Scaife and Wylie:

New Lower Iodides of Thorium. 1039.

By D. E. SCAIFE and A. W. WYLIE.

Three lower iodides of thorium have been characterised, viz., thorium triiodide, α -thorium di-iodide, and β (high temperature) thorium di-iodide. As the temperature is raised these iodides, undergo peritectic transformation as follows: thorium tri-iodide into β -thorium di-iodide at 746°, and β -thorium di-iodide into thorium metal at 864° . Solid-state transition of α -di-iodide into the β modification occurs sluggishly at 600-700°. These relationships are summarised in the form of an equilibrium diagram for the system thorium-iodine. Evidence for a fourth iodide of thorium at I/Th 3·3-3·4 is discussed but its existence is doubted.

Distinct X-ray diffraction patterns have been obtained for all lower iodides. That for β -thorium di-iodide has been indexed on the basis of a hexagonal unit cell with $a_0 = 9.21$ Å, $c_0 = 3.74$ Å. That for α -thorium di-iodide can be indexed on the basis of a hexagonal unit cell with $a_0 = 8.00$ Å, $c_0 = 7.87$ Å. The diffraction pattern for thorium tri-iodide is complex and does not resemble that of expected structure types.

Microscopical observation shows that β -thorium di-iodide is opaque, and golden with metallic reflection. Thorium tri-iodide is black, faintly translucent, and shows a strong blue-green dichroism and probably contains the ion Th³⁺. Both these two iodides and α -thorium di-iodide, which is difficult to characterise microscopically, are vigorously decomposed by water without formation of solid residues or coloured solutions.

In their survey of the important group of actinide element halides Katz and Sheft¹ comment on the confused state of knowledge concerning lower halides of thorium. An equilibrium diagram of the system thorium-iodine is now suggested which establishes the three phases, thorium tri-iodide and α - and β -thorium di-iodide. Thorium monoiodide does not appear to exist. One di-iodide phase was recently reported by Clark and Corbett² who also refer to a phase of composition $I/Th \leq 3.4$. Evidence for an iodide of thorium in the region I/Th $3\cdot 3$ — $3\cdot 4$ has been sought but its existence is doubted.

EXPERIMENTAL

Materials.-Dry iodine was prepared from melted analytical grade iodine by pumping, followed by distillation and condensation in a vacuum of $<10^{-4}$ mm. Its water content was less than 1 p.p.m.³ Electrolytic thorium, from the United Kingdom Atomic Energy Authority, contained 100—104 p.p.m. oxygen, 6—15 p.p.m. nitrogen, 5—6 p.p.m. hydrogen, <600 p.p.m. chloride, and insignificant quantities of other impurities. Its lattice spacing was 5.085 Å in agreement with the accepted value for pure thorium.⁴ High purity thorium carbide-iodide was also available for critical experiments. It contained <25 p.p.m. each of carbon, oxygen, or nitrogen.⁵

Preparation of Lower Iodides.—All initial preparations were made by heating various ratios of thorium and thorium tetraiodide in metal containers owing to the strong interaction between lower iodides of thorium and glass. Stock quantities of pure tetraiodide were prepared in Pyrex glass by reacting thoroughly degassed thorium with iodine vapour at 300° .⁶ The product was finally sublimed in vacuo at 430° and transferred to gas-tight metal containers.

Before reaction with tetraiodide, degassed thorium metal was reduced to a loose powder by subjecting it to several hydriding and dehydriding cycles according to the procedure of Witt,

¹ Katz and Sheft, "Advances in Inorganic Chemistry and Radiochemistry," Academic Press Inc., N.Y., 1960, Vol. 2, p. 195. ² Clark and Corbett, Inorg. Chem., 1963, 2, 460.

^a Mills and Reid, J. Inorg. Nuclear Chem., 1964, 26, 893.
^a Evans and Raynor, J. Nuclear Materials, 1959, 3, 281.
⁵ Reid, Wilmshurst, and Wylie, J. Electrochem. Soc., 1963, 110, 429.
⁶ Scaife and Wylie, "Proceedings of the Second International Conference on the Peaceful Uses of mice Proceedings of the Second International Conference on the Peaceful Uses of Mice Second Atomic Energy," Geneva, 1958, Vol. 4, p. 215.

Nylin, and McCullough.⁷ The final product, which contained substantially lower quantities of chloride than the starting material, was degassed at $700^{\circ}/10^{-6}$ mm. and transferred from Pyrex vessels into sealed metal containers.

