128. *The Conductivity of Univalent Electrolytes in Water.*

By Robert A. Robinson and Cecil W. Davies.

Some years ago an empirical equation was put forward (Davies, *Trans. Faraday Soc.*, 1927, **23**, 351) which represented with fair accuracy, up to a concentration of at least $1 \cdot 0N$, the conductivity figures of Kohlrausch for a number of completely dissociated uni-univalent salts at 18°. The value of this equation lay in the fact that it was free from any arbitrary constant dependent on the nature of the salt, so that it could be utilised as a standard of behaviour to which all normal completely dissociated salts could be expected to conform. The basis of this equation has not been regarded with much confidence by some later writers on the subject, and it therefore seemed of interest to apply to it a further test rendered possible by the accurate measurements of Shedlovsky (*J. Amer. Chem. Soc.*, 1932, **54**, 1411) on lithium, sodium, potassium, and hydrogen chlorides at 25°.

Before discussing the data at higher concentrations, it will be necessary to consider those for the most dilute solutions. In a previous paper (Davies, this vol., p. 432) it has been shown that the equation proposed by Shedlovsky for potassium chloride does not agree as closely as it should with the measurements for the most dilute solutions, and leads to a Λ_0 value that is too low by $0 \cdot 04\%$. The same is true for sodium chloride. The ten measurements made by Shedlovsky * below $0 \cdot 001N$ agree somewhat better with the equation $\Lambda = 126 \cdot 50 - 88 \cdot 56\sqrt{C} + 40C$, than with the Shedlovsky equation, which gives $\Lambda_0 = 126 \cdot 46$. The results for dilute hydrochloric acid solutions are more erratic, but appear to lead to $\Lambda_0 = 426 \cdot 25$ or $426 \cdot 3$ rather than to the value $426 \cdot 16$ derived by Shedlovsky, and in the same way the value $\Lambda_0 = 115 \cdot 11$ for lithium chloride is preferred to Shedlovsky's value $115 \cdot 03$. These values are used in the following calculations.

The empirical equation previously proposed was based on the discovery that at concentrations too high for Onsager's limiting equation $\Lambda_0 - \Lambda = b\sqrt{C}$ to be obeyed, the conductivity decrease was still proportional to the factor b, the Onsager slope. The dependence of the conductivity on concentration was complex, and the relation was used in the form $\Lambda_0 - \Lambda = b \cdot f(C)$, where the value of $f(C)$ at any concentration had to be

Table I.

C	0·001	0·002	0·005	0·01	0·02	0·05	0·07	0·10
$f(C)$	0·03122	0·04382	0·06683	0·09112	0·12254	0·17531	0·19708	0·22350
$(\sqrt{C} - C + 0 \cdot 001)$	0·03162	0·04372	0·06671	0·09100	0·12242	0·17461	0·19558	0·21723

Lithium chloride : $\Lambda_0 = 115 \cdot 11$; $b = 85 \cdot 95$.

Λ, obs.	112·46	111·35	109·36	107·31	104·55	100·12	98·14	95·86
Λ, calc.	112·43	111·34	109·36	107·28	104·58	100·04	98·17	95·89
Δ	+0·03	+0·01	±0	+0·03	−0·03	+0·08	−0·03	−0·03

Sodium chloride : $\Lambda_0 = 126 \cdot 50$; $b = 88 \cdot 53$.

Λ, obs.	123·76	122·71	120·62	118·47	115·69	110·92	—	106·72
Λ, calc.	123·74	122·62	120·58	118·43	115·66	110·99	—	106·72
Δ	+0·02	+0·09	+0·04	+0·04	+0·03	−0·07	—	±0

Potassium chloride : $\Lambda_0 = 149 \cdot 92$; $b = 93 \cdot 85$.

Λ, obs.	146·97	145·83	143·68	141·36	138·38	133·37	—	128·94
Λ, calc.	146·99	145·81	143·65	141·37	138·42	133·47	—	128·94
Δ	−0·02	+0·02	+0·03	−0·01	−0·04	−0·10	—	±0

Hydrochloric acid : $\Lambda_0 = 426 \cdot 27$; $b = 156 \cdot 7$.

Λ, obs.	421·36	419·39	415·80	412·00	407·23	399·08	395·44	391·31
Λ, calc.	421·38	419·40	415·79	411·99	407·07	398·80	395·38	391·24
Δ	−0·02	−0·01	+0·01	+0·01	+0·16	+0·28	+0·06	+0·07

evaluated from the data for one or more salts. The equation is now applied to Shedlovsky's figures in Table I ; this shows the values of $f(C)$ which best fit the data, and the subsequent

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* All Shedlovsky's values quoted in this paper have been increased by $0 \cdot 028\%$ in order to convert them to the new Jones and Bradshaw standard (cf. Shedlovsky and Brown, *J. Amer. Chem. Soc.*, 1934, **56**, 1069).

