

In summary, Figure 3 provides good evidence that the infrared assignments and hence the Mo-O force constants are probably correct, none being subject to any large random error. Figures 4 and 5 then show that the various estimates of bond orders are plausible and consistent over the series of compounds. Naturally, each bond order might be incorrect by several tenths of a unit, but it seems unlikely that errors, either random or systematic, could be much greater than that. Thus,

Mo-O bonds appear to exhibit the same qualitative relationships between bond orders and the two observable properties, bond lengths and bond force constants, as do bonds between pairs of light atoms and the Mo-C bonds in molybdenum carbonyl and its derivatives. Similar correlations may then reasonably be expected for other series of bonds from transition metals to light atoms, and their existence should prove useful in establishing and correlating the electronic structures of compounds containing such bonds.

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## A Light-Scattering Investigation of the Hydrolytic Behavior of Thorium in Aqueous Perchlorate Media

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The hydrolytic polymerization of thorium in solutions corresponding to 0.0, 1.0, 1.6, 2.0, and 3.0 bound hydroxide ions per thorium atom ( $\bar{n} = 0.0, 1.0, \text{etc.}$ ) has been investigated by the light-scattering technique at 25°. For each hydroxyl number, Th concentrations were varied between approximately 0.01 and 0.10 *M* in supporting electrolyte of 1.00 *M* NaClO<sub>4</sub>. The degree of hydrolysis of the thorium ion is found to affect markedly the magnitude and the manner in which the turbidity, refractive index increment, and density vary with thorium concentration. Changes in pH and ultraviolet absorption spectra with degree of hydrolysis are less pronounced. An unhydrolyzed and uncomplexed Th<sup>4+</sup> ion is confirmed at  $\bar{n} = 0.0$ , while the species [Th(OH)(ClO<sub>4</sub>)<sub>2</sub>]<sup>+</sup> is found at  $\bar{n} = 1.0$ . At hydroxyl numbers 1.6 and 2.0, average polymerization numbers of *ca.* 2.3 and 2.9 are found. Extremely large thorium aggregates containing 140–150 thorium atoms per particle are indicated in clear solutions at  $\bar{n} = 3.0$ . The measurements on all series appear to be equilibrium values at 25°, although slow kinetics cannot be ruled out for the later stages of hydrolysis.

### Introduction

Prior to 1947, studies of the aqueous solution chemistry of thorium had led to uncertain or no conclusions as to the nature of the hydrolyzed thorium species present in solution. The first isopolycation of thorium, [Th<sub>4</sub>O<sub>4</sub>]<sup>8+</sup>, was suggested from the results of e.m.f.<sup>2</sup> and freezing-point depression<sup>3</sup> measurements on hydrolyzed thorium solutions. Alternatively, e.m.f. titration of the aqueous nitrate with NaOH led Kasper<sup>4</sup> to propose only the mononuclear species, [Th(OH)]<sup>3+</sup>.

Rather complete pH titration studies<sup>5,6</sup> have been interpreted by the "core-plus-links" hypothesis<sup>7</sup> in terms of chain-like thorium aggregates of general formula [Th{(HO)<sub>3</sub>Th}<sub>*n*</sub>]<sup>(*n*+4)+</sup>. All values of *n* from 1 to considerably greater than 6 were found, with no upper limit to *n* being reached.<sup>8</sup> Later, [Th<sub>2</sub>(OH)<sub>2</sub>]<sup>6+</sup> and [Th<sub>2</sub>(OH)]<sup>7+</sup> were reported<sup>9</sup> for the earlier stages of hydrolysis.

