

The Oxides of Uranium. Part IV. The System $\text{UO}_2\text{-ThO}_2\text{-O}$.*

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Several mixed crystals having the general formula $\text{U}_x\text{Th}_{1-x}\text{O}_2$ were oxidised at temperatures of 100—1000°. Oxidation under appropriate conditions yielded cubic phases; no other structures were formed when $x < 0.5$. The densities of the cubic oxidised phases showed that oxygen entered interstitial positions in the original lattice. When $x > 0.5$, the amount of interstitial oxygen that could be accommodated was limited to 1.4 atoms per unit cell. When $x < 0.5$, the concentration of interstitial oxygen came to a reversible equilibrium with the ambient oxygen pressure at high temperatures. The unit cell contracted as the average uranium valency increased from 4.0 to 5.0 and began to expand as the uranium valency increased from 5.0 to 5.5. This result indicates that isolated uranium cations with more than 5 positive charges cannot exist in these crystals.

URANIUM DIOXIDE is capable of absorbing oxygen at low temperatures, the extra oxygen entering interstitial positions in the fluorite lattice (Anderson and Alberman, *J.*, 1949, S 303; Anderson *et al.*, unpublished work). The nonstoichiometric oxides so formed are metastable and split up on high-temperature vacuum annealing to UO_2 , U_3O_8 , and a cubic oxide U_4O_9 which probably contains one interstitial oxygen atom in every unit cell of the original dioxide lattice; all the oxides form U_3O_8 when heated in oxygen at high enough temperatures for this phase to be nucleated. The extension of this work to include the oxidation of uranium dioxide-thorium dioxide mixed crystals has enabled the study of interstitial anions in the fluorite lattice to be carried further, since at some compositions fluorite phases with extra oxygen in interstitial positions are stable over a wide range of temperature and oxygen content.

Hund and Niessen (*Z. Elektrochem.*, 1952, 56, 972) prepared a series of oxide mixed crystals by heating mixtures of thorium and uranyl nitrates in air and annealing the products in air at 1200°, and found that a fluorite phase extended from 0 to 56.5 moles % of uranium oxide. The oxygen content of these preparations was not determined. On the basis of density measurements they postulated that anomalous mixed crystals containing an intact cation sub-lattice and interstitial oxygen occurred above 50 moles % of UO_n and possibly below 15 moles % of UO_n , but that at intermediate uranium concentrations the anion sub-lattice was intact and the extra oxygen was accommodated by the occurrence of cation vacancies.

In this study, we started always with fully reduced specimens of uranium dioxide-thorium dioxide mixed crystals, containing a normal fluorite anion sub-lattice, with U^{4+}

* Part III, *J.*, 1953, 1731.

and Th^{4+} randomly distributed over the cation positions. The additional oxygen in the oxidised phases was measured during their preparation or determined by analysis. The structure and density could then be determined as a function of oxygen content for each mixed crystal. We have found no evidence that any types of defects other than interstitial anions are introduced into any of the fluorite phases in the course of oxidation. It was possible to determine the composition limits of the fluorite phases and the effect on the size of the unit cell of introducing interstitial oxygen. Structures other than fluorite were formed by complete oxidation of the uranium-rich mixed crystals.

EXPERIMENTAL

Preparation.—The starting materials were solutions of "AnalaR" uranyl nitrate and "AnalaR" thorium nitrate, analysed gravimetrically. Uranium was weighed as U_3O_8 after precipitation with ammonia solution, and thorium as ThO_2 after precipitation as oxalate or sebacate. Aliquot portions of these solutions were mixed and run slowly into an excess of ammonia solution with vigorous stirring. The precipitating conditions were those used by Trzebiatowski and Selwood (*J. Amer. Chem. Soc.*, 1950, **72**, 4504), except that ammonium nitrate was not added when a fine particle product was desired, especially at the higher uranium concentrations. The precipitates were centrifuged, washed, and dried at 120° . The highly coloured, glassy products were ground, ignited in air at $450\text{--}600^\circ$, and reduced with hydrogen or carbon monoxide at $900\text{--}1400^\circ$; carbon monoxide was preferred because of the danger of hydrogen chemisorption (L. E. J. Roberts, unpublished work). For the reduction, the samples were placed in alumina boats inside a Mullite tube which was heated by a radiation furnace. The gases were purified by passage over hot palladium-asbestos or hot copper and through potassium hydroxide or magnesium perchlorate. The oxides were cooled in the flowing gas and their homogeneity was proved by X-ray examination. The apparent cell edge was an accurate linear function of composition, in agreement with Slowinski and Elliott's data (*Acta Cryst.*, 1952, **5**, 768).

