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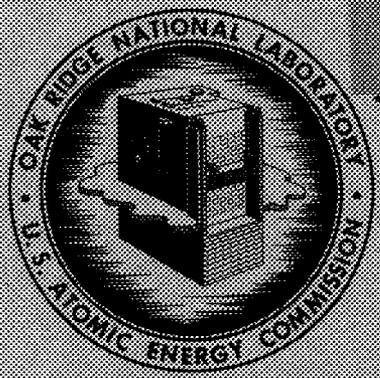
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HYDROLYSIS OF U(VI): ACIDITY MEASUREMENTS IN
 CHLORIDE SOLUTIONS AND ABSORPTION SPECTRA
 IN CHLORIDE AND PERCHLORATE SOLUTIONS

R. M. Rush
 J. S. Johnson
 K. A. Kraus

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R. M. Rush, J. S. Johnson, and K. A. Kraus

Page	Errata
1	Under ACIDITY MEASUREMENTS (C), <i>for</i> . . . pH Electrode No. 142138). <i>read</i> . . . pH Electrode No. 124138).
3	Table 1, column 3, line 30, <i>for</i> 1.9999, <i>read</i> 0.9999
7	Table 2, column 1, line 5, <i>for</i> 1.054 ± 0.075 , <i>read</i> 1.053 ± 0.075 ; line 7, <i>for</i> 1.011 ± 0.082 , <i>read</i> 1.101 ± 0.082 ; column 6, line 2, <i>for</i> 0.0082^a , <i>read</i> 0.0116^a
9	Table 3, column 6, line 6, <i>for</i> 0.0218^b , <i>read</i> 0.0281^b
10	Table 4, column 1, line 2, <i>for</i> 0.666 ± 0.06 , <i>read</i> 0.666 ± 0.060 ; column 3, line 6, <i>for</i> 0.998 ± 0.008 , <i>read</i> 0.999 ± 0.008 ; column 4, line 2, <i>for</i> 0.2 ± 1.1 , <i>read</i> -0.2 ± 1.1

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ABSTRACT

In separate publications, the authors have presented interpretations of acidity data (based on emf measurements) and optical absorption measurements of hydrolyzed U(VI) solutions in chloride and perchlorate media. In this report they give the primary data and a description of the computational programs used to analyze the acidity measurements.

INTRODUCTION

A study of the hydrolysis of U(VI) in chloride and perchlorate media by ultracentrifugation and acidity measurements has recently been published.¹ It seems likely that workers with special interest in the topic might find useful a more detailed presentation of the acidity data than was given there. This report contains tables of results obtained with cells having a liquid junction, which was the basis of the interpretation earlier reported, and without liquid junction. In addition, optical absorption curves of hydrolyzed U(VI) chloride and perchlorate solutions in the region 3650 to 5000 Å are presented.

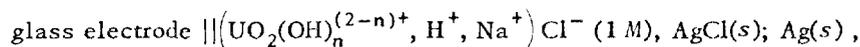
Some details of the least squares program by which acidity measurements were analyzed are given.

ACIDITY MEASUREMENTS

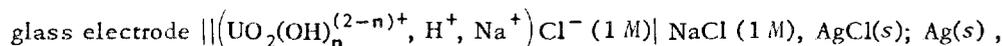
Acidity measurements were carried out at 25.0°C with a vibrating reed electrometer.² The cell was arranged so that three electrodes were immersed in the solution:

- (A) A Beckman No. 41262 glass electrode with a silver-silver chloride inner electrode and with the inner buffer solution replaced by 0.1 M HCl.
- (B) A silver-silver chloride electrode of the thermal-electrolytic type, prepared as outlined by Taniguchi and Janz.³
- (C) A dual-glass junction filled with 1 M NaCl and containing a silver-silver chloride electrode (these are parts of Leeds and Northrup Miniature pH Electrode No. ~~142138~~ 124138).

The potentials of the nonjunction cell,



and of the junction cell,



¹R. M. Rush, J. S. Johnson, and K. A. Kraus, *Inorg. Chem.* **1**, 378 (1962).

²K. A. Kraus, R. W. Holmberg, and C. J. Borkowski, *Anal. Chem.* **22**, 341 (1950).

³H. Taniguchi and G. J. Janz, *J. Electrochem. Soc.* **104**, 123 (1957).

were obtained from the potential of the silver-silver chloride electrode in the solution (B) vs the glass electrode (A) and the junction electrode (C).

For the junction measurements the acidity c_H (moles H^+ /liter) was taken to be given by

$$\log c_H = \log (c_H)_{Std} + \frac{E_{U(VI) Soln} - E_{Std}}{59.16} \quad (1a)$$

The nonjunction measurements yield

$$\begin{aligned} \log \frac{a_{\pm HCl}^2}{(a_{\pm HCl})_{Std}^2} &= \log \frac{c_H c_{Cl}}{(c_H c_{Cl})_{Std}} \cdot \frac{y_{\pm HCl}^2}{(y_{\pm HCl})_{Std}^2} \\ &= \frac{E_{U(VI) Soln} - E_{Std}}{59.16}, \end{aligned} \quad (1b)$$

where c_{Cl} is the free chloride concentration (moles/liter). With the assumption that the activity coefficients of HCl are the same in the U(VI) solutions and the standard solutions and that free chloride equals stoichiometric chloride (i.e., that the fraction of total chloride complexed by the U(VI) species is unimportant), an expression for $\log c_H$ may also be obtained from Eq. (1b). The potential E , expressed in millivolts, increases with acidity in this convention. The slope, $\Delta E / \Delta \log c_H$, was found to approach the ideal value, 59.16 mv, as the acidity decreased, and this value was therefore used to compute the acidities of the uranium solutions (which were mostly between 10^{-3} and 10^{-5} M H^+) from the potentials and concentrations of the standards.