The hydrolysis of thorium in perchlorate and in chloride solutions was studied potentiometrically<sup>10</sup> as a function of acidity and thorium concentration ( $2.5 \times 10^{-4}$  to  $1.5 \times 10^{-3}$  *M*) by Kraus and Holmberg. Their data were in agreement with those of Hietanen,<sup>5</sup> but their conclusions differed. A longer range of hydrolysis, with hydrolyses reversible up to *n* = 2, was concluded. The existence of unhydrolyzed Th(IV) was confirmed and stability constants for [Th(OH)<sub>2</sub>]<sup>2+</sup> and [Th<sub>2</sub>(OH)<sub>2</sub>]<sup>6+</sup> were reported. The hydrolysis constant for the first mononuclear step was calculated as  $5 \times 10^{-5}$ . Ultracentrifuge experiments<sup>11</sup> carried out on perchlorate solutions have indicated polymeric thorium species to be the principal hydrolysis products except in early stages, where mononuclear species are probably more important. Only monomeric products have been reported elsewhere,<sup>12,13</sup> while the higher polymers [Th<sub>5</sub>(OH)<sub>12</sub>]<sup>8+</sup> and [Th<sub>7</sub>(OH)<sub>18-21</sub>]<sup>*n*+</sup> have been suggested as superimposing upon monomeric and dimeric species to yield an average polymerization number of four.<sup>14</sup> Dimeric and trimeric "core-plus-

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links" species in solution at room temperature, and higher polymers at elevated temperatures, have been indicated from the results of recent ion-exchange studies.<sup>15,16</sup>

Finally, optical turbidity measurements have been used<sup>17</sup> to determine the solubility product of Th(OH)<sub>4</sub>. Simultaneous pH measurements made during the addition of base were explained on the basis of Th<sup>4+</sup> and [Th(OH)<sub>2</sub>]<sub>n</sub><sup>2n+</sup> as the principal species, but the possibility of [Th(OH)]<sup>3+</sup> could not be excluded by the data.

In view of the inconclusive and conflicting literature concerning the nature of the hydrolysis products of thorium, we felt that, at the very least, the results of a light-scattering study of the system might settle the degree of aggregation at various stages of hydrolysis.

### Experimental

**Stock Thorium and NaClO<sub>4</sub> Solutions.**—Stock thorium solutions were prepared by precipitating approximately 0.25 mole of hydrous ThO<sub>2</sub> from a large volume of the aqueous nitrate and washing with distilled water until the supernatant liquid reached a pH of 7–8. In some cases, significant amounts of thorium were lost by peptization in this procedure. The assumed 0.25 mole of ThO<sub>2</sub> was dissolved in a volume of standardized 70–72% HClO<sub>4</sub> (found 11.69 *M*) necessary to give solution compositions of Th(ClO<sub>4</sub>)<sub>4</sub> (series A), Th(OH)<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub> (series C), and Th(OH)<sub>3</sub>-ClO<sub>4</sub> (series D). The resulting solutions were diluted to 500 ml. with distilled water. Individual stock solutions were prepared directly or indirectly from these solutions, as described below.

**Series A Stock,  $\bar{n} = 0.0$ .**—Two different crystalline products obtained by slow evaporation at room temperature of the Th(ClO<sub>4</sub>)<sub>4</sub> solution<sup>18</sup> gave solutions free from chloride but containing excess HClO<sub>4</sub>. (Found: Th, 0.4753 *M*; ClO<sub>4</sub><sup>-</sup>, 2.116 *M*; ClO<sub>4</sub><sup>-</sup>:Th, 4.452.) The excess HClO<sub>4</sub> was neutralized with standard NaOH, yielding a Th(ClO<sub>4</sub>)<sub>4</sub> solution in dilute NaClO<sub>4</sub>.

**Series B Stock,  $\bar{n} = 1.0$ .**—This was prepared by the addition of sufficient standard NaOH to the series A stock so as to neutralize the free acid and result in a solution containing one added OH<sup>-</sup> per Th atom. (Found: Th, 0.2614 *M*.)

**Series C Stock,  $\bar{n} = 1.6$ .**—Considerable losses of ThO<sub>2</sub> during washing led to a final solution composition of higher ClO<sub>4</sub><sup>-</sup>:Th than the intended 2:1. (Found: Th, 0.4875 *M*; ClO<sub>4</sub><sup>-</sup>, 1.158 *M*; ClO<sub>4</sub><sup>-</sup>:Th, 2.38.) This was used as a stock solution of hydroxyl number 1.6.

**Series D Stock,  $\bar{n} = 2.0$ .**—Some series C stock solution was titrated with standard NaOH so as to increase OH:Th to 2:1. (Found: Th, 0.3886 *M*.)

