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SUBJECT: Calculation of the Diffusion Coefficient of Pertechnetate and Perrhenate Ions from Conductivity Measurements

TO: Those Listed

FROM: P. F. Thomason

Abstract

During the polarographic studies of technetium it became necessary to determine the diffusion coefficient of TcO_4^- ion. In order to calculate the number of electrons involved in the polarographic reduction process by means of the Ilkovic equation $\left(id = 607\ n\ D^{1/2}\ C\ m^{2/3}\ t^{1/6}\right)$ the diffusion coefficient (D) must be known. Therefore specific conductance measurements of $KReO_4$ and $KTcO_4$ solutions were made. From these data the diffusion coefficient of ReO_4^- and TcO_4^- ions were calculated.

Discussion

At infinite dilution, the equivalent conductance and diffusion coefficient of an ion are related by an equation derived by Nerst. This equation as given by Meites and Thomas[1] is as follows:

$$D^{o} = \frac{RT}{zF^{2}y}\lambda^{o} = 2.67 \times 10^{-7} \frac{\lambda^{o}}{z}$$

where R = molar gas constant

T = absolute temperature

Fy = Faraday

z = charge on the ion (valence)

λ^{o} = equivalent conductance at infinite dilution

Therefore if the equivalent conductance at infinite dilution and the charge (valence) of an ion are known the diffusion coefficient can be calculated. Lingane[2] has calculated the diffusion coefficient of ReO_4^- ion to be 1.37 x 10^{-5} cm^2/sec from his conductivity measurements. We have repeated his measurements and the specific conductance of solutions of $KReO_4$ and $KTcO_4$ were measured and the equivalent conductance calculated. The equivalent conductances at various concentrations were plotted versus the square root of the concentration on rectilinear graph paper. The equivalent conductance at infinite dilution was obtained by extrapolation of these straight line points to essentially zero concentration.

The values for the equivalent conductance were inserted in the Nerst equation and the diffusion coefficient for both ReO_4^- and TcO_4^- ions were calculated.

Experimental

Apparatus and Materials

Serfass Conductivity Bridge Model RCM-15 Conductivity Cell - medium Conductivity type No. 9-367 (Fisher Scientific Company)

Distilled water - conductivity 1.2×10^{-6} ohms^{-1}/cm

$KTcO_4$ - Pure salt obtained from R. H. Busey

$KReO_4$ - Reagent grade - A. D. Mackay Inc. (New York)

KCl - Reagent grade - Bakers analyzed

The conductivity cell was calibrated by measuring the conductance of a 0.0200 molar KCl solution. The cell constant of 0.73 was obtained from these measurements. All conductance measurements were made at 25°C.

A standard solution of $KReO_4$ was made by weighing a portion of the salt and dissolving in distilled water. Aliquots of this solution were diluted with distilled water to give the following concentrations: 0.00125, 0.0025, 0.005, and 0.01 molar $KReO_4$. The specific conductance of these solutions was measured and the data are shown in Table I.

Table I

Specific Conductance of $KReO_4$ Solutions

Concentration molarity of $KReO_4$	Conductance (meter reading) micro ohms^{-1}	Cell Constant	Specific Conductance micro ohms^{-1}/cm
0.01	1650	0.73	1204
0.005	840	0.73	610
0.0025	430	0.73	310
0.00125	220	0.73	160

The equivalent conductance (specific conductance x volume (in cc) for 1 gram equivalent) was calculated for these solutions and found to be 120, 122, 124, and 128 reciprocal ohms ($ohms^{-1}/cm^2$) respectively. These values were plotted versus the square root of concentration. On extrapolation to infinite dilution the equivalent conductance of $KReO_4$ was found to be 130 $ohms^{-1}/cm^2$. Correcting for equivalent conductance of the potassium ion (74.5 ohm^{-}/cm^2 Chemistry Handbook Value) the equivalent conductance for ReO_4^- ion was found to be 55.5 $ohms^{-1}/cm^2$ at 25° C. From the Nerst equation:

$$\text{Diffusion Coefficient } (D^o) \text{ of } ReO_4^- = \frac{RT\lambda^o}{zF^2Y} = 2.67 \times 10^{-7} \times \frac{55.1}{1} = 1.47 \times 10^{-5} \text{ cm}^2/\text{sec}$$

This value is somewhat higher than Lingane's value who obtained the equivalent conductance of 51.3 $ohms^{-1}/cm^2$ for ReO_4^- ion. He calculated the diffusion coefficient to be 1.37×10^{-5} cm^2/sec.

Solutions of $KTcO_4$ were made in a similar manner and the specific conductance measured. The data are given in Table II.

Table II

Specific Conductance of $KTcO_4$ Solutions

Concentration molarity of $KTcO_4$	Conductance (meter reading) micro $ohms^{-1}$	Cell Constant	Specific Conductance micro $ohms^{-1}/cm$
0.00438	695	0.73	507
0.00219	330	0.73	241
0.00109	170	0.73	124

The equivalent conductance was calculated from these data and found to be 116, 120, and 129 $ohms^{-1}/cm^2$ respectively. These values were plotted versus the square root of concentration. By extrapolation to infinite dilution the equivalent conductance of $KTcO_4$ was found to be 133 ohms^{-1}/cm^2. Correcting for the equivalent conductance of potassium ion (74.5) ohms^{-1}/cm^2) the equivalent conductance for TcO_4^- ion was found to be 58.5 ohms$^-$/cm^2 at 25°C. From the Nerst equation the diffusion coefficient was calculated to be 1.56×10^{-5} cm^2/sec.

It will be desirable to repeat these measurements when more $KTcO_4$ becomes available as the equivalent conductance values do not fall exactly on a straight line. However, as the polarographic diffusion current varies only with the square root of the diffusion coefficient an error of 10% in the value is not critical for use in the Ilkovic equation. More precise conductivity measuring equipment also would be desirable when these measurements are repeated.

The n value for the polarographic reduction of TcO_4^- ion in phosphate buffer solution of pH 7.0 was calculated from the Ilkovic equation.

$$id = 607\ n\ D^{1/2}\ C\ m^{2/3}\ t^{1/6}$$

$$= 0.313\ \mu amp = 607 \times 1.74 \times 10^{-2} \times \sqrt{1.56 \times 10^{-5}} \times 2.33n$$

$$n = 3.2$$

From these calculations it might be assumed that the reduction could take place as follows:

$$TcO_4^- + 3e \rightarrow Tc^{+4} \quad (E\ 1/2 = 0.68\ v\ vs\ S.C.E.)$$

References

1. Louis Meites and Henry C. Thomas "Advanced Analytical Chemistry", page 155 McGraw-Hill Book Company, New York, 1958.

2. J. J. Lingane, J. Am. Chem. Soc. 64, 1001-1007, (1942).

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