683. *Some Aspects of the System Uranium Trioxide–Water.*

By J. K. DAWSON, E. WAIT, K. ALCOCK, and D. R. CHILTON.

Uranium trioxide in contact with water at about 180° gives an ortho-rhombic hydrate, $UO_3,0.8H_2O$, with the cell dimensions $a = 10.23 \pm 0.01$, $b = 6.89 \pm 0.01$, $c = 4.28 \pm 0.01$ Å. These dimensions appear to vary slightly with deviation of the water content from 0.8 mole per uranium atom. Between 200° and 280° another phase appears, $UO_3,1.0H_2O$, also orthorhombic with cell dimensions $a = 5.638 \pm 0.005$, $b = 6.273 \pm 0.005$, $c = 9.925 \pm 0.005$ Å, space-group *Pbca*. The hemihydrate, $UO_3,0.5H_2O$, is stable in water above 280°. A further phase, possibly due to a relatively high pH and probably triclinic, was observed when the uranium trioxide was heated in water at 230° in contact with glass.

Some of the properties of these hydrates are described, together with observations on the preparation of pure anhydrous uranium trioxide from uranyl nitrate.

PREVIOUS investigations on the hydrated oxides of uranium indicated that the trioxide is stable in water, up to high temperatures, and that over the range 70—300° (approx.) it forms a monohydrate.[1] The system is quite complex, however, and Katz and Rabinowitz quoted the following four crystalline modifications observed by D. T. Vier : (i) α-UO_3,H_2O, large six-sided orthorhombic basal tablets; (ii) β-UO_3,H_2O, small orthorhombic prismatic tablets with slightly larger unit cell than the α-form; (iii) γ-UO_3,H_2O, six-sided columnar crystals, with X-ray diffraction pattern similar to that of the α- and the β-form, but perhaps belonging to a different system : contains <0.9 mole of H_2O per uranium atom; (iv) δ-UO_3,H_2O, triclinic, giving a complex X-ray diffraction pattern. The last form may be due to impurities.

Very few details were given of the preparation and the relations between these various forms, and the present investigation was undertaken to obtain more extensive information in the range 180—320°. The particular form of UO_3,H_2O obtained may be sensitive to the presence of traces of impurities, such as the soluble uranyl ion, and so some observations are made also on the preparation of uranium trioxide free from all contaminants down to a level of a few parts per million.

EXPERIMENTAL

The thermogravimetric curves were obtained by use of a quartz helix balance. A sample (about 100 mg.) was suspended in a platinum boat on the end of a 35-cm. extension fibre from the lower end of the helix. The temperature of the sample was raised linearly at about 2°/min.

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[1] " The Chemistry of Uranium, Part I," National Nuclear Energy Series, VIII—5, edited by Katz and Rabinowitz, McGraw-Hill Book Co., New York, 1951, pp. 281—283.

by feeding a furnace surrounding the platinum boat from a variable transformer which had a spindle turned by a motor-actuated cam.[2] Weight changes caused the vertical movement of an index fibre at the lower end of the helix and this was measured by a cathetometer; the sensitivity of the system was 0·85 mm./mg. The helix was surrounded by a glass tube which was connected by a ground joint to a quartz tube surrounding the platinum boat, and the system was evacuated to 0·1 mm. for a short time before each experiment in order to ensure the absence of moisture on the helix.

Preliminary experiments showed that all forms of hydrated uranium trioxide were converted into U_3O_8 at about 700° after 1 hr. in air. This was used as the basis for the determinations of water content, any change in weight between the sample and U_3O_8, after allowance for the decrease of oxygen content $UO_3 \longrightarrow UO_{2·67}$, being attributed to loss of water. Before analysis, samples of hydrate were normally dried on a sintered-glass disc at room temperature in a current of air for 5 hr. The validity of the method was checked by separate experiments. For instance, 1·457 g. of orthorhombic II hydrate were heated in a nitrogen stream to 450° for 90 min. and the nitrogen was subsequently passed through a weighed tube containing magnesium perchlorate. The increase in weight of the latter was 0·086 g.; and the water content corresponds to $UO_3,1·00H_2O$. The loss of weight of the uranium trioxide agreed within experimental error with the gain of the magnesium perchlorate.

A similar experiment with a sample consisting almost entirely of orthorhombic I hydrate showed that 0·993 g. lost 50·1 mg. of water, corresponding to a formula of $UO_3,0·85H_2O$. The thermogravimetric curves of both hydrates also supported these figures.

At the beginning of this investigation no steel autoclaves were available and so attempts were made to bring about the reaction of uranium trioxide with high-temperature water in glass tubes of 2 mm. wall thickness and about 15 ml. capacity. In order to prevent contamination of the product with silica, some of the experiments were performed with the uranium trioxide contained in a platinum tube inside the glass tube. Tubes (20 mm. diam.) would usually withstand the steam pressures at these temperatures provided that care was taken to ensure a symmetrical seal. The tubes were heated in a furnace fitted with a metal safety screen, and in the first experiments the slurries were agitated by continuously rotating the tubes end-over-end; later experiments were performed without agitation in order to grow more perfect crystals.

Subsequently the slurries were heated in stainless-steel autoclaves which could be agitated by rocking if desired. Usually 2 g. of uranium trioxide were heated with 80 ml. of water, but occasionally the scale was increased to 50 g. of oxide.

