differently from the nondeuterated crystals seems to point in this direction.

Even though we do not claim to know all the answers to the electronic structures of $Ni(CN)_4{}^{2-}$ we do think that the basic idea, namely a change in geometry for some of the excited states, is correct. Measurements at liquid helium temperature are planned and should be

of great help in order to settle the outstanding questions.

The Hydrolysis of Thorium(IV) at 0 and 95°[1]

By C. F. BAES, Jr., NORMAN J. MEYER,[2] and C. E. ROBERTS

The hydrolysis of thorium(IV) in 1 m (Na)ClO$_4$ was measured at 0 and 95° to establish better the reactions which occur and their temperature coefficients. Potentiometric measurements were made primarily with the quinhydrone electrode at 0° and with the glass electrode at 95°. Measurements of the solubility of ThO$_2$ as a function of acidity together with the potentiometric results at low hydrolysis were consistent with formation of ThOH^{3+}, Th(OH)$_2{}^{2+}$, and Th$_2$(OH)$_2{}^{6+}$, initial hydrolysis products proposed at 25° by previous investigators. Their results along with the present measurements were compared with numerous possible schemes of hydrolysis products, Th$_x$(OH)$_y{}^{(4x-y)+}$, by means of a general least-squares computer program. Two schemes of four species—(I) x,y: 1,1; 1,2; 2,2; 5,12 and (II) x,y: 1,1; 1,2; 2,3; 6,15—approximate the data, but yield systematic deviations which are similar at all three temperatures. Two schemes of five species—(III) x,y: 1,1; 1,2; 2,2; 3,6; 6,15 and (IV) x,y: 1,1; 1,2; 2,2; 4,8; 6,15—fit the data within the expected experimental error, scheme IV being the better. The assumption of six or more hydrolysis products is not justified by the accuracy of the measurements. The equilibrium quotients found for the formation of the five species in scheme IV from Th^{4+} and H$_2$O were: log $Q_{x,y}$ = (0°) −4.32, −8.48, −5.60, −22.79, and −43.84; (25°) −4.12, −7.81, −4.61, −19.01, and −36.76; (95°) −2.29, −4.50, −2.55, −10.49, and −20.63. The indicated average enthalpy and entropy changes per OH$^-$ bound in the polymeric species were nearly constant at ~7.3 kcal. and ~13.6 cal./°K., respectively.

Thorium(IV) ion, when compared to other tetravalent cations, is unusually resistant to hydrolysis at 25°. At moderate concentrations, its hydrolysis is first detectable at a pH below 3. The hydroxyl number, $\bar{n}$ (*i.e.*, the average number of OH$^-$ ions bound per Th^{4+} ion present) rises rapidly with pH until hydrolytic precipitation occurs at $\bar{n} \sim 2.5$ and pH ~ 4. Thorium hydrolysis thus is accessible to study over a fairly wide range in $\bar{n}$ and over a convenient range in pH.

The hydrolytic behavior of Th^{4+} has been widely investigated at room temperature.[3] Potentiometric studies of Kraus and Holmberg,[4] Hietanen,[5] and Hietanen and Sillén[6] are perhaps the most extensive. At present, however, no generally accepted scheme of hydrolysis products has appeared to account for the observed behavior of this ion. The previous potentiometric studies have made it clear that highly polymerized hydrolysis products Th$_x$(OH)$_y{}^{(4x-y)+}$ are involved, and this is also shown by the preliminary ultra-

centrifuge results of Johnson and Kraus,[7] as well as by cryoscopic measurements of Souchay.[8]

From their results in 1 M NaClO$_4$ at 25°, Kraus and Holmberg[4] concluded that Th(OH)$_2{}^{2+}$ and Th$_2$(OH)$_2{}^{6+}$ definitely were formed. The species ThOH^{3+} was found to be surprisingly unstable compared to UOH^{3+} and PuOH^{3+}. While additional, more polymeric hydrolysis products were evident, Kraus and Holmberg felt that insufficient data were available to establish them reliably.

Hietanen[5] chose to interpret her results in terms of the following "core-link" mechanism of continuous polymerization

$$Th_2(OH)_3{}^{5+}, Th_3(OH)_6{}^{6+}, Th_4(OH)_9{}^{7+} \ldots\ldots Th_x(OH)_{3x-3}{}^{(n+3)+}$$
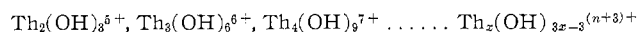
This scheme, however, fails to account properly for the careful measurements of Kraus and Holmberg at low $\bar{n}$ values.

Lefebvre[9] later re-examined these two sets of data and concluded that the following simpler scheme described the hydrolysis process

$$Th(OH)_2{}^{2+}, Th_2(OH)_2{}^{6-}, Th_6(OH)_{12}{}^{8+}$$
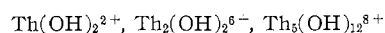
(1) Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corporation.

(2) Summer research participant with the Oak Ridge National Laboratory, 1961–1962, sponsored by the Oak Ridge Institute of Nuclear Studies.

(3) J. Bjerrum, G. Schwarzenbach, and L. G. Sillén, "Stability Constants; Part II, Inorganic Ligands," The Chemical Society, London, 1958, p. 6.

(4) K. A. Kraus and R. W. Holmberg, *J. Phys. Chem.*, **58**, 325 (1954).

(5) S. Hietanen, *Acta Chem. Scand.*, **8**, 1626 (1954).

(6) S. Hietanen and L. G. Sillén, *ibid.*, **13**, 533 (1959).

(7) Described in ref. 4, pp. 329, 330.

(8) P. Souchay, *Bull. soc. chim. France*, **15**, 227 (1958).

(9) J. Lefebvre, *J. chim. phys.*, **55**, 227 (1958).

up to $\bar{n} = 2$, the first two species being those proposed definitely by Kraus and Holmberg and the pentamer being in the series proposed by Hietanen.

The present study of thorium(IV) hydrolysis at 95 and 0°, the second in a series of hydrolysis investigations at this laboratory which include elevated temperature measurements,[10] was undertaken not only to establish the temperature dependence of the hydrolysis of this ion, but also in the hope that data at temperatures other than 25° would provide enough additional information to establish clearly the important hydrolysis products formed.
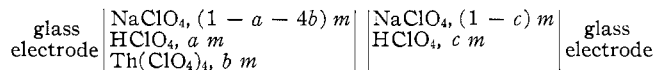
In addition to the glass electrode concentration cell described previously,[10] a hydrogen electrode concentration cell was used at 95°. At 0° glass electrodes and quinhydrone electrodes were used. The results obtained at 95 and 0°, as well as the published results of others at 25°, were analyzed in terms of possible hydrolysis schemes by the nonlinear least-squares computer program of Rush.[11]

Experimental Procedures and Results

(1) **Reagents.**—All thorium-containing solutions were made from a single 0.5 m Th(ClO$_4$)$_4$ solution prepared as follows: Th(NO$_3$)$_4$·xH$_2$O of high purity[12] was fumed with excess reagent grade HClO$_4$ on a sand bath until no detectable nitrate remained. The solution was then diluted to a thorium concentration of 0.5 m. The total equivalent cation concentration was determined by ion exchange with Dowex 50 in the hydrogen form, followed by titration of the eluate with standard base. The excess acid present was determined most accurately from the hydrolysis titration results at 0°, wherein hydrolysis was not appreciable below a pH value of 2.6.[13] This important quantity was checked by two methods: (1) replacement of Th^{4+} ion with Li$^+$ ion by resin ion exchange followed by titration of the free acid with standard base[14] and (2) addition of excess potassium oxalate to complex the Th^{4+}, followed by titration with standard base. The thorium concentration of the stock solution calculated from the difference between the total cation equivalent concentration and the concentration of excess acid was consistent with the amount of thorium nitrate starting material used and with direct chemical analysis.[15]

The sodium perchlorate (G. F. Smith reagent grade) stock solutions, used to control the total perchlorate concentration at 1 m, were first acidified with HClO$_4$, purged with nitrogen to remove CO$_2$, and then carefully neutralized with sodium hydroxide. Concentration was determined by evaporating an aliquot and drying to constant weight. The sodium hydroxide and perchloric acid stock solutions were prepared from reagent chemicals and standardized on a weight basis. It was found that the quinhydrone (Eastman) could be used without further purification. All solutions used in the measurements were prepared by weight.

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

(11) Described by R. M. Rush, J. S. Johnson, and K. A. Kraus, Oak Ridge National Laboratory Report ORNL-3278 (1963).

(12) Prepared by Lindsay Light and Chemical Co. Total detectable metallic impurities other than sodium was <100 p.p.m.; chloride, sulfate, and phosphate totaled ~50 p.p.m.

(13) C. F. Baes, Jr., *Inorg. Chem.*, **4**, 588 (1965).

(14) L. O. Gilpatrick and H. F. McDuffie in Oak Ridge National Laboratory Report ORNL-2931 (1960), pp. 127–129.

