CCXXX.—*The Dissociation Constants of Organic Acids. Part IV. The Mobilities of the Sodium, Potassium, and Hydrogen Ions at 25°, and the Determination of Cell Constants at 25°.*

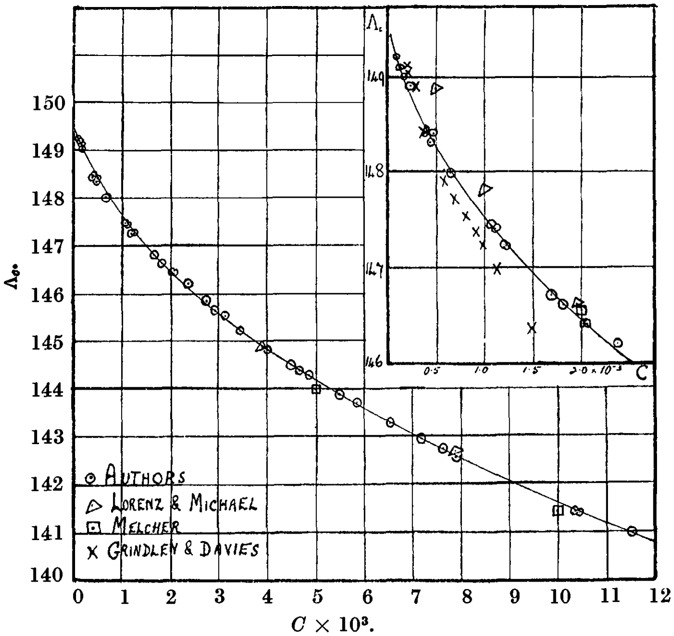
By George Harold Jeffery and Arthur Israel Vogel.

For the accurate determination of the dissociation constants of dibasic acids at 25°, at least three constants are necessary, *viz.*, the mobilities of the sodium, potassium, and hydrogen ions at this temperature. In order to calculate these, data for the variation of conductivity with dilution (up to $0{\cdot}0001N$) for iodic acid, potassium chloride, potassium iodate, and sodium chloride at 25° are required. Apart from the work of Kraus and Parker (*J. Amer. Chem. Soc.*, 1922, **44**, 2429) on iodic acid, no trustworthy conductivity measurements over an extensive range of concentration are available for these substances. The present research was therefore undertaken.

The measurements on potassium chloride are of particular interest in view of their bearing upon the determination of cell constants at 25°, at which temperature most conductivity determinations are now carried out. Since the publication of Kohlrausch, Holborn, and Diesselhorst's absolute data for $N/10$-, $N/50$-, and $N/100$-potassium chloride solutions at 18° (*Wied. Ann.*, 1898, **64**, 417; Ges. Abh., 1911, **2**, 737; Kohlrausch and Holborn, "Das Leitvermögen der Elektrolyte," 1916, p. 77), these have formed the basis of all accurate conductivity work, and have been almost exclusively employed for the determination of cell constants. In view of the limited range of conductivity cells, workers in dilute solutions have preferred to determine the cell constant over the same range of concentration as the actual measurements. For this purpose Kohlrausch and Maltby's data for potassium chloride at 18° (*Wiss. Abhandl. Phys.-Techn. Reichsanstalt*, 1900, **3**, 156; Ges. Abh., 1911, **2**, 826) have been utilised by Hartley and his collaborators (compare Frazer and Hartley, *Proc. Roy. Soc.*, 1925, **109**, *A*, 351), the equation $\Lambda_c = 129{\cdot}91 - 80{\cdot}75\,C^{0{\cdot}5}$, valid up to $0{\cdot}002N$, being employed for the computation of the specific conductivity. Davies (*Trans. Faraday Soc.*, 1929, **25**, 129) has suggested the equation $\Lambda_c = 129{\cdot}85 - 79{\cdot}8\,C^{0{\cdot}5}$. The disadvantages of this procedure for accurate work at 25° are that (1) it necessitates troublesome adjustments of thermostats and (2) the formula is applicable only over a limited range. Both of these are overcome by the experimental figures for potassium chloride at 25° now available over the concentration range $0{\cdot}0001$—$0{\cdot}01N$.

For the determination of the cell constant, Frazer and Hartley's procedure (*loc. cit.*) was adopted for the dilute solutions at 18°, the specific conductivity being computed from their formula and also by Ferguson and Vogel's formula, $\Lambda_c = 130{\cdot}04 - 61{\cdot}26\,C^{0{\cdot}452}$ (*Phil. Mag.*, 1925, **50**, 971). Both formulæ gave results in excellent agreement over their common range of applicability; the latter, however, has the advantage of being valid over the whole range 0·0001—0·01N with an accuracy of about 0·03%. The cell constant was also determined at 25° by Parker and Parker's method (*J. Amer. Chem. Soc.*, 1924, **46**, 312) with 0·01N-potassium chloride, and differed from that determined in dilute solution by approximately 0·15%. A small difference is to be expected, for Parker and Parker have shown (*loc. cit.*) that the conductivity of 0·01N-potassium chloride as determined by Kohlrausch and Maltby is 0·15% too high. The cell constant employed in the calculations was the mean of both methods. The absolute accuracy is therefore probably about 1 part in 1000 parts, but the relative accuracy is greater than this.

