

[CONTRIBUTION FROM THE LABORATORIES OF THE ROCKEFELLER INSTITUTE FOR  
MEDICAL RESEARCH]

## THE DETERMINATION OF THE IONIZATION CONSTANT OF ACETIC ACID, AT 25°, FROM CONDUCTANCE MEASUREMENTS

BY DUNCAN A. MACINNES AND THEODORE SHEDLOVSKY

RECEIVED DECEMBER 11, 1931

PUBLISHED APRIL 6, 1932

A number of years ago one of the authors published recalculations of the ionization constants of some weak acids, using the most accurate data then available.<sup>1</sup> In these computations, allowance was made for effects due to interionic attractions. These attractions are functions of the ion concentrations and are made evident by their effects on the ion activities and on the ion mobilities.

In the paper mentioned the law of mass action for the ionization of a weak acid was expressed as follows

$$K = \frac{\alpha^2 \gamma_{H^+} \gamma_{A^-}}{(1 - \alpha) \gamma_{HA}} \quad (1)$$

in which  $K$  is the ionization constant,  $\alpha$  is the degree of dissociation,  $C$  is the total concentration and  $\gamma_{H^+}$ ,  $\gamma_{A^-}$  and  $\gamma_{HA}$  are the activity coefficients of the hydrogen ion, the anion and the undissociated acid, respectively.<sup>2</sup>

The effect of interionic attractions on the activity coefficients of ions has been dealt with in the well-known papers of Debye and Hückel. The computation of the degree of dissociation,  $\alpha$ , from conductance measurements is influenced by interionic forces in that it is necessary to take account of the effect of such forces on the mobilities of the ions. According to the Arrhenius theory, the degree of dissociation  $\alpha = \Lambda_c / \Lambda_0$  in which  $\Lambda_c$  is the equivalent conductance at the concentration  $C$  and  $\Lambda_0$  is the equivalent conductance at infinite dilution. This theory involves the assumption that the ion mobilities do not change with the concentration. To show this let  $U_c^+$ ,  $U_c^-$ ,  $U_0^+$  and  $U_0^-$  be the mobilities of the positive and negative ions at the concentration  $C$  and at infinite dilution. Since

$$\Lambda_c = \alpha F(U_c^+ + U_c^-) \quad (2)$$

and

$$\Lambda_0 = F(U_0^+ + U_0^-) \quad (3)$$

( $\alpha = 1$  in the latter case) then

$$\frac{\Lambda_c}{\Lambda_0} = \frac{\alpha F(U_c^+ + U_c^-)}{F(U_0^+ + U_0^-)} \quad (4)$$

Thus,  $\Lambda_c / \Lambda_0 = \alpha$  only if  $U_c^+ + U_c^- = U_0^+ + U_0^-$ . This can be true only if the mobilities do not change, or by an improbable compensation.

<sup>1</sup> MacInnes, *THIS JOURNAL*, **48**, 2068 (1926).

<sup>2</sup> Sherrill and Noyes, *ibid.*, **48**, 1861 (1926), obtained this equation independently and tested it with data on the ionization of the second hydrogen from dibasic acids. See also Davies, *J. Phys. Chem.*, **29**, 977 (1925).

Debye and Hückel<sup>3</sup> and more recently Onsager<sup>4</sup> have shown that changes in ion mobilities with concentration are to be expected, on theoretical grounds, even in very dilute ion solutions. Transference data give conclusive evidence that such changes occur at higher concentrations. The original Arrhenius assumption, *i. e.*,  $\alpha = \Lambda_c/\Lambda_0$ , is therefore inaccurate at any concentration.

