

S 51. *The Lower Valency States of Thorium.*

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The possible existence of compounds of bivalent or trivalent thorium has some current interest in relation to the position of thorium in the Periodic System, and the so-called "actinide" theory of the heavy elements. Such compounds might indicate whether unutilised valency electrons are disposed in the cerium-like ($5f$) or the zirconium-hafnium-like ($6d$) configuration.

Thorium di- and *tri-iodide* have now been prepared and found to be deeply coloured compounds, analogous in every respect to the lower zirconium and hafnium iodides. They are formed by reduction of the tetraiodide with varying quantities of metallic thorium at $450-550^\circ$. The tri-iodide is perceptibly volatile; it undergoes reversible dissociation to tetra- and di-iodide at $550-600^\circ$. Above 600° , both lower iodides disproportionate into the tetraiodide and metallic thorium.

The compounds are hygroscopic and react vigorously with water, forming a thorium(IV) salt and hydrogen equivalent to the reducing power. A complete analytical balance sheet can thereby be obtained, the Th : H ratio characterising the product and the Th : (H + I) ratio (ideally 4) serving as a check on the unavoidable side reaction of thorium tetraiodide with the glass. The two compounds have been unambiguously identified in this way, although not isolated completely free from each other. The compounds have been further characterised by their X-ray diffraction patterns. The di-iodide has been found to have a hexagonal layer-lattice structure, related to the C6 type, with $a = 4.13$ and $c = 7.02$ Å.

RECENT discoveries of the trans-uranic elements, a new transition series arising from the occupation of the $5f$ electron levels, have directed attention to our scanty knowledge of the chemistry of the elements following actinium in the Periodic Table. In particular, the stage at which the occupation of the $5f$ levels commences, through the crossing-over of the energies of the $6d$ and $5f$ states, is not known, although some evidence bearing on this point should be provided by chemical relationships with the rare earths, and with the A-sub-group elements higher in the Periodic Table.

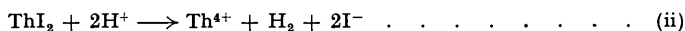
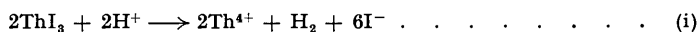
The elements of Group IVA (titanium, zirconium, hafnium) have a 3F ground state with d and s electrons external to an inert-gas core, as is typified by zirconium, with the configuration $KLM 4s^2 4p^6 4d^2 5s^2$. These elements are quadrivalent in most of their stable compounds, although compounds of bivalent and trivalent titanium are well known, and the lower halides of zirconium and hafnium have been described. As is general, the ease of reduction to these lower valency states decreases as the atomic number increases.

Thorium is quadrivalent in all its compounds described hitherto, but if—as has generally been considered—thorium is the analogue of the Group IVA elements, with the ground state Th, $KLMNO 6s^2 6p^6 6d^2 7s^2$, one might expect potentially variable valency, as shown by the existence of lower halides resembling in physical and chemical properties those of zirconium and hafnium. In addition to the Group IVA relationship, the chemistry of thorium is frequently stated to resemble that of quadrivalent cerium. The analogy is, in fact, very limited; Th^{4+} and Ce^{4+} are both inert-gas-like ions, of similar ionic radius; analogies of crystal structures and of complex-salt formation from these ions have little bearing on the sequence of electronic levels outside the xenon- and radon-like cores. The compounds of trivalent cerium are derived from the ion Ce^{3+} , $KLM 4s^2 4p^6 4d^{10} 4f^1 5s^2 5p^6$, and differ entirely from the compounds of trivalent zirconium or hafnium; these differences are not only in reactivity, arising from the energetics of the oxidation-reduction process but, more significantly, in the crystal structure and colour of the compounds concerned, which indicate the greater polarisability of the odd d electrons in Zr^{3+} as compared with the screened odd f electrons in Ce^{3+} . Compounds of bivalent cerium analogous to zirconium di-iodide do not exist. We concluded that from the existence and properties of lower halides of thorium the true chemical affinities of thorium might be deduced. As is shown below, the analogy with zirconium and hafnium is close; this conclusion was also reached by Hayek and Rehner (*Experientia*, 1949, 5, 114) in a publication dealing with the formation of thorium tri-iodide, which appeared after the completion of the work described here.

