[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF INDIANA UNIVERSITY]

The Electrical Conductance of Aqueous Solutions. II. Lithium, Sodium and Potassium Perchlorates at 25°

BY JAMES HOMER JONES

The measurements of Davies and Robinson[1] on the electrical conductance of dilute solutions of thallous perchlorate, and those of Van Rysselberghe[2] on magnesium perchlorate are apparently the only ones made on metallic perchlorates in water at 25° since 1926. Some of the earlier measurements at 25° on the perchlorates here studied are listed in the footnotes.[3]

Since the earlier measurements disagree considerably, the electrical conductances of lithium, sodium and potassium perchlorates have been redetermined.

The limiting conductance of the perchlorate ion in water at 25° was assigned a value of 67.94 by Davies[1] based on the conductance of thallous perchlorate. Lange[4] in his review assigns a conductance of 67 to the perchlorate ion which is the same value listed by Davies in his book on conductance.[5]

Experimental

Apparatus.—The apparatus used has been described in an earlier paper.[6] The cell constants of the conductance cells were redetermined and found to be substantially unchanged. The platinization of the electrodes was checked by measuring the resistances of the cells at 500, 1000 and 2000 cycles per second and found to be adequate. The ice-point of the platinum resistance thermometer was checked periodically. The individual dial resistors for the hundred-ohm dial and the thousand-ohm dial were checked against standard resistors calibrated by the Bureau of Standards. The values for the one ohm dial and 10 ohm dial were accepted at face value. The values of the resistances measured were kept above 1000 ohms whenever possible. The temperature control approximates ±0.001°.

Purification of Materials.—Best grade potassium perchlorate was recrystallized twice from conductivity water, dried at 250° and stored in a vacuum desiccator. Anhydrous sodium perchlorate was recrystallized twice from butanol, washed thoroughly with dry ether and then dried at 250° and stored. The lithium perchlorate was made from pure lithium carbonate and perchloric acid. The lithium carbonate was purified by solution in hydrochloric acid and precipitation with resublimed ammonium carbonate and ammonium hydroxide. The solution of lithium perchlorate was evaporated until it solidified on cooling and was then fused in platinum. Each sample was freshly fused in a platinum boat at 300-350° before using.

Density of the Solutions.—The densities of several solutions of each of the salts were determined at 25°. The data may be represented within 0.01% by means of the equations

$LiClO_4$ $0.9971 + 0.0623m$ = density
$NaClO_4$ $0.9971 + 0.0768m$ = density
$KClO_4$ $0.9971 + 0.0863m$ = density

where m refers to the concentration expressed as moles per 1000 g. of solution. No recorded values were found for comparison.

Data

All solutions were prepared either directly by weighing the salt and the water, or by weight dilution. All weights were corrected to vacuum. The cell constants were determined using the standards of Jones and Prendergast.[7]

The observed values for the conductances of solutions of various concentrations are given in Table I where c is the molar concentration and Λ is the equivalent conductance.

TABLE I

EQUIVALENT CONDUCTANCES OF SOLUTIONS AT 25°

$LiClO_4$		$NaClO_4$		$KClO_4$	
c	Λ	c	Λ	c	Λ
0.10544	88.17	0.099801	98.63	0.10596	114.90
.090352	89.08	.076764	100.00	.083130	117.18
.083170	89.59	.053993	101.99	.075068	118.90
.064896	90.98	.038510	103.80	.053458	121.10
.049409	92.43	.031954	104.73	.029702	125.35
.034482	93.95	.020353	106.90	.029163	125.59
.020391	96.12	.012634	108.76	.023838	126.95
.017555	96.60	.0090099	109.96	.018222	128.40
.011891	98.06	.0048058	111.86	.014315	129.70
.0050844	100.51	.0041725	112.14	.010131	131.40
.0044629	100.85	.0027320	113.20	.009089	131.88
.0020410	102.41	.0013613	114.38	.0087067	132.06
.0009674	103.54	.0007151	115.30	.0077881	132.54
.0006777	103.91			.0064104	133.28
				.0040351	134.82
				.0031150	135.58
				.0025208	136.08
				.0015280	137.22
				.0007355	138.26
				.00051512	138.74

Discussion

The limiting conductances of these salts were determined first by the Shedlovsky[8] relation that plots of

$$\Lambda_0' = \frac{\Lambda + \beta\sqrt{c}}{1 - \alpha\sqrt{c}} \ vs.\ c$$

are usually straight lines for strong uni-univalent electrolytes up to concentrations of about 0.1 molar. Table II summarizes the observed and calculated values for Λ at rounded concentrations.