There was a slight drift of electrode potentials of standards (from 0.1 to 0.2 mv/day); consequently, standard acids (ca. 0.003 or 0.001 M H^+ with NaCl added to give 1 M total chloride) were measured each day, usually before and after a series.

The most concentrated (0.1 M) U(VI) solutions were prepared by weight from unhydrolyzed uranium(VI) chloride (containing known excess acid), NaOH, and NaCl stock solutions, and the other concentrations were prepared by weight dilution with 1 M NaCl. The hydroxyl numbers n (number of hydroxides bound per uranyl) were obtained from the stoichiometry with a correction for free acid.

The results of these measurements are given in Table 1 and Fig. 1.

The differences between junction and nonjunction measurements (Table 1 and Fig. 1) are negligible for U(VI) concentrations ≤ 0.01 M; for 0.1 and 0.03 M U(VI), if the junction potential is neglected, the differences indicate some complexing of chloride both by UO_2^{2+} and by at least one hydrolyzed species.

It might be expected that estimates of the extent of chloride complexing could be made from the potentials between the two silver-silver chloride electrodes, at least in 0.03 and 0.1 M U(VI) solutions. Such estimates would require that an estimate of junction potential be made and that activity coefficient variations have only a small effect on the potentials. We found that junction potentials for the cracked glass junction used could be computed by the Henderson Equation within about 0.2 mv for HCl-NaCl solutions of known concentration and for different known concentrations of NaCl on the two sides of the junction. However, with the uranyl solutions in question estimates are hampered by a lack of knowledge of

Table 1. Acidity Measurements on Hydrolyzed U(VI) in 1 M Total Chloride

n	(c_M) _{total}	c_{Cl}	$-\log c_H$ (Junction)	$-\log c_H c_{Cl}$ (Nonjunction)	n	(c_M) _{total}	c_{Cl}	$-\log c_H$ (Junction)	$-\log c_H c_{Cl}$ (Nonjunction)
0.1446	0.000990	1.0003	4.019	4.020	0.7082	0.010329	1.0000	4.094	4.099
0.1844	0.000991	1.0002	4.061	4.061	0.8054	0.010335	1.0002	4.167	4.170
0.2628	0.000990	1.0003	4.183	4.188	0.9024	0.010344	1.0002	4.247	4.249
0.3503	0.000990	1.0003	4.265	4.270	1.0050	0.010365	1.0000	4.346	4.368
0.4389	0.000996	1.0003	4.345	4.349	1.0815	0.010366	1.0000	4.420	4.423
0.5313	0.000990	1.0003	4.423	4.427	1.1769	0.010361	0.9997	4.525	4.527
0.6330	0.000990	1.0003	4.500	4.504	1.2732	0.010360	0.9999	4.645	4.648
0.7280	0.000988	1.0003	4.564	4.566	1.3593	0.010495	0.9974	4.773	4.783
0.8223	0.000993	1.0003	4.631	4.631	1.3620	0.010535	0.9991	4.774	4.834
0.9181	0.000992	1.0000	4.678	4.678	1.4302	0.010487	0.9976	4.887	4.899
1.0179	0.000994	1.0000	4.764	4.769	0.0718	0.03232	1.0004	3.112	3.124
1.0928	0.000995	1.0000	4.826	4.826	0.1147	0.03231	1.0000	3.236	3.249
1.1864	0.000994	1.0000	4.910	4.910	0.2090	0.03231	1.0005	3.393	3.408
1.2812	0.000994	1.0000	4.994	4.995	0.3049	0.03229	1.0004	3.514	3.527
1.3656	0.001007	0.9998	5.101	5.102	0.4013	0.03237	1.0003	3.603	3.612
1.3685	0.001013	0.9999	5.084	5.085	0.4995	0.03232	1.0003	3.686	3.695
1.4351	0.001007	0.9998	5.208	5.208	0.6064	0.03225	0.9996	3.768	3.780
0.1094	0.003091	1.0003	3.721	3.727	0.7048	0.03226	0.9995	3.846	3.859
0.1477	0.003102	1.0002	3.801	3.806	0.8024	0.03235	0.9998	3.929	3.937
0.2339	0.003099	1.0003	3.936	3.941	0.8998	0.03236	1.0005	4.020	4.042
0.3257	0.003092	1.0003	4.029	4.034	1.0029	0.03241	1.0002	4.127	4.156
0.4187	0.003115	1.0003	4.106	4.106	1.0797	0.03243	0.9999	4.204	4.244
0.5142	0.003099	1.0003	4.186	4.188	1.0800	0.03236	1.0000	4.206	4.245
0.6186	0.003094	1.0003	4.265	4.266	1.2721	0.03238	0.9996	4.469	4.520
0.7152	0.003094	1.0003	4.338	4.338	1.3738	0.03249	1.0000	4.734	4.705
0.8114	0.003103	1.0003	4.408	4.411	0.0624	0.10108	1.0006	2.833	2.839
0.9076	0.003101	1.0001	4.479	4.480	0.1078	0.10091	0.9994	2.950	2.984
1.0095	0.003107	1.0000	4.558	4.562	0.2038	0.10110	1.0008	3.129	3.163
1.0853	0.003113	1.0000	4.631	4.632	0.3011	0.10099	1.0007	3.247	3.281
1.1801	0.003109	1.0000 0.9999	4.726	4.726	0.3981	0.10111	1.0002	3.342	3.375
1.2758	0.003107	1.0000	4.831	4.832	0.4969	0.10100	1.0003	3.426	3.458
1.3614	0.003148	0.9992	4.937	4.938	0.6041	0.10097	0.9981	3.514	3.537
1.4318	0.003149	0.9993	5.051	5.052	0.7029	0.10091	0.9979	3.605	3.627
0.0864	0.010309	1.0004	3.402	3.406	0.8008	0.10105	0.9989	3.685	3.708
0.1265	0.010330	1.0002	3.512	3.516	0.8985	0.10125	1.0016	3.778	3.818
0.2179	0.010343	1.0003	3.655	3.659	1.0019	0.10133	1.0005	3.894	3.940
0.3124	0.010314	1.0003	3.757	3.760	1.0791	0.10118	1.0000	3.986	4.043
0.4073	0.010370	1.0003	3.848	3.852	1.1748	0.10121	0.9978	4.110	4.177
0.5045	0.010330	1.0003	3.931	3.935	1.2716	0.10128	0.9988	4.294	4.365
0.6104	0.010301	1.0001	4.016	4.019					

