

Studies on the Hydrolysis of Metal Ions

IX. The Hydrolysis of the Thorium Ion, Th⁴⁺

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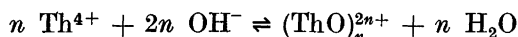
*Department of Inorganic Chemistry, The Royal Institute of Technology,
Stockholm 70, Sweden*PREVIOUS WORK ON Th⁴⁺ HYDROLYSIS

Denham¹ measured [H⁺] in various Th(SO₄)₂ solutions with a hydrogen electrode. He found that *E* varied with time — in one case it changed by 17 mV in the course of 11 days.

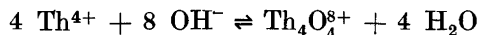
Hildebrand² and Britton³ titrated various thorium salt solutions with OH⁻, using hydrogen electrodes. Their chief aim was to study the precipitation of the hydroxyde or of basic salts. In their measurements, both the ionic strength and the total concentration of thorium varied, so that it is hard to make calculations on the basis of their data.

Chauvenet and Tonnet⁴ measured the changes in conductivity and the amount of heat evolved on mixing Th⁴⁺ (as chloride) and OH⁻ in various proportions. They found a not too distinct bend at the ratio 1 Th per 2 OH⁻, from which they concluded that the reaction was: ThCl₄ + 2 H₂O → Th(OH)₂Cl₂ + 2 HCl. Chauvenet and Souteyrand-Franck⁵ similarly concluded that Th(OH)₂(NO₃)₂ is formed in nitrate solutions.

Schaal and Faucherre⁶ measured pH in 0.12 C, 0.25 C, and 0.5 C thorium perchlorate and nitrate solutions and varied the ratio Th/OH by adding alkali. The ionic strength was kept constant by means of sodium perchlorate or nitrate. They assumed *a priori* that the following reaction occurs:

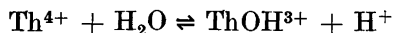


From their data they concluded $n = 4$ and thus the reaction would be:



Souchay⁷ claimed that his measurements on the freezing-point depression of thorium nitrate solutions also indicate the presence of this tetramer.

From investigations on thorium nitrate solutions, Kasper⁸ concluded that thorium forms mononuclear hydroxyl complexes according to the reaction



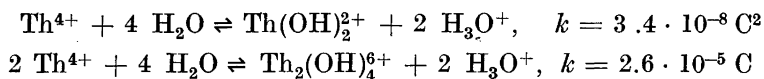
and that the equilibrium constant for this reaction is about 10^{-3.4}.

It has thus sometimes been assumed that thorium forms mononuclear complexes and sometimes that a polynuclear complex is formed:

The present work was started in 1947 to throw more light on the nature of the complexes and if possible to determine the equilibrium constants involved; the greater part of the experimental work was completed in 1948, but a few complementary measurements were made as late as in 1953. The results, and the main conclusions given here, were presented at the Symposium on coordination chemistry in Copenhagen, August 1953.

When the measurements and calculations to be given in the following had already been completed, Dr. Kurt A. Kraus of Oak Ridge was kind enough to send us a manuscript by Kraus and Holmberg⁹. They have studied the hydrolysis of thorium in perchlorate and chloride solutions by EMF measurements with a glass electrode, using either the same ionic medium as ourselves, 1 C NaClO₄, or 1 C NaCl, at 25° C.

Kraus and Holmberg assumed the following reactions, and approximate equilibrium constants:



Since these reactions could not explain the data completely, they concluded that other complexes are also formed. As will be seen their data agree excellently with the present work, although our conclusions differ considerably.

METHOD

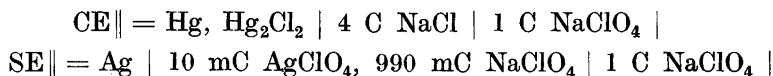
The present investigation was carried out as a series of potentiometric titrations at 25° C, adding NaOH to thorium perchlorate solutions containing initially a slight excess of HClO₄. All solutions were made to contain 1 C ClO₄ by adding NaClO₄. In each titration the total thorium concentration *M* was kept constant in order to make the calculations simpler. Since the hydrogen ion and thorium concentrations were kept low compared with the concentration of perchlorate ion, we may assume that the activity factors remained constant, and hence that concentrations could be used instead of the activities in the calculations¹⁰.

To study the mechanism of hydrolysis, it would have been desirable to know the concentrations of both H⁺ and Th⁴⁺. It seems, however, that nobody has ever been able to produce an electrode reversible to Th⁴⁺, so we must be content with measuring

$$[\text{H}^+] = h \quad (1)$$

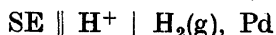
The hydrogen ion concentration *h* could be measured with a glass, quinhydrone, or hydrogen electrode. The quinhydrone electrode was used in the majority of the experiments because it is accurate and easy to work with. To check that no error is introduced by complex formation between quinhydrone and thorium, the hydrogen electrode was used in a few titrations.

The following two types of reference electrodes were used:



A calomel electrode was used for the first titrations but, later on, silver electrodes were used since they proved more stable. The salt bridge always contained 1 C NaClO₄.

The cells for measuring the hydrogen ion concentration may thus be written:



For any of these cells, E (in mV) can be written in the form

$$E = E_0 + E_j + 59.16 \log h$$

Here E_0 is a constant, different for each type of cell, h is the hydrogen ion concentration, and E_j the liquid junction potential¹⁰, which is an approximately linear function of h .

An example of a titration will be given below. Each titration generally started with an acid-base titration (without any thorium present) from which E and $E_j(h)$ were obtained. Then thorium ions were added, first in one large amount, and then simultaneously with the addition of NaOH, so that the total thorium concentration M was kept constant.

For each point of the following titration one could calculate h from E , using E_0 , E_j and equation (2). From the composition of the solution, the analytical hydrogen ion excess H (assuming all Th to be present as Th⁴⁺) was known. Then one could calculate (cf. VIII, 6; [OH⁻] is negligible in all Th solutions studied here)

$$Z = \frac{h-H}{M} \quad (3)$$

Z is the average number of protons split off per Th, or of OH bound per Th. For the following discussion, the experimental data are conveniently plotted in the form $Z(\log h)_M$.

For convenience, the concentrations h and M will generally be expressed in mC, except in the final equilibrium constants, where C is the unit.

