations (23) and (24) of Jones and Josephs, THIS JOURNAL, **50**, 1049 (1928).

[15] Parker and Parker, *ibid.*, **46**, 312 (1924).

[16] Since this paper was written, Jones and Bradshaw [*ibid.*, **55**, 1780 (1933)] have reported new values for the specific conductances of potassium chloride. Their value for the 0.01 *D* solution is 0.062% higher than that given by Parker and Parker. If the new value be adopted, our cell constants and all our values of Λ should be increased by that amount, but our values of C_i, K' and K would be unaffected. The data of Shedlovsky, THIS JOURNAL, **54**, 1411 (1932), and of MacInnes and Shedlovsky, *ibid.*, **54**, 1429 (1932), with which we later compare certain of our measurements, would only be raised by 0.028%, since their cell constants were determined with 0.1 *D* potassium chloride. In general, the agreement for the dilute solutions is improved in the cases of sodium chloride and sodium acetate, but is not improved in the case of hydrochloric acid.

[17] Determined by Lawrence S. Darken and Harry F. Meier in this Laboratory.

$$\mathrm{Na^+ + A^-};\quad \Lambda = 90.02 - 80.37\sqrt{C_i} + 67.7\,C_i(1 - 0.2276\sqrt{C_i}) \qquad (11)$$

$$\mathrm{H^+ + A^-};\quad \Lambda = 389.64 - 148.56\sqrt{C_i} + 142.6\,C_i(1 - 0.2276\sqrt{C_i}) \qquad (12)$$

Our experimental results are compared with those calculated from equations (8), (9) and (11) in Table I.

TABLE I

HCl

$C \times 10^3$	0.23042	0.45545	0.75166	1.3684	2.2406
Λ (obs.)	423.79	422.91	421.74	420.45	418.99
Λ (calcd.)	423.67	422.74	421.84	420.44	418.96
$C \times 10^3$	3.2561	4.5471	6.2065	8.0627	10.839
Λ (obs.)	417.59	416.18	414.68	413.26	411.51
Λ (calcd.)	417.61	416.19	414.69	413.27	411.48
$C \times 10^3$	15.063	20.055	24.822	31.097	
Λ (obs.)	409.25	407.09	405.35	403.40	
Λ (calcd.)	409.25	407.09	405.36	403.42	

NaCl

$C \times 10^3$	0.084837	0.33408	0.65245	1.4386	2.2142	
Λ (obs.)	125.61	124.90	124.28	123.17	122.44	
Λ (calcd.)	125.58	124.80	124.19	123.16	122.42	
$C \times 10^3$	3.2289	4.4206	5.7219	7.5809	8.3718	
Λ (obs.)	121.65	120.90	120.20	119.36	119.05	
Λ (calcd.)	121.66	120.91	120.22	119.38	119.06	
$C \times 10^3$	9.3286	11.443	13.845	15.883	18.784	22.299
Λ (obs.)	118.68	117.97	117.24	116.69	115.98	115.19
Λ (calcd.)	118.69	117.97	117.24	116.68	115.97	115.19

$CH_2ClCOONa$

$C \times 10^3$	0.6619	1.2613	1.8209	2.594	3.527
Λ (obs.)	88.17	87.12	86.68	86.12	85.43
Λ (calcd.)	88.00	87.25	86.71	86.10	85.48
$C \times 10^3$	4.039	5.005	5.841	6.496	7.077
Λ (obs.)	85.18	84.69	84.24	83.97	83.71
Λ (calcd.)	85.18	84.67	84.27	83.97	83.73

Our results for hydrochloric acid and sodium chloride are in good agreement with those of Shedlovsky[18] but are higher than those of Jeffery and Vogel.[19] From equation (12) and the conductances of monochloroacetic acid given in Table II, the remainder of the table was constructed.

If log $(K' \times 10^3)$ be plotted against $\sqrt{C_i}$, the first six points, excluding the first, fall on a straight line, the equation of which is

$$\log (K' \times 10^3) = 0.1449 + 1.011\sqrt{C_i} \qquad (13)$$

From this it is apparent that nearly the theoretical slope has been obtained and that $K = 1.396 \times 10^{-3}$, which is the average of the first six values in Table II, again excluding the first value. Above 0.01 normal the curve falls below the limiting slope and the values of K decrease. This decrease

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(18) Shedlovsky, THIS JOURNAL, **54**, 1411 (1932).

(19) Jeffery and Vogel, *J. Chem. Soc.*, (NaCl), 1715 (1931); (HCl), 400 (1932).

