THE ACTINIDE OXIDES

By L. E. J. Roberts

(Atomic Energy Research Establishment,
Harwell, Didcot)

To regard the elements of atomic number higher than actinium as forming an actinide (5*f*) series is chiefly of value in correlating and explaining the chemistry of the later members and the emergence of the group valency of three.[1] The chemistry of the oxides illustrates the general tendency for higher valencies to be preferred by the earlier members of the series; the ideal formulæ of the main oxide phases are given in Table 1. The uranium and plutonium oxides are of great technical interest in the nuclear-energy industry, and many papers given at the Second Geneva Conference on the Peaceful Uses of Atomic Energy (1958) summarise various aspects of technological work. The present Review is concerned with the structures of individual oxides and of the mixed oxide phases formed from them, and with the surface chemistry and the mechanisms of some of their reactions. The oxidation reactions have received particular attention since they may illustrate some features of solid-state reactions of general importance.

Table 1. *Ideal formulæ of important oxide phases.*

	ThO	PaO	UO	NpO	PuO	AmO	—
Ac_2O_3	—	—	—	—	Pu_2O_3	Am_2O_3	Cm_2O_3
	ThO_2	PaO_2	UO_2	NpO_2	PuO_2	AmO_2	CmO_2
		($PaO_{2.3}$)	U_4O_9				
		Pa_2O_5	U_3O_8	Np_3O_8			
			UO_3				

Monoxide phases

The formation of monoxides by all the elements from thorium to americium has been reported,[2] usually on the basis that an oxide film with the sodium chloride structure, has been identified on a specimen of metal. The structure, definitely established by the relative intensities of the *X*-ray diffraction lines, is typical of most semi-metallic MX phases irrespective of the metal structure or its atomic radius.[3] An early report of the preparation of americium monoxide by reduction of the sesquioxide with hydrogen has not been confirmed.[4]

Many attempts to prepare uranium monoxide by the direct reaction of the dioxide with metallic uranium have failed and it is possible that the

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[1] Katz and Seaborg, "The Chemistry of the Actinide Elements," Methuen, London, 1957.

[2] Zachariasen, *Acta Cryst.*, 1952, **5**, 19.

[3] Rundle, *Acta Cryst.*, 1949, **1**, 180.

[4] Penneman and Asprey, *Proc. Geneva Conf.*, 1956, 7, 355.

"UO" phase always contains some carbon or nitrogen;[5] similar phases have been made by heating uranium carbide with the dioxide above 1600°, and one nearly pure specimen had the composition $UC_{0.57}O_{0.43}$.[6] The monoxide phase does not appear during the oxidation of solid metallic uranium at low temperatures, but it does appear on the outer surface, not at the metal–oxide interface, when partially oxidised specimens are annealed. This unusual sequence suggests that nucleation of uranium monoxide is possible only when it is catalysed by nitride or carbide at a free surface.[7] The deliberate addition of a little carbon resulted in the formation of much more of the monoxide phase, in such quantity that carbon could have been only a minor constituent.

It seems certain that pure or nearly pure monoxide phases can be prepared but that they are semi-metallic interstitial compounds, similar to, and miscible with, the MC and the MN phase, and are not truly the oxides of the elements in a bivalent state. The lower oxides, said to occur in the black residues left when metallic thorium or uranium is dissolved in hydrochloric acid,[8] are not related to the monoxide phases described here; their character is not yet clearly established.

Dioxides and related phases

The dioxides are the most important and most characteristic oxides of the early members of the actinide series. They are high-melting, refractory oxides with the fluorite (CaF_2) structure (Fig. 1a); the regular, but not linear contraction of the unit cell with increasing atomic number is an expected effect of the increasing number of *f* electrons.[9] The relative stability of the dioxides is characteristic of the series. Thorium dioxide is the only regular oxide of thorium. The final oxides formed on pyrolysis in air of

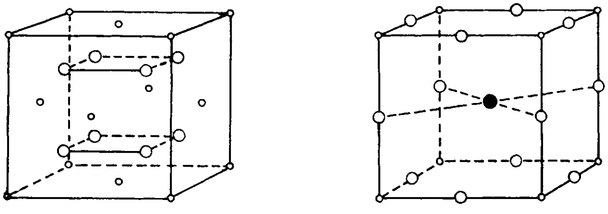

Fig. Ia.

Fig. Ib.

FIG. 1. (a) *The fluorite structure*, MO_2.
Small circles = M; large circles = O.
(b) *The perovskite structure*, ABO_3.
Full circle = A; small open circles = B; large open circles = O.

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[5] Rundle, Baenziger, Wilson and McDonald, *J. Amer. Chem. Soc.*, 1948, **70**, 99.

[6] Vaughan, Melton and Gerds, U.S.A.E.C. Report BMI-1175, 1957.

[7] Williams and Westmacott, *Rev. Metallurgie*, 1956, 189.

[8] Katzin, *J. Amer. Chem. Soc.*, 1958, **80**, 5908; Young, *J. Inorg. Nuclear Chem.*, 1958, **7**, 418.

[9] Asprey, Ellinger, Fried, and Zachariasen, *J. Amer. Chem. Soc.*, 1955, **77**, 1707.

proactinium and uranium compounds are Pa_2O_5 and U_3O_8, but uranium dioxide may be formed by reducing the higher oxides with hydrogen at 300—600°, while Pa_2O_5 is reported to be more stable, being reduced to the dioxide in hydrogen at 1500°. Ignition of neptunium and plutonium salts in air gives the dioxides. Plutonium dioxide is partially reduced in hydrogen at high temperatures, americium dioxide loses oxygen when heated to 800° in a vacuum, and curium dioxide is only formed under 1 atm. or more of oxygen. The dioxides are convenient starting materials for the preparation of quadrivalent compounds.[10] The relevance of the surface chemistry of these oxides to their general chemistry is a consequence of the small particle size, or high specific surface, of many preparations; as a result, surface reactions can account for measurable changes in the overall stoicheiometry.

(a) *The Oxidation of Uranium Dioxide.*—The uranium oxide in equilibrium at low temperatures with oxygen at atmospheric pressure is the trioxide UO_3, and, above 700°, U_3O_8, but the formation of either is apparently inhibited by a kinetic barrier. The trioxide can be prepared by oxidation, at low temperatures in 1 atm. of oxygen, of uranium dioxide of large surface area,[11] whereas a highly crystalline oxide, UO_2 or U_3O_8, can be oxidised to trioxide only under high oxygen pressures. The formation of U_3O_8 is occasionally noticed when dioxide of small particle size is exposed to air at room temperature, but this is probably due to a sudden local rise in temperature, and a highly crystalline dioxide is oxidised at low temperatures to yield fluorite-type oxides, U_3O_8 being formed as a second step, at temperatures above 200°.[12]

The oxidation of uranium dioxide at low temperatures is interesting since the mobile species is oxygen, and the structure of the products very closely related to that of the dioxide itself. The first process is a chemisorption measurable at $-183°$ which is rapid in the presence of an excess of oxygen,[13] but a slow process of chemisorption follows rapid physical adsorption when the oxygen is added in small increments.[14] The heat of adsorption decreases regularly with surface coverage from an initial value of 50 kcal./mole to values typical of physical adsorption when 50—80% of the surface uranium ions have reacted with an oxygen molecule.[15]

The chemisorption is succeeded by a slow process which eventually leads to the absorption of about 5 times as much oxygen and can be followed at all temperatures between $-138°$ and 50°.[16] The extent of the oxidation at these temperatures is simply proportional to the surface area

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[10] Smiley and Brater, *Progr. Nuclear Energy, Series III*, 1958, **2**, 107; and ref. 1.