Of the Group IVA elements, only quadrivalent titanium can be reduced in aqueous solution. The anhydrous tetrahalides have, however, been reduced to the trihalides by hydrogen ($TiBr_4$; Young and Schumb, *J. Amer. Chem. Soc.*, 1930, 52, 4233) or aluminium ($ZrCl_4$, Ruff and Walstein, *Z. anorg. Chem.*, 1923, 128, 96; $ZrBr_4$, Young, *J. Amer. Chem. Soc.*, 1931, 53, 2148; $HfBr_4$, Schumb and Morehouse, *ibid.*, 1947, 69, 2969). In the present work it appeared more promising to use metallic thorium as reducing agent, for the work of de Boer and Fast (*Z. anorg.*

Chem., 1930, **187**, 177) had shown that in the system of zirconium halides the reversible reactions $3\text{ZrI}_4 + \text{Zr} \rightleftharpoons 4\text{ZrI}_3$ and $2\text{ZrI}_3 \rightleftharpoons \text{ZrI}_2 + \text{ZrI}_4$ take place readily at 450–600°.

In a semi-theoretical review of the thermodynamic properties of the heavy elements in their several valency states, based on Seaborg's "actinide" theory, Brewer (MDDC., 1543) has predicted that the tervalency of thorium should be doubtful but that its trichloride might be the most stable lower halide. Analogy with the chemistry of zirconium and hafnium suggested that the iodides would be prepared more readily than the chlorides and bromides. This conclusion has been borne out by experiment. *Thorium di- and tri-iodide* have been prepared as deeply coloured compounds, very similar to the anhydrous lower iodides of the Group IV_A metals, and decomposed by water according to the equations:



EXPERIMENTAL.

Reaction of Thorium Metal with Thorium Tetraiodide.—Thorium tetraiodide was prepared by direct union of the elements in a flask carrying three side arms with a glass septum in the neck (see Fig. 1). This was joined by one side arm to a vacuum system, consisting of a McLeod gauge, rotary oil pump, and a mercury diffusion pump, and through another side arm to an iodine reservoir. The apparatus was evacuated to 10^{-3} mm., and the whole apparatus flamed out. Dry air was admitted to the apparatus, and the side arm *D* opened. 3 Mg.-atoms of thorium were introduced, then the side arm was drawn off as close to the neck of the flask as possible. 6 Mg.-mols. of iodine were introduced into the iodine reservoir through side arm *E* which was then sealed in turn. The iodine reservoir was immersed in liquid air, the whole apparatus evacuated and the thorium thoroughly out-gassed by heating it with a luminous tipped Bunsen flame. When cool, the apparatus was sealed and drawn off from the vacuum system at constriction *A*. The liquid-air bath was removed, and the reservoir allowed to warm to room temperature. When the thorium had been heated to approximately 400°, the iodine was sublimed over into the thorium flask, where an exothermic reaction took place and yellow thorium tetraiodide was formed. Any remaining iodine was sublimed into the thorium flask, and the iodine reservoir then sealed and drawn off at the constriction *B*. The flask and contents were placed in an oven at 475° for several hours in order to complete the reaction.

FIG. 1.

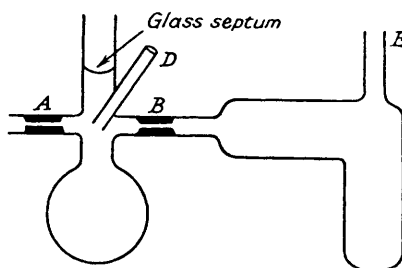
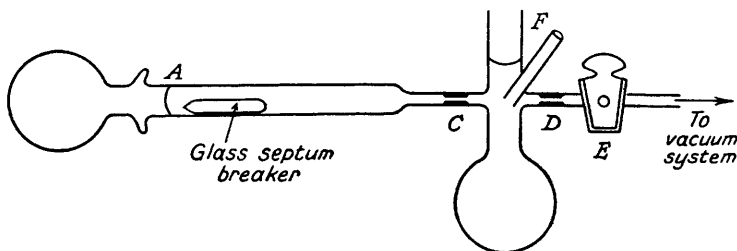


FIG. 2.