EXPERIMENTAL

Reagents

Thorium perchlorate solutions were prepared as follows: Thorium nitrate (Kebo puriss.) was moistened with water and then heated with 70–72 % perchloric acid (Kebo p.a.) on a sand bath at 150–180° C until no trace of nitric acid could be detected in the residue with the Fe³⁺ + H₂SO₄ reaction. Water was added to make the Th concentration about 0.1 C. For analysis thorium was precipitated with oxine¹¹ and determined as ThO₂. In the determination of ClO₄⁻, the solution was passed through an ion exchanger saturated with H⁺. The total amount of ClO₄⁻ was then found by titrating the eluate (H⁺ClO₄⁻) with standard sodium hydroxide.

Perchloric acid solutions, about 0.1 C, were prepared from HClO₄ p. a. 70–72 %.

Sodium hydroxide solutions, 0.1, 0.5, or 1 C, were prepared by adding water, free from carbon dioxide, to NaOH (p. a.); actually a small amount of carbonate would not affect the measurements very much, since at the low pH studied it would be present chiefly as H₂CO₃. The NaOH solutions were kept in polyethylene bottles (in the first experiments in

glass bottles with an inner coating of paraffin) and analyzed either by evaporating a known volume with a small excess of HCl, drying at 360° C in an oven, and weighing the residue as NaCl, or by titration against KIO₃ according to Oesper¹², or against standard HCl.

Quinhydrone (Merck p. a.) was at first recrystallized from 50 % ethanol-water. Later on, the commercial preparation was used directly since no positive reaction was found for iron or acid impurities.

Silver perchlorate solutions were prepared by adding an excess of Ag₂O to a boiling solution of HClO₄. The undissolved material was filtered off and the content of Ag⁺ in the clear solution was measured by Volhard's method employing a silver wire as primary standard.

Sodium perchlorate was prepared either by recrystallizing commercial NaClO₄ repeatedly from alcohol or by mixing HClO₄ and NaHCO₃ solutions. The stock solutions were analyzed by evaporating and drying at 125° C or 250° C.

The solutions S₀ etc. for the titrations (see below) were prepared by mixing appropriate amounts of these stock solutions.

Apparatus

The cell was of the same construction as described in previous papers from this Institute¹³. It was kept in a paraffin oil thermostat, 25.0 ± 0.1° C, which was placed in a thermostat room at approximately 25° C.

When a quinhydrone electrode was used, the solution was stirred with nitrogen gas.

Table 1. Summary of titrations.

No	M	Concentrations in mC				Volumes added (ml)					Electrodes	
		S ₀ H ⁺	S ₁ OH ⁻	S ₂ H ⁺	S ₂ Th ⁴⁺	S ₀	S ₁	S ₂	S ₂ + S ₁	S ₁	for h	ref.
1	1.00	49.95	70.00	0.72	2.00	30.00	17.00	47.00	9.00	9.00	Q	SE
2	1.00	29.78	50.00	0.72	2.00	30.00	15.00	45.00	10.00	10.00	Q	SE
3	1.00	29.70	50.00	0.72	2.00	49.00	24.00	72.00	15.00	15.00	H	SE
4	2.00	29.75	50.00	1.44	4.00	49.00	24.00	73.00	31.00	31.00	H	SE
5	2.00	29.75	50.00	1.44	4.00	35.00	16.00	51.00	23.00	23.00	Q	SE
6	5.00	49.93	70.00	3.60	10.00	33.00	20.00	53.00	45.00	45.00 ^a	Q	SE
7	5.00	30.00	49.80	3.60	10.00	30.00		30.00	68.00	68.00	Q	CE
8	5.00	30.31	95.62	-9.35	20.00	90.00		30.00	17.00	51.00	Q	CE
9	5.00	30.31	50.00	-9.35	20.00	90.00		30.00	41.50	124.50	Q	CE
10	10.00	30.00	80.00	7.20	20.00	80.00		80.00	110.00	110.00	Q	CE
11	10.00	50.16	95.62	-9.35	20.00	40.00		40.00	83.00	83.00	Q	CE
12	10.00	50.16	95.62	-9.35	20.00	40.00		40.00	73.00	73.00	Q	CE
13	10.00	50.00	94.09	-9.35	20.00	40.00		40.00	48.00	48.00	Q	CE
14	10.00	b	198.6	7.20	20.00	b			20.00	20.00	H	SE
15	10.00	c	198.6	7.20	20.00	c			20.00	20.00	Q	SE
16	20.00	50.00	156.2	-18.70	40.00	40.00		40.00	100.00	100.00	Q	CE
17	20.21	50.00	158.9	14.10	40.42	30.00		30.00	112.00	112.00	Q	CE
18	20.00	30.00	159.5	13.93	40.00	30.00		30.00	100.00	100.00	Q	CE
19	20.00	30.05	202.79	13.93	40.00 ^d	30.00		30.00	50.00	50.00 ^d	Q	CE

^a Titration 6: At the end of the usual titration, 49.63 ml of the solution was removed and a back-titration was started, adding 40.40 ml S₂ + 40.40 ml S₃ (49.93 mC H⁺) in portions. Another 49.63 ml was removed, and 20.00 ml S₂ + 20.00 ml S₃ was added in portions.

^b Titration 14 started with 69.63 ml (15.00 mC H⁺, 10.00 mC Th) to which (S₁+S₂) was added in portions.

^c Titration 15 started with 70.00 ml (15.00 mC H⁺, 10.00 mC Th) to which (S₁+S₂) was added in portions.

^d Titration 19: At the end of the usual titration, 70.00 ml S₃(89.79 mC H⁺) and 70.00 ml S₂ were added in portions.

Table 2. Data for titration 5, see also Table 1.

Acid-base titration			
S_1 ml	$H = h$ mC	E mV	E'_0 mV
0.00	29.75	76.07	163.24
1.00	27.53	77.95	163.13
4.00	21.57	83.85	162.76
6.00	18.08	88.19	162.56
8.00	14.91	93.02	162.44
12.00	9.39	104.67	162.21
16.00	4.73	122.07	162.00

Thorium titration					
$S_1 = S_2$ ml	H mC	E mV	$\log h$ (mC)	h mC	Z
0.00	3.08	131.97	0.506	3.20	0.06
1.00	2.56	136.22	0.433	2.71	0.07
3.00	1.56	146.86	0.252	1.78	0.11
5.00	0.64	160.54	0.021	1.04	0.20
6.00	0.20	167.83	-0.103	0.70	0.29
7.00	-0.22	173.90	-0.205	0.62	0.42
8.00	-0.62	178.03	-0.275	0.53	0.57
9.00	-1.02	180.67	-0.320	0.48	0.75
11.00	-1.77	185.54	-0.402	0.39	1.08
12.00	-2.13	187.74	-0.439	0.36	1.24
14.00	-2.81	192.04	-0.512	0.31	1.56
16.00	-3.40	197.52	-0.604	0.25	1.82
18.00	-4.05	204.19	-0.717	0.19	2.12
20.00	-4.62	212.32	-0.855	0.14	2.38
22.00	-5.16	224.48	-1.060	0.09	2.62
23.00	-5.42	232.38	-1.194	0.06	2.74

Hydrogen (nitrogen) gas was obtained from a cylinder and freed from oxygen by passing the gas through a column filled with activated copper¹⁴. It was then saturated with water vapor by bubbling it through 1 C NaClO₄.