The product of each experiment was examined visually under a projection microscope at × 1000 magnification. X-Ray diffraction photographs were obtained on the powders by use of a Guinier-type focusing camera with negligible background.[3] Cu-$K\alpha$ radiation was used in all cases; wavelengths were taken as $K\alpha_1 = 1·54051$ Å and $K\alpha_2 = 1·54433$ Å. Samples were approximately five microns thick. In cases where suitable crystals were available, single-crystal Weissenberg methods were also used to supplement the powder data. A micromanipulator technique was necessary for mounting the very small crystals and this will be described elsewhere.
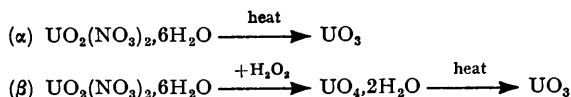
RESULTS and DISCUSSION

The following five crystallographically distinct hydrate phases were obtained during the course of this investigation and they are described here in order to aid the discussion of results : (i) $UO_3,2H_2O$, obtained only as very small particles, by reaction of anhydrous UO_3 with water at room temperature. (ii) $UO_3,0·8H_2O$, orthorhombic I, thin yellow rods about 10 μ long and showing straight extinction between crossed polaroids. When these were heated in air, there was a slight loss of weight up to 250°, but most of the water was not eliminated below ~300° (see Fig. 1). This phase is probably the same as Vier's γ-UO_3,H_2O (p. 3531). (iii) $UO_3,1·0H_2O$, orthorhombic II, crystallised as orthorhombic tablets, sometimes up to 150 μ long, with symmetrical extinction between crossed polaroids. It was almost colourless under the microscope. Thermogravimetric curves showed that this hydrate had remarkable stability in air, there being no loss of weight up to at least 360°. Rapid dehydration occurred at 400°. (iv) $UO_3,?H_2O$, monoclinic, or triclinic. This phase (III) was obtained in the presence of " Pyrex " glass at 230° and was observed

[2] Ball and Adams, *J. Sci. Instr.*, 1951, **28**, 47.
[3] D'Eye. A.E.R.E. C/R—1524.

in the form of stubby triclinic prisms, about 10 µ long. Sometimes it was observed also as large flat intensely yellow plates.* (v) $UO_3,0\cdot5H_2O$, monoclinic, usually twinned, as short oblique-ended laths.

(a) *The Conversion of Hydrated Uranyl Nitrate into Uranium Trioxide.*—There are several routes by which trioxide may be obtained from the readily available nitrate; the two most promising appeared to be :

$$(\alpha) \quad UO_2(NO_3)_2,6H_2O \xrightarrow{\text{heat}} UO_3$$

$$(\beta) \quad UO_2(NO_3)_2,6H_2O \xrightarrow{+H_2O_2} UO_4,2H_2O \xrightarrow{\text{heat}} UO_3$$

The decomposition of thermally unstable organic uranyl compounds was not favoured owing to the possibility of obtaining lower oxides.[4] Thermal decomposition curves for uranyl nitrate hexahydrate are shown in Fig. 2 for ignition in air and *in vacuo*. There
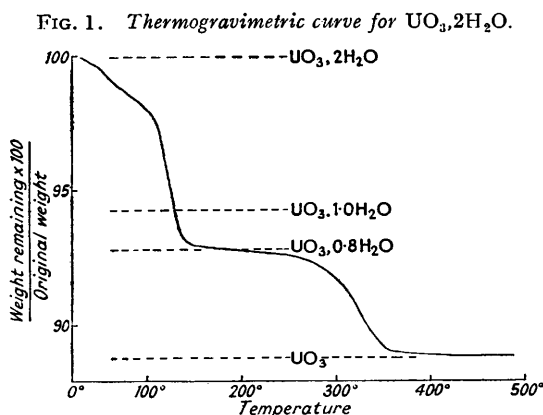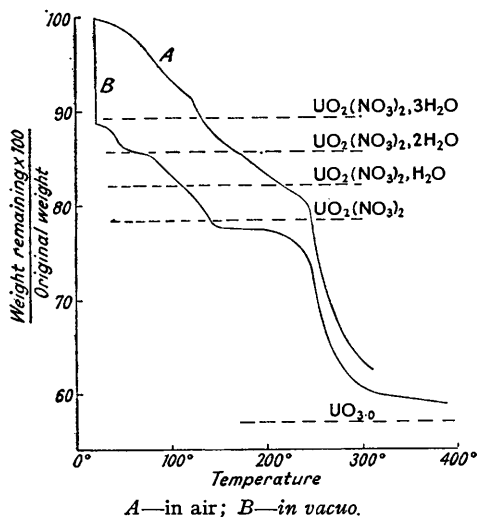

FIG. 1. *Thermogravimetric curve for $UO_3,2H_2O$.*

FIG. 2. *Thermogravimetric curves for uranyl nitrate hexahydrate.*

A—in air; B—in vacuo.

was only a slight difference in decomposition temperature by the two methods. The formation of pure uranium trioxide by this method is complicated, as the decomposition temperature of the nitrate is close to the stability limit in air of the oxide. Suitable temperatures quoted by earlier workers [5] have varied between 250° and 500°. Our results indicate that the temperature should be greater than 300°. According to an isobar for 10 mm. pressure of oxygen,[6] uranium trioxide begins to lose oxygen when heated above 430°. Consequently, the optimum temperature for the production of the trioxide by nitrate decomposition is about 400°. However, when this was performed in a tube furnace with a slow current of air passing over the sample, it was found that the residual nitrogen content of the oxide after 1 hour's heating was in the range 450—700 p.p.m. (*i.e.*, up to 0·28% expressed as nitrate ion) and that further heating was not effective in removing this. The amount of residual nitrogen could be reduced by recycling the material through

