Absorption Spectrum of Complexed Rhenide.—The distinction between the rhenide state in sulfuric acid and that in hydrochloric acid might lead one to expect a difference in the ultraviolet absorption in the two cases and an experimental comparison of the rhenide absorption in the two media seemed worthwhile.

To this end, 0.5 mM rhenide solutions in the 2 N acids were prepared by reduction with amalgamated zinc. Comparison solutions of the 2 N acids containing no rhenium were contacted with zinc under comparable conditions. The solutions were aged in the covered absorption cells for *ca.* 30 minutes prior to reading. The absorption data were determined from 240 to 1050 mμ. At each wave length the instrument was set to read 100% transmission on the proper solvent before reading the transmission of the corresponding rhenide solution. Cross comparison of the solvents showed only small differences below 300 mμ and negligible differences above this region. The solutions were at 25° when read. Readings were taken every 5 mμ from 240 to 350 mμ, every 10 mμ from 350 to 500 mμ, every 20 mμ from 500 to 600 mμ, every 25 mμ from 600 to 900 mμ, and at 950, 1000 and 1050 mμ. The minimum usable slit width was employed throughout. The absorption curves (Fig. 4) show quite significant differences between the near ultraviolet absorption spectra of rhenide in sulfuric acid and in hydrochloric acid.

Acknowledgment.—The authors wish to thank the Atomic Energy Commission for the predoctoral fellowship given C. L. R. and the Research Corporation for the use of equipment purchased under a Frederick Gardner Cottrell Grant.

WEST LAFAYETTE, IND. RECEIVED DECEMBER 7, 1950[10]

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[10] Original manuscript received August 6, 1949.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

The Diffusion Coefficient of Silver Nitrate in Dilute Aqueous Solution at 25°

BY HERBERT S. HARNED AND CLARENCE L. HILDRETH, JR.

The diffusion coefficient of silver nitrate has been determined by the conductometric method in dilute solutions. The results are found to be in agreement with the theory of Onsager and Fuoss.

The determination of the diffusion coefficient of silver nitrate contained in this communication supplements accurate results recently obtained with lithium, sodium[1] and potassium[2] chlorides and potassium nitrate.[3] The apparatus and experimental technique employed in these conductometric determinations has been described in detail[2] and requires no amplification. The results for silver nitrate contained in the second column of Table I are of comparable accuracy with those of the alkali halides and potassium nitrate.

TABLE I

THE OBSERVED AND CALCULATED DIFFUSION COEFFICIENTS OF SILVER NITRATE IN WATER AT 25°

c	$\mathfrak{D} \times 10^5$ Observed	$\mathfrak{D} \times 10^5$ Calcd.
0.00000	...	(1.7675)
.00285	1.718	1.721
.00322	1.719	1.718
.00427	1.711	1.712
.00496	1.708	1.708
.00628	1.701	1.702

The values in the third column of this table were computed from the theoretical equations for a uni-univalent electrolyte[4,5,6]

$$\mathfrak{D} = 16.629 \times 10^{10} T (\overline{\mathfrak{M}}/c) \left(1 + c\frac{\partial \ln y_\pm}{\partial c}\right) \quad (1)$$

where

$$(\overline{\mathfrak{M}}/c) \times 10^{20} = 1.0748 \left(\frac{\lambda_1^0\lambda_2^0}{\lambda_1^0 + \lambda_2^0}\right) - \frac{22.148}{\eta_0(DT)^{1/2}} \frac{\sqrt{c}}{(1 + A'\sqrt{c})} \left(\frac{\lambda_1^0 - \lambda_2^0}{\lambda_1^0 + \lambda_2^0}\right)^2 + \frac{9.304 \times 10^7}{\eta_0(DT)^2} c\phi(A'\sqrt{c}) \quad (2)$$

