zinc nitrate solutions. The fact that the two curves in Fig. 1 converge to the same point at infinite dilution, which is in agreement with Nernst's limiting value, may be considered as an independent check on the reliability of the present measurements.

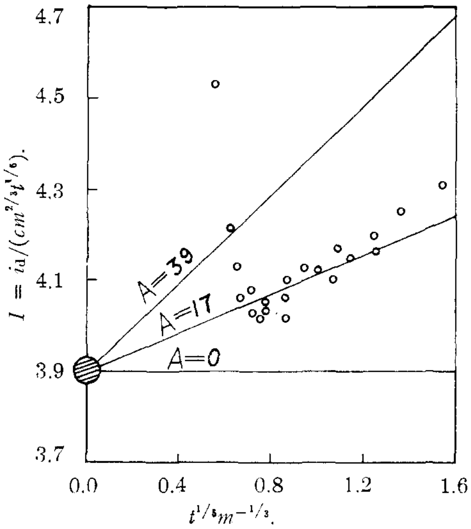

Fig. 4.—Comparison of equation 5 with polarographic diffusion current data for Zn(II) ion in 1.0 *F* NH_4OH + 1.0 *F* NH_4Cl solution containing 0.01% by wt. of gelatin.[9]

It may also be of interest to point out that the tracer-diffusion coefficient of Zn(II) ion in 1.0 *F* NH_4OH + 1.0 *F* NH_4Cl solution is 45% higher than that of Zn(II) ion at infinite dilution. This shows that the tetrammino-zinc ion, $Zn(NH_3)_4^{++}$, diffuses much faster than the simple hydrated Zn^{++} ion in solutions of equivalent concentrations.

Data in Table IV also show clearly that gelatin has no appreciable effect on the tracer-diffusion coefficient of Zn(II) ion in 1.0 *F* NH_4OH + 1.0 *F* NH_4Cl solution containing less than 0.1% of gelatin. This result is not unexpected for it is well-known that proteins in general combine with ions of the transition metals in a manner similar to the combination of these metal ions with ammonia and amino acids to form complex ions and metal–chelate compounds. Since in the solutions listed in Table V the concentrations of gelatin are negligibly small as compared to the great excess of competing ammonia molecules, the fraction of Zn(II) bound to gelatin in such solutions must be negligibly small. Consequently, the tracer-diffusion coefficient of Zn(II) ions in these solutions should be practically unaffected by the presence of gelatin.

Comparison of the Tracer-diffusion Coefficient of Zn(II) Ion with Polarographic Diffusion Current Data.—By using the tracer-diffusion coefficient of the Zn(II) ion in 1.0 *F* NH_4OH + 1.0 *F* NH_4Cl solution determined in the present work, the "diffusion current constant," $I = i_d/(cm^{2/3}t^{1/6})$, is calculated as linear functions of $t^{1/6}m^{-1/3}$. The calculated results are plotted in Fig. 4 as three straight lines corresponding to A = 0, 17 and 39, respectively. The experimental points in Fig. 4 are taken from the careful measurements of Lingane and Loveridge.[2] Examination of Fig. 4 shows clearly that the deviation of equation 1 with A = 39 or A = 0 from the experimental values is much larger than that with A = 17. But the agreement between the experimental points and equation 1 with A = 17 does not seem satisfactory enough for us to conclude definitely that the latter is valid. More work in this direction is desirable.

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New Haven, Connecticut

[Contribution from the Oak Ridge National Laboratory]

The Electrical Conductivity of Uranyl Sulfate in Aqueous Solution[1]