FIG. 1.



Potassium chloride at 25°.

The collected results for potassium chloride at 25° are shown in Fig. 1, the equivalent conductivity Λ_c being plotted against the concentration; the figures of previous workers (Melcher, quoted by Noyes and Falk, *J. Amer. Chem. Soc.*, 1912, **34**, 470; Lorenz and Michael, *Z. anorg. Chem.*, 1921, **116**, 161; Grindley and Davies, *Trans. Faraday Soc.*, 1929, **25**, 129) are also indicated.

Lorenz and Michael's data are inaccurate owing to their use of the Ostwald method of dilution; it is surprising that their results are expressed to 1 part in 14,000 parts when the cell constant as determined with $N/50$-potassium chloride is given as 0·2580. Grindley and Davies's figures are confined to the range 2—15 × $10^{-4}N$ and are shown in the enlarged inset. Our data are considered to be more trustworthy for the following reasons: (1) the accuracy in the actual conductivity measurements was greater, and the general technique better; (2) two conductivity cells were used, and consequently the presence of any systematic error is unlikely; (3) five series of determinations were made representing 36 concentrations distributed over the whole range; (4) a run carried out at 18° (the cell constant determined by Parker and Parker's method only was employed) for concentrations over the range 1·5—78 × 10^{-4} gave results in good agreement with Kohlrausch and Maltby's figures. These are shown below, Λ_c (calc.) being computed from the equation $\Lambda_c = 130{\cdot}04 - 61{\cdot}26\ C^{0{\cdot}452}$.

Potassium chloride at 18°.

Cell constant 0·034003. $\kappa = 0{\cdot}651$ gemmho.

$C \times 10^4$	1·556	6·578	15·14	28·63	52·81	77·83
Λ_c (obs.)	129·10	127·95	126·80	125·66	124·10	123·19
Λ_c (calc.)	128·88	127·81	126·78	125·70	124·31	123·22

The electrical conductivity of aqueous solutions of sodium chloride at 25° has been measured over limited ranges of concentration by Melcher (*loc. cit.*), by Lorenz and Michael (*loc. cit.*), and by Thomas and Marum (*Z. physikal. Chem.*, 1929, **143**, 198). The present authors' results, which cover the complete concentration range 0·0001—0·01N, are plotted in Fig. 2, which includes the figures of previous workers. The results for a run at 18° are given in Table II.

Potassium iodate was similarly investigated at 25°. One run was carried out at 18° in order to compare the results directly with those of Kohlrausch (*Berl. Ber.*, 1900, 1002; Ges. Abh., 1911, **2**, 943) (see Table II). The agreement was satisfactory.

The extrapolation to infinite dilution possesses particular importance since Λ_0 is required for the calculation of x in the Debye–Hückel–Onsager equation, which is of the type $\Lambda_c = \Lambda_0 - xC^{0{\cdot}5}$. For water at 25° the equation reduces to $\Lambda_c = \Lambda_0 - (0{\cdot}228\ \Lambda_0 + 59{\cdot}8)\ C^{0{\cdot}5}$ for uni-univalent electrolytes (Onsager, *Physikal. Z.*, 1927, **28**, 292; Hartley, *Ann. Reports*, 1931, **27**, 331). Four formulæ of importance are available for the calculation of Λ_0 for strong electrolytes, *viz.*,

(1) $\Lambda_0 = \Lambda_c + xC^{0\cdot5}$ (Kohlrausch).

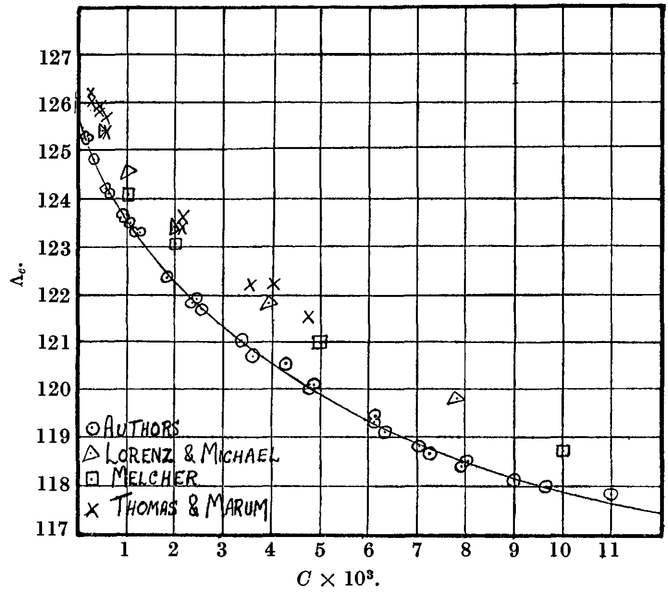
(2) $\Lambda_0 = \Lambda_c + \Lambda_c^p C^{0\cdot5}$ (Kohlrausch, *Berl. Ber.*, 1900, 1002; Ges. Abh., 1911, **2**, 944).