[11] Boulle, Jarg, and Berges, *Compt. rend.*, 1951, **233**, 1281.

[12] Jolibois, *Compt. rend.*, 1947, **224**, 1395; Aronson, Roof, and Belle, *J. Chem. Phys.*, 1957, **27**, 137.

[13] Roberts, *J.*, 1954, 3332; 1955, 3939.

[14] Ferguson and McConnell, *Proc. Roy. Soc.*, 1957, *A*, **241**, 67.

[15] McConnell and Roberts, "Chemisorption ", ed., W. E. Garner, Butterworths Scientific Publ., London, 1956, 218.

[16] Anderson, Roberts, and Harper, *J.*, 1955, 3946.

of the dioxide; this process results in all preparations of uranium dioxide containing an excess of oxygen after exposure to air. The few measurements available indicate that the density increases as oxidation proceeds, after an initial fall which may plausibly be ascribed to the formation of the chemisorbed layer. The absorptive capacity of the uranium dioxide for oxygen can be regenerated by annealing at a temperature where it is known that migration of oxygen into the lattice does occur, and therefore oxidation at room temperature probably produces an oxidised layer on each particle of uranium dioxide. Infrared lines characteristic of amorphous trioxide UO_3 have been observed when very small (100 Å) particles are oxidised at room temperature,[17] but the density and *X*-ray evidence for rather larger particles that are oxidised slowly (so that the process is isothermal) are not in accord with the formation of trioxide, suggesting rather penetration of the lattice by oxygen and formation of a layer of one of the tetragonal, pseudo-cubic phases containing interstitial oxygen.[16,18] The mechanism of such a low-temperature reaction is of considerable interest; the energy liberated by the chemisorptive process may cause a rearrangement of the oxygen ions.[19]

Bulk oxidation occurs above 80° by a process having an activation energy of 20—25 kcal./mole; oxidation in air proceeds to a limit between $UO_{2\cdot33}$ and $UO_{2\cdot38}$, finally causing some distortion of the lattice from cubic to tetragonal symmetry and a contraction of the unit cell, although the surface area is unchanged and individual particles are virtually unaltered.[16,21] The regular increase in the density of a given sample of uranium dioxide as oxidation proceeds shows that the product contains oxygen in interstitial sites in the uranium dioxide lattice.[20,21] Kinetic results indicate a diffusion-controlled, and not a phase-boundary, reaction but do not distinguish between diffusion into the dioxide down a concentration gradient and diffusion through a thickening layer of product as the rate-determining step.[22,12] A distinction is possible, in principle, by *X*-ray studies but difficult to make because of overlapping diffraction lines. The profiles of the lines on *X*-ray powder photographs have been interpreted in terms of a concentration gradient throughout the uranium dioxide particle, causing a regular contraction of the lattice,[21] and as showing the initial formation of a skin of tetragonal oxide, $UO_{2\cdot33}$.[20] Two recent studies with the *X*-ray diffractometer, an inherently more powerful tool, provide evidence of the formation of a tetragonal phase having $c/a = 1{\cdot}01$ or $0{\cdot}99$ in the early stages of the reaction, with the eventual formation of a tetragonal phase having $c/a = 1{\cdot}03$ when the composition has reached $UO_{2\cdot33}$—$UO_{2\cdot35}$.[17,18] This is probably the best account to date of the oxidation of

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[17] Hoekstra, Santoro, and Siegel, *J. Inorg. Nuclear Chem.*, 1961, **18**, 166.
[18] Belbeoch, Piekarski, and Perio, *J. Nuclear Materials*, 1961, **3**, 60.
[19] Anderson and Gallagher, 4th Internat. Symp. Reactivity of Solids, 1960.
[20] Blackburn, Weissbart and Gulbransen, *J. Phys. Chem.*, 1958, **62**, 902.
[21] Anderson, Symp. Peaceful Uses of Atomic Energy in Australia, 1958.
[22] Alberman and Anderson, *J.*, 1949, 5303.

rather large uranium dioxide particles at ordinary pressures, but it is to be remembered that different mechanisms may hold for different particle sizes[18] and that oxidation at low pressures ceases at compositions below $UO_{2.27}$.[16] The oxidation rate is instantly changed by changing the ambient oxygen pressure, as is the case for the room-temperature oxidation.[16] Since the heat of chemisorption covers the whole range 4—55 kcal./mole, it is clear that some of the surface oxygen will be reversibly absorbed above 100°, and this oxygen may be concerned with the rate-determining concentration gradient.

(b) *Stable Phases in the Uranium Dioxide—Oxygen System.*—The phases formed directly during the oxidation of uranium dioxide below 250° are unstable at high temperatures; the stable phases at high temperatures are a non-stoicheiometric UO_{2+x} phase, the cubic or pseudocubic U_4O_9 phase, and the orthorhombic U_3O_{8-x} phase, which is discussed below. The system does not easily lend itself to the usual anneal-and-quench techniques because of the extremely rapid oxygen diffusion in UO_{2+x};[23] the apparent diffusion coefficient characteristic of all interstitial oxygen atoms in UO_{2+x} is $\sim 3 \cdot 10^{-8}$ cm.^{2}/sec. at 750°.

Gronvold[24] studied the UO_2–U_4O_9 system by high-temperature *X*-ray measurements from 20° to 900° and his results are shown in Fig 2; a metallographic study by Schaner is in reasonable agreement at low O:U ratios.[25] Higher solubilities of oxygen in uranium dioxide below 400°

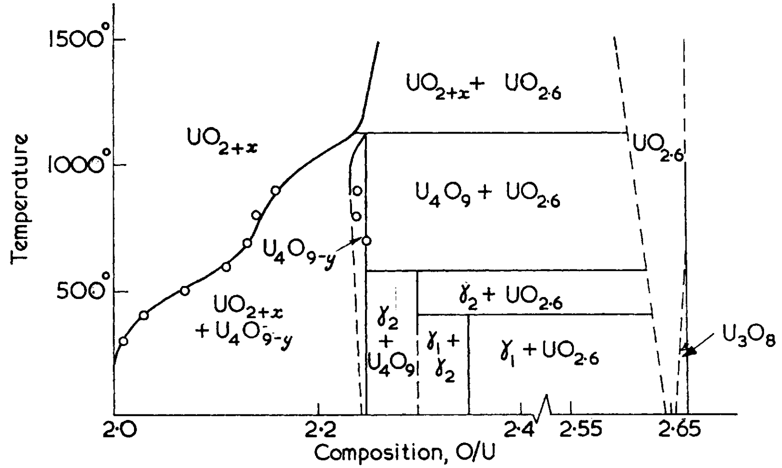

FIG. 2. *Portion of* U–O_2 *phase diagram. Circles denote* X*-ray results* (taken from Gronvold, *J. Inorg. Nuclear Chem.*, 1955, **1**, 357).