**Series D Stock,  $\bar{n} = 3.0$ .**—The solution prepared from the reaction of ca. 0.25 mole of ThO<sub>2</sub> with 0.25 mole of HClO<sub>4</sub> remained slightly turbid after vigorous stirring at room temperature for 3 days. Filtration through medium-porosity sintered glass gave a solution which still showed a strong Tyndall beam. After final dilution to 500 ml. and after standing 2 weeks, a perceptible turbidity persisted. Unlike all other stock solutions, the thorium in this solution was only partially absorbed on Dowex 50W-X8; consequently the perchlorate content was determined by the tetraphenylarsonium chloride method after addition of HCl to destroy any colloidal ThO<sub>2</sub>. (Found: Th, 0.4650 *M*; ClO<sub>4</sub><sup>-</sup>, 0.4849 *M*; ClO<sub>4</sub><sup>-</sup>:Th, 1.04.)

Concentrated stock solutions of NaClO<sub>4</sub> were prepared by dissolving the recrystallized 1-hydrate in sufficient distilled water so as to give a final concentration of at least 6 *M*.

**Analyses.**—Thorium was determined gravimetrically as the

oxide.<sup>19</sup> Perchlorate was determined either by passing aliquots of the solution through a Dowex 50W-X8 ion-exchange column and titrating the eluted HClO<sub>4</sub> or by precipitation with tetraphenylarsonium chloride and weighing as (C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>AsClO<sub>4</sub>.<sup>20</sup> Stock solutions of NaClO<sub>4</sub> were analyzed as before.<sup>21</sup>

**Experimental Solutions.**—For each series of stock Th solutions, experimental solutions containing 0.01–0.10 *M* Th were prepared by taking aliquots of the freshly-analyzed stock and diluting to 100 ml. after addition of the calculated volume of NaClO<sub>4</sub> so as to give a supporting electrolyte concentration of 1.00 *M*. That NaClO<sub>4</sub> already present in any stock solution (series A, B, and C) was taken into account in the adjustment to unit molarity of NaClO<sub>4</sub>.

All experimental solutions prepared were visibly clear, including those of hydroxyl number 3.0 (series D). Presumably the addition of NaClO<sub>4</sub> and dilution had the effect of eliminating whatever was responsible for the visible turbidity of the parent stock solution.

**Light-scattering measurements** were made with a Brice-Phoenix photometer (Model 1974), dry, thiophene-free benzene being used as our secondary-type standard. The value 7.71 × 10<sup>-4</sup> cm.<sup>-1</sup> was taken as the absolute turbidity of benzene.<sup>22</sup> The instrument calibration was checked by determining the molecular weight of raffinose (found, 508 ± 10; calcd. for anhydrous C<sub>18</sub>H<sub>32</sub>O<sub>16</sub>, 504). One 3-cm. square scattering cell was used for all measurements with 4358 Å. light. No dissymmetry was found for the series D solutions using a special cylindrical cell; measurements between 50 and 130° gave an average dissymmetry ratio of 1.02 ± 0.02. Solutions were clarified by filtration through 450-*mμ* Millipore filters directly into the scattering cell.

Each value given for the turbidity represents an average of 12–20 measurements taken over 5–15 filtrations. In almost every case, the turbidity was constant after an initial five filtrations. The turbidity of the 1.00 *M* NaClO<sub>4</sub> background was taken as the limiting turbidity of each series of solutions as the Th concentration approached zero; this was subtracted from the gross turbidity of the solution to give the excess turbidity, τ\*, due to the thorium species.

Refractive index increments were obtained as previously described.<sup>21</sup>

**Other Measurements.**—Densities were determined pycnometrically at 25°. The pH of each experimental solution was measured at 25° using a Leeds and Northrup pH indicator standardized with saturated aqueous potassium hydrogen tartrate. Ultraviolet absorption measurements were made with a Perkin-Elmer Model 202 recording spectrophotometer.