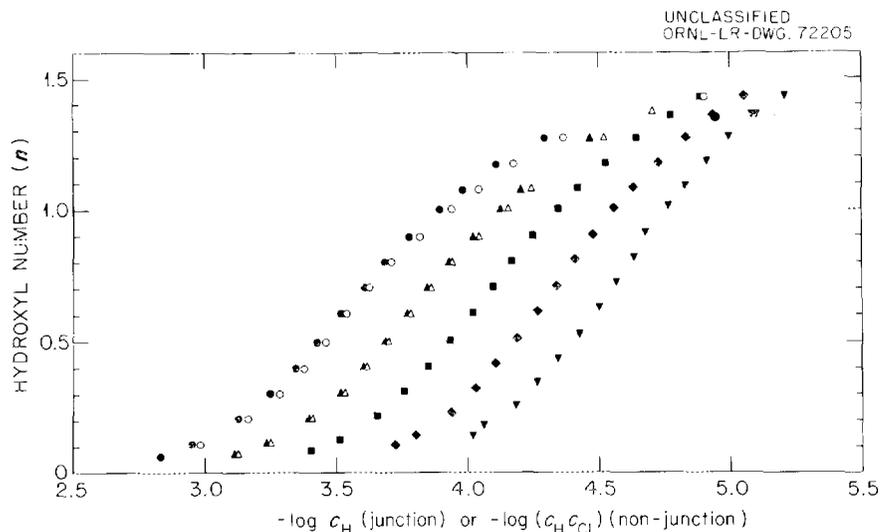


Fig. 1. Hydrolysis of U(VI) in 1 M Chloride. Junction measurements are shown as solid symbols and nonjunction measurements as open symbols. Only the junction points are shown where the difference is 0.006 in $\log c_H$ or less. Symbols represent M U(VI) as: ●, 0.1; ▲, 0.03; ■, 0.01; ◆, 0.003; ▼, 0.001.

the mobilities of the hydrolyzed and complexed U(VI) species. Estimates with the data available⁴ gave values in the range 0.1–1 mv. An estimate of the effects that might be expected from activity coefficient variations, based on an analogy with the system $BaCl_2-HCl-H_2O$,⁵ came to about 0.5–1.0 mv. Since the total difference in potential between the silver–silver chloride electrodes amounted to at most 3.5 mv, and since such estimates of junction potential and nonideality are very uncertain at the present state of knowledge, we conclude that only qualitative information concerning chloride complexing may be obtained from the data. This conclusion is confirmed by the results of a computation assuming constancy of activity coefficients but in which corrections for junction potentials were attempted; this computation indicated chloride complexing, the extent being greater in solutions containing relatively more species expected to bind chloride, but the correlation between number of chlorides bound per U(VI) in the 0.03 and 0.1 M U(VI) solutions was poor.

COMPUTATION

Hydrolysis Constant Program

In the interpretation of emf results, there are two interlocking problems: to identify the species present in appreciable amounts and to find the formation quotients $k_{i,j}$ for these species which give the

⁴R. D. Brown *et al.*, *J. Am. Chem. Soc.* **76**, 1532 (1954); C. A. Kraus, USAEC A-360 (Oct. 26, 1942).