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[23] Belle, Geneva Conf., 1958, paper P/2404.
[24] Gronvold, *J. Inorg. Nuclear Chem.*, 1955, **1**, 357.
[25] Schaner, *J. Nuclear Materials*, 1960, **2**, 110.

were reported by Vaughan *et al.*[26] from high-temperature *X*-ray evidence; however, their materials were originally annealed at 450° and it is possible that the U_4O_9 phase is slow to nucleate at 450° for O:U ratios approaching 2·0. The phase boundaries at higher temperatures and higher O:U ratios are more reliably determined by measuring equilibrium oxygen pressures and applying the phase rule: the pressure at a given temperature is independent of composition when two solid phases are present. Oxygen pressures have been measured from 950° to 1150° by an effusion method,[27] from 880° to 1080° by a high-temperature e.m.f. method,[28] and from 1000° to 1450° by direct tensimetric means.[29] The agreement between these three investigations is very good, except that Blackburn[27] places the upper limit of the U_4O_9 phase at a higher O:U ratio than that in Fig. 2. There may be a small region of homogeneity of the U_4O_9 phase at low temperatures.[26]

At least two tetragonal phases, based on distortions of the fluorite structure in the composition range $UO_{2.25}$—$UO_{2.40}$, can be preserved indefinitely below 500°, although their thermodynamic stability is still open to doubt. These are the γ_1 phase,* having $a = 5{\cdot}381$ Å, $c = 5{\cdot}556$ Å, $c/a = 1{\cdot}030$, stable from 180° to about 400°, and the γ_2 phase, having $a = 5{\cdot}406$ Å, $c = 5{\cdot}491$ Å, $c/a = 1{\cdot}016$, stable from 200° to about 550°. The composition of the γ_1 phase has been variously given as $UO_{2.33}$ to $UO_{2.38}$, and that of the γ_2 phase as $UO_{2.30}$ to $UO_{2.35}$.[17,18,21,30] There is no doubt that the γ_1 phase is richer in oxygen than γ_2, since the reaction $\gamma_1 \rightarrow \gamma_2 + U_3O_8$ occurs between 360° and 460°; similarly the γ_2 phase must be richer in oxygen than U_4O_9, since the reaction $\gamma_2 \rightarrow U_4O_9 + U_3O_{8-x}$ occurs above 550°. Both phases may exist over a range of composition. Hoekstra *et al.*[17] point out that the tetragonal phases should be described in terms of a body-centred tetragonal cell.

It also seems certain that metastable cubic phases can be prepared at temperatures below those at which the UO_{2+x} phase is stable.[21,30] Cubic phases with O:U $< 2{\cdot}0$ have also been reported, on the evidence of cell edges greater than those for UO_2 itself. While it seems possible that the dioxide could lose oxygen at high temperatures under very reducing conditions, the compositions of these phases have not been established by analysis. A UO_{2-x} phase would be expected to be re-oxidised very rapidly in air, which may explain why similar results have not been recorded more often.

Density measurements prove conclusively that the U_4O_9 structure is related to that of UO_2 by the inclusion of interstitial oxygen, 1 oxygen atom per unit cell (see Fig. 1a). *X*-Ray powder patterns show all the strong lines of the dioxide lattice, displaced because the unit cell has contracted

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* The notation is that used by Perio.

[26] Vaughan, Bridge, and Schwartz, U.S.A.E.C. Report BMI-1241.

[27] Blackburn, *J. Phys. Chem.*, 1958, **62**, 897.

[28] Aronson and Belle, *J. Chem. Phys.*, 1958, **29**, 151.

[29] Roberts and Walter, *J. Inorg. Nuclear Chem.*, in the press.

[30] Anderson, *Bull. Soc. chim. France*, 1953, 781; Perio, *ibid.*, p. 840.

($a = 5{\cdot}438$ Å; cf. $a = 5{\cdot}468$ Å for UO_2), and a large number of superstructure lines at high angles.[24] It is clear that the uranium atoms must have remained very close to the f.c.c. fluorite positions and that the true unit cell of the structure must be very large. Entropy values reveal that U_4O_9 is highly ordered compared with the UO_{2+x} phase.[29] The positions of the oxygen atoms cannot be deduced readily from X-ray data because of the large difference between the scattering factors of uranium and oxygen atoms. From neutron diffraction data Andresen *et. al.*[31] proposed a tetragonal structure for U_4O_9, with $a_0 = 2\sqrt{(2a)}$, and $c = 2a$, where $a = 5{\cdot}438$ Å. In principle the positions of the oxygen atoms can be determined in this way. However, the resolving power of neutron diffractometers may be insufficient to reveal the structure of a very large unit cell from work on powders and a single-crystal study would be preferable. Perio and his colleagues[32] have recently studied single crystals of U_4O_9 by X-ray methods and report that the structure is in fact cubic, with $a_0 = 4a$, and have proposed a model with the interstitial oxygen atoms disposed in an ordered fashion on positions equivalent to the ($\frac{1}{2}\frac{1}{2}\frac{1}{2}$) position in the original cell (see Fig. 1a).

Most measurements of the densities of the tetragonal γ_1 and γ_2 phases show that these phases, like U_4O_9, contain interstitial oxygen atoms relative to the UO_2 structure;[17,20,21] the low densities occasionally reported,[33] which would indicate cation vacancies in the structure, may be due to the presence of a little U_3O_8 in the annealed specimens. The tetragonal symmetry indicates that the ordering of the interstitial oxygen atoms is different from that in U_4O_9, and that the cations have moved further from the fluorite positions. Different formulations of the true unit cells have been proposed,[17,21] but the structures have not been determined; if the true unit cells are even larger than that of U_4O_9, their resolution will be a formidable undertaking.

The difficulty of attaining single, homogeneous phases on cooling material to room temperature has marred much work on the electrical and magnetic properties of the system. It seems clear, however, that UO_{2+x} is a metal-deficient, p-type semiconductor, while U_4O_{9-x} and U_3O_{7-x} (the γ_1 phase) are metal-excess, n-type semiconductors; this confirms the view that these are regular, ordered phases.[34]

(c) *The* NpO_2–O_2, PuO_2–O_2, *and* PaO_2–O_2 *Systems*.—The behaviour of neptunium and plutonium dioxide towards oxygen bears no resemblance to that of uranium dioxide. Both are inert in oxygen: plutonium dioxide, treated with atomic oxygen gave no evidence of higher oxide formation, nor did neptunium dioxide when heated in oxygen or nitrogen dioxide.[35]

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[31] Andresen, Enlarged Symp. on Reactor Materials, Stockholm, Oct. 1959.

[32] Belbeoch, Piekarski, and Perio, C.E.A. Report, 1960.

[33] Gronvold and Haraldsen, *Nature*, 1948, **162**, 69.

[34] Willardson, Moody, and Goering, *J. Inorg. Nuclear Chem.*, 1958, **6**, 19; Vaughan, Bridge, and Schwartz, U.S.A.E.C. Report BMI-1241, 1957.

[35] Gruen, Koehler, and Katz, *J. Amer. Chem. Soc.*, 1949, **73**, 1478.

