ACTA CHEMICA SCANDINAVICA 22 (1968) 265–280

Studies on the Hydrolysis of Metal Ions

60. Hydrolysis of the Thorium(IV) Ion in 3 M (Na)Cl Medium

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The hydrolysis equilibria of Th^{4+} have been studied at 25°C in the medium 3 M (Na)Cl, using hydrogen (and occasionally glass) electrodes, in a concentration range for Th between 0.100 M and 0.0001 M. Table 2 and Fig. 1 give the data in the form $Z(\log h)_B$. A large number of combinations of hydrolysis products $Th_q(OH)_p$ were tried in order to get the best fit with the data, using the generalized least-squares program LETAGROP. The "best" set was sought under different conditions: I) $q \leq 4$, thus at most 4 Th in a complex, II) $q \leq 5$, III) $q \leq 6$, and IV) no restriction on q. The "best" combinations of complexes and equilibrium constants on each assumption are given in Table 3 as IB, IIB, IIIB, and IVB. It is concluded that hexanuclear complexes are an important product, even if, in view of Johansson's recent X-ray work,[9] they are not likely to be regular octahedra.

The hydrolysis of the thorium ion, Th^{4+}, has been studied by several authors. For a relatively complete list of investigations up to 1963, we refer to *Stability Constants*,[1] work before 1954 is discussed by Hietanen.[2]

There has been a general agreement in later years that polynuclear complexes are formed. We shall denote by the (p,q) complex the species or group of species, which may be described by the formula $Th_q(OH)_p^{(4q-p)+}$. As usual, this formula includes species containing more (or less) of the solvent, H_2O, and various amounts of the medium ions, since such species cannot be distinguished by equilibrium studies with a constant ionic medium.

We shall denote by β_{pq} the equilibrium constant for the formation of the (p, q) complex, by the reaction

$$p\,H_2O + q\,Th^{4+}\ (b) \rightleftharpoons Th_q(OH)_p^{(4q-p)+}\ (c_{pq}) + H^+\ (h);\ c_{pq} = \beta_{pq}\,h^{-p}b^q \quad (1)$$

As usual, the aim of equilibrium analysis is to find the "best" mechanism, thus the combination of sets $(p,q,\ \beta_{pq})$ that gives the best agreement with the experimental data. Since the complexes may also contain anions from the

medium, there is a definite possibility that the set of complexes may not be the same in different media, *e.g.* in nitrate, chloride, and perchlorate media.

For *nitrate* solutions, Souchay [3] and Faucherre [4] have interpreted glass electrode and freezing point data in terms of the (8,4) complex only. Johansson [9] has recently studied hydrolyzed Th nitrate solutions by X-ray diffraction and found evidence also for complexes with $q > 4$.

For *perchlorate* media (usually 1 M $(Na)ClO_4$) there are several sets of emf measurements. Schaal and Faucherre [5] (from emf data) concluded that the main product is the (8,4) complex, $Th_4(OH)_8^{8+}$ (or $Th_4O_4^{8+}$). In 1954, Hietanen [2] made a more extensive study with H_2 and quinhydrone electrodes. It was obvious that a single polynuclear complex (p,q) did not suffice to explain the data, and, because of the limitations on computation methods at that time, she chose an approximation that involved only two parameters and gave a reasonable agreement, namely a series of complexes $(3\ n,\ n+1)$. Kraus and Holmberg,[6] from glass electrode data concluded that the mononuclear (1,1) and (2,1), the binuclear (2,2), and in addition other undesignated complexes exist. Lefebvre,[7] from the same data, calculated the equilibrium constants for (2,1), (2,2), and (12,5), and found evidence for heptanuclear complexes (18 to 21, 7). Baes, Mayer and Roberts [8] measured with the quinhydrone electrode at 0° and glass electrode at 95°. They also treated the data of Kraus and Holmberg.[6] They concluded a mechanism with the species (1,1), (2,1), (2,2), (8,4), and (15,6) ("scheme III"), or possibly one ("scheme IV") with (6,3) instead of (8,4). Johansson [9] in this laboratory has recently made X-ray studies of quite concentrated thorium perchlorate solutions at various degrees of hydrolysis.

In *chloride solutions*, working with 0.5 and 0.7 M Th self-medium, Hietanen and Sillén [10] found evidence for complexes with one or two OH, which they interpreted as (1,2) and (2,2); actually this method gives information on the number of OH ions per complex (p) whereas the number of Th (q) must be concluded from comparisons with other media.

In this laboratory, Johansson [9] has made an X-ray study on hydrolyzed Th chloride solutions of high concentrations.

The present work is concerned with measurements using hydrogen (and sometimes glass) electrodes, in the medium 3 M (Na)Cl. An attempt has been made to cover a wide concentration range, and to use some of the recent techniques — *e.g.* coulometric titration at low Th concentrations — that may increase the precision of the measurements. A preliminary result of the present study has been published earlier.[11]

EXPERIMENTAL

Reagents and analysis

Sodium chloride, Merck *p.a.* or Baker *p.a.* was used after heating to 360°C.

Hydrochloric acid, Kebo, was standardized against $KHCO_3$ or Tl_2CO_3, and checked against standard NaOH.

Sodium hydroxide solutions were prepared as usual. A 50 % solution of NaOH *p.a.* was left standing in a polyethylene bottle for several days, after which the clear solution was pipetted out and diluted with de-aerated water. The dilute alkaline solution was

standardized against hydrazine sulfate, and against HCl; the two methods agreed within better than 0.1 %.

Sodium hydrogen carbonate solution was prepared from $NaHCO_3$, Merck *p.a.* and analysed against HCl.

Thorium chloride solutions for the coulometric experiments, which were made after the "buret" titrations, were prepared from $ThCl_4(H_2O)_8$ *p.a.* Lindsay Rare Earth Chemicals, West Chicago, Ill. Before that material was available, thus for the earlier set of titrations, we started from $Th(NO_3)_4(H_2O)_4$, Kebo *puriss.*, which had to be freed from traces of Fe. Three methods of preparation were used; it should be remembered that for this type of work it is not necessary to start with a pure solid of stoichiometric composition since the excess or deficit of H^+ (H_0) will at any rate be determined during the experiments.

1) Fe was removed by dissolving the nitrate in 6 M HCl and extracting with isopropyl ether according to Dodson *et al.*[12] The aqueous phase was heated under an infrared lamp, adding conc. HCl or water at intervals, until no trace of nitrate could be detected.