rows of figures show, for each of the chlorides investigated by Shedlovsky, the degree of agreement between the conductivity calculated from the Λ_0, b, and $f(C)$ values shown, and the observed conductivity, taken from a curve of the experimental results in the case of lithium chloride, and from Table 6 of Shedlovsky's paper for the other three electrolytes. The agreement is very satisfactory; it is as good, in fact, as the agreement between the observed values and the values calculated from Shedlovsky's equations, although these contain an additional arbitrary constant that varies from salt to salt. The empirical equation can therefore be applied with some confidence to any univalent electrolyte at 25°, using the $f(C)$ values listed in Table I. For intermediate values of the concentration, $f(C)$ can be found by interpolation; but between $0.002N$ and $0.02N$, $f(C)$ is satisfactorily represented by $f(C) = \sqrt{C} - (C - 0.001)$, as is shown in the table.

Shedlovsky has also examined potassium nitrate, a salt which does not show a normal conductivity curve, and for which a dissociation constant $K = 1.3$ has been derived from the conductivities at 18°. For this salt the figures at the lower concentrations, when plotted by the method of Onsager (*Physikal. Z.*, 1927, **28**, 277), give $\Lambda_0 = 144.90$. The conductivities at the higher concentrations are uniformly lower than the values calculated by the empirical equation just discussed, and if the discrepancy is attributed to incomplete dissociation, and the dissociation constant calculated in the usual way (Davies, "Conductivity of Solutions," 1933, p. 109), the results shown below are obtained :

Potassium nitrate : $\Lambda_0 = 144.90$.

C	0·01	0·02	0·05	0·07	0·10
Λ	135·82	132·41	126·31	123·56	120·40
Λ_x	136·46	133·56	128·79	126·78	124·38
α	0·9954	0·9914	0·9808	0·9746	0·9680
K	1·72	1·68	1·60	1·59	1·66

Here, C represents the equivalent concentration and Λ the observed conductivity; Λ_x, found by successive approximations, is the conductivity that a solution of this ionic concentration should have according to our equation, α is the degree of dissociation, and K, the dissociation constant, is $f^2\alpha^2C/(1 - \alpha)$, where f, the ion-activity coefficient, has been taken from the data of Robinson (*J. Amer. Chem. Soc.*, 1935, **57**, 1165). The values of K are satisfactorily constant.

The results of applying the same treatment to silver nitrate are as follows :
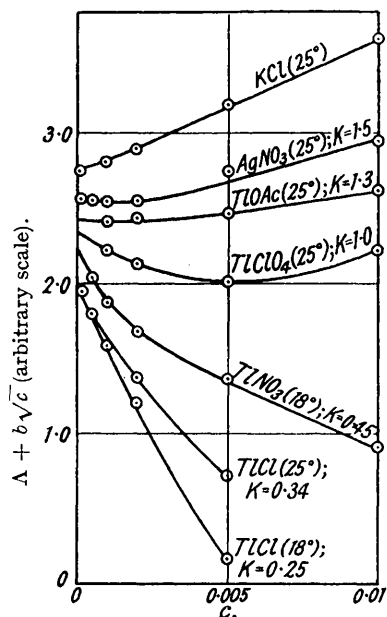
Silver nitrate : $\Lambda_0 = 133.42$.

C	0·01	0·02	0·05	0·10
Λ	124·76	121·41	115·24	109·14
Λ_x	125·22	122·41	117·80	113·56
α	0·9963	0·9918	0·9783	0·9611
K	2·14	1·76	1·48	1·45

The last two values, corresponding to solutions in which more than 1% of the salt is undissociated, are much more reliable than the first two, but the variations of K are not covered in this case by the probable error of the conductivity measurements, and it is possible that the treatment of this salt is complicated by the presence of complex ions, since the transference numbers reported by McInnes, Shedlovsky, and Longsworth (*Chem. Rev.*, 1933, **13**, 29) are also abnormal. The value found from the data at 18° was $K = 1.20$, there being no evidence of a change of K with changing concentration.

Conductivity Measurements with Thallous Salts.—Other interesting cases in which anomalous conductivities find a reasonable explanation in incomplete dissociation occur with thallous salts. Davies has already shown that this is true of the chloride and nitrate at 18°, and Robinson (*J. Amer. Chem. Soc.*, 1937, **59**, 84) has suggested that the very low activity and osmotic coefficients of thallous perchlorate and acetate at 25° may also be due to incomplete dissociation. We have now measured the conductivities of thallous perchlorate and acetate at 25° up to a concentration of $0.01N$. The salts were prepared from the purified carbonate, and recrystallised three times, conductivity water being used for the last recrystallisation. The apparatus and methods employed in the conductivity measure-

ments have been described in a previous paper (Davies, this vol., p. 432). Two runs were made with each salt, and the experimental figures are given in Table II. For thallous perchlorate the normal solvent correction has been applied, but for thallous acetate a combined solvent and hydrolysis correction was necessary, and this has been calculated by a method previously outlined (Davies, *Trans. Faraday Soc.*, 1932, **28**, 607), it being assumed that a small part (0·07 gemmho) of the solvent's conductivity was attributable to saline impurities and that the residue (0·47 gemmho for Run 3, and 0·37 gemmho for Run 4) was due to carbon dioxide.