This is the more remarkable in the case of neptunium dioxide, since a higher oxide, Np_3O_8, is well known and is probably the stable oxide in air below about 200°; the Np_3O_8 structure can be preserved in high pressures of oxygen up to 500°. Np_3O_8 decomposes to give NpO_2 directly in low oxygen pressures above 400°, with no evidence of any intermediate oxide.[36,37]

Both neptunium and plutonium dioxide preparations do absorb some oxygen when heated in oxygen after having been fully reduced by exposure to hydrogen or carbon monoxide at 500—800°.[38] The reaction is measurable above 200° and oxygen contents as high as $PuO_{2.09}$ have been reported.[39] The absorption is greater the larger the surface area, and the oxygen absorbed never exceeds an amount equivalent to a monolayer;[40] it may be noted that an apparent change of about 0·07 in the O:Pu ratio is caused by the adsorption of a monolayer of oxygen by oxide particles of 0·05 μ diameter—that is, a preparation of surface area 10 m.^{2}/g., and larger specific surfaces are often recorded for preparations of these refractory oxides. The size of the unit cell showed no significant change on oxidation and reduction. These observations all suggest that these are surface processes; such a chemisorption, operative only above 200°, is presumably an activated process, quite different from the adsorption of oxygen by a reduced surface of uranium dioxide, resembling rather the high-temperature chemisorption found on thorium dioxide.[41]

The properties of protactinium dioxide are of great interest. Three cubic, fluorite-type oxides have been reported.[42] The dioxide is a black solid obtained by reducing higher oxides in hydrogen at 1550°, and the composition must be close to PaO_2 since the cell constant ($a_0 = 5{\cdot}505$ Å) falls between those of the dioxides of thorium and uranium. Diprotactinium pentoxide ($a_0 = 5{\cdot}455$ Å) is prepared by heating a protactinium(V) hydroxide precipitate to 500° in air, and its formula has been deduced from the white colour. Another black, cubic oxide of intermediate composition is prepared by heating the pentoxide to 1800° *in vacuo*, as well as a black tetragonal oxide having $a = 3{\cdot}835$ Å, $c = 5{\cdot}573$ Å. Densities could not be determined on the 50 μg. samples used. However, the contraction from dioxide to pentoxide, 0·050 Å for a change in oxidation number of one unit, is similar to the initial contraction of UO_2 to U_4O_9 (0·030 Å for an oxidation number increase 4 → 4·5) and it seems probable that the cubic pentoxide is related to protactinium dioxide by inclusion of interstitial oxygen. The unit cell of the tetragonal phase may be expressed as the face-centred cell with $a = 5{\cdot}42$ Å, $c = 5{\cdot}573$ Å, $c/a = 1{\cdot}03$, which is similar to

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[36] Gruen and Katz, *J. Amer. Chem. Soc.*, 1950, **71**, 2106.
[37] Roberts and Walter, U.K.A.E.A. Report, A.E.R.E. R-3624, 1961.
[38] Roberts, Adwick, Rand, Russell, and Walter, Geneva Conf. 1958, paper P/26.
[39] Drummond and Welch, *J.*, 1957, 4781.
[40] Jackson and Rand, U.K.A.E.A. Report, A.E.R.E. R-3636.
[41] Roberts and Walter, personal communication.
[42] Sellers, Fried, Elson, and Zachariasen, *J. Amer. Chem. Soc.*, 1954, **76**, 5935.

the tetragonal γ phases in the uranium–oxygen system. The fluorite phases in the protactinium–oxygen system may therefore resemble the similar phases of the uranium–oxygen system, but the precise course of the oxidation of protactinium dioxide is not yet clear; both analytical and density data are needed.

(d) *Related Mixed Oxide Phases.*—The actinide dioxides form complete solid solutions with one another and with cerium dioxide, and extensive cubic solid solutions with zirconium dioxide. The cell constant of the solid solutions varies linearly with the molar composition, indicating that the cations are distributed at random on the cation sites.[38,43]

The oxidation properties of such solid solutions which contain uranium dioxide are similar to those of this oxide itself. Solid solutions of uranium dioxide in thorium dioxide have been most intensively studied; chemisorption is measurable at —183° on surfaces prepared by crushing crystals,[13,44] and two kinetically distinct processes occur, one at 0—25° and one above 100°. Prolonged oxidation at high temperatures of solid solutions containing more than 60 moles % of uranium dioxide yields U_3O_8-like structures, but only cubic phases are formed by oxidising solid solutions more dilute in this dioxide; these cubic phases contain oxygen in interstitial positions,[45] up to a limiting composition $U_yTh_{1-y}O_{2.33}$ if $y \geqslant 0{\cdot}5$. The cell constant contracts at first on oxidation but passes through a minimum when the oxidation number of the uranium is about 5·0, and then expands as oxidation proceeds. The behaviour is very regular; the change in cell constant consequent upon oxidation, per mole of uranium ions (*i.e.*, $\Delta a/y$, for $U_yTh_{1-y}O_2 \rightarrow U_yTh_{1-y}O_{2+x}$), depends only on the oxidation number reached by the uranium and is independent of y.[45] Identical values of $\Delta a/y$ for a given oxidation number are found from Gronvold's values[24] for the UO_{2+x} phases, when $y = 1$. At high temperatures, equilibrium oxygen pressures can be measured over the oxidised cubic phases, and the thermodynamic behaviour of the $U_yTh_{1-y}O_{2+x}$ system is very regular from $y = 1$ to $y = 0{\cdot}01$, with the heat of solution of oxygen in the crystals falling as the uranium dioxide concentration falls below 50%.[38,46]

There is no indication that plutonium(IV) and neptunium(IV) show any more tendency to oxidise as components of solid solutions than as dioxide. ThO_2–PuO_2 and CeO_2–PuO_2 solid solutions do not absorb extra oxygen when heated in air, and NpO_2–UO_2 solid solutions behave similarly to ThO_2–UO_2 solid solutions, the neptunium(IV) apparently acting as an inert diluent.

The behaviour of these "regular" solid solutions of the MO_2 structure towards oxygen thus confirms and extends the general properties of the

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[43] Mulford and Ellinger, *J. Amer. Chem. Soc.*, 1958, **80**, 2023; Wolten, *ibid.*, 1958, **80**, 4772; Mulford, *J. Phys. Chem.*, 1958, **62**, 146; Rudorff and Valet, *Z. anorg. Chem.*, 1953, **271**, 257; Duwez, *J. Amer. Ceram. Soc.*, 1957, **40**, 321.

[44] McConnell, *J.*, 1958, 947.

[45] Anderson, Edgington, Roberts, and Wait, *J.*, 1954, 257.