In the cells with quinhydrone, two Pt foils were used as inert electrodes. They were first cleansed in nitric acid (1 : 1), washed with water, and ignited in an alcohol flame. The hydrogen electrodes were lightly palladinated Pt foils¹⁵. Ag electrodes were prepared and coated with AgI as usual in this laboratory¹⁰.

The E of the cells were measured with a Jensen compensator (type 10 A) and a Multi-flex galvanometer, or with a valve potentiometer (Radiometer PHM 3).

PROCEDURE AND SURVEY OF THE DATA

The basis of the calculations are the 19 titrations which are summarized in Table 1. M gives the total thorium concentration which was constant in the "thorium part" of each titration. For a titration, three solutions S_0 , S_1 , and S_2 were usually prepared: besides Na⁺ and ClO₄⁻, S_0 contained H⁺, S_1 OH⁻, and S_2 Th⁴⁺ and H⁺. Columns 3—6 in Table 1 give for each solution the concentrations of the ions, leaving out Na⁺ and ClO₄⁻, which were added to make all solutions contain 1 000 mC ClO₄⁻.

The following columns give the amount of each solution which was added in the course of a titration. As an illustration, titration 5 will be described —

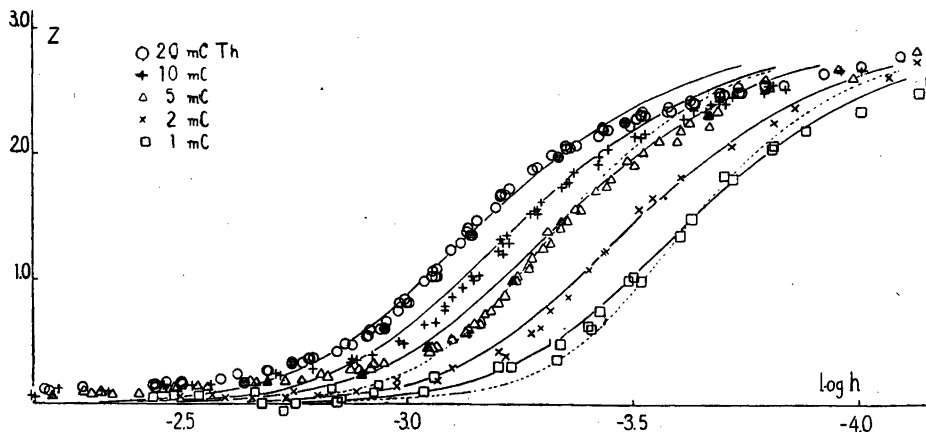


Fig. 1. Hydrolysis of Th^{4+} . Vertical axis: Z = average number of OH^- bound per Th . Horizontal axis: $\log h$ (C scale). The symbols for experimental points at various values for M (total Th concentration) are given to the left in the figure. Shaded circles and triangles: reverse titrations. Curves: $Z(\log h)$ calculated for the various M values with hypothesis IIIa, $\log k_0 = -7.50$ and $k = 1.0$ (full-drawn) or $k_0 = 0.5$ (broken).

the detailed data for it are given in Table 2. Titrations 1–6, which were really the most recent ones, were done in essentially the same way.

Titration 5 started with an acid-base titration. The titration vessel initially contained 35.00 ml of the acid solution S_0 . To this solution, an almost equivalent amount of hydroxide solution S_1 was added in portions from a buret and E was measured after each new addition. Then $E'_0 = E - 59.16 \log h$ (2) could be calculated and plotted against h . Here, of course, the analytical hydrogen ion excess H was equal to $[H^+] = h$. The diagram $E'_0(h)$ was used in the latter part of the titration for calculating h , the quantity sought for, from E . For instance, in the latter part of titration 5 the equation $E'_0 = 161.77 + 0.049 h$ was used.

For all the acid-base titrations in experiments 1–6, the points $E'_0(h)$ fell upon parallel straight lines with the slope 0.048 mV/mC. In similar experiments in this laboratory, Biedermann found the slope 0.064 ± 0.002 , whereas the present author in 1948 found values ranging between 0.070 and 0.082 in sixteen acid-base titrations (average 0.077). Whatever the reason for this discrepancy, it makes little difference in the curve $Z(\log h)$. In the calculations the value 0.048 or 0.049 was used for the recent titrations (1–6, 14, 15) and 0.077 for the older ones (7–13, 16–19).

At the end of the acid-base titration in experiment 5, the total volume was 51.00 ml. An equal volume, 51.00 ml, of the thorium solution S_2 was now added. The pH of the mixture was then successively increased by addition of small portions of $NaOH$ (S_1). To keep the thorium concentration M constant = 2.00 mC throughout the experiment, an equal volume of S_2 was added for each addition of S_1 . After each addition of ($S_1 + S_2$), E was measured repeatedly until it became constant, usually within 15–20 min. The titration was interrupted when a precipitate appeared, as was indicated by the fact that E began to drift.

In titrations 7—13 and 16—19, first 30 or 40 ml of acid (S_0) and then an equal volume of Th solution S_2 were added. Finally the solution was titrated with ($S_1 + S_2$) just as in the latter part of titrations 1—6. The value for E_0 was calculated either from the E obtained with only S_0 or from E after the first addition of S_2 , neglecting the hydrolysis of Th^{4+} in this rather acid solution.

In titrations 14 and 15, the initial solution already contained Th^{4+} and H^+ (see footnote, Table 1).

Reversibility. Two special titrations, 6 and 19, were carried out in both directions: first a basic solution S_1 was added as usual, and then acid and, of course, thorium were added in portions (see footnotes in Table 1). The points from the back titrations are shaded in Fig. 1. They are seen to fall on the same curves as the forward titration points, so one may conclude that reversible equilibria have been studied.