2) After removal of Fe by extraction, Th was precipitated with $(NH_4)_2CO_3$ solution, filtered off, and ignited. When ThO_2 was heated in a stream of Cl_2 and CCl_4, $ThCl_4$ sublimed and was then used for making the solutions. The product was pure but the yield was small.

3) Thorium nitrate was dissolved in water, and KIO_3 solution added. Thorium iodate precipitated and was filtered off, washed and dissolved in HCl. Iodine was removed by heating under an infrared lamp. The remainder, $ThCl_4$ and some KCl, was dissolved in water, ammonium carbonate solution was added, and the precipitate was washed, heated and dissolved in HCl. No trace of alkali metals could be detected by a spectrographic method.

Most of the earlier experiments were made with method 1, but no significant difference in results was found with different preparation methods.

For the analyses, Th was precipitated with oxine, ignited and determined as ThO_2. Total chloride was found by passing the solution through a H^+-saturated cation exchanger, and titrating the eluate with standard NaOH. In some cases AgCl was precipitated from the original thorium chloride solution. The results agreed within ± 0.1 %.

Apparatus and procedure

All measurements were performed in an oil thermostat at 25 $\pm$ 0.1°C. $[H^+] = h$ was determined electrometrically in cells of the type

$$\text{SE/equilibrium solution, } H^+/H_2,\text{Pt} \qquad (2)$$

In a few cases we used cells

$$\text{SE/equilibrium solution, } H^+/\text{glass electrode} \qquad (3)$$

The reference half cell was

$$\text{SE} = \text{Ag,AgCl/3 M NaCl (saturated with AgCl)/3 M NaCl/} \qquad (4)$$

The electrode vessel and the salt bridge were of the same type as described in previous papers from this laboratory.[13] In cell (2), a platinized Pt electrode was used. The earlier part of the work was made as emf titrations, adding $NaHCO_3$ (or in a few cases NaOH) solution from one buret, and Th solution from another, so as to keep the total Th concentration (B) and the ionic medium (3 M (Na)Cl) constant, and to decrease the analytical H^+ excess, H, which became negative in the course of the titration. In some experiments the direction was reversed, HCl being added to a solution with negative H. In others, ionic medium and thorium solution were mixed, keeping one in the buret, and the other in the equilibrium vessel, so as to keep Z roughly constant whereas B varied.

In some "flask titrations" a series of solutions of different B and Z were prepared and kept in a thermostat room at 25°C; after various times they were placed in the oil thermostat, and hydrogen and reference electrodes inserted.

In some later experiments, especially at low concentrations, the composition was changed by a coulometric method developed by Biedermann and Ciavatta in this laboratory.[14] Into the equilibrium solution in cell (2) were inserted a Pt-net as the coulometric

cathode, and the connecting tube to another Wilhelm bridge, which contained 3 M NaCl and the anode, a silver-coated Pt foil electrode. At the anode (separated from the equilibrium solution) soluble chloroargentate complexes were formed, and the cathode reaction was

$$H^+ + e^- \longrightarrow \tfrac{1}{2} H_2 \qquad (5)$$

so that H^+ was removed from the equilibrium solution.

The current source was a coulometric analyzer, Leeds and Northrup Co. The current strength was 6.430 mA for the higher Th concentrations, and 0.6430 mA for the lower ones. The solution was stirred by bubbling H_2 during the electrolysis, to avoid precipitation because of local excess of OH^-.

Hydrogen gas was taken from a cylinder and freed from oxygen by passing through a column of activated copper, or of Deoxo.

SYMBOLS

$b = [Th^{4+}]$; $B = [Th]_{total}$; H = analytical H^+ excess concentration (often negative); $h = [H^+]$; $Z = (h - H)B^{-1}$ average number of OH bound per Th; β_{pq} = formation constant of the (p,q) complex (1); U = error-square sum, here = $\sum(Z_{calc} - Z_{exp})^2$ (10); $\sigma(Z)$ = standard deviation in Z; F_σ = "sigfak", rejection criterium; a complex is rejected if $\beta_{pq} > F_\sigma\, \sigma(\beta_{pq})$.

EVALUATION OF DATA

If a set of complexes (p,q) are formed, the equilibrium law (1), and the conditions for mass balance give for the total concentration of Th

$$B = b + \sum q\, \beta_{pq}\, h^{-p} b^q \qquad (6)$$

and for the number of moles of OH^- bound to Th per liter

$$BZ = \sum p\, \beta_{pq}\, h^{-p} b^q \qquad (7)$$

The analytical H^+ excess concentration is

$$H = h - BZ \qquad (8)$$

The primary experimental data are H, h, and B. B is presumably known quite accurately from the analyses. The free H^+ concentration, h, is determined from the E of cells (2) or in a few cases (3). For cell (2) we have

$$E = E_0 + 59.15 \log h - 29.58 \log p(H_2) + E_j;\ E_j = jh \qquad (9)$$

For the glass electrode we have a similar equation, without the $p(H_2)$ term.

In most of our series of experiments, the first points were at such high values h that BZ could be neglected in (8) and $h \approx H$. Hence these points could be used for constructing a Gran [15] diagram which gave both H in the original solution, and E_0 in eqn. (9). At first the calculation was made only graphically; later on, the data, E and added volume (or charge), were inserted into the general minimizing program Letagrop to find the values for E_0 and H_0 that gave the best agreement. The standard deviation of E_0 came out between 0.01 and 0.04 mV, and that of H_0 between 1 and 3 μM (thus 10^{-6} M).

By the application of trivial stoichiometry, and eqns. (8) and (9), these calculations gave sets of data $Z(\log h)_B$.

At some of the highest B values, E_0 was also taken from the most acidic points but H_0 was taken from the analytical data. At any rate, the Letagrop adjustment of "δZ" is a first check on H_0.

Now, the aim was to find a mechanism that gave a good agreement, which was defined as a low value for the error square sum

$$U = \sum(Z_{calc} - Z_{exp})^2 \tag{10}$$

In this equation, Z_{exp} is obtained from eqn. (8):

$$Z_{exp} = (h-H)B^{-1} \tag{11}$$

using for h the value calculated from E, and for B and H the values from analysis, including the information from the Gran diagram.