[46] Aronson and Clayton, *J. Chem. Phys.*, 1960, **32**, 749.

pure dioxides. Some new features are shown by the "anomalous" solid solutions of fluorite-structure formed by dissolving oxides of bivalent and tervalent metals in the actinide dioxides. Extensive solid solutions are formed with many of these oxides but not with oxides of metals of small ionic radius—magnesium, beryllium, aluminium. Always, solid solutions are formed with an intact cation sub-lattice and charge balance maintained by vacancies appearing in the anion sub-lattice.[47]

Oxygen can be incorporated to fill the anionic vacancies by forming uranium(V) or uranium(VI) in place of uranium(IV). Since the diminution of the lattice energy caused by the formation of vacancies must be considerable, it is not surprising that some oxides such as magnesium oxide, which do not form appreciable solid solutions with uranium dioxide, can dissolve in the latter to about 35 moles % if the conditions are oxidising enough to enable the complete fluorite lattice, MO_2, to be retained.[47,48] There is a considerable tendency to form a complete MO_2 lattice even where a genuine uranium(IV) solid solution can be formed. Solid solutions of uranium dioxide and yttrium trioxide, with the uranium as uranium(IV), could only be obtained at 1000° by finally reducing in sealed tubes with metallic uranium, and could only be preserved in the complete absence of oxygen. The brown preparations absorbed oxygen rapidly in air at temperatures of —20° to +20° and eventually formed black, fluorite-type phases with a contracted cell and a composition close to $MO_{2.0}$.[49] This rapid bulk oxidation at room temperature and below occurred even with coarsely crystalline preparations and is entirely different from the limited oxidation of the outer layers of uranium dioxide at these temperatures.

The cell constants for the UO_2–Y_2O_3, UO_2–Y_2O_3–O, and MgO–UO_2–O systems are summarised in Fig. 3; it may be noted that the cell constant for the last system at 33 moles % of MgO agrees with that given for MgU_2O_6, a fluorite-type oxide prepared by the decomposition of magnesium uranates.[50] This is close to the solubility limit for magnesium oxide, and the formal charge number of the uranium is 5·0. It is also extremely difficult to oxidise the solid solution $U_{0.5}Y_{0.5}O_2$ beyond this composition, at which the oxidation number of the uranium is 5·0. These facts may indicate, but do not prove, the existence of uranium(V) in these compounds.

These MO_2 structures can be oxidised beyond this composition and, in air, the uranium-rich materials may be further oxidised to U_3O_8-like structures or to U_3O_8 itself. The cubic solid solutions of U_3O_8 and another oxide are special cases of this general type and the oxidation number of the uranium cannot be assumed to remain 5·33 (equiv. to U_3O_8).[51] The cubic

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[47] Lang, Knudsen, Fillimore, and Roth, N.B.S. Circular 568, 1956; Budnikov, Tresviatsky, and Kushakovsky, Geneva Conf., 1958, paper P/2193.

[48] Anderson and Johnson, *J.*, 1953, 1731.

[49] Anderson, Ferguson, and Roberts, *J. Inorg. Nuclear Chem.*, 1955, **1**, 340; Ferguson and Fogg, *J.*, 1957, 3679.

[50] Hoekstra and Katz, *J. Amer. Chem. Soc.*, 1952, **74**, 1683.

[51] Hund and Peetz, *Z. anorg. Chem.*, 1952, **267**, 189; **271**, 6; Hund, Peetz, and Kottenhahn, *ibid.*, 1955, **278**, 184.

oxides MO_{2+x} contain interstitial oxygen, and the cube cell-edge contracts below the $MO_{2.0}$ value, but not as sharply as when anionic vacancies are being filled.

Fig. 3 includes data for NpO_2–Y_2O_3 solid solutions; these can be seen to resemble the UO_2–Y_2O_3 behaviour (curve No. 1) rather than that of the $U_yY_{1-y}O_2$ solid solutions (curve 2).[38] The cell constants of the NpO_2–Y_2O_3 solid solutions do not change when they are fired in air or reduced in contact with metallic uranium.[52] The neptunium is then in the neptunium(IV) state, and this experiment shows that the resistance of neptunium to oxidation in fluorite-type oxides does not depend on the space available, and the contrast between the behaviour of these anion-deficient solid solutions of neptunium and uranium is even sharper than that between the dioxides of these elements themselves.

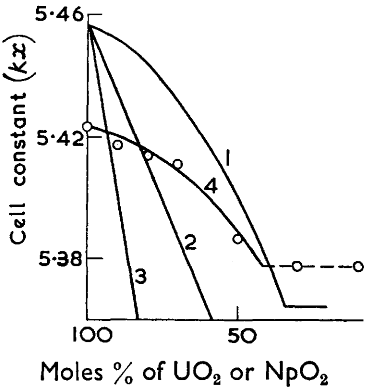

FIG. 3. *Cell dimensions of cubic phases*: 1, UO_2–$YO_{1.5}$; 2, $U_yY_{1-y}O_2$; 3, $U_yMg_{1-y}O_2$; 4, NpO_2–$YO_{1.5}$.

The quadrivalent actinide oxides are also capable of forming structures of the perovskite type (Fig. 1b) with alkaline-earth oxides. Perovskite, or distorted perovskite, structures have been reported for $CaUO_3$, $SrUO_3$, $BaUO_3$,[47] $BaThO_3$,[53] and $BaPuO_3$.[54] The structure of the $CaUO_3$ phase is open to doubt and it has been proposed that it has the rare-earth "type C" structure—essentially a fluorite structure with an ordered arrangement of anion vacancies.[55]

Lower oxides, M_2O_3—MO_2

Here are found the closest analogies between the oxide systems of the actinide and the lanthanide elements. The rare-earth oxides commonly exist as the hexagonal "A" form or the cubic "C" form, which is closely

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[52] Rand and Jackson, U.K.A.E.A. Report, A.E.R.E. R-3635.

[53] Smith and Welch, *Acta Cryst.*, 1960, **13**, 653.

[54] Russell, Harrison, and Brett, U.K.A.E.A. Report A.E.R.E. R-3044, 1960.

[55] Alberman, Blakey and Anderson, *J.*, 1951, 1352.

related to the fluorite structure; the oxides with larger cations have C-type polymorphic forms at low temperatures.[56] Known structures in the actinide series are as in Table 2. The sesquioxide Pu_2O_3 is prepared by reducing plutonium dioxide PuO_2 with metallic plutonium in a closed crucible at 1500°, Am_2O_3 by reducing the dioxide with hydrogen, and Cm_2O_3 by heating the product of the decomposition of the oxalate at 600° in a vacuum, while curium dioxide is made by heating the last material in 1 atm. of oxygen and cooling the product slowly.

TABLE 2.

Ac_2O_3	Type A	$a = 4{\cdot}07$ Å,	$c = 6{\cdot}29$ Å
Pu_2O_3	Type A	$a = 3{\cdot}84$ Å,	$c = 5{\cdot}96$ Å
$PuO_{1.6}$	Type C	$a = 11{\cdot}04$ Å	
Am_2O_3	Type A	$a = 3{\cdot}82$ Å,	$c = 5{\cdot}97$ Å
Am_2O_3	Type C	$a = 11{\cdot}03$ Å	
Cm_2O_3	Type C	$a = 11{\cdot}00$ Å	

The "type C" form of plutonium sesquioxide is not a polymorphic form of Pu_2O_3 but a separate oxide with a composition about $PuO_{1.6}$,[57] that the ordered type-C structure can tolerate some additional oxygen has been demonstrated in several studies of mixed-oxide phases. Phases other than PuO_2, $PuO_{1.6}$, and the hexagonal Pu_2O_3 do not occur in samples of composition Pu_2O_3–PuO_2 quenched from high temperatures, but equilibration experiments show that one more stable phase, of composition about $PuO_{1.8}$, exists above 600°;[58] here is another example of a very rapid phase transformation.