All transfers, weighings, and other operations were carried out in an evacuable glove box whose argon atmosphere could be maintained at a dew point of -60° or better. Equilibrations and quenchings were carried out in sealed capsules made from small-bore tantalum tubing, pre-closed at one end. After filling these were sealed in argon by cold welding in a set of jaws designed to operate in a hand press in the glove box. Finally the flattened ends of the capsules were arc welded in argon to ensure a perfect seal. Platinum capsules were sealed by the same technique except that the final seal was made by fusion in a small oxygen-coal gas flame, the body of the capsule being cooled in water. A somewhat more convenient procedure, due to A. G. Turnbull, consisted in flattening a piece of gold wire, inserting it between the flattened walls of the capsule end (above the cold weld) and fusing it in a flame at a lower temperature. Fidelity of the seals was checked by boiling the weighed capsules in water and reweighing after cooling. The capsule was weighed again after heating, very few being rejected because of leaks.

The sealed tantalum capsules were heated in evacuated tubes of "Supremax" glass or clear quartz and quenched in less than 3 sec. by dropping these into a bucket of cold water. Several platinum capsules were quenched at a faster rate by fusing a supporting wire thread and allowing them to drop straight into water.

Tantalum suffers little or no attack by molten iodides and is quite unaffected by thorium metal at the temperature of these experiments.⁵ Platinum suffers little attack in the absence of thorium but a reaction at the capsule walls occurring with free thorium metal causes formation of various black, strongly adherent intermetallic compounds,⁸ and changes in the composition of the capsule contents. Further mention of these changes will be made later.

Microscopical Examination.—Slides were prepared in the glove box for examination in transmitted, polarised, and reflected light. Fluorocarbon oil, dried and purified by prolonged heating *in vacuo* was a satisfactory immersion medium. Most conventional high refractive index media reacted chemically with the specimens.

The reaction of lower iodides with water was examined optically on a microscope slide.

X-Ray Powder Diffraction.—X-Ray diffraction measurements were made by means of a Philips Debye–Scherrer type powder camera of 11.46 cm. diameter, using $Cu-K_{\alpha}$ radiation and nickel filter. Finely ground samples were loaded into 0.3 mm. Lindemann glass capillaries in the glove box and sealed off. Pyrex capillaries were used for some mixtures which showed superficial reaction with Lindemann glass. Films were calibrated for absorption and other errors by incorporating a small amount (ca. 10%) of high-purity degassed thorium dioxide in the sample, the correct positions of the thorium dioxide lines being calculated from the extrapolated lattice constant. Secondary calibrations could be made in the event of thorium dioxide lines obscuring lines of the samples. Films of samples containing excess of thorium metal could be calibrated directly in the basis of Nelson–Riley extrapolation of the lattice constant of the metal; this constant never differed significantly from that of the starting material, showing that the thorium was substantially free of any alloying elements.

Line positions were measured with a precision of better than 0.02 mm. by means of a Pye travelling microscope. Scatter of results for different films of the same sample did not exceed $\pm 0.03 \text{ mm}$. Line intensities were judged by eye; some intensities were measured with a Joyce microdensitometer.

Some measurements were taken with a Philips diffractometer, and also with a Guinier-type focusing camera, using in the latter case airtight sample holders designed in these Laboratories. Results were in good agreement with Debye–Scherrer measurements

Except in the region I/Th $3\cdot 2$ — $3\cdot 5$ the quality of films was generally good, and the phases comprising each sample could be identified with certainty. Results reported for the pure phases are the averages of at least six separate films on at least three separate samples.

Differential Thermal Analyses.—All differential thermal analysis (D.T.A.) was carried out in sealed platinum capsules of $\frac{3}{16}$ in. (i.d.) $\times \frac{3}{4}$ in. long either on unchanged mixtures of thorium and its tetraiodide or on mixtures pre-equilibrated by heating in tantalum and subsequently quenched. Preliminary experiments showed that the formation of intermetallic

⁷ Witt, Nylin, and McCullough, U.S.A.E.C. Report SEP-221, 1956.

⁸ Thomson, Acta Cryst., 1962, 15, 1308.

platinum thorium compounds at the wall of the container was a slow, exothermic process which was not responsible for any of the sharp peaks observed on the D.T.A. recordings.

The D.T.A. apparatus was conventional although a sensitive amplifying system with full half-scale deflection $40 \,\mu v$ was employed. The technique was to rest the capsule and an identical reference capsule containing ignited alumina on the tips of the differential couple. The weight of the capsule was usually sufficient to obtain adequate contact and signals of usable size. The capsules were supported in alumina collars which also served to insulate them from the nickel block. An all-alumina block was also used satisfactorily. Capsules filled with pure sodium chloride pre-melted *in situ* were used to calibrate the equipment.