TABLE II

MONOCHLOROACETIC ACID

$C \times 10^3$	$L \times 10^3$	Λ	$C_i \times 10^3$	α	$K' \times 10^3$	$K \times 10^3$
1.814	5.593	225.32	1.062	0.585	1.500	1.390
4.048	9.675	174.67	1.844	.456	1.543	1.396
5.222	11.405	159.61	2.176	.417	1.554	1.394
6.230	12.765	149.74	2.438	.391	1.567	1.397
8.407	15.389	133.77	2.944	.350	1.587	1.398
9.464	16.525	127.93	3.164	.334	1.589	1.394
14.113	20.996	108.72	4.030	.286	1.611	1.389
18.824	24.866	96.54	4.782	.254	1.629	1.386
24.44	28.930	86.51	5.574	.228	1.647	1.384
30.19	32.615	78.95	6.293	.208	1.657	1.377

has been observed with acetic acid by MacInnes and Shedlovsky.[5] For both acids log K decreases approximately linearly with C_u, the concentration of the un-ionized acid. Further examples and a discussion of this relation will appear in a later paper from this Laboratory.

From a plot of log K' against $\sqrt{C_i}$ it is evident that equation (13) may be written

$$\log k' = \log K + a\sqrt{C_i} \tag{14}$$

where a in the dilute range approaches the theoretical value, 1.013, but decreases with concentration. Since $C_i^2/C_u = K'$, it follows that

$$\log K' = \log K + a(K')^{1/4}\, C_u^{1/4} \tag{15}$$

and since K' increases with concentration it may be expected that log K' should be a linear function of $C_u^{1/4}$, at least in the region of concentration in which the "medium effect" is not pronounced. This relation holds for monochloroacetic acid. If the acid is sufficiently weak, C_u may be replaced by C, the total acid concentration, and log K' and C_i may then be calculated from C. Even with an acid as strong as monochloroacetic the data can be represented by

$$\log (K' \times 10^3) = 0.1449 + 0.1794C^{1/4} \tag{16}$$

Excluding the first result, this equation reproduces the measured values of K' to within ±0.18% and the values of C_i to within ±0.07% and, therefore, gives a satisfactory method for calculating C_i from C. If this method be applied to MacInnes and Shedlovsky's[5] data on acetic acid, the results up to 0.01 N are given by the equation

$$\log (K' \times 10^5) = 0.24378 + 0.06074C^{1/4} \tag{17}$$

Above this concentration, the measured values of log K' fall below those calculated using equation (17) and the deviation is linear with C, which is to be expected if this is due to the "medium effect." Accordingly, a term in C was added to equation (17) giving

$$\log (K' \times 10^5) = 0.24378 + 0.06302C^{1/4} - 0.1256C \tag{18}$$

This equation reproduces K' to within ±0.10% and the values of C_i to within ±0.04%. It should be borne in mind that equations (16) and (18) reproduce the values of K' and C_i for the two acids, respectively, as measured by a conductance ratio in which $\Lambda_{(H^+ + A^-)}$ has been corrected for interionic forces but not for the presence of the un-ionized portion of the acid. More properly these are only apparent values except in the concentration range in which equation (2) is obeyed.

We have carried out similar measurements on acetic acid and its sodium salt in cell A. Our results agree with those of MacInnes and Shedlovsky[5] and not with those of Jeffery and Vogel.[20] Briefly, our results for sodium acetate are given by the equation

$$\Lambda = 90.91 - 80.57\sqrt{C_i} + 89.7C_i(1 - 0.2276\sqrt{C_i}) \qquad (19)$$

and our value of K is 1.759×10^{-5}. Our equivalent conductances for the acid are slightly higher than those of MacInnes and Shedlovsky.[5] This is probably due to the fact that our first conductivity water was not good enough for the measurements with such a weak acid. Their lower value, 1.753×10^{-5}, or 1.754×10^{-5} obtained by Harned and Ehlers[21] for electromotive force measurements is to be preferred.

Summary

Using a "flask" cell and bright platinum electrodes, the conductances of hydrochloric and monochloroacetic acids and their sodium salts have been measured and reported.

The results with all the strong electrolytes (those mentioned above and sodium acetate for which the equation only is given) confirm Onsager's equation as a limiting law, and up to our highest concentration, 0.03 N, agree with Shedlovsky's extension of Onsager's equation.

It has been shown that the theoretical constant of the limiting law of Debye and Hückel correctly represents the dependence of the activity coefficient of monochloroacetic acid upon its ionic concentration. Using this limiting law, the thermodynamic ionization constant of the acid is found to be 1.396×10^{-3}.

The values of the constant for acetic acid obtained by Harned and Ehlers and by MacInnes and Shedlovsky have been confirmed.

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(20) Jeffery and Vogel, *J. Chem. Soc.*, 2829 (1932).

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