(3) $\Lambda_0 = \Lambda_c + BC^n$ (Ferguson and Vogel, *loc. cit.*).

(4) $\Lambda_0 = \Lambda_c + \alpha C^{0\cdot5} + \beta C$ (Debye and Hückel, *Physikal. Z.*, 1923, **24**, 305).

Formula (1) is valid up to 0·002N and its *form* has been deduced theoretically by the Debye–Hückel–Onsager theory for very low concentrations Formula (2) holds up to 0·1N for uni-uni- and uni-bi-valent electrolytes and was introduced by Kohlrausch in order to calculate Λ_0 from data in relatively concentrated solutions (compare Kohlrausch and Grüneisen, *Berl. Ber.*, 1904, 1215; Ges. Abh., 1911, **2**, 1078) : it has the disadvantage that the constants are determined with relative difficulty. Equation (3) holds for uni-univalent electrolytes up to about 0·01N and the constants B and n are readily determined by a graphical method (Ferguson and Vogel, *loc. cit.*). Its theoretical basis is at present obscure, but it is possible that it may be correlated with deviations from Coulomb's law owing to association and other factors (compare Williams, *Chem.*

FIG. 2.



Sodium chloride at 25°.

Reviews, 1931, **8**, 319). Recently, Ferguson and Vogel (*Trans. Faraday Soc.*, 1931, **27**, 285) have expressed equation (3) in the form $\Lambda_0 = \Lambda_c + BC^{0\cdot5\pm\delta}$ owing to the significant clustering of the values of n about 0·5, the value of δ being zero under the conditions of the Debye–Hückel–Onsager theory. The constants in formula (4) were determined by Debye and Hückel by the method of least squares and these values of Λ_0 were employed by them and by Onsager (*loc. cit.*) in testing the agreement of the theoretically deduced equation (1) with experiment. The type of results for Λ_0 for uni-univalent electrolytes computed with the aid of the four formulæ from Kohlrausch and Maltby's data at 18° can be seen by reference to Table I.

TABLE I.

Electrolyte.	(1).	(2).	(3).	(4).
KCl	129·91	130·10	130·04	129·93
NaCl	108·87	108·99	109·02	108·89
LiCl	98·99	98·88	99·07	98·93
KNO_3	126·40	126·50	126·39	126·46
$NaNO_3$	105·30	105·33	105·48	105·34
$LiNO_3$	95·18	95·18	95·40	95·24

It is apparent that, where data for strong electrolytes extend to about 0·0001*N*, the values of Λ_0 determined by independent methods agree to about 0·1%. Only formulæ (1) and (3) have been employed in the present work.

The equations for the conductivity–concentration curves at 25° over the whole observed concentration range (up to 0·01*N*) are :

$$\text{KCl},\ \Lambda_c = 149\cdot83 - 101\cdot6\,C^{0\cdot547} \quad . \quad . \quad . \quad . \quad . \quad (5)$$

$${}^*\text{NaCl},\ \Lambda_c = 126\cdot18 - 117\cdot4\,C^{0\cdot551} \quad . \quad . \quad . \quad . \quad (6)$$

$$\text{KIO}_3,\ \Lambda_c = 115\cdot45 - 58\cdot7\,C^{0\cdot384} \quad . \quad . \quad . \quad . \quad . \quad (7)$$

* For NaCl at 25° the equation holds with accuracy up to a concentration of 0·006*N* only.

Equations (5) and (6) are put forward for use in the determination of cell constants at 25°. The specific conductivity at any concentration is calculated from the appropriate value of the equivalent conductivity computed from equation (5) or (6) and compared with the conductivity observed in the cell, and the cell constant obtained by division. For 18° the corresponding equations are (Ferguson and Vogel, *loc. cit.*) :

$$\text{KCl},\ \Lambda_c = 130\cdot04 - 61\cdot26\,C^{0\cdot452} \quad . \quad . \quad . \quad . \quad . \quad (8)$$

$$\text{NaCl},\ \Lambda_c = 109\cdot02 - 54\cdot24\,C^{0\cdot443} \quad . \quad . \quad . \quad . \quad (9)$$

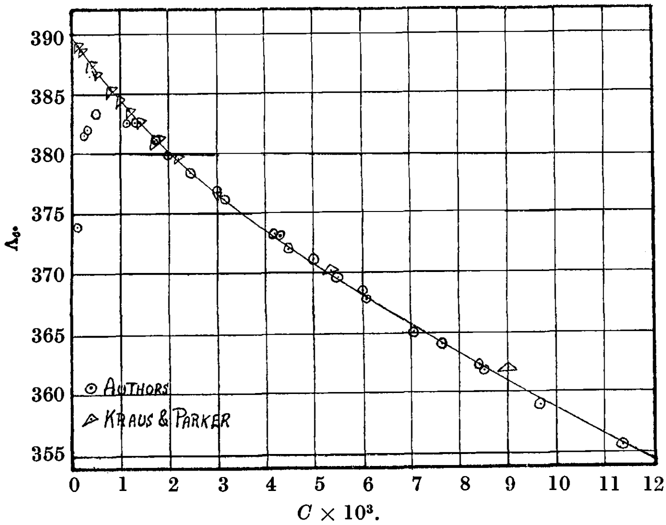
By plotting the equivalent conductivity against the square root of the concentration, satisfactory straight lines were obtained from the lowest measured concentration up to about 0·002*N*, and the values of Λ_0^s have been determined by direct extrapolation of these straight lines. The slopes of these lines (x, obs.) are here compared with those calculated (x, calc.) from the Debye–Hückel–Onsager equation

$$\Lambda_c = \Lambda_0 - (0{\cdot}228\ \Lambda_0 + 59{\cdot}8)\ C^{0{\cdot}5}:$$

