[CONTRIBUTION FROM THE CHEMISTRY DIVISION OF THE ARGONNE NATIONAL LABORATORY]

Higher Oxides of the Lanthanide Elements. Terbium Dioxide[1]

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In our investigation of the comparative chemistry of the lanthanide and actinide elements, atomic oxygen has been used to convert lower oxides of praseodymium, terbium and uranium to PrO_2, TbO_2 and UO_3, respectively. No evidence for higher oxide formation has been obtained with Y, La, Nd, Sm, Eu, Gd, Yb, Hf and Th. Pure TbO_2 was identified crystallographically and has the fluorite structure with $a_1 = 5.213 \pm 0.002$ Å. Evidence for continuous transitions from cubic Pr_2O_3 to PrO_2 and from cubic Tb_2O_3 to TbO_2 has been obtained. The "actinide contraction" observed with +4 actinide compounds is shown to have its counterpart in the lanthanide dioxides.

The recent elaboration of the actinide hypothesis and the synthesis of a number of transuranium elements[3] have stimulated interest in the comparative chemistry of these elements with corresponding elements in the lanthanide series. The structure and properties of the oxide systems of the actinide and lanthanide elements are of particular interest, for in addition to the comparative aspects is the bearing these systems have on the general problem of non-stoichiometric compounds, of which they are typical examples.[4]

In a recent communication, the higher oxides of the actinide elements were discussed and the preparation of Np_3O_8 was reported.[5] The present paper concerns itself primarily with the higher oxides of the lanthanide elements. Of the lanthanide oxides, those of praseodymium have hitherto received most study.[6–10] Oxides of terbium, the only other lanthanide element besides cerium and praseodymium for which an oxidation state greater than three has definitely been observed, are less well known owing partly to the lack of pure materials.[11] The oxides Tb_4O_7 and Tb_6O_{11} had, however, been characterized, but TbO_2 has not previously been prepared in pure form.[9]

The conditions likely to yield higher oxidation states of the lanthanide elements must be chosen with care. Thus, treatment of Tb_2O_3 with molecular oxygen even under high temperature and pressure conditions which convert the lower praseodymium oxide to PrO_2[8] only yields the oxide Tb_6O_{11}.[9] A low temperature reaction, therefore, appeared essential for the formation of still higher terbium oxides. Preliminary experiments indicated that the method of Sabatier and Senderens[12] involving NO_2 as an oxidizing agent, and which yields higher neptunium oxides[5] failed to yield well defined higher oxides with Pr_2O_3 or Tb_2O_3. Atomic oxygen, whose intense oxidizing power had been demonstrated many times in the past,[13–17] was therefore investigated. The results obtained with this reagent form the subject of this paper.

Experimental

Apparatus.—Atomic oxygen was generated by electrode discharge in an apparatus similar to that of Harteck and Kopsch.[18] The apparatus, shown in Fig. 1, differs from that of Harteck and Kopsch in that removable rather than fixed electrodes are used. The U-tube (25 mm. i.d.) of 2 meters total length was fitted at each end with female standard taper (34/45) water-cooled joints into which aluminum electrodes were placed. The aluminum electrodes were machined to 34/45 standard taper, and the upper portion was hollowed out to permit water cooling. Details of the electrodes are shown in Fig. 2. Because of the ease with which they may be removed and replaced and their ability to dissipate heat, these electrodes appear to have definite advantages over the conventional metal–glass seals usually used for this type of work.

Power was supplied by a 3750-v. transformer controlled through a variac. A stable discharge could be maintained for several hours when a 500-ma. choke was used in series with the transformer. Heating was not excessive at a current of 250 ma. in the pressure range 0.5–3 mm. of oxygen.

