[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF INDIANA UNIVERSITY]

The Electrical Conductance of Aqueous Solutions. III. Potassium Metaperiodate and Potassium Perrhenate at 25°

BY JAMES HOMER JONES

Studies in this and other laboratories have shown that the conductances of many potassium salts deviate negatively from the Debye–Hückel limiting law in dilute solutions. The slopes of the Shedlovsky function, $\Lambda_0' = \Lambda + \beta\sqrt{c}/1 - \alpha\sqrt{c}$ *vs. c*, are much lower than the slopes of the corresponding sodium and lithium salt, and deviate from the predicted straight line in dilute solution. One means of accounting for such behavior is to assume incomplete dissociation of the potassium salts. In order that this behavior might be further studied, two salts, potassium metaperiodate and potassium perrhenate, were selected which might show more pronounced deviations.

Pushin and Tutundzie[1] measured the electrical conductance of potassium perrhenate in 1930. Their work is not of a high order of accuracy and the conductance of the most dilute solution they recorded (0.001 M) is more than one per cent. higher than the curve they used for extrapolation to infinite dilution. All other points out to 0.02 molar are on a straight line when the equivalent conductance is plotted against the square root of concentration. No work on potassium metaperiodate at 25° was found in the literature.

Experimental

Apparatus.—The apparatus used has been described in a previous paper.[2] The cell constants were checked using the standard solutions proposed by Grinnell Jones.[3] The resistances of the hundreds ohm dial and the thousands ohm dial were checked against standard resistors calibrated by the Bureau of Standards. The resistors in the ten ohm dial and one ohm dial were accepted at face value. The resistance values of the cells were normally kept above one thousand ohms. The temperature control approximates ±0.001°.

Purification of Materials.—Potassium metaperiodate was recrystallized three times from water and dried at 150°. Each sample used was dried in a platinum boat at 180° for ten hours before using. The stock solid was analyzed iodimetrically and showed a purity of 99.95 ± 0.05 per cent. The potassium perrhenate was similarly crystallized and dried. It was analyzed gravimetrically by precipitation with tetraphenylarsonium chloride as outlined by Willard and Smith.[4] The purity found was 99.96 ± 0.07 per cent.

Data

Density Measurements.—The densities of several solutions of each salt were determined at 25° using Weyl specific gravity bottles. Duplicate weights with the same twenty-five milliliter bottle agreed within at least 1.5 mg. These densities may be expressed by the following equations to within 0.01%

$$d_{KReO_4} = 0.99707 + 0.2330m$$
$$d_{KIO_4} = 0.99707 + 0.1685m$$

In these equations m refers to the concentration expressed in moles per 1000 g. of solution.

Conductance Data.—All solutions were made either directly by weighing the salt and water or by weight dilution with all weights corrected to vacuum. The conductivity water used had a specific conductance ranging from 8×10^{-7} to 11×10^{-7} reciprocal ohms. The observed values for the equivalent conductances of solutions of various concentrations are given in Table I where Λ is the equivalent conductance and c is the molar concentration.

TABLE I

EQUIVALENT CONDUCTANCES OF SOLUTIONS AT 25°

$KReO_4$		KIO_4	
c	Λ	c	Λ
0.030705	113.90	0.020421	115.67
.018988	116.44	.016823	116.67
.018169	116.71	.010570	118.75
.014639	117.64	.0095498	119.09
.012002	118.53	.0093787	119.22
.010284	119.15	.0055778	120.99
.0080024	120.03	.0045175	121.70
.0042208	122.00	.0034732	122.36
.0036452	122.44	.0033106	122.51
.0024432	123.36	.0015560	124.22
.0017732	124.04	.0012938	124.57
.0012745	124.64	.00072096	125.36
.0010634	124.98	.00049401	125.71
.00066531	125.71		
.00038123	126.41		

Discussion

The limiting conductances of these salts were determined by graphical extrapolation of large scale plots of the Shedlovsky[5] function. The plots were constructed large enough that 1 mm. on the scale was equivalent to 0.01 conductance unit. The plots of the Shedlovsky function are shown in Fig. 1.

These plots show clearly that both the potassium metaperiodate and potassium perrhenate deviate from the predicted straight lines in dilute solutions just as many other potassium salts do. This deviation, however, is not as much as expected. It is about the same order of magnitude as that for such potassium salts as the bromate, nitrate and perchlorate. Above concentrations of 0.005 molar, the points all fall on a straight line. The slope of this line is 50.5 for the metaperiodate (about the same as potassium nitrate and perchlorate); and 70.3 for the perrhenate (about the same as potassium bromate).

The limiting conductances found by graphical extrapolation are 128.15 and 127.87 for potassium perrhenate and potassium metaperiodate, respectively.

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[1] Pushin and Tutundzie, *Z. anorg. allgem. Chem.*, **193**, 420 (1930).

[2] J. H. Jones, THIS JOURNAL, **66**, 1115 (1944).

[3] Grinnell Jones and B. C. Bradshaw, *ibid.*, **55**, 1780 (1933).

[4] Willard and Smith, *Ind. Eng. Chem., Anal. Ed.*, **11**, 305 (1939).