Salt.	Λ_0^s.	x, obs.	x, calc.	Δ.
KCl	150·05	79·2	94·0	−19·8
NaCl	126·18	83·5	87·3	− 4·4
KIO_3	114·57	100·3	85·9	+16·8

Δ is the percentage deviation of the observed value from the theoretical, *i.e.*, $\Delta = 100(x, \text{obs.} - x, \text{calc.})/x, \text{calc.}$ (compare Copley, Murray-Rust, and Hartley, J., 1930, 2497). It will be observed that Δ is negative for sodium and potassium chlorides, and positive for potassium iodate.

FIG. 3.



Iodic acid at 25°.

Measurements have also been made of the electrical conductivity of aqueous solutions of iodic acid at 25° over the range 1—100 × $10^{-4}N$. These results are plotted in Fig. 3. The conductivity–concentration curve passes through a maximum at a concentration of about $10^{-3}N$. Similar results were obtained by Kraus and Parker (*J. Amer. Chem. Soc.*, 1922, **44**, 2429) with lime-glass cells, but the maximum was lower. Unfortunately, apart from two isolated observations at concentrations of 1·6 and 3·6 × 10^{-3}, no figures are available for comparison for Pyrex-glass cells. Kraus and Parker, however, investigated the conductivity in quartz cells chiefly in dilute solutions up to a concentration of about $2 \times 10^{-3}N$ (their results are indicated by triangles in Fig. 3; for the sake of clarity only a few of these are shown at low concentrations); no maximum was observed, indicating that the latter is largely due to impurities dissolved from the containing vessels.

Onsager (*Physikal. Z.*, 1927, **28**, 292) has shown that the square-root relation $\Lambda_0 = \Lambda_c + xC^{0\cdot5}$ does not hold for iodic acid, a parabola being obtained on plotting Λ_c against $C^{0\cdot5}$, so that this method cannot be employed for extrapolation to Λ_0. Ferguson and Vogel (*Trans. Faraday Soc.*, 1931, **27**, 285), however, find that the equation

$$\Lambda_0 = \Lambda_c + 2187\ C^{0\cdot880}$$

accurately represents Kraus and Parker's results, and this leads to a mean value of Λ_0 of 389·6 for iodic acid at 25°. It appears that results in Pyrex-glass cells do not differ appreciably from those in quartz cells at concentrations greater than $0{\cdot}002N$ (compare Randall and Scott, *J. Amer. Chem. Soc.*, 1927, **49**, 636); hence, by the use of an extrapolation formula which holds over a large concentration range, extrapolation to Λ_0 should be possible although, owing to the limited concentration range, too great an accuracy cannot be expected, nor can any great significance be attached to the values of the other constants of the formula. Equations (2) and (3) are available. We have applied equation (3) to our results at concentrations exceeding 2×10^{-3} and find that $\Lambda_0 = \Lambda_c + 910{\cdot}3\ C^{0\cdot732}$, leading to 389·8 as the value for the conductivity at infinite dilution.

In view of the good agreement with Λ_0 deduced from Kraus and Parker's observations in dilute solution, we have carried out a series of measurements upon iodic acid at 18° in Pyrex cells over the concentration range $0{\cdot}0001$—$0{\cdot}01N$. The results were similar to those at 25° (see Experimental). At concentrations above $0{\cdot}002N$, the conductivity–concentration curve can be expressed by the equation $\Lambda_0 = \Lambda_c + 384{\cdot}1\ C^{0\cdot577}$, which gives a mean value of Λ_0 of 351·0 for iodic acid at 18°. Measurements will be made in the near future in silica cells in order to obtain trustworthy values for conductivities at low concentrations and also for Λ_0 at 18°.

These experiments indicate clearly that silica cells should be employed for measurements with acids at concentrations below $2 \times 10^{-3}N$.* The work on dibasic acids of one of us (J., 1929, 1476, 1487) will therefore require revision and will be repeated in quartz cells. The early work is regarded as preliminary in character owing to the many assumptions made in the calculations

* No difficulties of this character seem to have been experienced by Murray-Rust and Hartley (*Proc. Roy. Soc.*, 1929, **126**, *A*, 85) in their work with acids in methyl and ethyl alcohol.

and the use of constants which the present research shows to be appreciably in error.