Figure 1 shows the plots of the Shedlovsky function.

It will be noted that potassium perchlorate does not behave in the manner predicted by the Shedlovsky equation. The much lower slope and the

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(1) C. W. Davies and R. A. Robinson, *J. Chem. Soc.*, 574 (1937).

(2) Pierre Van Rysselberghe and J. M. Magee, THIS JOURNAL, **65**, 737 (1943).

(3) (a) Harry C. Jones, Carnegie Institute Bulletin No. 170 (1912); (b) Noyes, Boggs, Farrell and Stewart, THIS JOURNAL, **33**, 1654 (1911); (c) Ostwald, "Lehrbuch der allgemeinen Chemie," 1891-1905.

(4) Jörn Lange, *Z. physik. Chem.*, **A188**, 284-315 (1941).

(5) C. W. Davies, "The Conductivity of Solutions," John Wiley and Sons, Inc., New York, N. Y., 1933, p. 208.

(6) J. H. Jones, THIS JOURNAL, **66**, 1115 (1944).

(7) Grinnell Jones and M. J. Prendergast, *ibid.*, **59**, 731 (1937).

(8) T. Shedlovsky, *ibid.*, **54**, 1405 (1932).

TABLE II

c	$LiClO_4$ obs.	$LiClO_4$ calcd.	$NaClO_4$ obs.	$NaClO_4$ calcd.	$KClO_4$ obs.	$KClO_4$ calcd.
0.0005	104.18	104.14	115.64	115.58	138.76	137.99
.001	103.44	103.42	114.87	114.82	137.87	137.17
.002	102.46	102.44	113.80	113.77	136.62	136.00
.005	100.57	100.55	111.75	111.77	134.16	133.74
.010	98.61	98.61	109.59	109.65	131.46	130.95
.020	96.18	96.19	106.96	106.94	127.92	127.90
.050	92.20	92.38	102.40	102.39	121.62	121.66
.070	90.52	90.96	100.52	100.49	118.79	118.77
.100	88.56	....	98.43	98.49	115.20	115.25
	$\Lambda_0 = 105.98$		$\Lambda_0 = 117.48$		$\Lambda_0 = 140.04$	
	$A = 84.52$		$A = 87.22$		$A = 92.57$	
	$B = 112.0$		$B = 92.6$		$B = 49.0$	

$$\Lambda = \Lambda_0 - A\sqrt{c} + Bc(1 - 0.2294\sqrt{c})$$

deviation upward of the curve in dilute solutions have been observed in a good many other potassium salts such as potassium nitrate, potassium bromate and potassium chlorate. Even potassium chloride shows a slight upward deviation in dilute solutions from the predicted straight line. Two checks were made to insure that the measured conductances were correct. First, a new sample of potassium perchlorate was obtained and the conductances of dilute solutions were redetermined with good checks. Secondly, two solutions of sodium chloride (0.05*m* and 0.01*m*) were prepared and their equivalent conductances determined. These checked the equivalent conductances reported by Shedlovsky[9] to within one-tenth of a conductance unit.