(15) All direct thorium analyses were performed by the Oak Ridge National Laboratory Analytical Chemistry Division. For samples containing <5 mg. of Th/ml., a spectrophotometric thoron method was used [P. F. Thomason, M. A. Perry, and W. M. Byerly, *Anal. Chem.*, **21**, 1239 (1959)]. For samples containing 5–25 mg. of Th/ml., a volumetric method was used [J. Körbl and R. Pribil, *Chemist Analyst*, **45**, No. 4, 102 (1956)]. For the 0.5 m thorium stock solution, a gravimetric oxalate method was used.

(2) **Potentiometric Measurements.**—The potentiometric circuit (which employed a vibrating reed electrometer as a nul-detector), the glass electrode concentration cell, and the titration procedures used at 95° all have been described previously.[10] For the present measurements, the cell may be represented as

$$\begin{array}{c}\text{glass}\\\text{electrode}\end{array}\left|\begin{array}{l}\text{NaClO}_4, (1 - a - 4b)\, m\\\text{HClO}_4,\, a\, m\\\text{Th(ClO}_4)_4,\, b\, m\end{array}\right|\left|\begin{array}{l}\text{NaClO}_4, (1 - c)\, m\\\text{HClO}_4,\, c\, m\end{array}\right|\begin{array}{c}\text{glass}\\\text{electrode}\end{array}$$

At the high acid concentrations involved in the initial hydrolysis of Th^{4+} at 95° (<0.01 m), the reproducibility of the glass electrodes was found to be unsatisfactory. As a consequence, a hydrogen electrode was substituted for the glass electrode in the above cell in some of these measurements. This electrode consisted of a platinum capillary (0.032-in. o.d. × 0.020-in. i.d.) connected through an electrically insulating Teflon block to the hydrogen supply. The lower end of the capillary, which dipped into the solution, was crimped in order that with an internal hydrogen pressure 50 p.s.i. greater than the cell pressure a slow stream of hydrogen emerged from the (platinized) tip. The arrangement is shown in Figure 1. At the beginning of a run, air was removed from the cell solution by successive partial evacuation and filling with hydrogen while stirring the cell solution and bubbling hydrogen through the electrodes. During a titration, the hydrogen partial pressure above the solutions (typically 200 p.s.i.) rose slowly, partly because of the introduction of hydrogen through the electrodes and partly because of the titrating solution added to the cell, which decreased the gas volume. After each addition of titrant, the cell potential was followed until it became constant. This often required many minutes, making this electrode relatively less convenient to use than the rapidly responding glass electrode. (The equilibration time presumably could be decreased by inserting a stirring magnet in the reference compartment as well as in the working compartment.) Since both electrode compartments were exposed to the same hydrogen pressure in this cell arrangement, it was not necessary to measure the hydrogen pressure.

Measurements of the hydrolysis of Th^{4+} at 0° were first made with a conventional glass electrode–calomel electrode arrangement similar to that used previously in the study of UO$_2^{2+}$ hydrolysis at 25°.[10] The cell was thermostated in an ice bath. The apparatus was enclosed in an aluminum cabinet which provided the necessary electrostatic shielding. Because rate effects were encountered (*vide infra*) the potential drifts with time associated with the glass electrode interfered seriously with the measurements. Consequently, a quinhydrone electrode concentration cell was substituted for those measurements at 0°. It was a symmetrical arrangement of two cell compartments (with provision for stirring) connected by a column of electrolyte (1 m NaClO$_4$). Asbestos fibers, sealed in the glass wall of each cell, formed the liquid junctions. Nitrogen gas was bubbled slowly through the two cell solutions to prevent oxidation of the quinhydrone.

A transient precipitation usually occurs when an increment of base is added to thorium solutions. Normally this precipitate, produced by local excesses of base, dissolves more or less readily on mixing, depending upon the pH. No difficulty from this effect was noted in the measurements below $\bar{n} = 1.8$ at 95°; however, at 0° it appeared that precipitate so formed did not readily redissolve. This would account for rate effects noted in runs involving addition of base to acidic solutions. Even when periods up to 0.5 hr. were allowed between additions of base, the $\bar{n}$ values obtained often were higher than values found at the same acidity in reverse titrations (addition of acid to initially hydrolyzed thorium). This effect was the more serious as $\bar{n}$ increased, but was appreciable even at the lowest $\bar{n}$ values when the thorium concentration was highest (~0.02 m). To avoid this difficulty three titrations were carried out by the following procedure: A hydrolyzed thorium stock solution ($\bar{n} \sim 2.3$) was carefully prepared by gradual addition of base with stirring and gentle heating. Three dilutions (to ~0.02, ~0.006, and ~0.002 m thorium) were prepared from this solution and used as the
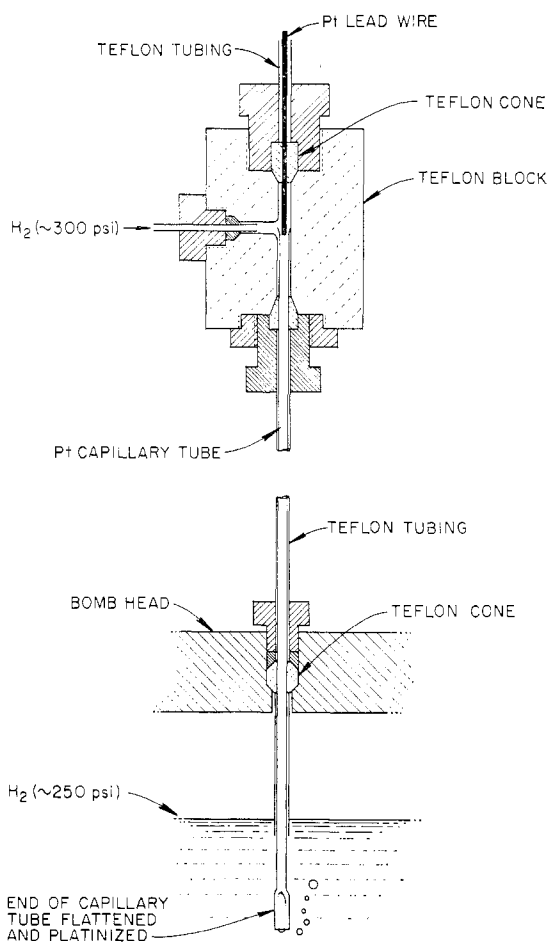
Figure 1.—High temperature–high pressure hydrogen electrode arrangement.

initial solutions to which acid was added to runs at 0°. Though the stock solution and its dilutions stood for 1–2 weeks before use, no precipitation was observed, and in the runs equilibrium appeared rapid. Moreover, the results obtained (Figure 3) were in agreement with a number of results from other titrations run in the reverse manner at low thorium concentrations.

In the hydrolysis measurements at 95°, $\bar{n} < {\sim}1.8$, the equilibria were evidently rapidly attained and reversible, concordant results being obtained by the addition of base to initially unhydrolyzed solutions or by the addition of acid to initially hydrolyzed solutions (Figure 3). In the region of $\bar{n} \sim 1.8$ and above, a drift in cell potential toward higher acidities was encountered, caused by hydrolytic precipitation. Analogous behavior has been found[4] at 25° at $\bar{n}$ values > 2. In several experiments at 95°, the changing acidity accompanying precipitation was followed for several days with the hydrogen electrode without the system reaching equilibrium, and it became clear that considerable supersaturation had occurred before initial precipitation.

(3) **ThO₂ Solubility Measurements at 95°.**—Hydrolyzed, supersaturated thorium solutions of known composition were prepared, placed in Pyrex tubes or in Teflon bottles equipped with tight-fitting Teflon caps, and seeded with finely divided ThO₂. These containers were then clamped to a rotating support which was immersed in an oil bath controlled at 95.0 ± 0.1°. The sample tubes were tumbled for various periods from 10 to 100 days to ascertain whether or not equilibrium had been reached. The Teflon containers were used in the longest equilibrations.