Precipitation. When the total thorium concentration M was 20 mC, a visible precipitate was formed at $\log h$ values between -3.80 and -3.90 (C scale) while in this range, E also became irregular. With $M = 2$ mC, the solution did not get distinctly opaque until $\log h = -4.70$. However E began to drift already at $\log h = -3.80$.

The value of E_0 for SE or CE proved to be quite constant, if measurements were made on the same day or with a few days' interval were compared. However, a slow change of the E_0 was often observed with the CE. On one occasion, a change as great as 4.0 mV was observed with a CE after the lapse of a few months. Since our calculations contain only the differences $E_0 - E$ in a single titration, this long-time variation in E_0 did not influence the results.

With hydrogen electrodes (experiments 3, 4, 14), the $Z(\log h)$ curves agreed very well with those obtained with quinhydrone electrodes and thus there is no reason to assume an appreciable error from thorium-quinhydrone complexes. With thorium solutions of the lowest M value (1 mC) and low h (1—5 mC), the E with the hydrogen electrode kept drifting indefinitely and would not become stable, whereas the quinhydrone electrode, as usual, gave reproducible potentials very quickly. Remarkably enough it was found that if one waited only about ten minutes after each addition, measured the E (without waiting for the drift to stop) and then made a new addition, the points obtained agreed satisfactorily with those from the quinhydrone titrations.

Table 3 gives $\log h$ and Z for one titration at each of the five M values used (1, 2, 5, 10, and 20 mC). The complete data are given in Figures 1 and 3 — titrations with the same M are seen to agree very well in Fig. 1.

GENERAL COMPOSITION OF THE COMPLEXES

The present data are condensed in Fig. 1, which gives $Z(\log h)_M$. If only mononuclear complexes were formed, Z would be a function of h only, and independent of M , and all points in Fig. 1 would fall on the same curve. Obviously this is not so, and one may conclude that Th^{4+} hydrolyses with the formation of polynuclear complexes. If there are mononuclear complexes they do not seem to be important in any part of the curves except perhaps for very low M and Z values — here the data are, however, not accurate enough to permit any certain conclusions.

Table 3. Z (log h) for six titrations.

Titration 1 (1 mC Th)		Titration 4 (2 mC Th)		Titration 6 (5 mC Th)		Titration 12 (10 mC Th)		Titration 16 (20 mC Th)	
log h	Z	log h	Z	log h	Z	log h	Z	log h	Z
0.567	0.05	0.410	0.045	0.661	0.09	1.232	0.08	1.169	0.08
0.520	0.07	0.347	0.05	0.600	0.11	1.120	0.09	1.008	0.086
0.465	0.07	0.271	0.045	0.531	0.12	0.902	0.10	0.797	0.10
0.341	0.09	0.199	0.07	0.446	0.14	0.683	0.13	0.538	0.18
0.168	0.12	0.114	0.10	0.274	0.19	0.494	0.16	0.416	0.20
0.063	0.16	0.023	0.14	0.179	0.23	0.294	0.24	0.313	0.27
-0.061	0.23	-0.067	0.20	0.084	0.29	0.124	0.36	0.232	0.33
-0.205	0.32	-0.218	0.38	-0.049	0.43	0.019	0.50	0.122	0.47
-0.338	0.50	-0.296	0.62	-0.101	0.51	0.083	0.78	0.060	0.61
-0.426	0.74	-0.358	0.86	-0.164	0.68	-0.144	1.03	0.020	0.74
-0.491	1.01	-0.436	1.22	-0.217	0.89	-0.208	1.32	-0.038	0.98
-0.628	1.55	-0.540	1.66	-0.244	1.02	-0.270	1.57	-0.098	1.24
-0.811	2.07	-0.809	2.34	-0.276	1.17	-0.359	1.78	-0.155	1.47
-1.156	2.58	-0.166	2.78	-0.311	1.40	-0.517	2.14	-0.228	1.73
				-0.372	1.58	-0.659	2.36	-0.321	1.97
				-0.486	1.94	-0.838	2.54	-0.424	2.15
				-0.604	2.19	-1.004	2.68	-0.538	2.30
				-0.983	2.62			-0.635	2.40
								-0.733	2.49
								-0.832	2.67
								-0.920	2.64
								-1.008	2.71
								-1.091	2.78
								-1.194	2.85
								-1.284	2.90
								-1.345	2.93

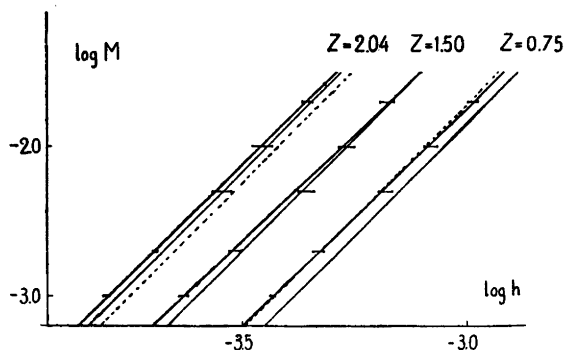


Fig. 2. Calculation of curve spacing: corresponding values for $\log h$ and $\log M$ are given for three Z values. Thick lines: "best" line drawn through experimental data. Thin lines: calculated for hypothesis IIIa, $\log k = -7.50$, $k_0 = 1.0$ (full-drawn) or 0.5 (broken).

One may try to apply to these data the general methods for treating polynuclear complexes that have been given by Sillén (ABI¹⁶, ABII¹⁷) and transformed by Hietanen and Sillén (part VIII¹⁸) to a form suitable for hydrolysis reactions.

An inspection of the curves in Fig. 1 suggests that the curves $Z(\log h)$ for different M values are parallel. To determine the quantity (cf. VIII, 14)

$$\left(\frac{\partial \log M}{\partial \log h}\right)_Z = -R \quad (4)$$

the diagram Fig. 2 was constructed. For each of three Z values (2.04, 1.50, and 0.75) a horizontal line was drawn in Fig. 1, and the $\log h$ values were read where the line intersected the $Z(\log h)$ curves for the five different M values. The bars in Fig. 2 indicate the inaccuracy.

As seen from Fig. 2, a straight line can be drawn through the data for each Z value. The slopes of the "best" lines were found to be 2.95, 2.80, and 2.93, and thus equal to 3 within the limits of error. Now if the derivative in (4) is constant and equal to 3 this means (cf. VIII, 15a, $t = -R = 3$) that Z should be a function of

$$x = \log M - 3 \log h \quad (5)$$

To check whether this is so, the data were recalculated, plotting (cf. VIII, 18)

$$y = \frac{1}{3} Z \quad (6)$$

as a function of x . As seen from Fig. 3, the points fall very nicely on a single curve, within the limits of experimental error. (The choice of $y = \frac{1}{3} Z$ instead of Z is for convenience when comparing our data with the equations and curves calculated for y in ABI¹⁷.)