Because of the non-reversibility of the various phase reactions, the most directly useful D.T.A. results were obtained on the first heating of previously equilibrated and quenched samples. Subsequent heating and cooling cycles disturb this equilibrium; Fig. 1 shows such a



FIG. 1. D.T.A. record for the composition I/Th 2.05

First cycle with pre-equilibrated material, second cycle immediately following. Heating rate 8°/min. (Arrows indicate where temperatures were read for melting, freezing.)

heating cycle, in which the composition of $\text{ThI}_{2.05}$ is heated to 930° and cooled at the same cooling rate (10°/min.). The appearance of extra peaks and changes in intensity of existing peaks on cooling and subsequent cycles is typical, and results from the presence of phases not in equilibrium at this composition because of the slowness of the phase reactions on cooling.

Repeated heating of mixtures of thorium metal and thorium tetraiodide in platinum capsules in the D.T.A. system gave useful information on the various horizontals existing in the system. The complicating feature for compositions containing initially large amounts of thorium metal, *viz.*, the gradual withdrawal of thorium from the sample by alloying with the platinum of the capsule walls, does not introduce significant amounts of platinum into the melt. Indeed use may be made of this, in that the progressive change of average composition causes certain D.T.A. peaks to disappear and others to appear.

All capsules were analysed after D.T.A. by chemical, microscopical, and X-ray methods.

Analytical Methods.—Although materials made by us were not pyrophoric, the lower iodides required careful hydrolysis in an atmosphere of ammonia to prevent loss of iodine. Samples in a partially covered weighing bottle were placed in a covered beaker containing a small quantity of concentrated ammonia solution and were allowed to stand for several hours in a

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closed vessel. After this treatment the product could be dissolved in IN-perchloric acid with negligible loss of iodine. Unchanged thorium, which does not dissolve in dilute perchloric acid, was filtered off, ignited, and weighed as oxide. Soluble thorium was determined by E.D.T.A. titration with xylenol orange indicator. A pH of 2.0 for the initial solution, lower than suggested by Barnett and Milner,⁹ was essential for accurate results. Any free iodine present was reduced by boiling with hydroxylamine hydrochloride. Iodine was determined by Lang's iodine-cvanide method,¹⁰ special precautions being taken to prevent loss of iodine from acidified





 \bigcirc , Results for D.T.A. Horizontals represent the average for many results, not all of which are shown. \triangle Equilibrated samples quenched from these points (cf. Table 1).

iodide solutions.¹¹ Satisfactory summations were obtained and the precision of the iodine and thorium determinations was such that the I/Th molar ratios in the samples were accurate to ± 0.02 unit for both thorium di- and tri-iodides.

RESULTS AND DISCUSSION

Fig. 2 summarises the experimental findings as an equilibrium diagram which is expected to differ little from a true condensed-phase diagram in which equilibria are determined

⁹ Barnett and Milner, U.K.A.E.A. Report A.E.R.E. C/R 2307, 1958.

¹⁰ See Böttger and Oesper, "Newer Methods of Volumetric Analysis," Chapman and Hall, London, 1939, p. 38.

¹¹ Pilkington and Smith, to be published.

under a total pressure equal to the vapour pressure of the system itself. The system is quite complex, much of it lying in temperature regions not accessible to earlier workers operating with glass equipment. Slow rates of reaction (cf. Table 1) add to the difficulty of experimental investigation. For convenience the results will be discussed in terms of three sub-systems.

The Sub-system Thorium-Thorium Di-iodide.-This section of the diagram is relatively

TABLE 1.

Quenching data.

