

428. *The Dissociation Constants of Organic Acids.*
Part VI. Acetic Acid.

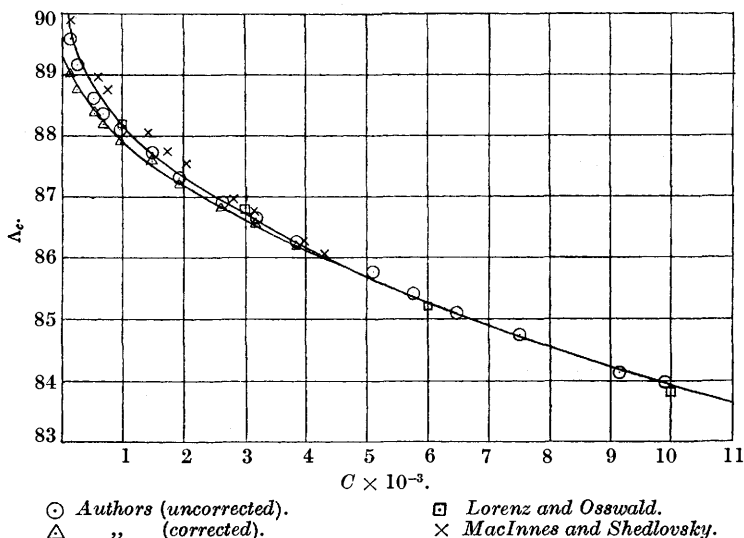
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THE only trustworthy measurements of the conductivity of aqueous solutions of acetic acid at 25° are those of Kendall (J., 1912, **101**, 1275; *Medd. K. Vetenskapsakad. Nobel-Inst.*, 1913, **2**, No. 38), made in a glass cell with equilibrium water and covering the range 0.0005—1*N*. In view of the effect of the material of the cell on the conductivities of aqueous solutions of strong acids (compare this vol., p. 400), we have carried out new measurements in a silica cell of the Hartley and Barrett type; we also effected dilution, not by Ostwald's method (as used by Kendall), but by that of Whetham (*Phil. Trans.*, 1900, **194**, 321), in which, to a known weight of pure solvent, are added successive portions of a solution of the solute from a weight pipette. When the work was completed, MacInnes and Shedlovsky (*J. Amer. Chem. Soc.*, 1932, **54**, 1429) described similar determinations on acetic acid in a Jena-glass cell of special design. The three sets of results are in satisfactory agreement, as can be readily seen by drawing the conductivity-concentration curve, and hence it appears that for a weak acid the material of the cell and the method of dilution have but little influence.

For the calculation of the Ostwald dissociation constant, Kendall assumed the conductivity at infinite dilution to be 387.9, this figure being based on his own value (J., 1912, **101**, 1275) of the limiting mobility of the hydrogen ion and Bredig's value (*Z. physikal. Chem.*, 1894, **13**, 218) of 40.7 for the acetate ion. We have made new determinations of the conductivity over the concentration range 0.0001—0.01*N* of both sodium and potassium acetate. These results have been corrected for hydrolysis (see p. 2835), and the conductivity at infinite dilution computed by Ferguson and Vogel's method (*Phil. Mag.*, 1925, **50**, 971). Sodium acetate gives $\Lambda_0 = \Lambda_c + 93.42 C^{0.598} = 89.45$, whilst potassium acetate gives $\Lambda_0 = \Lambda_c + 150.5 C^{0.686} = 113.44$, leading to values of 39.7 and 40.0 respectively for the limiting mobility of the acetate ion; the figures used for the mobilities of the sodium and potassium ions

were those previously determined (J., 1931, 1722) with n_K for potassium chloride = 0.490. This leads to a value for Λ_0 of $348.0 + 39.85 = 387.85$, 348.0 being the limiting mobility of the hydrogen ion (this vol., p. 400). MacInnes and Shedlovsky (*loc. cit.*) made measurements on sodium acetate in the presence of excess ("several tenths of a per-cent.") of acetic acid, claiming that this prevented hydrolysis; the results were then corrected for the presence of the excess acid. This procedure is clearly unsatisfactory, as shown by Fig. 1, in which the results obtained are compared with our

FIG. 1.