It is gratifying that the data of Kraus and Holmberg⁹ fit in very well with the same curve as the present data if they are plotted in an $y(x)$ diagram.

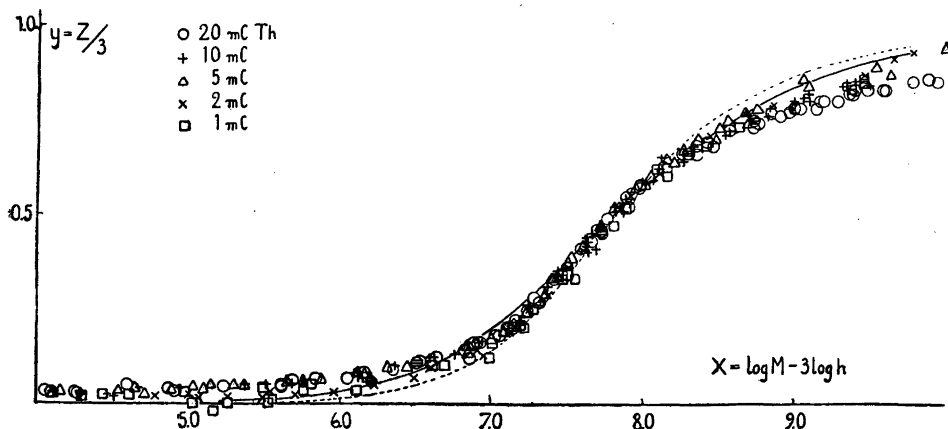
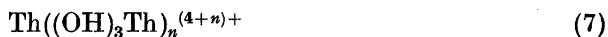


Fig. 3. Data in Fig. 1, recalculated to the form $y(x)$, assuming $t = 3$: $x = \log M - 3 \log h$ (C scale), $y = Z/3$. Symbols for experimental points as in Fig. 1. Curves calculated for hypothesis IIIa, $\log k = -7.50$, $k_0 = 1.0$ (full-drawn) or 0.5 (broken).

In Fig. 4 only a part of the points from each investigation, chosen at random, have been plotted so as not to overcrowd the diagram.

Now, as proved in (ABI, 16—19; cf. VIII, 15) the fact that Z (or y) is a function of $x = \log M - 3 \log h$ implies that all complexes formed in appreciable amounts can be written in the form



This conclusion seems to be reliable within the range of M and h studied, to judge from the good coherence of the points in fig. 3 or 4. However, to decide whether only one complex (one value for n) or several are formed, we must analyze the curve $y(x)$.

DIRECT ANALYSIS OF $y(x)$

As shown in (ABII, 14, 15) one may use the function $y(x)$ to calculate

$$\log(1 + g) = \int_{-\infty}^x y \, dx + \log(1 - y) + y \log e \quad (8)$$

$$\log u = x - y \log e - \int_{-\infty}^x y \, dx \quad (9)$$

Here (VIII, 31, 32; ABII, 2, 3, 3a)

$$u = mh^{-t} = [\text{Th}^{4+}]h^{-3} \quad (10)$$

$$g = f(u) = \sum k_n u^n \quad (11)$$

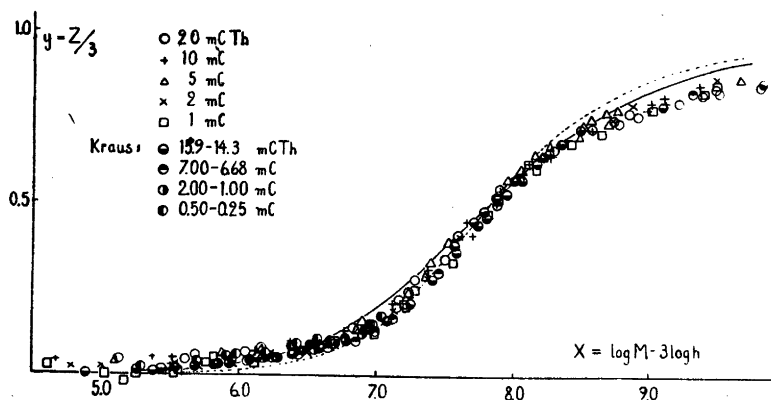
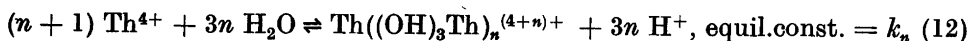


Fig. 4. Comparison of present data with those of Kraus and Holmberg⁹, recalculated to the form $y(x)$ assuming $t = 3$. Symbols: see left side of figure. Curves calculated for hypothesis IIIa as in Fig. 3.

and k_n is the equilibrium constant for the formation of the n :th complex from the metal ion and water, in this case for the reaction (VIII, 29)



An average curve was drawn through the points of Fig. 3 (in a recalculation, Fig. 4 was used; but this made very little difference). The y values were read at 0.2 intervals of x (Table 4), and the integral $\int y dx$ calculated by trapezoidal integration. Thus u and g could be calculated from (8) and (9).

This procedure involves no extra assumption apart from the one — strongly corroborated by the data in Figs. 3 and 4 — that only complexes of formula $\text{Th}((\text{OH})_3\text{Th})_n^{4+n}$ need be considered.

One might think of using the data $g(u)$ for calculating the various k_n in (11). It may not be too hard to find a set of k_n that gives an acceptable agreement with $g(u)$. However, because of the limited accuracy of the data, this can

Table 4. Average points $y(x)$ and primary values for "direct analysis".

x	y	$\log u + \delta \log(1 + g) - \delta$	x	y	$\log u + \delta \log(1 + g) - \delta$		
5.2	0.012	5.1948	-0.0000 ₃	7.6	0.394	7.1721	0.2104
5.4	0.017	5.3897	0.0029	7.8	0.484	7.2452	0.2674
5.6	0.021	5.5842	0.0066	8.0	0.568	7.3035	0.3320
5.8	0.030	5.7752	0.0116	8.2	0.640	7.3514	0.4049
6.0	0.040	5.9638	0.0185	8.4	0.694	7.3946	0.4911
6.2	0.050	6.1505	0.0272	8.6	0.736	7.4334	0.5882
6.4	0.062	6.3341	0.0381	8.8	0.765	7.4707	0.7004
6.6	0.080	6.5121	0.0517	9.0	0.792	7.5032	0.8149
6.8	0.110	6.6800	0.0694	9.2	0.816	7.5320	0.9328
7.0	0.155	6.8340	0.0929	9.4	0.840	7.5560	1.0481
7.2	0.216	6.9704	0.1239	9.6	0.860	7.5773	1.1688
7.4	0.300	7.0826	0.1625	9.8	0.875	7.5973	1.2996