The arc was usually operated at an oxygen pressure of 1–2 mm. The gas flow rate was about 4.5 liters of oxygen per hour corresponding to a gas velocity of about 10 meters per second in the vicinity of the sample. A thin platinum foil placed in the position normally occupied by the sample was heated to 1000° (optical pyrometer); this corresponds to an atomic oxygen content of about 15%, based on the data of Harteck and Kopsch.[18]

Procedure.—The samples were introduced into the reaction chamber on a holder. One type of holder consisted of a platinum disk, silver-soldered to a covar joint, to which were affixed a nichrome heating element and a thermocouple; the other type of holder was very similar but consisted of a quartz disc rather than platinum. Samples for treatment with atomic oxygen were prepared by placing 0.5–1 mg. of the appropriate substance on the platinum or quartz holder, adding a drop of purified tetraethylene glycol and distributing the suspension evenly over the surface. The glycol was then evaporated under a heat lamp leaving a coherent film of the substance on the plate. The sample was exposed to atomic oxygen for approximately 10 minutes. It was often found necessary to raise the over-all temperature of holder and sample by means of the nichrome elements in order to induce a reaction. Generally, an experiment was performed by first allowing the temperature of the sample to reach the value sustained by recombination, then to increase it to 450° with the auxiliary heaters and finally to

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[3] G. T. Seaborg, *Chem. Eng. News*, **23**, 2190 (1945); **24**, 1192 (1946); **25**, 358 (1947); *American Scientist*, **36**, 361 (1948); *Nucleonics* **5**, 16, November, 1949.

[4] For a comprehensive review of the non-stoichiometric compounds, see J. S. Anderson, *Ann. Reports Chem. Soc.*, **43**, 104 (1946).

[5] J. J. Katz and D. M. Gruen, THIS JOURNAL, **71**, 2106 (1949).

[6] P. H. M.-P. Brinton and H. A. Pagel, *ibid.*, **45**, 1460 (1923).

[7] W. Prantdl and K. Hüttner, *Z. anorg. allgem. Chem.*, **149**, 225 (1925).

[8] P. H. M.-P. Brinton and H. A. Pagel, THIS JOURNAL, **51**, 42 (1929).

[9] W. Prandtl and G. Rieder, *Z. anorg. allgem. Chem.*, **238**, 225 (1938).

[10] J. K. Marsh, *J. Chem. Soc.*, 15–17 (1946).

[11] D. M. Yost, H. Russell, C. S. Garner, "The Rare Earth Elements and Their Compounds," J. Wiley and Sons, Inc., New York, N. Y., 1947.

[12] P. Sabatier and J. B. Senderens, *Ann. chim. phys.*, [7] **7**, 356, 384, 396 (1896).

[13] J. J. Thompson, *Proc. Phys. Soc.* (*London*), **40**, 79 (1928).

[14] W. C. Schumb and H. Hunt, *J. Phys. Chem.*, **34**, 1919 (1930).

[15] E. N. Kramer and V. W. Meloche, THIS JOURNAL, **56**, 1081 (1934); H. Rheinboldt, A. Hersel and K. Schwenger, *Ber.*, **63B**, 1865 (1930).

[16] H. Damianovich and J. Piazza, *Anales inst. invest. cient. technol.*, **1**, 45, 49, 54, 58 (1932); **2**, 23 (1933).

[17] O. E. Kurt with T. E. Phipps, *Phys. Rev.*, **34**, 1357 (1929).

[18] P. Harteck and U. Kopsch, *Z. physik. Chem.*, **12**, 327 (1931).