### Results and Discussion

The light-scattering data were interpreted in the usual manner.<sup>23,24</sup> The data were treated for a pseudo-three-component system consisting of solvent (component 1), a monodisperse polymer (component 2), and supporting electrolyte (component 3). In such a system, the degree of polymerization *N* is related to the excess turbidity, τ\*, due to the thorium-containing solute by

$$1/N_{z'} = \frac{H''M'\phi\psi'^2}{\tau^*} - \frac{z'^2M'}{2M_3} \quad (1)$$

$$H'' = \frac{32000\pi^3n^2}{3N\lambda^4} \quad (2)$$

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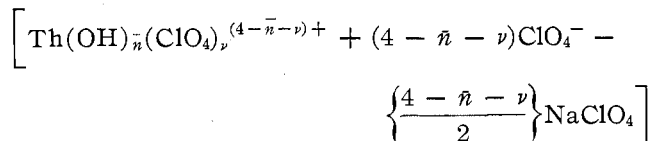
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where  $\phi$  is the solvent volume fraction,  $N$  is Avogadro's number,  $n$  is the refractive index of the solution, and  $\lambda$  is the wave length of the light.  $M'$ ,  $z'$ , and  $\psi'$  are the molarity, charge, and differential refractive index of the "monomeric" component.<sup>25</sup> For the thorium system, the monomeric component is defined according to the hydroxyl number,  $\bar{n}$ , by



The definitions of  $z'$ ,  $\psi'$ , and  $M_3$  then follow as

$$z' = (4 - \bar{n} - \nu)$$

$$\psi' = \partial n / \partial M' - (z'/2) \partial n / \partial M_3$$

$$M_3 = 1.00 + (z'/2)M'$$

with  $M'$  the total thorium molarity. The corrections of  $\bar{n}$  for free  $[\text{H}^+]$  were found to be practically negligible and were not made.

**Refractive Index Increments, Volume Fractions, Apparent Molar Volumes, and pH of Solutions.**—Subtraction of the  $\text{NaClO}_4$  contribution from the gross  $\Delta n$  of the solution gave  $\Delta n$  for the thorium species. Plots of the resultant  $\Delta n$  as a function of  $M'$  gave straight lines with zero intercept and slope  $\partial n / \partial M'$ . Values of  $\psi'$  were then calculated using  $z'$  as a parameter by use of the  $\partial n / \partial M_3$  data of Goehring.<sup>26</sup>

Solvent volume fractions,  $\phi$ , and apparent molar volumes,  $\Phi$ , for the monomeric component were calculated as before.<sup>21</sup> The former varied between approximately 0.94 and 0.95 for all solutions. The average values calculated for  $\Phi$  were:  $\bar{n} = 0.0$ , 134 ml. mole<sup>-1</sup>;  $\bar{n} = 1.0$ , 70 ml. mole<sup>-1</sup>;  $\bar{n} = 1.6$ , 94 ml. mole<sup>-1</sup>;  $\bar{n} = 2.0$ , 89 ml. mole<sup>-1</sup>; and  $\bar{n} = 3.0$ , 48 ml. mole<sup>-1</sup>. The low value calculated for the  $\bar{n} = 1.0$  series is inexplicably out of line with the usual trend toward lower values of  $\Phi$  with increasing hydroxyl number, but is possibly related to the point of transition from mononuclear to polynuclear species above  $\bar{n} = 1.0$ .

Table I gives  $\Delta n$  and  $\tau^*$  for the thorium solute species and  $\phi$  and pH values for the solutions studied. Values found for  $\partial n / \partial M'$  were: series A,  $5.43 \times 10^{-2}$  l. mole<sup>-1</sup>; series B,  $4.82 \times 10^{-2}$  l. mole<sup>-1</sup>; series C,  $4.14 \times 10^{-2}$  l. mole<sup>-1</sup>; series D,  $3.77 \times 10^{-2}$  l. mole<sup>-1</sup>; and series E,  $3.17 \times 10^{-2}$  l. mole<sup>-1</sup>. As usual,  $\partial n / \partial M'$  decreased with  $\bar{n}$ , with a plot of this quantity *vs.*  $\bar{n}$  showing distinct inflections near  $\bar{n} = 0.6$  and  $\bar{n} = 2.1$ ; this is undoubtedly related to marked changes in the stage of hydrolysis and/or state of aggregation of the refracting particles.