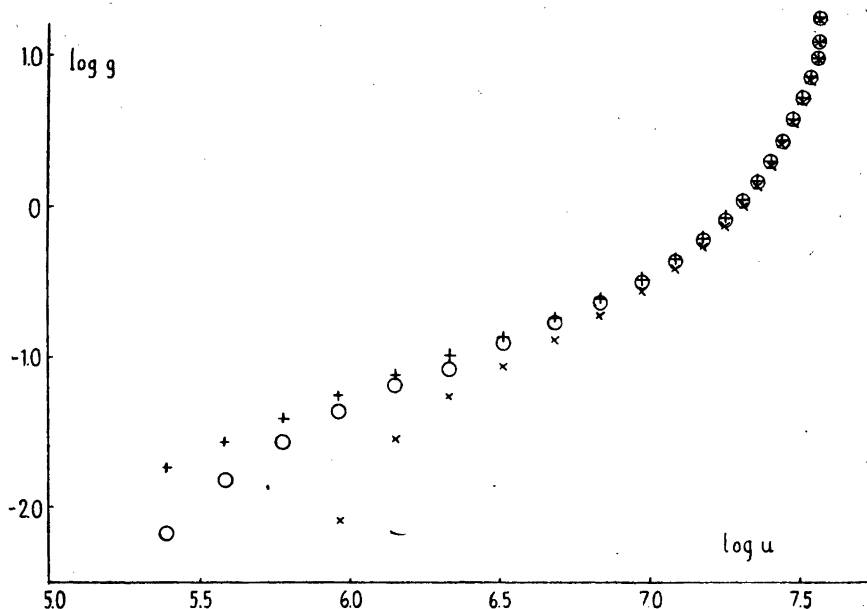


Fig. 5. Direct analysis of $y(x)$ curve: $\log g$ as a function of $\log u$. The residual integral δ was assumed to be 0.0050 (+), 0 (O), or -0.0150 (x).

probably be achieved in several ways. We have hence preferred another way of approach. From (ABII, 73) we have

$$\frac{d \log g}{d \log u} = \bar{n} = \frac{\sum n c_n}{\sum c_n} \quad (13)$$

where \bar{n} is the average number of $\text{Th}(\text{OH})_3$ "links" per complex.

Table 4 gives the values for $\log(1+g)$ and $\log u$ primarily obtained assuming the residue integral

$$\delta = \int_{-\infty}^{5.2} y \, dx \quad (14)$$

to be zero. In the following calculations, the values $\delta = 0.0050$ (crosses +), $\delta = 0$ (circles O) and $\delta = -0.0150$ (x) were used; Fig. 5 shows $\log g$ as a function of $\log u$, and Fig. 6 \bar{n} as a function of x , with these three values.

For x values below 7.0, the curves for the three δ values are seen to differ considerably. One would expect \bar{n} to approach the value 1 asymptotically for low x , but this is not achieved with any δ value. It should be remembered that the \bar{n} values in this range are very sensitive to small errors in y .

For $x > 7$, a reasonable variation of δ , which may also include the error in the integral between $x = 5.2$ and 7.0, does not influence the general course of the curves very much.

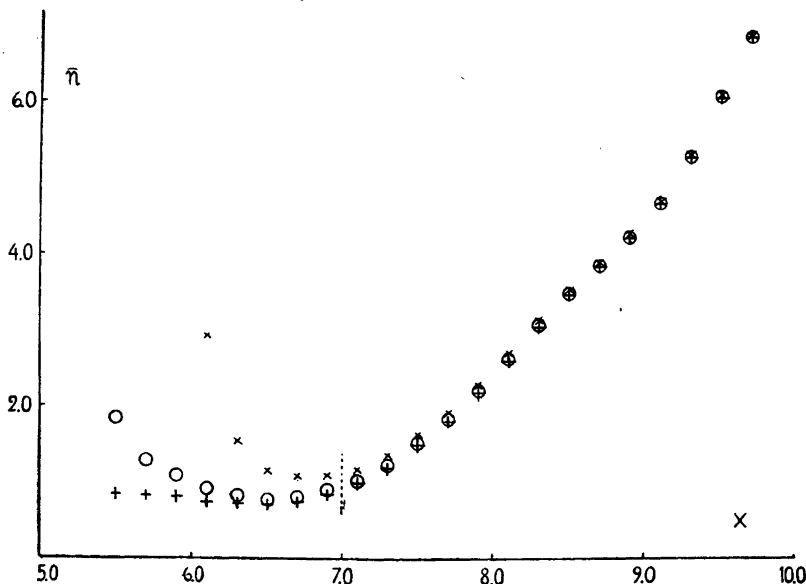


Fig. 6. Direct analysis of $y(x)$ curve: \bar{n} as a function of x . Symbols as in Fig. 5.

If only one complex had existed, one would expect the \bar{n} curve to be a horizontal line at the corresponding n value. If two complexes had predominated over all others, \bar{n} would give two almost horizontal shelves, with a transition curve between them. Finally, if there were a maximum value for n , \bar{n} should approach this n_{\max} with increasing x .

As a matter of fact, as far as the data go, \bar{n} is seen to increase with x , and even the slope increases. Thus there is no indication that one or two complexes are more important than all others and if there is a maximum value for n it must be much greater than 6.

The \bar{n} curve may be compared with the results of the preliminary ultracentrifugations of thorium perchlorate solutions quoted by Kraus and Holmberg⁹: "aggregates were found in the vicinity of $Z = 2$ with tetramers possibly occurring for Z just less than 2, and considerably larger polymers for Z larger than 2". (Kraus' symbol has been replaced by Z to conform with the present paper). It should be noted that a "tetramer" with 4 Th would correspond to $n = 3$ (cf. eq. 7).

Fig. 6, which follows from the present equilibrium data, and from Kraus' and Holmberg's own equilibrium data, gives however no indication of a sudden change at $Z = 2$ ($x \approx 8.3$ according to Fig. 3), nor of the prevalence of tetramers.