The flask containing the tetraiodide was joined by a constriction to one of the three side arms of a similar flask. Another side arm was connected by a constriction and tap to a liquid-air trap and then to a vacuum system. After evacuation and flaming out of the apparatus, from 1 to 6 mg.-atoms of thorium, according to the product desired, were added through side arm *F* (see Fig. 2), which was then sealed and drawn off. The apparatus was again evacuated and the thorium out-gassed at 10^{-3} mm. After tap *E* had been closed, the apparatus was removed from the vacuum system, and the glass septum *A* broken. The apparatus was again connected to the vacuum system, and the liquid-air trap evacuated.

By opening tap *E* any residual gases and/or free iodine could be pumped off. The tetraiodide was sublimed into the flask containing the thorium whilst the apparatus was subjected to continuous pumping. Then, after the apparatus had been sealed and drawn off at constriction *D*, the flask which had contained the tetraiodide was sealed and drawn off at constriction *C*.

After several hours' heating, the flask was removed from the oven and examined. No thorium tetraiodide was visible, but a black powder and a sublimate with a metallic lustre were seen on the walls of the flask. This clearly indicated that a lower halide had been formed.

Analysis.—By analogy with the lower halides of zirconium, the lower halides of thorium are likely to react with water, evolving hydrogen and forming a thorium (IV) salt in solution (cf. equations i and ii, above). If this reaction is quantitative, the volume of hydrogen liberated is a direct measure of the reducing power of the thorium. According to our observations this is the case, although Hayek and Rehner (*loc. cit.*) state that the primary reaction with water is one of disproportionation:



In experiments with *thorium di-iodide*, at least, the full quota of hydrogen was liberated rapidly, any metallic thorium remaining as a residue and reacting slowly with the (somewhat acid) solution being attributable to excess of thorium present in the preparation. Our results may, perhaps, not exclude the partial occurrence of this reaction with *thorium tri-iodide*, even though most of the material reacts according to equation (i).

For the purposes of analysis the flask containing the lower halide was joined to a tap-funnel and to a Toepler pump. The septum was perforated, and 10 c.c. of air-free water were run in *in vacuo*. A vigorous exothermic reaction took place, and the hydrogen gas was withdrawn and measured. The solution, filtered from pieces of broken septum and unchanged thorium, was analysed for thorium and iodine by precipitation as thorium oxalate and silver iodide, respectively.

A complete analytical balance sheet was thereby obtained in each experiment; the ratio Th : I : H should be 1 : 3 : 1 for ThI_3 and 1 : 2 : 2 for ThI_2 . Results obtained for preparations with varied initial quantities of thorium tetraiodide and thorium metal are collected in Tables I and II.

TABLE I.

I : Th > 3 : 1.

Expt.	Thorium, milliatoms.	ThI_4 , millimols.	Reaction temp.	Time of heating, hrs.	Th : I : H.	H + I.	ThI_3 , %.
(1)	1	3	515°	20	1 : 3.49 : 0.74	4.23	74.2
(2)	$\frac{1}{2}$	3	515	20	1 : 3.54 : 0.585	4.12	58.5
(3)	1	3	475	66	1 : 3.39 : 0.729	4.11	72.5
(4)	1	3	450	49	1 : 3.53 : 0.609	4.14	61.1
(5)	$\frac{3}{4}$	3	450	48	1 : 3.23 : 0.803	4.03	80
(6)	1	3	555	24	1 : 3.26 : 0.718	3.98	71.6

TABLE II.

I : Th < 3 : 1.

Expt.	Thorium, milliatoms.	ThI_4 , millimols.	Temp.	Time, hrs.	Th : I : H.	H + I.	ThI_3 , % (assuming ThI_2 - ThI_3 system).
(1)	3.26	3	475°	12	1 : 2.76 : 1.25	4.01	24
(2)	3	3	535	38	1 : 2.5 : 1.5	4	50
(3)	2	3	555	24	1 : 2.5 : 1.49	3.99	50
(5)	4	3	555	48	1 : 2.1 : 1.86	3.98	90
(6)	6	3	555	48	1 : 2.2 : 1.88	4.06	80
(7)	4	3	555	144	1 : 2.12 : 1.84	3.96	88

Results and Discussion.—It is convenient to consider separately the experiments designed to produce the tri-iodide, with initial ratios I : Th > 3 : 1 (Table I), and those designed to produce the di-iodide (I : Th < 3 : 1) (Table II).