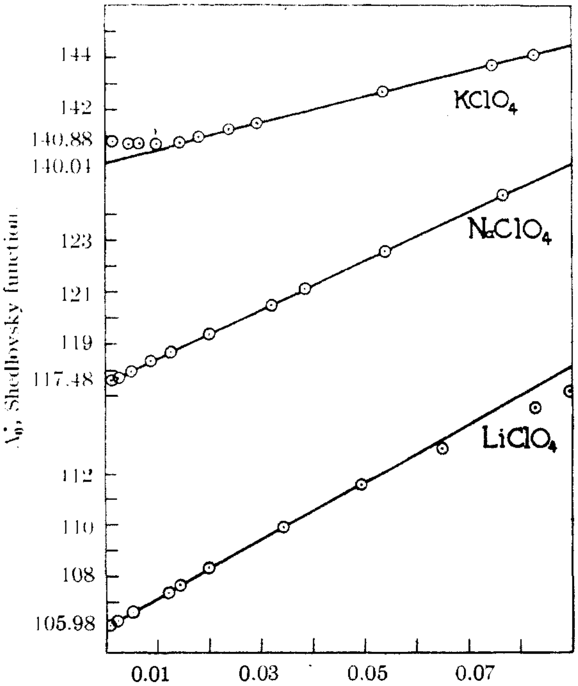

Fig. 1.—Shedlovsky function to evaluate the limiting conductance.

The behavior of potassium perchlorate was not unexpected since Scatchard,[10,11] Prentiss, and P. T. Jones had found that the freezing points of potassium perchlorate solutions were abnormal, and that the j-values became even more positive than those predicted by the Debye–Hückel limiting law. Among the other salts Scatchard, Prentiss and Jones studied were potassium chlorate and nitrate although the j-values of these salts were always above the limiting law.

The Shedlovsky plot for potassium perchlorate can be extrapolated satisfactorily to infinite dilution even though it is not a straight line. The Λ_0 value so obtained is 140.88. Lithium and sodium perchlorates behave normally, and the extrapolated straight line yields values for Λ_0 of 105.98 and 117.48, respectively.

The limiting conductances were also obtained by extrapolation on the Onsager Equation, *i. e.*, Λ *vs.* $\sqrt{c}$ for solution more dilute than 0.005 molar. A plot of this function is given in Fig. 2.

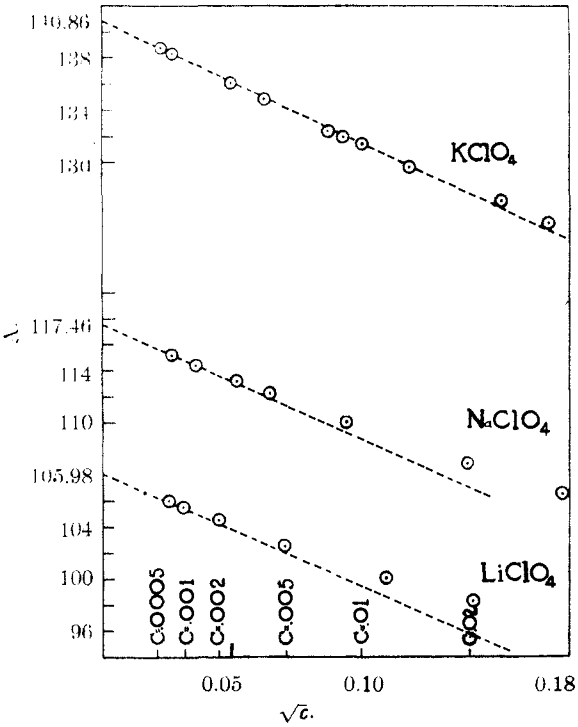

Fig. 2.—Equivalent conductance *vs.* $\sqrt{c}$; dotted lines are limiting slope.

By application of the method of least squares, the following values of Λ_0 were obtained

Salt	Λ_0	Slope
Potassium perchlorate	140.90	−95.57
Sodium perchlorate	117.43	−81.13
Lithium perchlorate	105.83	−74.80

The value obtained for lithium perchlorate is

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(9) T. Shedlovsky, THIS JOURNAL, **54**, 1414 (1932).

(10) G. Scatchard, S. S. Prentiss and P. T. Jones, *ibid.*, **56**, 805 (1934).

(11) *Ibid.*, **54**, 2690 (1932).

low because the large scale plot of Λ *vs.* $\sqrt{c}$ shows detectable curvature over the range used.

When electrolytes behave as potassium perchlorate does, Davies[12] has shown that it is possible to evaluate the limiting conductance by assigning finite equilibrium constants to the salt, and finding the value of Λ_0 which yields the most consistent values for the equilibrium constants at various low concentrations. Using potassium chloride as the reference curve for normal uni-univalent electrolytes; the conductance values of Shedlovsky[9] for potassium chloride; and the activity coefficients of Scatchard[10] for potassium perchlorate; the data in Table III were obtained. The limiting conductance that yielded the most consistent values of K was 140.83.

