$E = -0.665$, exclusive of liquid potentials. The potential of the normal calomel electrode we have found in the preceding paper to be -0.2776. The absolute potential, therefore, of the above electrode is -0.943. Hence we may obtain the normal potential of this electrode from the equation $-0.943 = E^\circ_{298} - (0.05915/5)\log(H^+)^6(IO_3^-)$. Assuming the degree of dissociation of $0.001M$ HIO_3 to be 0.97, the concentration of each ion is $0.00097M$;

$$E^\circ_{298} = -1.193;\ \Delta F^\circ_{298} = -5EF' = 137590. \tag{21}$$

$I(s) + 3/2O_2 + \ominus = IO_3^-$ —Combining Equation 21 with the value we have used above for the free energy of formation of liquid water and of hydrogen ion, we find

$$\Delta F^\circ_{298} = -32270 \tag{22}$$

This value is in surprisingly good agreement with the one obtained above. The latter calculation is by far the more reliable of the two and can hardly be in error by more than 200 calories.

In concluding we wish to express our obligation to the Rumford Fund of the American Academy of Arts and Science for financial aid in this investigation.

Summary.

We shall not summarize here the various subsidiary calculations used in this paper, but merely repeat the final values of the free energy of formation of the iodine compounds investigated.

TABLE VI.

Substance.	ΔF°_{298}.	Equation.	Substance.	ΔF°_{298}.	Equation.
$I(s)$	0		$HI(g)$	310	11
$I(l)$	460	1	I^-	—12304	13
$I_2(g)$	4640	4	I_3^-	—12216	15
$I(g)$	16965	7	HIO(aq.)	—23300	17
I_2(aq.)	3926	8	IO_3^-	—32270	22

BERKELEY, CALIFORNIA.

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF ILLINOIS.]

A SENSITIVE CRITERION OF THE PRECISION AND OF CONSTANT ERRORS IN THE CONDUCTANCE DATA OF WEAK ELECTROLYTES, THE DETERMINATION OF THE MOLAR CONDUCTANCE OF ORGANIC ELECTROLYTES AT ZERO CONCENTRATION AND A STUDY OF THE CORRECTION FOR THE SPECIFIC CONDUCTANCE OF THE CONDUCTIVITY OF WATER.

BY C. G. DERICK.

Received August 26, 1914.

I. "Calculated" λ_0 as a Criterion of Precision.

If the ideal mass law for weak electrolytes is given the form $k = (\alpha^2/1 - \alpha)$ or $k = c\lambda/\lambda_0(\lambda_0 - \lambda)$, since $\alpha = \lambda/\lambda_0$, is assumed to hold exactly in any given case, it is possible to calculate the value of the conductance at zero concentration or infinite dilution from two measurements of its conductance at two different concentrations. If λ and λ_1 represent the molar conductances of this electrolyte at the concentrations C and C_1, respectively, then $k = c\lambda^2/\lambda_o(\lambda_o - \lambda) = c_1\lambda_1^2/\lambda_o(\lambda_o - \lambda_1)$ from which $\lambda_o = \lambda\lambda_1(c\lambda - c_1\lambda_1)/(c\lambda^2 - c_1\lambda_1^2)$.[1]

Since the ideal mass law in the above form can only hold rigorously where the nature of the solution no longer changes with change in concentration, it is obvious that the mass law in this form is never rigorously obeyed.

Yet there may exist electrolytes which obey it accurately enough so that our measurements do not detect any deviations at small concentrations. Fortunately, data are fast being accumulated which show to what degree the ideal mass law in the above form is approximated and may be used, therefore, to draw valuable conclusions concerning the behavior of electrolytes, as, for example, the calculation of the molar conductance at zero concentrations in the manner just described. The recent accurate work of Kendall[2] upon the conductance of acetic acid in aqueous solution at 25° warrants one in believing that this acid very closely approximates the ideal mass law in the above form, and it may be used in the calculation of the molar conductance of acetic acid at zero concentration, which value will hereafter be called the "calculated" λ_o. Table I, that follows, gives the results of these calculations for all possible combinations of the dilutions measured by Kendall together with the corresponding values for its molar conductance and ionization constant.

As stated in the introductory paragraphs to the article, in order to calculate λ_o, as has been done in the table, the mass law in the above form is assumed to be approximated to such a degree that experimental errors in the measured values of λ and λ_1, and C and C_1 are not greater than those introduced by the difference in values for the ionization constant corresponding to these concentrations, since these values are made identical in the calculations. The values given by Kendall for the ionization constant corresponding to the different concentrations or dilutions, as seen from the table, justify the above assumptions and it is evident that small differences in these values do not influence the "calculated" λ_o appreciably. The concentrations, at which the constant for ideal mass law in the above form is most accurately known, may be determined as follows: The percentage error introduced into the ionization constant by errors in λ and λ_o (C is assumed to have a negligible error, *i. e.*, is a

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[1] Kohlrausch and Holborn, "Leitvermögen der Elektrolyte," **1898**, p. 103.

[2] *J. Chem. Soc.*, **101**, 1283 (1912); and *Meddelanden fran K. Vetenskapsakademiens Nobelinstitut*, **2**, 38 (1913).

TABLE I.