Equation 2 may be used to compute degrees of dissociation if values of the expression  $F(U_{c^+} + U_{c^-})$ , which we will call  $\Lambda_e$ , are known. Since  $\Lambda_c$  is the conductance of a mole of acid, the proportion  $\alpha$  of which is in the form of ions,  $\Lambda_e$  is evidently the conductance of a mole of *ions* in a condition in which their mobilities retain the values they have at the concentration  $C$ . Since we have good evidence that strong electrolytes are completely dissociated, at least in dilute solution, values of  $\Lambda_e$  may be readily found from the following considerations. Let NaAc represent the sodium salt of the weak acid (acetic acid for instance) whose degree of dissociation is desired, then

$$\Lambda_{e_{\text{HAo}}} = \Lambda_{c'_{\text{HCl}}} - \Lambda_{c'_{\text{NaCl}}} + \Lambda_{c'_{\text{NaAc}}}$$

in which the  $\Lambda_{c'}$  values are the equivalent conductances of the substances indicated at the ion concentration  $C'$ . For completely dissociated substances this ion concentration is also the stoichiometric concentration, whereas  $\Lambda_{e_{\text{HAo}}}$  is the equivalent conductance of a mole of completely dissociated acetic acid at the *ion* concentration  $C'$ . Thus for the computation of the degree of dissociation  $\alpha = \Lambda_c/\Lambda_e$  a value of  $\Lambda_e$  must be found which corresponds to the ion concentration of the solution of the weak acid whose measured equivalent conductance is  $\Lambda_c$ . This involves a short series of approximations. In the previous paper<sup>1</sup> it was shown that for relatively strong acids, such as *o*-nitrobenzoic acid and *o*-chlorobenzoic acid, with ionization constants  $6.0 \times 10^{-3}$  and  $1.2 \times 10^{-3}$ , respectively, true constants for Equation 1 were obtained over the range of concentrations for which data were available. It was, however, rather disturbing to find that the data for the relatively weak acetic acid indicated a definite trend (from  $1.74 \times 10^{-5}$  to  $1.78 \times 10^{-5}$ ) of the "constant" in the concentration range 0.07 to 0.002 mole per liter. We felt that it was important to find out whether this drift in the ionization constant was due to inaccuracy of the data available or to the assumptions involved in the computation. In addition, an accurate value of the ionization constant of acetic acid is desirable in other connections. It was decided therefore to obtain, with all possible accuracy, data on the conductance of the acid, and of the other substances (sodium chloride, hydrochloric acid and sodium acetate) involved in the calculation of the ionization constant of this acid.

<sup>3</sup> Debye and Hückel, *Physik. Z.*, **24**, 305 (1923).

<sup>4</sup> Onsager, *ibid.*, **27**, 388 (1926); **28**, 277 (1927).

### Experimental

The conductances were determined with the bridge<sup>5</sup> and cells described in a paper from this Laboratory.<sup>6</sup> The data on sodium chloride and hydrochloric acid used in the computations are also reported in the latter paper. The basis for the conductivity values is that a solution containing 7.47896 g. of potassium chloride in 1000 g. of water (weights in air *vs.* brass) has a specific conductance of 0.012852<sub>4</sub> at 25°.

(a) Solutions of Acetic Acid.—C. P. synthetic acetic acid (Niacet Co., U. S. P.) was purified by distilling the material from 2% by weight of potassium permanganate, using an efficient fractionating column.<sup>7</sup> The product was again distilled from a little chromic anhydride. This was followed by a final fractional distillation. Freezing point measurements were made on the separate fractions. After the first quarter of the material was distilled, later fractions, which were kept for use, gave constant freezing points. The purified acid had a freezing point of 16.54° on a thermometer which had been compared with a carefully calibrated platinum resistance thermometer. The specific conductance of the pure acid at 25° was  $1.4 \times 10^{-8}$  mhos.

We are indebted to Dr. L. G. Longworth, of this Laboratory, for a very careful analysis of this acid by the differential potentiometric method recently described.<sup>8</sup> A solution of approximately 0.2 *N* sodium hydroxide used in the titration was calibrated to an accuracy of better than 0.01% against pure benzoic acid from the Bureau of Standards. This solution, which was nearly carbonate free, was kept in large paraffin-lined flasks which were connected with a carbon dioxide absorbing train. By titration of a stock solution, and of small samples of the acid weighed on a micro balance, the purified material was found to be 100.04 ± 0.01% acetic acid. An interesting check on this figure was obtained from the freezing point. Using the cryoscopic constant obtained from De Visser's data<sup>9</sup> and taking Bousfield and Lowry's<sup>7</sup> value of 16.60 ± 0.005° for the freezing point of the pure acid and the freezing point for our acid given above, the value obtained for the strength of the acid is 100.037%, if it is assumed that the freezing point lowering is due to a trace of acetic anhydride.