| Molar comp. ^a | | Thermal history | | | | | | | | | | | |
|-----------------------------|--------------|-----------------|--|------------|-----------|----------------|----------------------------|---------------------------|--|--|--|--|--|
| | | r | | Equi- | | 0 1 |) | | Phases present | | | | |
| Over- all | Solu- ble | Reac | tion | libra | tion | Quench- ing | ζ <u> </u> | K-Ray | | | | | |
| I/Th | I/Th | °c | hr. | °c | hr. | °c | Major | Minor | Microscopical examination | | | | |
| 0·87 ₃ | 2.05 | 600 800 | $\begin{array}{c} 110\\ 170 \end{array}$ | 600 | 120 | b | β -ThI ₂ | α-ThI ₂ | Lightly sintered mass of bronze yellow opaque material with small amount of adhering | | | | |
| 1.45 | | 450 | 65 | 500 500 | 160 47 | Ь | Th | ${ m ThI}_3$ ${ m ThI}_4$ | black opaque phase. No 1h metal visible. Lumps of "iodide" thorium starting metal heavily coated with black opaque phase. Also ca. 20% of thorium tetraiodide; some translucent dichroic phase and few clear laths of oxyiodide. Equilibration time inadequate. | | | | |
| 1.31 | 2.21 | | | 600 | 115 | 600 | α -ThI ₂ | Th ThI ₃ | Coarse grey free-flowing powder giving metal- lic streak. Rich in black opaque phase, some particles having dull bronze sheen. Some free thorium visible. | | | | |
| 1.71 | 2.73 | 500 | 67 | 500 | 47 | Ь | ThI_3 | Th α-ThI₂vw | Coarse, free flowing powder, bulk consisting of radiating aggregates of elongated black crystals; $<5\%$ of bronze yellow phase; <5% laths of oxyiodide. Some opaque crystals translucent at thin edges and di- chroic; others translucent, brown. Equi- librium time inadequate | | | | |
| 1.90 | | 600 | 230 | 500 | 572 | 600 | α -ThI ₂ | Th ThI ₃ vw | Unsintered black powder with few lightly sintered bronze yellow lumps. Most parti- cles opaque, 10% translucent thin edges only and dichroic. | | | | |
| 2.04 | 2.19 | 800 600 | $\begin{array}{c} 20\\120\end{array}$ | 800 | 145 | 800 | β -ThI ₂ | ThI_3 | Sintered mass of opaque bright golden yellow metallic phase. Less than 20% of dark, adhering phase translucent at thin edges only and dichroic | | | | |
| $2 \cdot 11$ | $2 \cdot 40$ | 800 | 25 | 700 | 93 | 700 | β -ThI ₂ | ThI_{3} | Heavily sintered dull bronze yellow phase. | | | | |
| 3.02 | 3 ·10 | 700 | 36 | 700 | 93 | 700 | ThI ₃ | | Black homogeneous sintered powder, parti- cles fairly well crystallised and translucent at thin edges only; dichroic. No tetra- iodide noted. | | | | |
| 3.08 | 3.12 | 600 | 220 | 600 | 596 | 600 | ThI₃ | | Homogeneous black powder, free-flowing. Crystal development poor; translucent thin edges only; strongly dichroic. No tetra- iodide visible; few needles of oxyiodide present. | | | | |
| 3·24 ¢ | 3.24 | 700 | 69 | 600 | 69 | b | ThI₃ | ThOI ₂ | Mixture of black particles and semi-trans- parent aggregates of highly refracting, violet-brown needles. Black material trans- lucent, strongly dichroic. Mixture only partially melted. | | | | |
| 3.50 d | 3.50 | 500 | 89 | 700 | 46 | b | ThI ₄ | ThOI ₂ vw | Mixture of abundant tetraiodide plates, laths, etc., and black opaque, dichroic particles. Definitely melted. Few prisms and other sections of colourless thorium oxyiodide particles present. | | | | |

^a Made from thorium metal and thorium tetraiodide unless stated otherwise. ^b Allowed to cool slowly *in situ*. ^c Made from β -thorium di-iodide and thorium tetraiodide. Weight changes of 3 mg. in 3 g. of sample suggest a small leak with this capsule. ^d Made from thorium tri-iodide and thorium tetraiodide.

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simple. The only phase reactions below 950° are the transition between α - and β -thorium di-iodide:

(Low temp.)
$$\alpha$$
-ThI₂ $\longrightarrow \beta$ -ThI₂

occurring between 600 and 700°, and the peritectic decomposition of β -thorium di-iodide at 864°:

$$2\beta$$
-ThI₂(solid) \longrightarrow Th(solid) + ThI₄(liquid)

This peritectic line extends right across the diagram from I/Th < 0.87 to ~ 3.2 in agreement with the results of Clark and Corbett.²

Metallic, golden β -thorium di-iodide formed by reaction of thorium tetraiodide and thorium at 800° (sol. Th, 43.9_6 ; sol. I, 52.7_5° ; I/Th (sol.), 2.19; free Th 3.29°) has the morphological characteristics summarised in Table 2. Its X-ray pattern (Table 3b) shows general agreement with that reported by Clark and Corbett² for the "metallic di-iodide" phase except that they included a line not due to β -thorium di-iodide. The data can be provisionally indexed on the basis of a hexagonal unit cell with $a_0 = 9.21$ Å, $c_0 = 3.74$ Å. The structure does not appear to be related to the cadmium hydroxide structure nor to the strontium or barium di-iodide variants of the lead chloride structure.

Because of the slowness of reaction as well as the likelihood of a low heat of transition, the transition temperature between α - and β -thorium di-iodide could not be located by D.T.A. methods. Quenching experiments (Table 1) suggest that it occurs between 600