Conductance data.[1]

v.	λ.	$k_a^{25°} \times 10^{-5}$
13.57	6.086	1.845
27.14	8.591	1.851
54.28	12.09	1.849
108.56	16.98	1.849
217.1	23.18	1.851
434.2	33.22	1.849
868.4	46.13	1.850
1737.0	63.60	1.854
3474.0	87.17	1.855
6948.0	116.8	1.870
∞	387.7	...

"Calculated" λ_0.		
Dilutions.		λ_0.
12.57 and	27.14	766
	54.28	449
	108.56	359
	217.1	416
	434.2	402
	868.4	399
	1737.0	399
	3474.0	396
	6948.0	400
27.14 and	54.28	348
	108.56	311
	217.1	389
	434.2	384
	868.4	388
	1737.0	532
	3474.0	391
	6948.0	458

"Calculated" λ_0.		
Dilutions.		λ_0.
54.28 and	108.56	290*
	217.1	402
	434.2	391
	868.4	392
	1737.0	395
	3474.0	393
	6948.0	399
108.56 and	217.1	551*
	434.2	434*
	868.4	414*
	1737.0	408*
	3474.0	401*
	6948.0	403*

"Calculated" λ_0.		
Dilutions.		λ_0.
217.1 and	434.2	379*
	868.4	388
	1737.0	393
	3474.0	392
	6948.0	398
434.2 and	868.4	394
	1737.0	398
	3474.0	394
	6948.0	400
868.4 and	1737.0	400*
	3474.0	381
	6948.0	401
1737.0 and	3474.0	390
	6948.0	401
3474.0 and	6948.0	409

constant for the given case) is easily obtained by differentiating the logarithmic form of expression $k = C\lambda^2/\lambda_0(\lambda_0 - \lambda)$, whence

$$dk/k = [(2\lambda_0 - \lambda)/(\lambda_0 - \lambda)][d\lambda/\lambda - d\lambda_0/\lambda_0].$$

As the solutions become more concentrated, λ approaches zero as its limit when $dk/k = 2[d\lambda/\lambda - d\lambda_0/\lambda_0]$. On the other hand, as the solution becomes more dilute, λ approaches λ_0 as its limit, when $dk/k = \infty\,(d\lambda/\lambda - d\lambda_0/\lambda_0)$. Obviously, the ionization constant is least influenced by errors in λ and λ_0 the greater the concentration, which, however, must never be so great that the degree of ionization ceases to be measured by the expression $\alpha = \lambda/\lambda_0$ with the requisite accuracy for the above discussion. For most weak electrolytes, the value of this upper limit of concentration is in the neighborhood of 0.02 N according to recent investigations. Thus, for Kendall's measurements the value 1.849×10^{-5}

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[1] Uncorrected for the specific conductance of the conductivity water.

may be taken as the ionization constant of acetic acid according to his data. The error in this value may be greater or less than that in λ or λ_o accordingly as $d\lambda/\lambda$ and $d\lambda_o/\lambda_o$ are of the opposite or the same sign, respectively. Before the correct weight can be given to this value for the ionization constant for acetic acid the amount and the direction of the errors in λ and λ_o must be ascertained. However, it is sufficiently obvious that acetic acid very closely approximates the mass law and that a correct value for its "calculated" λ_o may be found as described.

It is now necessary to determine which value of "calculated" λ_o is most free from the errors in λ and λ_1 or which value is most sensitive to these errors if the "calculated" λ_o is to be used as a criterion of the accuracy of the conductance data. In a similar manner to that in which the percentage error in the ionization constant was found, and again assuming that the errors in C and C_1 are negligible, the percentage error in λ_o with those in λ and λ_1 may be calculated from the expression:

$$\frac{d\lambda_o}{\lambda_o} = \frac{C_1\lambda_1[C_1\lambda_1^2 + C\lambda^2 - 2C\lambda\lambda_1]}{[C\lambda - C_1\lambda_1][C\lambda^2 - C_1\lambda_1^2]}\frac{d\lambda}{\lambda} + \frac{C\lambda[C_1\lambda_1^2 + C\lambda^2 - 2C_1\lambda\lambda_1]}{[C\lambda - C_1\lambda_1][C\lambda^2 - C_1\lambda_1^2]}\frac{d\lambda_1}{\lambda_1}$$

Letting $a = \dfrac{C_1\lambda_1[C_1\lambda_1^2 + C\lambda^2 - 2C\lambda\lambda_1]}{[C\lambda - C_1\lambda_1][C\lambda^2 - C_1\lambda_1^2]}$, $b = \dfrac{C\lambda[C_1\lambda_1^2 + C\lambda^2 - 2C_1\lambda\lambda_1]}{[C\lambda - C_1\lambda_1][C\lambda^2 - C_1\lambda_1^2]}$

and solving for their numerical values in the following cases, using the data given in Table I, the results of Table II are obtained:

TABLE II.