The calculated Z could be found in principle by eliminating b from eqns. (6) and (7), assuming B, h, and the β_{pq} to be known. However, we wished to include the possibility that there was a small analytical error in the evaluation of the Gran diagram. For chemical reasons it seemed reasonable to assume that H was more accurately determined in those solutions of acid or alkali that were free from Th than in the Th solution; an error of H in the Th solution would correspond to a constant error δZ. So, we set, in the final calculations

$$Z_{calc} = Z \text{ (from eqns. 6 and 7)} + \delta Z \tag{12}$$

This error might be different in different "titrations" so it was used as a group parameter, k_s in the Letagrop calculations.[16]

As usual, we saw no point in weighting the error squares in (10) although this could easily have been done in the program: the selection of the experimental points in various concentration ranges is an important factor, and we think it is reasonable to assume that the uncertainty in Z is roughly the same in experiments of various B, rather than for instance that in $B\bar{Z}$, or in log Z.

THE DATA

The $Z(\log h)_B$ curves obtained by glass electrode titrations did not differ systematically from those obtained with a hydrogen electrode, but they gave a greater spread, and a much lower accuracy was obtained in determining H_0 from the Gran diagram. Hence, at the end all glass electrode titrations were left out from the final evaluation.

Our data obtained with hydrogen electrodes are given in Table 2, and a survey is given in Fig. 1.

Ten total concentrations B were used between 0.0001 and 0.1 M. We have coulometric data for 0.1 through 1 mM, and data with buret additions from 0.25 to 100 mM. In the Letagrop calculations, however, the "buret" data were used only between 2 and 100 mM since the coulometric data were considered more accurate; there were no systematic deviations, as may be seen from Table 2.

Table 1. Experiments on aging of Th solutions at relatively high Z values and various $B = [\mathrm{Th}]_{tot}$

Date 19/9 −57			26/9 −57		2/10 −57	
B mM	Z	log h	Z	log h	Z	log h
20.00	1.518	−3.447	precipitation			
10.00	1.529	−3.538	1.530	−3.525	1.530	−3.523
5.00	1.546	−3.629	1.549	−3.609	1.549	−3.607
2.00	1.585	−3.766	1.585	−3.754	1.587	−3.756
1.00	1.633	−3.877	1.647	−3.831	1.650	−3.823
0.50	1.702	−3.966	1.732	−3.936	1.735	−3.930
0.25	1.791	−4.139	1.880	−4.016	1.891	−4.005

Date 29/9 −57			5/10 −57	
B mM	Z	log h	Z	log h
2.00	1.110	−3.655	1.110	−3.655
1.00	1.169	−3.771	1.170	−3.769
0.50	1.258	−3.890	1.260	−3.886
0.25	1.378	−4.024	1.376	−4.025

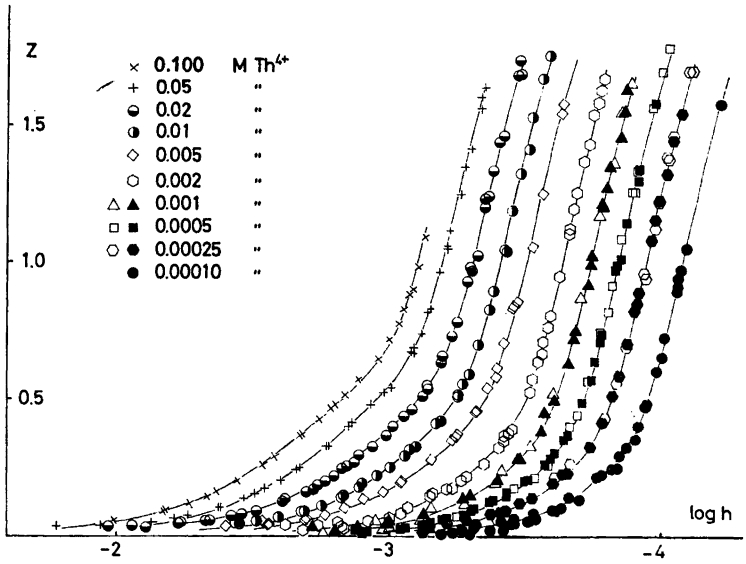

Fig. 1. Hydrolysis of Th^{4+}: Z = average number of OH^- bound per Th^{4+}, as a function of log h for various total concentrations, B, of Th. The black symbols for B = 0.00010 M through 0.001 M refer to coulometric titrations, the rest are buret titrations. Curves: calculated with mechanism IIIB. Numerical values are given in Table 1.

For the calculations, 158 points were selected which can be distinguished in Table 2 since for these points the values −log h and Z are followed by the deviation $1000(Z_{calc} - Z_{exp})$.

Table 2. Experimental data $(-\log h, Z)_B$ for hydrolysis of Th^{4+} in 3 M (Na)Cl medium. For the points used in the Letagrop calculations also $1000(Z_{calc} - Z_{exp})$ is given, using the set III b (Table 3) of equilibrium constants and δZ. Points marked with an asterisk were obtained by interpolation of titrations at "constant Z" (really constant H/B).

$B = 0.100$ M
1.987, 0.055, −8; 2.177, 0.091, −2; 2.264, 0.117, +1; 2.331, 0.143, +3; 2.441, 0.199, +5; 2.575, 0.290, +4; 2.681, 0.375, +3; 2.785, 0.468, −1; 2.887, 0.570, −11; 3.001, 0.717, −15; 3.053, 0.828, −8; 3.072, 0.882, −4; 3.107, 0.985, +19; 3.132, 1.090, +16; 2.154, 0.092; 2.346, 0.161; 2.517, 0.260; 2.653, 0.365; 2.725, 0.427; 2.782, 0.480; 3.017, 0.775; 3.067, 0.903; 3.118, 1.068;
2.171, 0.089; 2.363, 0.159; 2.534, 0.258; 2.670, 0.364; 2.742, 0.427; 2.799, 0.479; (2.857, 0.554;) *3.117, 1.007; *2.958, 0.647; *2.834, 0.515;

$B = 0.050$ M
1.778, 0.035; 1.942, 0.038; 2.126, 0.053; 2.260, 0.075, −12; 2.375, 0.106, −9; 2.465, 0.140, −6; 2.541, 0.175, −1; 2.654, 0.244, +3; 2.769, 0.330, +6; 2.850, 0.402, +4; 2.931, 0.480, −0; 3.008, 0.542, +17; 3.088, 0.689, −7; 3.139, 0.818, −5; 3.182, 0.964, +3; 3.219, 1.117, +4; 3.274, 1.350, +11; 3.335, 1.606, −7;
2.210, 0.064; 2.379, 0.106; 2.505, 0.154; 2.599, 0.203; 2.669, 0.249; 2.775, 0.329; 2.863, 0.412; 2.979, 0.525; 3.117, 0.740; 3.151, 0.829; 3.210, 1.050; 3.261, 1.249; 3.302, 1.416; 3.336, 1.564; 3.349, 1.640;
3.212, 1.010; *3.269, 1.350; *3.093, 0.716;