⁵H. S. Harned and R. Gary, *J. Am. Chem. Soc.* **76**, 5924 (1954).

best fit to the data. The formation quotients are defined as

$$k_{i,j} = \frac{k_{i,j}^0}{G_{i,j}} = \frac{[(\text{UO}_2)_i(\text{OH})_j^{(2i-j)^+}][\text{H}^+]^j}{[\text{UO}_2^{2+}]^i} = \frac{c_{i,j} c_{\text{H}}^j}{c_{1,0}^i}, \quad (2)$$

where $k_{i,j}^0$ is the formation constant, $G_{i,j}$ is the appropriate activity coefficient ratio, and brackets and the symbol c indicate concentration in moles per liter. The decision on which species are present depends on which scheme, when the best values of quotients have been determined, gives the best representation of the data, and is consistent with other information (e.g., results of equilibrium ultracentrifugation) available.

The concentration dependence of hydroxyl number at a fixed acidity immediately indicates that polynuclear products must be present in hydrolyzed U(VI) solutions. A convenient procedure to obtain the best values of $k_{i,j}$ for a given scheme (the word "scheme" is used here to denote a set of postulated species) is a least squares computation. Our program for effecting this is written in IBM 709 FORTRAN language and consists of a general least squares program⁶ and a subroutine which calculates the dependent variable (hydroxyl number n) for a given set of formation quotients (guesses on the first cycle) and the independent variables [acidity c_{H} and total uranium concentration $(c_{\text{M}})_{\text{total}}$]. In the least squares computation, the partial derivatives $(\partial n / \partial k_{i,j})$ are approximated numerically by incrementing the formation quotients and recomputing n . These derivatives are then used to form the normal equations⁷ which are solved directly for the changes in the constants. New values of the formation constants are then calculated, and the process is repeated with these new values. This cyclic procedure is continued until the standard deviation (in hydroxyl number) is constant and the changes in the constants become negligible.

The Newton-Raphson method for the solution of equations⁸ is used by the subroutine to calculate the free uranyl concentration $c_{1,0}$ to within one part in 10^6 . The method is applied to the equation

$$f(c_{1,0}) = \sum i c_{i,j} - (c_{\text{M}})_{\text{total}} = \sum i \frac{k_{i,j} c_{1,0}^i}{c_{\text{H}}^i} - (c_{\text{M}})_{\text{total}} = 0. \quad (3)$$

The calculated hydroxyl number then is $\sum j c_{i,j} / (c_{\text{M}})_{\text{total}}$. An alternate subroutine was written in which the acidity c_{H} is the dependent variable and the hydroxyl number n and total uranium concentration $(c_{\text{M}})_{\text{total}}$ are the independent variables. The same method is used to solve the following equations for the acidity c_{H} and free uranyl concentration $c_{1,0}$ to within one part in 10^6 :

$$F(c_{\text{H}}, c_{1,0}) = \sum j c_{i,j} - n(c_{\text{M}})_{\text{total}} = \sum j \frac{k_{i,j} c_{1,0}^i}{c_{\text{H}}^i} - n(c_{\text{M}})_{\text{total}} = 0, \quad (4)$$

$$G(c_{\text{H}}, c_{1,0}) = \sum i c_{i,j} - (c_{\text{M}})_{\text{total}} = \sum i \frac{k_{i,j} c_{1,0}^i}{c_{\text{H}}^i} - (c_{\text{M}})_{\text{total}} = 0. \quad (5)$$

⁶W. R. Busing and H. A. Levy, ORNL TM-271 (1962).

⁷H. Margenau and G. M. Murphy, *The Mathematics of Physics and Chemistry*, 2d ed., pp 517-19, Van Nostrand, New York, 1956.

⁸*Ibid.*, pp 492-93.

Converged values of formation quotients obtained on the basis of both of these procedures varied only slightly (see Table 2). Most of the results given in this report were obtained with a version of the program utilizing the values of $k_{i,j}$ directly. More recent versions utilize $\log k_{i,j}$.

Anion Complexing

When complexing by a univalent ligand L^- occurs, interpretation of the acidity data by the above procedure actually gives rather than $k_{i,j}$ an apparent formation quotient

$$k_{i,j}^a = \frac{(c_{i,j} + \sum_{l=1} c_{i,j,l}) c_H^j}{(c_{1,0} + \sum_{l=1} c_{1,0,l})^i}, \quad (6)$$

where $c_{i,j,l}$ is the concentration of $(UO_2)_i(OH)_j L_l^{(2i-j-l)^+}$ and $c_{1,0,l}$ is the concentration of $UO_2 L_l^{(2-l)^+}$. If the complex formation constant is

$${}^{i,j}k_{i,j,l} = \frac{c_{i,j,l}}{c_{i,j} c_L^l}, \quad (7)$$

where c_L is the concentration of free ligand, Eq. (6) becomes

$$k_{i,j}^a = k_{i,j} \frac{(1 + \sum_{l=1} {}^{i,j}k_{i,j,l} c_L^l)}{(1 + \sum_{l=1} {}^{1,0}k_{1,0,l} c_L^l)^i}, \quad (8)$$

where $k_{i,j}$ is the formation quotient defined by Eq. (2). In these experiments, free chloride varied only slightly in the different solutions, and therefore the value of $k_{i,j}^a$ is constant to a good approximation. In cases where a large fraction of total anion is bound, however, it would be desirable to take complexing into consideration.