Sodium acetate at 25°.

uncorrected and corrected results. The data of Lorenz and Osswald (*Z. anorg. Chem.*, 1920, **114**, 209) are also shown.

The values of the classical dissociation constants are given on p. 2837; the figures for MacInnes and Shedlovsky's results up to ca. 0.01N are shown below. Our mean value for K_1 is 1.813×10^{-5}

$C \times 10^4$	0.2801	1.114	1.532	2.184	10.28	13.63
$K_1 \times 10^5$	1.800	1.801	1.797	1.799	1.808	1.813
$C \times 10^4$	24.14	34.41	59.12	98.42	128.3	
$K_1 \times 10^5$	1.816	1.819	1.825	1.831	1.829	

It is now generally agreed that figures thus calculated require correction for the effects of the interionic attraction, which results in the mobilities varying with concentration and hence invalidating Arrhenius's original assumption as to the method of calculation of the degree of dissociation α . MacInnes (*J. Amer. Chem. Soc.*, 1926, **48**, 2068; see also Noyes and Sherrill, *ibid.*, 1926, **48**, 1861)

has suggested that a more nearly correct degree of dissociation α' can be obtained by comparing the measured equivalent conductivity with that of an equivalent of the ions at the same *ion* concentration, a quantity represented by Λ_c . If independent migration of ions is assumed, the conductivity of completely dissociated acetic acid HOAc corresponding to any particular ion concentration c' can be computed from such relations as the following :

$$\Lambda_c \text{HOAc} = \Lambda_c \text{HCl} - \Lambda_c \text{KCl} + \Lambda_c \text{KOAc} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$= \Lambda_c \text{HCl} - \Lambda_c \text{NaCl} + \Lambda_c \text{NaOAc} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$= \Lambda_c \text{C}_6\text{H}_5\text{SO}_3\text{H} - \Lambda_c \text{C}_6\text{H}_5\text{SO}_3\text{Na} + \Lambda_c \text{NaOAc} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$$= \Lambda_c \text{HIO}_3 - \Lambda_c \text{KIO}_3 + \Lambda_c \text{KOAc} \quad . \quad . \quad . \quad . \quad . \quad (4)$$

A short series of approximations (see p. 2837; also MacInnes, *J. Amer. Chem. Soc.*, 1926, **48**, 2069; MacInnes and Shedlovsky, *ibid.*, 1932, **54**, 1434; compare Banks, J., 1931, 3341) is necessary for the calculation of the ionic concentration c' . We have tested the validity of the assumption by applying expressions (1)—(4) to run 3, and expressions (1) and (2) to all the runs, and find that it holds satisfactorily (see Experimental); the conductivity values employed were those previously determined (Jeffery and Vogel, J., 1931, 1715; this vol., p. 400). MacInnes and Shedlovsky tacitly assume the validity of expression (2) in computing their results.

The thermodynamic or true dissociation constant has been computed from the corrected values of the degree of dissociation (compare MacInnes, *J. Amer. Chem. Soc.*, 1926, **48**, 2068). The activity coefficients of the ions γ_i were assumed to be equal, and were calculated from the Debye-Hückel equation $\log \gamma_i = 0.505 c'^{0.5}$ (cf. LaMer and Goldman, *J. Amer. Chem. Soc.*, 1929, **51**, 2636; Davies, *ibid.*, 1932, **54**, 1698); that of the undissociated acid was taken as unity. The mean values of the thermodynamic and the classical dissociation constant are 1.776×10^{-5} and 1.813×10^{-5} respectively. The final value for the former differs appreciably from that of MacInnes and Shedlovsky (1.753×10^{-5}) and is to be attributed (1) to the approximate conductivity values for sodium acetate used by those authors, and (2) to their different method of calculating Λ_0 for acetic acid, which they found to be 390.59.