$B = 0.020$ *M*
2.224, 0.046, +2; 2.342, 0.058, +4; 2.459, 0.079, +5; 2.513, 0.093, +6; 2.612, 0.125. +9; 2.696, 0.161, +12; 2.766, 0.199, +15; 2.845, 0.257, +11; 2.937, 0.326, +16; 3.056, 0.439, +12; 3.139, 0.550, −4; 3.194, 0.656, −16; 3.295, 0.982, −22; 3.352, 1.234, −25; 3.401, 1.438, −18; 3.475, 1.737;
2.058, 0.038; 2.236, 0.051; 2.420, 0.073; 2.608, 0.125; 2.736, 0.186; 2.824, 0.244; 3.014, 0.398; 3.139, 0.547; 3.229, 0.730, −6; 3.285, 0.931; 3.348, 1.200; 3.381, 1.334; 3.478, 1.736; 2.719, 0.169; 2.800, 0.218; 2.872, 0.268; 2.992, 0.366; 3.084, 0.460; 3.192, 0.632; 3.250, 0.781; 3.301, 0.966; 3.364, 1.240; 3.416, 1.461; 3.471, 1.681;
*3.142, 0.536; *3.324, 1.024; *3.381, 1.334; *3.478, 1.736;

Back titration: 3.125, 0.513; 2.890, 0.302; 2.619, 0.142; 2.331, 0.058; 2.112, 0.030; 1.963, 0.021; 1.621, 0.008; 1.385, 0.004; 1.294, 0.002;

$B = 0.010$ M
2.434, 0.045; 2.512, 0.054; 2.593, 0.068; 2.674, 0.088; 2.752, 0.113; 2.826, 0.142; 2.891, 0.177, +3; 3.006, 0.250, +10; 3.099, 0.326; 3.189, 0.420, +10; 3.247, 0.508, +1; 3.293, 0.591, +10; 3.428, 1.037; 3.513, 1.413;
2.443, 0.045, −11; 2.519, 0.056, −11; 2.685, 0.090, −5; 2.832, 0.148, −2; 2.955, 0.220, +2; 3.057, 0.295, +7; 3.173, 0.409, +3; 3.250, 0.518; 3.268, 0.554; 3.421, 1.038; 3.523, 1.530; 3.427, 1.037; 2.438, 0.054; 2.675, 0.098; 2.899, 0.193; 3.075, 0.317; 3.280, 0.581; 3.364, 0.826; 3.419, 1.043; 3.500, 1.404; 3.590, 1.754, −17;
3.326, 0.697, −5; 3.381, 0.896, +1; 3.419, 1.056, +8; 3.448, 1.189, +6; 3.479, 1.324, +8; 3.563, 1.670, −17;

$B = 0.005$ M
2.397, 0.034; 2.534, 0.056; 2.907, 0.134; 3.229, 0.352, −8; 3.395, 0.612, −12; 3.468, 0.855, +2; 3.560, 1.250, +22; 3.634, 1.580, −8;
2.556, 0.040, −0; 2.693, 0.060; 2.764, 0.078, −2; 2.837, 0.100; 2.978, 0.160, −2; 3.045, 0.195; 3.156, 0.277, +1; 3.246, 0.365; 3.316, 0.453; 3.361, 0.541; 3.419, 0.705; 3.453, 0.833;
2.557, 0.046; 2.695, 0.066, −6; 2.766, 0.080; 2.838, 0.106, −9; 2.980, 0.165; 3.047, 0.200, −2; 3.158, 0.284, −4; 3.248, 0.372, −9; 3.318, 0.460, −13; 3.363, 0.528, −4; 3.420, 0.713; 3.455, 0.840;
*3.391, 0.582; *3.525, 1.059, +54; *3.629, 1.546;

$B = 0.002$ M
2.812, 0.050, −14; 3.071, 0.105, −3; 3.153, 0.145, −4; 3.213, 0.175, +1; 3.284, 0.220, +7; 3.351, 0.265, +19; 3.403, 0.325, +13; 3.449, 0.390, +8; 3.515, 0.525, +6; 3.559, 0.665, +6; 3.593, 0.805, +3; 3.625, 0.950, +3; 3.675, 1.195, −9; 3.732, 1.430, +2; 3.787, 1.671, −37;
2.565, 0.006; 2.682, 0.018; 2.835, 0.026; 3.023, 0.069; 3.233, 0.175; 3.424, 0.347; 3.588, 0.804; 3.684, 1.254; 3.787, 1.671;
2.654, 0.008; 2.828, 0.035; 3.044, 0.086; 3.264, 0.204; 3.434, 0.377; 3.526, 0.574; 3.578, 0.763; 3.659, 1.125; 3.711, 1.372; 3.776, 1.628;
Back titration: 3.745, 1.540; 3.654, 1.105; 3.564, 0.710; 3.420, 0.370; 3.159, 0.155; 2.922, 0.055; 2.707, 0.040;
*3.766, 1.585; *3.655, 1.110; *3.548, 0.640;

$B = 0.001$ M, coulometric titrations:
2.803, 0.014, +1; 2.892, 0.025, −1; 2.990, 0.045, −7; 3.133, 0.079, −7; 3.298, 0.148, −5; 3.397, 0.204, +7; 3.476, 0.279, +6; 3.572, 0.449, −28; 3.608, 0.493, +7; 3.676, 0.719, +3; 3.738, 0.993, +6; 3.797, 1.271, +7; 3.863, 1.549, +9;
2.721, 0.034; 2.888, 0.029; 2.997, 0.044; 3.132, 0.077; 3.298, 0.143; 3.473, 0.277; 3.605, 0.488; 3.683, 0.749; 3.742, 1.025; 3.808, 1.299; 3.864, 1.581;
2.807, 0.019; 2.897, 0.029; 2.988, 0.050; 3.121, 0.083; 3.272, 0.138; 3.481, 0.283; 3.560, 0.382; 3.658, 0.627; 3.728, 0.916; 3.780, 1.154; 3.850, 1.457;