(a) *Thorium tri-iodide system.* If the systems with I : Th > 3 : 1 attain chemical equilibrium during heating, they must, according to the phase rule, be univariant, with two solid phases present. If—as proved to be the case—complete reaction is not achieved, some metallic thorium may remain in excess. The metallic thorium available had an oxygen content up to 0.5% (equivalent to nearly 5% ThO_2), and this may have adversely affected the reaction. From analytical data alone it would be impossible to distinguish mixtures of the tri-iodide with excess of tetraiodide from mixtures of di-iodide with excess of tetraiodide. However, in such experiments as Nos. 1, 3, and 6 (Table I), the latter alternative would involve the presence of a relatively large excess of tetraiodide, which would be easily visible by reason of its bright yellow colour. In fact, only a trace of yellow tetraiodide was detectable and removable by sublimation at low temperatures (200°), and no diffraction lines of this iodide were identified in the X-ray

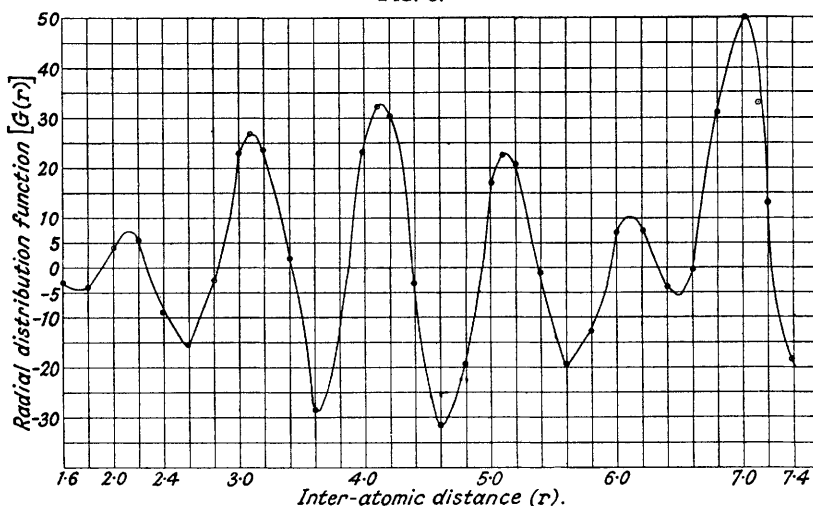
diffraction pattern. Hence, the product of reaction under the conditions specified was undoubtedly the tri-iodide, with some excess of unchanged tetra-iodide.

From Table I it is seen that the duration and temperature of heating, within the range 450—550°, had no effect on the apparent yield of tri-iodide. The maximum apparent yield of 70% may be due to a coating of tri-iodide on the thorium, preventing further reaction with the tetraiodide. Alternatively, it would be explained if a portion of the tri-iodide underwent disproportionation according to equation (iii), as suggested by Hayek and Rehner. It can readily be shown that the simultaneous occurrence of reactions (i) and (iii) lowers the Th : H ratio, whilst preserving the ratio $\text{Th} : (\text{I} + \text{H}) = 1 : 4$. In Table I the latter ratio is, in general, greater than 1 : 4, and this is probably to be attributed to the known reaction between tetraiodide and glass (Fischer, *Z. anorg. Chem.*, 1939, **242**, 161), whereby ThO_2 and SiI_4 are formed. In the analysis the iodine present as SiI_4 is necessarily determined along with that present in the ThI_3 - ThI_4 system.