A variation of the computer program provides for the inclusion of complexed species and the calculation of their overall formation constants. In this case the Newton-Raphson method is used to solve the following equations for $c_{1,0,0}$ and c_L to within one part in 10^6 :

$$\begin{aligned} F(c_L, c_{1,0,0}) &= \sum_{i,j,l} i c_{i,j,l} - (c_M)_{\text{total}} \\ &= \sum_{i,j,l} i \frac{k_{i,j,l} c_{1,0,0}^i c_L^l}{c_H^j} - (c_M)_{\text{total}} = 0, \end{aligned} \quad (9)$$

$$\begin{aligned} G(c_L, c_{1,0,0}) &= \sum_{i,j,l} l c_{i,j,l} + c_L - (c_L)_{\text{total}} \\ &= \sum_{i,j,l} l \frac{k_{i,j,l} c_{1,0,0}^i c_L^l}{c_H^j} + c_L - (c_L)_{\text{total}} = 0, \end{aligned} \quad (10)$$

where $(c_L)_{\text{total}}$ is the stoichiometric ligand concentration and

$$k_{i,j,l} = \frac{c_{i,j,l} c_H^j}{c_{1,0,0}^i c_L^l} \quad (11)$$

The calculated hydroxyl number is then $\sum_{i,j,l} j c_{i,j,l} / (c_M)_{\text{total}}$. In all of the programs, interpretation of the data obtained with a nonjunction cell includes provision for converting the product $c_H c_{Cl}$ [obtained from Eq. (1b) by assuming that the activity coefficient ratio $\gamma_{\pm HCl}^2 / (\gamma_{\pm HCl})_{\text{Std}}^2$ is unity] to c_H through division by c_L .

RESULTS

Hydrolyzed Uranyl Chloride

Analysis of the junction measurements by the program have been presented elsewhere.¹ Briefly, of those tested, the scheme⁹ consisting of (2,2)-(3,4)-(3,5) and of (1,1)-(2,2)-(3,4)-(3,5) gave the best fit to the data. The results and standard deviations are summarized in Table 2. The schemes fit both sets of measurements satisfactorily, and no conclusive answer concerning whether the (1,1) species is present in

⁹The species are identified by the values of i and j of Eq. 2; e.g., (2,2) corresponds to the species $(\text{UO}_2)_2(\text{OH})_2^{2+}$ and (3,5) to the species $(\text{UO}_2)_3(\text{OH})_5^+$.

Table 2. Tests of Various Hydrolysis Schemes with Acidity Measurements in 1 M Chloride Solutions; Values Given Are the Formation Quotients and Their Standard Errors (\pm) for the Species Assumed and the Standard Deviation of the Fit to the Observed Data (σ)

$k_{2,2} \times 10^6$	$k_{3,4} \times 10^{13}$	$k_{3,5} \times 10^{17}$	Other		σ (in n)
			(i,j)	$k_{i,j}$	
Junction Measurements					
0.668 \pm 0.015	4.72 \pm 0.13	1.048 \pm 0.023			0.0098
0.692 \pm 0.013	4.70 \pm 0.14	1.112 \pm 0.021			0.0082 ^a 0.0116
0.629 \pm 0.018	4.68 \pm 0.12	1.063 \pm 0.023	(1,1)	$(2.30 \pm 0.69) \times 10^{-6}$	0.0092
1.099 \pm 0.053		1.80 \pm 0.10			0.0437
1.054 \pm 0.075 1.053		1.82 \pm 0.11	(1,1)	$(2.6 \pm 3.2) \times 10^{-6}$	0.0438
0.91 \pm 0.11	-0.7 \pm 1.7		(4,6)	$(0.70 \pm 0.12) \times 10^{-18}$	0.0485
1.011 \pm 0.082 1.101		1.80 \pm 0.11	(3,3)	$(-3 \pm 69) \times 10^{-11}$	0.0440
Nonjunction Measurements					
0.687 \pm 0.015	3.83 \pm 0.13	1.006 \pm 0.023			0.0104
0.659 \pm 0.019	3.81 \pm 0.12	1.013 \pm 0.023	(1,1)	$(1.67 \pm 0.73) \times 10^{-6}$	0.0102
1.045 \pm 0.065		1.587 \pm 0.083	(1,1)	$(0.8 \pm 2.8) \times 10^{-6}$	0.0390
0.966 \pm 0.068		1.10 \pm 0.14	{ (1,1) (2,3)	{ $(-3.4 \pm 2.8) \times 10^{-6}$ $(0.92 \pm 0.26) \times 10^{-11}$	0.0371

^aValues obtained with $-\log c_H$ as dependent variable and n and $(c_M)_{\text{total}}$ as independent variables. The standard deviation σ is thus in terms of $-\log c_H$.

appreciable amounts under these conditions is obtained, either on the basis of standard deviations or of deviations between observed hydroxyl numbers and values computed from the quotients listed. The species fractions $F_{i,j} = (ic_{i,j}/c_M)_{\text{total}}$ in the various species for the (2,2)-(3,4)-(3,5) scheme at three uranium concentrations are shown in Fig. 2.