To prepare the most dilute solutions it was not possible to weigh out small quantities of the glacial acid with sufficient accuracy. It was, therefore, necessary to prepare stock solutions of about 0.1 *N* concentration, weighed increments of which were successively added to the conductivity water in the cell. A difficulty was encountered in dealing with these acetic acid stock solutions. On making titrations on successive days it was found that the acid was growing weaker at the rate of about 0.01% per day. This was not due to attack on the glass wall of the container as a solution of hydrochloric acid showed no such decrease. The effect was finally found to be due to growth of organisms, probably bacteria, in the acetic acid solution. It was overcome, with the kind help of Dr. Alexis Carrel and assistants, by the use of the following sterile technique.

A solution of approximately the concentration desired was made from the pure acid and conductivity water, and was sealed in a half-filled round-bottomed Pyrex flask. This flask was placed in an autoclave at about 15 pounds' steam pressure for an hour or two on three successive days, to make sure that any spores present were killed. The flask was then opened and the solution was transferred to the flask shown in Fig. 1. This flask had also been sterilized. The transfer took place in a chamber

<sup>5</sup> Shedlovsky, *THIS JOURNAL*, **52**, 1793 (1930).

<sup>6</sup> Shedlovsky, *ibid.*, **54**, 1411 (1932).

<sup>7</sup> Bousfield and Lowry, *J. Chem. Soc.*, **99**, 1432 (1911).

<sup>8</sup> MacInnes and Cowperthwaite, *THIS JOURNAL*, **53**, 555 (1931).

<sup>9</sup> De Visser, *Rec. trav. chim.*, **12**, 101 (1893).

which had been sprayed free of dust. The flask is similar to that described by MacInnes and Dole<sup>10</sup> with the addition of a close-grained alundum filter, F. With this arrangement the acid can be forced out by a pressure of gas without fear of contamination by bacteria. Acid, in this flask, kept its concentration to within  $\pm 0.01\%$  for a month.

The data on the conductance of acetic acid are given in Columns 1 and 3 of Table II. Of these data the measurements of solutions having concentrations below 0.01 *N* were made in the quartz flask cell<sup>6</sup> with a cell constant of 0.58895. Above that concentration the measurements at round values were made in pipet cells,<sup>6</sup> and the others in a Pyrex flask cell with a cell constant of 8.2183.

(b) **Solutions of Sodium Acetate.**—The solutions of dilute sodium acetate cannot readily be prepared to the desired accuracy in the concentrations by weighing out the dry salt or the trihydrate, since neither of these compounds can be obtained with sufficient stoichiometric purity. Also it is necessary to control the hydrolysis of the

salt. The following procedure was therefore adopted. Sodium bicarbonate, which can be readily obtained free from the potassium salt and other impurities, was heated in an electric furnace at about 280° to yield sodium carbonate. A stock solution of this material (about 0.1 *N*) was prepared and was titrated electrometrically against standard hydrochloric acid, with an accuracy of about 0.01%. To prepare a solution of sodium acetate from this material, about 1 g. of the glacial acetic acid was weighed out into a quartz ampoule on a micro balance. The necessary amount of the sodium carbonate solution to nearly but not quite neutralize the acid was weighed out into a weighed glass-stoppered flask and the ampoule was dropped into it. The excess of acid was several tenths of a per cent. This flask was then carefully

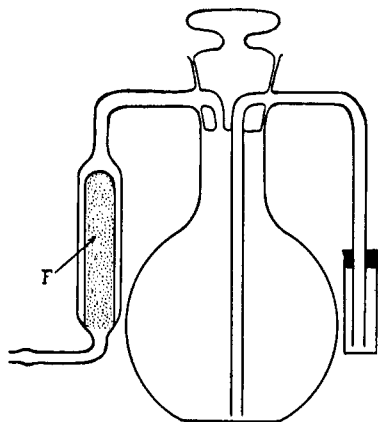


Fig. 1.

heated to drive off carbon dioxide, which was evolved with practically no spray. After cooling, the flask was again weighed. The concentration of sodium acetate was computed from the known quantity of sodium present. Dilute solutions were prepared by adding small weighed amounts of this stock solution to conductivity water in the cell.