C.	C_1.	k_C.	k_{C_1}.	a.	b.
1/54.28	1/108.56	1.849×10^{-5}	1.849×10^{-5}	—110.5	+111.2
1/54.28	1/434.2	1.849×10^{-5}	1.849×10^{-5}	— 33.4	+ 34.4
1/54.28	1/6948	1.849×10^{-5}	1.870×10^{-5}	— 5.3	+ 6.3
1/108.56	1/217.1	1.849×10^{-5}	1.851×10^{-5}?	—151.1?	+151.9?
1/217.1	1/434.2	1.851×10^{-5}	1.849×10^{-5}	— 71.5	+ 72.5
1/434.2	1/868.4	1.849×10^{-5}	1.850×10^{-5}	— 51.6	+ 52.7
1/868.4	1/1737.0	1.850×10^{-5}	1.854×10^{-5}	— 36.0	+ 37.3

From Table II it is seen that the error in "calculated" λ_o for acetic acid is never greater than that in λ or λ_1, depending upon which is most in error, as long as $d\lambda/\lambda$ and $d\lambda_1/\lambda_1$ have the same sign, since (a) and (b) always have opposite signs. This appears to be the case with Kendall's data. As long as this is true the "calculated" λ_o may be found with the same accuracy whatever combinations of λ and λ_1 (C and C_1) are employed, provided the ideal mass law in the above form is approximated with sufficient accuracy. In other words, the "calculated" λ_o is an equally sensitive criterion of the precision of the molar conductances under these conditions whatever the values of C and C_1.

If, however, $d\lambda/\lambda$ and $d\lambda_1/\lambda_1$, are opposite in sign, then the error in "calculated" λ_o is greater the greater the value of C and C_1, since (a) and (*b*) always have opposite signs. Table II shows that for Kendall's data on acetic acid, that the "calculated" λ_o, found by using concentration which are as different as possible, is least affected by errors in λ and λ_1 when $d\lambda/\lambda$ and $d\lambda_1/\lambda_1$ are opposite in sign. Thus in the series of values of "calculated" λ_o in which $C = 1/54.32$ (Table I) is the common concentration, when $C_1 = 1/6948$, the "calculated" λ_o is 399; while the average of all the values of "calculated "λ_o for all possible combinations of concentrations from 1/54.32 to that of 1/6958, excluding those marked by the asterisks, is 398 with a mean error of ±6 for each value. It is also clear that "calculated" λ_o is a much more sensitive criterion of the precision of the conductance data when C and C_1 are as near in value as possible if $d\lambda/\lambda$ and $d\lambda_1/\lambda_1$ are opposite in sign.

II. "Calculated" λ_o as a Criterion of Constant Errors.

The mathematical methods for the determination of the precision of experimental results have been very accurately developed and employed for conductance data, but such methods are of little value where constant errors are present. It is the presence of constant errors in most of the conductance data of weak electrolytes that renders the same useless when quantitative conclusions are to be drawn. Therefore, more attention must be paid to the development of methods for the detection of such constant errors in conductance data.

In the present discussion, fortunately, the molar conductance at zero concentration for weak electrolytes, like acetic acid, which closely approximate the ideal mass law in the above form, may be determined, independently of the conductance data for the acid, by the following well-known method:

$$\lambda_o RCO_2H = \lambda_o RCO_2Na + \lambda_o H^+ - \lambda_o Na^+$$

The mobilities of the hydrogen and sodium ions are known from conductance and transference measurements upon strong acids and their salts. The molar conductances of the sodium or other salts of the weak acid are extrapolated to zero concentration by one of the well-known methods in order to determine their molar conductance at zero concentration. In this manner, by independent measurements, the molar conductance at zero concentration of a weak electrolyte may be determined. Such a value for λ_o will be spoken of as determined by the salt method in the following discussion:

A comparison of the "calculated" λ_o for weak electrolytes like acetic acid with that obtained for the same acid by the salt method offers a means of detecting constant errors in conductance data. This means assumes that the conductance data for the salt is fairly accurately known and, similarly for the values of the mobilities of the sodium and hydrogen ions. It is not necessary that the weak electrolyte approximate the ideal mass law, in the above form, as accurately as does acetic acid in order that "calculated" λ_0 may be used to detect constant errors in conductance data, as will be shown from the discussions in the following sections. It must be pointed out, however, that the conductance at zero concentration for most uni-univalent salts of weak electrolytes falls between the limits 80 and 90 while the mobility of the hydrogen ion at 25° for aqueous solution has been given the limits 338 and 365.[1] Obviously, fairly large errors in the molar conductance at zero concentration for the sodium salt will not introduce a correspondingly large error in the λ_0 value determined by the salt method, since the former value is additive in the above equation to the mobility of hydrogen and sodium ions. Similarly it is not necessary that the mobility of the sodium ion be known with anything like the accuracy with which the mobility of the hydrogen ion must be known, since the value of the former is 52 compared 338 to 365 for the latter at 25°. Unfortunately, the uncertainty is greatest concerning the mobility of the hydrogen ion, which should be most accurately known.

Kendall, in the article referred to above, has recently attempted to ascertain the most accurate value for the mobility of the hydrogen ion at 25°. His indirect method consisted in the calculation of the ideal mass law constant from his measurements of the conductance of cyanoacetic, *o*-nitrobenzoic, *o*-chlorobenzoic, etc., acids at concentrations where these acids very closely approximated this law. These calculations were made with varying values for the mobility of the hydrogen ion, provided it was always in the neighborhood of 350 and that value was chosen for this mobility which gave the most consistant mass law constant at the smaller concentrations. His method gave him the value 347.2, provided the specific conductance of water was not greater than 0.9×10^{-6}. No correction was made for such water.