In order to obtain very well crystallised samples for X-ray work, samples of the mixed crystals were pelleted and heated in dynamic vacuum in thoria crucibles to $1700\text{--}2100^\circ$; such treatment also sufficed for the original reduction. The vacuum furnace was described by Alberman (*J. Sci. Instr.*, 1950, **27**, 280). The sintered pellets were broken in an iron percussion mortar and finely ground in an agate mortar. Although crystallinity was improved, the high-temperature annealing produced no significant change in the cell-size of homogeneous products. Homogeneous products were usually, but not always, obtained by the gaseous reduction method; they were always obtained after high-temperature annealing.

The only major impurity found was cerium, present to the extent of 0.4% * in the thorium nitrate. The colours of the mixed crystals changed from uranium dioxide-brown at high uranium concentrations to a "uranous" green at 25 moles % of uranium dioxide; the green colour became progressively lighter as the U^{4+} ions were further diluted with Th^{4+} .

X-Ray Measurements.—Samples were exposed in 0.3-mm. thin-walled Pyrex capillaries in 9-cm. or 19-cm. Unicam cameras. $\text{Cu-K}\alpha$ radiation was used with a nickel filter; λ_{α_1} was assumed to be 1.537396 k.X.U., and λ_{α_2} 1.541232 k.X.U. Values of a_{100} at $\theta = 90^\circ$ were found by extrapolation from a values calculated above $\theta \sim 50^\circ$, Nelson and Riley's method (*Proc. Phys. Soc.*, 1945, **57**, 160) being used. Values of a_{100} could be obtained accurate to ± 0.0003 k.X.U. from 19-cm. photographs of well-crystallised samples, and to ± 0.001 k.X.U. from good 9-cm. photographs. Poorly crystalline phases gave photographs with no resolution of the $\text{K}\alpha_1\text{--}\alpha_2$ doublets, and the a_{100} values were accurate to only ± 0.003 k.X.U.

Density Measurements.—These were carried out by using either helium or toluene as the displaced fluid. The densities in helium were measured after outgassing at $200\text{--}300^\circ$ and were reproducible to within $\pm 0.3\%$. The densities in toluene were measured by weighing small, open glass bulbs containing the powders first in air and then in toluene, the liquid being admitted after evacuation at $100\text{--}150^\circ$, flushing with toluene vapour at room temperature and again outgassing; corrections were made for the weight and buoyancy of the empty bulbs. This method seems more accurate than the usual pycnometric method when the quantities of solid available are small. With 3 g. (0.3 c.c.) samples, the densities were reproducible to $\pm 0.3\%$. The two methods, when directly compared on the same samples, yielded results in agreement to $\pm 0.3\%$.

Oxidation Measurements and Analysis.—The oxygen absorbed by the reduced phases by

* We are indebted to the Spectrographic Group at A.E.R.E. for this analysis.

oxidation at 100—900° was estimated by gain of weight and by gas-volumetric methods. The gas measurements were the more accurate because the relative increase in weight was small. For the gas measurements, a sample was weighed into a small Vitreosil U-tube, which was connected through capillary lines to a U-tube mercury manometer, of which one limb was a gas burette; the apparatus could be evacuated through a conventional high-vacuum system. The sample could be heated by a small furnace. The dead spaces in the leads and bulbs were determined with helium. B.O.C. "Spectroscopically Pure" oxygen was used for the oxidation experiments without further purification. Preparations which could have oxidised appreciably in air at room temperature (Part V, following paper) were reduced with carbon monoxide at 600—800° and pumped at 800° immediately before the oxidation experiment.