After equilibration, the samples were quickly cooled and transferred to centrifuge tubes. After centrifuging for 3 hr. at 20,000 r.p.m., the mother liquor was sampled and analyzed for thorium

TABLE I

SOLUBILITY OF ThO₂ in 1 m (Na)ClO₄ AT 95°[a]

Initial solution		Final solution		Calcd. OH/Th ratio in solid $(m_H - m_{H,0})/(m_{t,0} - m_t)$
$m_{t,0}$[b]	$m_{H,0}$[c]	m_t[b]	m_H[c]	
0.02887	−0.02353	0.01753	0.02085	3.91
0.02135	−0.01741	0.01202	0.02257	4.29
0.009710	−0.007937	0.003317	0.01730	3.95
0.003739	−0.003079	0.000319	0.01043	3.95
0.001931	−0.001609	0.000039	0.00586	3.95
0.0009640	−0.0008214	0.000013	0.00318	4.21

[a] Samples equilibrated in Teflon bottles for 100 days. [b] Thorium molality. [c] Formal acid molality; minus sign signifies base concentration.

by the thoron method[15] and for acid by alkalimetric titration in the presence of excess oxalate. The results obtained indicated (Table I) that the solid phase was ThO₂ and this was confirmed by electron diffraction examination of the solid phase in an electron microscope.[16] From the observed variation of the solubility results as a function of the formal acidity (m_H) and equilibration time (Figure 2), it appeared that equilibrium was reached in 10 days with $m_H < 0.01\ m$. Increasingly longer times appeared necessary as m_H increased to 0.02 m. There was no indication of interference from dissolved silica from the Pyrex vessels used in the two shorter equilibrations.
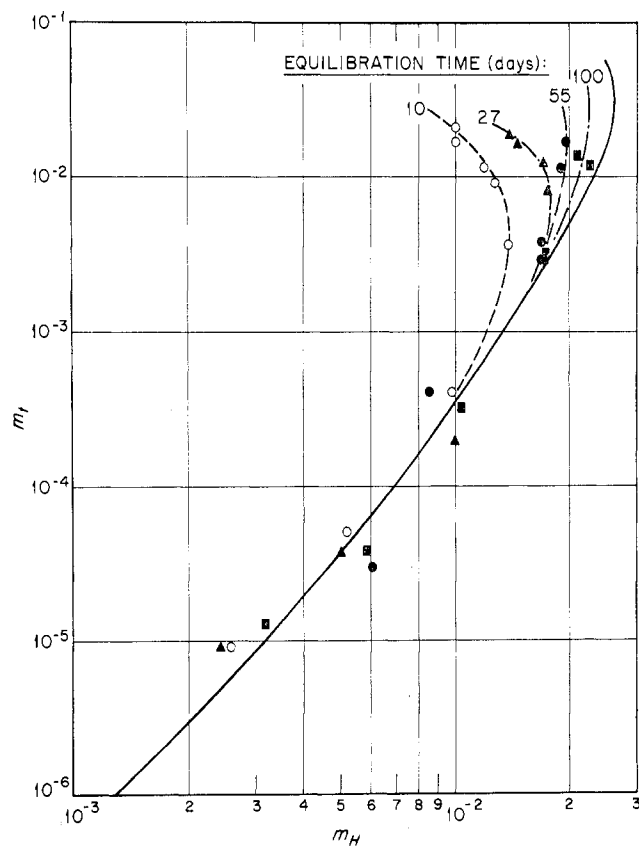
Figure 2.—The solubility of ThO₂ as a function of formal acidity of 1 m (Na)ClO₄ at 95°: solid curve calculated from eq. 9 and 10 with log Q_s = 4.26, log $Q_{1,1}$ = −2.26, and log $Q_{1,2}$ = −4.54.

(4) **Data Reduction and Results.**—The conversion of observed potential changes (ΔE), as a function of composition

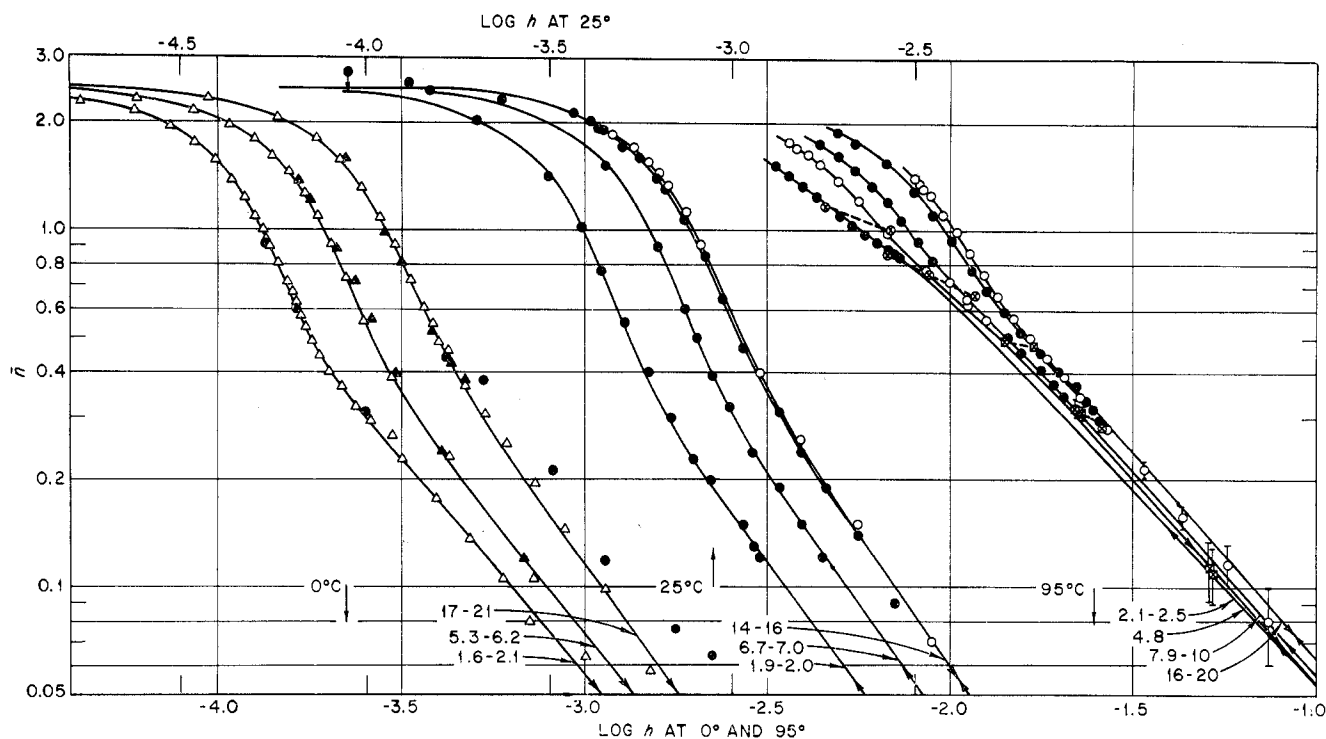(16) Performed by T. E. Wilmarth, Analytical Chemistry Division, Oak Ridge National Laboratory.

Figure 3.—The hydrolysis of Th^{4+} in 1 m (Na)ClO$_4$ from 0 to 95°: circles, glass electrode data; triangles, quinhydrone data; squares, hydrogen electrode data; open symbols, decreasing $\bar{n}$; filled symbols, increasing $\bar{n}$; crossed symbols, increasing m_t. The numbers refer to the range of $m_t \times 10^3$ which decreases in the direction indicated by arrow heads. The 25° data, a portion of Kraus and Holmberg's results,[4] have been shifted to the right. The curves are calculated from scheme IV, Table V.

changes during the titrations, to the hydroxyl number ($\bar{n}$, the average number of OH$^-$ ions bound per Th^{4+} ion present) was carried out as described previously.[10,13] The relationship assumed between ΔE and the acidity h was

$$\Delta E = \frac{RT}{F} \ln (h_r/h) - \Sigma D_i(i_r - i) \qquad (1)$$

where i denotes the concentration of each ion present and the subscript r denotes values at the reference point in the titration. From the Henderson equation, the liquid junction potential coefficients, D_i, for each ion can be calculated from the equivalent conductance (λ_i) and charge of the ion, with sign (Z_i)[10]

$$D_i = \frac{RT\lambda_i}{Z_i F \Sigma(i\lambda_i)} \qquad (2)$$

In the present measurements, since the total perchlorate concentration was constant at 1 m, the concentration change of Na$^+$ can be eliminated in eq. 1

$$\Delta E = \frac{RT}{F} \ln (h_r/h) - \Sigma(D_i - Z_iD_{Na})(i_r - i) \qquad (3)$$

The resulting coefficients of the liquid junction terms reflect the replacement of Na$^+$ by one of the other cations present—H$^+$, Th^{4+}, or Th$_x$(OH)$_y^{(4x-y)+}$. Calculations of the last term on the right in eq. 3 were made in which all the hydrolysis products indicated by a typical hydrolysis scheme were included. They showed that the terms containing the concentrations of Th^{4+} and Th$_x$(OH)$_y^{(4x-y)+}$ could be replaced by a term containing the total thorium concentration with negligible error. Hence the following equation was used in treating the data.

$$\Delta E = \frac{RT}{F} \ln (h_r/h) - (D_H - D_{Na})(h_r - h) -$$
$$(D_{Th} - 4D_{Na})(m_{t,r} - m_t) \qquad (4)$$

Observed values of the two liquid junction potential coefficients are compared with calculated values in Table II. The coefficient ($D_{Th} - 4D_{Na}$) was not measured at 95° since hydrolysis was found to be appreciable at all acidities measured.

TABLE II

LIQUID JUNCTION POTENTIAL COEFFICIENTS[a] IN 1 m (Na)ClO$_4$

	($D_H - D_{Na}$), mv., kg., mole^{-1}		($D_{Th} - 4D_{Na}$),[a] mv., kg., mole^{-1}	
Temp., °C.	Observed	Calculated[b]	Observed	Calculated[b]
0	62	74	−38	−36
95	41	46	…	−53

[a] Coefficients in eq. 4. [b] Calculated by eq. 2: λ_{H^+}, λ_{Na^+}, and $\lambda_{ClO_4^-}$ were taken from R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Academic Press, Inc., New York, N. Y., 1955, p. 454; $\lambda_{Th^{4+}}$ was assumed to be 30 and 200 cm.^{2} ohm^{-1} equiv.$^{-1}$ at 0 and 95°, respectively.