A stoichiometric solution of sodium acetate has the disadvantages that it is considerably hydrolyzed and its conductivity is therefore very sensitive to traces of carbon dioxide, since these would react with the liberated hydroxide. The sodium acetate in a solution containing a slight excess of acetic acid is, however, not hydrolyzed and the ionization of carbonic acid is repressed. The solution is, in fact, buffered against these effects. On the other hand, the conductivity of the solutions thus prepared must be corrected for the conductance due to the very slight ionization of the excess acid. This forms a part of the total solvent correction, which includes the conductivity of pure water in the given solution, and a further correction for conductivity due to a trace of neutral salt if the water had been stored in a Vitreosil container. From *P<sub>H</sub>* determinations on the solutions the hydrogen-ion concentration may be computed with sufficient accuracy. This figure and the ion product ( $H^+$ )( $OH^-$ ) =  $K_w$  of water gives the hydroxyl-ion concentration. Since in these measurements the solution was slightly acid, the difference between the hydrogen and hydroxyl concentrations must be balanced by acetate-ion concentration in excess of that arising from the sodium acetate. The

<sup>10</sup> MacInnes and Dole, *THIS JOURNAL*, 51, 1124 (1929).

magnitude of the correction for the trace of salt was arrived at as follows. The conductivity water from the Vitreosil container also contains a trace of carbonic acid. This was shown in two ways. In the first place, by blowing nitrogen, carefully freed from carbon dioxide, through the water in the conductivity cell the conductance slowly dropped from 3 or  $4 \times 10^{-7}$  to a minimum of about  $1.5$  to  $2 \times 10^{-7}$ . Furthermore, when brom thymol blue, isohydric to  $P_H$  7, was added to a fresh sample of water the color corresponded to about  $P_H$  6.5. However, after the purified nitrogen had been run through the water for about an hour, the color changed to that of  $P_H$  7, and continued passage of gas produced no change. It was thus concluded that the current of gas removed the last traces of carbonic acid and that the minimum conductance measured was due to the pure water plus a minute amount of neutral salt. Since the conductance of pure water at  $25^\circ$  is  $0.55 \times 10^{-7}$ , that due to the trace of salt can be found by subtracting this value from the minimum conductance obtained as described above.<sup>11</sup> The complete solvent correction which was applied to the conductivity measurements of the solutions of sodium acetate was a sum of the neutral salt correction to which were added the conductances of hydrogen, hydroxyl and excess acetate ions computed as already described.<sup>12</sup> The  $P_H$  value used in these computations was that of the final solution after the concentration had been built up to about  $0.005 N$  by successive additions of the stock solution. This  $P_H$  was assumed to be constant throughout the measurements since the mixture is a buffer. Also the  $0.005 N$  solution had very nearly the same  $P_H$  as the stock solution, typical values being  $P_H = 6.60$  and  $P_H = 6.72$ , respectively. The  $P_H$  measurements were made electrometrically in the usual Clark apparatus, by Mr. Donald Belcher.

The conductance data on sodium acetate at  $25^\circ$  are given in Table I, which also includes a comparison of the observed values with those obtained from the equation

$$\Lambda_{NaAc} = 90.97 - 80.48 \sqrt{C} + 90C(1 - 0.2274 \sqrt{C}) \quad (5)$$

TABLE I  
EQUIVALENT CONDUCTANCES OF SODIUM ACETATE SOLUTIONS AT  $25^\circ$

$C \times 10^4$	$\Lambda$ obs.	$\Lambda$ cal.	$C \times 10^4$	$\Lambda$ obs.	$\Lambda$ cal.
0.99051	90.11	90.17	17.463	87.74	87.76
1.8627	89.92	89.90	20.683	87.52	87.45
5.9058	88.96	89.07	27.973	86.96	86.96
7.3205	88.90	88.86	31.332	86.75	86.74
7.6201	88.76	88.82	39.725	86.28	86.25
14.237	88.03	88.06	41.243	86.16	86.17
15.256	87.95	87.96	43.016	86.07	86.08

<sup>11</sup> The water used in the measurement of the acetic acid solutions was collected directly into the transparent quartz cell. This water had an initial conductivity 1 to  $2 \times 10^{-7}$  lower than the water which had been stored in the Vitreosil container. It has been assumed, therefore, that the salt came from the latter container, and consequently no salt correction was required in the case of the acetic acid measurements.