The "A" form of americium sesquioxide was obtained by reduction above 800° and the "C" form by reduction at 600°.[59] Decomposition of americium dioxide in a vacuum begins at about 700° and has been followed as far as $AmO_{1.85}$; one log p–$1/T$ plot showed a very distinct break at 1270° and a composition $AmO_{1.88}$, but X-ray examination of the intermediate oxides has not been reported.[60] The black oxide formed by igniting curium oxalate in air has the fluorite structure with a larger cell than that of the dioxide, and is presumably oxygen-deficient.[9]

Although the facts reported are few, it seems that the oxide systems between M_2O_3 and MO_2 do not resemble closely the corresponding rare-earth oxides, where a series of ordered intermediate phases occurs at low temperatures, with larger ranges of homogeneity at high temperatures.[61] It is worth considering whether the radiation damage self-inflicted on the actinide oxides by α-decay may be expected to hinder the

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[56] Roth and Schneider, *J. Res. Nat. Bur. Stand.*, 1960, **64A**, 309.

[57] Holley, Mulford, Huber, Head, Ellinger, and Bjorklund, Geneva Conf., 1958, paper P/701.

[58] L. E. Russell, personal communication.

[59] Templeton and Dauben, *J. Amer. Chem. Soc.*, 1953, **75**, 4560.

[60] Asprey, U.S.A.E.C. Report UCRL-329 (Revised), 1949.

[61] Bevan, *J. Inorg. Nuclear Chem.*, 1955, **1**, 49; Brauer and Gingerich, *Angew. Chem.*, 1957, **69**, 480.

formation of ordered phases. The half-lives of the isotopes concerned are: ^{239}Pu 2·4.10^4; ^{241}Am 470; ^{244}Cm 18 years. Approximate calculation of the effect of α-particle decay, in which the recoiling heavy nucleus displaces many atoms from their rest positions by collision, shows that the percentages of the atoms in the dioxides so displaced in one month are: 0·1% for ^{239}Pu, 5% for ^{241}Am, and 100% for ^{244}Cm.[62] Such results can hardly affect the structures of plutonium oxides, but may be important in the curium–oxygen system.

A series of double oxides containing plutonium(III) has been reported: $BaPuO_3$, $PuAlO_3$, $PuUO_3$, and $PuCrO_3$; all have the perovskite structure, and their formation apparently stabilises the plutonium(III) state, since they are relatively readily formed under reducing conditions.[54]

Oxides $MO_{2.5}$—$MO_{2.7}$

Triuranium octaoxide, U_3O_8, is the oxide formed by the ignition of uranium compounds in air or 15 cm. of oxygen at temperatures below 900°, followed by slow cooling. It is orthorhombic with a density, 8·3 g./c.c., much lower than that of uranium dioxide. An analogous neptunium phase, $NpO_{2.64\pm0.03}$, can be prepared by treating neptunium hydroxides with nitrogen dioxide at 300—450°, or by heating neptunium(V) and neptunium(VI) compounds in air at 275—450°.[37] A second form of Pa_2O_5, also white but orthorhombic and not cubic, was prepared fortuitously during attempted fluorination of a protactinium oxide, presumably by hydrolysis, and was identified as Pa_2O_5 from its colour and by analogy with the structures of Nb_2O_5 and Ta_2O_5.[63] These compounds must be quite closely related structurally; evidence from the decomposition of U_3O_8 and UO_3, and the heat treatment of U_3O_8, discloses a large family of orthorhombic or pseudo-hexagonal phases, whose interrelations are very complex. Their elucidation is difficult for the reasons already discussed, namely, the difficulty of fixing oxygen positions in the presence of uranium atoms, particularly when the true unit cell is very large, and the need for precise measurement of composition and the attainment of equilibrium.

The main orthorhombic phases are listed in Table 3, the small pseudo-cell being always given, together with the true cell when this has been reported. No attempt has been made to include all the observations when agreement between those of different observers is reasonable. The data for the hexagonal α-UO_3 phase are included for comparison.

Zachariasen drew attention to the close similarity between the uranium positions in U_3O_8 and in the α-UO_3 phase. This is brought out by Fig. 4a, which shows the *c* axis projection of the assumed unit cell of U_3O_8, with the hexagonal unit cell of α-UO_3 outlined (dotted). Along the *c*-axis, perpendicular to the plane shown in Fig. 4a, stretch endless chains of

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[62] D'Eye and Roberts, U.K.A.E.A. Report A.E.R.E. C/M 306.

[63] Sellers, Fried, Elson, and Zachariasen, *J. Amer. Chem. Soc.*, 1954, **76**, 5935; Holser, *Acta Cryst.*, 1956, **9**, 196.

–U–O–U–O–atoms in α-UO_3: it is assumed that certain of these oxygen atoms between the uranium–oxygen layers are missing in U_3O_8: these are indicated by a dotted ring. For true hexagonal symmetry, the ratio of the axes a_0/b_0 of the equivalent orthorhombic pseudo-cell would be $\sqrt{3}$, *i.e.*, 1·732, as is obvious from Fig. 4a: the actual ratio for U_3O_8 is 1·69. This

TABLE 3. *Cell dimensions of orthorhombic* U_3O_8*-like phases.*

Composition	a (Å)	b (Å)[a]	c (Å)[a]	Ref.
U_3O_8	6·717	3·99 (×3)	4·150	67
	6·723	3·975 (×3)	4·143 (×2)	65
α-UO_3	6·878	(3·971)	4·168	[b]
β-U_3O_8	7·05	3·81 (×3)	4·143 (×2)	66
Trigonal U_3O_8	6·815	(3·938)	4·136	[c]
$UO_{2.6}$	6·751	3·97 (×8)	4·143 (×2)	66
($UO_{2.5}$)	6·73	3·96 (×8)	4·143 (×2)	5
Np_3O_8	6·579	4·080	4·182	37
β-Pa_2O_5	6·92	4·02	4·18	63

[a] The factor by which a dimension of the pseudo-cell must be multiplied to give the dimension of the true cell is given in parentheses.
[b] Zachariasen *Acta Cryst.*, 1948, **1**, 265.
[c] Siegel, *Acta Cryst.*, 1955, **8**, 617.

structure was altered in detail by a neutron diffraction study by Andresen.[64] In this structure (Fig. 4b), every uranium atom is bonded to an oxygen directly above and below, and the oxygen atoms in the uranium sheets are

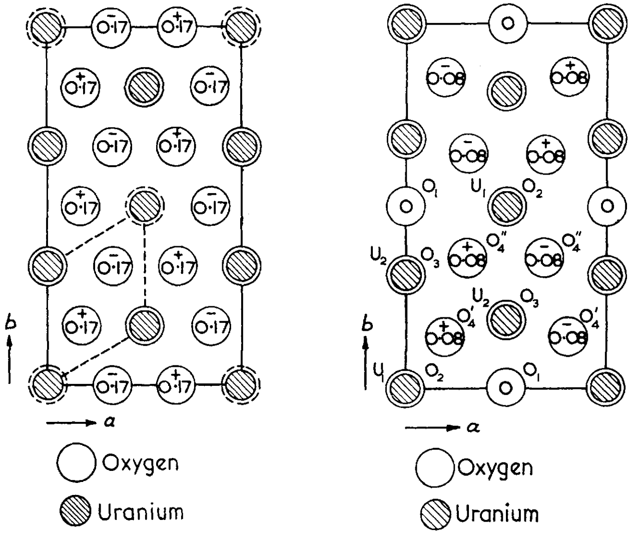

FIG. 4. c-*Axis projections of* (a) *previously assumed unit cell of* U_3O_8, (b) *derived unit cell of* U_3O_8. (Reproduced, by permission, from *Acta Cryst.*, 1958, **11**, 612.)