* *Added July 30th,* 1956.—Investigations performed on other systems since the submission of this paper indicate that the "phase III hydrate" is probably a uranyl silicate, $(UO_2)_2SiO_4,3H_2O$ or $(UO_2)_3Si_2O_7,2H_2O$. The same substance has been prepared by the action of uranyl sulphate solution at 300° on fused silica vessels (Davidge, Lock, and Wait, unpublished work) and from the reaction between uranyl fluoride solution and silica (Marshall and Secoy, personal communication). In the experiments reported above, it was presumably formed by reaction of the residual soluble uranium content of the oxides with the walls of the glass capsules.

[4] " The Chemistry of Uranium," p. 317.
[5] *Ibid.*, pp. 319, 320.
[6] Biltz and Muller, *Z. anorg. Chem.*, 1927, **163**, 295.

the structural changes $UO_3,2H_2O \rightleftharpoons UO_3$ by alternate washing with water and heating at 400°. Orange-yellow uranium trioxide prepared by decomposition of uranyl nitrate or peroxide reacts rapidly with water at room temperature, producing the dihydrate with evolution of considerable heat. However, the dihydrated and the monohydrated trioxide decompose to give a red anhydrous oxide which is less reactive towards water; for reconversion into the dihydrate this requires either to be left much longer in contact with water at room temperature or to be hydrated at a rather higher temperature.

The decomposition temperature of the hydrated trioxide was considered to be 400° since this is above the stability limit of either the orthorhombic I or the orthorhombic II monohydrate phase, as determined by thermogravimetric curves, and yet below the reported stability limit of the anhydrous oxide. Fig. 1 shows the thermogravimetric curve for $UO_3,2H_2O$ which decomposes at about 140° to the orthorhombic I form, $UO_3,0.8H_2O$, which in turn decomposes to uranium trioxide above about 360°.

An alternative method of reducing the nitrate content of the oxide involves the crystal-structure changes orthorhombic I, $UO_3,0.8H_2O \rightleftharpoons$ anhydrous UO_3. The anhydrous oxide as prepared by direct decomposition of the nitrate is readily converted into $UO_3,0.8H_2O$ in a current of steam at 120°. If the temperature is raised to 420° and passage of steam continued, the hydrate is decomposed to the original anhydrous phase and some of the nitrate is removed in the steam. In one such experiment carried over five cycles, between 120° and 420°, the sample being held at the limiting temperatures for 30 min. at

FIG. 3. *Thermogravimetric curve for* $UO_4,2H_2O$.
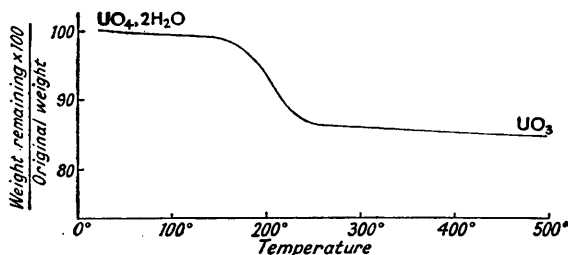
each stage, the nitrogen content was reduced from a starting value of 600 to 5 p.p.m. A disadvantage of this process was the sintering of the sample in the later stages.

(b) *Conversion of Uranium Peroxide into Uranium Trioxide.*—The preparation of pure uranium trioxide from the nitrate *via* the peroxide was also a long process. The uranium peroxide was precipitated from dilute aqueous uranyl nitrate solution by addition of dilute hydrogen peroxide; it was then centrifuged and required many washings in order to free the supernatant liquid from nitrate ion (" nitron " reagent). However, this process gave after ignition of the precipitate an anhydrous trioxide with a nitrogen content of about 30 p.p.m. After being dried overnight at 100° in air, the precipitate had the composition $UO_4,2.0H_2O$ according to the weight change observed on igniting a sample in air to U_3O_8.

Previous results [7] on the thermal decomposition of hydrated uranium peroxide are not very consistent. A thermogravimetric curve obtained with $UO_4,2.0H_2O$ is shown in Fig. 3. There were no plateaux between the starting material and UO_3 and it appeared that loss of oxygen and water occurred simultaneously, in agreement with Kraus's results.[8] Uranium trioxide for the hydrations was produced at about 375° (tube furnace) in a slow current of air during 1 hr.

(c) *The System* UO_3–H_2O.—The results of heating uranium trioxide with water are given in Table 1 for oxide obtained by direct thermal decomposition of the nitrate, and in Table 2 for oxide obtained by decomposition of peroxide. One of the difficulties attending this investigation was the apparent complexity of the UO_3–oxygen system, so that allowance had to be made for use as starting material of various types of uranium trioxide. A brief

[7] Summarised in " The Chemistry of Uranium," pp. 290—292.
[8] Kraus, reported in " The Chemistry of Uranium," p. 290.

