CCCXXVIII.—*The Mobility of the Perchlorate Ion in Methyl Alcohol.*

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The perchlorate ion is of special interest in methyl-alcoholic solutions both on account of its exceptionally high mobility and of its value for finding the mobilities of bivalent metals, since it has been shown by F. A. Philbrick and K. B. Ross in this laboratory that the perchlorates of a number of bivalent metals are strong electrolytes in this solvent.

Frazer and Hartley (*Proc. Roy. Soc.*, 1925, **109**, *A*, 351) assigned a value of 69·4 to the mobility of the perchlorate ion at 25° in methyl alcohol based on Philbrick's measurements of the conductivity of sodium perchlorate. Further measurements have now been made of the conductivities of solutions of the perchlorates of lithium, sodium, and silver at 25° over a range of concentration 0·0001*N* to 0·002*N* with a view to getting a more accurate value for the mobility of the perchlorate ion.

Methyl alcohol was purified by the method described by Hartley and Raikes (J., 1925, **127**, 524) and its dryness was tested by measuring its viscosity. The specific conductivity of the sample used in each series of measurements is stated in the tables of results.

Lithium perchlorate was prepared by heating Merck's lithium nitrate with perchloric acid, and recrystallising the salt twice from water. It was dried to constant weight by heating at 300° in a Richards bottling apparatus in which the salt could be heated and bottled in a current of dried air.

Sodium perchlorate was prepared by dissolving sodium carbonate in perchloric acid. The anhydrous salt was recrystallised from water above 50° and centrifuged. It was dried to constant weight in an air-bath at 250—270°.

Silver perchlorate was prepared from pure assay silver by the method recommended by Hill (*J. Amer. Chem. Soc.*, 1921, **43**, 254). The nitrate was first made and converted into the oxide by the addition of caustic soda solution. Slight excess of the oxide was then heated with 60% perchloric acid solution, and the solution of silver perchlorate filtered and evaporated until crystals began to form. The salt was then recrystallised from benzene and dried to constant weight for 12 hours at 120°.

The resistance measurements were carried out as described by Frazer and Hartley (*loc. cit.*) in a conductivity cell designed by Barrett and Hartley (J., 1913, **103**, 789). About 250 g. of alcohol were placed in the cell, and a series of additions of salt solution were made from a weight burette, the resistance being measured after each addition. The cell constant was determined by measuring the resistance of a series of aqueous solutions of potassium chloride at 18° as described by Frazer and Hartley (*loc. cit.*). The means of two series of determinations were $0{\cdot}03948_2$ and $0{\cdot}03942_5$, giving a final mean of $0{\cdot}03945_4$ in good agreement with a previous mean value of $0{\cdot}03945_6$.

TABLE I.

	κ.	$c \times 10^4$.	$100\sqrt{c}$.	Λ_c obs.	Λ_c calc.	Diff.
Lithium perchlorate : $\Lambda_0 = \Lambda_c + 258\sqrt{c}$; $\Lambda_0 = 110{\cdot}50$.						
Series *a*	0·105	1·2863	1·134	107·55	107·57	−0·02
		2·1939	1·481	106·67	106·68	−0·01
		3·3276	1·824	105·76	105·79	−0·03
		4·9352	2·222	104·71	104·77	−0·06
		7·8521	2·802	103·22	103·27	−0·05
Series *b*	0·086	1·1676	1·080	107·80	107·71	+0·09
		2·1926	1·481	106·73	106·68	+0·05
		3·7707	1·942	105·52	105·49	+0·03
		5·6449	2·376	104·36	104·37	−0·01
		9·7881	3·129	102·40	102·43	−0·03
Sodium perchlorate : $\Lambda_0 = \Lambda_c + 290\sqrt{c}$; $\Lambda_0 = 116{\cdot}50$.						
Series *a*	0·138	1·4627	1·209	112·97	112·99	−0·02
		2·4318	1·559	112·02	111·98	+0·04
		3·7478	1·934	111·83	110·89	−0·06
		5·7517	2·398	109·54	109·54	±0·00
		9·3164	3·052	107·71	107·65	+0·06
Series *b*	0·061	1·1266	1·061	113·40	113·42	−0·02
		2·2003	1·483	112·16	112·20	−0·04
		3·5368	1·881	111·01	111·05	−0·04
		5·7591	2·400	109·49	109·54	−0·05
		9·1420	3·024	107·78	107·73	+0·05
Silver perchlorate : $\Lambda_0 = \Lambda_c + 277\sqrt{c}$; $\Lambda_0 = 121{\cdot}15$.						
Series *a*	0·262	1·5627	1·250	117·03	117·69	−0·65
		2·7317	1·653	116·35	116·57	−0·22
		4·2863	2·070	115·36	115·42	−0·06
		6·7881	2·605	113·97	113·93	+0·04
		9·5985	3·098	112·63	112·57	+0·06
		14·1630	3·763	110·84	110·73	+0·07
Series *b*	0·146	1·3590	1·166	117·46	117·92	−0·46
		2·5405	1·594	116·55	116·73	−0·18
		4·2188	2·054	115·42	115·46	−0·04
		6·1936	2·489	114·28	114·26	+0·02
		9·5848	3·096	112·63	112·57	+0·06
		13·8941	3·728	110·85	110·82	+0·03
Series *c*	0·161	1·3204	1·149	117·73	117·97	−0·24
		2·3941	1·547	116·89	116·86	+0·03
		3·6300	1·905	115·94	115·87	+0·07
		5·0585	2·249	115·03	114·92	+0·11
		7·3469	2·710	113·73	113·64	+0·11
Series *d* (by F. A. Philbrick)	0·084	1·3968	1·182	117·85	117·88	−0·03
		2·7815	1·668	116·58	116·53	+0·05
		5·1613	2·272	114·82	114·86	−0·04
		9·0148	3·003	112·82	112·83	−0·01
		13·8284	3·719	110·84	110·85	−0·01