The mobilities of the potassium, sodium, chloride, iodate, and hydrogen ions at 25° can be computed from the values of Λ_0 deduced from the relation $\Lambda_0 = \Lambda_c + BC^n$ for sodium and potassium chlorides, potassium iodate, and iodic acid with the aid of the transport number for potassium chloride. The following table contains the results for a transport number for the potassium ion in potassium chloride of 0·497 (Kohlrausch and Maltby, Ges. Abh., 1911, **2**, 892; this forms the basis of all the calculations of Kohlrausch and of Ferguson and Vogel) and of 0·490 (MacInnes and Dole, *J. Amer. Chem. Soc.*, 1931, **53**, 1362).

Kation transport number of KCl.	Mobilities of ions.				
	$K^{\cdot}$.	$Na^{\cdot}$.	Cl'.	IO_3'.	$H^{\cdot}$.
0·497	74·5	50·8	75·4	41·0	348·6
0·490	73·4	49·8	76·4	42·0	347·6

A preliminary value for the mobility of the hydrogen ion at 18°, based on the value of Λ_0 of 351·0 for iodic acid deduced in the present work and of 34·0 for the mobility of the iodate ion (Ferguson and Vogel, *Phil. Mag.*, 1925, **50**, 971), is 317·0.

Parker (*J. Amer. Chem. Soc.*, 1923, **45**, 2017) has described measurements with aqueous solutions of hydrochloric acid in silica cells at 25°. These have been discussed by Ferguson and Vogel (*Trans. Faraday Soc.*, 1931, **27**, 285). New data for hydrochloric acid will be published in the near future.

EXPERIMENTAL.

Conductivity Water.—This was prepared as described by Jeffery and Vogel (this vol., p. 1201).

Preparation of Materials and Solutions.—Potassium chloride. Kahlbaum's purest salt was recrystallised twice from conductivity water, the separated crystals being removed in the first crystallisation by filtration through a Jena-glass Büchner funnel with a glass filter disc, and in the second recrystallisation the mother-liquor was decanted, the crystals partially dried at 100°, and then fused in platinum. Two specimens were prepared. All the operations in this and the following purifications were conducted in Pyrex-glass vessels which had been soaked in chromic–sulphuric acid mixture and steamed for 12 hours with steam generated from distilled water, before use.

Sodium chloride. Kahlbaum's purest material was dissolved in conductivity water, precipitated with redistilled absolute alcohol, and filtered through a Jena-glass filter. This operation was repeated and the product fused in platinum [Found : Cl, (1) 60·68, (2) 60·64. Calc.: 60·66%].

Potassium iodate. Kahlbaum's "pure for analysis" salt was recrystallised twice from hot water (neutral solutions were always obtained), dried in the steam oven, and stored in a vacuum desiccator over concentrated sulphuric acid until required. The substance was analysed by precipitation as silver salt, the silver iodate dissolved in the filtrate being estimated by the addition of excess of potassium iodide and sulphuric acid and titration of the liberated iodine with standard sodium thiosulphate (Kraus and Parker, *J. Amer. Chem. Soc.*, 1922, **44**, 2431) (Found : $0{\cdot}2394_2$ g. Taken : $0{\cdot}2392_2$ g.).

Iodic acid. Kahlbaum's iodic acid "for analysis" was purified by three crystallisations from conductivity water in the presence of a little pure nitric acid as recommended by Kraus and Parker (*loc. cit.*) [Found: (1) $0{\cdot}3043_5$ g., (2) $0{\cdot}2133_1$ g. Taken : (1) $0{\cdot}3041_3$, (2) $0{\cdot}2133_4$ g.].

All solutions were made up by weight as described in Part I (J., 1929, 1480).

Measurement of Conductivity.—The experimental procedure was the same as described by Vogel (*loc. cit.*), the only modifications being the use of the new type of low-inductance decade resistance box made by the Cambridge Instrument Co., and a Sullivan valve oscillator adjusted to a frequency of 1000 cycles. Successive additions of weighed amounts of solution were made to a known weighed amount of water in the cell, and the resistance was determined after each addition. The same sample of conductivity water was employed for the preparation of the solutions as that contained in the cell.

Temperature Control.—The thermostats were filled with distilled water (a little thymol was added to minimise the growth of algæ) and were electrically controlled by mercury–toluene thermo-regulators : the temperature was constant at 18° ± 0·01° and at 25° ± 0·01°. Temperatures were measured on standard thermometers recently calibrated at the N.P.L.

Calculation of the Concentrations.—All the concentrations are expressed in g.-mols. per litre of solution at the temperature at which the run was carried out. The concentrations are known, in the first instance, in weight normalities, and in order to convert them into volume normalities, the density at the temperature of the run of the final solution in the cell was determined with a carefully calibrated pycnometer, and a linear variation of density with concentration was assumed.

Conductivity Cells.—Two cells of the Hartley and Barrett type (J., 1913, **103**, 789) were employed in the runs, and a small Kohlrausch-type cell of about 35 c.c. capacity (compare Vogel, *loc. cit.*) was used for the measurement of the specific conductivity of the solvent, since this was outside the range of the other cells. All the electrodes were coated with grey platinum.