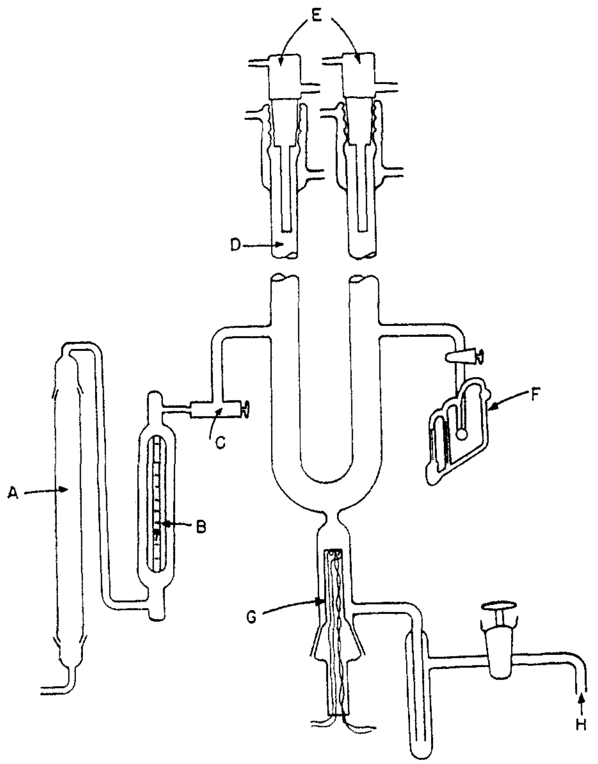

Fig. 1.—Atomic oxygen apparatus: A, drying tower fitted with P_2O_5; B, Fischer–Porter flowrator; C, needle valve; D, discharge tube; E, removable aluminum electrodes; F, tilting McLeod gage; G, sample holder with heater and thermocouple; H, vacuum provided by a Cenco Megavac and Hypervac in parallel.

allow the temperature to fall again to the recombination value. Since most of the reactions were accompanied by color changes some visual indication of the course of a particular experiment could usually be had. Also, by heating the products in vacuum, a higher oxide could be decomposed and then treated with atomic oxygen once more. It was thus possible not only to make qualitative observations regarding the thermal stability of several of the oxidation products but also to eliminate spurious results by repeating the oxidation process on the same sample.

Homogeneous oxidation products were obtained only when the sample thickness did not exceed that produced by 0.5–1 mg. of material per square centimeter of surface. It was therefore necessary to rely for the identification of the products on X-ray diffraction methods. For this, the sample holder was removed from the reaction chamber at the conclusion of an exposure; the sample was collected and transferred to an X-ray capillary. Precision measurements of lattice constants were then made on the X-ray diffraction patterns which were taken on a 9-cm. Debye camera. The lattice constants were evaluated by a least squares method using back reflection lines. Excellent patterns were obtained in all cases.

Materials.—The praseodymium oxide was a sample highly purified by Dr. F. H. Spedding and his group at Iowa State College by resin exchange methods. It contained less than 0.2% of Ce, La and Nd by spectroscopic analysis.

The terbium oxide was a Hilger Co. sample found to be exceedingly pure by Dr. Mark G. Inghram of this Laboratory by mass spectroscopic analysis.

The other rare earth oxides used in this work were samples of the purest materials available from the Hilger Co.

The uranium compounds contained less than 0.01% impurity by spectroscopic analysis. U_3O_8 was obtained by ignition of uranyl nitrate at 700° in air.

The neptunium employed was a very pure sample supplied to us by Dr. J. C. Hindman as a solution of Np(V) (10 mg./ml.) in 1 *M* $HClO_4$.