It is necessary to discuss the claims made by Shedlovsky (*J. Amer. Chem. Soc.*, 1932, **54**, 1405, 1411) for the new method of calculating Λ_0 and for the new type of conductivity cell, and also to reply to his criticism concerning pipette conductivity cells, by means of which most of the recent conductivity work in aqueous and non-aqueous solutions has been carried out (cf. Kraus and Parker, *J. Amer. Chem. Soc.*, 1922, **44**, 2449; Parker, *ibid.*, 1923,

45, 2033; Hartley and collaborators, *Proc. Roy. Soc.*, 1925—1930, J., 1930—1931; Vogel, J., 1929, 1480). Shedlovsky (*loc. cit.*) employs the equation

$$\Lambda_0 = \frac{\Lambda_c + \beta C^{0.5}}{1 - \alpha C^{0.5}} - BC \dots \dots \dots (5)$$

where α , β , and B are constants, for the calculation of the conductivity at infinite dilution. This is of the familiar square-root equation form

$$\Lambda_0 = \Lambda_c + xC^{0.5} \dots \dots \dots (6)$$

to which another adjustable constant B has been added. It is doubtful whether this new expression, with an additional adjustable constant, has any advantage over the square-root formula or the ‘ n ’ equation of Ferguson and Vogel. Indeed, the square-root equation holds accurately for Shedlovsky’s own experimental results for potassium, sodium, and hydrogen chlorides at 25° over a considerable concentration range, and the use of his expression seems quite unnecessary. Further, the values for Λ_0 deduced from Shedlovsky’s equation for potassium and sodium chlorides at 18° have actually been exceeded experimentally by Wieland (*J. Amer. Chem. Soc.*, 1918, 40, 146) and by Kohlrausch and Maltby (“*Ges. Abh.*,” 1911, 2, 886).

Shedlovsky deduces theoretically that the use of cells with dipping electrodes, *e.g.*, those described by Kraus and Parker (*J. Amer. Chem. Soc.*, 1922, 44, 2429), Parker (*ibid.*, 1923, 45, 1366, 2017), and Hartley and Barrett (J., 1913, 103, 786), introduces errors in conductivity measurements which tend to produce apparent variations in cell constants, and he has designed a cell which is claimed to be free from this objection. The new cell appears to be less suitable than the Hartley and Barrett cell for the numerous runs and routine work which are involved in this series of researches. In view of the fact that most of the recent work in aqueous and non-aqueous solutions has been carried out in cells with dipping electrodes, it is important to consider whether Shedlovsky’s theoretical deduction is supported by experiment. In the first place, where data are available for conductivity cells with dipping electrodes but of different design, such as the Hartley and Barrett type and that used by Kraus and Parker (*loc. cit.*), it is found that they give consistent results; *e.g.*, the present authors’ measurements with iodic acid (J., 1931, 1715; this vol., p. 400) agree well with those of Kraus and Parker. No good agreement is obtained for hydrochloric acid when comparison is made with Parker’s figures (*J. Amer. Chem. Soc.*, 1923, 45, 2017), but this is attributed to his use of phosphoric oxide as a drying agent, for this substance enters into the slow reaction $2P_2O_5 + 3HCl = POCl_3 + 3HPO_3$.