<sup>12</sup> The formula for the total water correction,  $L$ , for dilute solutions of sodium acetate prepared as described above is

$$L = (L_S + 0.350 C_{H^+} + 0.196 C_{OH^-} + 0.041 C_{Ac^-})$$

in which  $L$  is the total correction to the measured specific conductance,  $C_{H^+}$  is the hydrogen-ion concentration =  $10^{-P_H}$ ,  $C_{OH^-} = 10^{-14}/C_{H^+}$ , and  $C_{Ac^-} = C_{H^+} - C_{OH^-}$ .  $L_S$  is the conductance due to neutral salt. The coefficients of the concentration terms are the limiting conductances of the ions times  $10^{-3}$ .

This equation is of the same form as those used in expressing the conductance of hydrochloric acid and sodium chloride solutions.<sup>6</sup>

### Discussion of Results

As stated in our introduction, the degree of dissociation,  $\alpha$ , is obtained from the ratio  $\Lambda_c/\Lambda_e$ , or, possibly more convenient for computation, the ion concentration  $C_i = \alpha C$  may be found from

$$C_i = \frac{1000 \bar{L}}{\Lambda_e} \quad (6)$$

in which  $\bar{L}$  is the specific conductance of a solution and  $\Lambda_e$  depends upon the ion concentration in the solution. Values of  $\Lambda_e$  (the conductance of completely dissociated acetic acid) as a function of the ion concentration are given by the equation

$$\Lambda_{e_{\text{HAc}}} = 390.59 - 148.61 \sqrt{C_i} + 165.5 C_i (1 - 0.2274 \sqrt{C_i}) \quad (7)$$

which was in turn obtained from the equation

$$\Lambda_e = \Lambda_{\text{HCl}} - \Lambda_{\text{NaCl}} + \Lambda_{\text{NaAc}} \quad (8)$$

in which  $\Lambda_{\text{HCl}} = 426.04 - 156.70 \sqrt{C} + 165.5 C (1 - 0.2274 \sqrt{C})$ ,  $\Lambda_{\text{NaCl}} = 126.42 - 88.53 \sqrt{C} + 89.5 C (1 - 0.2274 \sqrt{C})$  from the accompanying paper by Shedlovsky<sup>6</sup> and  $\Lambda_{\text{NaAc}}$  is given by Equation 5 of this communication. This, of course, involves the assumption that Kohlrausch's law of independent ion migration holds at the ion concentrations involved. That no appreciable error arises from this assumption will be shown, from newly obtained data, in a paper to appear shortly from this Laboratory.

To find a value of  $\Lambda_e$  corresponding to an ion concentration  $C_i$ , involved a short series of approximations. A first approximation was made with the limiting value of  $\Lambda_e$ , *i. e.*,  $\Lambda_0$ , giving  $C_i = 1000 \bar{L}/\Lambda_0$ ; from this ion concentration a value of  $\Lambda_e$  was found from Equation 7. A new estimate of  $C_i$  was then made, followed by another of  $\Lambda_e$ , until repetition did not change the result. Usually three approximations were sufficient. From the resulting  $C_i$  values a series of values of

$$K' = \frac{\alpha^2 C}{1 - \alpha} = \frac{C_i^2}{(C - C_i)} \quad (9)$$

were obtained. These are given in Column 5 of Table II. It will be recalled that  $K'$  is the mass action "constant" uncorrected for changes in activity coefficients.