Table V, with the subsequent discussion, offers convincing proof of the correctness of this value for the mobility of the hydrogen ion at 25° for transition electrolytes in aqueous solution. For, in Kendall's work, he must assume the mass law and draw his conclusion from the mass law constant, which is in reality reasoning in a circle; since he had no independent measurements to justify his assumption of the mass law for his measurements. The calculation of the "calculated" λ_0 from the conductance data of these acids, as has been done in Table V, while also assuming the mass law, gives a value which may be checked by independent measurements and thus justify the assumption of the mass law. This procedure entirely substantiates the conclusions drawn by Kendall as to the mobility of the hydrogen ion at 25° for transition electrolytes, which is apparently, as the theories demand, the same value as for strong electrolytes.

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[1] See article by Kendall mentioned above.

In the case of weak electrolytes ($k < 10^{-4}$) Kendall justly states that his method for determining the mobility of the hydrogen ion is not sensitive, since large variations in this value do not influence the ionization constant to anything like the extent that it does for the transition electrolytes. In fact the water correction, which has a slight influence for the transition electrolytes, is of much more importance than slight variation in the value for the mobility of hydrogen ions upon the ionization constants of weak electrolytes, as will be discussed later. However, in accordance with theory, Kendall uses the value 347 for the mobility of the hydrogen ion in acetic acid at 25°, and calculates what he considers the best ionization constant for acetic acid at 25°, as was seen in Table I. In this case the unsatisfactoriness of his method, when applied to weak electrolytes for the solution of this problem, becomes very evident, since he did not choose the best value for the conductance of acetic acid at zero concentration, *i. e.*, the best value for the mobility of the hydrogen ion, which gives the best mass law constant for his data. In determining the molar conductance at zero concentration for acetic acid, Kendall used the value for the mobility of the acetate ions at 25° which was determined many years ago by Ostwald[1] and compiled by Bredig,[2] which, when expressed in reciprocal ohms, is 40.7. Since the limits for the mobility of the hydrogen ion at 25° are 338 and 365, the limits for the molar conductance at zero concentration of acetic acid at 25° are 379 and 406, accepting the mobility of the acetate ion as 41. Obviously, that value, for λ_0 for acetic acid, which will give the best mass law constant is found by assuming the mass law to hold, and solving for λ_0 from the conductance data of the acid as was done in Section I. This value for "calculated" λ_0 was found to be 398, which value is well within the above limits. Table III gives the values for the ionization constant of acetic acid determined by using this "calculated" λ_0 value, together with those of Kendall, using his data for λ and λ_0.

TABLE III.

	Ionization constant × 10^{-5}.			Ionization constant × 10^{-5}.	
Dilutions.	Kendall.	Author.	Dilutions.	Kendall.	Author.
13.57	1.845	1.749	434.2	1.849	1.750
27.14	1.851	1.752	868.4	1.850	1.750
54.28	1.849	1.752	1737.0	1.854	1.750
108.56	1.849	1.749	3474.0	1.855	1.749
217.1	1.851	1.750	6948.0	1.870	1.755

Kendall's measurements and interpretation give the average value for the ionization constant of acetic acid at 25° as 1.852×10^{-5} with a mean error in each value of $\pm 7 \times 10^{-8}$, while the author's interpretation gives the average value 1.750×10^{-5} with the mean error in each

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[1] *Z. physik. Chem.*, **2**, 45 (1889).

[2] *Ibid.*, **13**, 218 (1894).

value of $\pm 2 \times 10^{-8}$. In the term $(\lambda_0 - \lambda)$ employed in these calculations, λ was rounded off to a whole number, except where the decimal was close to 0.5 of a unit, so that the above results for the ionization constant are as uniform as possible, since the value for λ_0 is not known to a fraction of a whole unit. This value is practically the same as that obtained by Ostwald[1] when his results are expressed in international units, using the accepted values for the mobilities of the sodium and hydrogen ions at 25° (51.2 and 347). Kendall stated that Ostwald obtained the value 1.80×10^{-5} for this constant, but overlooked the fact that the values for these mobilities had changed since Ostwald made his calculations.

The fact that Kendall's data for acetic acid give the value 398 for the "calculated" λ_0 while the salt method gives 388 means that some constant error is present in these data, if the mobility of the hydrogen ion at 25° is 347 for such weak electrolytes. This constant error may be due to the fact that no correction was made for the specific conductance of the water used in the dilutions (see last section).

Finally, it is interesting to note that this value for "calculated" λ_0 for acetic acid is much closer to that obtained by the salt method by using the mobility of the hydrogen ion as 365 as suggested by Noyes and Sammuel.[2]

III. Application of the Criterion, "Calculated" λ_0 to other Data upon the Conductance of Acetic Acid.

In order to test the precision of, and constant errors in, the conductance data for acetic acid that follow, the "calculated" λ_0 was determined for all possible combinations of concentrations as given in Table IV.

TABLE IV.

Conductance Data.