Further, by the determination of the cell constant at 25° in a Hartley cell with 0.01*N*-potassium chloride by Parker and Parker's method (*J. Amer. Chem. Soc.*, 1924, **46**, 312), we have been able to reproduce Kohlrausch and Maltby's results at 18° (*op. cit.*, 1911, **2**, 826) for potassium chloride, sodium chloride, and potassium iodate over the range 0.0001—0.01*N* (*J.*, 1931, 1715) to within about 1 part in 1000; better absolute agreement could not be expected owing to the slight difference between Parker and Parker's and Kohlrausch and Maltby's value for the specific conductivity of 0.01*N*-potassium chloride. Our results clearly indicate (1) that our conductivity technique, if Kohlrausch and Maltby's results be taken as standard, is satisfactory, and (2) that there is no apparent variation in cell constant over the range 0.0001—0.01*N* for the above-mentioned substances, and hence the conductivity figures may be regarded as trustworthy to at least 0.1%. Frazer and Hartley's method of determination of cell constants (*Proc. Roy. Soc.*, 1925, **109**, A, 351; see also Part IV), in which the specific conductivity of a series of solutions of potassium chloride is measured at 18° over the concentration range in which the cell is to be employed, appears to us to be preferable to the single determination by the Parker and Parker method, especially in view of the limited concentration range of each cell (cf. Washburn, *J. Amer. Chem. Soc.*, 1916, **38**, 2431) and the simultaneous check on the constancy of the cell constant thus made. Both methods give results agreeing to about 1 part in 1000, provided all the solutions measured are within the concentration range of the cell, as can be seen from Table I, which gives typical results for four Hartley cells by both methods.

TABLE I.

Cell Constants with Potassium Chloride at 25°.

Pyrex Cell S.		Pyrex Cell V.	
$C \times 10^4$.	<i>K</i> .	$C \times 10^4$	<i>K</i>
2.736	0.034263	3.616	0.027835
9.368	0.034243	9.759	0.027814
28.64	0.034237	21.39	0.027833
52.94	0.034252	35.26	0.027840
	Mean 0.034249	75.41	0.027820
0.01 <i>N</i>	0.034210		Mean 0.027828
		0.01 <i>N</i>	0.027996
Silica Cell R.		Silica Cell Q.	
$C \times 10^4$.	<i>K</i> .	$C \times 10^4$	<i>K</i>
3.763	0.025860	4.364	0.026760
17.27	0.025852	12.07	0.026750
29.39	0.025866	24.53	0.026746
47.40	0.025854	32.92	0.026762
75.62	0.025876		Mean 0.026758
	Mean 0.025861	0.01 <i>N</i>	0.026738
0.01 <i>N</i>	0.025848		

We regard our results for potassium and sodium chlorides at 25°, when referred to Kohlrausch and Maltby's figures for potassium chloride at 18° as standard, as accurate to within 0.1%. Shedlovsky's determinations (*loc. cit.*) with his new cell differ by nearly 0.5% for potassium chloride, exhibit variations above 0.001*N* which may be as high as 0.3% for sodium chloride, and agree reasonably well over the range 0.005—0.003*N* for hydrochloric acid when compared with our own results (J., 1931, 1715; this vol., p. 400).

EXPERIMENTAL.

Preparation of Materials and Solutions.—*Acetic acid.* Specimen 1. B.D.H. "A.R." Acid, m. p. 16.00°, was distilled with pure Ac_2O and pure CrO_3 (Orton and Bradfield, J., 1927, 984). After rejection of the first fraction (about 10% of the whole) a middle fraction boiling constantly at 118°/758 mm. was collected. Its "bromine absorption number" (Orton, Edwards, and King, J., 1911, 100, 1178) was 0.10 and the Ac_2O content 0.004% (Orton and Bradfield, *loc. cit.*).

Specimen 2. A pre-war sample of Kahlbaum's 99—100% acid, m. p. 15.85°, treated as above, gave a fraction with Br absorption number 0.20 and Ac_2O content 0.001%.

For the actual runs a little of the purified acid was distilled in the all-Pyrex still previously described (this vol., p. 509), the first few c.c. of the acid were rejected, and then the requisite quantity collected directly in a large silica weighing bottle attached to the end of the condenser by a rubber bung carrying a CaCl_2 guard tube: the acid was thus weighed directly. Conductivity water, of the same sp. conductivity as that employed in the runs, was added, and the bottle reweighed. This formed the stock solution. Independent stock solutions were prepared for each run.