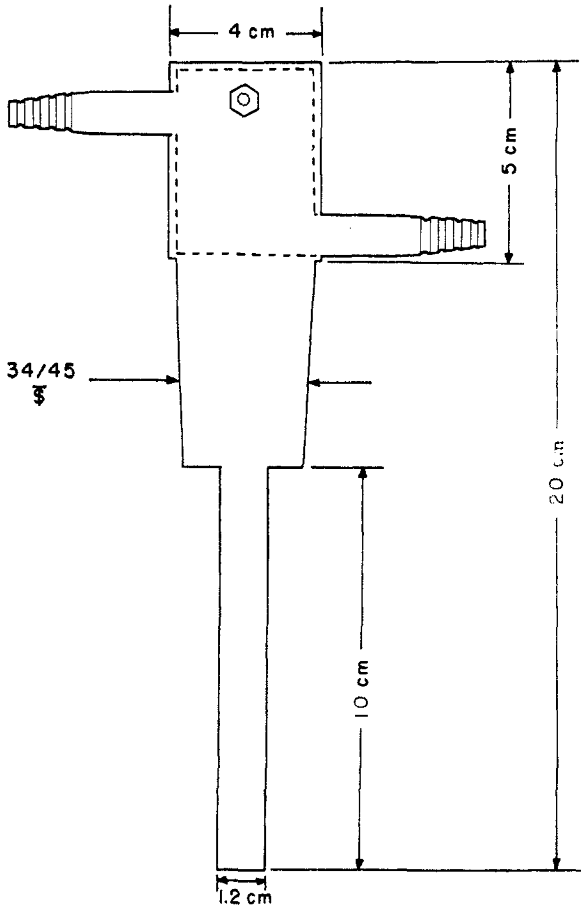

Fig. 2.—Removable aluminum electrode for atomic oxygen apparatus.

Results and Discussion

In general, the structures and properties of the rare earth oxides are well known. The sesquioxides have been extensively studied by Goldschmidt,[19] Zachariasen[20] and others. They exhibit three crystallographic forms: (a) cubic "face centered," (b) hexagonal, (c) type "B" (monoclinic or trigonal). Each phase inhabits a definite temperature region. The dioxides of cerium and praseodymium have the fluorite structure while Pr_6O_{11} and Tb_4O_7 give diffraction patterns, the strongest lines of which correspond to a cubic face-centered lattice. There are, however, a few weak lines in both patterns which have not been indexed. A pure phase of TbO_2 has not been reported previously.

Higher Oxides of Praseodymium.—The composition of the various oxidation products obtained here has been established from the lattice parameters of the praseodymium oxides determined by McCullough.[21] His data appear to be the best values in the literature; for "C" type Pr_2O_3, McCullough finds a_1 = 5.570 ± 0.002 Å., for Pr_6O_{11}, a_1 = 5.468 ± 0.001 Å., and for PrO_2, a_1 = 5.394 ± 0.002 Å. There is thus a contraction in the lattice as the oxidation state of the metal is

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[19] V. M. Goldschmidt, F. Ulrich, T. Barth and G. Lunde, *Geochemische Verteilungsgesetze*, Vol. IV, V, Oslo, 1925.

[20] W. H. Zachariasen, *Norsk. Geol. Tids.*, **9**, 310 (1927).

[21] J. D. McCullough, THIS JOURNAL, **72**, 1386 (1950).

TABLE I

REACTIONS OF PRASEODYMIUM AND TERBIUM OXIDES WITH ATOMIC OXYGEN

			Product			
			Major phase		Minor phase	
Expt.	Starting material[a]	Temp., °C.	Lattice constant, Å.	Composition	Lattice constant, Å.	Composition
		Praseodymium Oxides				
1	Hexagonal $Pr_2O_3 + Pr_6O_{11}$	250	5.380 ± 0.003	$PrO_{2.02}$	5.454 ± 0.008	$PrO_{1.90}$
2	Same as No. 1	450	5.380 ± 0.003	$PrO_{2.02}$	5.6 (estimated)	
3	Same as No. 1	450	5.380 ± 0.003	$PrO_{2.02}$	None	
4	Pr_6O_{11}	150	5.53	$PrO_{1.65}$	None	
5	Pr_6O_{11}[b]	900	5.399 ± 0.002	$PrO_{1.90}$	None	
6	PrO_{2-x}	150	5.399 ± 0.002	$PrO_{1.99}$	None	
7	Same as[c] No. 1	350	Unidentified		5.380 ± 0.003	$PrO_{2.02}$
8	Product Expt. 7 heated in vacuum	250	5.380 ± 0.003	$PrO_{2.02}$	None	
		Terbium Oxides				
9	Tb_4O_4	350	5.213 ± 0.002	TbO_2	None	
10	Tb_2O_3	450	5.212 ± 0.005	TbO_2	5.265 ± 0.005	$TbO_{1.83}$
11	Tb_2O_3[c]	250	5.276 ± 0.005	$TbO_{1.79}$	None	

[a] Lattice constants: Pr_6O_{11}, 5.53 Å.; PrO_{2-x}, 5.399 ± 0.002 Å.; Tb_2O_3, 5.359 ± 0.003 Å.; Tb_4O_7, 5.290 ± 0.005 Å.
[b] Treated with O_2 at 20 atm. [c] Oxidized with NO_2 gas.

increased, similar to that observed in many other oxide systems. By the use of a plot of McCullough's data (see Table II and Fig. 3) the composition of a particular praseodymium oxide can be established from its lattice parameter.