**Ultraviolet Absorption Spectra.**—Little quantitative information could be gathered from the absorption measurements between 1900 and 3900 Å., nor could any spectral trend be noted as the degree of hydrolysis increased. All series of solutions showed complete

TABLE I  
EXPERIMENTAL TURBIDITIES (4358 Å.), REFRACTIVE INDEX INCREMENTS (4358 Å.), SOLVENT VOLUME FRACTIONS, AND pH

Series, $\bar{n}$	$M'$	$10^3 \tau^*$	$10^3 \Delta n$	$\phi$	pH
A, 0.0	0.0143	0.50	0.798	0.953	2.62
	0.0285	0.80	1.606	0.951	2.48
	0.0428	1.26	2.351	0.949	2.40
	0.0570	1.50	3.142	0.947	2.31
	0.0713	1.82	3.907	0.945	2.24
	0.0856	2.05	4.724	0.943	2.18
	0.0998	2.37	5.462	0.940	2.15
	0.1141	2.77	6.223	0.938	2.16
	0.1426	3.10	7.814	0.935	2.07
	B, 1.0	0.0105	0.55	0.553	0.955
0.0183		0.94	0.970	0.953	2.92
0.0261		1.34	1.306	0.952	2.90
0.0523		2.60	2.553	0.951	2.75
0.0784		3.94	3.826	0.949	2.70
0.1046		5.30	5.113	0.946	2.62
C, 1.6	0.0097	1.02	0.449	0.954	3.13
	0.0243	2.36	1.009	0.953	3.02
	0.0340	3.54	1.427	0.951	3.00
	0.0486	5.27	2.046	0.950	2.97
	0.0729	7.64	3.055	0.947	2.93
	0.0971	9.71	4.028	0.944	2.88
	0.1214	12.33	5.030	0.942	2.85
	D, 2.0	0.0117	1.18	0.467	0.954
0.0194		1.97	0.760	0.953	3.24
0.0272		2.91	1.014	0.952	3.20
0.0350		3.69	1.328	0.951	3.17
0.0466		4.88	1.794	0.950	3.15
0.0583		6.06	2.193	0.949	3.14
0.0777		8.20	2.908	0.947	3.10
0.0972		10.34	3.663	0.945	3.08
0.1166		12.33	4.428	0.943	3.06
E, 3.0		0.0093	36.90	0.297	0.955
	0.0139	56.10	0.442	0.955	3.10
	0.0232	93.40	0.629	0.954	3.06
	0.0325	117.5	1.028	0.953	3.02
	0.0465	165.4	1.489	0.952	2.98
	0.0697	254.3	2.212	0.951	2.95
	0.0930	337.5	2.894	0.949	2.92
	0.1162	417.4	3.676	0.948	2.88

absorption in the range 2000–2400 Å. and very weak absorption near 3000 Å. Extinction coefficients calculated at 3000–3050 Å. were approximately 2.5 l. mole<sup>-1</sup> for all hydrolyzed solutions (series B–D) and approximately 1.9 l. mole<sup>-1</sup> for the unhydrolyzed solutions (series A). All solutions were transparent in the visible region.

**Degrees of Polymerization and Estimated Charges for the Thorium Species.**—Figures 1 and 2 show plots of  $1/N_z$  as a function of  $M'$  with  $z'$  as a parameter. In none of the series does the degree of polymerization appear to be appreciably concentration dependent. For hydroxyl number 0.0, a degree of polymerization of ca. 0.9 is found at  $z' = 4+$ ; an unhydrolyzed and uncomplexed species,  $[\text{Th}(\text{OH})_n]^{4+}$ , is therefore indicated. These findings are in agreement with those of Kraus and Holmberg<sup>10</sup> and with a recent determination of charge on thorium in  $\text{HClO}_4$  based on Donnan membrane measurements.<sup>27</sup> Similarly, a mononuclear spe-