$B = 0.001$ M, buret titrations:
2.574, 0.006; 2.676, 0.013; 2.757, 0.018; 2.951, 0.059; 3.158, 0.105; 3.413, 0.240; 3.606, 0.522; 3.702, 0.870; 3.778, 1.215; 3.850, 1.547; 3.522, 0.335; 3.388, 0.194; 3.278, 0.116; 3.117, 0.059; 3.011, 0.029; 2.842, 0.016; 2.834, 0.008;
2.980, 0.034; 3.076, 0.038; 3.287, 0.123; 3.397, 0.204; 3.572, 0.449; 3.680, 0.750; 3.740, 0.999; 3.820, 1.364; 3.885, 1.655;
*3.769, 1.170; *3.877, 1.633; *3.870, 1.635;
Back titration:
3.816, 1.389; 3.762, 1.125; 3.638, 0.622; 3.401, 0.241; 3.325, 0.181; 3.252, 0.135; 3.176, 0.108; 3.115, 0.076; 3.050, 0.066; 3.005, 0.033; 2.825, 0.023;

$B = 0.0005$ M, coulometric titrations:
2.917, 0.016; 3.040, 0.026, −2; 3.143, 0.040, +0; 3.271, 0.076, −3; 3.431, 0.146, +0; 3.605, 0.300, −7; 3.742, 0.568, +10; 3.785, 0.734, +13; 3.847, 1.012, +22; 3.908, 1.296, +17; 3.976, 1.582, +3;
2.899, 0.008; 3.060, 0.028; 3.121, 0.040; 3.203, 0.060, −6; 3.299, 0.092, −9; 3.381, 0.128, −9; 3.501, 0.200, −6; 3.571, 0.260; 3.642, 0.348, −6; 3.707, 0.484, −12; 3.773, 0.706; 3.835, 0.984; 3.912, 1.340;
2.914, 0.010; 3.080, 0.032; 3.133, 0.040; 3.258, 0.076; 3.332, 0.102; 3.414, 0.140; 3.504, 0.198; 3.596, 0.282; 3.675, 0.394; 3.733, 0.544; 3.777, 0.706; 3.839, 0.982;
Back titration:
3.870, 1.144; 3.831, 0.968; 3.754, 0.636; 3.709, 0.490; 3.654, 0.364; 3.510, 0.204; 3.436, 0.162; 3.371, 0.126; 3.313, 0.098; 3.215, 0.064; 3.155, 0.050; 3.057, 0.038; 2.875, 0.020;

$B = 0.0005$ M, buret titrations:
3.253, 0.074; 3.303, 0.088; 3.358, 0.102; 3.463, 0.172; 3.576, 0.262; 3.665, 0.398; 3.727, 0.564; 3.774, 0.740; 3.816, 0.914; 3.850, 1.088; 3.905, 1.334; 3.963, 1.566; 4.024, 1.786;
*3.886, 1.260; *3.996, 1.702; *3.891, 1.258, *3.800, 0.820;
Back titration:
3.692, 0.441; 3.628, 0.306; 3.585, 0.258; 3.543, 0.214; 3.457, 0.148; 3.373, 0.110; 3.304, 0.072; 3.238, 0.037; 3.130, 0.030; 3.045, 0.016; 2.913, 0.018; 2.747, 0.002; 2.662, 0.010;

$B = 0.00025$ M, coulometric titrations:
3.148, 0.035, −7; 3.213, 0.046, −9; 3.287, 0.061, −11; 3.376, 0.080, −7; 3.482, 0.117, −2; 3.608, 0.190, +3; 3.742, 0.325, +12; 3.845, 0.586, −2; 3.916, 0.888, −5; 3.974, 1.155, +1; 4.041, 1.446, −1;
3.412, 0.088, −7; 3.524, 0.138, −1; 3.654, 0.228, +4; 3.786, 0.412, +5; 3.876, 0.699, +5; 3.902, 0.822; 3.962, 1.082, +18; 4.017, 1.323; 4.072, 1.543;

Back titration:
3.992, 1.230; 3.907, 0.844; 3.819, 0.512; 3.640, 0.224; 3.430, 0.089; 3.319, 0.043 3.128, 0.011;

B = 0.00025 M, buret titrations:
3.188, 0.024; 3.286, 0.060; 3.671, 0.264; 3.796, 0.428; 3.872, 0.688; 3.933, 0.960; 3.988, 1.220; 4.040, 1.464; 4.098, 1.700;
*3.941, 0.940; *4.024, 1.378; *4.010, 1.390;

B = 0.0001 M, coulometric titrations:
3.193, 0.006; 3.232, 0.010, +11; 3.267, 0.020, +4; 3.311, 0.030, −1; 3.410, 0.050, −6; 3.459, 0.060, −6; 3.532, 0.080, −6; 3.659, 0.140, −11; 3.778, 0.220, −4; 3.941, 0.470, +3; 4.069, 0.970, +2; 4.211, 1.580, −5;
3.297, 0.005; 3.372, 0.020; 3.460, 0.040; 3.541, 0.060; 3.632, 0.100, +14; 3.818, 0.240, +18; 3.873, 0.320; 3.914, 0.400; 3.980, 0.600; 4.009, 0.720, −16; 4.057, 0.940, −24;
3.325, 0.010; 3.421, 0.020; 3.511, 0.050; 3.597, 0.090; 3.681, 0.140; 3.763, 0.210; 3.847, 0.290; 3.947, 0.480; 3.998, 0.650; 4.057, 0.910; 4.089, 1.050;
3.227, 0.022; 3.297, 0.019; 3.358, 0.023; 3.451, 0.040; 3.530, 0.057; 3.617, 0.088; 3.701, 0.128, +26; 3.841, 0.244; 3.906, 0.350; 3.978, 0.560; 4.055, 0.893;

EQUILIBRATION

At the highest Z values there came a point where creeping of the potential, and sometimes a visible opalescence, showed that a precipitate had been formed. Such points were left out, and the present work is concerned only with clear solutions. However, there were certain signs of slow equilibration at the highest Z values, and a number of checks were made to study whether really reversible equilibria had been obtained.

Back titrations were made, adding HCl from a buret after the solution had reached a certain Z value by coulometric titration or by buret titration with $NaHCO_3$. The turning points were at $Z = 0.513$ for 0.020 M Th, at $Z = 1.540$ for 0.002 M Th, at $Z = 1.380$ for $B = 0.001$, and $Z = 0.441$ for $B = 0.0005$. As seen from Fig. 1 and Table 2, these points coincided (within the experimental accuracy) with points from the first part of the titration, with decreasing H and increasing Z.