Ostwald[3] 25°.			Jones[4] 25°.			Van't Hoff[5] 19.1°.	
v.	λ.	$k_a^{25} \times 10^{-5}$.	v.	λ.	$k_a^{25} \times 10^{-5}$.	v.	λ.
8	4.61	1.75	2	2.089	1.69	18.53	7.110
16	6.48	1.74	8	4.342	1.83	37.07	9.970
32	9.19	1.68	32	8.699	1.86	74.15	14.03
64	12.81	1.73	128	17.11	1.84	148.3	19.76
128	18.03	1.74	512	33.24	1.82	296.6	27.53
256	25.23	1.74	1024	45.87	1.81	593.2	38.16
512	34.23	1.63	2048	63.00	1.80	1186.4	49.60
1024	48.90	1.74				2372.8	71.65
						4745.6	97.36
						9491.2	129.7

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[1] *Z. physik. Chem.*, 3, 170 (1889).

[2] *Ibid.*, 43, 49 (1903).

[3] *Ibid.*, 3, 174 (1889).

[4] H. C. Jones, "Electrical Conductivity, etc., of Certain Salts and Organic Acids."

[5] *Z. physik. Chem.*, 2, 779 (1889).

TABLE IV (*continued*).

Calculated λ_0.

Ostwald.		Jones.		Van't Hoff.	
Solutions.	λ_0.	Solutions.	λ_0.	Solutions.	λ_0.
8 and 16	151	2 and 8	— 28.2	18.54 and 37.07	117
32	645	32	— 82.2	74.17	237
64	234	128	— 348.0	148.3	382
128	1647	512	+1900	296.6	331
256	358	1024	698	593.2	318
512	216	2048	524	1186.4	312
1024	366	8 and 32	—1279	2372.8	319
16 and 32	—468	128	+ 434	4745.6	344
64	+279	512	345	9491.2	349
128	351	1024	329	37.07 and 74.15	446*
256	412	2048	334	148.3	582*
512	222	32 and 128	434	296.6	384*
1024	388	512	288	593.2	344
32 and 64	135	1024	292	1186.4	328
128	236	2048	308	2372.8	329
256	321	128 and 512	301	4745.6	353
512	185	1024	301	9491.2	363
1024	205	2048	317	74.15 and 148.3	740*
64 and 128	509	512 and 1024	301	296.6	369
236	539	2048	325	593.2	333
512	211	1024 and 2048	344	1186.4	322
1024	414			2372.8	325
128 and 256	562			4745.6	350
512	183			9491.2	361
1024	402			148.3 and 296.6	269*
256 and 512	128			593.2	289*
1024	373			1186.4	298*
512 and 1024	—695			372.8	302*
				4745.6	340*
				9491.2	355*
				296.6 and 593.2	299*
				1186.4	317
				2372.8	315
				4745.6	347
				9491.2	361
				593.2 and 1186.4	336
				2372.8	320
				4745.6	355
				9491.2	359
				1186.4 and 2372.8	281*
				4745.6	334
				9491.2	346
				2372.8 and 4745.6	406*
				9491.2	392*
				4745.6 and 9491.2	384*

The criterion establishes the fact that the measurements by Ostwald and by Jones lack precision and contain constant errors that render them valueless from a quantitative standpoint when compared to those by Kendall. Further, the criterion establishes the second fact that the errors in λ and λ_1 are often in opposite directions since the value for "calculated" λ_0 may suddenly jump from —468 to +279 in the case of Ostwald's measurements, or from —1279 to +434 in the case of those by Jones (see Table IV).

The fact that the ionization constants calculated from the measurements of Ostwald, as well as from those by Jones, show a much greater precision than the corresponding values for "calculated" λ_0 must be attributed in part to the fact that there is a compensation in the errors of λ by those of λ_0 since the previous section shows that

$$dk/k = [(2\lambda_0 - \lambda)/(\lambda_0 - \lambda)][d\lambda/\lambda - d\lambda_0/\lambda_0].$$

In other words, the errors in λ and λ_0 must be in the same direction so that $d\lambda/\lambda$ and $d\lambda_0/\lambda_0$ have the same sign. Further, fairly large differences in the values for λ_0 do not greatly influence the value for the mass law constant of acetic acid. These facts make it clear that the use of the criterion, "calculated" λ_0 is much more sensitive as a test for the precision of, and of constant errors in, the conductance data of weak electrolytes than the ionization constant and that its use is indispensible at present, if accurate quantitative conductance data of such electrolytes is desired.

The measurement by van't Hoff and L. Th. Reicher give values for "calculated" λ_0 which fall, as a rule, close to the value determined by the sodium salt method. The average value for "calculated" λ_0 of all the calculations from the dilution 37.07 to that of 9491.2, neglecting those marked by the asterisks, is 345 with a mean error of ±19 in each value. The most probable value for this quantity by the salt method is not far from 352 at 19.1°.

Finally, the measurements by Kendall (Table I), although they possess satisfactory precision, contain constant errors, provided the mobility of the hydrogen ion at 25° is 347, as maintained by Kendall for acetic acid, since the "calculated" λ_0 is 398 while Kendall chose 388 by the salt method.

IV. Application of the Criterion of "Calculated" λ_0 to the Conductance Data of Transition Electrolytes.

In the case of transition electrolytes, Kendall[1] has pointed out for cyanoacetic, *o*-chlorobenzoic, *o*-nitrobenzoic acids, etc., that fairly consistent values for their ionization constants are obtained for solutions sufficiently dilute, provided an arbitrary value was chosen for the mobility of the hydrogen ion (347) and that the specific conductance for the conductivity water was not greater than 0.90×10^{-6}. In general, it is believed that all electrolytes approximate very accurately the mass law in the

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[1] See reference above.