By Robert D. Brown, W. B. Bunger, William L. Marshall and C. H. Secoy

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The conductance of uranyl sulfate in aqueous solution has been determined at 0°, 25°, 50°, 90°, 125° and 200° in concentrations ranging from 10^{-4} to 7.28 *N*. A value of Λ^0_{25} = 131 $ohms^{-1}$ $cm.^2$ $equiv.^{-1}$ has been obtained when correction is made for the conductivity of H^+, $U_2O_5^{++}$ and HSO_4^- present from hydrolysis. This corresponds to a value for $\lambda^0_{UO_2^{++}}$ of 51 $ohms^{-1}$ $cm.^2$ $equiv.^{-1}$. The degree of dissociation of uranyl sulfate into simple ions at 25° has been determined from conductivity data and tentative values for the mean activity coefficients have been calculated. These values have been used to determine the dissociation constant. Conductometric titrations with sulfuric acid of uranyl sulfate solutions containing dissolved UO_3 show that UO_3 behaves as a weak base in aqueous solution and exhibits a strong buffering action.

The conductivity of uranyl sulfate in aqueous solution has been investigated at several temperatures and in various concentrations. The only previous work of this nature is that of Dittrich[2] and of Jones.[3] Each of these investigators measured the conductivity of uranyl sulfate at 25° in concentrations ranging from one equivalent per liter of solution to 1/4096 equivalent per liter. There is wide disagreement between the two sets of experimental data. The present results are in good agreement with the work of Dittrich.

Experimental

Materials.—A stock solution of uranyl sulfate, prepared by dissolving pure UO_2 in C.P. sulfuric acid and adjusting the uranium/sulfate ratio on the basis of analytical deter-

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[1] Presented before the 123rd Meeting of the American Chemical Society, Los Angeles, Calif., March 15–19, 1953.

[2] C. Dittrich, *Z. physik. Chem.*, **29**, 449 (1899).

[3] H. C. Jones, Carnegie Inst. Wash. Publ. No. 170 (1912).

TABLE I

CONDUCTANCE DATA

0°		25°		50°		90°		125°		200°	
C^a	Λ	C^a	Λ	C^a	Λ	C^a	Λ	C^b	Λ	C^b	Λ
0.0001008	83.13	0.0001	175.34	0.0000991	290.62	0.0000968	521.60	0.0001	590.0		
.000504	62.33	.0005	127.20	.0004955	198.79	.000484	289.20	.0005	320.0		
.001008	54.05	.001	106.51	.000991	159.34	.000968	227.23	.001	236.0	0.001	235.9
.002526	43.31	.005	63.18	.004955	85.92	.00484	107.42	.005	110.4	.005	124.8
.01263	26.29	.01	49.21	.00991	65.33	.00968	79.53	.01	81.4	.01	105.4
.02526	20.71	.05	27.65	.04955	35.99	.0484	45.24	.05	48.6	.05	66.0
.0982	13.13	.1	22.18	.0991	29.28	.0968	38.53	.1	42.08	.1	55.0
.3992[b]	9.37	.5	14.43	.4955	20.53	.484[b]	28.64	.5	34.28	.5	39.8
1.0[b]	6.43	1.0	11.59	.991	17.03	.968[b]	24.43	1.0	26.78	1.0	33.4
3.075[b]	2.51	4.66	2.78	2.504[b]	9.59	2.520[b]	14.49	2.52	18.00	2.52	20.6
6.065[b]	0.465			4.66[b]	4.69	4.66[b]	7.77	4.66	10.07		
				7.28[b]	1.02						

[a] C, concentration in equivalents per liter. [b] Concentrations on 25° basis.

minations, was used to make up solutions of other concentrations by dilution with conductivity water using calibrated apparatus.

Baker and Adamson reagent grade KCl, carefully recrystallized, was used to determine the conductivity cell constants. This material was purified as follows: fresh material was dissolved in conductivity water, filtered and saturated with chlorine generated from C.P. hydrochloric acid and $KMnO_4$. The excess chlorine was boiled off and the KCl was precipitated by HCl generated from C.P. sulfuric and hydrochloric acids. This precipitate was washed with water and redissolved in conductivity water from which it was recrystallized twice. The resulting crystals were dried in a desiccator and fused in a platinum dish surrounded by an atmosphere of nitrogen. This material was weighed on a semi-micro balance in the quantity required for 0.1 and 0.01 demal solutions according to the data of Jones and Bradshaw[4] and added to the necessary amounts of water, all weighings being reduced to vacuum.