The experimental results are summarized in Table I. Atomic oxygen at 250° on a mixture of hexagonal Pr_2O_3 and Pr_6O_{11} (made by reducing Pr_6O_{11} with hydrogen at 600°) results in two crystalline oxide phases with lattice constants 5.380 ± 0.003 Å. and 5.454 ± 0.008 Å., respectively (Expt. 1). The major phase is PrO_2 but the minor phase has a lattice constant intermediate between that of PrO_2 and Pr_6O_{11}. This observation is at variance with that of McCullough,[21] who was unable to obtain a homogeneous phase of intermediate composition by heating intimate mixtures of the two oxides, but confirms the work of R. L. Martin[22] who found a monophasic region with composition range $PrO_{1.75}$ to PrO_2, depending on the thermal history of the sample.

Other samples of the Pr_2O_3–Pr_6O_{11} mixtures were treated with atomic oxygen at 450° using a quartz sample holder in Expt. 2 and a platinum sample holder in Expt. 3. In the first case, two crystalline oxide phases resulted, the major phase being PrO_2. In the second case, pure PrO_2 was produced.

Since these oxidations were carried out at pressures of 1–2 mm., the dissociation pressure of PrO_2 at 450° must lie below this value. However, when the PrO_2 made in Expt. 3 was heated in a high vacuum at 450° for 15 minutes, cubic Pr_2O_3 (a_1 = 5.568 ± 0.005 Å.) resulted. The cubic form is the low temperature modification of Pr_2O_3.[19] It has also been observed by Marsh.[10]

The starting material for Expt. 4 was Pr_6O_{11} prepared by igniting $NH_4Pr(NO_3)_4$ in air at 1000°. This material had a lattice constant of 5.53 Å. indicating that it was somewhat deficient in oxygen. Treatment with atomic oxygen at 150° had no effect on the cell constant. The same material when treated with molecular oxygen under pressure at 900° (Expt. 5) yielded an oxide of composition close to PrO_2 (a_1 = 5.399 Å.). This latter material was not further altered by treatment with atomic oxygen at 150° (Expt. 6).

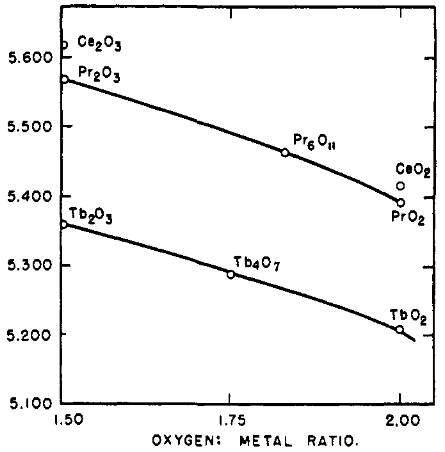

Fig. 3.—Change of lattice parameters with oxygen content.

It was of interest to determine the effect of NO_2 on a sample of the Pr_2O_3–Pr_6O_{11} mixture, since NO_2 appears to yield the same products as does atomic oxygen in the case of uranium oxide oxidations.[5] At 350°, NO_2 yielded two crystalline oxide phases (Expt. 7). The minor phase (≈40%) was PrO_2 (a_1 = 5.380), but the major phase exhibited a complex pattern which has not yet been identified. The product was analyzed for nitrogen and was found to have adsorbed NO_2 to the extent of 1/2 mole NO_2/mole of Pr_6O_{11}. It is of interest to note that when this material was treated with atomic oxygen at 250° after having been heated to 400° in a vacuum, a monophasic crystalline oxide was produced having the lattice parameter of PrO_2 (Expt. 8). It appears that NO_2 oxidation is incapable of forming pure PrO_2 under the conditions employed here.