Cell Constants.—These were determined for the Hartley cells by measuring the resistance of aqueous solutions of potassium chloride at 18° over a concentration range from about 0·0002 to about 0·002*N*. The value of the specific conductivity at the concentrations employed was calculated from the data of Kohlrausch and Maltby using both the equation

$$\Lambda_c = 129{\cdot}91 - 80{\cdot}75\, C^{0{\cdot}5} \quad . \quad . \quad . \quad . \quad (A)$$

(Frazer and Hartley, *Proc. Roy. Soc.*, 1925, **109**, *A*, 355) and the equation

$$\Lambda_c = 130{\cdot}04 - 61{\cdot}26\, C^{0{\cdot}452} \quad . \quad . \quad . \quad . \quad (B)$$

(Ferguson and Vogel, *loc. cit.*). Typical sets of results for the two cells are shown below.

Cell.	$C \times 10^4$.		Equation A.	Equation B.
S	2·386		0·034235	0·034226
	6·570		0·034261	0·034252
	23·14		0·034241	0·034259
		Mean	0·034246	0·034246
V	2·764		0·027815	0·027805
	8·647		0·027819	0·027810
	24·63		0·027833	0·027847
		Mean	0·027822	0·027820

The cell constants were also determined by Parker and Parker's method (*loc. cit.*) with 0·01*N*-potassium chloride at 25°; typical results were : Cell S, 0·034003 (before resealing) and 0·034208 (after resealing); Cell V, 0·027804.

The values used throughout in the calculations were : Cell S, for runs with potassium chloride only, $0{\cdot}03401_3$, and for other substances, $0{\cdot}03422_8$ (this change was due to resealing of the Pyrex-glass supports at the four corners of the platinum plates); Cell V, $0{\cdot}02781_5$. The cell constant of the Kohlrausch cell, determined at 25° with 0·01*N*-potassium chloride by Parker and Parker's method only, was 0·2390.

The cell constants were determined at frequent intervals throughout the research but no appreciable variation was detected.

Solvent Correction.—The solvent correction for the salts was applied by subtracting the specific conductivity of the water from that of the solution in each case. No correction for solvent conductivity was made for the solutions of iodic acid.

Results.—The following tables give the experimental values for the equivalent conductivity Λ_c of the substances investigated at various concentrations C, expressed in g.-equivs. per litre. Entirely independent solutions were used for each series of measurements of the same electrolyte. The letter in parenthesis refers to the Hartley cell employed.

The mean values of Λ_0^s and x deduced from the square-root relation $\Lambda_c = \Lambda_0^s - xC^{0{\cdot}5}$, which holds up to about 0·002N, for each salt are given at the head of the appropriate section of the table. Likewise the mean values of Λ_0^n evaluated from the equation $\Lambda_0^n = \Lambda_c + BC^n$, the constants of which are also given, are included at

Series.	κ.	$C \times 10^4$.	Λ_c obs.	Λ_c calc.	Diff.	Λ_0^n.
Potassium chloride at 25° (M = 74·56).						
$\Lambda_0^s = \Lambda_c + 79{\cdot}2\ C^{0{\cdot}5}$. $\Lambda_0^s = 150{\cdot}05$.						
$\Lambda_0^n = \Lambda_c + 101{\cdot}6\ C^{0{\cdot}547}$. $\Lambda_0^n = 149{\cdot}83$.						
1 (S) First specimen	0·779	1·029	149·19	149·22	−0·03	149·86
		3·649	148·41	148·54	−0·13	149·76
		12·00	147·24	147·31	−0·07	149·81
		23·76	146·20	146·19	+0·01	149·93
		40·05	144·80	—	—	149·83
		58·69	143·69	—	—	149·82
		78·84	142·64	—	—	149·84
		115·3	140·96	—	—	149·82
2 (S) First specimen	0·781	0·977	149·21	149·27	−0·06	149·86
		3·984	148·45	148·47	−0·02	149·86
		18·26	146·61	146·67	−0·06	149·84
		31·10	145·51	145·09	−0·42	149·84
		46·78	144·35	—	—	149·76
		103·7	141·40	—	—	149·76
3 (V) First specimen	0·802	2·474	148·81	148·80	−0·01	149·90
		6·517	147·99	148·03	−0·04	149·83
		12·23	147·23	147·28	−0·05	149·83
		20·41	146·41	146·47	−0·06	149·85
		29·26	145·60	145·76	−0·16	149·79
		45·00	144·48	—	—	149·78
		65·33	143·25	—	—	149·75
4 (S) Second specimen	0·802	1·582	149·01	149·05	−0·04	149·86
		4·600	148·40	148·35	−0·05	149·92
		11·00	147·40	147·42	−0·02	149·85
		20·63	146·40	146·45	−0·05	149·86
		34·18	145·20	145·42	−0·22	149·80
		48·31	144·27	—	—	149·78
		76·24	142·77	—	—	149·84
		104·6	141·39	—	—	149·79
5 (V) Second specimen	0·821	1·405	149·11	149·11	0·00	149·91
		4·351	148·30	148·40	−0·10	149·78
		10·58	147·43	147·43	0·00	149·83
		16·98	146·70	146·79	−0·09	149·79
		27·41	145·81	145·90	−0·09	149·85
		55·01	143·86	—	—	149·77
		71·72	142·93	—	—	149·76

the head of the tables.* Col. 1 gives the values of κ, the specific conductivity of the solvent, expressed in gemmho, determined with the Kohlrausch cell; col. 2 gives the value of the concentration; col. 3, the observed equivalent conductivity Λ_c; col. 4, the values of Λ_c calculated from the given values of Λ_0^s and x; col. 5 is the difference between Λ_c obs. and Λ_c calc.; and col. 6 contains the values of Λ_0^n computed for each concentration from the appropriate constants B and n.