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[64] Andresen, *Acta Cryst.*, 1958, **11**, 612.

rearranged, giving 6 oxygen atoms surrounding an U_I atom and 7 surrounding an U_{II} atom. Andresen points out that the dimensional changes in going from α-UO_3 to U_3O_8 refer to the *a* and *b* axes, and not the *c* axis. The uranium–oxygen distance in the chains along the *c* axis is the shortest of all, 2·07 Å, and these oxygen atoms are sometimes referred to as the "uranyl" oxygen atoms, for reasons to be discussed. A rather similar structure was arrived at by Chodura and Maly,[65] from *X*-ray measurements of single crystals grown at 1100°C.

The composition range of the U_3O_8 phase itself is narrow at low temperatures. There is general agreement that a closely related phase, which we shall term the $UO_{2.6}$ phase, is formed at slightly lower oxygen content. The phase limits are not precisely known; they were determined[66] as $UO_{2.56}$ to $UO_{2.65}$ on the basis of annealing UO_2–U_3O_8 mixtures in evacuated quartz tubes at 1200°. It seems certain that a single crystal of this phase was studied by Rundle *et al.*[5] and showed the large unit cell given in Table 3. The β-U_3O_8 structure was obtained by heating crystals of $UO_{2.64}$ in oxygen at 750°, and the trigonal U_3O_8 or U_3O_{8-x} phase by heating U_3O_8 in a closed capillary tube. The latter (trigonal) phase has a truly hexagonal arrangement of uranium atoms. These phases are probably related by different ordering in the uranium–oxygen sheets.

The Np_3O_8 phase has been prepared apparently free of other phases with compositions of $NpO_{2.64}$ to $NpO_{2.58}$; it should probably be referred to as the $NpO_{2.6}$ phase. Some superstructure lines have been observed and the true cell is probably large; the relation to the U_3O_8 structure could probably only be found by neutron-diffraction methods; the ratio *a*/*b* for Np_3O_8 is low and the *c* value larger than in U_3O_8.[37]

Phases of this general type can certainly contain cations of more than one kind; they have been prepared by the oxidation of cubic mixed oxide phases (see p. 450) and by the reduction of some uranates.

Uranium trioxides and the uranates

Uranium is the only one of these elements to form oxides with all the metal atoms in the sexivalent state. At least five crystalline forms of uranium trioxide are known, and the usual one, made by heating the hydrated peroxide in air at 400°, is amorphous. The preparation and interconversion of the various forms has recently been summarised by Hoekstra and Siegel[67] and their notation is used here. The heats of formation of all five crystalline forms are very close, ranging from −293 to −295 kcal./mole; all other forms can be converted into the yellow γ-form by heating in oxygen at 650°/40 atm.; the γ-form itself is usually prepared by igniting uranyl nitrate hexahydrate in air at 400—600°.

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[65] Chodura and Maly, Geneva Conf., 1958, paper P/2099.

[66] Hoekstra, Siegel, Fuchs, and Katz, *J. Phys. Chem.*, 1955, **59**, 136.

[67] Hoekstra and Siegel, Geneva Conf., 1958, paper P/1548; *J. Inorg. Nuclear Chem.*, 1961, **18**, 154.

The crystal structures of only the α- and the δ-form are well known, though the oxygen positions even in the α-trioxide have been deduced from steric considerations. The hexagonal crystal structure of this ($a = 3{\cdot}963$, $c = 4{\cdot}16$ Å) has already been described. The δ-form is cubic, with the ReO_3 structure, which is related to the perovskite structure (Fig. 1b) by the omission of the central "A" cation. This form of uranium trioxide has been prepared by dehydrating the monohydrate in air at 415° and can apparently exist over a range of composition. The original report[68] gave the composition as $UO_{2.82}$ with cell edge $a = 4{\cdot}146 \pm 0{\cdot}005$ Å, but the stoicheiometric form can be prepared if sufficient time is allowed. This is the only structure in which uranium is co-ordinated to six oxygen atoms with which it forms equivalent bonds; the δ-form can then be regarded as made up of three-dimensional U–O–U chains similar to those along the *c* axis of the hexagonal α-trioxide form. The structure of molydenum trioxide is somewhat similar.[69] It is clear that the crystal structures of the other forms of uranium trioxide are considerably more complex; that of the stable γ-form has been reported as orthorhombic and as monoclinic.[70]

The decomposition of uranium trioxide to U_3O_8 is normally irreversible since re-oxidation can be effected only in high pressures of oxygen. Many intermediate phases have been identified, the course of the decomposition depending on the type of trioxide and on the ambient oxygen pressure.[67,71] The structures observed are related to the α-UO_3 and α-U_3O_8 structures. One well-characterised phase is the $UO_{2.9}$ phase, which is stable over a 150° temperature range in air; it is orthorhombic with $a = 6{\cdot}90$ Å, $b = 3{\cdot}91$ Å, $c = 4{\cdot}15$ Å, which is the characteristic *c*-axis length for the U–O–U–O chains.

Hydrated Uranium Trioxides.—The product of the reaction between uranium trioxide and water at room temperature, after air-drying, is $UO_3,2H_2O$. The thermal decomposition[72] of the dihydrate in air and in vacuum yields α-UO_3,H_2O, of variable composition down to at least $UO_3,0{\cdot}8H_2O$, and $UO_3,0{\cdot}5H_2O$. β-UO_3,H_2O was prepared by heating the anhydrous trioxide with water at 180° and by hydrolysis of uranyl acetate solution at 110°.[73] These compounds have been termed uranic acids, but the older nomenclature is adhered to here in order not to suggest a simple relation between the structures of these compounds and those of the uranates, in which radicals such as UO_4^{2-} cannot be identified. However, infrared spectra do indicate the presence of hydroxyl groups in $UO_3,2H_2O$ and in α-UO_3,H_2O.[74]

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

[69] Hägg and Magneli, *Rev. Pure Appl. Chem.* (*Australia*), 1954, **4**, 235.

[70] Perio, *Bull. Soc. chim. France*, 1953, 776; Connolly, *Acta Cryst.*, 1959, **12**, 949.

[71] Wait, U.K.A.E.A. Report A.E.R.E. R-3623.

[72] Hüttig and von Schroeder, *Z. anorg. Chem.*, 1922, **121**, 243; Gentile, Talley, and Collopy, *J. Inorg. Nuclear Chem.*, 1959, **10**, 114; Dawson, Wait, Alcock, and Chilton, *J.*, 1956, 3531.

[73] Bergstrom and Lundgren, *Acta Chem. Scand.*, 1956, **10**, 673.

[74] Deane, U.K.A.E.A. Report A.E.R.E. R-3411.