$\mathfrak{D}$ is the diffusion coefficient in cm.^{2} sec.,$^{-1}$ T the absolute temperature, c is in moles per liter, and $y_\pm$ is the activity coefficient of silver nitrate. D is the dielectric constant of water, η_0 its viscosity, and λ_1^0, and λ_2^0 are the equivalent ionic conductances of the silver and nitrate ions, respectively, at infinite dilution. $A'\sqrt{c}$ equals κa, where κ is the reciprocal radius of the ionic atmosphere and "a" is the mean distance of approach of the ions according to the Debye and Hückel theory. The exponential integral function of the theory $c\phi(A'\sqrt{c})$ may be interpolated from data given in tables.[5,6]

The activity coefficients obtained from isopiestic vapor pressure measurements by Robinson and Stokes[7] were employed to evaluate the thermodynamic term in equation (1) and the mean distance of approach of the ions, a. Utilizing the familiar Debye and Hückel equations, "a" was found to equal 3.03 Å. and consequently $A'\sqrt{c} = 0.995\sqrt{c}$. This procedure leads to the numerical equation for the thermodynamic term

$$\left(1 + c\frac{\partial \ln y_\pm}{\partial c}\right) = 1 - \frac{0.5862\sqrt{c}}{(1 + 0.995\sqrt{c})^2} - 0.2395c - c\psi(d) \quad (3)$$

estimated to be valid from 0 to 0.5 molar concentration. The numerical equation for the density term is

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[1] Harned and Hildreth, THIS JOURNAL, **73**, 650 (1951).

[2] Harned and Nuttall, *ibid.*, **69**, 736 (1947); **71**, 1460 (1949). Harned and Blake, *ibid.*, **72**, 2265 (1950).

[3] Harned and Hudson, *ibid.*, **73**, 652 (1951).

[4] Onsager and Fuoss, *J. Phys. Chem.*, **36**, 2689 (1932).

[5] Harned and Owen, "The Physical Chemistry of Electrolytic Solutions," 2nd Ed., Reinhold Publishing Corp., New York, N. Y., pp. 178, 593.

[6] Harned, *Chem. Revs.*, **40**, 462 (1947).

[7] Robinson and Stokes, *Trans. Faraday Soc.*, **45**, 612 (1949).

$$c\psi(d) = \frac{0.00810c - 0.003903c^{3/2}}{0.99704 + 0.00810c - 0.00260c^{3/2}} \quad (4)$$

The mobility term was computed by substituting the values: $D = 78.54$,[8] $\eta_0 = 8.949 \times 10^{-3}$,[9] $T = 298.16$, $\lambda_1^0 = 61.92$ and $\lambda_2^0 = 71.44$ in equation (2). The values of the limiting conductances of the silver and nitrate ions were those obtained by MacInnes, Shedlovsky and Longsworth.[10] The equation for the mobility term reduces to the numerical form

$$(\overline{\mathfrak{M}}/c) \times 10^{20} = 35.6512 - \frac{0.08241\sqrt{c}}{1 + 0.995\sqrt{c}} + 18.959c\phi(0.995\sqrt{c}) \quad (5)$$

The third column in Table I contains the results computed by equations (1), (3), (4) and (5). With the exception of the result at the lowest concentration, the agreement of the observed results with theory is remarkably good.

A more detailed description of the calculation is illustrated in Fig. 1. In this figure, the upper (solid) curve represents the calculation by the complete theory and the lower (solid) curve the result obtained by the limiting law of the theory[6] which for silver nitrate becomes

$$\mathfrak{D} \times 10^5 = 1.7675 - 1.040\sqrt{c} \quad (6)$$

The plot which lies between these results is obtained when $(\mathfrak{M}/C \times 10^{20})$ is constant and equal to its value at zero concentration. The difference between the center and top curve represents the calculated effect of electrophoresis. There seems to be little doubt from the positions of the circles representing the experimental results that the mobility term is required for the calculation.