In "flask titrations", E was measured in the same solution immediately after mixing, and after a week (for some also after two weeks). Table 1 indicates that for Z values below 1.7, there is no serious creep with time. Only Z values lower than 1.7 were used in the calculations.

PRELIMINARY TREATMENT

The data were first treated with a general integration method,[17] which gave the average composition $(\bar{p},\bar{q})$ of the complexes. After that a number of complexes that were thus indicated as possible were tried in Letagrop, our generalized least square program. Preliminary calculations[11] indicated mono, di-, and hexanuclear complexes: (2,1), (1,2), (2,2), (3,2), (14,6), (15,6). By that time it seemed natural to conclude that the hexanuclear complexes were likely to contain regular Th octahedra, similar to the Bi_6, Ce_6, and U_6 octahedra known from other evidence.

G. JOHANSSON'S X-RAY DATA

Dr. Georg Johansson in this laboratory has recently made an X-ray investigation[9] of hydrolyzed Th nitrate, chloride, and perchlorate solutions with no other ions added. The nitrate data have been more thoroughly analysed, but the chloride and perchlorate data are quite similar.

The solutions contained up to 3 M Th and $\bar{Z}$ was between 0 and 3.

At all $\bar{Z}$ values > 0, the radial distribution curve showed a peak at 4.0 Å, which is very close to the Th—Th distance in the group $(NO_3)_3(H_2O)_3Th(OH)_2Th(H_2O)_3(NO_3)_3$ found by him in a crystal structure.[9] At $\bar{Z} > 1$ there were smaller peaks at 6.5 and 7.6 Å (at $\bar{Z} > 2$) that he interpreted as partly due to Th—Th distances. He could also estimate the number of neighbors.

Now, if our preliminary equilibrium constants could be applied to his data (admittedly in a different medium), the (2,2) complex should predominate at $\bar{Z} \approx 1$, which fitted the picture. At higher $\bar{Z}$, the (14,6) and (15,6) complexes would presumably take over. The closest Th—Th distance in a larger complex might well also be close to ≈4.0 Å. However, with a regular Th_6 octahedron one would have expected a secondary peak at $4.0\sqrt{2} = 5.6$ Å, which was not observed.

Even if the regular octahedron could be excluded, the data did not suffice to establish with certainty the structure of the larger complexes.

SEARCH FOR THE "BEST" MECHANISM

In order to find out how good was the equilibrium evidence for large complexes, we decided to evaluate the data — by Letagrop adjustment — under four different assumptions,

I No complex with $q > 4$.
II No complex with $q > 5$
III No complex with $q > 6$
IV No restriction on q

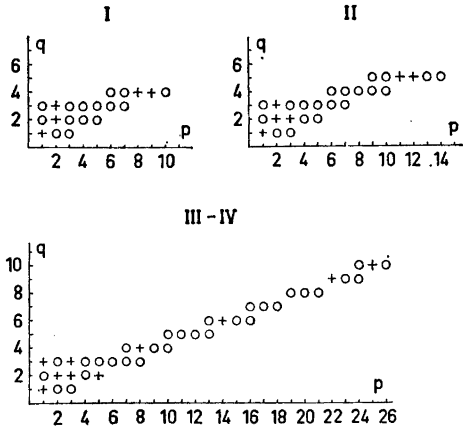

Fig. 2. Survey of species (p,q) tested with the assumptions I (no $q > 4$), II (no $q > 5$), III (no $q > 6$) and IV (no restriction on q). Crosses indicate species that remained in the "final" set of species and equilibrium constants. Circles indicate species (p,q) that were rejected, which means that when (p,q) was combined with the "surviving" species, at the minimum it came out with $\beta_{pq} < F_\sigma \sigma(\beta_{pq})$.

For each of these assumptions, Letagrop was used to search for the mechanism — set of (p,q, β_{pq}) — that gave the best fit with the data.

A) assuming no systematic errors, hence all $\delta Z = 0$

B) treating the systematic errors δZ as unknown parameters to be adjusted, together with the equilibrium constants, to give the best fit.

Fig. 2 shows which complexes (p,q) have been tested in cases I, II, and IV. Those marked with a cross were those that remained in the "best" combination and those with a circle were found not to diminish the error square sum significantly, if they were added to the combination of the "crosses".

Table 3. "Best" combinations of equilibrium constants log β_{pq} for Th^{4+} hydrolysis in 3 M Na(Cl) as found by Letagrop. I: $q \leq 4$; II: $q \leq 5$; III: $q \leq 6$; IV: no restriction on q. A: assuming no systematic error δZ; B: adjusting for δZ.

(p,q)	I A	I B	II A	II B
1,1	−4.60 ± 0.20	−4.52 ± 0.13	−4.77 ± 0.18	−4.57 ± 0.13
1,2				
2,2	−4.83 ± 0.08	−4.90 ± 0.06	−4.74 ± 0.06	−4.90 ± 0.08
3,2	—	—	−9.14(< −8.84)	−8.68 ± 0.12
5,2	—	—	—	—
1,3	—	—	—	—
2,3	−4.05(< −3.70)	—	−3.92 ± 0.24	−4.53(< −4.24)
3,3	—	—	—	—
8,4	−20.97(< −20.75)	—	—	—
9,4	−24.26 ± 0.11	−24.22 ± 0.08	—	—
11,5	—	—	−28.56 ± 0.10	−29.61(< −29.57)
12,5	—	—	−32.56 ± 0.13	−32.24 ± 0.10
14,6	—	—	—	—
25,10	—	—	—	—
$\sigma(Z)$	0.044	0.030	0.023	0.014

III A	III B	III′ A	IV A	IV B
−5.23(−4.98)	−5.14 ± 0.22	−5.28(< −4.99)	−5.04 ± 0.25	−4.97 ± 0.16
		−2.64(< −2.43)		
−4.75 ± 0.05	−4.78 ± 0.04	−4.78 ± 0.06	−4.74 ± 0.05	−4.76 ± 0.04
−8.71 ± 0.10	−8.72 ± 0.08	−8.67 ± 0.10	−8.93(< −8.72)	−8.94 ± 0.20
−17.32(< −17.11)	−17.16 ± 0.14	−17.39(< −17.13)	−17.09 ± 0.18	−16.99 ± 0.11
−1.35 ± 0.23	−1.50 ± 0.23	—	−1.19 ± 0.19	−1.36 ± 0.18
—	—	—	—	—
−6.90 ± 0.20	−6.86 ± 0.14	−6.92 ± 0.23	−6.86 ± 0.19	−6.83 ± 0.13
—	—	—	−21.06(< −20.85)	−21.11 ± 0.22
—	—	—	—	—
—	—	—	—	—
—	—	—	—	—
−36.38 ± 0.04	−36.42 ± 0.03	−36.38 ± 0.04	−36.56 ± 0.13	−36.58 ± 0.10
—	—	—	−65.29(< −65.09)	−65.35 ± 0.21
0.015	0.011	0.016	0.013	0.010

These calculations were made with the "species selector" in Letagrop. The results are summarized in Table 3, and the deviations in Z for various concentrations are indicated in Fig. 3 for I, II, and III.