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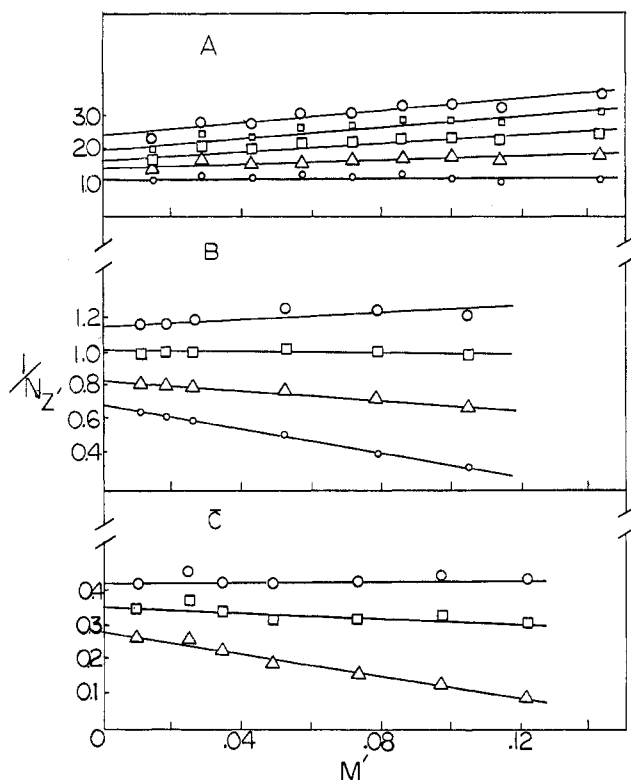


Figure 1.—Series A,  $\bar{n} = 0.0$ :  $\circ$ ,  $z' = 0$ ;  $\square$ ,  $z' = 1$ ;  $\square$ ,  $z' = 2$ ;  $\Delta$ ,  $z' = 3$ ;  $\circ$ ,  $z' = 4$ . Series B,  $\bar{n} = 1.0$ :  $\circ$ ,  $z' = 0$ ;  $\square$ ,  $z' = 1$ ;  $\Delta$ ,  $z' = 2$ ;  $\circ$ ,  $z' = 3$ . Series C,  $\bar{n} = 1.6$ :  $\circ$ ,  $z' = 0$ ;  $\square$ ,  $z' = 1$ ;  $\Delta$ ,  $z' = 2$ .

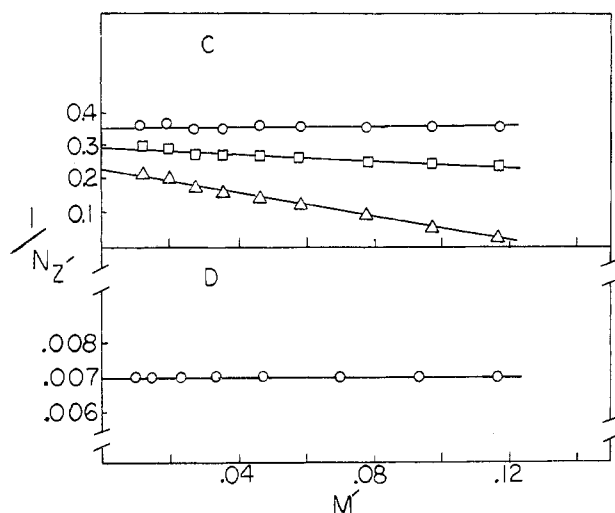


Figure 2.—Series C,  $\bar{n} = 2.0$ :  $\circ$ ,  $z' = 0$ ;  $\square$ ,  $z' = 1$ ;  $\Delta$ ,  $z' = 2$ . Series D,  $\bar{n} = 3.0$ :  $\circ$ ,  $z' = 0$ .

cies is found at  $\bar{n} = 1.0$ , with  $z' = 1+$ . The low charge requirement is attributed to gegenion association with the hydrolyzed species, and an ion of the form  $[\text{Th}(\text{OH})(\text{ClO}_4)_2]^+$  is suggested for these conditions. The lack of a marked dependence of  $1/Nz'$  on concentration at this stage is somewhat in disagreement with the results of e.m.f. studies,<sup>5,6,8,10</sup> the latter showing contributions by polymeric thorium species. Unfortunately, the turbidity measurements do not give meaningful data below  $0.01 M$  Th concentration, where the concentration dependence would be most significant.