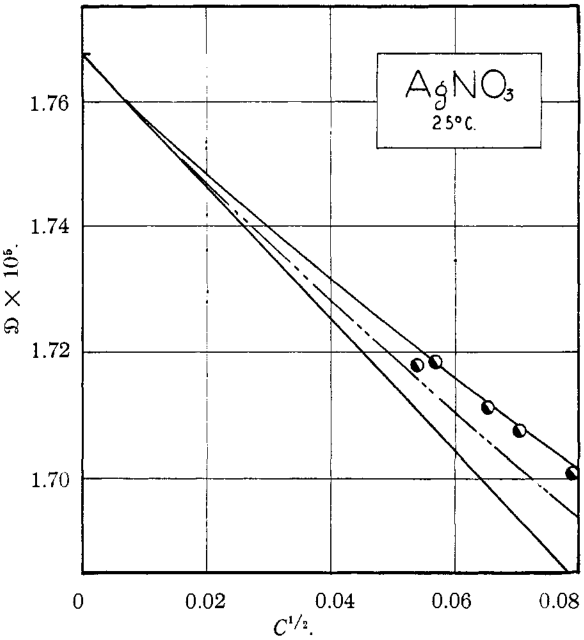

Fig. 1.—Upper curve represents complete theory. Lower curve represents the limiting law (Eq. 6). The intermediate curve was obtained by assuming constancy of $(\overline{\mathfrak{M}}/c)$.

NEW HAVEN, CONN. RECEIVED FEBRUARY 26, 1951

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[8] Ref. 6, p. 118.

[9] Ref. 6, p. 128.

[10] MacInnes, Shedlovsky and Longsworth, THIS JOURNAL, **54**, 2758 (1932).

[CONTRIBUTION FROM THE METCALF RESEARCH LABORATORY OF BROWN UNIVERSITY]

Properties of Electrolytic Solutions. LII. Conductance of Some Salts of Acetone

BY MAURICE J. MCDOWELL[1] AND CHARLES A. KRAUS

To fill some gaps in the list of ion conductances in acetone, the conductances of a number of salts were determined in this solvent. Thus, the conductances of the ammonium, the tetramethyl-, tetrapropyl- and tetraamylammonium ions have been determined. The conductances of octadecyltributyl- and dioctadecyldibutylammonium ions have been determined as also has been that of the chloride ion. Dissociation constants have been evaluated on the basis of the Fuoss analysis. Some comparisons are made of dissociation constants and ion conductances in different solvents.

I. Introduction

Reynolds and Kraus[2] have measured the conductance of a number of salts in acetone at 25°. For purposes of intercomparison of ion conductances and dissociation constants of electrolytes in different solvents, the earlier measurements in acetone leave a number of gaps which the present investigation is intended to fill. In particular, the conductances of several symmetrical quaternary ammonium salts have been measured so as to provide data on the conductances of the quaternary ammonium ions from tetramethyl- to tetra-*n*-amyl, inclusive. The conductances of the octadecyltributyl- and the dioctadecyldibutylammonium ions have been determined. The conductances of the chloride and the ammonium ions have likewise been evaluated.

II. Experimental

1. **Apparatus, Procedure and Materials.**—The electrical measuring apparatus and the thermostat were the same as those of Reynolds.[2] The temperature was controlled at 25 ± 0.002°.

With the exception of tetrabutylammonium chloride, with which the dilution method was employed, all measurements were carried out according to the procedure described by Daggett, Bair and Kraus[3] for aqueous solutions. The conductance cell of the erlenmeyer type had a capacity of approximately 1 liter. Salt samples were weighed out on a microbalance in quartz cups. Since acetone is insensitive to carbon dioxide, samples were introduced into the cell as it rested in the thermostat. The cell was provided with a magnetic stirrer.

Acetone[4] was purified according to the method of Rey-

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[1] Ethyl Corporation Fellow (1947-1948); University Fellow (1948-1949); Metcalf Fellow (1949-1950) in Brown University.

[2] M. B. Reynolds and C. A. Kraus, THIS JOURNAL, **70**, 1709 (1948).

[3] H. M. Daggett, E. J. Bair and C. A. Kraus, *ibid.*, **73**, 799 (1951).

[4] This material was kindly furnished by the Tennessee Eastman Company of Kingsport, Tennessee.