TABLE 1. *Results of heating nitrate-derived UO_3 with water.*

Starting material	No.	Temp. (°)	Time (hr.)	Container	Agitation	Soluble uranium (p.p.m.)	Soluble "N" (p.p.m.)	Soluble "N" in solid product (p.p.m.)	pH	H_2O (mole per U atom)	Colour	X-Ray Major	X-Ray Minor	Optical Major	Optical Minor	Large yellow plates
UO_3 from nitrate	1	180	24	Glass	+	1836	152		4·1	0·99	Pale yellow	II + III		II + III		
	2	200	"	"	++	53	150		5·6	0·98	Yellow	II + III		II + III		+
	3	230	"	"	—	36	190		5·8	0·91	"	I	II	II + III	(I)	
	4	180	"	Steel	—	148	14		4·5	0·89	"			Very small		
	5	180	48	"	—	<10	2	<5	6·4	1·00	Pale yellow			II		
	6	230	24	"	—	34	4	<5	5·3	1·00	Pale green			II		
	7	180	"	Glass	—	9790	195		4·1	0·98	Yellow			II		
	8	180	"	"	—	3717	109		4·4	0·99	Pale yellow			II		
	9	230	"	Steel	—	350	64	8	4·9	1·00	"			III	III	
	10	230	168	"	—	1300	69	<5	4·3	1·01	Bright yellow			II		
	11	230	"	"	+	340	30	<5	4·3	0·99	Yellow			II		
UO_3 (II) from UO_3,H_2O	12	180	24	Glass	++	109	415	<5	7·1	0·99	Pale yellow			III		+
	13	230	"	Steel	—	85	32	<5	6·9	0·86	",, green			III	(I)	
	14	180	"	"	—	13	3		6·1	1·01	",, green			II		
	15	280	"	"	—	20	1		6·0	1·02	Mustard	II		II		
	16	320	"	"	—	14	<1			0·50	",,	$UO_3,0.5H_2O$	$UO_3,0.5H_2O$	$UO_3,0.5H_2O$		
UO_3 (I) from nitrate, but recycled through $UO_3,2H_2O$	17	180	70	Glass	—	21	5		7·3	0·93	Yellow			I + II	I, III	
	18	180	24	"	—	<30	15	32	6·9	0·89	Yellow-green	II	III	II + III	III	+++
	19	230	"	Pt	—	240	5	<5		0·97	Yellow	II	III	II + III	III	
	20	230	"	Glass	—	160	6		7·0	0·92	Pale green	II		II + III	I (20)	
	21	230	"	Pt	—	7	<5			0·93	Green	II	I	II (80)	I (20)	
	22	230	70	"	—	<10	<5	32		0·95	Pale green	II	I	II + III	I	
	23	230	"	"	—	<10	5	30	6·1	0·92		II	I	II (80)	I	
	24	230	0·5	"	—			32		0·91	Yellow-green			II	I (20)	
	25	230	5	"	—			32		0·88	Green			II	I	
	26	290	30	Steel	—										$UO_3,0.5H_2O$	

Notes on Tables 1 and 2.

1. The experiments have been arranged in groups with the same starting material and not in chronological order.

2. Experiments in which agitation is indicated were performed by rotating the glass tubes end-over-end at about 1 rev./sec. and by rocking the steel autoclaves above and below horizontal at 0·5 cycle/sec.

3. In uranium trioxide obtained directly from uranyl nitrate ignition, the soluble uranium content could be varied by washing with water at room temperature before heating.

4. The following abbreviations are used to describe the product: I = orthorhombic I hydrate, $UO_3,0.8H_2O$; II = orthorhombic II hydrate, $UO_3,1.0H_2O$; III = phase III.

When two components are in approximately equal amount, this is indicated by a + sign between them. Parentheses round a minor phase indicate that this was present in trace amount only; figures in parentheses are number percentages obtained by counting under the microscope.

TABLE 2. *Results of heating peroxide-derived* UO_3 *with water.*

	Starting material	Temp.	Time (hr.)	Container	Agitation	Soluble uranium (p.p.m.)	Soluble "N" (p.p.m.)	"N"(p.p.m.) in solid product	pH
27		180	24	Glass	+		6	17	7·4
28		180	,,	,,	—	150			6·3
29		180	,,	Steel	—	30	<1	<5	6·0
30	UO₃ (I) from peroxide	180	88	,,	—	14			6·7
31		180	24	,,	—	<10		<5	5·2
32		230	,,	Glass	—	<10	38		7·0
33		230	,,	Steel	—	<10	<5		6·7
34		230	240	,,	—	<10	<5	18	7·0
35	UO₃ from	180	12	,,	—	<10	<2		6·2
36	peroxide	180	24	Glass	—		<5		6·8
37	recycled	180	,,	,,	—	25	154		5·9
38	through	230	,,	,,	—	<10	<5		6·7
39	UO₃,2H₂O	230	,,	Steel	—	17	1		6·5
40		180	,,	Glass	—				6·7
41		180	,,	Steel	—	17	<1	<5	6·6
42		230	,,	Glass	—		<5		6·7
43	Red UO₃ (I)	230	,,	Steel	—	13	3		6·6
44	from	230	,,	Glass	—		130	6	7·7
45	UO₃,0·8H₂O	230	,,	Steel	—	468	26		4·7
46		230	,,	,,	—	<10	1	<5	7·0
47		230	,,	,,	—	21	5	<5	5·2
48		230	,,	,,	—	2	<10		5·7