Some oxidations were carried out at 120 atm. pressure. The samples were placed in open silica tubes inside a stainless-steel tube ($\frac{1}{8}$ " o.d., $\frac{1}{4}$ " i.d.), which was connected through high-pressure lines and valves to a B.O.C. gauge and an oxygen cylinder. The mixture of nitrogen dioxide and oxygen obtained by heating lead nitrate *in vacuo* was used as the oxidising gas in a few experiments, as had been done by Katz and Gruen (*J. Amer. Chem. Soc.*, 1949, **71**, 2106) in a study of the oxidation of UO_2 , U_3O_8 , and NpO_2 . In our experiments the oxidising gas was circulated at about 1 atm. pressure over the previously outgassed sample by means of a thermal-gradient pump.

The products of such oxidations, and some other samples, were analysed for oxygen in excess of $\text{MO}_{2.00}$ by reduction with carbon monoxide and measurement of the carbon dioxide produced. The oxidised samples were evacuated at temperatures below 200°, when no oxygen was lost, and heated to 800° in a closed system, any oxygen evolved being measured and then pumped off after isolation of the sample. When measurable pressures of oxygen were no longer generated the sample was cooled, pure carbon monoxide was admitted, and the sample heated again to 800°. Carbon monoxide was streamed over the sample until no more dioxide could be frozen out of the issuing gas in a liquid-oxygen trap. The carbon dioxide collected was expanded into a known volume, and the pressure and temperature were measured. The oxygen content of the original sample was then calculated as (vol. of oxygen + 0.5 vol. of carbon dioxide) found, and the sample was recovered in the fully reduced state and could be used again. The results of gas-volumetric measurements of oxygen absorbed and of analyses by the above method were in good agreement. Results on gain of weight were also in general agreement when allowance was made for their lower accuracy.

RESULTS AND DISCUSSION

Structure of the Oxidised Phases.—Mixed crystals of all compositions—even those containing only 1% of uranium dioxide—oxidised rapidly at temperatures below 400°. The preparative conditions, analyses, and X-ray characteristics of many of the oxidised phases are collected in Table I. Where the conditions of oxidation are not quoted, the sample was oxidised in 5—15 cm. of oxygen, or in air. Many of the products were annealed in sealed, evacuated tubes. The compositions are expressed both as the additional oxygen atoms per "molecule" of mixed crystal and as the average valency reached by the uranium. Preparations referred to as "C.C." were crushed crystals, formed by high-temperature annealing and pulverising; the others were the products of reduction in carbon monoxide or hydrogen. The cell-edge measurements in Table I refer to f.c.c., fluorite, phases.

The oxidised phases were always cubic fluorite phases when the temperature of oxidation was lower than 200°. At higher temperatures, mixed crystals containing more than 80 moles % of uranium dioxide formed other structures, and finally a U_3O_8 -like structure. The fluorite oxidised phases of mixed crystals containing less than 78 moles % of dioxide were stable in air at all temperatures up to 1400°, though oxidation in high-pressure oxygen broke the cubic structure of the mixed crystal containing 66 moles % of uranium dioxide. Oxidation under any conditions of mixed crystals containing less than 50 moles % of uranium dioxide yielded only fluorite phases. These results differ from those reported by Hund and Niessen (*loc. cit.*), who found U_3O_8 and a limiting fluorite phase after roasting in air samples with more than 56.5 moles % of dioxide. The discrepancy is probably due to the different methods of preparation. Hund and Niessen prepared the oxidised phases directly from hydroxides containing hexavalent uranium; the nucleation of U_3O_8 might have been facilitated by this procedure.