$(\Lambda + b\sqrt{c})$ calculated from Onsager's equation for various electrolytes.

TABLE II.

Conductivities of Thallous Perchlorate and Acetate at 25°.

Thallous perchlorate ($M = 303\cdot85$).

Run No.	$C \times 10^4$.	Λ.	Run No.	$C \times 10^4$.	Λ.
1	1·7372	141·36	1	37·436	136·71
2	4·0891	141·16	2	58·103	135·45
1	9·823	139·71	1	77·535	134·32
1	18·999	138·45	2	98·002	133·42
2	26·049	137·76			

Thallous acetate ($M = 263\cdot41$).

Run No.	$C \times 10^4$.	Λ.	Run No.	$C \times 10^4$.	Λ.
4	4·3160	113·84	4	48·560	109·73
3	6·4852	113·42	3	58·726	109·10
4	11·584	112·78	4	78·072	108·16
3	21·956	111·62	3	93·088	107·51
4	28·086	110·10	4	147·34	105·24
3	40·553	110·21			

From a graph of these results we have read off conductivities at round concentrations and thence calculated $(\Lambda + b\sqrt{c})$ from Onsager's equation. These values of $(\Lambda + b\sqrt{c})$ are plotted against the concentration in the figure, which also shows similar plots for a typical, completely dissociated salt, potassium chloride, and an incompletely dissociated electrolyte, silver nitrate. For comparison, data for thallous chloride and nitrate are also included, the values of Kohlrausch and Steinwehr (*Sitz. Berl. Akad.*, 1902, 581) and of Bray and Winninghof (*J. Amer. Chem. Soc.*, 1911, **33**, 1663) being used. This method of plotting conductivity results not only makes it possible to decide whether a salt is completely dissociated or not, but also gives an approximate estimate of the degree of dissociation and the dissociation constant.

TABLE III.

	Thallous chloride at 18°.			Thallous chloride at 25°.			
C	0·002	0·005	0·01	0·002	0·005	0·01	0·01607
a	0·9928	0·9830	0·9698	0·9952	0·9886	0·9757	0·9642
K	0·25	0·24	0·25	0·37	0·36	0·31	0·31

	Thallous nitrate at 18°.			Thallous perchlorate at 25°.			Thallous acetate at 25°.		
C	0·002	0·005	0·01	0·002	0·005	0·01	0·002	0·005	0·01
a	0·9955	0·9912	0·9843	0·9982	0·9958	0·9931	0·9985	0·9978	0·9941
K	0·39	0·47	0·48	1·00	1·00	1·14	1·20	1·32	1·33

The conductivity values at infinite dilution are 115·63 for thallous acetate and 142·65 for the perchlorate. Taking $\Lambda_0(KCl) = 149\cdot92$, $\Lambda_0(Cl) = 76\cdot39$, and $\Lambda_0(NaCl) = 126\cdot50$,

we have $\Lambda_0(\text{Na}) = 50\cdot11$, and if from MacInnes and Shedlovsky's results (*J. Amer. Chem. Soc.*, 1932, **54**, 1429) we use $\Lambda_0(\text{NaOAc}) = 91\cdot03$, then $\Lambda_0(\text{OAc}) = 40\cdot92$, $\Lambda_0(\text{Tl}) = 74\cdot71$, and $\Lambda_0(\text{ClO}_4) = 67\cdot94$.

Table III gives the degree of dissociation and dissociation constant for some thallous salts, calculated in the same way as for potassium and silver nitrates.

SUMMARY.

It is shown that the change of conductivity with concentration in the case of lithium, sodium, potassium, and hydrogen chlorides at 25° can be expressed within the experimental error by : (1) Onsager's limiting equation up to $0\cdot001N$, (2) the equation $\Lambda = \Lambda_0 - b(\sqrt{C} - C + 0\cdot001)$ between $0\cdot002$ and $0\cdot02N$, and (3) the equation $\Lambda = \Lambda_0 - b \cdot f(C)$ above $0\cdot02N$, $f(C)$ being an empirical function of the concentration and the same for all electrolytes.

The data for potassium and silver nitrates are anomalous but can be accounted for by assuming incomplete dissociation, K being $1\cdot6$ and $1\cdot5$ respectively at 25° compared with $1\cdot3$ and $1\cdot2$ at 18°.

The conductivities of solutions of thallous perchlorate and acetate have been measured at 25° up to a concentration of $0\cdot01N$, and the dissociation constants of a number of thallous salts have been calculated.

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