[5] T. Shedlovsky, THIS JOURNAL, **54**, 1405 (1932).

The limiting conductances were also evaluated by the mathematical extrapolation of the curves for Λ *vs.* $\sqrt{c}$. The method of least squares applied to the data for dilute solutions gave the following values for the limiting conductances

Salt	Λ_0	Slope	Theor. slope
KIO_4	127.92	−94.08	−89.61
$KReO_4$	128.20	−97.08	−89.68

The extrapolated value obtained by Pushin and Tutundzie[1] was 125.7 for potassium perrhenate.

The data were also plotted according to a method proposed by Shedlovsky[6] in which an extrapolation function of the form $1/\Lambda = (1/\Lambda_0) + k\sqrt{c}$ is used. The data for solutions more dilute than 0.01 molar fell on straight lines and yielded values of Λ_0 of 127.95 for potassium metaperiodate and 128.25 for potassium perrhenate. These values are somewhat higher than those obtained by either of the other two methods but the extrapolation is rather long and steep. The agreement between the various methods of evaluating Λ_0 is considered satisfactory. The values accepted for Λ_0 are 127.90 for the metaperiodate and 128.20 for the perrhenate. These are believed accurate to within ±0.07 conductance unit.

Mobilities of the Anions.—Since the mobility of the potassium ion at infinite dilution and 25° is well known (73.52 on the Jones and Bradshaw[3] standard), it is possible to calculate the mobilities of the metaperiodate ion and the perrhenate ion using the limiting conductances of the potassium salts measured in this investigation. This would yield the following values: metaperiodate ion, 54.38 ± 0.07 and perrhenate ion, 54.68 ± 0.07.

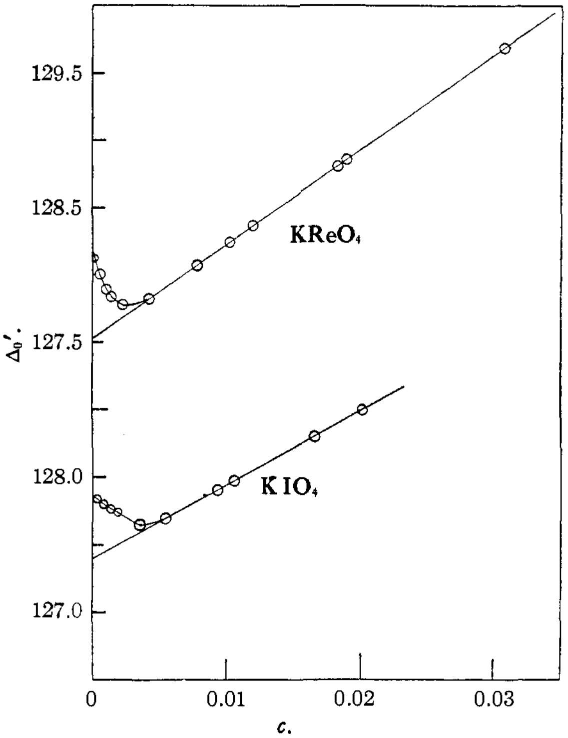

Fig. 1.—Plots of Shedlovsky function.

Summary

The electrical conductances of aqueous solutions of potassium metaperiodate and potassium perrhenate were measured over the concentration range 0.0004 *m* to approximate saturation.

The limiting conductances were determined by three independent methods with satisfactory agreement.

The densities of the solutions were determined with an accuracy of approximately 1 part in 15,000.

The limiting conductances of the anions were determined using the recorded value for the potassium ion and the measured values for the salts from this investigation.

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[6] T. Shedlovsky, *J. Franklin Inst.*, **225**, 739 (1938).

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Derivatives of the Methylchlorosilanes. IV. Amines

BY ROBERT O. SAUER AND R. H. HASEK[1]

In the first paper[2] of this series which described the hydrolysis and alcoholysis products of trimethylchlorosilane attention was directed toward the unstable nature of trimethylsilanol as compared with triethylsilanol and its higher homologs. We now report a parallel study of the ammonolysis and aminolysis products of this chlorosilane.

Stock and Somieski[3] treated chlorosilane vapor with ammonia and isolated the tertiary amine $(H_3Si)_3N$, b. p. 52°. With excess ammonia presence of the primary and secondary amines was assumed; neither, however, was isolated. Aminosilane presumably condensed with itself producing ammonia and disilazine, $H_3SiNHSiH_3$; the latter decomposed slowly with the formation of silane and the non-volatile polysilazine, $(H_2SiNH)_x$. Chlorosilane with methylamine and with ethylamine yielded[4] N-methyldisilazine, b. p. 32°, and N-ethyldisilazine, b. p. 66°, respectively.

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[1] Present address: Tennessee Eastman Corp., Kingsport, Tenn.

[2] Sauer, THIS JOURNAL, **66**, 1707 (1944).

[3] Stock and Somieski, *Ber.*, **54**, 740 (1921).

[4] Emeleus and Miller, *Nature*, **142**, 996 (1938); *J. Chem. Soc.*, 819 (1939).