	H₂O (mole per U atom)	Colour	Product X-Ray Major	X-Ray Minor	Optical Major	Optical Minor	Large yellow plates	Remarks
27	0·83	Yellow	I	III	I		+	
28		,,			I + II			
29	0·90	,,	I	II	I	II		
30	0·99	Green	II	I	II	I		
31	0·98	Yellow-green			II	(I)		
32	0·84	Bright yellow			III	II	+	
33	0·98	Pale green	II		II			
34	0·98	Green	II		II		+	
35	0·92	Yellow-green			I	II		
36	0·87	Yellow			I	(II)		
37		Bright yellow			I	II		Added NaNO₃
38	0·86	Yellow			III	II (I)	+	
39	0·90	Green-yellow			II (86)	I (14)		
40	0·97	Pale yellow			II	I		
41	0·95	Yellow-green			II (66)	I (34)		
42	0·91	Yellow			II + III		+	
43	0·99	Pale green			II (88)	I (12)		
44					III	II	+	
45		Yellow-green			II			Added NaNO₃
46		Pale green			II			,, sodium silicate
47		,,			II			,, silica
48		,,			II			,, boric acid

description of the anhydrous oxide phases is given in the X-ray crystallographic section (p. 3540), but for clarity their derivation is shown here :

UO_3 obtained by thermal decomposition of uranyl nitrate, of $UO_3,2H_2O$, and of $UO_3,0·8H_2O$, is crystallographically the same and is designated UO_3, phase (I). According to which of the three source materials is used, however, the oxide may differ in such properties as residual soluble uranyl ion.

UO_3 produced from $UO_3,1·0H_2O$ (orthorhombic II) by thermal degradation usually shows an oxygen deficiency and has a cubic structure. It is termed UO_3, phase (II), and is brown or red as compared with the yellow-orange of UO_3 (I).

The results are discussed below in terms of the temperature of reaction between the uranium trioxide and water. In cases where relative amounts of the hydrate phases are

given for any one product, these amounts were obtained by visual analysis under the microscope and the figures quoted in col. 14 of Tables 1 and 2 are number percentages.

(i) *Reaction at* 180°. Uranium trioxide obtained by decomposition of nitrate and heated with water in glass or in steel for up to 48 hr. gave orthorhombic II phase as the major product, the soluble uranium content varying over the range 148—9790 p.p.m. (runs 1, 7, 8, 4, and 5).

However, the trioxide prepared by decomposition of peroxide gave the hydrate orthorhombic I phase, or a mixture of this with orthorhombic II, when heated with water for 24 hr. in glass (runs 27 and 28). In steel, for the same time, the major phase obtained was orthorhombic I, but that obtained after 88 hr. was orthorhombic II (runs 29 and 30).

A sample of uranium trioxide from decomposition of peroxide was washed with water at room temperature in an attempt to remove any remaining traces of soluble uranyl ion. This lead to formation of $UO_3,2H_2O$, which was dehydrated at 400°. Heating the oxide obtained (phase I) with water in glass for 24 hr. or in steel for 12 hr. produced orthorhombic I hydrate as the major phase. This uranium trioxide was evidently quite similar to the original material obtained direct from peroxide.

Anhydrous oxide (phase II), obtained by thermal decomposition of orthorhombic II hydrate, when heated with water in glass at 180° for 24 hr., produced only orthorhombic II hydrate in the presence of a soluble uranium content of 109 p.p.m. and 1840 p.p.m. of nitrate in solution (run 12), but with a soluble uranium content of 21 p.p.m. and 22 p.p.m. of nitrate the product consisted of orthorhombic I and II hydrates in about equal amounts (run 17). Reaction of trioxide (II) with steam at 120° also gave pure orthorhombic II hydrate.

It appears that at 180° orthorhombic I hydrate is unstable relative to orthorhombic II hydrate, some evidence having been obtained for its conversion into the latter (*a*) on lowering the pH for heating any particular kind of trioxide with water (runs 29, 31, 28, 27, 36, 35), (*b*) on prolonged heating with water (runs 17, 18), (*c*) by decomposing the orthorhombic I hydrate thermally and attempting its re-formation in water at 180° (runs 40, 41), and (*d*) on heating in water above 200° (see below). Both orthorhombic hydrate phases were stable in air at room temperature.

(ii) *Reaction at* 230°. Uranium trioxide formed by thermal decomposition of either the nitrate or the peroxide produced orthorhombic II hydrate when heated with water at 230° in steel for 1—10 days and in the presence of soluble uranium ($<$10—350 p.p.m.) (runs 6, 9, 10, 11, 33, 34). In one run (no. 22), thermally decomposed orthorhombic II hydrate, when again heated for 24 hr. with water in platinum, yielded mainly orthorhombic II hydrate with about 20% of orthorhombic I hydrate. Other experiments with the same type of oxide in platinum inserts in the glass tubes gave some evidence that the orthorhombic I hydrate may be formed first but is converted into orthorhombic II hydrate or into phase III on prolonged heating (runs 24, 25, 22, 20, 23). The orthorhombic II hydrate from experiments in which the uranium trioxide was heated with water in glass at this temperature, was usually mixed with varying amounts of phase III which made the product bright yellow (runs 3, 13, 19, 32).