A small particle-size preparation of $U_{0.90}Th_{0.10}O_2$ was oxidised at temperatures below 200° to give cubic phases; the X-ray lines tended to broaden in the direction caused by a cell contraction, in a manner strongly reminiscent of the behaviour of uranium dioxide

TABLE I. Preparation, analyses, and structures of $U_xTh_{1-x}O_{2+y}$.

x	y	Valency of U	Details of oxidation		X-Ray results		Remarks
			Treatment	Temp.	a_{100} , k.X.U.		
0.90	0	4.0	—	—	5.468		
	0.21	4.47	Oxidised	155°	5.459	Broad lines	
			Annealed	400	5.443		
	0.30	4.67	Oxidised	150	—		
			Annealed	400	5.444		
	0.35	4.79	Oxidised	140	5.441		
Annealed			500	—	Lines split		
0.90 (C.C.)	0	4.0	—	—	5.471		
	0.14	4.31	Oxidised	340	—		
			Annealed	800	5.454		
	0.31	4.68	Oxidised	440	5.443		
			Annealed	800	5.443		
	0.25	4.55	Oxidised	305	5.471		
			Annealed	590	5.448		
	0.35	4.77	Oxidised	270	5.441		
			Annealed	590	5.448		
	0.39	4.87	Oxidised	350	5.442	— Faint	
	0.40	4.89	Oxidised	305	5.442	+ Phase B	
	0.44	4.97	Oxidised	450	5.442	+ Phase B	
			Annealed	500	5.443	+ Phase B	
	0.63	5.39	Annealed	700	5.446	+ Phase B	
Oxidised			600	—	(Orthorhombic)		
0.82	0	4.0	—	—	5.480		
	0.14	4.35	Oxidised	130	5.472		
			Annealed	700	5.459		
	0.32	4.79	Oxidised	150	—		
			Annealed	185	5.449		
	0.53	5.29	Oxidation	600	5.455		
0.78 (C.C.)	0	4.0	—	—	5.485	(Orthorhombic)	
	0.33	4.85	Oxidation	900	—		
0.76 (C.C.)	—	—	Oxidation	900	5.457		
	0	4.0	—	1400	5.453		
0.76 (C.C.)	0.051	4.13	Oxidation	275	5.499	Broad lines	
			Annealed	310	5.481		
	0.17	4.46	Annealed	700	5.488		
			Oxidised	300	5.499		
	0.34	4.88	Oxidised	650	5.476		
			Annealed	310	5.477		
0.66 (C.C.)	0	4.0	—	—	5.501		
	0.34	5.07	Oxidised	500	5.479		
	0.47	5.43	Oxid. 100 atm. O ₂	550	—	(Low symmetry)	
0.50	0	4.0	—	—	5.524		
	0.31	5.26	Oxid. 100 atm. O ₂	500	5.510		
0.38	0	4.0	—	—	5.536		
	0.16	4.83	Oxidised	420	5.537		
			Annealed	420	5.523		
0.13	4.68	Oxidised	700	—			
		Annealed	800	5.527			
0.24	0	4.0	—	—	5.556		
	0.081	4.67	Oxidised	360	5.555		
			Annealed	400	5.548		
	Annealed	800	5.549				
Annealed	800	5.550					

(J. S. Anderson, to be published). The oxidation stopped at a composition $MO_{2.35}$; rise of temperature by 20° caused no further oxidation. This product was poorly crystalline but apparently cubic, the cell edge having contracted from $a = 5.466$ to 5.441 k.X.U. When this product was annealed at 400° *in vacuo*, the cube lines tended to split and a phase of lower symmetry was formed, which has not yet been fully investigated. The loss of cubic