Because hydrolysis was appreciable at even the highest acidities measured at 95° the reference acidity (h_r, eq. 4) in acid–base titrations could not be determined directly. Instead the extent of hydrolysis in this region was first determined by the stepwise addition of thorium to relatively acidic solutions initially free of thorium, wherein the reference acidity was established by the known initial acidity. The hydrogen electrode was used in most of these measurements. The results were used to establish h_r in the other, acid–base, titrations. While it was necessary to use the calculated value of ($D_{Th} - 4D_{Na}$) in treating these data, the fair agreement of other calculated with observed values of the coefficients in Table II suggests that the calculated value here is not in error by more than ±10 mv. m^{-1}. The resulting uncertainty in $\bar{n}$ (*cf.* Figure 3) is significant only for a few results at the highest acidities studied.

The hydrolysis results obtained with the glass electrode at 95° and with the quinhydrone electrode at 0° are listed in Table III. The data points for each run are listed in the order in which

Table III
Thorium(IV) Hydrolysis Results in 1 m (Na)ClO$_4$

0°						95°					
$m_t \times 10^3$	$-\log h$	$\bar{n}$	$m_t \times 10^2$	$-\log h$	$\bar{n}$	$m_t \times 10^2$	$-\log h$	$\bar{n}$	$m_t \times 10^3$	$-\log h$	$\bar{n}$
20.6	4.028	2.315	5.45	3.006	.064	20.0	2.097	1.403	9.66	1.715	.374
20.2	3.840	2.072	5.43	2.879	.035	20.0	2.090	1.366	9.52	1.759	.413
19.8	3.735	1.828	5.40	2.760	.023	20.0	2.078	1.318	9.37	1.805	.456
19.5	3.672	1.583	5.38	2.665	.013	20.0	2.058	1.251	9.23	1.853	.508
19.1	3.610	1.339	5.33	2.514	.004	20.0	2.032	1.117	9.09	1.902	.564
18.7	3.590	1.094				20.0	1.985	.991	8.95	1.952	.637
18.5	3.521	.911	2.06	4.373	2.329	20.0	1.948	.871	8.82	2.001	.724
18.2	3.479	.728	2.02	4.222	2.141	20.0	1.911	.750	8.67	2.049	.823
18.1	3.441	.607	1.98	4.129	1.931	20.0	1.869	.661	8.46	2.092	.943
18.0	3.418	.546	1.95	4.062	1.761	20.0	1.825	.576	8.44	2.135	1.065
17.9	3.399	.486	1.91	4.008	1.571	20.0	1.780	.502	8.32	2.177	1.200
17.9	3.367	.426	1.87	3.962	1.381	20.0	1.733	.443	8.21	2.218	1.339
17.8	3.329	.367	1.85	3.929	1.238	20.0	1.689	.392	8.10	2.261	1.479
17.7	3.277	.309	1.82	3.899	1.096	20.0	1.647	.347	7.99	2.308	1.621
17.6	3.215	.252	1.81	3.879	1.001	20.0	1.569	.280	7.88	2.359	1.762
17.5	3.139	.197	1.80	3.870	.954	20.0	1.468	.215			
17.5	3.054	.145	1.79	3.860	.906	20.0	1.361	.158	4.77	2.440	1.770
17.4	2.945	.098	1.78	3.838	.813	20.0	1.240	.117	4.77	2.437	1.764
17.3	2.820	.058	1.76	3.814	.719	20.0	1.126	.081	4.77	2.419	1.705
17.3	2.676	.031	1.75	3.797	.674				4.77	2.392	1.632
17.2	2.542	.015	1.75	3.791	.626				4.77	2.358	1.539
17.0	2.327	.001	1.74	3.777	.590	19.9	1.599	.304	4.77	2.310	1.386
			1.73	3.762	.525	19.8	1.611	.314	4.77	2.252	1.208
6.19	4.220	2.333	1.72	3.743	.490	19.7	1.633	.335	4.77	2.169	.986
6.13	4.067	2.156	1.72	3.722	.447	19.4	1.669	.368	4.77	2.064	.785
6.07	3.970	1.979	1.71	3.696	.405	19.2	1.706	.403	4.77	1.952	.624
6.01	3.900	1.802	1.70	3.655	.365	18.9	1.755	.459	4.77	1.847	.498
5.95	3.853	1.624	1.70	3.628	.327	18.6	1.805	.523	4.77	1.752	.412
5.90	3.808	1.446	1.69	3.587	.292	18.3	1.852	.598	4.77	1.689	.347
5.84	3.756	1.268	1.68	3.526	.267	18.0	1.897	.683			
5.78	3.730	1.090	1.68	3.501	.229	17.8	1.939	.760	2.51	2.136	.850
5.73	3.693	.912	1.66	3.407	.177	17.4	1.966	.936	2.50	2.139	.858
5.68	3.653	.735	1.65	3.316	.136	17.0	2.049	1.109	2.50	2.143	.863
5.63	3.605	.559	1.64	3.278	.106	16.6	2.102	1.285	2.49	2.151	.871
5.57	3.528	.388	1.62	3.152	.080	16.2	2.176	1.523	2.47	2.164	.891
5.52	3.372	.231	1.61	3.081	.062	15.8	2.261	1.761	2.43	2.201	.934
5.48	3.141	.105	1.60	3.019	.049	15.6	2.310	1.878	2.39	2.235	.984
			1.58	2.963	.036				2.35	2.270	1.037
						10.00	1.632	.320	2.31	2.306	1.101
						9.98	1.635	.324	2.28	2.339	1.169
						9.96	1.640	.328	2.24	2.374	1.248
						9.92	1.651	.333	2.21	2.408	1.333
						9.84	1.672	.346	2.18	2.443	1.425
									2.15	2.478	1.525

they were obtained. At 0°, only the data from the reverse titrations are included, owing to difficulty with irreversible precipitation accompanying the addition of base in forward titrations. Figure 3 includes, in addition to these data, a few results of the forward titrations at 0°, the hydrogen electrode data at 95°, and a portion of the results of Kraus and Holmberg[4] at 25°.

(5) **Data Analysis.**—The computer program used for comparing various possible hydrolysis schemes with both the present results and the published results at 25° has been described by Rush, Johnson, and Kraus.[11] A chosen set of hydrolysis products, Th$_x$(OH)$_y$ (which will be referred to as a scheme) was tested by specifying the values of the integers x and y for each species assumed and a guessed value of its formation quotient, $Q_{x,y}$

$$Q_{x,y} = t_{x,y}h^y/t^x \qquad (5)$$

where t, $t_{x,y}$, and h are, respectively, the concentrations of Th^{4+}, Th$_x$(OH)$_y$$^{(4x-y)+}$, and H$^+$. In the computation, the expression for the total concentration of thorium

$$m_t = t + \Sigma x Q_{x,y}(t^x/h^y) \qquad (6)$$

was solved for the unhydrolyzed thorium concentration, t, by successive approximation for each data point (m_t and h being specified). The hydroxyl number was next calculated

$$\bar{n} = \frac{\Sigma y Q_{x,y}(t^x/h^y)}{m_t} \qquad (7)$$

The standard deviation of $\bar{n}_{calcd}$ from the observed value $\bar{n}$— $\sigma(\bar{n}) = [\Sigma(\bar{n} - \bar{n}_{calcd})^2/(\text{no. obsd.} - \text{no. adj. parameters})]^{1/2}$—was determined for all the data points, and in a series of refinements by a least-squares procedure[17] the whole operation was repeated varying the $Q_{x,y}$ values to find those formation quotient values which yield the minimum $\sigma(\bar{n})$ value. These "best" Q values and their estimated uncertainties were reported, as well as $\sigma(\bar{n})$. For each data point, $\bar{n}_{calcd}$ and the calculated concentrations of each of the assumed species were also reported.

Occasionally tests of assumed hydrolysis schemes did not converge to a set of best $Q_{x,y}$ values: If the initial values of $Q_{x,y}$ were poor guesses, successive "refinements" sometimes produced increasing $\sigma(\bar{n})$ values. This process stopped when one of the $Q_{x,y}$ values became either very large or very small. If $\sigma(\bar{n})$

(17) H. Margenau and G. M. Murphy, "The Mathematics of Physics and Chemistry," 2nd Ed., D. Van Nostrand Co., New York, N. Y., 1956, pp. 517–519.

proved to be insensitive to one or more of the assumed $Q_{x,y}$ values (corresponding to unimportant species), these quotients would vary widely, becoming either small or large, again terminating the computation. This difficulty could sometimes be overcome by specifying a larger value for the increments of $Q_{n,y}$ which were specified to determine the derivative $\partial(n_{calcd})/\partial(Q_{x,y})$ numerically in the computation. In spite of this precaution, a $Q_{x,y}$ value occasionally would persist in becoming very small and its estimated uncertainty could become very large. In further testing of a scheme in which this occurred, the species corresponding to this formation quotient was not included.