Phase III was not obtained pure and so evidence on its composition is rather scanty; there seem to be some indications that the water content is $<$0·9 mole per uranium atom (*e.g.*, run 1). In attempts to determine the cause of its formation, samples of trioxide were heated with water in steel, with the addition of 2% of sodium nitrate, sodium silicate, silica, or boric acid, but in each case the product consisted of only orthorhombic II hydrate (runs 45, 46, 47, 48). A similar addition of sodium nitrate did not produce any phase III at 180° (run 37), although in three cases (runs 1, 8, and 27) this phase was observed from experiments in glass tubes at this temperature. Perhaps the high content of soluble uranyl ion caused these conversions. There is some evidence that a relatively high pH may cause the conversion into phase III at 230°; *e.g.*, thermally decomposed orthorhombic I hydrate [UO_3 (I)] heated in glass for 24 hr. gave a higher proportion of phase III at pH 7·7 than at 6·7 (runs 42 and 44). Uranium trioxide (I), obtained by thermal decomposition of $UO_3,2H_2O$ which in turn was obtained by hydrating the anhydrous oxide produced from peroxide, when heated in water for 24 hr. at 230° also gave a product consisting mainly of

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orthorhombic II hydrate when the experiment was performed in steel, but phase III in glass (runs 39 and 38).

In some of the experiments, a different form of uranium trioxide hydrate appeared to be formed as a minor constituent. This formed very large, flat, yellow plates and was observed most often in runs which had been performed at 230° and at relatively high pH (see col. 14 of Tables 1 and 2). In all cases except one it was associated with the appearance of phase III hydrate, and the fact that it is another growth habit of this phase was later proved by single-crystal X-ray diffraction photographs.

(iii) *Reaction above* 230°. Uranium trioxide (II) was heated with water in steel for 24 hr. at 280° and produced pure orthorhombic II hydrate, but at 320° a new phase appeared (runs 15 and 16). This formed pale yellow, oblique-ended laths and its composition as shown by analysis was $UO_3,0.5H_2O$. Uranium trioxide (I), from ignition of nitrate heated with water at 290°, gave mainly orthorhombic II hydrate with 9% of hemihydrate (run 26). Evidently the orthorhombic II hydrate is unstable with respect to the hemihydrate in water above 280°; there is no evidence, however, that either $UO_3,0.8H_2O$ or $UO_3,0.5H_2O$ occurs as intermediate in the thermal degradation in air of the monohydrate. These results are in general agreement with those of American workers; Katz and Rabinowitz [9] give results which indicate that the hemihydrate is stable in water above 325° and is slowly converted into the monohydrate below 300°.

X-Ray crystallographic data.

$UO_3,2H_2O$. Identical Guinier powder photographs were obtained from dihydrate specimens prepared by the action of water at room temperature on UO_3 (I) obtained by decomposition of either nitrate or peroxide, and by vapour-phase hydration at room temperature of UO_3 (I) of very small particle size.

The visually estimated intensities of the diffraction lines and the measured $\sin^2 \theta$ values are given in Table 3. The existence of a number of summation relations involving pairs of $\sin^2 \theta$ values makes it probable that the symmetry is monoclinic or higher, and the absence of any appreciable number of summation relations of triplets of independent $\sin^2 \theta$ values together with the presence of large numbers of very weak reflections also indicates a monoclinic structure. It has not proved possible to index the reflections unambiguously.

$UO_3,0.8H_2O$. Hydrate specimens of composition near to $UO_3,0.8H_2O$, referred to as orthorhombic I phase, were obtained from liquid-water reactions described above and by hydration of UO_3 (I) in steam at 120°. Guinier diffraction photographs of the various specimens showed that the diffraction patterns were basically the same. Small differences in the positions of certain lines of the pattern between one specimen and another were attributed to a variation of cell constant with water content. This effect is being investigated further and will be reported later.

The powder photograph was indexed on the basis of an orthorhombic unit cell: $a = 10.23 \pm 0.01$, $b = 6.89 \pm 0.01$, $c = 4.28 \pm 0.01$ Å. The unit cell has a volume of 301.7 Å³ and contains four formula units of the ideal composition $UO_3,1.0H_2O$. The calculated and observed values of $\sin^2 \theta$ are given in Table 4 together with the reflection indices. All reflections observed have $(h + k)$, $(k + l)$, and $(h + l)$ equal to $2n$, which indicates a face-centred space-group.

The uranium atoms lie in four-fold special positions, $(000)(\frac{1}{2}\frac{1}{2}0)(\frac{1}{2}0\frac{1}{2})(0\frac{1}{2}\frac{1}{2})$. The cell dimensions for this phase are close to those given by Zachariasen [10] for a "UO_3,H_2O" of prismatic tablet form.

$UO_3,1.0H_2O$. Specimens of composition $UO_3,1.0H_2O$, orthorhombic II phase, were obtained by the reaction of liquid water with uranium trioxide under a variety of conditions in the temperature range 200—280°. The samples were examined by powder and single-crystal X-ray diffraction methods; the crystal system was orthorhombic and the cell dimensions as deduced from measurements of the Guinier photographs were : $a = 5.638 \pm 0.005$, $b = 6.273 \pm 0.005$, $c = 9.925 \pm 0.005$ Å. The volume of the unit cell was

[9] Katz and Rabinowitz, *ibid.*, p. 289.
[10] Zachariasen, reported in " The Chemistry of Uranium," p. 285.

TABLE 3. *Diffraction data on* $UO_3,2H_2O$.