symmetry implies an ordering of the previously randomly arranged additional oxygen in the fluorite lattice, and is analogous to the formation of tetragonal phases with compositions between $\text{UO}_{2.30}$ and $\text{UO}_{2.39}$ in the uranium oxide system. Oxidation above 200° to compositions below $\text{MO}_{2.30}$ gave a two-phase product, one being the unoxidised material and the other a cubic phase with $a = 5.442$ k.X.U. Oxidation beyond $\text{MO}_{2.35}$ caused the appearance of a few lines of a new phase (denoted "phase B" in Table 1) which could be indexed fairly satisfactorily on the basis of a simple cubic cell having $a = 7.45$ k.X.U., and the fluorite phase with $a = 5.442$ k.X.U. persisted. As oxidation proceeded, the lines of "phase B" became stronger relative to the cubic phase. The composition of "phase B" has not yet been established, but it seems fair to conclude from the results in Table 1 that the fluorite phase with $a = 5.442$, stable at high temperatures, had a composition close to $\text{MO}_{2.32}$. The one case where some unoxidised material was still present when the average composition was slightly richer in oxygen than $\text{MO}_{2.32}$ could be explained by some formation of "phase B," the lines being too faint to appear. Finally, oxidation at 600° caused the complete disappearance of the fluorite structure; the product was almost certainly one phase and its structure was probably orthorhombic because of the strong similarity of the X-ray diffraction pattern to that of U_3O_8 , though the positions of the diffraction lines showed that the cell size differed from that of U_3O_8 . A complete structure determination has not been carried out, but low-angle lines on the X-ray pattern could be satisfactorily indexed by analogy with the U_3O_8 lines, and preliminary values of the cell constants are $a = 6.75$, $b = 3.97$, $c = 4.15$ k.X.U. Zachariasen's values for U_3O_8 are $a = 6.70$, $b = 3.98$, $c = 4.14$ k.X.U. (National Nuclear Energy Series VIII—5, 271). The oxidation of $\text{U}_{0.82}\text{Th}_{0.18}\text{O}_2$ below 200° yielded fluorite phases and stopped at the composition $\text{MO}_{2.32}$. The fluorite phases were stable towards high temperatures *in vacuo*, but oxidation at high temperatures again gave a U_3O_8 -like phase, presumably orthorhombic; preliminary values of the cell constants are $a = 6.81$, $b = 3.94$, $c = 4.17$ k.X.U.

The oxidation in air or low-pressure oxygen of mixed crystals containing less than 80 moles % of uranium dioxide always yielded cubic phases, but oxidation of $\text{U}_{0.66}\text{Th}_{0.34}\text{O}_2$ in 120 atm. of oxygen at 550° broke the fluorite structure to give a phase of lower symmetry, shown by the splitting of the low-angle lines of the diffraction pattern; the structure could not be determined since the lines were very diffuse.

The products of the oxidation in air at 200 — 400° of mixed crystals containing less than 80 moles % of uranium dioxide were sometimes single fluorite phases and sometimes mixtures of two fluorite phases, one of which was the unoxidised material. Oxidation to completion—a limit when no more oxygen could be absorbed by the solid—at low or high

TABLE 2.

x in $\text{U}_x\text{Th}_{1-x}\text{O}_2$	Oxidation treatment :		Composition limit of fluorite phase :		x in $\text{U}_x\text{Th}_{1-x}\text{O}_2$	Oxidation treatment :		Composition limit of fluorite phase	
	Max. temp.	Conditions	U valency	y in MO_{2+y}		Max. temp.	Conditions	U valency	y in MO_{2+y}
1.0	180°	5—15 cm. O_2	4.58	0.29	0.24	360	5—15 cm. O_2	5.31	0.16
0.90	120	"	4.70	0.315		450	120 atm. O_2	5.38	0.17
0.82	185	"	4.79	0.32			"	5.45	0.18
0.78	400	"	4.85	0.33		400	1 atm. NO_2	5.40	0.18
0.76	570	"	4.88	0.34	0.146	370	5—15 cm. O_2	5.36	0.096
0.66	500	"	5.07	0.34		450	120 atm. O_2	5.46	0.11
0.50	320	Air	5.21	0.30	0.063	400	5—15 cm. O_2	5.08	0.034
	500	120 atm. O_2	5.26	0.32		450	100 atm. O_2	5.37	0.043
0.38	500	Air	5.16	0.22	0.030	500	5—15 cm. O_2	4.94	0.014
	650	120 atm. O_2	5.26	0.24	0.010	420	"	4.51	0.0026
	400	1 atm. NO_2	5.39	0.27					

temperatures always gave a single-phase product, and the intermediate two-phase materials gave a single-phase product after annealing in evacuated sealed tubes at $\sim 800^\circ$.