The structure of only the β-UO_3,H_2O phase has been described in detail.[73] It is orthorhombic, $a = 6{\cdot}29$, $b = 5{\cdot}64$, $c = 9{\cdot}93$ Å; the uranium atoms lie on a face-centred array, forming $UO_2(OH)_2$ layers with linear UO_2 groups perpendicular to the sheets. This appearance of uranyl (UO_2) groups, as distinct from U–O–U chains, is repeated in the uranate structures, discussed below.

The Uranates.—Uranates have been prepared by addition of alkali to aqueous solutions of uranyl salts, by the decomposition of double salts, by heating the oxide UO_3 or U_3O_8 with oxides, hydroxides, or carbonates, and by the reaction of U_3O_8 with alkali or alkaline-earth chlorides in the air. The last reaction has been used for making single crystals. All the uranates are insoluble in water. They are more stable thermally than uranium trioxide; thus, MgU_2O_7 is stable to 850° in a vacuum and Li_2UO_4 to 1300° in air, although the most stable form of uranium trioxide decomposes at 700° in air.

Recent studies by Russian authors and by J. S. Anderson and his collaborators have considerably extended our knowledge of the alkali-metal uranates.[75] Polybasic uranates, such as Li_4UO_5, are most easily prepared for the lower members of the series, and the more complex polyuranates are more easily prepared the larger the alkali-metal atom. $Cs_2U_6O_{19}$ and $Rb_2U_6O_{19}$ are known, but the lithium series apparently stops at $Li_2U_3O_{10}$. Many structural data exist for the alkali-metal uranates, for the uranates of Group II elements, and for lead uranates.

Detailed structural results have been published for $CaUO_4$, $MgUO_4$,[76] and $BaUO_4$.[77] The $CaUO_4$ structure (Fig. 5) is related to that of α-uranium

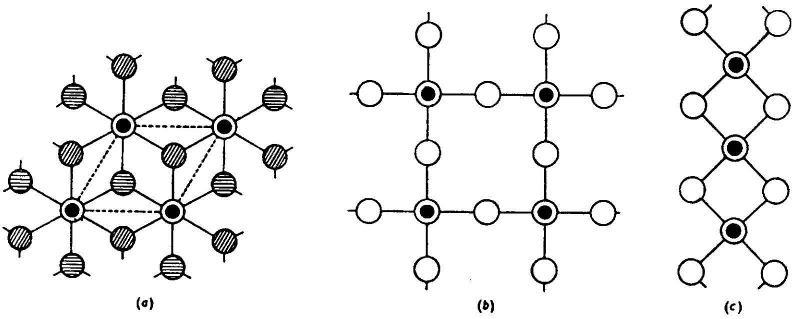

FIG. 5. *Layers and chains of atoms observed in uranate structures, shown in somewhat idealised form,* (a) $CaUO_4$; (b) $BaUO_4$; (c) $MgUO_4$. ⊙, U atom with O_I above and below; o, O_{II}. (Reproduced, by permission, from *Acta Cryst.*, 1954, **7**, 795.)

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[75] Efremova, Ippolitova, Simanov, and Spitsyn, *Proc. Acad. Sci.* (*U.S.S.R.*), 1959, **124**, 115; Kovba, Ippolitova, Simanov, and Spitsyn, *ibid.*, 1958, **120**, 465; J. G. Allpress, Thesis, Melbourne, 1960; D. G. Kepert, M.Sc. Thesis, Melbourne, 1960.

[76] Zachariasen, *Acta Cryst.*, 1948, **1**, 281; 1954, **7**, 788.

[77] Samson and Sillén, *Arkiv Kemi, Min., Geol.*, 1947, **25**, *A*, 1.

trioxide; each uranium atom is bonded to two "primary" O_I atoms, perpendicular to the layer shown in Fig. 5, and to the six "secondary" O_{II} atoms shown, which are alternately above and below the plane illustrated, the distances being U—O_I = 1·91 Å, U—O_{II} = 2·29 Å. The $UO_2(O_2)$ layers form infinite nets with the calcium atoms between them; uranyl groups can be identified, instead of the U–O–U chains of α-UO_3. One form of $CdUO_4$ is similar,[78] and also one form each of Li_2UO_4, Na_2UO_4, and K_2UO_4.

More analogies with other structures can be drawn when uranium has the more usual co-ordination number of six. This is so in the $BaUO_4$ structure, which is pseudotetragonal, with the uranium co-ordinated by two O_I and four O_{II} atoms, the oxygen octahedra sharing corners to make infinite nets of the type shown in Fig. 5, with barium atoms between the $(UO_2)O_2$ layers. Similar structures have been reported for one polymorphic form of the alkali-metal monouranates[75] and for $PbUO_4$.[79] In the α-Li_2UO_4 structure, which is similar to that of K_2NiF_4 and other oxides such as La_2NiO_4, the lithium ions lie between the O_I atoms, and U–O_I–Li–Li–O_I–U strings are formed along the *c*-axis of the tetragonal cell. In the $MgUO_4$ structure, each uranium atom is again bonded to two O_I and four O_{II} atoms, but the oxygen octahedra share two edges to form infinite strings (Fig. 5); one form of $CdUO_4$is similar.[78] The U–O_I and U–O_{II} distances in these compounds are not constant, but fall into a regular sequence when the number of bonds made to a given atom is taken into account.[80] Zachariasen has suggested that polyuranates may be formed by sharing the O_I atoms which lie above and below the orthouranate layers or chains, and a structure in which this occurs has been suggested for MgU_3O_{10} and ZnU_3O_{10}.[78]

At high temperatures or under mildly reducing conditions the uranates lose oxygen and other structures are found. Compounds formally involving uranium(v) have been reported to have the perovskite structure (*e.g.*, $NaUO_3$, KUO_3[75]), where uranium–oxygen chains are formed in all directions. This structure is often found for ABO_3 compounds when the A_2BO_4 compound has the K_2NiF_4 structure. U_3O_8-like compounds, orthorhombic with the characteristic *c*-spacing of 4·14 Å, have been observed in the decomposition of alkali-metal uranates and in the CdO–UO_3 system.[78] Finally, under more reducing conditions, fluorite phases are often formed, of the type already described (p. 451).

The uranate structures show clearly the tendency to form collinear, symmetrical MO_2 groups, common to all the actinides from uranium to americium but to few other elements. No pure oxide phase of this type has been described for elements other than uranium, though Np_3O_8 is

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[78] Ippolitova, Simanov, Kovba, Polonina, and Beresnikova, *Radiokhimiya*, 1959, **6**, 660.

[79] Frondel and Barnes, *Acta Cryst.*, 1958, **11**, 562.

[80] Zachariasen and Plettinger, *Acta Cryst.*, 1959, **12**, 526.

probably a related structure and the oxyfluoride, $KAmO_2F_2$, has the $CaUO_4$ structure, with $(AmO_2)^+$ groups.[81] In view of the extra stability of the uranates over uranium trioxide, it is possible that neptunates and plutonates could be made.

The author thanks many friends and colleagues for information and discussions, and in particular, Professor P. L. Robinson and Dr. E. Wait for reading this manuscript.

[81] Asprey, Ellinger, and Zachariasen, U.S.A.E.C. Report AECD-3554.