Discussion

(1) **Initial Hydrolysis.**—At 95°, the tendency of the log $\bar{n}$ vs. pH curves at various thorium concentrations to converge at low $\bar{n}$ values (Figure 3) gives clear evidence that the principal initial hydrolysis products are mononuclear. The initial slope—$(\partial \log \bar{n}/\partial\text{pH})_{m_t}$—here is $\sim$1.2, suggesting these principal initial species to be ThOH^{3+} and Th(OH)$_2$$^{2+}$.

Further evidence for these species is offered by the ThO$_2$ solubility results at 95° (Figure 2). For ThO$_2$-saturated solutions

$$\text{ThO}_2(\text{s}) + 4\text{H}^+ \rightleftharpoons \text{Th}^{4+} + 2\text{H}_2\text{O} \qquad Q_\text{S} = t/h^4 \quad (8)$$
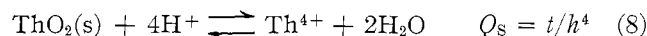
Substitution of $Q_\text{S}h^4$ for t in the expression for m_t (eq. 6) gives

$$m_t = Q_\text{S}h^4 + \Sigma\, xQ_{x,y}Q_\text{S}^x h^{4x-y} \qquad (9)$$

The observed dependence of m_t on m_H varies between the second and fourth power below $m_\text{H} = 0.015$, suggesting that $4x - y$ in the above equation varies between 2 and 4. This is consistent with Th(OH)$_2$$^{2+}$, ThOH^{3+}, and Th^{4+}. The smooth curve shown in Figure 2—calculated assuming these three species with log $Q_{1,2} = -4.54$, log $Q_{1,1} = -2.26$, and log $Q_\text{S} = 4.26$—compares well with the data. The upward break of both this curve and the data at acidities above 0.015 results because the formal acidity m_H which is plotted becomes significantly less than the actual acidity h as the concentration of hydrolysis products becomes appreciable compared to m_H

$$h - m_\text{H} = \Sigma\, tQ_{x,y}Q_\text{S}^x h^{4x-y} \qquad (10)$$

The values $Q_{1,1}$ and $Q_{1,2}$ used here approximate those given by schemes of four or five hydrolysis products which fit all the hydrolysis data at 95° (Table V). The other species, all having $4x - y$ values greater than 4, were found by calculation to be insignificant in the ThO$_2$-saturated solutions.

At 0° the initial slope of the $\bar{n}$ vs. pH curves (Figure 3) is nearly 2, but since here $\bar{n}$ is clearly a function of the thorium concentration, at least one polynuclear species —probably Th$_2$(OH)$_2$$^{2+}$—must be present at the lowest $\bar{n}$ values measured.

Thus, as Kraus and Holmberg pointed out,[4] at least three species are necessary to account just for the initial hydrolysis of Th^{4+}. The three species indicated by the data at 95° and 0°—$x,y = 1,1$; 1,2; 2,2—are precisely the ones they proposed to account for their extensive result at low $\bar{n}$ values at 25°. To account fully for the observed hydrolysis behavior it appears
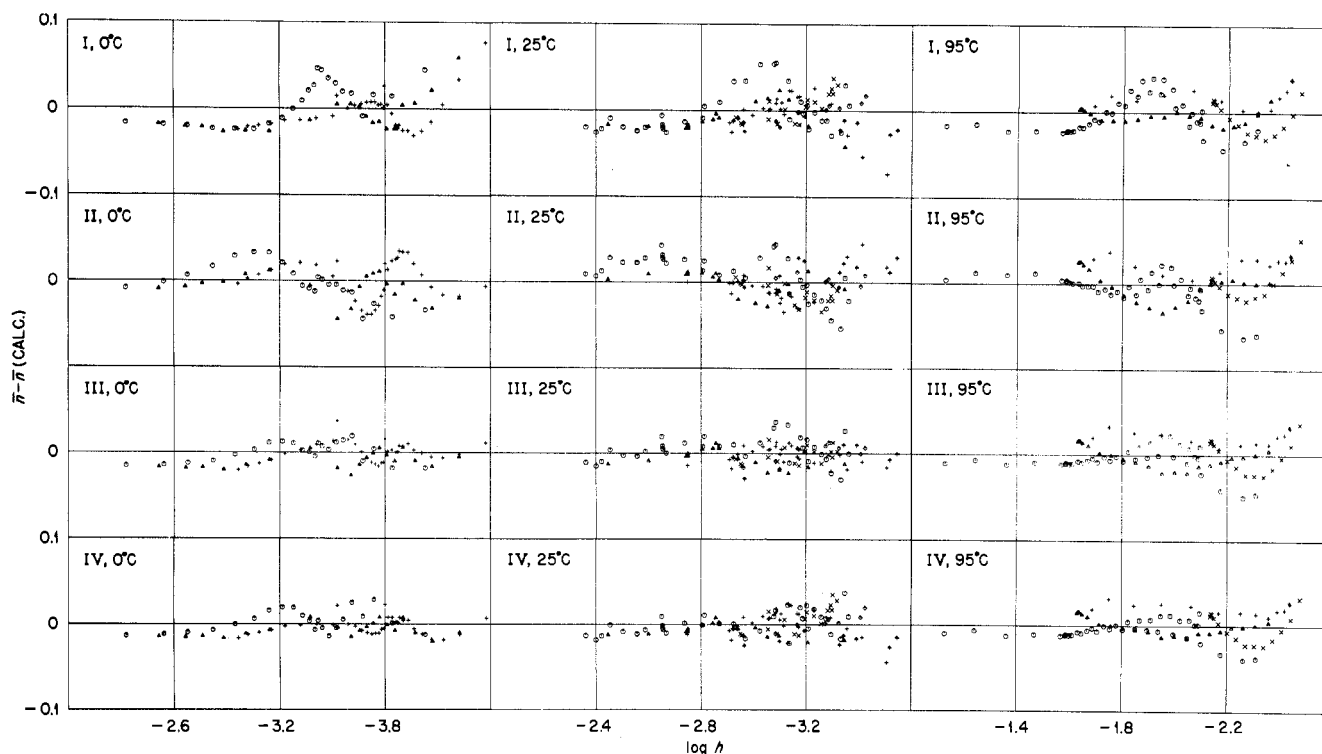
Figure 4.—Deviation plots obtained with schemes I–IV; the $\sigma(\bar{n})$ and $Q_{x,y}$ values are listed in Table V.

TABLE IV

STANDARD DEVIATION OF CALCULATED FROM OBSERVED $\bar{n}$ VALUES FOR VARIOUS THORIUM HYDROLYSIS SCHEMES

[VALUES LISTED ARE $\sigma(\bar{n}) \times 10^3$]

(A) Four Species: 1,1; 1,2; 2,y; x,y

Fourth species[a]	Third species										
	—0°—		—25°—						—95°—		
	2,2	2,3	2,1	2,2	2,3	2,4	None	2,1	2,2	2,3	2,4
5,11	74	94		38	45				35	54	
4,9	67	79		36	41		44	33	33	44	44
7,16	43	72		25					26	47	
6,14	32	55		20	47		45	37	22	38	43
5,12	24	32	49	21	19	42	32	30	19	25	31
7,17	32	34		33	24				30	30	
4,10	43	33	54	37	29	47	22	22	22	15	18
6,15	45	21			20		39	39	31	21	28
7,18	70	45		39	30				44	28	
5,13	70	46		52	28				36	23	
6,16		68			36						34

(B) Five Species: 1,1; 1,2; 2,2; x,y; x,y

Fifth species[a]	Fourth species											
	None	2,3	3,4	3,5	3,6	3,7	4,7	4,8	4,9	4,10	5,10	5,12
					0°							
5,12	24	20	21	21	23		21	22	24			
7,17	32	21		16	17		15	14	19			
6,15	45	20		18	13	28	20	12	15	39	15	22
7,18	70	45			25	37		25	14	42		21
8,21									19			
					25°[b]							
7,17	33	19					17	14				
6,15	39	19			16			15	16			
7,18		29							15			
					95°							
7,17	30						19	19				
6,15	31	20			18			15	18			
7,18	44								18			

(C) Five Species: 1,1; 1,2; 2,2; 2,2x; x,2.5x

Fifth species[a]	Fourth species						
	3,6	4,8	5,10	3,6	4,8	3,6	4,8
4,10		32					
6,15	13	12	15	13	15	18	15
8,20	20	16					
10,25	28	23					

[a] Species are listed in order of increasing OH/Th ratio. [b] Values at 25° are based on data of Kraus and Holmberg.[4]

that at least four hydrolysis products must be assumed, since the maximum value of $\bar{n}$ which has been observed is >2 and since more highly polymeric hydrolysis products evidently are formed.