The Compositions of the Cubic Oxidised Phases.—The highest oxygen concentrations found in the fluorite phases, and the conditions of oxidation employed, are summarised in Table 2. The determination of these limits in the cases of the crystals containing 90 and 82 moles % of uranium dioxide has been discussed above. The limit of $\text{UO}_{2.29}$ is quoted

for uranium dioxide itself since this is the highest oxygen content observed without definite evidence of the formation of a tetragonal oxide. In the other cases, the limit was determined by oxidising in air or in 5—15 cm. of oxygen for a long time at low temperatures and slowly raising the temperature in stages, allowing time for the oxidation to have apparently ceased at each temperature. At high temperatures the oxygen content began to decrease. The values in Table 2 are the highest observed, which were usually reached at $\sim 400^\circ$. The oxygen content of fluorite phases formed by oxidation with high-pressure oxygen and with nitrogen dioxide are also included.

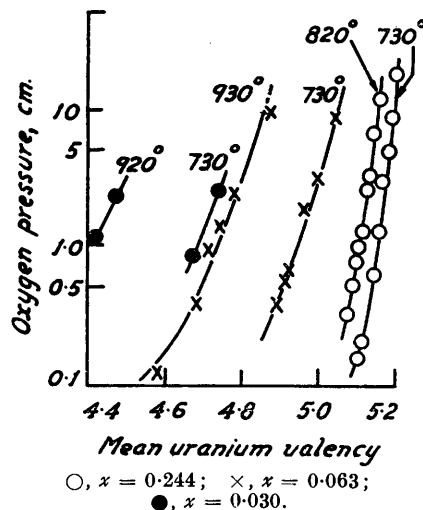
The mixed crystals having a uranium dioxide content of greater than 50% all oxidised to a gross composition of $\text{MO}_{2.32}$ — $\text{MO}_{2.34}$ while retaining the fluorite structure, irrespective of the average uranium valency reached. The composition limit is thus dependent essentially on the geometry of the structure—on the additional oxygen that can be accommodated in the volume of the whole crystal; the density results presented below prove that the additional oxygen in the fluorite phases always enters interstitial positions. The composition limit tends to rise slightly as the uranium dioxide content decreases from 100 to 66 moles %, in accordance with the continuous expansion of the unit cell as Th^{4+} replaces U^{4+} .

Geometrical considerations cannot limit the amount of oxygen entering the crystals which are dilute in uranium. The maximum theoretical valency of uranium is 6. The maximum valency reached by the uranium in these experiments was 5.46, reached by oxidising $\text{U}_{0.15}\text{Th}_{0.85}\text{O}_2$ with high-pressure oxygen. The crystals more dilute in uranium actually took up less oxygen per uranium atom than the crystals with 15 and 25 moles % of uranium dioxide under the same oxidation treatment. These compositions are determined by thermodynamic considerations and not by purely structural factors.

The oxygen content of the mixed crystals in the dilute uranium range was a function of the temperature and the pressure of oxygen. Results for several mixed crystals are plotted in Fig. 1, the equilibrium pressures being plotted on a logarithmic scale for convenience; these equilibria could be approached from either direction, the time taken to come to equilibrium varying from about 15 min. at 600° to 2 min. at 900° . It was not possible to make equilibrium measurements at pressures greater than 30 cm., but the compositions reached on oxidation for at least 24 hr. at 120 atm. and at 500 — 600° were in reasonable agreement with extrapolated curves. These results and those in Table 2 illustrate that the compositions of the solid phases are determined by the magnitude of the free-energy changes on transfer of oxygen from the gas phase into the solid and that these are dependent on the particular configuration of uranium ions in the solid; the oxidised phases cannot be regarded as solid solutions of thorium dioxide and any known higher oxide of uranium.