Sodium chloride at 25° (M = 58·45).

$\Lambda_0^s = \Lambda_c + 83{\cdot}5\,C^{0{\cdot}5}$. $\Lambda_0^s = 126{\cdot}18$.

$\Lambda_0^n = \Lambda_c + 117{\cdot}4\,C^{0{\cdot}551}$. $\Lambda_0^n = 126{\cdot}18$.

Series.	κ.	$C \times 10^4$.	Λ_c obs.	Λ_c calc.	Diff.	Λ_0^n.
1 (V)	0·819	2·952	124·82	124·74	+0·08	126·15
		9·045	123·67	123·67	0·00	126·14
		12·30	123·29	123·25	+0·04	126·22
First specimen		25·44	121·68	121·97	−0·29	126·05
		48·60	120·10	—	—	126·34
		70·20	118·82	—	—	126·46
		89·96	118·10	—	—	(126·86)
		109·7	117·85	—	—	(127·62)
2 (V)	0·845	1·111	125·30	125·30	0·00	125·92
		5·542	124·21	124·21	0·00	126·09
		11·66	123·29	123·33	−0·04	126·13
Second specimen		23·48	121·81	122·13	−0·32	125·99
		33·46	121·05	—	—	126·13
		42·30	120·54	—	—	126·32
		61·25	119·42	—	—	(126·55)
		79·05	118·40	—	—	(126·56)
3 (V)	0·802	1·193	125·25	125·27	−0·02	126·06
		9·210	123·61	123·65	−0·04	126·11
		18·03	122·33	122·63	−0·30	125·94
First specimen		35·90	120·71	—	—	125·99
		47·74	120·01	—	—	126·19
		61·05	119·30	—	—	(126·86)
		72·41	118·65	—	—	126·42
		96·33	117·99	—	—	(127·09)
4 (S)	0·748	1·424	125·21	125·18	+0·03	126·10
		5·771	124·10	124·17	−0·07	126·03
Second specimen		10·53	123·50	123·47	+0·03	126·19
		24·13	121·90	122·08	−0·18	126·14
		63·22	119·12	—	—	126·33
		80·35	118·53	—	—	(126·76)
5 (S)	0·811	1·404	125·28	125·19	+0·09	126·16
		6·788	124·19	124·00	+0·19	126·30
		16·31	122·80	122·81	−0·01	126·22
		25·82	121·46	121·94	−0·48	125·87
First specimen		36·93	120·68	—	—	126·05
		47·49	120·14	—	—	126·30
		57·94	119·60	—	—	126·48
		71·39	118·92	—	—	(126·71)
		86·38	118·21	—	—	(126·81)

---

* The values in parenthesis were not employed in the calculations.

Potassium iodate at 25° (M = 214·03).

$\Lambda_0^s = \Lambda_c + 100\cdot3\ C^{0\cdot5}$. $\Lambda_0^s = 114\cdot57$.

$\Lambda_0^n = \Lambda_c + 58\cdot7\ C^{0\cdot384}$. $\Lambda_0^n = 115\cdot45$.

Series.	κ.	$C \times 10^4$.	Λ_c obs.	Λ_c calc.	Diff.	Λ_0^n.
1 (S)	0·800	*0·776	114·21	113·29	+0·92	(115·78)
		5·331	112·13	112·23	−0·13	115·39
		9·670	111·36	111·47	−0·11	115·39
		19·91	110·07	110·09	−0·02	115·48
		37·06	108·66	108·46	+0·20	115·53
		54·41	107·43	—	—	115·42
		74·13	106·30	—	—	115·26
		88·84	105·58	—	—	115·18
2 (V)	0·760	1·905	113·20	113·19	+0·01	115·40
		7·448	111·66	111·83	−0·17	115·37
		15·49	110·71	110·62	+0·09	115·62
		27·71	109·49	109·29	+0·20	115·63
		44·61	108·08	—	—	115·45
		63·11	106·91	—	—	115·33
		77·47	105·88	—	—	114·99
		95·81	104·98	—	—	114·90
3 (V)	0·801	*1·054	114·00	113·54	+0·46	(115·75)
		3·188	112·91	112·71	+0·13	115·58
		37·89	108·60	108·40	+0·20	115·52
		48·79	107·75	—	—	115·38
		55·26	107·38	—	—	115·38
		66·66	106·72	—	—	115·32
		92·58	105·31	—	—	115·06

* The minima were not very sharp.

Iodic acid at 25° (M = 175·94).