(2) **Four Hydrolysis Products.**—With the aid of the general least-squares computer program, the data in Table III, along with the results of Kraus and Holmberg at 25°,[4] were used to test numerous schemes of four hydrolysis products. We chose not to include in the data the few results reported by Kraus and Holmberg at $\bar{n} > 2$ since they were derived from titrations involving the addition of base to the hydrolyzing solutions and it was feared, as in the present measurements at 0°, that these results might have been affected by precipitation.

The standard deviation of calculated from observed $\bar{n}$ values, $\sigma(\bar{n})$, obtained with the various schemes of four species tested are summarized in Table IV (A). In every case $ThOH^{3+}$ and $Th(OH)_2^{2+}$ were assumed as the first two species. Various dimers, usually $Th_2(OH)_2^{6+}$ or $Th_2(OH)_3^{5+}$, were tried as the third species. As the fourth species tetramers to heptamers were tested. These are arranged in Table IV in the order of increasing y/x ratio since the values of $\sigma(\bar{n})$ were found to be strongly a function of this ratio. This may be seen from the values listed for the schemes 1,1; 1,2; 2,2; x,y and 1,1; 1,2; 2,3; x,y at each temperature, wherein $\sigma(\bar{n})$ decreases with increasing y/x until a minimum is reached, respectively, at $y/x \sim 2.4$ and ~ 2.5, and then increases. As expected, the 0° data are the most sensitive to y/x for the fourth species since these data contained the highest $\bar{n}$ values.

Two schemes of four species were found to be most consistent with the data

I 1,1; 1,2; 2,2; 5,12 $\sigma(\bar{n}) = 0.024, 0.021, 0.019$

II 1,1; 1,2; 2,3; 6,15 $\sigma(\bar{n})$ = 0.021, 0,020, 0,021

(the three values of $\sigma(\bar{n})$ for each refer, respectively, to the 0, 25, and 95° data). All other schemes listed gave a $\sigma(\bar{n})$ value >0.03 at at least one temperature. The less extensive tests with other dimers gave in every case poorer fits than were obtained when the 2,2 or 2,3 species were assumed. In a few other tests (not listed), substitution of various trimers for the 2,2 or 2,3 species also gave poorer fits to the data. Thus it appears likely that schemes I and II are the best possible choices of four species to account for the data at all three temperatures. These "best" choices, however, are not especially good fits (Figure 4). The deviations are largely systematic rather than random and, furthermore, in each scheme they are similar in appearance at all three temperatures. While systematic errors in one set of data might produce such deviations, it seems very unlikely that systematic errors at all three temperatures would produce qualitatively similar deviations. Hence it may reasonably be concluded that at least five hydrolysis products must be assumed to account properly for the data.

(3) **Five Hydrolysis Products.**—The search for more consistent schemes of five hydrolysis products was undertaken with the realization that probably no clearly unique scheme could be identified since systematic errors present in the data or insensitivity of the data to various combinations of so many species would produce good fits to more than one scheme. Yet, $\bar{n}$ vs. pH data are probably the best kind of data with which to investigate so complicated a hydrolysis process and the progress made in identifying consistent schemes, as well as in eliminating others, should be useful when additional evidence becomes available.

In all schemes of five species tested (Table IV (B, C)) the first three species were assumed to be $ThOH^{3+}$, $Th(OH)_2^{2+}$, and $Th_2(OH)_2^{6+}$. As the fourth species principally trimers and tetramers were tested. These tests were largely limited to the 0° results since these seemed to be the most sensitive. Again it appeared that $\sigma(\bar{n})$ was largely a function of the ratio y/x for the final species. In addition, the best fits were obtained when y/x for the fourth species was 2.

The arrays of $\sigma(\bar{n})$ values listed for the 0° data in Table IV (B) indicate the best schemes to be

III 1,1; 1,2; 2,2; 3,6; 6,15 $\sigma(\bar{n})$ = 0.0126, 0.0128, 0.0175

IV 1,1; 1,2; 2,2; 4,8; 6,15 $\sigma(\bar{n})$ = 0.0117, 0.0145, 0.0154

While the $\sigma(\bar{n})$ values at 25° do not favor scheme IV, those for scheme IV at 0 and 95° were among the lowest ones obtained with any scheme at these temperatures. In other tests at 0°, listed in Table IV (C), the degree of polymerization of the fourth and fifth species was varied while holding their y/x ratios at 2 and 2.5, respectively, with the result that scheme IV remained the "best" choice. The deviation plots obtained with schemes III and IV, as expected, showed more nearly random scatter of the data (Figure 4).

The poorer fit of scheme IV compared to scheme III at 25° is not necessarily significant for the following reason: In listing their results, Kraus and Holmberg did not specify the thorium concentration for each point in the three runs which covered the full range of $\bar{n}$ values, but instead indicated only the initial and final values of the thorium concentrations. In using all their results below $\bar{n}$ = 2, we interpolated values of the thorium concentration at each point in these three runs and, in so doing, may easily have introduced significant errors. The remaining extensive results of Kraus and Holmberg—confined to $\bar{n}$ values less than 0.52 but with specified thorium concentrations ranging from 2×10^{-4} to 1.5×10^{-2} M—were tested separately with the following results.

V 1,1; 1,2; 2,2; 2,3; (6,15) $\sigma(\bar{n})$ = 0.0087 (25°)

III 1,1; 1,2; 2,2; 3,6; (6,15) $\sigma(\bar{n})$ = 0.0094 (25°)

IV 1,1; 1,2; 2,2; 4,8; (6,15) $\sigma(\bar{n})$ = 0.0096 (25°)

(The final 6,15 species was included here with a fixed formation quotient; its contribution was negligible in all three cases.) Thus schemes III, IV, and a scheme (V) which includes the four species originally selected by Kraus and Holmberg all are quite consistent with low $\bar{n}$ values at 25°.

In other tests: Lefebvre's[9] scheme

VI 1,2; 2,2; 5,12; (6,y) $\sigma(\bar{n})$ = 0.030 (25°)

wherein the last species, 6,18–6,21, may be neglected at $\bar{n}$ < 2, was found to give a relatively poor fit to the data of Kraus and Holmberg. Hietanen's data[5] at 25° were found to give higher $\sigma(\bar{n})$ values and to be less sensitive to the various schemes tested. In addition, here $\bar{n}$ values were on the average ~0.1 higher than Kraus and Holmberg's values. Attempts were made to test the scheme

VII 1,1; 1,2; 2,2; 2,3; (3,6); (4,9); 5,12; 6.15
$\sigma(\bar{n})$ = 0.0106, 0.117, 0.0171

which contains all the species proposed by Kraus and Holmberg and by Hietanen. The 3,6 and 4,9 species, shown in parentheses, were rejected repeatedly in the computations, the $Q_{3,6}$ and $Q_{4,9}$ values becoming either very large or very small. Without these two species, the remaining scheme of six was similar to scheme IV in over-all fit to the data.

While the numerous tests listed in Table IV do not reveal a clearly unique hydrolysis scheme, nonetheless they do reveal what to some may seem a surprising sensitivity of the data to as many as five assumed equilibria. This is illustrated by the variation of $\sigma(\bar{n})$ with the y/x ratios of those species which were varied. Of course, in the relatively few cases at 0° wherein the maximum y/x ratio assumed is lower than the maximum observed $\bar{n}$ values a relatively poor fit is expected, but in the other cases a correlation was also found. The sensitivity of $\sigma(\bar{n})$ to the assumed degree of polymerization (Table IV (C) is also noteworthy in view of the rather high polymers assumed.

(4) **Errors.**—The extent to which this sensitivity may be accepted as real depends directly upon (1) the

TABLE V

FORMATION QUOTIENTS FOR THORIUM HYDROLYSIS PRODUCTS IN 1 m (Na)ClO$_4$

Temp., °C.	\-log $Q_{x,y}$					$\sigma(n)$
Scheme I	1,1	1,2	2,2	5,12		
0	4.24 ± 0.04	8.83 ± 0.16	5.45 ± 0.03	34.84 ± 0.03		0.024
25[a]	4.16 ± 0.05	7.72 ± 0.04	4.52 ± 0.02	29.26 ± 0.02		0.021
95	2.25 ± 0.02	4.51 ± 0.01	2.51 ± 0.04	16.36 ± 0.02		0.019
Scheme II	1,1	1,2		2,3	6,15	
0	4.38 ± 0.05	...		8.86 ± 0.02	43.77 ± 0.03	0.021
25	4.13 ± 0.04	8.63 ± 0.27		7.60 ± 0.01	36.81 ± 0.02	0.020
95	2.30 ± 0.02	4.56 ± 0.01		4.40 ± 0.03	20.60 ± 0.03	0.021
Scheme III	1,1	1,2	2,2	3,6	6,15	
0	4.23 ± 0.02	9.73 ± 0.65	5.62 ± 0.02	17.80 ± 0.02	43.78 ± 0.02	0.0126
25[a,b]	4.07 ± 0.03	7.95 ± 0.05	4.67 ± 0.03	15.01 ± 0.03		0.0094
25[a]	4.00 ± 0.02	8.05 ± 0.07	4.72 ± 0.03	14.99 ± 0.02	36.81 ± 0.02	0.0128
95	2.26 ± 0.02	4.54 ± 0.01	2.60 ± 0.04	8.59 ± 0.04	20.61 ± 0.03	0.0175
Scheme IV	1,1	1,2	2,2	4,8	6,15	
0	4.32 ± 0.02	8.48 ± 0.03	5.60 ± 0.02	22.79 ± 0.02	43.84 ± 0.02	0.0117
25[a,b]	4.12 ± 0.03[c]	7.81 ± 0.03[c]	4.64 ± 0.02	18.64 ± 0.03		0.0096
25[a]	4.15 ± 0.04	7.70 ± 0.03	4.61 ± 0.02[c]	19.01 ± 0.02[c]	36.76 ± 0.02	0.0145
95	2.29 ± 0.02	4.50 ± 0.01	2.55 ± 0.03	10.49 ± 0.03	20.63 ± 0.02	0.0154