From Equation 1 it may be seen that the thermodynamic ionization constant  $K$  is related to  $K'$  by

$$K = K' \frac{\gamma_i^2}{\gamma_u} \quad (10)$$

TABLE II

EQUIVALENT CONDUCTANCES AND IONIZATION CONSTANT VALUES OF ACETIC ACID AT 25°

Total concn. $C \times 10^3$	Ion concn. $C_1 \times 10^4$	$\Lambda_e$	$\Lambda_0$	$K' \times 10^6$	$K \times 10^6$
0.028014	0.15107	390.02	210.32	1.768 <sup>2</sup>	1.752 <sup>2</sup>
.11135	.36491	389.68	127.71	1.778 <sup>7</sup>	1.753 <sup>8</sup>
.15321	.44049	389.61	112.02	1.777 <sup>5</sup>	1.750 <sup>2</sup>
.21844	.54101	389.49	96.466	1.781 <sup>0</sup>	1.750 <sup>7</sup>
1.02831	1.2727	388.94	48.133	1.797 <sup>4</sup>	1.750 <sup>8</sup>
1.36340	1.4803	388.81	42.215	1.803 <sup>0</sup>	1.752 <sup>8</sup>
2.41400	2.0012	388.52	32.208	1.809 <sup>0</sup>	1.750 <sup>3</sup>
3.44065	2.4092	388.32	27.191	1.814 <sup>0</sup>	1.749 <sup>8</sup>
5.91153	3.1929	387.99	20.956	1.823 <sup>0</sup>	1.748 <sup>7</sup>
9.8421	4.1557	387.61	16.367	1.832 <sup>0</sup>	1.746 <sup>9</sup>
12.829	4.7591	387.41	14.371	1.834	1.743
20.000	5.975	387.05	11.563	1.840	1.738
50.000	9.524	386.19	7.356	1.849	1.721
52.303	9.7542	386.07	7.200	1.854	1.723
100.000	13.496	385.29	5.200	1.846	1.695
119.447	14.763	385.07	4.759	1.847	1.689
200.000	18.992	384.41	3.650	1.821	1.645
230.785	20.371	384.15	3.391	1.814	1.633

in which  $\gamma_i$  is the mean activity coefficient of the ions and  $\gamma_u$  that of the undissociated acid. Thus

$$\log K = \log K' + 2 \log \gamma_i - \log \gamma_u \quad (11)$$

However, from the Debye-Hückel theory in its limiting form

$$-\log \gamma_i = 0.5065 \sqrt{C_1} \quad (12)$$

and also in the limit  $\gamma_u = 1$ . Thus

$$\log K = \log K' - 1.013 \sqrt{C_1} \quad (13)$$

This limiting equation accounts with surprising accuracy for the measurements at the five or six lowest concentrations, as is shown in Fig. 2, in which the logarithms of  $K'$  are plotted against the square roots of the corresponding ion concentrations. In this plot the solid line  $e$  has the theoretical slope 1.013 of Equation 13. The excellent agreement between the theory and the experimental results for the more dilute solutions is also shown in Column 6 of Table II, in which the values of the thermodynamic constant  $K$  computed from Equation 13 are listed. For the lower range of concentrations these vary but slightly from a mean of  $1.752 \times 10^{-6}$ .<sup>13</sup> Above an acid concentration of about 0.01  $N$  the computed values of the ionization constant decrease.

There are a number of reasons why this should be the case. In the first place we have used the limiting form of the Debye-Hückel equation

<sup>13</sup> In our recent "Letter to the Editor," THIS JOURNAL, 53, 2419 (1931), the slightly lower values of  $K$  resulted from calculations made before our complete data on the conductivity of hydrochloric acid were available.

for computing the activity coefficients of the ions. If account is taken of the size of the ions, instead of Equation 13 we have

$$-\log \gamma = 0.5065 \frac{\sqrt{C}}{1 + 0.327 a \sqrt{C}} \quad (14)$$

(where  $a$  is the distance of closest approach of ions in Ångström units). This equation is valid for the ion concentrations involved in our computations if  $a$  is greater than  $3 \text{ \AA}$ .<sup>14</sup> In the second place the assumption that the activity coefficient of the undissociated acid  $\gamma_u$  is unity is true only at sufficiently low concentrations. The correction for this deviation is relatively small. It can be evaluated, however, from freezing point