$\Lambda_0^n = \Lambda_c + 910\cdot3\ C^{0\cdot732}$. $\Lambda_0^n = 389\cdot8$.

1 (V)	0·752	†1·170	373·98	—	—	—
		6·088	383·38	—	—	—
		11·60	382·62	—	—	—
First specimen		19·87	379·93	—	—	389·51
		31·33	376·20	—	—	389·57
		41·96	373·33	—	—	389·89
		60·03	368·46	—	—	389·98
		85·24	361·80	—	—	389·62
2 (S)	0·773	†3·266	382·14	—	—	—
		13·18	382·67	—	—	—
		24·57	378·42	—	—	389·61
Second specimen		44·75	372·05	—	—	389·42
		50·01	371·20	—	—	390·03
		60·94	367·71	—	—	389·48
		84·12	362·32	—	—	389·87
		113·3	355·66	—	—	389·93
3 (V)	0·856	†2·551	381·71	—	—	—
		17·52	381·22	—	—	389·96
		29·97	376·88	—	—	389·83
Second specimen		42·95	373·17	—	—	390·01
		55·12	369·65	—	—	389·87
		70·29	365·92	—	—	390·08
		76·64	364·09	—	—	389·83
		95·74	359·05	—	—	389·85

† After the first addition only there was a gradual decrease in conductivity during the first half hour and then it attained a constant value.

Iodic acid at 18°.

$\Lambda_0^n = \Lambda_c + 384{\cdot}1\ C^{0{\cdot}577}$. $\Lambda_0^n = 351{\cdot}0$.

Series.	κ.	$C \times 10^4$.	Λ_c obs.	Λ_c calc.	Diff.	Λ_0^n.
1 (V)	0·709	†1·281	338·43	—	—	—
		6·829	344·23	—	—	—
		12·19	343·62	—	—	—
First specimen		20·15	341·55	—	—	351·27
		30·90	337·56	—	—	351·28
		44·29	334·19	—	—	351·11
		67·42	329·21	—	—	350·73
		86·33	325·96	—	—	350·77
2 (V)	0·688	†2·395	340·95	—	—	—
		5·844	343·53	—	—	—
		15·17	341·89	—	—	—
Second specimen		25·34	338·88	—	—	351·12
		35·82	335·98	—	—	350·92
		48·13	333·25	—	—	350·97
		65·88	330·01	—	—	351·24
		89·43	325·70	—	—	351·02
3 (S)	0·688	†1·630	338·27	—	—	—
		4·271	343·44	—	—	—
		9·316	343·06	—	—	—
First specimen		21·46	339·59	—	—	350·71
		34·19	336·55	—	—	351·09
		50·06	332·89	—	—	350·91
		66·73	329·27	—	—	350·65
		107·0	322·92	—	—	(349·34)

TABLE II.

Sodium chloride at 18° (Second specimen).

Cell constant $0{\cdot}02781_5$. $\kappa = 0{\cdot}560$.

Λ_c calc. was computed from the formula $\Lambda_c = 109{\cdot}02 - 54{\cdot}24\ C^{0{\cdot}443}$.

$C \times 10^4$	6·198	11·51	21·25	34·00	46·75	68·31	86·97
Λ_c obs.	106·91	106·65	105·45	104·67	103·97	102·95	102·49
Λ_0 calc.	106·96	106·32	105·47	104·65	103·99	103·06	102·39

Potassium iodate at 18°.

Cell constant $0{\cdot}02781_5$. $\kappa = 0{\cdot}471$.

Λ_c calc. was computed from the formula $\Lambda_c = 98{\cdot}54 - 61{\cdot}07\ C^{0{\cdot}460}$.

$C \times 10^4$	5·753	15·38	29·31	63·87	96·70
Λ_c obs.	96·65	95·57	94·33	92·55	90·87
Λ_c calc.	96·57	95·44	94·36	92·59	91·31

TABLE III.

$C \times 10^4$.	KCl.	NaCl.	KIO_3.	HIO_3 (25°).	HIO_3 (18°).
1·0	149·20	125·30	113·60	—	—
5·0	148·25	124·34	112·25	—	—
10·0	147·50	123·48	111·25	—	—
20·0	146·45	122·20	109·98	380·06	340·22
30·0	145·55	121·25	109·10	376·80	337·52
40·0	144·80	120·47	108·40	373·77	335·06
50·0	144·15	119·83	107·70	370·98	332·80
60·0	143·55	119·30	107·05	368·30	330·80
70·0	143·02	118·80	106·48	365·70	328·95
80·0	142·50	118·38	105·94	363·20	327·20
90·0	142·02	118·05	105·44	360·80	325·55
100·0	141·55	117·80	104·95	358·50	323·96

Λ_c *at Round Concentrations.*—The values of the equivalent conductivity at round concentrations are given in Table III. Interpolation was carried out on a Λ_c–C graph drawn with a flexible spline.

The authors' thanks are due to the Council of this College, the Royal Society (to A. I. V.) and the Chemical Society (to G. H. J.) for grants which have helped to defray the very heavy cost of this research.

UNIVERSITY COLLEGE, SOUTHAMPTON. [*Received, May 27th,* 1931.]