The experimental results are given in Table I. With each substance are given the mean values found graphically for Λ_0, its conductivity at infinite dilution, and for x, the coefficient in the Kohlrausch equation $\Lambda_c = \Lambda_0 - x\sqrt{c}$. Col. 1 gives the specific conductivity (κ) of the solvent in each series, the value of which was subtracted from the conductivity of each solution, col. 2 the concentration in g.-equivs. per l. × 10^4, col. 3 the value of $100\sqrt{c}$, cols. 4 and 5 respectively the values of Λ_c observed and of Λ_c calculated from the mean values of Λ_0 and x, and col. 6 gives the difference Λ_c obs. $-$ Λ_c calc.

Discussion of Results.

The differences in the last column of the tables show that, with the exception of the values of the more dilute solutions of silver perchlorate, the results are in good accordance with the equation $\Lambda_c = \Lambda_0 - x\sqrt{c}$. In the case of silver perchlorate the values of the equivalent conductivity obtained for solutions of concentration less than $N/3000$ were considerably lower than those calculated from the equation. The degree of divergence was different for different series, being greatest with solvent of highest conductivity. It appears, therefore, that the discrepancy is connected with the purity of the solvent and similar behaviour has been noticed by Frazer and Hartley in the case of silver nitrate. Moreover, the results of Getman and Gibbons for silver nitrate show a maximum in the region of $0{\cdot}001N$; these authors give no details of the purity of their solvent, but owing to their method of purification its conductivity was probably high. Silver salts thus appear to be very sensitive to solvent impurity. Constant stirring was necessary to obtain consistent readings with silver solutions, otherwise the resistance changed continuously.

Onsager has modified the Debye–Hückel theory of the variation of equivalent conductivity with concentration so as to take into account the Brownian motion of the ions, and has derived the following expression for x in the equation $\Lambda_c = \Lambda_0 - x\sqrt{c}$ for a uni-univalent electrolyte in any solvent :

$$x = \left[\frac{5{\cdot}78 \times 10^5}{(DT)^{3/2}}\Lambda_0 + \frac{58{\cdot}0}{(DT)^{1/2}\eta}\right]\sqrt{2}$$

which for methyl alcohol at 25° (D, the dielectric constant $= 30{\cdot}3$; η, the viscosity $= 0{\cdot}00545$) reduces to

$$x = 0{\cdot}957\,\Lambda_0 + 158{\cdot}1.$$

The observed and the calculated values of x for the salts examined are given in Table II, and it will be seen that in each case there is good agreement with the theoretical value.

TABLE II.

	Λ_0.	$l_{0ClO_4^-}$.	x, obs.	x, calc.
$LiClO_4$	110·50	70·90	258	264
$NaClO_4$	116·50	70·80	290	270
$AgClO_4$	121·15	68·95	277	274

Col. 3 of Table II gives the values for the mobility of the perchlorate ion obtained by subtracting from the values of Λ_0 the mobilities of the respective kations found by Frazer and Hartley. The values from the first two salts are in good agreement, and the low value obtained from silver perchlorate suggests that the mobility of the silver ion (52·2) given by Frazer and Hartley is too high. It was derived from their measurements with silver nitrate, the conductivity of which diminished with concentration to an abnormal extent, x obs. being 451 and x calc. 266. These values show that silver nitrate is associated in dilute solutions and that the value for Λ_0 found by extrapolation may be too high owing to the steepness of the curve. As silver perchlorate behaves normally, it probably yields a more correct value for Λ_0, and by subtracting the mean value for the perchlorate mobility given by the lithium and sodium salts, *viz.*, 70·85, we obtain a more likely value of 50·3 for the mobility of the silver ion.

It is remarkable that the perchlorate ion should have a mobility of 70·8 when the mobility of the simple chloride ion is only 51·3. The perchlorate ion is actually faster than any monatomic ion in methyl alcohol, the next fastest being cæsium with a mobility of 62·3. In water the velocities of the chlorine and perchlorate ions are almost identical. In the crystalline state the chlorine ion behaves as a sphere of diameter 3·44 Å., while the perchlorate ion occupies a considerably larger volume. According to Zachariasen (*Z. Krist.*, 1930, **73**, 141) the ClO_4^- group is tetrahedral, the distance from chlorine to oxygen being 1·56 Å., and the mean distance from oxygen to oxygen being 2·51 Å. The reason for the abnormal mobility of the more complex ion in solution may be that it is less solvated in consequence of the weaker electrical field in its neighbourhood, due to its larger size.

Summary.

1. The conductivities of solutions of the perchlorates of lithium, sodium, and silver have been measured in methyl alcohol at 25° at concentrations varying from 0·0001*N* to 0·002*N*.

2. The variation of conductivity with concentration is in each case in close agreement with the Debye–Hückel–Onsager theory.

3. The mobility of the perchlorate ion is found to be 70·85, and that of the silver ion 50·3, in methyl alcohol at 25°.

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[*Received, August* 15*th*, 1930.]