TABLE V.

Cyanoacetic acid.			*o*-Chlorobenzoic acid.			*o*-Nitrobenzoic acid.		
v.	λ.	$k_a^{25°} \times 10^{-3}$.	v.	λ.	$k_a^{25°} \times 10^{-3}$.	v.	λ.	$k_a^{25°} \times 10^{-3}$.
20.80	96.2	0.398	150.1	134.6	0.1293	32	139.7	6.72
41.60	127.1	0.389	300.2	174.0	0.1286	64	179.0	6.60
83.20	164.5	0.381	600.4	218.0	0.1284	128	221.0	6.45
166.4	207.3	0.375	1201.0	262.6	0.1284	256	265.0	6.33
332.8	252.4	0.372	2402.0	302.1	0.1279	512	303.6	6.28
665.6	294.4	0.372	4804.0	333.0	0.1286	1024	333.5	6.27
1331.0	329.2	0.372	9608.0	353.7	0.1288	2048	353.6	6.29
2662.0	353.2	0.371	∞	380.2		4096	365.3	6.18
5324.0	368.3					∞	379.2	
∞	385.9							

Cyanoacetic acid.			
Dilutions.			λ_0.
20.80	and	41.60	302.2
		83.20	350.1
		166.4	361.0
		332.8	370.4
		665.6	377.5
		1331.0	380.5
		2662.0	383.4
		5324.0	384.7
41.60	and	83.20	357.4
		166.4	366.6
		332.8	374.2
		665.6	379.8
		1331.0	382.8
		2662.0	384.2
		5324.0	385.2
83.20	and	166.4	372.3
		332.8	378.1
		665.6	382.4
		1331.0	384.2
		2662.0	384.9
		5324.0	385.6
166.4	and	332.8	381.6
		665.6	384.6
		1331.0	385.4
		2662.0	385.5
		5324.0	385.9
332.8	and	665.8	386.3
		1331.0	386.0
		2662.0	385.8
		5324.0	386.1
665.8	and	1331.0	385.9
		2662.0	385.8
		5324.0	386.1
1331.0	and	2662.0	385.8
		5324.0	386.1
2662.0	and	5324.0	386.3

o-Chlorobenzoic acid.			
Dilutions.			λ_0.
150.01	and	300.2	251.7
		600.4	348.9
		1201.0	340.3
		2402.0	357.9
		4804.0	368.5
		9608.0	374.2
300.2	and	600.4	379.8
		1201.0	379.5
		2402.0	380.2
		4804.0	380.3
		9608.0	380.4
600.4	and	1201.0	380.4
		2402.0	379.7
		4804.0	380.3
		9608.0	380.4
1201.0	and	2402.0	379.4
		4804.0	380.3
		9608.0	380.4
2402.0	and	4804.0	380.8
		9608.0	380.6
4804.0	and	9608.0	380.5

o-Nitrobenzoic acid.			
Dilutions.			λ_0.
32	and	64	356.1
		128	362.3
		256	367.4
		512	372.2
		1024	375.5
		2048	377.4
		4096	378.0
64	and	128	364.2
		256	369.3
		512	373.6
		1024	376.3
		2048	377.0
		4096	378.3
128	and	256	372.1
		512	375.4
		1024	377.4
		2048	378.4
		4096	378.5
256	and	512	377.3
		1024	378.4
		2048	379.0
		4096	378.8
512	and	1024	379.1
		2048	379.3
		4096	379.0
1024	and	2048	379.3
		4096	378.9
2048	and	4096	378.7

form here discussed, if measurements can be made, on solutions sufficiently dilute, with the necessary degree of accuracy. It is interesting, therefore, to apply the criterion of "calculated" λ_0 to such electrolytes which have been so carefully measured, these results are given in Table V, as calculated from the data given by Kendall.

Since Kendall finds that, at and below a certain concentration, constant values are obtained for the mass law constant, it would be expected that a similar behavior would be found in the values for "calculated" λ_0. For each acid given in Table V, it is seen that the values for "calculated" λ_0 regularly increase to a constant maximum value. This increase in value should be steady for increasing dilution or decreasing concentration and never fluctuate from greater to lesser to greater, etc., values. If such is the case, the criterion, "calculated" λ_0, demonstrates the lack of precision due to errors in the measurements. The extreme sensitiveness of the criterion detects such errors even in the very accurate data of Kendall for *o*-chlorobenzoic acid given in Table V. The application of "calculated" λ_0 as a test of the precision of the conductance data of transition electrolytes is, therefore, obvious.

To detect the presence of constant errors, the average maximum constant value for "calculated" λ_0 must be compared with the value for λ_0 obtained independently by the salt method as shown under Section II. If no maximum constant value is obtained in any given case, it is obvious that the conductances of more dilute solutions must be measured, but for most organic electrolytes it will be unnecessary to measure solutions more dilute than 0.0005 *N*. A graph, obtained by plotting λ_0 as ordinates against the dilution as abscissae will often give much information concerning what dilutions must be measured in order that constant values for "calculated" λ_0 may be obtained. However, this graphic method will not give the correct value for "calculated" λ_0, since a range of dilution is employed in its calculation. The application of this criterion of constant errors to the data of Table V is given in next section.