The results at hydroxyl numbers 1.6 and 2.0 indicate

the presence in solution of small hydrolytic aggregates with polymerization numbers (taken at face value) near 2.3 and 2.9, respectively. At  $\bar{n} = 1.6$ , the data correspond closely to a low-charged dimeric species, but a distribution of dimeric and trimeric units would agree as well with the observed degree of polymerization. A low-charged trimer is suggested at  $\bar{n} = 2.0$ . The low charge required for concentration independence in these cases is similar to that found for polymerized lead(II) species.<sup>21,28</sup> It is perhaps coincidental that the estimate of  $z' = 0$  requires approximately one hydroxyl-bridged  $\text{ClO}_4^-$  per coordinated hydroxide ion. Oxyanion bridging has been proposed earlier<sup>8,12</sup> for hydrolyzed thorium ions and has been discussed<sup>29</sup> in relation to similar bridging of anions found in the solid state for the basic salts  $\text{Th}(\text{OH})_2\text{SO}_4$ <sup>30</sup> and  $\text{Th}(\text{OH})_2\text{CrO}_4 \cdot \text{H}_2\text{O}$ <sup>31</sup> by X-ray examination. Here infinite  $[\text{Th}(\text{OH})_2]^{2+}$  chains bridged by sulfate and chromate are found. It is also interesting to note from this work that the chain-like structure persisted in solid  $\text{Th}(\text{OH})_2\text{SO}_4$  prepared by hydrothermal synthesis over the entire temperature range  $50$ – $200^\circ$ , while the analogous U(IV) compound showed repeating  $[\text{U}(\text{OH})_2]^{2+}$  units when prepared at low temperatures, but reverted to distinct  $[\text{U}_6\text{O}_4(\text{OH})_4]^{12+}$  units when synthesized at higher temperatures. The marked hydrolytic difference between Th(IV) and U(IV), Pu(IV) has also been noted by Kraus and Holmberg.<sup>10</sup>

Extremely large aggregates were found at hydroxyl number 3.0. The data here indicate  $z' = 0$  and polymeric species containing approximately 140–150 thorium atoms per solute particle. Under these conditions of incipient precipitation of thorium (3.5 equivalents of  $\text{OH}^-$  per Th atom results in complete precipitation<sup>32</sup>), the possibility of colloidal species is ruled out on the basis of three independent observations in this work: (1) the constancy of the turbidity of the solutions over repeated ultrafine filtrations; (2) the absence of any dissymmetry of the scattering particles; and (3) the fact that the refractive index increment was found unchanged when measured before and after all other measurements and operations. Such interpretation of the results at this stage of hydrolysis is qualitatively in agreement with previous studies on extensively-hydrolyzed thorium solutions.<sup>33,34</sup>

It is interesting to speculate on the length of an extended  $[\text{Th}(\text{OH})_2]^{2+}$  zigzag chain in solution containing 150 thorium atoms. Using the X-ray data of Lundgren<sup>31</sup> and following the structure found in basic thorium chromate, the value  $450 \text{ \AA}$ ., or about 10% of the wave length of light used in this work, seems to be an upper limit for the longest dimension of such an ion. A particle of this size would not be expected to show

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dissymmetry. Furthermore this length is certainly an overestimate since coiling of chains and/or cross linking would result in a decrease in the longest dimension of the particle.

The results of the present study seem to be best summarized by a hydrolytic process for thorium whereby a continuous series of aggregates are formed above  $\bar{n} = 1.0$ , beginning with the formation of dinuclear and trinuclear species near hydroxyl number 1.5–2.0 and leading to the formation of very large particles prior to precipitation of hydrous oxide or basic salts above hydroxyl number 3.0. Although no measurements were made between hydroxyl numbers 2.0 and 3.0, the existence of polymers of intermediate molecular weight seems quite likely in this range. Such a continuous polymerization scheme for hydrolysis would lend cre-

dence to the hypothesis that hydrous oxide or basic salt structures are approximated in solution prior to precipitation, but the validity of this theory and the general nature of this phenomenon are subject to the results of considerable further work along these lines.

Finally, the results of this work are believed to be of the usual accuracy obtained in light-scattering work, the polymerization numbers reported being most likely accurate to within less than  $\pm 10\%$ .