Apparatus and Method.—The conductance cells employed were of the design recommended by Jones and Bollinger.[5]

Resistance was measured with a Jones conductance bridge manufactured by Leeds and Northrup Company. This bridge has built-in shielding and additional external shielding was added in order to reduce the capacitance and inductive effects. It was not feasible to control room temperature and humidity within the limits recommended by the manufacturer; however, it is not believed that this caused appreciable error, since it was found possible to reproduce measurements within a few hundredths of a per cent. under varying room conditions.

Accessory equipment consisted of a Hewlett–Packard sine wave generator (20 to 30,000 cycles), a General Radio amplifier and a Dumont 208-B oscilloscope. Most resistance measurements were made at 1500 cycles, and with the above equipment it was possible to obtain bridge readings to 0.001 ohm.

For resistance measurements, the conductivity cell was immersed in an oil-filled constant temperature bath. This bath could be maintained at a temperature somewhat below the desired value by a small refrigerating unit operating through a copper coil and brought to temperature by knife blade heating elements activated by a thermoregulator operating through a merc-to-merc relay. Auxiliary heat was supplied by a similar heater with manual control. By careful regulation of the auxiliary heater, temperature control to ±0.005° was achieved.

The temperature of the bath was measured with a Leeds and Northrup platinum resistance thermometer and Mueller bridge assembly. The bridge has a National Bureau of Standards Certificate and the resistance thermometer used was calibrated against another of the same type having a N.B.S. certificate.

In order to obtain experimental data above 100°, a bomb was constructed to hold a small pressure cell made of heavy-wall Pyrex tubing. The solution was sealed inside the cell and the cell placed inside the bomb. The vapor pressure was approximately balanced by admission of nitrogen to the bomb. Electrical connection to the outside was made through conventional pressure fittings with soapstone glands. This cell gave results reliable to an estimated ±5% at 200° in the more concentrated (0.001 N) solutions.

It was shown, however, by both conductometric and spectrographic methods that considerable solution of the Pyrex glass took place at this temperature. The conductivity of a solution was measured at room temperature before and after use in the high temperature cell. The equivalent conductance of a 0.001 N UO_2SO_4 solution increased by 20 $\text{ohms}^{-1}\ \text{cm.}^2\ \text{equiv.}^{-1}$ after being subjected to a temperature of 200° for two hours. A sample of 0.1 N UO_2SO_4 was held in the bath for a period of 16 to 18 hours and then removed and a spectrographic determination of boron was obtained. The solution was found to contain 8.2 μg. of boron per ml., which showed considerable solution of the Pyrex glass.

Results and Discussion

The equivalent conductances of the several solutions at the temperatures indicated are shown in Table I. Since a plot of the equivalent conductance, Λ, *vs.* $C^{1/2}$, where C is concentration in equivalents per liter, approaches the conductance axis asymptotically it is not possible to obtain a satisfactory value of Λ° by extrapolation to zero concentration. Accordingly a more definitive treatment than the application of the Onsager equation was sought.

Of the several extrapolation methods by which the equivalent conductance of a weak electrolyte at infinite dilution may be determined, the methods of Shedlovsky[6] and of Fuoss and Kraus[7] were tried. These give essentially identical results. The final extrapolation plots using the Fuoss and Kraus method are shown in Fig. 1. Estimated values of Λ° are given on the graph.

Such values of Λ° are not satisfactory for use in attempting to evaluate the dissociation constant for uranyl sulfate since no allowance has been made for the contribution to the conductivity of other ionic species such as the H^+ ion, the HSO_4^- ion and the $U_2O_5^{++}$ ion. These are all most probably present and, at least in the case of the H^+ ion, their contribution to conductivity is a major factor. An attempt to correct for these factors is impossible at any temperature other than 25° because of the lack of necessary data. The method by which corrections were applied to the 25° data follows.

Although one cannot positively identify or

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(4) G. Jones and B. C. Bradshaw, THIS JOURNAL, **55**, 1780 (1933).