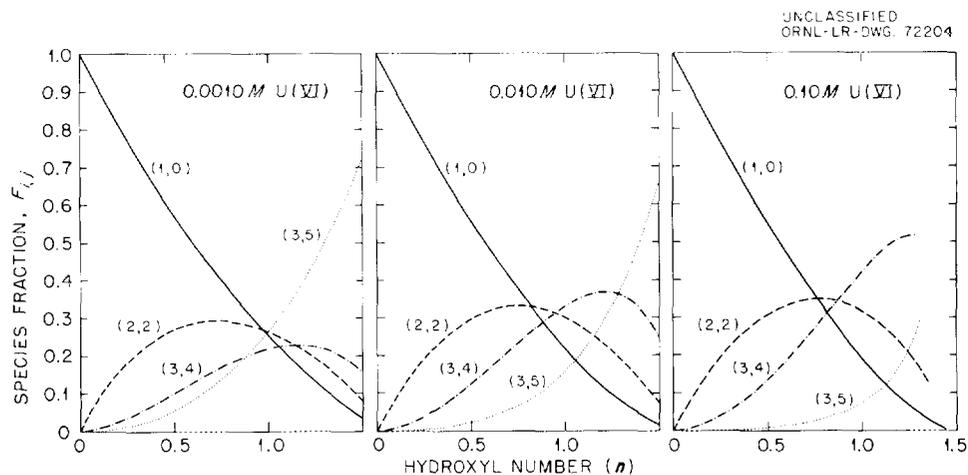


Fig. 2. Fraction Curves for Hydrolyzed U(VI) Chloride Solutions. Formation constants are $k_{2,2} = 0.67 \times 10^{-6}$, $k_{3,4} = 4.7 \times 10^{-13}$, and $k_{3,5} = 1.0 \times 10^{-17}$.

Many studies¹⁰ have indicated that unhydrolyzed complex UO_2Cl^+ is present in appreciable amounts under our experimental conditions; the greater importance of the (3,4) species in chloride than in perchlorate media¹ suggests that it also complexes chloride. From spectrophotometric measurements,¹¹ it appears that the (2,2) and (3,5) species do not complex much, if any, chloride. We therefore attempted to interpret the acidity data by Eqs. (9-11), with inclusion of chloride complexed species of the (1,0) and (3,4) species. The uncertainties of the formation quotients obtained supported the statement made earlier on the basis of potential differences between junction and nonjunction silver chloride electrodes that our measurements are not sensitive enough to chloride complexing to yield information about it.

Hydrolyzed Uranyl Perchlorate

Tests of various hydrolytic schemes for U(VI) in 1 M NaClO_4 by the computational program, using the acidity measurements of Ahrland,¹² have been reported,¹ and tests using acidity and optical absorption measurements of our own are to be published.¹¹ The results shown in Table 3 indicate that the (3,4) species is not present, at least in significant amounts, in perchlorate solutions, and that the data can be

¹⁰J. Bjerrum, G. Schwarzenbach, and L. G. Sillén, *Stability Constants*, Part II, The Chemical Society, London (1958).

¹¹R. M. Rush and J. S. Johnson, submitted for publication in the *Journal of Physical Chemistry*.

¹²S. Ahrland, *Acta Chem. Scand.* **3**, 374 (1949).

Table 3. Tests of Various Hydrolysis Schemes Based on Acidity Measurements of Ahrland¹² in 1 M Perchlorate Solutions; Values Given Are the Formation Quotients and Their Standard Errors (\pm) for the Species Assumed and the Standard Deviation of the Fit to the Observed Data (σ)

$k_{2,2} \times 10^6$	$k_{3,4} \times 10^{13}$	$k_{3,5} \times 10^{17}$	Other		σ (in n)
			(i,j)	$k_{i,j}$	
1.100 \pm 0.032		1.835 \pm 0.066			0.0313
0.996 \pm 0.065		2.01 \pm 0.15			0.0339 ^a
1.138 \pm 0.035		1.776 \pm 0.069			0.0288 ^b
1.093 \pm 0.048	0.08 \pm 0.46	1.82 \pm 0.10			0.0314
1.197 \pm 0.090	-2.42 \pm 0.80	2.51 \pm 0.23			0.0295 ^a
1.050 \pm 0.050	1.13 \pm 0.48	1.58 \pm 0.10			0.0218 ^b 0.0281^b
0.837 \pm 0.042		1.856 \pm 0.054	(1,1)	$(1.74 \pm 0.24) \times 10^{-5}$	0.0251
1.104 \pm 0.033		1.926 \pm 0.083	(2,1)	$(5.3 \pm 3.0) \times 10^{-4}$	0.0309
		5.07 \pm 0.92	(2,1)	$(1.65 \pm 0.30) \times 10^{-2}$	0.1229

^aGlass electrode measurements only.

^bQuinhydrone electrode measurements only.

fitted with either a (1,1)-(2,2)-(3,5) or a (2,2)-(3,5) scheme. The "core-link" model,¹³ postulated¹⁴ on the basis of Ahrland's measurements, was shown to be inconsistent with ultracentrifugation results.

The species UO_2OH^+ has been postulated by a number of workers, but in many cases, their conclusions are suspect because polymeric species were not considered. The question of the importance of the (1,1) in both chloride and perchlorate solutions at these concentrations and at 25°C is unresolved by our results. The work of Baes and Meyer¹⁵ indicates that it is present in substantial amounts at 94°C in nitrate solution, but the formation quotient they give for 25° is very small.