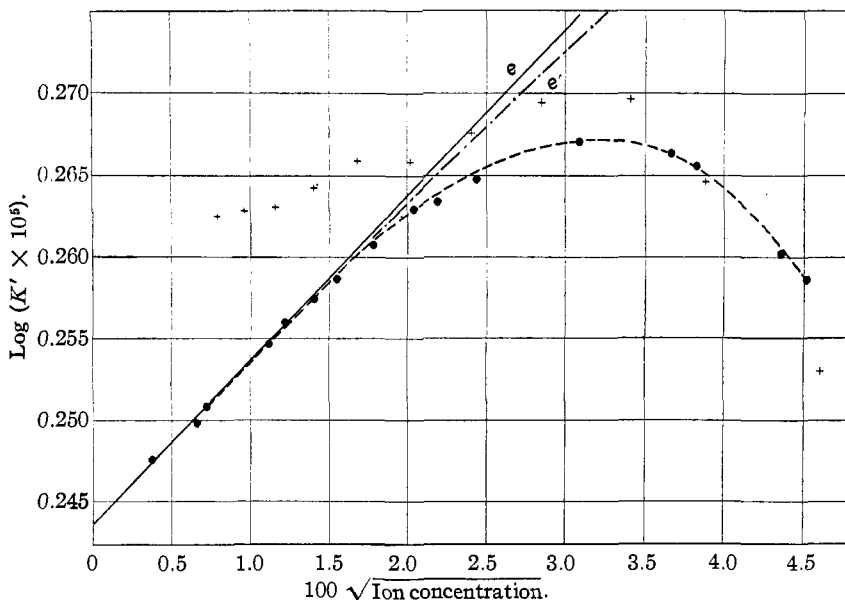


Fig. 2.—●, MacInnes and Shedlovsky; +, Kendall.

measurements, as has been shown by Lewis and Randall.<sup>15</sup> Although both of these effects are in the right direction, they are not nearly large enough to account for the observed deviations. This is shown in Fig. 2 where the broken line  $e'$  represents the variation of  $K'$  which would be expected if the activity coefficients were modified to allow for the two foregoing effects. In this calculation it has been assumed that  $a$  is of the order of  $4 \text{ \AA}$  Ångström units, as can be roughly estimated from crystal structure data. It will be observed that the effects of ion size and activity coef-

<sup>14</sup> Gronwall, La Mer and Sandved, *Physik. Z.*, 29, 358 (1928), give a further extension of the theory which must be used for small ions or higher valences.

<sup>15</sup> Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., 1923, pp. 284, 290.

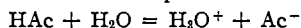


ficients of the undissociated material are not sufficient to account for the variation of  $K'$  observed.<sup>16</sup>

In computing  $K$  it has been assumed that the accumulation of undissociated acetic acid with increasing concentration has no effect on the solvent. The properties of undissociated acetic acid are, however, quite different from those of water. For instance, the acid has a low dielectric constant, less than 10 per cent. of that of water, and its presence in undissociated form in the aqueous solutions would be expected to influence the *mobilities* as well as the activities of the ions. In our computation it has been necessary, with the data at hand, to assume that the solvent is pure water. This is evidently incorrect at the higher concentrations, and will lead to greater errors the weaker the electrolyte. We expect, in the near future, to study the effect of the change of the medium on the mobilities of the ions.<sup>17</sup>

Referring to Fig. 2 it is seen that line  $e$ , as has been mentioned, represents the Debye-Hückel theoretical limiting slope, *i. e.*, the constant  $2A = 1.013$  in the expression  $-\log \gamma_i^2 = 2A \sqrt{C_i}$ . Although this line is evidently in close agreement with the data for the lower concentrations, it is nevertheless a limiting equation, and deviations from it must be considered for obtaining the most probable value of the constant  $K$  from the

<sup>16</sup> The change of the activity of the solvent must also be considered at higher concentrations since the ionization in its simplest terms is



Also see Kendall, *THIS JOURNAL*, 39, 2323 (1917).