I	$\sin^2 \theta_{obs.}$	I	$\sin^2 \theta_{obs.}$	I	$\sin^2 \theta_{obs.}$	I	$\sin^2 \theta_{obs.}$	I	$\sin^2 \theta_{obs.}$	I	$\sin^2 \theta_{obs.}$
vvw	0·0065	vvw	0·0233	vvw	0·0535	w	0·0794	vvw	0·1194	w } Diff.	0·1457
vvw	0·0079	vvw	0·0251	s	0·0571	vvw	0·0856	vw	0·1227	w }	0·1475
s	0·0110	vvw	0·0299	ms	0·0591	vw	0·0888	w+	0·1280	m+	0·1545
vvw	0·0141	mw	0·0440	vvw	0·0681	m	0·0903	w+	0·1365	vvw	0·1612
vvw	0·0154	s	0·0462	vvw	0·0690	mw	0·0926	w+	0·1391	vvw	0·1653
vvw	0·0158	ms	0·0485	vw	0·0710	w	0·1115	m–	0·1435	vvw	0·1688
vvw	0·0172	vw	0·0491	vw	0·0737	vvw	0·1153			vw	0·1762

TABLE 4. *Diffraction data on* $UO_3,0·8H_2O$.

Index	$\sin^2 \theta_{calc.}$	$\sin^2 \theta_{obs.}$	$I_{obs.}$	Index	$\sin^2 \theta_{calc.}$	$\sin^2 \theta_{obs.}$	$I_{obs.}$	Index	$\sin^2 \theta_{calc.}$	$\sin^2 \theta_{obs.}$	$I_{obs.}$
200	0·0227	0·0227	s	222	0·2024	0·2023	w	313	0·3555	0·3558	w
020	0·0500	0·0500	ms	600	0·2045	0·2044	vw	800	0·3635	0·3639	vvw
111	0·0506	0·0505	s	402	0·2206	0·2204	w	622	0·3842	0·3838	w
220	0·0727	0·0727	m	240	0·2227	0·2225	w	351	0·3960	0·3958	w
400	0·0909	0·0907	mw	620	0·2545	0·2543	w	640	0·4045	0·4046	vw
311	0·0961	0·0959	m	422	0·2706	0·2705	w	133	0·4101 }	0·4101	wd
002	0·1297	0·1298	mw	531	0·2869	0·2871	w	820	0·4135 }		
420	0·1409	0·1408	mw	440	0·2909	0·2908	vw	442	0·4206 }	0·4218	wd
131	0·1506	0·1504	m	113	0·3101	0·3101	w	731	0·4232 }		
202	0·1524	0·1526	m	711	0·3233	0·3231	w	513	0·4463	0·4462	w
022	0·1797	0·1797	w	042	0·3297	0·3292	vvw	060	0·4500	—	
511	0·1869	0·1868	mw	602	0·3342	0·3338	vw	333	0·4555	0·4561	w
331	0·1960	0·1959	mw	151	0·3506 }	0·3514	wd				
040	0·2000	0·2002	vw	242	0·3524 }						

TABLE 5. *Diffraction data on* $UO_3,1·0H_2O$.

hkl	$\sin^2 \theta_{calc.}$	$\sin^2 \theta_{obs.}$	I	hkl	$\sin^2 \theta_{calc.}$	$\sin^2 \theta_{obs.}$	I	hkl	$\sin^2 \theta_{calc.}$	$\sin^2 \theta_{obs.}$	I
002	0·0241	0·0241	m+	211	0·0959	0·0958	vvw	131	0·1607	0·1603	m
111	0·0398	0·0396	s	004	0·0965	0·0965	w	204	0·1713	0·1714	m–
020	0·0604	0·0603	m+	202	0·0989	0·0989	m	115	0·1846	0·1847	m
021	0·0664	0·0663	vvw	122	0·1032	0·1031	vw–	311	0·1893	0·1893	m
200	0·0748	0·0748	m	104	0·1152	0·1151	vvw	133	0·2089	0·2086	m
022	0·0846	0·0844	m	220	0·1352	0·1350	m	006	0·2272	0·2172	w
133	0·0881	0·0880	m+	024	0·1569	0·1566	m–	224	0·2317	0·2315	m
210	0·0899	0·0900	vvw	222	0·1593	0·1594	m	313	0·2376	0·2375	m

TABLE 6. *Diffraction data on phase III hydrate.*

I	$\sin^2 \theta_{obs.}$	I	$\sin^2 \theta_{obs.}$	I	$\sin^2 \theta_{obs.}$	I	$\sin^2 \theta_{obs.}$	I	$\sin^2 \theta_{obs.}$	I	$\sin^2 \theta_{obs.}$
s	0·0151	s	0·0288	m	0·0562	m–	0·0961	m–	0·1095	vvw	0·1255
vw	0·0229	vw	0·0414	m	0·0667	vw	0·0973	m–	0·1173	vvw	0·1290
m+	0·0259	m+	0·0531	m–	0·0759	vvw	0·1032	vw	0·1221	m–	0·1357
w	0·0274	m+	0·0536	s	0·0806						

TABLE 7. *Diffraction data for* $UO_3,0·5H_2O$.