(5) G. Jones and G. M. Bollinger, *ibid.*, **53**, 411 (1931).

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

(7) R. M. Fuoss and C. A. Kraus, THIS JOURNAL, **55**, 476 (1933).

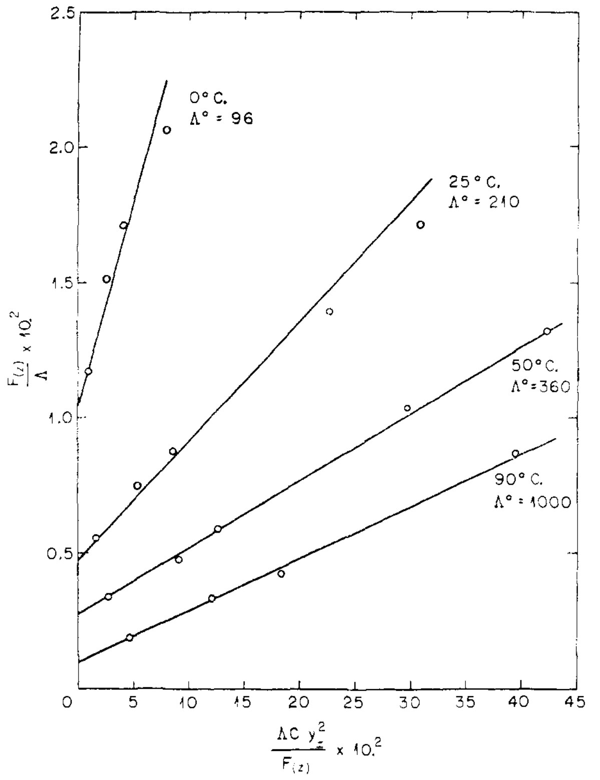

Fig. 1.—Fuoss and Kraus extrapolation plot for uranyl sulfate.

specify the concentration of the various ions in a given solution of UO_2SO_4, it seems probable that in addition to UO_2^{++}, $SO_4^{=}$ and H^+ ions there are appreciable amounts of $U_2O_5^{++}$ and HSO_4^- ions. The following dissociation and hydrolysis pattern was assumed.

$$UO_2SO_4 \rightleftharpoons UO_2^{++} + SO_4^{=} \quad (1)$$

$$2UO_2^{++} + H_2O \rightleftharpoons U_2O_5^{++} + 2H^+ \quad (2)$$

$$H^+ + SO_4^{=} \rightleftharpoons HSO_4^- \quad (3)$$

For the purpose of making corrections for the effect of reactions 2 and 3 on the conductivity, complete initial dissociation into UO_2^{++} and $SO_4^{=}$ ions was further assumed. It is possible to approximate the ionic concentrations from the pH measurements of MacInnes and Longsworth[8] and the accepted value for the dissociation constant for the equilibrium

$$HSO_4^- \rightleftharpoons H^+ + SO_4^{=} \quad K = 0.010$$

If this is done a hydrolysis correction after the method of Owen and Gurry[9] can be applied to the measured conductance of a UO_2SO_4 solution of known concentration.

Equation 2 shows that one equivalent of $U_2O_5^{++}$ is produced and two equivalents of UO_2^{++} disappear per equivalent of H^+ formed. From equation 3 it is seen that one equivalent of H^+ and one mole of $SO_4^{=}$ disappear to produce one equivalent of HSO_4^-. The conductivity has thereby been increased due to fast moving H^+ replacing the slower UO_2^{++} ions and decreased by the replacement of $SO_4^{=}$ by slower HSO_4^-. Hence two corrections are necessary, one to account for the increase and the other to account for the decrease in conductivity.