V. A Simple and Accurate Method for the Determination of the Molar Conductance at Zero Concentration of Organic Electrolytes.

In Section I it was shown that electrolytes of the strength of acetic acid obeyed the ideal mass law in the form $k = C\lambda^2/\lambda_0(\lambda_0 - \lambda)$ for all concentrations below 0.02 *N*, within the error of the present measurements.

In Section II it was shown that the molar conductance of such electrolytes at zero concentration could be calculated from any two values of its molar conductance at two different concentrations, provided such concentrations are below 0.02 *N*, with the same degree of accuracy with which this value can be determined by the salt method, and in fact to a much greater degree of accuracy if no choice is made between the limiting values 338 and 365 for the mobility of the hydrogen ion at 25° in aqueous solution.

In Section IV it has just been shown that, assuming the ideal mass law to hold for transition electrolytes, and determining the values for "calculated" λ_0 at different concentrations, a regularity in the increase in these values with decreasing concentration was obtained, ceasing in a maximum constant value, below which concentration the ideal mass law is approximated to such a degree of accuracy that our measurements can detect no deviations. Obviously this maximum constant value for the molar conductance of the electrolyte must be identical with the same value obtained by the salt method if measurements and theories are correct.

From Table V it is seen that for cyanoacetic acid that the last thirteen values for "calculated" λ_0 are practically constant and are the maximum values obtained. In fact their average value is 385.9, while a mean error of ±0.2 is present in each value. The value chosen by Kendall from the salt method is 385.9 and an exact coincidence is obtained, as must be the case if the measurements and theories are accurate. Similarly for *o*-chlorobenzoic acid the last fourteen values for "calculated" λ_0 are constant and maximum in value. Their average maximum value is 380.3 while a mean error of ±0.4 is present in each value. Kendall chose for this constant 380.2 by the salt method. For *o*-nitrobenzoic acid, the last eight values for "calculated" λ_0 are constant and maximum. The average maximum value is 379.0 and a mean error of ±0.2 is present in each value, while the salt method gives the value 379.2 according to Kendall. The data for this acid show how much more sensitive the criterion "calculated" λ_0 is than the criterion the mass law constant for the determination of the approximation of an electrolyte to the ideal mass law, but less strikingly than the calculations given in Section III.

VI. Mobility of the Hydrogen Ion at 25°.

Section IV shows that the molar conductance at zero concentration for any organic electrolyte may be determined from the values of "calculated" λ_0 with the same degree of accuracy as by the salt method. Since this is the case this constant may be freed from the uncertainty attached to the mobility of the hydrogen ion when it is determined by the salt method. However, for the detection of constant errors in conductance data it is necessary to calculate λ_0 by both methods, and it is therefore necessary to know the velocity of the hydrogen ion at 25°. Kendall varied the value for this constant between certain limits, choosing that value which gave the best *precision* in the values for the ionization constant of the electrolyte concerned, which, he states, is "347.2 at 25°

with a maximum divergence of ±0.4." However, he did not always choose the correct value for λ_0 which would give the best *precision* in the values for the ionization constant. He should have assumed the mass law and calculated the value for λ_0 from his data, as has been done in this paper. These statements are supported by the facts given in Table III for acetic acid. He chose 387.7 as the molar conductance at zero concentration for acetic acid while his data gives 398, which would mean that the mobility of the hydrogen ion at 25° is 357 instead of 347 as he claims. However, for the other electrolytes considered in this paper, the "calculated" λ_0 checks within the experimental error the λ_0 value obtained by the salt method, when the mobility of the hydrogen ion is taken as 347. It is, therefore, probable that the data given by Kendall for acetic acid contains constant errors which account for the high value of the mobility of the hydrogen ion, obtained from the same by the calculation of the "calculated" λ_0. At present it would seem that the mobility of the hydrogen ion at 25° is 347, as claimed by Kendall and others, at least for the transition electrolytes.

VII. The Application of the Correction for the Specific Conductance of the Conductivity Water to the Conductance Data of Organic Electrolytes.

Since the "calculated" λ_0 as a criterion offers a method for the determination of the accuracy with which a given electrolyte approximates the ideal mass law in the form here discussed, it may be used to decide whether or not a correction for the specific conductance of the water used in the dilution of the organic acid should be applied to the conductance data of such acids. The method is simply to calculate the values for "calculated" λ_0 for the corrected and uncorrected data and compare the same with the value of λ_0 obtained by the salt method. This is possible, since the water corrections, necessary for the determination of λ_0 by the salt method, are far less influential than in the "calculated" λ_0 values and do not affect the former value by more than a few tenths of a per cent. at the most. This is easily seen when one considers the manner in which the λ_0 value is obtained by the salt method, which necessitates the measurement of the conductance of a strong acid, like hydrochloric acid, where the water correction is far less influential than in the case of a weak acid like acetic acid, and of the conductance of a salt, where the water correction is a large factor. But the mobility of the cation, like sodium (51.2 at 25°), so obtained is additive to a much larger quantity, that of the mobility of the hydrogen ion (347 at 25°), from the hydrochloric acid, and hence does not need to be known with anything like the accuracy with which the value for the latter must be known.