| | β-ThI, | ThI _{3.0} | $\mathrm{Th}\mathrm{I}_4$ | | | |
|-------------------------------|---|--|--|--|--|--|
| Reflected light | 1 2 | | - | | | |
| Colour | Golden, metallic | Black | Clear yellow | | | |
| Habit | Often in indefinite aggre- gates with numerous facets. Well crystall- ised specimens ^b often in lustrous six-sided plates with profile angles seldom if ever regular, 112 ± 2 and $124 \pm 2^\circ$ seemingly characteristic. Re- entrant angles and rhombic plates ob- served occasionally. | Poorly crystalline lumps occasionally showing small polygonal facets. Sometimes in more elongated particles. | Usually plates or columnar growths. Sometimes micro-crystalline. | | | |
| Hardness, frac- ture, etc. | Soft, with metallic streak. Cleavage parallel to basal faces. | Brittle, with conchoidal fracture. | Brittle, with characteristic cleavage directions. | | | |
| Particle size (μ) | 20-100 | 560 | 20-200 | | | |
| Transmitted light | | | | | | |
| Colour and trans- parency | Totally opaque | Opaque except in small fragments or edges of larger ones viewed in strong light, when translucency apparent. | Clear sulphur yellow, high refractive index. | | | |
| Refraction and extinction | | Doubly refracting, sharp extinction. | Doubly refracting, strong- ly birefringent, biaxial. ^e Extinction angle in white light varies with dispersion except for sections perpendicular to plane of optic axes. | | | |
| Selective absorp tion | | Shows marked dichroism violet to olive green. | Not dichroic. | | | |
| " See text for | discussion on thorium di-id | odide. ^b Prepared $>750^\circ$, | <850°. ^e Thorium tetra- | | | |

TABLE 2.

Some morphological and optical properties of thorium iodides.^a

^a See text for discussion on thorium di-iodide. ^b Prepared >750°, <850°. ^c Thorium tetraiodide is known to have orthorhombic symmetry.¹¹ [Note added in proof: Forrester, Templeton, and Zalkin, *Inorg. Chem.*, 1964, **3**, 639, have shown that ThI₄ has monoclinic symmetry.] and 700°. The sluggishness of this transformation is shown by the result for a composition I/Th = 0.87 heated to 800° to form β -thorium di-iodide and subsequently heated for 120 hours at 600°; only about a quarter of the initial product was transformed to α -thorium di-iodide. The phase α -thorium di-iodide is therefore best prepared at approximately 600° when thorium metal is the only impurity (Table 1, sample I/Th 1.31). At temperatures much below 600° the rates of reaction and transition are both very slow and a non-equilibrium distribution of phases may result. For example mixtures of thorium and thorium tetra-iodide (I/Th 1.71) heated for a long period at 500° (Table 1) consisted mainly of thorium and thorium tri-iodide, the X-ray pattern of the latter being identical with that of tri-iodide obtained at higher temperatures.

The X-ray pattern of α -thorium di-iodide is in rough agreement with that reported by D'Eye, Ferguson, and McIver for their " black di-iodide " except that they did not report two low angle lines.¹¹ This pattern cannot be attributed to presence of oxyiodide in the samples of D'Eye et al.¹² as claimed by Clark and Corbett.² Despite some close coincidences in line positions the pattern of α -thorium di-iodide is quite distinct from, though closely related to that of, β -thorium di-iodide. The structure of α -thorium di-iodide does not appear to belong to the cadmium hydroxide type with the lattice constants claimed in an early Paper of D'Eye and Anderson,¹³ nor to the lead chloride type. The diffraction pattern reported in Table 3(a) can be provisionally indexed on the basis of an hexagonal unit cell with $a_0 = 8.00$ Å, $c_0 = 7.87$ Å. This unit cell is related to that found for the β -di-iodide in that c_0 for the α compound closely approximates $\sqrt{3/2} a_0$ for the β compound. This relationship may indicate that the unit cells derived from the two diffraction patterns are sub-multiples of the true unit cells. It would be more reasonable to expect similar a_0 values but different c_0 values for the two forms, and indeed, the pattern for the α -di-iodide can be partially indexed [Table 3(a)] on the basis of an hexagonal unit cell with $a_0 = 9 \cdot 10$ Å, $c_0 = 6.93$ Å. However two lines cannot be accounted for by this procedure and indexing is less satisfactory than with $a_0 = 8.00$ Å, $c_0 = 7.87$ Å.

| TABLE | 3. |
|-------|----|
|-------|----|

| Х- | Rav | powder | diffraction | data | for | lower | thorium | iodides. |
|----|-----|--------|-------------|------|-----|-------|---------|----------|
|----|-----|--------|-------------|------|-----|-------|---------|----------|