TESTING SIMPLE MECHANISMS

The independent determination of, say, even the first 6 or 8 k_n values would require a greater accuracy than the present data allow. It was then tested whether the $y(x)$ curve could not be approximately described by some of the simple one- or two-parameter mechanisms discussed in ABII and part VIII.

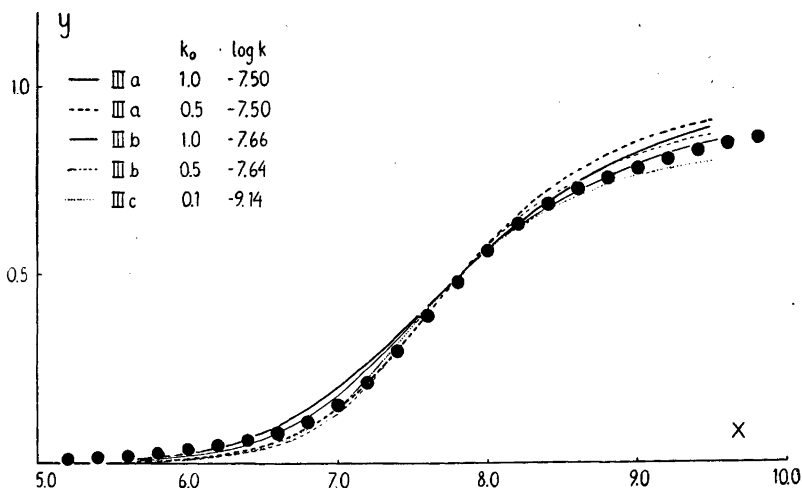


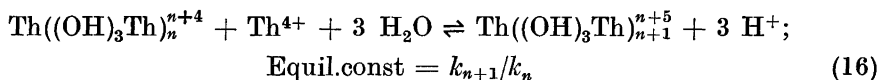
Fig. 7. Curves $y(x)$ calculated for the simplified mechanisms indicated to the left in the figure. Dots: smoothed values from experimental data, Figs. 3 and 4.

The hypotheses denoted as I (precipitate formed) and II (only one complex formed) could immediately be ruled out since no acceptable fit could be found with the $y(x)$ curves calculated according to ABII. Thus, more than one polynuclear complex must be formed in the solution — the same conclusion was reached from the "direct analysis" above.

With the hypotheses involving the formation of an unlimited series of complexes: IIIa, IIIb, and IIIc, the fit was considerably better. The three hypotheses assume the following formulas for k_n (ABII 28; VIII 36)

$$\text{IIIa: } k_n = k_0 k^n; \text{ IIIb: } k_n = k_0 n k^n; \text{ IIIc: } k_n = \frac{k_0 k^n}{n} \quad (15)$$

We may remember that the ratio k_{n+1}/k_n is the equilibrium constant for the addition of a new link:



With IIIa this ratio is a constant k . With IIIb, $k_{n+1}/k_n = k(1 + n^{-1})$; it decreases somewhat with increasing n but tends to a limiting value k . With IIIc, the ratio is equal to $k(n + 1)^{-1}$ and thus tends to zero with increasing n .

The best fits with the experimental points were obtained with the following sets of constants:

$$\text{IIIa: } k_0 = 0.5 \text{ to } 1.0; \log k \approx -7.50$$

$$\text{IIIb: } k_0 = 0.5 \text{ to } 1.0; \log k \approx -7.65$$

$$\text{IIIc: } k_0 = \text{about } 0.1; \log k \approx -9.15$$

Fig. 7 gives five curves calculated with these constants; the dots are taken from the average experimental curve (Table 4). All the calculated curves in Fig. 7 are fairly close to the experimental points although each deviates slightly in some part of the x range.

Details of calculations

For IIIa, $\log k$ was read off to be about -7.5 directly from the $y(x)$ diagram, Fig. 3 or 4, using equation (ABII, 33): $\log k = \log 2 - x_{\frac{1}{2}}$. To study the spread, $\log k$ was also calculated separately for each curve in Fig. 1, using the equation $\log k = \log 2 - \log M + 3 \log h_{\frac{1}{2}}$; $h_{\frac{1}{2}}$ and $x_{\frac{1}{2}}$ are the values at $y = \frac{1}{2}$. For $M = 1, 2, 5, 10,$ and 20 mC, $\log k = -7.60, -7.55, -7.45, -7.49,$ and -7.54 was found; average $\log k = -7.53 \pm 0.07$. The average curve gave $\log k = -7.54$.

k_0 was found using equation (ABII, 37): $k_0 = y(1 - 10^x(1 - y))^2(10^x(1 - 2y)^2)^{-1}$. The abscissa x was measured for $y = 0.2, 0.3, 0.4, 0.5, 0.6, 0.7,$ and 0.8 , and for each value $10^x = 2 \cdot 10^{(x - x_{\frac{1}{2}})}$ was calculated (ABII, 36). There was a trend in k_0 for high y : $0.62, 0.82, 0.85, \dots, 0.76, 1.00, (2.19)$.

For IIIb, equation (ABII, 40) was used: $\log k = \log(1 + v_{\frac{1}{2}}) - x_{\frac{1}{2}}$, where $v_{\frac{1}{2}}$ is calculated from $2k_0v_{\frac{1}{2}}^2 = (1 - v_{\frac{1}{2}})^2$. For $k_0 = 0.5$, $\log k = -7.64$ and for $k_0 = 1.0$, $\log k = -7.66$ were found.

For IIIc, equations (ABII, 44) were similarly used.

The comparison of the experimental data with the calculated curves for unlimited mechanisms suggests that the ratio k_{n+1}/k_n approaches a value around $10^{-7.65}$ with increasing n . This is the value for k found with IIIb; moreover, in the "direct analysis", u seems to tend to a limiting value about $10^{7.65}$ ($v \rightarrow 1, u \rightarrow k^{-1}$ for IIIa and IIIb, cf. ABII, 31, 38, 6). The ratio k_{n+1}/k_n for low n , and the first constant k_1 may be somewhat higher, perhaps in the neighbourhood of $10^{-7.50}$.

From the experimental data one might try to calculate the first k_n more exactly. We shall not do so at present.