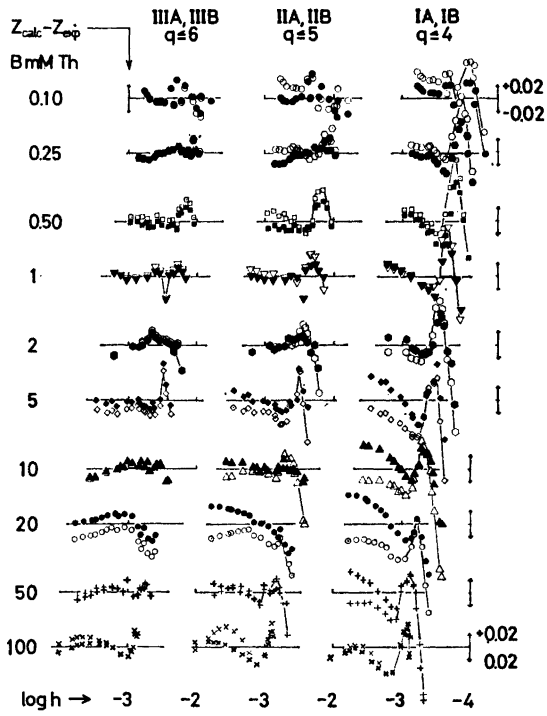

Fig. 3. Deviations ($Z_{calc} - Z_{exp}$) for various "best fit" mechanisms, IA through IIIB. Symbols mainly like in Fig. 1. The filled or blacker symbols are the "B" mechanisms, where correction has been made for an analytical error δZ, the others are the A mechanisms. The arrows to the extreme right indicate $\pm$ 0.02 in Z.

Our strategy has been as usual, to start with all $\delta Z = 0$ and find the set of species that give the "best" agreement (the "A" set) and after that to adjust the δZ. In this process, some earlier accepted equilibrium constants may become so small as compared to their $\sigma(\beta)$ that they are rejected by the species selector and do not appear in the "B" set. However, we have not tried to add, while varying the δZ, complexes that were not accepted with $\delta Z = 0$.

I. With $q \leq 4$, $\sigma(Z)$ came out as high as 0.044 with all $\delta Z = 0$, and as 0.030 with δZ adjusted. The direction of the systematic deviations at high Z values (Fig. 3) indicates that the experimental curves are steeper than the calculated ones.

II. With $q \leq 5$, the value for $\sigma(Z)$ becomes smaller than with I: 0.023 with $\delta Z = 0$, and 0.014 with δZ adjusted. There is still a systematic deviation indicating steeper experimental curves, but smaller than for I.

In both cases one has to assume the analytical errors δZ to be of the order of 0.02—0.06 for I and up to 0.05 for II (Table 4). Moreover there is a

Table 4. Analytical errors $100 \times \delta Z$, calculated for various titrations by Letagrop adjustment to best fit.

B, total concentration of Th^{4+} in M	I B	II B	III B	IV B
0.10	4.46 ± 0.92	3.18 ± 0.62	−0.55 ± 0.25	−0.90 ± 0.30
0.05	6.15 ± 0.91	3.86 ± 0.56	−0.15 ± 0.20	−0.67 ± 0.17
0.02	6.91 ± 0.88	5.27 ± 0.51	2.53 ± 0.34	2.16 ± 0.36
0.01	5.35 ± 0.87	2.76 ± 0.51	0.47 ± 0.20	0.05 ± 0.20
0.005	4.93 ± 0.91	2.73 ± 0.52	1.46 ± 0.39	1.35 ± 0.31
0.002	2.35 ± 0.99	−0.03 ± 0.58	0.14 ± 0.34	0.20 ± 0.31
0.001	4.86 ± 0.99	−1.34 ± 0.58	−0.06 ± 0.33	0.05 ± 0.27
0.00050	−1.05 ± 0.95	−2.91 ± 0.59	−0.61 ± 0.25	−0.50 ± 0.23
0.00025	−1.79 ± 0.95	−3.32 ± 0.61	−0.14 ± 0.18	−0.02 ± 0.14
0.00010	−2.68 ± 0.98	−4.11 ± 0.65	−0.35 ± 0.32	−0.73 ± 0.33

systematic drift of δZ which comes out negative for low B and positive for high B. This is in the direction to be expected if the experimental curves $Z(\log h)_B$ are more crowded than the calculated ones.

From our knowledge of the experimental procedure we would have expected the systematic δZ to be at most of the order of 0.01, and either to be fairly constant throughout a series of solutions, or to vary irregularly.

III. A considerably better agreement was obtained if also hexamers were allowed, (also given in Fig. 3). The value for $\sigma(Z)$ drops to 0.015 without δZ adjustment, 0.011 with adjustment, which is quite reasonable. A slight improvement was found by adding (24,10) and (8,4) (mechanism IV) which gave $\sigma(Z) = 0.013$ without, and 0.010 with adjustment of δZ. In III'A, (1,3) was replaced by (1,2) which gave a somewhat higher $\sigma(Z) = 0.016$ for $\delta Z = 0$.

As compared with I and II, the various sets under III came out with more reasonable values for $\sigma(Z)$ and for δZ.

We may thus conclude from the emf data that explanations with all $q \leq 4$, or $q \leq 5$ do not give an acceptable agreement with the data; the disagreement persists to quite low concentrations of Th so that it would be very hard to put the blame on activity factors.

On the other hand, assuming hexamers, an acceptable agreement with the data is obtained which may be slightly improved by adding other species. So, by the standards hitherto used there is good evidence for hexanuclear species.

The X-ray data [9] indicate that they are not regular octahedra. It seems risky to attempt a structure model on the present evidence, but we hope that someone will some day find a crystal structure that gives a good clue.