| (a) | α -ThI ₂ (calculated for hexagonal unit cells). | | | | | | (b) | β-ThI | 2 (calc | ulated | (c) ThI_{3} | | | | |
|-------------|---|--------|-----------------|----------------|--------------------|----------------|------------------|----------|----------------|---------------------------|------------------------|---------------|-------------|-----------------|----------|
| | | | | | | | | | · | | | | | | |
| đ | T/T * | (obs) | (calc) | 461 | sin ₂ 0 | 1.1.1 | đ | 1/1 + | $sin_2 \theta$ | sin ₂ θ | 1.1.1 | | 11 | hl _a | |
| ~ | 1/10 | (005.) | (Calc.) | 2 00 | caic. | 0 10 | u | 1/101 | (005.) | (calc.) | <i>nKi</i> | d | 1/10 † | d | 1/10 † |
| | | | $a_0 = c$ | 5·00, 7·87. | $a_0 = c_0 =$ | 9·10, 6·93. | | | $a_0 =$ | $9.12, c_0 =$ | = 3.74. | | | | |
| 7.89 | 9 | 0.0095 | 0.0096 | 001 | 0.0096 | 100 | 7.92. | 9 | 0.0095 | 0.0095 | 100 | 8.02 | 7 | 1.772 | 2 |
| 7.13 | 2 | 0.0117 | 0.0124 | 100 | 0.0124 | 001 | 3.42 | 3 | 0.0506 | 0.0513 | 101 | 3.22- | 5 | 1.731 | 2 |
| 0.044 | - | 0.0501 | (0.0496 | 200 | (0.0496 | 002 | 3.02 | 4 | 0.0650 | 0.0665 | 210 | 3.09 | 8 | 1.696 | 2 |
| 0.3440 | 2 | 0.0201 | 10.0508 | 102 | 10.0508 | 201 | 2.884 | 7 | 0.0713 | 0.0703 | 111 | 3.01 | - - 4 | 1.669 | 3 |
| 3.14 | 3 | 0.0599 | 0.0592 | 201 | 0.0592 | 102 | 2.63. | 10 | 0.0852 | 0.0855 | 300 | 2.940 | 7 | 1.640 | 5 |
| 2·80 | 2 | 0.0757 | 0.0756 | 112 | | | 2.33 | 6 | 0.1092 | 0.1083 | 211 | $2 \cdot 825$ | 7 | 1.603 | 7 |
| 9.69 | 6 | 0.0864 | € 0.0864 | 003 | 0.0864 | 300 | $2 \cdot 24_{0}$ | 1 | 0.1182 | 0.1140 | 220 | 2.754 | 5 | 1.572 | 8 |
| 2.021 | 0 | 0.0004 | 1 0.0868 | 210 | | | 2.20 | 5 | 0.1216 | 0.1235 | 310 | 2.709 | 3 | 1.536 | 3 |
| 2.32_{0} | 1 | 0.1102 | 0.1116 | 300 | 0· 1 116 | 003 | 1.980 | 10 | 0.1513 | 0.1520 | 4 00 | $2 \cdot 674$ | 10 | 1.511 | 6 |
| 1.998 | 10 | 0.1487 | 0.1488 | 220 | 0.1200 | 302 | 1.716 | 2 | 0.2015 | 0.1995 | 410 | $2 \cdot 514$ | 3 | 1.406 | 3 |
| 1.966 | 6 | 0.1534 | 0.1536 | 004 | 0.1536 | 400 | 1.639 | 6 | 0.2208 | 10.9992 | 201 | $2 \cdot 486$ | 3 | 1.392 | 2 |
| 1.939 | 4 | 0.1579 | 0.1284 | 221 | | | 1.626 | 1 | 0.2245 | 50.2223 | 321 | $2 \cdot 454$ | 3 | 1.377 | 3 |
| 1.723 | 2 | 0.1998 | 0.1980 | 303 | ∫0•1980 | 303 | 1.588 | 4 | 0.2353 | € 0.2337 | 212 | 2.371 | 2 | 1.353 | 3 |
| 1 120 | ~ | 0 1000 | | 000 | 0.2016 | 410 | 1 000 | | 0 2000 | 0.2375 | 500 | $2 \cdot 251$ | 2 | 1.336 | 3 |
| 1.588 | 7 | 0.2353 | { 0.2352 | 223 | 0.2364 | 313 | 1.567 | 4 | 0.2416 | 0.2413 | 411 | $2 \cdot 186$ | 2 | 1.316 | 2 |
| | | | 0.2356 | 320 | | | 1.402 | 4 | 0.3019 | 0.2983 | 331 | $2 \cdot 162$ | 2 | 1.302 | 2 |
| 1.400 | 6 | 0.3027 | 10.3010 | 500 | € 0·3010 | 005 | 1.329 | 8 | 0.3329 | 0.3363 | 511 | 2.147 | 2 | 1.289 | 2 |
| | | | 0.3024 | 224 | 0.3032 | 314 | 1.303 | 1 | 0.3495 | 0.3477 | 322 | 2.006 | 9 | 1.268 | 2 |
| 1.304 | 2 | 0.3490 | 10.3472 | 420 | 0.34/2 | 512 | 1 000 | - | 0.0400 | (0.3515 | 430 | 1.984 | ž | 1.256 | 2 |
| 1.159 | 0 | 0.4469 | (0.3516 | 300 | (0.3516 | 203 | 1.145 | 1 | 0.3622 | 0.3667 | 412 | 1.836 | Ð | 1.042, | 2 |
| 1.199 | 2 | 0.4407 | 0.4404 | 600 | (0.4472 | 424 | 1.120 | | 0.4695 | 0.4617 | 011 | 1.804 | 2 | 0.801 | 4 |
| 1.124_{1} | 2 | 0.4695 | 0.4704 | 700 | 10.4729 | 400 | 1.104 | 0 | 0.49629 | 0.4009 | 303, 312 | 1.791 | 4 | 0.801 | 4 |
| 1.054 | 2 | 0.5228 | 0.5329 | 610 | 0.5226 | 441 | 0.084 | ê | 0.6197 | 0.4302 | 220 | | | | |
| 1.0045 | 5 | 0.0000 | 0.0332 | 010 | (0.5968 | 719 | 0.966 | 9 | 0.6355 | 0.6365 | 790 | | | | |
| 0.995 | 2 | 0.5989 | 0.6072 | 443 | 0.5980 | 541 | 0.925 | 2 | 0.6030 | 0.6935 | 810 | | | | |
| 0 0002 | 2 | 0 0000 | 0 3012 | 110 | 0.5986 | 515 | 0.900 | ĩ | 0.7315 | 0.7353 | 214 811 | | | | |
| | | | • | D1 4 | 1 1 1 - 1 | | | | | | | | | | |
| | * Photoelectric densitome | | | | | | | uremen | ts. | T Est | imated by | eye. | | | |
| | | | | | | | | | | | | | | | |