TABLE III

c	$\gamma_{\pm}$	KCl $\Lambda_{\text{obs.}} - \Lambda_{\text{L.L.}}$	KClO$_4$ $\Lambda_{\text{obs.}} - \Lambda_{\text{L.L.}}$	Δ	K
0.001	0.965	0.10	−0.03	0.13	1.03
.002	.951	.20	− .08	.28	.91
.005	.923	.51	− .12	.63	.91
.010	.893	.96	− .10	1.06	.99
.020	.853	1.90	+ .08	1.82	1.02

In Table III, Δ is the "conductance deficiency" of potassium perchlorate and $K = (\gamma\pm)^2c/(1 - \alpha)$ where $1 - \alpha$ is the degree of association. The limiting conductance of potassium perchlorate so evaluated agrees well with that evaluated by the other two methods; the three values for the limiting conductance being 140.90, 140.88 and 140.83. The last two values should be somewhat more accurate than the first which was obtained by extrapolation of Λ *vs.* $\sqrt{c}$. The most probable value of the limiting conductance is 140.86 ± 0.06.

The best values for the limiting conductances of sodium perchlorate and lithium perchlorate are 117.46 and 105.98 with about the same probable error as for potassium perchlorate.

Mobility of the Perchlorate Ion.—Using the limiting conductances obtained in this paper and the known conductances of the cations (K^+ = 73.52, Na^+ = 50.11, and Li^+ = 38.69), the limiting conductance of the perchlorate ion would be 67.34, 67.35, and 67.27, respectively. The average of these 67.32 with an estimated error of ±0.06 conductance unit is assigned as the limiting conductance of the perchlorate ion. This value is approximately 0.6 of a unit lower than that found by Davies.[1]

Summary

The electrical conductances of aqueous solutions of sodium, lithium and potassium perchlorates have been determined at 25° over the concentration range of 0.0005–0.1 molar. The limiting equivalent conductances have been evaluated by several methods.

The densities of the solutions of the three salts have been determined over the same concentration range.

The limiting conductance of the perchlorate ion has been calculated using the conductance data of this investigation and the known conductances of the cations.

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[12] C. W. Davies, *Trans. Faraday Soc.*, **23**, 351 (1927); *J. Chem. Soc.*, 2093 (1938); *ibid.*, 349 (1939).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE COLLEGE OF WASHINGTON]

The System Ammonium Selenate–Cupric Selenate–Water at 25°

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As a part of the more extensive problem of determining solubility relations in ternary systems of selenates, the system $(NH_4)_2SeO_4$–$CuSeO_4$–H_2O has been investigated at 25°. As mentioned in a previous communication,[1] relatively few selenate systems have been studied. From the meager data available on mutual solubility of two selenate salts in water, it appears that these systems follow closely the corresponding sulfate systems, although tendency toward compound formation appears to be less pronounced than in systems of sulfates.

Although the double salt, $(NH_4)_2Cu(SeO_4)_2 \cdot 6H_2O$ has been prepared by several investigators, no studies of mutual solubilities of the component salts have been reported.

Experimental

Procedures followed in solubility determinations were similar to those generally employed in investigations of this nature. Various mixtures of the component salts and water were made up such that considerable solid phase would be present at equilibrium and the mixtures agitated in an electrically controlled thermostat maintained at 25 ± 0.05° until equilibrium had been attained. The method of making up complexes of known composition was followed in some of the runs. Analyzed portions of the component salts and water were carefully weighed into glass-stoppered tubes of about 60-ml. capacity, followed by rotation at constant temperature.

The preparations of selenic acid and ammonium selenate have been described previously.[2] The copper salt was prepared from reagent quality cupric carbonate and selenic acid. The salt was recrystallized and air dried and stored over partially dehydrated cupric selenate. Analy-

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[1] Lawrence and King, THIS JOURNAL, **60**, 1987 (1938).

[2] Gilbertson and King, *ibid.*, **58**, 180 (1936); King, *J. Phys. Chem.*, **41**, 797 (1937).