The same facts are true of the conductance of the salt of the organic acid at zero concentration as for the cation. Hence in the value for λ_o, by the salt method, the water correction is of slight importance in comparison to this value when calculated from the conductance of the organic acid. Further, the question of the application of the water correction to salts has been fairly well agreed upon and it is usually applied, so that the only uncertainty which surrounds this correction to the λ_o value by the salt method is its application to the conductance of the strong acid (hydrochloric acid), from which the mobility of the hydrogen ion is obtained, where it is of minor influence, however.

The very accurate work of Kendall discussed in this paper shows that *no water correction should be applied to his data upon transition electrolytes if the specific conductance of the water is less than* 0.9×10^{-6}, since his uncorrected data give "calculated" λ_o values which agree with the values obtained by the salt method with an accuracy greater than 0.1% in the dilute solutions. Kendall found that he obtained a better constant for the mass law using his uncorrected data and, therefore, chose this data as the most accurate, which choice is justified by the application of the criterion "calculated" λ_o in this paper.

To realize what influence the water correction has upon the ionization constant and upon the criterion "calculated" λ_o the following tables have been compiled, using Kendall's data upon acetic acid discussed in Section I of this paper. In Table VI, Column I gives the dilution (v) of the measurement, II the corrected specific conductance ($\underline{L}^c$), III the corresponding uncorrected specific conductance ($\underline{L}^u$), IV the percentage influence of the water correction, V and VI the ionization constants for the uncorrected (k_a^u) and corresponding corrected data (k_a^c). Table VII gives the "calculated" λ_o values for the corrected (λ_o^c) and corresponding uncorrected (λ_o^u) data.

Table VI shows that the uncorrected data for the conductance of acetic acid give far more satisfactory ionization constants than the corrected data and that, even though the water correction is 1.69% of the total uncorrected specific conductance, it should be entirely neglected if acetic acid approximates the mass law within 0.1%.

Table VII shows that acetic acid does closely approximate the mass law and the correction for the specific conductance of the water should be neglected entirely for all concentrations for the data measured by Kendall. A comparison of the corrected and uncorrected ionization constants of acetic acid from Table VI with the corresponding corrected and uncorrected values for "calculated" λ_o from Table VII shows how much more sensitive the latter values are as a criterion of the precision of and constant errors in the conductance data for weak electrolytes. Numerous other

TABLE VI.

v.	$\underline{L}^c \times 10^4$.	$\underline{L}^u \times 10^4$.	$\underline{L}^u_{H_2O}$.	$ka^u_a \times 10^5$.	$k^c_a \times 10^5$.
13.57	4.476	4.485	0.204	1.845	1.839
27.14	3.156	3.165	0.284	1.851	1.839
54.28	2.218	2.227	0.404	1.849	1.833
108.56	1.555	1.564	0.575	1.849	1.826
217.1	1.088	1.097	0.820	1.851	1.821
434.2	0.7561	0.7651	1.17	1.849	1.804
868.4	0.5222	0.5312	1.69	1.850	1.784
1737.0	0.3571	0.3661(5)	2.46	1.854	1.754
3474.0	0.2406	0.2496	3.60	1.855	1.706
6948.0	0.1592	0.1682	5.35	1.870	1.639

TABLE VII.

Dilution series. v and v_1.		Calculated λ_o. λ^u_o.	λ^c_o.
13.57 and	27.14	766	443.0
	54.28	449	341.1
	108.56	359	319.6
	217.1	416	326.7
	434.2	402	313.8
	868.4	399	325.4
	1737.0	399	308.0
	3474.0	396	304.0
	6948.0	400	302.8
27.14 and	54.28	348	294.0
	108.56	311	296.0
	217.1	389	314.1
	434.2	384	305.5
	868.4	388	313.4
	1737.0	532	304.6
	3474.0	391	301.7
	6948.0	458	301.3
54.28 and	108.56	290	297.3
	217.1	402	320.4
	434.2	391	306.7
	868.4	392	306.4
	1737.0	395	305.2
	3474.0	393	301.9
	6948.0	399	301.5
108.56 and	217.1	551	338.6
	434.2	434	303.2
	868.4	414	307.8
	1737.0	408	306.0
	3474.0	401	302.2
	6948.0	403	301.7
217.1 and	434.2	379	293.6
	868.4	388	300.3
	1737.0	393	301.7
	3474.0	392	299.4
	6948.0	398	300.0
434.2 and	868.4	394	304.9
	1737.0	398	304.0
	3474.0	394	300.4
	6948.0	400	300.5
868.4 and	1737.0	400	303.3
	3474.0	381	299.2
	6948.0	401	299.9
1737.0 and	3474.0	390	296.7
	6948.0	401	299.0
3474.0 and	6948.0	409	300.4
λ_o by the salt method		=	387.7

measurements in this laboratory, which will be published shortly, confirm Kendall in neglecting entirely the correction for the specific conductance of the conductivity water. The advantage of this method in determining the question of the application of the water correction is that it is applicable to the given solution of a weak acid under the ordinary conditions of measurement and necessitates no other procedure than a simple calculation.

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