Another species, $(\text{UO}_2)_2(\text{OH})^{3+}$, has been postulated on the basis of acidity measurements in concentrated, slightly hydrolyzed uranyl perchlorate solutions.¹⁶ We have tested different interpretations of these data by the Hydrolysis Constant Program, and the results are shown in Table 4. It can be seen that a better fit is obtained with either a (1,1)-(2,2) or a (2,1)-(2,2) scheme than if only the (2,2) is postulated. From this, one might conclude that one of these species must contribute substantially to the hydrolysis. However, the acidities of the solutions are high (up to ca. 0.2 M), and the difficulties of accurate measurements of pH in this range cast some doubt on this conclusion. It is our view, from this survey and from the wide range of values quoted for $k_{1,1}$ by different workers, that further experiments, especially designed to elucidate this point (e.g., tracer or other high dilution experiments), will be necessary to decide the contribution of the (1,1) or the (2,1) species to room temperature U(VI) hydrolysis.

¹³L. G. Sillén, *Acta Chem. Scand.* **8**, 299, 318 (1954).

¹⁴S. Ahrland, S. Hietanen, and L. G. Sillén, *Acta Chem. Scand.* **8**, 1907 (1954); see also F. J. C. Rossotti, II, Rossotti, and L. G. Sillén, *Acta Chem. Scand.* **10**, 203 (1956).

¹⁵C. F. Baes, Jr., and N. J. Meyer, *Inorg. Chem.* **1**, 780 (1962).

¹⁶S. Hietanen and L. G. Sillén, *Acta Chem. Scand.* **13**, 1828 (1959).

Table 4. Tests of Various Hydrolysis Schemes Based on Acidity Measurements of Hietanen and Sillén¹⁶ in Perchlorate Self-Medium; Values Given Are the Formation Quotients and Their Standard Errors (\pm) for the Species Assumed and the Standard Deviation of the Fit to the Observed Data (σ); Only the Measurements with Glass Electrode Were Used

Under the conditions of these experiments, the (3,4) and (3,5) species are present in such small amount that their formation quotients are undetermined.

$k_{1,1} \times 10^4$	$k_{2,1} \times 10^4$	$k_{2,2} \times 10^6$	$k_{3,4} \times 10^{13}$	$k_{3,5} \times 10^{17}$	σ (in n)
1.4 M U(VI), 3 M (Na)ClO₄					
	2.01 \pm 0.10	0.474 \pm 0.038	1.2 \pm 1.4		0.0016
	1.94 \pm 0.06	0.507 \pm 0.009			0.0015
	2.00 \pm 0.09	0.484 \pm 0.028		23 \pm 26	0.0016
2.87 \pm 0.14		0.341 \pm 0.040	0.2 \pm 1.1		0.0016
		1.048 \pm 0.036		-370 \pm 50	0.0054
0.4 M U(VI), 1 M (Na)ClO₄					
	1.21 \pm 0.14	0.998 0.999 \pm 0.008			0.0020
0.666 \pm 0.06		0.874 \pm 0.016			0.0017
		1.088 \pm 0.021		-8.9 \pm 3.4	0.0040

SPECTROPHOTOMETRIC MEASUREMENTS

Spectrophotometric measurements have been carried out on 21 U(VI) solutions in chloride media and 9 solutions in perchlorate media. The compositions of these solutions are shown in Table 5.

The correlation of the optical absorption data with the hydrolysis schemes discussed earlier is reported elsewhere.¹¹ For those having an interest in the data, the spectra are shown in Figs. 3, 4, and 5. The molar absorptivity E is shown as a function of wavelength, where $E = A/(c_M)_{\text{total}}b$, $A = \log(I_0/I)$, I is the intensity of light transmitted by the solution and I_0 of that transmitted by a reference solution (1 M NaCl or 1 M NaClO₄), $(c_M)_{\text{total}}$ is the total stoichiometric U(VI) concentration in moles per liter, and b is the path length in cm. The absorbance A at 25 Å intervals was obtained from the spectrophotometer chart and converted to molar absorptivity E . These data are available in tabular form or as IBM punched cards.

The interpretation of these data and acidity measurements in perchlorate media¹¹ supports the statement that the (2,2) and (3,5) species do not complex much, if any, chloride and that the (3,4) species appears in appreciable amounts in chloride but not in perchlorate media. Formation quotients for the species in perchlorate media derived from these spectrophotometric and acidity measurements are also reported.¹¹

ACKNOWLEDGMENT

We wish to express our indebtedness to Neva Harrison for valuable technical assistance.