Densities of the Fluorite Phases.—The densities of several of the mixed crystals which oxidised to give fluorite phases only were measured before and after oxidation in air at 500° . The results are recorded in Table 3. The calculated densities were obtained from the measurements of the unit-cell edge, by assuming no vacancies and 4 MO_2 "molecules" per unit cell. The density always increased on oxidation, and the amount by which it increased was in reasonable quantitative agreement with a theoretical increase calculated by assuming that the oxygen entered interstitial positions in the MO_2 lattice, allowance being made for the cell contractions observed (Table 1 and below). These results prove that the oxygen enters interstitial positions in the fluorite lattice at all uranium con-

FIG. 1. Oxygen pressures in equilibrium with oxidised solid solutions, $\text{U}_x\text{Th}_{1-x}\text{O}_{2+n}$, plotted against the mean valency of the uranium.



centrations from 15 to 78 moles %, since any formation of cation defects would have been shown by a large fall of density on oxidation.

It is noteworthy that the measured densities of the reduced phases are always 2% and in one case nearly 6% lower than the calculated value. Such discrepancies are not due to poor penetration of pores in particles by the measuring fluid, since they occur even when helium is used; we have found similar results when measuring the densities of several

TABLE 3. *Densities of the fluorite phases, $U_xTh_{1-x}O_{2+y}$.*

Reduced phase			Oxidised phase		Density increase :	
x	d (g./c.c.) :		y	d (g./c.c.)	obs.	calc.
	obs.	calc.				
0.146	10.00	10.15	0.10	10.03	0.03	0.07
0.244	9.94	10.25	0.16	10.00	0.06	0.12
"	"	"	0.16	10.13	0.19	0.12
"	9.68	10.25	0.16	9.82	0.14	0.12
0.498	10.27	10.47	0.30	10.50	0.23	0.28
0.783	10.52	10.72	0.33	10.81	0.29	0.42

preparations of uranium dioxide itself by using helium. Densities 6–10% lower than theoretical may be due either to the occurrence of a large number of Schottky defects, equal numbers of vacant cation and vacant anion sites, in the reduced crystals, or to an imperfect packing of crystallites in the solid particles. We found that low densities occurred when the crystallite size, as gauged by the width of the X -ray diffraction lines, was much smaller than the particle size, as measured by gas-adsorption methods, and it is therefore probable that the low-density preparations had a faulty microstructure, though Schottky defects may have been present also. Microstructure faults may explain the low density of one preparation made by Hund and Niessen, which led them to postulate that cation defects and not interstitial anions occurred in some of the oxidised phases. The results in Table 3 illustrate that it is difficult to decide unequivocally the type of defect present on the basis of density measurements of the oxidised phases if the densities of the same preparations in the reduced state are not available for comparison. Our results show that cation defects are not introduced during the oxidation of these mixed crystals.

Variation of Cell Size with Composition.—The variation of cell size with amount of interstitial oxygen was studied in detail on crushed-crystal samples of the 14.6, 24.4, and 38.4 moles % uranium dioxide preparations. Most of the preparations were annealed at 600–800°; where this might have caused loss of oxygen, they were held for some hours at 400°. The oxidised phases were all single-phase and well crystallised. The results are plotted, as a_{100} against the average uranium valency reached, in Figs. 2*a*, *b*, and *c*. The behaviour is very similar in the three cases when they are compared on a basis of uranium valency reached. A regular and probably linear contraction of the unit cell occurs at first, a shallow minimum is reached around a uranium valency of 5.0, and the cell expands as the uranium valency increases to 5.5. In order to make a quantitative comparison, the quantity $\Delta a/x$ for all three crystals is plotted against average uranium valency in Fig. 3; here Δa is the difference in a between the oxidised and reduced crystal and x is the mole % of uranium dioxide in the reduced crystal. This is equivalent to plotting the cell contraction per unit concentration of interstitial oxygen against uranium valency. The points for the three crystals all lie near to one curve, and the $\Delta a/x$ values for a given valency are in reasonable agreement with similar values calculated for crystals of higher uranium content whose oxidation cannot be carried so far. Thus, at a uranium valency of 4.7, the crystals containing 90 and 82 mole % of uranium dioxide give $\Delta a/x$ values of 0.033 and 0.032, respectively, while the curve in Fig. 3 passes through $\Delta a/x = 0.031$. Further, the limiting straight line followed from a uranium valency of 4.0 to 4.4 has a slope of -0.044 per unit valency increase, or -0.09 k.X.U. per oxygen atom added, a value only slightly less than the value of -0.12 Å per oxygen atom found in the uranium dioxide–oxygen system by Perio (*Bull. Soc. chim.*, 1953, 256). It therefore seems that the cell contraction caused by a given quantity of interstitial oxygen per uranium atom is independent of the concentration of uranium in the crystal, at least as a first approximation.