A remarkably good approximation is obtained with the very simplest hypothesis, IIIa with $k_0 = 1$, implying that k_1 and all consecutive constants k_{n+1}/k_n (16) are alike. One then gets the very simple equations (cf. ABII, 34a):

$$x + \log k = \log y - 2 \log (1 - y) \quad (17)$$

thus for Th⁴⁺

$$\log M - 3 \log h - 7.50 = \log \frac{3Z}{(3 - Z)^2} \quad (18)$$

STRUCTURE OF THE COMPLEXES

The equilibrium data seem to indicate that a series of complexes Th((OH)₃Th)_n is formed with $n = 1, 2, 3$ etc. Although these data permit no conclusions on the shape of the complexes, it seems very plausible to assume that they are chain-like. It is tempting to compare these complexes with the chains (Th(OH)₂²⁺)_n found by Lundgren and Sillén^{19,20} in the crystal structures of thorium hydroxide sulfate and chromate (Fig. 8). Such a chain contains two parallel rows of hydroxide groups, with Th atoms on alternate sides so that

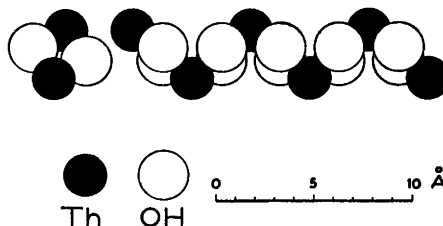
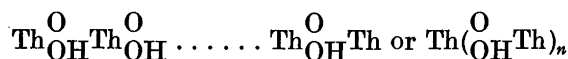


Fig. 8. $(Th(OH)_3^+)_n$ chain from thorium hydroxide sulfate or chromate^{19,20}

every Th is in contact with 4 OH, and every OH with 2 Th. If, in the pH range studied, one OH group out of two has lost its proton, we would have chains



which would be equivalent to $Th((OH)_3Th)_n$. By emf methods in constant ionic medium we cannot distinguish between 1 O^{2-} and 2 OH^- .

The assumption that half of the OH^- have lost a H^+ is not so unreasonable if it is remembered, for instance, that for each of $PO_2(OH)_2$ and PO_3OH^{2-} (i.e. $H_2PO_4^-$ and HPO_4^{2-}), there is a pH range of about 5 units within which this species is predominant.

The assumption that the hydrolysis products of Th^{4+} are chain-like complexes is further supported by the work of Dobry, Guinand, and Mathieu-Sicaud²¹ on colloidal thorium hydroxide, obtained by dialysis of dilute thorium chloride solutions. From observations on viscosity, light diffusion, and stream double refraction, and especially from electron microscope pictures, they concluded that the particles are thread-like, of diameter about 18 Å, and of average length 700 Å. The cross-section corresponds to bundles of perhaps some 20 or 30 of the simple chains of Fig. 8. Perhaps the simple chains are joined to bundles by O or OH during some of the later stages of the hydrolysis.

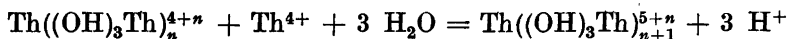
SUMMARY

The hydrolysis of the ion Th^{4+} in 1 C perchlorate medium at 25° C has been studied by electrometric titrations, using quinhydrone or hydrogen electrodes. The data were treated by the methods given in previous papers, ABI¹⁶, ABII¹⁷, and part VIII¹⁸.

Within the experimental accuracy, Z (the number of H^+ split off per Th), proved to be a function of the single variable $x = \log M - 3 \log h$ (M = total Th concentration, $h = [H^+]$). Hence it follows that all complexes formed in appreciable amounts can be written in the form $Th((OH)_3Th)_n^{4+n}$.

From a direct analysis of the experimental $y(x)$ curve ($y = \frac{1}{3} Z$) it is concluded that complexes with a number of different n values are formed, and that no one n value predominates. No upper limit for n was found and it was concluded that there must be n values considerably greater than 6.

A quite good approximation to the experimental data is obtained with the very simple assumption that the equilibrium constants for all successive steps ($n = 0, 1, 2, 3 \dots$):



are the same, $k = 10^{-7.50}$. ("IIIa, $k_0 = 1$ " in Figs 1, 3, 4, 7). The deviations indicate that the constant is really somewhat lower, perhaps about $10^{-7.65}$, for the higher n values.

In view of X-ray and electron microscope data^{19,20,21} it seems plausible that the complexes are chain-like, of formula $\text{Th}(\overset{\text{O}}{\text{OH}}\text{Th})_n^{4+n}$

The data agree well with those recently published by Kraus and Holmberg⁹, although our conclusions differ considerably.

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REFERENCES

1. Denham, H. G. *J. Chem. Soc. (London)* **93** (1908) 62; *Z. anorg. Chem.* **57** (1908) 388.
2. Hildebrand, J. H. *J. Am. Chem. Soc.* **35** (1913) 865.
3. Britton, H. T. S. *J. Chem. Soc. (London)* **127** (1925) 2110.
4. Chauvenet, E. and Tonnet, J. *Bull. soc. chim. France* **47** (1930) 701.
5. Chauvenet, E. and Souteyrand-Franck *Bull. soc. chim. France* **47** (1930) 1128.
6. Schaal, R. and Faucherre, J. *Bull. soc. chim. France* **14** (1947) 927.
7. Souchay, P. *Bull. soc. chim. France* **15** (1948) 143.
8. Kasper, J. *Diss.*, The Johns Hopkins University, Baltimore, Md, 1941.
9. Kraus, K. A. and Holmberg, R. W. *J. Phys. Chem.* **58** (1954) 325.
10. Biedermann, G. and Sillén, L. G. *Arkiv Kemi* **5** (1953) 425. (Part IV).
11. Hecht, F. *Z. anal. Chem.* **100** (1935) 98.
12. Oesper, P. *J. Chem. Educ.* **26** (1949) 588.
13. Forsling, W., Hietanen, S. and Sillén, L. G. *Acta Chem. Scand.* **6** (1952) 901. (Part III).
14. Meyer, F. R. and Ronge, G. *Angew. Chem.* **52** (1939) 637.
15. Hamer, W. J. and Acree, S. F. *J. Research Natl. Bur. Standards* **33** (1944) 87.
16. Sillén, L. G. *Acta Chem. Scand.* **8** (1954) 299 (AB I).
17. Sillén, L. G. *Acta Chem. Scand.* **8** (1954) 318 (AB II).
18. Hietanen, S. and Sillén, L. G. *Acta Chem. Scand.* **8** (1954) 1607. (Part VIII).
19. Lundgren, G. and Sillén, L. G. *Arkiv Kemi* **1** (1949) 277.
20. Lundgren, G. *Arkiv Kemi* **2** (1950) 535.
21. Dobry, A., Guinand, S. and Mathieu-Sicaud, A. *J. chim. phys.* **50** (1953) 501.

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