Higher Oxides of Terbium.—The terbium–oxygen system bears a close resemblance to the praseodymium–oxygen system. Cubic Tb_2O_3 was prepared by the reduction of Tb_4O_7 with hydrogen

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(22) R. L. Martin, *Nature*, **165**, 202 (1950).

at 600° (lattice constant a_1 = 5.359 ± 0.003 Å.). Ignition of Tb_2O_3 in air at 700° yielded the oxide Tb_4O_7 with a lattice constant of a_1 = 5.290 ± 0.005 Å. The value given by Goldschmidt[19] is a_1 = 5.275 Å. Our determination is thought to be more reliable since very pure terbium samples were used in this work.

The lattice parameter of TbO_2 was taken as a_1 = 5.202 Å. This value was chosen on the basis of the following considerations. The ratio of the lattice constants of cubic Pr_2O_3 and PrO_2 is 1.032. Assuming the lattices of cubic Tb_2O_3 and TbO_2 to have a similar relationship to each other, one calculates for the parameter of TbO_2 the value 5.202 Å. (The same result is obtained when crystal radii rather than lattice parameters are used in the calculation.)

The experimental results summarized in Table I were interpreted on the basis of a plot of lattice parameter *vs.* composition (see Table II and Fig. 3). Treatment of Tb_4O_7 with atomic oxygen at 350° (Expt. 9) results in a monophasic crystalline product which has the fluorite structure with a cell constant of 5.213 ± 0.002 Å. This is in good agreement with the assumed value for TbO_2. Treatment of Tb_2O_3 (a_1 = 5.359 ± 0.003 Å.) with atomic oxygen at 450° (Expt. 10) yields a crystalline diphasic product, the major phase of which is TbO_2 (a_1 = 5.212 ± 0.005 Å.). The minor phase has a lattice constant a_1 = 5.265 ± 0.005 Å. and may be the phase Tb_6O_{11} previously reported by Prandtl and Rieder.[9] The preparation of a pure phase of TbO_2 confirms the results of Prandtl and Rieder[9] and of Marsh[10] who obtained evidence for the existence of the dioxide from weight changes of mixtures of Tb_2O_3 and Y_2O_3 treated with molecular oxygen under pressure. The existence of phases intermediate between Tb_4O_7 and TbO_2 parallels the behavior in the praseodymium–oxygen system.

Reaction of NO_2 with Tb_2O_3 leads to an oxide with a parameter 5.276 ± 0.005 Å. (Expt. 11), thus indicating the formation of an oxide intermediate between Tb_4O_7 and Tb_6O_{11}. The formation of TbO_2 by oxidation with NO_2 has not been observed in any of a number of experiments. In the case of the rare earth oxides, there is thus less resemblance between the behavior of NO_2 and atomic oxygen than has been encountered in the case of the uranium oxides. Decomposition of TbO_2 at 450° in vacuum yields Tb_4O_7 (a_1 = 5.290 ± 0.005 Å.).

Attempted Preparation of Higher Oxides of Other Lanthanide Elements.—The only lanthanide element other than cerium, praseodymium and terbium for which an oxidation state greater than +3 is said to have been observed is neodymium.[23,24,25] In none of a series of experiments in which Nd_2O_3 was exposed to atomic oxygen over a range of temperatures was there any indication of higher oxide formation. Our results are entirely in agreement with those of Pagel and Brinton[8] and Popov and Glockler[26] who also failed to find a higher oxide of neodymium.

The sesquioxides of lanthanum, samarium, europium, gadolinium and ytterbium and the dioxide of hafnium were routinely exposed to atomic oxygen. In every case the diffraction patterns of the products were identical with those of the starting materials indicating that no higher oxides of these elements were formed. With amorphous HfO_2, evolution of light and conversion to a well-defined crystalline form was observed on treatment with atomic oxygen.