The change from cell contraction to cell expansion as the uranium valency passes

through 5.0 is accompanied by a marked change in colour. The crystals containing 25 and 15 moles % of uranium dioxide change from a pure green (U^{4+} colour) to grey-black as the uranium valency increases from 4 to 5; when this valency is 5.2, the colour is brown-black and at a valency of 5.4 the colour is a rich brown. The corresponding colour sequence of the crystal having 6 moles % of uranium dioxide is light green—straw—dirty straw—red-brown.

FIG. 2a. Variation of cell constant with oxidation state, for the solid solution $U_{0.38}Th_{0.62}O_2$.

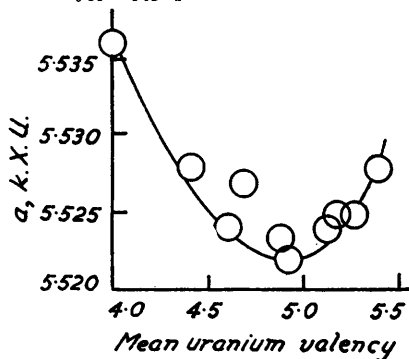


FIG. 2b. Variation of cell constant with oxidation state, for the solid solution $U_{0.24}Th_{0.76}O_2$.

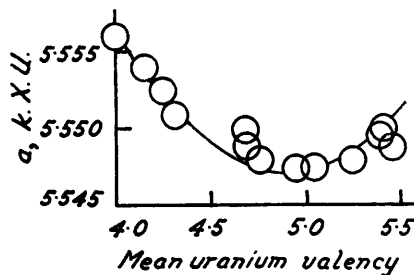
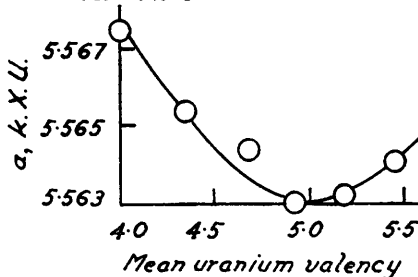
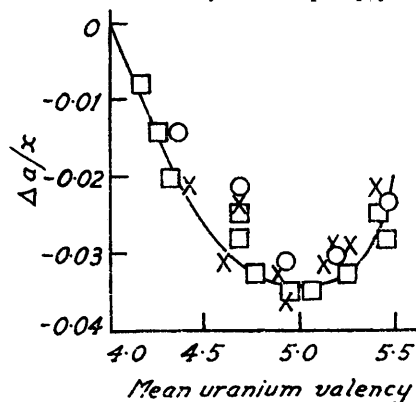


FIG. 2c. Variation of cell constant with oxidation state, for the solid solution $U_{0.18}Th_{0.82}O_2$.



○, $x = 0.146$; □, $x = 0.244$; ×, $x = 0.384$.

FIG. 3. Plot of $\Delta a/x$ against the average uranium valency in $U_xTh_{1-x}O_{2+y}$.



The minimum in the plot of Fig. 3 and the colour changes indicate that the type of interaction between uranium and oxygen alters as the uranium valency is increased beyond 5.0. That the cell contracts as interstitial oxygen is first added may be due to the contraction following upon an effective increase of charge outweighing the expansion due to the inclusion of additional oxygen. This might be expected if U^{5+} were formed instead of U^{4+} . The expansion of the cell as some of the uranium has to become hexavalent, whatever the concentration of interstitial oxygen in the crystal as a whole, would then mean that hexavalent uranium can only occur through the formation of groups such as $(UO)^{4+}$ or $(UO_2)^{++}$, with consequent lowering of the coulombic energy of the crystal. The formation of linear groups such as $(UO_2)^{++}$ is possible along the diagonals of the (110) planes.

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