I	$\sin^2 \theta_{obs.}$	I	$\sin^2 \theta_{obs.}$	I	$\sin^2 \theta_{obs.}$	I	$\sin^2 \theta_{obs.}$	I	$\sin^2 \theta_{obs.}$	I	$\sin^2 \theta_{obs.}$
vw	0·0111	vvw	0·0346	m	0·0573	vvw	0·0858	w	0·1342	vvw	0·1939
w	0·0125	vw	0·0437	vvw	0·0596	w	0·0896	vvw	0·1514	vw	0·2001
vw	0·0202	vvw	0·0462	w	0·0617	vw	0·0921	vvwd	0·1552	vvw	0·2069
vw	0·0224	vvw	0·0486	vvw	0·0763	vw	0·0939	vvw	0·1624	vw	0·2136
m–	0·0262	vvw	0·0499	vvw	0·0807	vw	0·0952	w	0·1730	vvw	0·2197
vw	0·0310	w	0·0533	vvw	0·0828	w	0·1296	vvw	0·1746		
m+	0·0335	m	0·0551	vvw	0·0847						

TABLE 8. *Diffraction data on* UO_3, *phase (I).*

I	$\sin^2 \theta_{obs.}$	I	$\sin^2 \theta_{obs.}$	I	$\sin^2 \theta_{obs.}$	I	$\sin^2 \theta_{obs.}$	I	$\sin^2 \theta_{obs.}$	I	$\sin^2 \theta_{obs.}$
mw	0·0139	sd	0·0638	wd {	0·1231	mw	0·1495	w	0·1929	mwd	0·2494
ms	0·0237	vw	0·0688	{	0·1238	w } d	0·1629	mw	0·1952	wd {	0·2547
vw	0·0257	sd	0·0758	vw	0·1252	w }	0·1642	m	0·1997	{	0·2563
s	0·0309	w	0·0785	w	0·1295	mwd {	0·1743	vvw	0·2025	vw	0·2736
vs	0·0497	mw	0·0854	w	0·1333	{	0·1760	vw	0·2145	vw	0·2855
ms	0·0559	vw	0·0995	vvw	0·1350	mw	0·1785	mw	0·2234		
vw	0·0567	w	0·1033	mw	0·1454	w	0·1852	mw	0·2329		

351 Å³, and on the assumption of an oxygen volume of about 19 Å³ the cell contained four formula units UO_3,H_2O.

The calculated and observed values of $\sin^2\theta$ together with the Miller indices and visually estimated intensities of the powder reflection lines are set out in Table 5. The indices of all the reflections except a few weak ones satisfy the conditions $(h + k) = (k + l) = (h + l) = 2n$. A close examination of the powder photographs and the single-crystal Weissenberg photographs discloses weak reflections with the indices (021), (104), (210), (211), (122). The conditions limiting all observed reflections are $(0kl)$, $k = 2n$; $(h0l)$, $l = 2n$; $(hk0)$, $h = 2n$; (hkl), no conditions. The space-group is consequently $Pbca$–O_{2h}^{15}.

The general position of $Pbca$ is 8-fold and the co-ordinates of two sets of 4-fold positions are: $(000)(\frac{1}{2}\frac{1}{2}0)(\frac{1}{2}0\frac{1}{2})(0\frac{1}{2}\frac{1}{2})$, $(00\frac{1}{2})(\frac{1}{2}\frac{1}{2}\frac{1}{2})(\frac{1}{2}00)(0\frac{1}{2}0)$. These differ only in the choice of origin and the point symmetry is $\bar{1}$. Hence the uranium atoms must lie in a set of four-fold positions on a face-centred lattice. In these positions they make maximum possible contribution to the reflections with $(h + k)$, $(k + l)$, and $(h + l)$ even, and zero contribution to all other classes of reflections. This accounts for the distribution of intensities observed, the very weak reflections being derived from oxygen-scattering only.

$UO_3,?H_2O$, Phase III. This substance appeared in the product of experiments in which uranium trioxide was heated with water at 230° in glass tubes. Both the chemical and X-ray analyses were hampered by the fact that it was never prepared with purity exceeding 50%. The powder diffraction photograph was extremely complex; the $\sin^2\theta$ values of the most prominent lines are presented in Table 6. The absence of any summation relations between these $\sin^2\theta$ values indicates that the crystals are probably triclinic.

$UO_3,0\cdot5H_2O$. The hemihydrate was produced as a pure phase by reaction of uranium trioxide with water at 320°. The crystals were yellow, oblique-ended laths about ten microns long. They were often irregularly fractured and striated in appearance, and they showed imperfect extinction between crossed polaroids. Because of extensive twinning of the crystals it has not proved possible to determine unit-cell dimensions; however, for identification purposes Table 7 gives the intensities and $\sin^2\theta$ of the most prominent powder diffraction lines.

UO_3 (I). Anhydrous uranium trioxide samples, obtained by thermal decomposition of uranyl nitrate, $UO_3,2H_2O$, or $UO_3,0\cdot8H_2O$ are crystallographically indistinguishable. They are also indistinguishable from the product of oxidation of lower uranium oxides with 130 atm. of oxygen at 700°. The X-ray pattern is complex and contains many weak lines; some summation relations which exist between pairs of $\sin^2\theta$ values indicate that the compound may be monoclinic. For identification purposes, the observed $\sin^2\theta$ values and visually estimated intensities are shown in Table 8.

UO_3 (II). Dehydration of orthorhombic II monohydrate in air at 415° produces a red trioxide with simple cubic structure and a unit cell dimension of $a = 4\cdot146 \pm 0\cdot005$ Å. If the monohydrate is heated very rapidly to this temperature specimens slightly deficient in oxygen (down to $UO_{2\cdot88}$) are produced.[11] The cell contains one formula unit UO_3, there being uranium at (000) and oxygen at $(\frac{1}{2}00)$, $(0\frac{1}{2}0)$, and $(00\frac{1}{2})$. The compound is isostructural with rhenium trioxide.

[11] Wait, *J. Inorg. Nuclear Chem.*, 1955, **1**, 309.