¹² D'Eye, Ferguson, and McIver, "Sixteenth Congress of the International Union or Pure and Applied Chemistry," Section on Inorganic Chemistry, Paris, 1957, p. 341.
 ¹³ D'Eye and Anderson, J., 1949, S244.

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Microscopically α -thorium di-iodide is not easy to categorise. Sometimes it appears as a dull black, poorly crystallised material with a faint bronze metallic sheen; at other times as small, black, lath-like particles which show a faint translucency and faint brownish-purple dichroism. These laths or needles, which are briskly decomposed by water with evolution of hydrogen gas, are to be distinguished from crystals of thorium oxyiodide which sometimes occur in small amount in samples into which traces of oxygen have been introduced from thorium or container materials. These are usually colourless and highly acicular in habit ¹³ but occasionally they may be coloured a pinkish-brown by some unidentified process. Non-reaction of thorium oxyiodide with thorium metal at 690° ruled out reduction of the oxyiodide as a source of this colour. However, the fact that thorium oxyiodide, whether coloured or not, dissolves in water without evolution of gas serves to distinguish it from α or β -thorium di-iodide and from thorium tri-iodide.

The existence of two phases with the properties described, explains most of the conflict in the early literature on the di-iodide region of the system thorium-iodine.

The Sub-system Thorium Di-iodide-Thorium Tri-iodide.—This section of the diagram is also simple. In addition to the $\alpha-\beta$ transition of thorium di-iodide and the peritectic reaction at 864°, there now appears the phase reaction:

$$2\text{ThI}_3(\text{solid}) \longrightarrow \beta - \text{ThI}_2(\text{solid}) + \text{ThI}_4(\text{liquid})$$

marked by a peritectic line at 746°. This line extends from I/Th = 2.0 to 3.25. The heat of the reaction at 746° appears to be somewhat less than the heat of the reaction at 864°. However complete release or absorption of heat may not occur at or near 746° because of incomplete reaction during thermal analysis. The D.T.A. peak for this peritectic reaction is in consequence often delayed and the signal prolonged. Microscopic examination of a sample consisting substantially of tri-iodide (I/Th = 3.20), after heating to 800° for 10 minutes before quenching, therefore revealed a considerable residue of unchanged tri-iodide as well as abundant β -thorium di-iodide and cryptocrystalline tetraiodide. X-Ray examination confirmed the presence of both lower iodide phases although the tetraiodide was apparently too poorly crystallised to give an X-ray pattern.

Thorium tri-iodide prepared by reaction of thorium metal and thorium tetraiodide at 700° (sol. Th, $36 \cdot 9_0$; sol. I, $62 \cdot 2_7 \%$; I/Th (sol) $3 \cdot 09$; free Th $0 \cdot 83 \%$) gives a distinct X-ray diffraction pattern (Table 3c) which has not yet been indexed. Optical and X-ray results suggest orthorhombic or lower symmetry. The compound is not isomorphous with uranium tri-iodide. The most characteristic optical property (Table 2) is the marked dichroism shown by small fragments or by thin edges of larger fragments in strong polarised light. Marked metallic characteristics are thus not exhibited. No evidence for other crystallographic forms of tri-iodide was obtained by D.T.A., X-ray, or microscopic examination.