Higher Oxides of the Actinide Elements.—Only two higher oxides of the actinide elements are presently known: UO_3 and Np_3O_8. Their preparation by means of NO_2 oxidation of lower oxides has been previously described.[5] It was of interest to compare the action of this oxidizing agent with that of atomic oxygen. With U_3O_8, the action of atomic oxygen results in a brick red UO_3 which is the same phase as that produced by reaction of U_3O_8 with NO_2. This phase is entirely distinct from three other known phases of UO_3.[27] The bearing which this observation has on the mechanism of NO_2 oxidations made it important to rule out the possibility that the present reaction was caused by small amounts of NO_2 formed in the arc from nitrogen impurities. To show conclusively that atomic oxygen is the active species in the present case, an experiment was performed in which a stream of molecular oxygen admixed with a small amount of NO_2 was passed over the sample under conditions of temperature and pressure leading to reaction in the presence of atomic oxygen. No oxidation was noted after 1.5 hours. Likewise, nitrogen–oxygen mixtures in the discharge gave results entirely comparable to those obtained with pure oxygen. Normally, of course, NO_2 oxidations are performed in an atmosphere of NO_2 at atmospheric pressure. The rate of U_3O_8 oxidation with atomic oxygen or NO_2 is negligible below 200° but goes to completion in a few seconds at 350°. The similarity in reaction conditions and the identity of the products of both reactions suggests the same fundamental mechanism for these two reactions.

Treatment of various samples of dried neptunium hydroxides with atomic oxygen has not led to a higher oxide which could be identified crystallographically. The production of an amorphous form of Np_3O_8 however is not completely ruled out. Clear patterns of Np_3O_8 in the past could be obtained only maintaining the oxide for several hours at 300° in an atmosphere of NO_2. Patterns of dried plutonium and americium hydroxides treated with atomic oxygen have not given evidence for higher oxide formation.

Some General Aspects of Actinide and Lanthanide Oxygen Systems.—The thallium oxide (Tl_2O_3) structure is the prototype of one of the common crystal forms of many rare earth sesquioxides. This so called "C" form[19,28] is perhaps most easily pictured as a distorted CaF_2 arrangement in which trivalent metal atoms replace calcium atoms and three-fourths of the fluorine positions are occupied

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(23) Brauner, *Collection Czechoslov. Chem. Commun.*, **5**, 279 (1933).

(24) Marc, *Ber.*, **35**, 2382 (1902).

(25) Meyer and Koss, *ibid.*, **35**, 3740 (1902).

(26) A. I. Popov and G. Glockler, This Journal, **71**, 4114 (1949).

(27) The results of S. Fried, N. R. Davidson and W. H. Zachariasen on the phase relationships of UO_3 will be reported by them in a subsequent communication.

(28) A. Iandelli, *Gazz. chim. ital.*, **77**, 312 (1947).

by oxygen ions, the remaining positions being vacant. A pure face centered cubic "fluorite" structure, however, is found for the lanthanide dioxides CeO_2, PrO_2 and TbO_2. In view of the close similarity between the Tl_2O_3 and CaF_2 structures, it is not surprising to find the existence of extensive solid solution ranges between "C" form lanthanide sesquioxides and lanthanide dioxides.[10,21,29] Our data indicate that there may be a continuous transition from cubic Pr_2O_3 to PrO_2 and cubic Tb_2O_3 to TbO_2. Compositions corresponding to Pr_6O_{11} and Tb_4O_7 may be thought of as representing particularly stable configurations just as U_6O_{17} appears as a point of marked stability in the monophasic region U_3O_8–UO_3. As the upper limit of the solid solution range is approached it becomes increasingly difficult to add oxygen because the lattice contracts. Indeed TbO_2 had only been prepared prior to this work in mixtures with other C-type sesquioxides which aided oxygen absorption by maintaining the Tl_2O_3 structure. The effect of oxygenation on the lattice parameters is brought out in Fig. 3. It is to be noted that the ratios of the cell constants of dioxide to sesquioxide is the same for the praseodymium and terbium systems. Evidence for the existence of phases intermediate between those shown in Fig. 3 was obtained from X-ray diffraction data as discussed in detail in the previous section. This material has been collected in Table II. The continuous range $UO_{1.75}$–$UO_{2.30}$ has been studied by Rundle, *et al.* Their data are also listed in Table II and show a contraction in the fluorite lattice of UO_2 as well. However, the changes in the parameters are less in this than in the lanthanide–oxygen systems for equal changes in oxygen content.