Reverting tc specific conductance, k, and designating k corrections for H^+ by Δk_1

$$1000\Delta k_1 = C_{H^+}\lambda_H$$

$$\Delta\Lambda_1 = 1000\Delta k_1/C$$

The second correction must be approximated since the ionic conductances of UO_2^{++} and $U_2O_5^{++}$ are not precisely known.[10] This was made by applying the H^+ correction over the range of concentration from 10^{-4} to 10^{-2} N and determining Λ° from a plot of Λ'^{-1} *vs.* $\Lambda'C$ where Λ' is the corrected equivalent conductance. This gave a value of Λ° in the neighborhood of 119, from which a value of $\lambda_{UO_2^{++}} = 39$ was derived. The second correction referred to above was then applied as

$$1000\Delta k_2 = C_{U_2O_5^{++}}(2\lambda_{UO_2^{++}} - \lambda_{U_2O_5^{++}}) + C_{HSO_4^-}(\lambda_{SO_4^{=}} - \lambda_{HSO_4^-})$$

$$\Delta\Lambda_2 = 1000\Delta k_2/C$$

$$\Lambda'' = \Lambda - \Delta\Lambda_1 + \Delta\Lambda_2$$

where Λ'' is the doubly corrected equivalent conductance. In this calculation $(2\lambda_{UO_2^{++}} - \lambda_{U_2O_5^{++}})$ was treated as if $\lambda_{U_2O_5^{++}} = \lambda_{UO_2^{++}} = 39$, which is justified on the grounds that $\lambda_{UO_2^{++}}$ is not precisely known, and a decrease from two ions UO_2^{++} to one of $U_2O_5^{++}$ would lead to a loss of at least half the conductivity due to UO_2^{++}.

The corrected conductance data were treated after the method of Fuoss and Kraus.[7] In these calculations the mean distance of closest approach of the oppositely charged ions was assumed to be 7 Å., which is one-half of the interionic distance calculated by Bjerrum's equation. The results are shown in Table II. At 25° this method leads to a value of 131 for the equivalent conductance of UO_2SO_4 at infinite dilution or a limiting conductance of 51 for the uranyl ion. The "dissociation constant," K, had an average value of 5.93×10^{-4} over the concentration range 5×10^{-5} to 5×10^{-3} M. The significance of dissociation constants for 2–2 electrolytes determined by conductance methods is questionable since the normal behavior for completely dissociated electrolytes

Table II

Corrected Conductance Data

c^a	Λ''^b	α^c	$y_{\pm}^d$	$K \times 10^{4e}$
0.00005	119.4	0.935	0.940	5.93
.00025	98.7	.794	.883	5.99
.0005	85.6	.702	.851	5.97
.0025	53.2	.464	.758	5.78
.005	42.12	.383	.709	5.98
.025	25.46	.281	.560	8.57
.05	22.11	$.26^f$	.48	11

[a] c, molar concentration. [b] Λ'' corrected equivalent conductance. [c] α, degree of dissociation. [d] $y_{\pm}$, mean molar activity coefficient (= y stoi./α). [e] K, dissociation constant. [f] Extrapolated value.

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(8) D. A. MacInnes and L. G. Longsworth, "Measurement and Interpretation of pH and Conductance Values of Aqueous Solutions of Uranyl Salts," AEC, MDDC-911, 1942.

(9) B. B. Owen and R. W. Gurry, This Journal, **60**, 3074 (1938).

(10) The values of MacInnes and Longsworth for 0.1 N solution ($\lambda_{UO_2^{++}} = 27.82$, $\lambda_{U_2O_5^{++}} = 18.5$) are in qualitative agreement with those used here for the limiting ion conductances.

of this type is unknown.[11] However, a comparison of our results with those of Davies[12] indicates that uranyl sulfate is a weaker electrolyte than magnesium sulfate since the comparable values of K are smaller by a factor of ten. A value of approximately 0.02 was obtained for the dissociation constant of uranyl sulfate by Ahrland[13] using both potentiometric and extinctiometric methods. It is the opinion of the authors that Ahrland's value should be regarded as more nearly correct because of the inherent weakness of the conductometric method. A comparison with the normal behavior of a completely dissociated 1–1 electrolyte is forced by the equations employed. These equations are probably not adequate to describe the normal behavior of a completely dissociated 2–2 electrolyte. If such is the true reason for the lack of agreement it is possible that the correct dissociation constant for magnesium sulfate is considerably larger than the value reported by Davies; in fact, perhaps as large as 0.2.