One must not forget that the solutions studied by Johansson had a different composition from ours; fewer anions, no Na^+, less free water, and much more Th. So there is the possibility that slightly different complexes may have been formed in his solutions.

Out of the complexes listed, perhaps (1,3) requires some attention. In earlier work with self-medium, we concluded the formation of the complex with one OH^- group and ascribed to it the formula Th_2OH^{7+} (+ an unknown number of anions and H_2O). This gave a reasonable fit with the data whereas

$ThOH^{3+}$ did not; we never discussed Th_3OH^{11+} (+ anions), perhaps since we had difficulties to imagine it geometrically. The present data seem to give a better agreement with the (1,3) complex than with the (1,2) complex, but one would like to have more evidence before one accepts it willingly.

RECALCULATION OF EARLIER DATA FOR PERCHLORATE MEDIUM

We have made some calculations on earlier data [2,6,8] for the medium 1 M $NaClO_4$. The Oak Ridge School [6,8] has made titrations with varying B; Ref. 8 gives the B values, for Ref. 6 we calculated B for each point by interpolation from the published data. To the set (1,1), (2,1), (2,4), (8,4), and (15,6) suggested by Baes *et al.* we tried to add (14,6) and a few other complexes that had been suggested by preliminary calculations for chloride medium; however, all were rejected by our species selector. We did not try make a very thorough test of various mechanisms because the range in B was narrow (0.0016 to 0.020) and because our main aim was to see whether our methods of calculation were equivalent.

The "best" values for log ($\beta \pm 3\ \sigma$) so found are given in Table 5 and compared with the log ($\beta \pm \sigma$) calculated by Baes *et al.*[8] One may especially compare "0°, A" with "0°,8" and "95°, A" with "95°,8". The agreement is excellent if it is observed that we give $3\sigma(\beta)$ and Baes *et al.* give $\sigma(\beta)$. Also $\sigma(Z)$ agrees very well. Hence it seems that our least-square programs give equivalent results for a "well-behaving" set of species. From the description in Ref. 8, however, we can see some practical advantages of Letagrop when it comes to testing many mechanisms and less well-behaving combinations, or to test for systematic errors.

Another conclusion is that both in Oak Ridge and Stockholm, one can nowadays get $\sigma(Z)$ around 0.010 in this type of measurements.

The old data of one of us [2] covered a narrow concentration range, 0.001 to 0.020 M, and was surely not of present-day accuracy. We have recalculated the data for $Z < 2$, using a larger set of data than given in the paper. Some more complexes were tried (Fig. 4), and rejected, after the systematic errors had been introduced. The resulting $\sigma(Z) = 0.028$ is large and shows that we may have learnt something in the meantime.

We think it would be desirable to have data over a broader concentration range for Th hydrolysis, and also in nitrate and perchlorate medium, with the accuracy that is possible today.

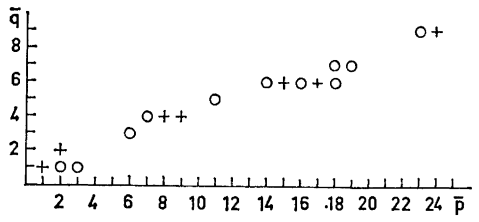

Fig. 4. Complexes (p,q) tested with hydrolysis data in perchlorate medium from Ref. 2. Symbols like in Fig. 2.

Table 5. Equilibrium constants, log ($\beta_{pq} \pm 3\sigma$) for Th^{4+} hydrolysis in 1 M (Na)ClO_4 medium, recalculated from Refs. 2, 6, 8.

1,1	2,1	2,2	8,4	15,6	$\sigma(Z)$	Data	Ref.
−4.33 ± 0.07	−8.48 ± 0.10	−5.60 ± 0.06	−22.79 ± 0.05	−43.84 ± 0.06	0.012	8	0° A
−4.31 ± 0.06	−8.46 ± 0.09	−5.59 ± 0.06	−22.80 ± 0.05	−43.81 ± 0.05	0.010	8	0° B
−4.32 ± 0.02	−8.48 ± 0.03	−5.60 ± 0.02	−22.79 ± 0.02	−43.84 ± 0.02	0.012	8	0° 8
−2.28 ± 0.06	−4.50 ± 0.02	−2.56 ± 0.12	−10.49 ± 0.09	−20.63 ± 0.07	0.015	8	95°, A
−2.25 ± 0.03	−4.51 ± 0.02	−2.59 ± 0.08	−10.44 ± 0.05	−20.61 ± 0.05	0.009	8	95°, B
−2.29 ± 0.02	−4.50 ± 0.01	−2.55 ± 0.03	−10.49 ± 0.03	−20.63 ± 0.02	0.015	8	95°, 8
−4.21 ± 0.13	−7.72 ± 0.07	−4.61 ± 0.06	−19.15 ± 0.01	−37.02 ± 0.06	0.015	6	25°, A
−4.23 ± 0.11	−7.69 ± 0.06	−4.61 ± 0.05	−19.16 ± 0.05	−37.02 ± 0.05	0.012	6	25°, B
−4.15 ± 0.04	−7.70 ± 0.03	−4.61 ± 0.02	−19.01 ± 0.02	−36.76 ± 0.02	0.015	6	25°, 8
−3.69 ± 0.01	−4.43 ± 0.01	—	−18.75 ± 0.01	−36.37 ± 0.12	0.042	2	25°, A
−3.71 ± 0.08	−4.44 ± 0.07	—	−18.78 ± 0.08	−36.42 ± 0.08	0.028	2	25°, B

A: calculated with Letagrop, $\delta Z = 0$; B: calculated with Letagrop δZ adjusted, 8: calculated by Baes *et al.* with Rush program at Oak Ridge.

The correction 1000 δZ was for data of Ref. 8 for 0° $+3 \pm 3$ to -11 ± 2; for 95° 2 ± 2 to 24 ± 16; for data of Ref. 6: 3 ± 3 to 23 ± 3; for data of Ref. 2: 10 ± 10 to 47 ± 4.

Acknowledgements. The present work has been supported by *Statens Naturvetenskapliga Forskningsråd (Swedish Natural Science Research Council)*. Dr. Georg Biedermann has given valuable advice about the coulometric method. We wish to thank Dr. Georg Johansson for many pleasant discussions. Dr. George Baldwin was kind enough to correct the English of the text.

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Received August 3, 1967.