TABLE II

OXYGEN CONTENT AND LATTICE PARAMETERS OF LANTHANIDE AND URANIUM OXIDES

Formula	Oxygen/metal ratio	Lattice constant,[a] Å.	Reference[b]
Ce_2O_3	1.50	5.622	28
CeO_2	2.00	5.41	19
Pr_2O_3	1.50	5.570	21
$PrO_{1.65}$	1.65	5.53	
Pr_6O_{11}	1.83	5.468	21
$PrO_{1.99}$	1.99	5.399	
PrO_2	2.00	5.394	21
$PrO_{2.02}$	2.02	5.380	
Tb_2O_3	1.50	5.359	
Tb_4O_7	1.75	5.290	
$TbO_{1.79}$	1.79	5.276	
Tb_6O_{11}	1.83	5.265	
TbO_2	2.00	5.213	
U_4O_7?	1.75	5.477	c
UO_2	2.00	5.458	c
$UO_{2.3}$	2.30	5.430	c

[a] The ratio of the lattice constants for $Ce_2O_3:CeO_2$ is 1.039; $Pr_2O_3:PrO_2$ is 1.032 and $Tb_2O_3:TbO_2$ is 1.029. [b] Present work unless otherwise indicated. [c] R. E. Rundle, N. C. Baenziger, A. S. Wilson and R. A. McDonald, THIS JOURNAL, **70**, 99(1948).

The experimental determination of the lattice parameter of TbO_2 now makes possible a comparison between lanthanides and actinides in the +4 oxidation state. As was to be expected, the same contraction effects are found in the +4 as in the +3 compounds.[30] Crystallographically, it is of interest to note that with the exception of ZrO_2 and HfO_2, the only dioxides possessing the fluorite structure are the lanthanide and actinide dioxides. (The reason is to be found in the criterion for stability of this lattice; *i.e.*, that the radius of the metal must be greater than 0.73 times the radius of the anion.) Figure 4 shows the slow, successive decrease in cell constants (crystal radii) with increasing atomic number characteristic of the filling of the f-shells in both actinide and lanthanide series. This comparison of quadrivalent actinides and lanthanides is unique since no series of quadrivalent lanthanide compounds other than the oxides are known.

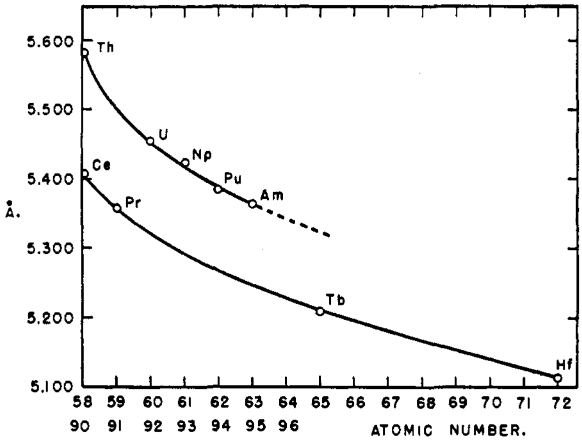

Fig. 4.—Lattice constants of actinide and lanthanide dioxides.

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(29) E. Zintl and U. Croatto, *Z. anorg. allgem. Chem.*, **242**, 79 (1939).

(30) W. H. Zachariasen, *Phys. Rev.*, **73**, 1104 (1948).