An interesting feature of the conductance data is the effect of temperature change. According to Walden's generalization, $\Lambda^\circ\eta_0$ = constant. In effect, for a completely dissociated electrolyte the conductance should be a function of the viscosity of the solvent. For UO_2SO_4 aqueous solution, however, a plot of $(\Lambda\eta_0)_{t^\circ C.}/(\Lambda\eta_0)_{0^\circ C.}$ *vs.* t°C., Fig. 2, gives a curve with a negative slope, indicating that fewer ions are present to carry the current at the more elevated temperatures than at lower temperatures. This indicates that there is an increase in association due perhaps to the decreased dielectric strength of the solvent at the higher temperatures.

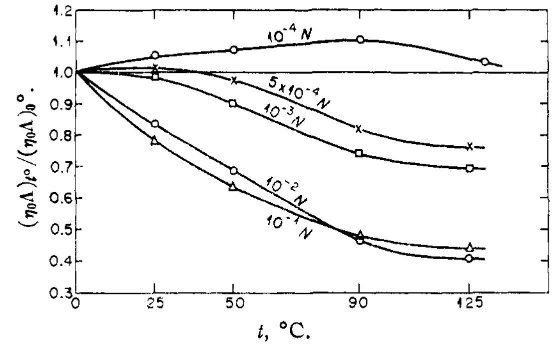

Fig. 2.—$\eta_0\Lambda$ of uranyl sulfate as a function of t, °C.

Conductometric Titrations.—It was desirable to have information concerning the variation of conductivity as a function of the ratio, UO_3/H_2SO_4, in order to determine both the characteristics of the curve and the titrimetric end-point. Uranyl sulfate solutions containing dissolved UO_3 were titrated at 25° with H_2SO_4. Clearly defined end-points were obtained in all cases by plotting the conductivity *vs.* ml. of standard acid added. These plots are shown in Fig. 3. The equivalent conductance in each case is in good agreement with that obtained in our previous work and a comparison of the conductometric end-point with the calculated stoichiometric end-point, given in Table III, shows good agreement.

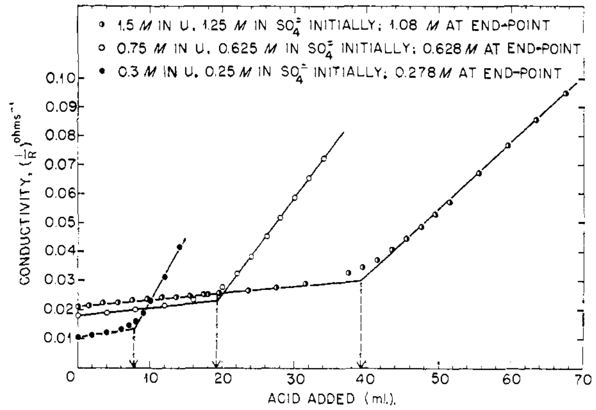

Fig. 3.—Conductometric titration of UO_3 in UO_2SO_4 solution with 1.281 N H_2SO_4; cell constant 0.501.

TABLE III

Initial U concn.	0.3 M	0.75 M	1.5 M
Calcd. vol. of acid (stoich. end-point)	7.81	19.52	39.03
Exptl. vol. of acid (conduct. end-point)	7.8	19.4	39.3

It is concluded that uranyl oxide behaves as a weak base in aqueous solution and shows a strong buffering action, as indicated by the small change in conductivity upon addition of sulfuric acid until the stoichiometric end-point is reached.

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(11) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 2nd ed., Reinhold Publ. Corp., New York, N. Y., 1950, p. 147.

(12) C. W. Davies, "The Conductivity of Solutions," 2nd ed., Chapman & Hall, Ltd., London, 1933, p. 109.

(13) S. Ahrland, *Acta Chem. Scand.*, **5**, 1151 (1951).