[a] These log $Q_{x,y}$ values, based on the data of Kraus and Holmberg in 1 M NaClO$_4$ (ref. 4), have been corrected from the molarity to the molality scale. The values on the molarity scale are more negative by a small amount: Δ log $Q_{x,y} = 0.020(y - x + 1)$. [b] These values are based on the data of Kraus and Holmberg at low $\bar{n}$ values wherein m_t was specified for each data point. [c] Values used in the calculations of ΔH, ΔF, and ΔS, Table VI.

accuracy of the measurements, (2) the accuracy of the liquid junction potential estimates, and (3) the constancy of ionic activity coefficients. The accuracy of the measurements was probably most affected by errors in solution composition. In addition, since at high $\bar{n}$ values the solutions at all temperatures were supersaturated with respect to hydrolytic precipitation, errors due to precipitation were possible, although the consistency of forward and reverse titrations indicates these errors to be small.

The experimental procedure used[13] should have reduced the liquid junction potential error to less than the liquid junction potential *variation* (usually ~0.5 mv.) during each titration. The liquid junction potential error was probably of the order of ±0.1 mv., corresponding to ~±0.4% errors in h, comparable to the random scatter of the data.

The errors caused by activity coefficient variations may be estimated roughly as follows: While activity coefficient measurements in 1:1–4:1 electrolyte mixtures are lacking, use of the equations given by Johnson, Scatchard, and Kraus[18] for BaCl$_2$–HCl mixtures shows that over the composition range 0 m BaCl$_2$–1 m HCl to 0.02 m BaCl$_2$–0.96 m HCl, $(\gamma_\pm)_{BaCl_2}$ decreases only 0.7% and $(\gamma_\pm)_{HCl}$ decreases only 0.5%. Though activity coefficients over the comparable range in Th(ClO$_4$)$_4$ mixtures involved here are expected to be larger, it seems not unreasonable to suppose that $\gamma_{Th^{4+}}$ and γ_{H^+} change no more than 2 and 1%, respectively. The resultant variations of $Q_{x,y}$ are estimated to be less than typical values of their statistical uncertainties (Table V).

Considering these various possible errors, the minimum $\sigma(\bar{n})$ values given by the better five-member schemes are probably as low as could reasonably be expected. While the random scatter is less than 0.01 in $\bar{n}$, the sum of possible systematic errors from all sources could easily be of this order.

(5) Conclusions.—Of the various species which appear in schemes I–IV, all of which have been proposed by one or more previous investigators, the monomers ThOH^{3+} and Th(OH)$_2^{2+}$ and the dimer Th$_2$(OH)$_2^{6+}$ seem to be well established by the appearance of the data at low $\bar{n}$ values. The hexamer Th$_6$(OH)$_{15}^{9+}$, which appears in three of the four best schemes, seems most probably to be the correct final product. Of the two schemes, III and IV, which contain these species the latter seems the better choice. The fact that schemes I and II both give fair agreement with the data may be rationalized as follows: In scheme I, the 5,12 species approximates the behavior of the two species 4,8 and 6,15; in scheme II, the 2,3 species approximates the behavior of the two species 2,2 and 4.8.

Of course this reasoning can be extended by supposing that the more polymeric species in scheme IV are in reality "standing in" for pairs of other species. Certainly this cannot be disproved. Indeed there is no doubt that replacing one or more numbers in scheme IV by pairs of species would yield slightly better fits (e.g., in scheme VI, 4,8 is replaced by 2,3 and 5,12). However, such a procedure is justified only if the errors in the data are completely random, since the general least-squares procedure then will distinguish between significant and insignificant species. In the present case, however, some systematic errors undoubtedly were present. The decision to examine five-member schemes was made only after it was found that the best four-member schemes gave deviations of calculated from observed $\bar{n}$ values which were larger than expected for such systematic errors and were similar at all three temperatures. The deviations found with the best five-member schemes, however, were not clearly sufficient to justify the assumption of six-member schemes.

(18) J. S. Johnson, G. Scatchard, and K. A. Kraus, *J. Phys. Chem.*, **63**, 793 (1959).
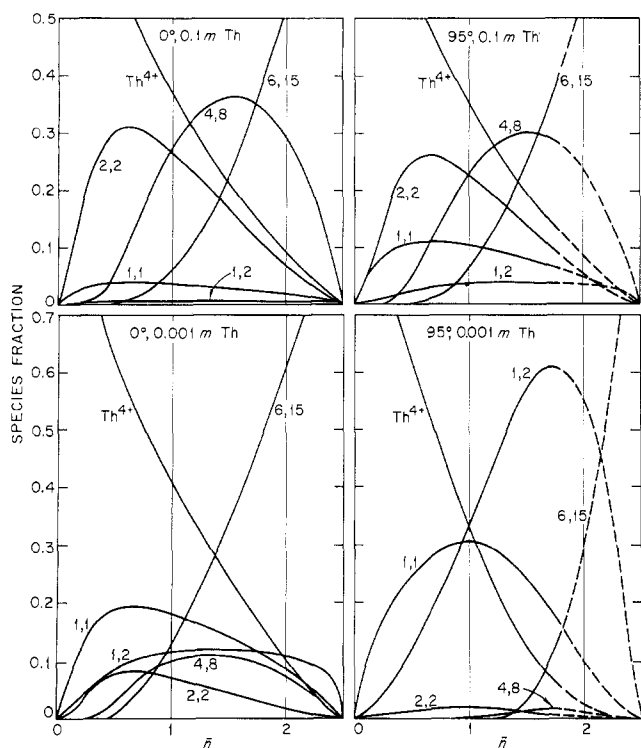
Figure 5.—Predicted distribution of thorium among the various hydrolysis products of scheme IV.

During the preparation of the present paper, Hietanen and Sillén reported[19] preliminary results of a similar computer analysis on their (as yet unpublished) data on thorium hydrolysis in 3 M NaCl at 25°. They report formation quotients for the species

VIII   1,2; 2,1; 2,2; 2,3; 6,14; 6,15
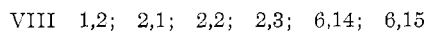
They found also that many other species, including 3,6 and 4,8, were rejected in their computations. For the reasons just stated we feel, however, that the rejection of the 3,6 and/or the 4,8 species to leave a six-member scheme is significant only if the discrepancies found with simpler schemes containing them are too large to be attributed to experimental error. With the present data, while the 2,3–6,14 species

IX   1,1; 1,2; 2,2; 2,3; 6,14; 6,15 $\sigma(\bar{n}) = 0.0143,$
                                                              $0.0119, 0.0185$
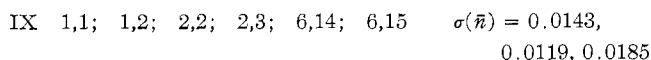
can replace the 3,6 or 4,8 species to give about the same over-all fit, the five-member scheme

X   1,1; 1,2; 2,2; 6,14; 6,15 $\sigma(\bar{n}) = 0.019, 0.021, 0.021$
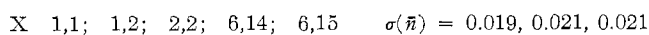
is clearly less consistent with the present data than scheme III or IV. Consequently, the 6,14 species can neither be confirmed nor ruled out by the present data. (In these tests, the 1,1 species was used in place of the 2,1 species proposed by Hietanen and Sillén because it seemed clearly indicated by the 95° data; at the lower temperatures this change should have only a small effect.) Since three species present in scheme VIII are common to scheme III and IV and since there is the possibility that the pair 2,3–6,14 may be replaced by the 3,6 or the 4,8 species, the new results of Hietanen

(19) S. Hietanen and L. G. Sillén, *Acta Chem. Scand.*, **18**, 1018 (1964).

and Sillén in 3 M (Na)Cl appear more consistent with the present results in 1 m (Na)ClO$_4$ than might have been expected.

The formation quotients $Q_{x,y}$ (eq. 4) obtained with schemes I–IV are listed in Table V. The ranges shown for log $Q_{x,y}$ represent approximately the computed standard deviations ($\pm$) of $Q_{x,y}$. In schemes I and II the 1,1 and 1,2 species are relatively unimportant at 0 and 25°, e.g., with scheme I, the formation quotient of the 1,2 species was computed to be negligible at 0°. With a few exceptions, values of the formation quotients are not grossly affected by the choice of scheme.