Sodium acetate. A weighed quantity of B.D.H. "A.R." acid, purified as described above, was treated with the calc. quantity of standard "A.R." NaOH aq., and the liquid evaporated to crystallisation. The product was recrystallised from conductivity H_2O , dried in an air-oven at 130°, and gently fused in Pt [Found: Na (by volumetric method of Dobbins and Byrd, *J. Amer. Chem. Soc.*, 1931, 53, 3288), 28.01. Calc.: 28.05%].

Potassium acetate. This was similarly prepared [Found: K (as K_2SO_4), 39.86. Calc.: 39.82%].

Conductivity Cells.—Four cells of the Hartley and Barrett type, two of silica, *R* (0.02586₈) and *Q* (0.02674₈), and two of Pyrex, *S* (0.03422₈) and *V* (0.02781₅), were employed for the actual runs, and a small Pyrex Kohlrausch cell (0.2390) for the measurement of the conductivity of the water. Cell constants were determined at frequent intervals by Jeffery and Vogel's method (J., 1931, 1719) with KCl at 25° and are shown in parentheses.

Conductivity Measurements.—The technique employed has been described in earlier papers of this series. It must be emphasised that the sliding contact of the bridge was earthed, as was also a special terminal on the resistance box which was thus shielded (cf. Shedlovsky, *J. Amer. Chem. Soc.*, 1932, 54, 1427).

Solvent Correction.—No correction was applied for the acid. Calculation (see Glasstone, "Electrochemistry of Solution," 1931, p. 148; Davies, "The

Conductivity of Solutions," 1930, p. 56) showed that the influence of the H_2CO_3 contained in the conductivity H_2O was negligible. The sp. conductivity of the H_2O used was subtracted from the total obs. conductivity for solutions of the salts.

Correction for Hydrolysis.—The hydrolysis of the acetate MOAc, where $M = Na$ or K , can be represented as $MOAc + H_2O \rightleftharpoons HOAc + MOH$. The degree of hydrolysis, a_h , at any mol. concn. c may be computed from the approximate relation

$$a_h = \sqrt{K_w/c \cdot K_{class.}} \dots \dots \dots (7)$$

where K_w is the ionic product of H_2O , taken as 9.9×10^{-15} (Roberts, *J. Amer. Chem. Soc.*, 1930, **52**, 3877), and $K_{class.}$ is the classical dissociation const. of AcOH, a preliminary value (1.814×10^{-5}) being deduced by calculating the limiting mobility of the OAc' ion from the uncorr. results for the acetates by the "n" formula. These were as follows :

$$\begin{aligned} NaOAc : \Lambda_0 &= \Lambda_c + 51.4 C^{0.433} = 90.72; & OAc' &= 40.9 \\ KOAc : \Lambda_0 &= \Lambda_c + 79.9 C^{0.552} = 114.15; & OAc' &= 40.7 \end{aligned}$$

Λ_0 for AcOH was taken as $348.0 + 40.8 = 388.8$. The use of expression (7) is justified since the degree of hydrolysis is small. Now $c = 1/v$ where v is the dilution; also the sp. conductivity $\kappa = \Lambda/v = \Lambda_c$, where κ is the sp. conductivity at concn. c . If $\kappa_{obs.}$ is the obs. (uncorr.) sp. conductivity of the acetate solution at any dilution v , then

$$\kappa_{obs.} \times 10^3 = a_h c \Lambda_v MOH + c(1 - a_h) \Lambda_v S + c a_h \Lambda_v HOAc \dots (8)$$