Table 5. Composition of U(VI) Solutions for Spectrophotometry (Anion Concentration Made Up with Sodium Salt)

$[c_{U(VI)}]_{total}$ (moles/liter)	n	Total Anion Concentration
Chloride		
0.1009	0.381	1.002
0.1008	0.674	1.000
0.1003	0.899	0.999
0.01003	0.000	0.995
0.01005	0.124	0.999
0.01007	0.213	0.999
0.01007	0.303	0.999
0.01004	0.416	0.998
0.01006	0.509	0.998
0.01003	0.611	0.997
0.01003	0.713	0.997
0.01006	0.789	0.998
0.01006	0.889	0.997
0.01007	0.980	0.999
0.01008	1.070	0.998
0.01001	1.205	0.997
0.01002	1.298	0.997
0.000997	0.450	1.000
0.001001	0.734	1.000
0.001007	0.994	1.000
0.000998	1.214	1.000
Perchlorate		
0.1000	0.420	0.982
0.01009	0.000	1.093
0.00998	0.429	1.000
0.01007	0.623	0.997
0.01005	0.806	0.994
0.000996	0.454	1.001
0.001004	0.638	1.001
0.001002	0.816	1.001
0.001011	1.003	1.000

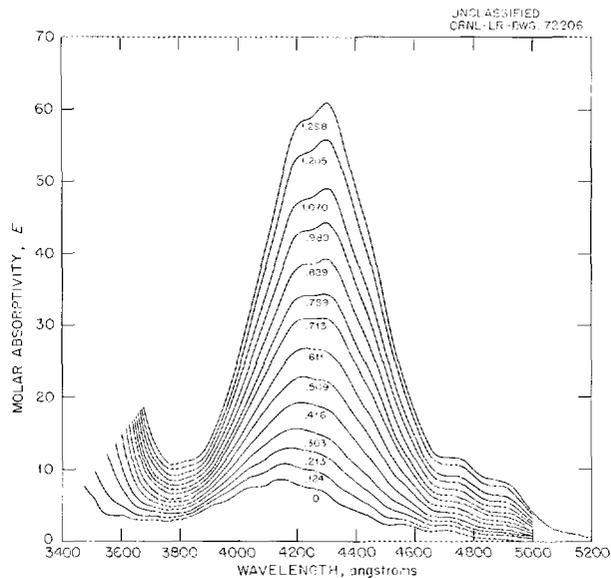


Fig. 3. Absorption Spectra of 0.01 M U(VI) Solutions in 1 M Chloride. Each curve is identified by the hydroxyl number n of the solution.

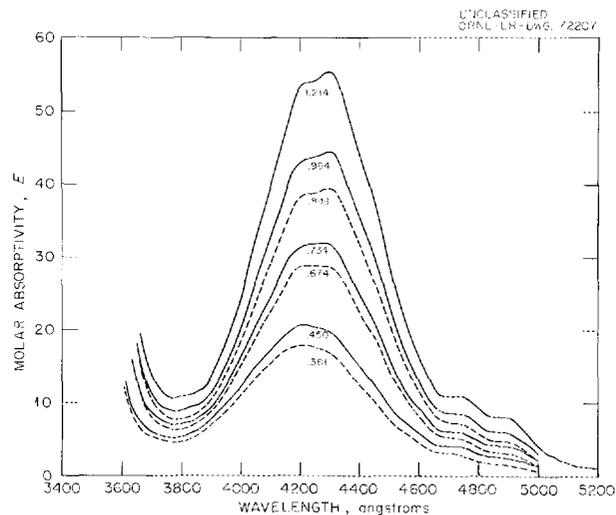


Fig. 4. Absorption Spectra of 0.001 M (—) and 0.1 M (---) U(VI) Solutions in 1 M Chloride. Each curve is identified by the hydroxyl number n of the solution.

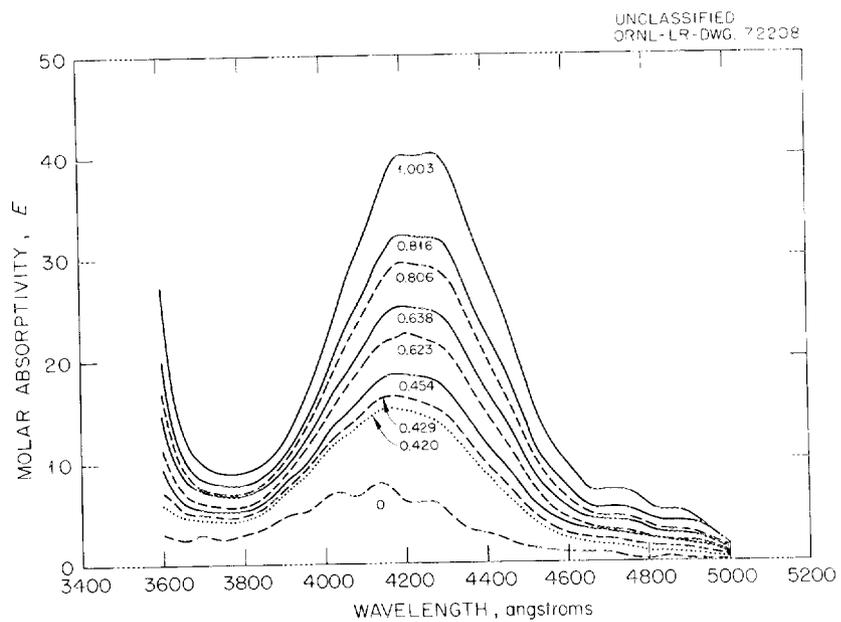


Fig. 5. Absorption Spectra of 0.001 M (—), 0.01 M (---), and 0.1 M (·····) U(VI) Solutions in 1 M Perchlorate. Each curve is identified by the hydroxyl number n of the solution.

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