The predicted distribution of thorium among the various hydrolysis products assumed in scheme IV is shown at 0 and 95° and at 0.001 and 0.1 m thorium in Figure 5. It is seen that temperature should have the greater effect on the relative abundance of monomeric *vs.* polymeric species at the lower thorium concentrations. There should be a maximum in the concentration of Th$_4$(OH)$_8^{4+}$ at $\bar{n} \sim 1.5$; however, its presence was found by calculation to have but little effect on the average degree of polymerization which would be measured by the ultracentrifuge or by light scattering. This, in addition to the uncertainty regarding the charge on the various hydrolysis products, makes these methods of confirming the present interpretation unpromising. While we have arbitrarily written the charge as $(4x - y)+$, it seems probable that at least the higher polymers incorporate or closely associate ClO$_4^-$ ions. Since the concentration of ClO$_4^-$ was constant in the measurements, its possible involvement in the equilibria does not affect the other conclusions drawn regarding the species formed, however.

For the five species in scheme IV, the logarithms of $Q_{2,2}$, $Q_{4,8}$, and $Q_{6,15}$ vary nearly linearly with $1/T°$K. $Q_{1,1}$ and $Q_{1,2}$, however, show a surprisingly small difference between the values at 25 and 0°. Based on these results values of ΔH, ΔF, and ΔS of reaction at 25° have been calculated[20] assuming ΔC_p to be independent of temperature (Table VI). These, of course, are not the usual thermodynamic quantities, the standard states being hypothetical 1 m solutions of the solutes

TABLE VI

ESTIMATED ENTHALPIES, FREE ENERGIES, AND ENTROPIES
OF REACTION[a]

25°, 1 m NaClO$_4$

$$x\text{Th}^{4+} + y\text{H}_2\text{O} \rightleftharpoons \text{Th}_x(\text{OH})_y{}^{(4x-y)+} + y\text{H}^+$$

Species	ΔH, kcal.	ΔF, kcal.	ΔS, cal./°K.	ΔC_{p_0}, cal./deg.
ThOH^{3+}	5.9	5.6	0.9	224
Th(OH)$_2^{2+}$	13.9	10.7	11.0	304
Th$_2$(OH)$_2^{6+}$	14.8	6.3	28.4	1
Th$_4$(OH)$_8^{8+}$	57.7	25.9	106.6	108
Th$_6$(OH)$_{15}^{9+}$	108.5	50.1	195.7	239

[a] Values were calculated as described in footnote 20, using values of log $Q_{x,y}$ in Table V, scheme IV.

in 1 m NaClO$_4$ as the solvent. The accuracy of these numbers is difficult to assess without certain knowledge

(20) The expression ln $Q_{x,y} = -A/RT - (B/R) \ln T + D$ was fitted to the values of $Q_{x,y}$ at the three temperatures; $\Delta H = A - BT$ and $\Delta C_p = -B$.

that scheme IV is correct—though, from the fair constancy of $Q_{x,y}$ values found for many individual species in the numerous schemes tested, it can be said that the numbers in Table VI are usefully accurate if the species to which they correspond do indeed exist. If scheme IV is correct, the ΔF and ΔH values may be good to a few tenths of a kcal.; the ΔC_p values are probably no better than ± 20 cal./deg.
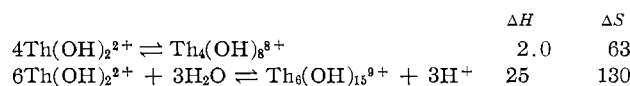
These approximate thermochemical values suggest a constancy of $\Delta H/y$ and $\Delta S/y$ for the polymeric species.

	ThOH^{3+}	Th-(OH)$_2{}^{2+}$	Th$_2$-(OH)$_2{}^{6+}$	Th$_4$-(OH)$_8{}^{8+}$	Th$_6$-(OH)$_{15}{}^{9+}$
$\Delta H/y$	5.9	7.0	7.4	7.22	7.23
$\Delta S/y$	0.9	5.5	14.2	13.3	13.0

These are the average enthalpies and entropies for the reaction shown in Table VI per OH$^-$ ion bound or H$^+$ ion produced. From the previous study of uranium-(VI) hydrolysis,[10] the corresponding values

	UO$_2$OH$^+$	(UO$_2$)$_2$(OH)$_2{}^{2+}$	(UO$_2$)$_3$(OH)$_5{}^+$
$\Delta H/y$	11	5.0	5.0
$\Delta S/y$	11	3	2

show roughly the same correlation. The entropy increases associated with thorium hydrolysis are seen to be much greater, owing presumably to the higher charge on the unhydrolyzed ion. The following polymerization reactions

	ΔH	ΔS
$4\text{Th(OH)}_2{}^{2+} \rightleftharpoons \text{Th}_4(\text{OH})_8{}^{8+}$	2.0	63
$6\text{Th(OH)}_2{}^{2+} + 3\text{H}_2\text{O} \rightleftharpoons \text{Th}_6(\text{OH})_{15}{}^{9+} + 3\text{H}^+$	25	130

evidently are favored far more by the accompanying entropy increase than they are hindered by the enthalpy increase. In the latter case, ~ 22 and 40, respectively, should be subtracted from ΔH and ΔS to correct for the three protons liberated.

CONTRIBUTION FROM THE INSTITUTE FOR ATOMIC RESEARCH AND
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Aquation of Chloropentaaquochromium(III) Ion Catalyzed by Mercury(II) Complexes[1]

BY JAMES H. ESPENSON AND JAMES P. BIRK

The aquo and chloro complexes of mercury(II) ion accelerate release of chloride ion from the primary coordination sphere of monochloropentaaquochromium(III) ion. For each mercury(II) species which enhances this aquation, the observed rates follow the equation $-\text{d ln [CrCl}^{2+}]/\text{d}t = (k_0 + k_{-1}[\text{H}^+]^{-1})[\text{Hg(II)}]$. The values of these rate constants for Hg^{2+} and HgCl$^+$ together with the activation parameters ΔH^* and ΔS^* for each reaction pathway were determined in media of constant unit ionic strength and constant perchlorate ion concentration. The mercury(II) species Hg^{2+} and HgCl$^+$ exert rate effects much larger than those of HgCl$_2$ and HgCl$_3{}^-$. A correlation is made of reaction rate with stability of the metal–chloride bond being formed; presumably chloride ion bridged transition states are involved here. Comparisons are presented between the activation parameters for the reaction Hg^{2+} + CrCl^{2+} and the electron-transfer reaction Cr^{2+} + CrCl^{2+}; the higher rate of the latter reaction is due almost entirely to its lower ΔH^*.

Introduction

Metal ions possessing affinity for halide ions increase the rate of aquation of halo complexes. The aquation rates of haloamminecobalt(III) ions are accelerated by mercury(II), silver(I), and thallium(III) ions.[2] The rates of aquation of dichlorotetraaquochromium(III) and chloropentaaquochromium(III) ions are increased by silver(I) ion.[3]

We report here on a study of the aquation of chloropentaaquochromium(III) ion enhanced by mercury(II) species. These effects are quite dramatic. At 25° and 1 M H$^+$, for example, the half-life for aquation of chlorochromium(III) ion is *ca.* 570 hr. In the presence of 0.10 M Hg^{2+} the half-life under the same condi-

tions is 87 sec.; with 0.10 M HgCl$^+$, it is 46 sec. The reactions taking place are[4]

$$\text{CrCl}^{2+} + \text{HgCl}_n{}^{2-n} = \text{Cr}^{3+} + \text{HgCl}_{n+1}{}^{1-n} \tag{1}$$
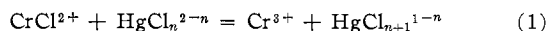
The relatively rapid reactions of aquomercury(II) ion and monochloromercury(II) ion have been studied in detail. The reactions involving the dichloro and trichloro complexes of mercury(II) are much slower; these slight enhancements of the aquation rate are not far beyond those reasonably attributable to medium effects.

Experimental

Reagents.—Chlorochromium(III) ion was prepared by reaction of chromium(II) ion and chlorine[5]; the complex was separated and purified by cation exchange on Dowex 50W-X8 resin. Chloride ion and chlorine were washed from the resin with 0.01 F

(1) Contribution No. 1578. Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

(2) J. N. Brønsted and R. Livingston, *J. Am. Chem. Soc.*, **49**, 435 (1927); (b) F. A. Posey and H. Taube, *ibid.*, **79**, 255 (1957); (c) A. M. Sargeson, *Australian J. Chem.*, **17**, 385 (1964).

(3) P. J. Elving and B. Zemel, *J. Am. Chem. Soc.*, **79**, 5855 (1957).

(4) In general, water in the coordination sphere will be omitted from chemical formulas.

(5) H. Taube and H. Myers, *J. Am. Chem. Soc.*, **76**, 2103 (1954).