(all the terms in this equation are sp. conductivities), where $\Lambda_v S$ is the mol. conductivity of the unhydrolysed salt at the dilution v . One may write $\kappa_{obs.} \times 10^3/c = \Lambda'_v S$, where $\Lambda'_v S$ is the obs. mol. conductivity of the hydrolysed salt at the dilution v . Owing to the production of alkali hydroxide, $\Lambda'_v S > \Lambda_v S$. Dividing (8) throughout by c , to give mol. conductivities, one obtains

$$\Lambda'_v S = a_h \Lambda_v MOH + (1 - a_h) \Lambda_v S + a_h \Lambda_v AcOH$$

or
$$\Lambda_v S = \frac{\Lambda'_v S - a_h \Lambda_v MOH - a_h \Lambda_v AcOH}{(1 - a_h)} \dots \dots \dots (9)$$

The values of the mol. conductivities at the respective dilutions for NaOH, KOH and AcOH were read off directly from the conductivity-concentration curves.

Results.—The following tables give the exptl. values of the equiv. conductivity, Λ_c obs., of the substances investigated at various concns. C , expressed in g.-equivs. per l. The capital letters S, V, Q, R refer to the cell employed. The mean values of Λ_0^n , evaluated from the equation $\Lambda_0^n = \Lambda_c + BC^n$, the values of the consts. of which are given, are included at the head of the table. Likewise the mean values of Λ_0^s and x deduced from the square-root relation $\Lambda_c = \Lambda_0^s - xC^{0.5}$ are incorporated in the tables. Col. 3 gives the values of the degree of hydrolysis, a_h ; col. 4 the values of the conductivity corrected for hydrolysis, Λ_c corr.; col. 5 the values of Λ_0^n calc. by the "n" formula; col. 6 the values of Λ_c calc. computed from the given values of Λ_0^s and x ; col. 7 is the difference between Λ_c obs. and Λ_c calc.; κ is the sp. conductivity of the H_2O used expressed in gemmhos, and M is the mol. wt.

For NaOAc, x calc. by the Debye-Hückel-Onsager equation (cf. J., 1931, 1720) is 80.2 and $\Delta = 36.7$; for KOAc x calc. is 85.7 and $\Delta = 49.0$.

Sodium Acetate at 25° (M = 82.04).

$$\Lambda_0^n = \Lambda_c + 93.42 C^{0.598}; \quad \Lambda_0^n = 89.45.*$$

$$\Lambda_0^s = \Lambda_c + 50.8 C^{0.5}; \quad \Lambda_0^s = 89.58.$$

$C \times 10^4$.	Pyrex cell V.			$\kappa = 0.811$.		Series 1S.		Diff.
	Λ_c obs.	α_+	Λ_c corr.	Λ_0^n .	Λ_c calc.			
1.285	89.60	0.00216	89.00	89.44	89.00		0.00	
5.368	88.62	0.00106	88.36	89.39	88.40		-0.04	
9.927	88.10	0.00078	87.89	89.38	87.98		-0.09	
19.71	87.31	0.00055	87.18	89.47	87.32		-0.14	
38.74	86.26	0.00039	86.20	89.44	(86.52)		(-0.32)	
57.78	85.41	—	85.41	(89.69)	(85.72)		(-0.31)	
75.24	84.75	—	84.75	(89.65)	—		—	
91.77	84.16	—	84.16	(89.75)	—		—	

	Pyrex cell S.			$\kappa = 0.840$.		Series 2S.		Diff.
	Λ_c obs.	α_+	Λ_c corr.	Λ_0^n .	Λ_c calc.			
2.808	89.16	0.00150	88.76	89.46	88.73		+0.03	
6.076	88.37	0.00093	88.20	89.41	88.24		-0.04	
14.87	87.71	0.00064	87.60	89.50	87.62		-0.02	
26.38	86.90	0.00048	86.80	89.48	86.87		-0.07	
32.06	86.64	—	86.64	89.55	86.70		-0.06	
51.09	85.77	—	85.77	(89.75)	(85.95)		(-0.18)	
64.91	85.10	—	85.10	(89.65)	—		—	
99.01	83.95	—	83.95	(89.92)	—		—	

* The values in parentheses were not employed in the calculation of the mean value of Λ_0^n .