(b) *Thorium di-iodide system.* Products from experiments with $\text{I} : \text{Th} > 3 : 1$ could, in accord with the analytical data, consist of di-iodide mixed with either tetra- or tri-iodide. The latter appears the more probable, since in experiments 1, 2, 3 (Table II) no tetraiodide was detectable visually or separable by sublimation at low temperatures. Moreover, in the absence of an excess of tetraiodide there is little reaction with the glass vessel during heating, as is shown by the satisfactory values found for the $\text{Th} : (\text{I} + \text{H})$ ratio (column 6). The optimum conversion into di-iodide was obtained at temperatures above 550°.

X-Ray Crystallographic Evidence.—For X-ray examination, samples approximating closely to the compositions ThI_2 and ThI_3 were introduced into thin-walled capillaries (0.3 mm. diam.) sealed on to the reaction vessel. Photographs were taken with filtered $\text{Cu-K}\alpha$ radiation. The existence of two compounds, distinct from each other and from the tetraiodide, was thereby clearly confirmed.

FIG. 3.



Thorium tri-iodide, after prolonged annealing in the evacuated capillary (48—200 hours at 550°), gave evidence of extensive recrystallisation; this compound is perceptibly volatile, and appears to form either largely oriented aggregates, or possibly a few mutually oriented crystals within the capillary. Two characteristic diffraction patterns have been observed, depending on the duration of the annealing, and it appears probable that the tri-iodide is dimorphous. Evidence available at present suggests that neither form is isomorphous with the rare-earth tri-iodides, but the study of the compound is incomplete.

Thorium di-iodide is not volatile, and does not undergo recrystallisation and orientation within the capillary. In order to derive the maximum information from the data, the interplanar spacings d_i and visually estimated intensities I_i and all the observed lines were combined by constructing the radial distribution function $G(r)$ (cf. Warren and Gingrich, *Physical Rev.*, 1934, **46**, 368; Medlin, *J. Amer. Chem. Soc.*, 1935, **57**, 1036; 1936, **58**, 1590) :

$$G(r) = \frac{2r}{\pi} \sum S_i \cdot I_i \sin S_i \cdot r \quad \text{where} \quad S_i = (4\pi \sin \theta) / \lambda$$

For computation this can more conveniently be converted into the equivalent form

$$G(r) = 4r \sum \frac{I_i}{d_i} \sin 2\pi \frac{r}{d_i}$$

The values of $G(r)$, between $r = 1.6$ A. and $r = 7.2$ A. are shown in Fig. 3; two strong, sharp peaks are shown at $r = 4.13$ A., $r = 7.02$ A., with smaller peaks at $r = 3.1_0$ A., $r = 5.1_2$ A. The interatomic distance 4.13 A. is within the range of I-I distances in metallic iodides; the size of the peak indicates that this coincides also with a Th-Th distance. The 3.10 A. peak may be taken as a Th-I distance, and the I-Th-I angle can then be calculated as approximately 84° , being somewhat sensitive to errors in the interatomic distances. It is evident that the thorium is in 6-fold co-ordination with iodine (I-Th-I angle ideally 90° for octahedral co-ordination). With this established, consideration shows that the radial distribution function is compatible only with a hexagonal layer-lattice structure, with $a = 4.13$ A., $c = 7.0_2$ A., $c/a = 1.7$. The magnitude of the 4.13 A. and 7.0₂ A. peaks is then due to the coincidence of Th-Th and I-I distances; the 5.1₂ A. peak is in the required position for the Th-I (second nearest neighbour) distance.

The observed diffraction pattern can, indeed, be satisfactorily indexed on this basis, and it may be concluded that thorium di-iodide crystallises, like other known di-iodides, in a layer-lattice structure related to the CdI_2 (C6) structure. Calculation of intensities, and direct comparison with the diffraction pattern of lead iodide, which is comparable in cell dimensions and in the relative scattering power of the atoms concerned, shows some anomalies, however. The elucidation of these must await further work, and the full presentation of the X-ray data is, accordingly, deferred to a later publication.

Conclusion.—The results given here show that thorium can display variability of valency, and that the compounds formed resemble in their types, reactions, and physical properties those of the Group IVA elements zirconium and hafnium. The inferences may legitimately be drawn that these lower halides, like those of zirconium and hafnium, are based on cations with unutilised $6d$ electrons, and that the occupation of $5f$ orbits comes into operation only with the elements of higher atomic number than thorium.

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