<sup>17</sup> Davies [*Phil. Mag.*, 4, 244 (1927)] finds that a constant can be obtained from Kendall's conductance data on acetic acid if the conductances are multiplied by the viscosity at each concentration. However, he obtains a higher value than we do for the constant; furthermore, he uses an empirical value of  $A = 0.393$  in the limiting equation  $-\log \gamma = A \sqrt{C}$  instead of the theoretical value  $A = 0.5065$  obtained by Debye and Hückel. He considers that this observation supports Milner's theory (which leads to a lower value of  $A$ ) rather than the Debye-Hückel theory, and also that it sustains Nonhebel's experimental value of  $A = 0.39$  obtained from *e. m. f.* data [Nonhebel, *Phil. Mag.*, 7, ii, 1085 (1926)]. Kendall's data may be readily shown to be of insufficient accuracy to decide the question. In Fig. 2 values of  $K'$ , which have been calculated from Kendall's data, are compared with our results. In these computations his conductances for acetic acid have been reduced to our basis and our data for the other electrolytes have been used. It will be seen that there is a progressive deviation of these values of  $K'$  from ours as the concentrations decrease. This is what would be expected from Kendall's procedure. His measurements on the more concentrated solutions were made first and the concentrations successively reduced by halves, the dilutions being carried out in air in a glass conductivity cell. The most dilute solution thus had the most handling and had the greatest contamination. Also any adsorption of the acid from the concentrated solutions would likewise tend to contaminate the dilute solutions. The apparent need for a viscosity correction to the data, for the more dilute solutions at least, thus arose from experimental error. As Davies has observed, there is no need for such a correction to the data for the stronger acids.

data. Accordingly least square computations were made on the eight and ten lowest points, using the equation

$$\log K' = \log K - 2A\sqrt{C_1} + BC_1$$

The results are given below

	$2A$	$B$	$K \times 10^5$
8 lowest points	0.9946	-0.023	1.7533
10 lowest points	1.041	-0.047	1.7526

Although the computed values of  $2A$  are, respectively, 2% below and 3% above the theoretical value 1.013, the corresponding variations in the activity coefficients, in the ion concentration range of these measurements, are of the order of a few hundredths of a per cent. Thus the values of  $2A$  are in complete agreement with the theory within the precision of the measurements.

These least square computations give us the limiting value of  $K = 1.753 \times 10^{-5}$ , which is also the result obtained in extrapolating from a plot of the  $K$  values in Table II against  $C_1$ . These constants agree excellently with the value  $1.75 \times 10^{-5}$  obtained in a very different manner (from e. m. f. measurements on cells without liquid junction) by Harned and Owen.<sup>18</sup>

### Summary

Conductance measurements at 25° are reported on aqueous solutions of acetic acid in the concentration range 0.00003  $N$  to 0.2  $N$ , and on solutions of sodium acetate (in which hydrolysis has been repressed) in the range 0.0001 to 0.004  $N$ .

With these data and measurements of hydrochloric acid and sodium chloride, given in an accompanying paper, values of the stoichiometric ionization constants ( $K'$ ) of acetic acid at 25° have been computed. In this computation it has been assumed that the strong electrolytes are completely dissociated and that, for the low ion concentrations involved, the Kohlrausch law of independent ionic mobilities holds. At high dilutions the relation between  $K'$  and the true (thermodynamic) ionization constant  $K$ , *i. e.*,  $K = K'\gamma_i^2$  (in which  $\gamma_i$  is the mean ionic activity coefficient) is confirmed if values of  $\gamma_i$  are calculated from the Debye-Hückel theory. In fact the data corresponding to solutions of acetic acid below 0.01  $N$  are in quantitative agreement with the theory. Above that concentration a strong "medium effect," which probably has its greatest influence on ionic mobilities, becomes apparent.

From the measurements at the higher dilutions the value obtained for the thermodynamic ionization constant  $K$  is  $1.753 \times 10^{-5}$ , which is in excellent accord with recent determinations by electromotive force methods.

NEW YORK, N. Y.

<sup>18</sup> Harned and Owen, *THIS JOURNAL*, **52**, 5079 (1930).