Potassium Acetate at 25° (M = 98.13).

$$\Lambda_0^n = \Lambda_c + 150.5 C^{0.686}; \quad \Lambda_0^n = 113.44.$$

$$\Lambda_0^s = \Lambda_c + 43.7 C^{0.5}; \quad \Lambda_0^s = 113.65.$$

	Pyrex cell V.			$\kappa = 0.730$.		Series 1S.		Diff.
	Λ_c obs.	α_+	Λ_c corr.	Λ_0^n .	Λ_c calc.			
1.415	113.65	0.00206	113.10	113.44	113.13		-0.03	
6.177	112.75	0.00099	112.53	113.37	112.56		-0.01	
11.53	112.25	0.00072	112.14	113.40	112.16		-0.02	
23.11	111.39	0.00051	112.29	113.51	(111.55)		(-0.26)	
48.22	110.00	—	110.00	(113.88)	(110.61)		(-0.61)	
72.85	109.09	—	109.09	(113.92)	—		—	
92.45	108.40	—	108.40	(114.00)	—		—	
111.0	107.80	—	107.80	(114.21)	—		—	

	Pyrex cell S.			$\kappa = 0.819$.		Series 2S.		Diff.
	Λ_c obs.	α_+	Λ_c corr.	Λ_0^n .	Λ_c calc.			
2.909	113.22	0.00144	112.83	113.39	112.90		-0.07	
7.096	112.65	0.00092	112.50	113.44	112.49		+0.01	
15.79	111.80	0.00062	111.70	113.50	(111.91)		(-0.21)	
30.27	110.85	0.00045	110.78	113.48	(111.25)		(-0.47)	
39.70	110.39	—	110.39	113.54	—		—	
53.40	109.90	—	109.90	(113.68)	—		—	
68.68	109.15	—	109.15	(113.89)	—		—	

Acetic Acid at 25° (M = 60.04).

The results are given below, together with the corresponding values of the classical dissociation consts., K_{class} , with $\Lambda_0 = 387.85$.

Series, etc.	$C \times 10^4$.	Λ_c .	$K_{\text{class.}} \times 10^5$.
1A.	1.873	102.5	1.782
Specimen 1.	25.62	31.59	1.840
$\kappa = 0.742$.	45.23	24.05	1.854
Cell Q.	65.27	20.06	1.832
	89.55	16.99	1.797
	113.2	15.42	1.863
2A.	1.772	103.9	1.744
Specimen 2.	9.400	50.60	1.841
$\kappa = 0.740$.	24.78	31.94	1.849
Cell Q	38.86	25.78	1.839
	56.74	21.48	1.842
	80.23	18.51	1.814
	92.16	16.99	1.850
	106.3	15.81	1.841
3A.	5.160	65.95	1.819
Specimen 1.	12.96	43.50	1.836
$\kappa = 0.717$.	25.78	31.43	1.842
Cell R.	68.71	19.58	1.844
	84.56	17.74	1.854
	112.2	15.41	1.844
			Mean 1.831

Calculation of Dissociation Constants.—For the computation of " Λ_c " of AcOH at any ion concn. c' , four expressions are available; these being identical with (1), (2), (3), and (4) when $\Lambda'_{c'}$ is substituted for Λ_c in each case. Let the ion concn. corresponding to the mol. concn. C be represented by c' , and κ_c soln. be the sp. conductivity of the solution at the concn. C . As a first approximation, using the limiting value of Λ_e , i.e., Λ_0 , $c' = 1000 \kappa_c$ soln./387.85. For this concn. c' an approx. value of Λ_e may be obtained with the aid of the conductivity-concentration curves of the substances given in equation (2) (the results are to be found in the present and earlier papers of this series). We have found that for,

$$\begin{aligned} \text{HCl, } \Lambda_c &= 423.67 - 1380 C^{0.929}, \\ \text{NaCl, } \Lambda_c &= 126.18 - 117.4 C^{0.551}, \\ \text{NaOAc, } \Lambda_c &= 89.45 - 93.42 C^{0.598}. \end{aligned}$$

Substituting in equation (2), we have

$$\Lambda_c \text{AcOH} = 386.94 - 1380 C^{0.929} - 93.42 C^{0.598} + 117.4 C^{0.551}.$$

With the new value of Λ_e , a fresh determination of the ionic concn. c'' was made and thence the corresponding value of Λ_e . Two approximations were found to be sufficient.