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## The Phase Equilibria and Crystal Chemistry of the Rare Earth Group VI Systems. III. Neodymium-Tellurium<sup>1</sup>

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The phases occurring in the neodymium-tellurium system are: NdTe, f.c.c.  $a = 6.278 \text{ \AA}$ , m.p. 2040°. A solid solution series  $\text{Nd}_3\text{Te}_4$ - $\text{Nd}_2\text{Te}_3$  which has a high temperature,  $\text{Th}_3\text{P}_4$ -type structure, whose cubic lattice constant varies from 9.434 to 9.424  $\text{ \AA}$ , respectively; a phase transition occurs at 1000° to an orthorhombic modification, Pbnm,  $a = 11.94 \text{ \AA}$ ,  $b = 12.24 \text{ \AA}$ ,  $c = 4.407 \text{ \AA}$ ;  $\text{Nd}_2\text{Te}_4$  melts at 1680° and  $\text{Nd}_2\text{Te}_3$  melts at 1620°. A solid solution series exists over the composition range  $\text{NdTe}_{1.74}$  to  $\text{NdTe}_2$ ; the tetragonal unit cell for  $\text{NdTe}_2$  has dimensions  $a = 4.419 \text{ \AA}$ ,  $c = 9.021 \text{ \AA}$ , space group  $P^{+}/nmm$ , and the compound melts at 1270°. The phase  $\text{Nd}_2\text{Te}_5$  is orthorhombic, pseudotetragonal,  $a = b = 4.380 \text{ \AA}$ ,  $c = 44.0 \text{ \AA}$ , space group Bmmb, and melts incongruently at 910°.  $\text{NdTe}_3$  is orthorhombic, Bmmb, and the dimensions of the pseudotetragonal cell are  $a = 4.350 \text{ \AA}$ ,  $c = 25.8 \text{ \AA}$ . The compound melts incongruently at 830°.

### Introduction

Two intermediate phases in the neodymium-tellurium system, NdTe and  $\text{Nd}_2\text{Te}_3$ , have been reported. Iandelli<sup>2</sup> found that NdTe was isostructural with NaCl, and  $\text{Nd}_2\text{Te}_3$  has been shown by Miller, *et al.*,<sup>3</sup> to exhibit solid solubility ranging to the composition  $\text{Nd}_3\text{Te}_4$ . The body-centered cubic  $\text{Th}_3\text{P}_4$ -type structure, which is frequently observed for rare earth-group VI compounds having the 2:3–3:4 composition range, is observed for  $\text{Nd}_2\text{Te}_3$ , although Miller<sup>3</sup> and Flahaut, *et al.*,<sup>4</sup> report a phase transformation to the orthorhombic system below 1000°. No complete investigation of the binary phase diagram has been reported and the aim of this investigation is to determine all the intermediate phases

which exist in this system and to study their crystal chemistry.

### Experimental

Neodymium ingots of 99.9% purity were obtained from the Nuclear Corporation of America and tellurium of 99.99% purity was obtained from the American Smelting and Refining Co. The region of the phase diagram 60–100 atom % Te was investigated by sealing the appropriate compositions of the elements in evacuated silica tubes and allowing them to react for at least 2 weeks at temperatures below 700°. Extensive reaction between neodymium metal and the silica surfaces occurred if the reaction temperature exceeded 700°. The intermediate phases  $\text{NdTe}_3$ ,  $\text{Nd}_2\text{Te}_5$ , and  $\text{NdTe}_2$ - $\text{NdTe}_{1.74}$  were prepared in this manner. Mixtures containing less than 60% tellurium did not yield satisfactory results because at temperatures below 700° equilibrium could not be established and higher temperatures caused the formation of  $\text{Nd}_2\text{O}_3$ . In order to prepare the neodymium-rich compounds the mixtures were allowed to prereact in silica tubes for approximately 100 hr. and then sealed into tantalum tubes. These specimens were then heated in a vacuum induction furnace at approximately 2000° for 2–5 min. This procedure was very satisfactory for the preparation of  $\text{Nd}_2\text{Te}_3$  and its solid solution compositions and for NdTe. The reacted, neodymium-rich, compositions can be equilibrated in silica tubes

(1) This work is being sponsored by a grant from the U. S. Air Force Office of Scientific Research.

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