The Sub-system Thorium Tri-iodide-Thorium Tetraiodide.—Principal feature of this region is a steeply rising liquidus curve with peritectic points at 864° , I/Th $3\cdot1$ — $3\cdot2$ and 746°, I/Th $3\cdot2$ — $3\cdot3$, respectively. The eutectic line between the tri- and tetra-iodide is placed at 554° and the eutectic point at I/Th $3\cdot8$ — $3\cdot9$.

The region between compositions I/Th 3·2 and 3·5 is very difficult to investigate experimentally, partly because of the poorness of the X-ray diffraction patterns, and partly because of the influence of oxyiodide impurity which finds its way into some samples despite all efforts to exclude it. Even small quantities of oxyiodide may be responsible for the small but easily detectable thermal effects at 650—660° (see Fig. 2). These effects could also be ascribed to a peritectically melting compound at I/Th 3·3 (see Fig. 2). Clark and Corbett ² mention such a compound at "I/Th $\leq 3\cdot4$." However it is pointed out that it is not necessary to postulate existence of a compound in this region. The appearance of D.T.A. peaks at 650—660° can also be ascribed to thermal halts in the ternary system: Thorium di-iodide-thorium tetraiodide. At this temperature it is suggested that eutectic lines of the ternary system may meet the peritectic line which

occurs at 746° in the binary system thorium di-iodide-thorium tetraiodide to give a ternary eutectic point and the thermal effect observed. Only a few moles per cent. of oxyiodide need be involved, and its presence would be difficult to detect by current analytical methods. Thorium oxyiodide is known not to undergo thermal reactions when heated to 900° in a closed system.¹⁴

Since no X-ray or microscopic results have been obtained to support the existence of an intermediate compound the balance of evidence therefore suggests that the oxyiodide may be responsible for the thermal effects at $650-660^{\circ}$.

No evidence has been found for terminal solid solution in this sub-system.

Further Observations on Lower Thorium Iodides.—Both α - and β -thorium di-iodides as well as thorium tri-iodide are vigorously decomposed by water with the evolution of hydrogen gas. Coloured solutions or solid residues are not formed, discounting suggestions in the early literature that disproportionation to metallic thorium can occur. Rapid hydrolysis also occurs in moist air.

Clark and Corbett² found that "thorium di-iodide" (actually the β-di-iodide) when heated in a vacuum begins to lose thorium tetraiodide by sublimation at $550-600^{\circ}$, disproportionation to metallic thorium being complete at 800°. We confirm this observation and extend it to both α - and β -di-iodides. The only vapour pressure data for iodides of thorium are those of Fischer, Gewehr, and Wingchen,¹⁵ which indicate that the pressure of thorium tetraiodide in contact with liquid tetraiodide reaches one atmosphere at 837°. However preliminary data due to Josim¹⁶ suggest that at 527° the vapour pressure of tetraiodide over "thorium tri-iodide" is approximately 0.1 mm., and over a phase described as "ThI_{1.8}" is approximately 0.003 mm. While these observations are not in serious conflict with the data presented here, it is clear that formidable difficulties face the experimenter in establishing a complete vapour pressure description of the system thoriumiodine. No reference was made by Josim to the volatility of thorium tri-iodide, which, although small, is believed to be the cause of rapid overall corrosion of glass and other containers.

Preliminary consideration has been given to the structures of the lower iodides. Clark and Corbett ² maintain that thorium "di-iodide" does not contain the ion Th²⁺, but exist as $Th^{4+}(I^{-})_{2}(e^{-})_{2}$. While the first assumption seems to be possible, the formulation of the " di-iodide " cannot be regarded as firmly established, particularly in view of the existence of a second crystallographic form of di-iodide which may have a different electronic structure. The electronic structure of thorium tri-iodide is also in doubt. If it is a compound of tervalent thorium it should be an insulator with a paramagnetic susceptibility which may, however, be very small. It is not clear whether the observations of Clark and Corbett² as to high resistance and qualitative diamagnetism, apply to thorium tri-iodide or to a mixed phase with $I/Th \leq 3.4$. In either case the evidence is not against the presence of tervalent thorium. Spectroscopic examination of thorium tri-iodide by transmission and reflectance methods has not given useful results, but the colours in transmission under the microscope are not inconsistent with the presence of the ion Th^{3+} . Further X-ray, magnetic, spectroscopic, and other work is in progress to determine whether thorium tri-iodide does indeed contain such an ion or whether it should be formulated as a mixed valency compound or a semiconductor with metal to metal bonding.

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¹⁴ Scaife, Turnbull, and Wylie, J., in the press.
 ¹⁵ Fischer, Gewehr, and Wingchen, Z. anorg. Chem., 1939, 242, 161.

¹⁶ Josim, U.S.A.E.C. Report NAA-SR-5350, 1960, Part VII, p. 35.