For the sake of brevity, only the final results are given in Table II. Λ_e has been deduced from expressions (1) and (2), K' is the dissociation const. computed from the corr. degree of dissociation, and $K_{\text{therm.}}$ is the true or thermodynamic dissociation const. deduced from the equation $\log K_{\text{therm.}} = \log K' - 1.010 c''^{0.5}$. Table III gives a similar set of results applied to series 3A but with the mean value of Λ_e deduced from equations (1), (2), (3), and (4): the difference is very small, indicating that the assumption of independent migration of ions is justified.

Λ_c at Round Concentrations.—The values for the equiv. conductivity at round concns. are given in Table IV. Interpolation was carried out on a Λ_c - C graph drawn with a flexible spline.

TABLE II.

$C \times 10^4$.	Λ_c .	Λ_e .	$c'' \times 10^4$.	$K' \times 10^5$.	$K_{\text{therm.}} \times 10^5$.
Series 1A.					
1.873	102.5	387.23	0.4966	1.794	1.773
25.62	31.59	387.13	2.0857	1.847	1.787
45.23	24.05	387.05	2.8089	1.858	1.788
65.27	20.06	386.95	3.3829	1.843	1.766
89.55	16.99	386.90	3.9310	1.806	1.725
113.2	15.42	386.82	4.5138	1.874	1.784
Series 2A.					
1.772	103.9	387.24	0.4764	1.751	1.722
9.400	50.60	387.20	1.2188	1.847	1.800
24.78	31.94	387.14	2.0439	1.838	1.780
38.86	25.78	387.07	2.5882	1.847	1.780
56.74	21.48	387.00	3.1494	1.851	1.777
80.23	18.51	386.91	3.8414	1.828	1.745
92.16	16.99	386.89	4.0471	1.864	1.779
106.3	15.81	386.85	4.3466	1.851	1.765
Series 3A.					
5.160	65.95	387.22	0.8960	1.802	1.763
12.96	43.50	387.20	1.4553	1.843	1.792
25.78	31.43	387.12	2.0925	1.849	1.789
68.71	19.58	386.96	3.4771	1.853	1.775
84.56	17.74	386.90	3.8813	1.865	1.783
112.2	15.41	386.83	4.4720	1.854	1.767

TABLE III.

Series 3A.					
5.160	65.95	387.73	0.8848	1.798	1.759
12.96	43.50	387.64	1.4535	1.838	1.788
25.78	31.43	387.50	2.0904	1.845	1.785
68.71	19.58	387.22	3.4748	1.851	1.773
84.56	17.74	387.12	3.8747	1.862	1.780
112.2	15.41	386.99	4.4702	1.853	1.764

TABLE IV.

$C \times 10^4$.	AcOH.	AcONa.*	AcOK.*	$C \times 10^4$.	AcOH.	AcONa.*	AcOK.*
1.0	—	89.07	113.10	50.0	22.75	85.70	109.91
2.0	104.0	88.87	113.00	60.0	20.78	85.25	109.49
5.0	64.50	88.56	112.68	70.0	19.24	84.90	109.14
10.0	48.70	88.06	112.24	80.0	17.96	84.53	108.79
20.0	35.18	87.23	111.48	90.0	16.92	84.19	108.48
30.0	29.32	86.67	110.88	100.0	16.20	83.86	108.16
40.0	25.45	86.18	110.37				

* Corrected for hydrolysis.

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