TABLE IV

POWDER DIFFRACTION DATA FOR TbOF

(Cr Kα, λ = 2.2909 Å.)

hkl[a] hex.	hkl, rhomb.	$\sin^2\theta$ Calcd.	$\sin^2\theta$ Obsd.	I, obsd.
006	222	0.1291	0.1284	w
102	110	.1327	.1325	ms
104	211	.1758	.1759	m
009	333	.2905	.2919	vw
107	322	.2941		
108	332	.3480	.3482	m
110	$10\bar{1}$	.3551	.3550	m+
201	$11\bar{1}$	.4771	.4768	w
1, 0, 10	433	.4771		
116	321	.4842	.4857[b]	m
202	200	.4878		
204	220	.5309	.5310	w
1, 0, 11	443	.5524	.5519	vw
119	432	.6456	.6478	w
207	331	.6493		
208	422	.7031	.7037	mw
1, 0, 13	544	.7246	.7232	vw
0, 0, 15	555	.8071	.8095	trace
1, 0, 14	554	.8215	.8215	w
2, 0, 10	442	.8322	.8316	w
211	$20\bar{1}$	.8323		
212	$21\bar{1}$	.8430	.8430	m+
1, 1, 12	543	.8716	.8713	w
214	310	.8861	.8857	m

[a] For an hexagonal cell with a = 3.844, c = 19.13, Z = 6.
[b] Diffuse.

to three decimal places. It should be remembered that the second decimal is in doubt on an absolute scale, but the third decimal is of significance in the *differences* of adjacent radii. For most correlative purposes, the absolute scale is of no consequence.

These radii are based primarily on the cubic oxides, with the radius of oxygen taken as 1.380 Å. in this structure (coördination six). The cell dimensions of the tetragonal oxychlorides,[14] the second most extensive isostructural set available, were used in an empirical way to help fix the values for the elements near lanthanum. The less extensive data on the monoclinic[15] and hexagonal chlorides and orthorhombic fluorides[16] were used to test the curvature of the plot of radius against atomic number. About as many deviations occurred in one direction as in the other.

TABLE V

CRYSTAL RADII OF TRIVALENT RARE EARTH IONS

Ion	Radius, Å.	Ion	Radius, Å.
La^{+++}	1.061	Tb^{+++}	0.923
Ce^{+++}	1.034	Dy^{+++}	.908
Pr^{+++}	1.013	Ho^{+++}	.894
Nd^{+++}	0.995	Er^{+++}	.881
Pm^{+++}	.979	Tm^{+++}	.869
Sm^{+++}	.964	Yb^{+++}	.858
Eu^{+++}	.950	Lu^{+++}	.848
Gd^{+++}	.938		

We wish to thank Mrs. Helena W. Ruben who took the diffraction photographs and performed some of the calculations, and Professor B. B. Cunningham and his students who supplied us with the rare earth trichlorides and the terbium compounds. The completion of this study was aided by a John Simon Guggenheim Memorial Fellowship (to D.H.T.) and by the kind hospitality of Professor G. Hägg and the Institute of Chemistry, University of Uppsala, Uppsala, Sweden. This research was supported by the Atomic Energy Commission.

[14] D. H. Templeton and C. H. Dauben, THIS JOURNAL, **75**, 6069 (1953).

[15] D. H. Templeton and G. F. Carter, *J. Phys. Chem.*, **58**, Nov. (1954).

[16] A. Zalkin and D. H. Templeton, THIS JOURNAL, **75**, 2453 (1953).

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY OF IOWA]

Praseodymium Oxides. II. X-Ray and Differential Thermal Analyses[1]

BY E. DANIEL GUTH,[2] J. R. HOLDEN, N. C. BAENZIGER AND LEROY EYRING

RECEIVED MAY 24, 1954

This is a study of oxides of praseodymium in the composition range Pr_2O_3 to Pr_6O_{11}. X-Ray powder diagrams of quenched samples were taken in order to investigate the structures of oxides of several compositions. High temperature X-ray powder diagrams were taken for a check on the quenching procedure. Differential thermal analyses were made to further illustrate the stepwise nature of oxidation and reduction in this system. The results indicate that under equilibrium conditions oxides with hexagonal, body-centered cubic, rhombohedral or face-centered cubic lattices are stable at various compositions. As Pr_6O_{11} is reduced to Pr_2O_3 it undergoes changes in lattice from face-centered cubic to rhombohedral to body centered cubic to hexagonal. Each of these lattices is found to be stable over a range of compositions. The rhombohedral lattice has not previously been reported.

Introduction

Dissociation pressure measurements on praseodymium oxides[3] indicate that in addition to the well-known oxides, Pr_2O_3 and Pr_6O_{11}, other oxides intermediate to them exhibit stability under equilibrium conditions at particular pressures up to one atmosphere of oxygen, and temperatures up to 1050°. Many previous workers have reported Pr_2O_3 and Pr_6O_{11}, but the nature of the region between these compositions has not been clearly understood. Through the techniques of X-ray diffraction and differential thermal analysis a study of this system has been carried out to further elucidate it.

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[1] Part of the data reported here was taken from a dissertation submitted by E. Daniel Guth to the Graduate College of the State University of Iowa.

[2] Research Division, Phillips Petroleum Co., Bartlesville, Oklahoma.

[3] R. Ferguson, E. Daniel Guth and L. Eyring, THIS JOURNAL, **76**, 3890 (1954).

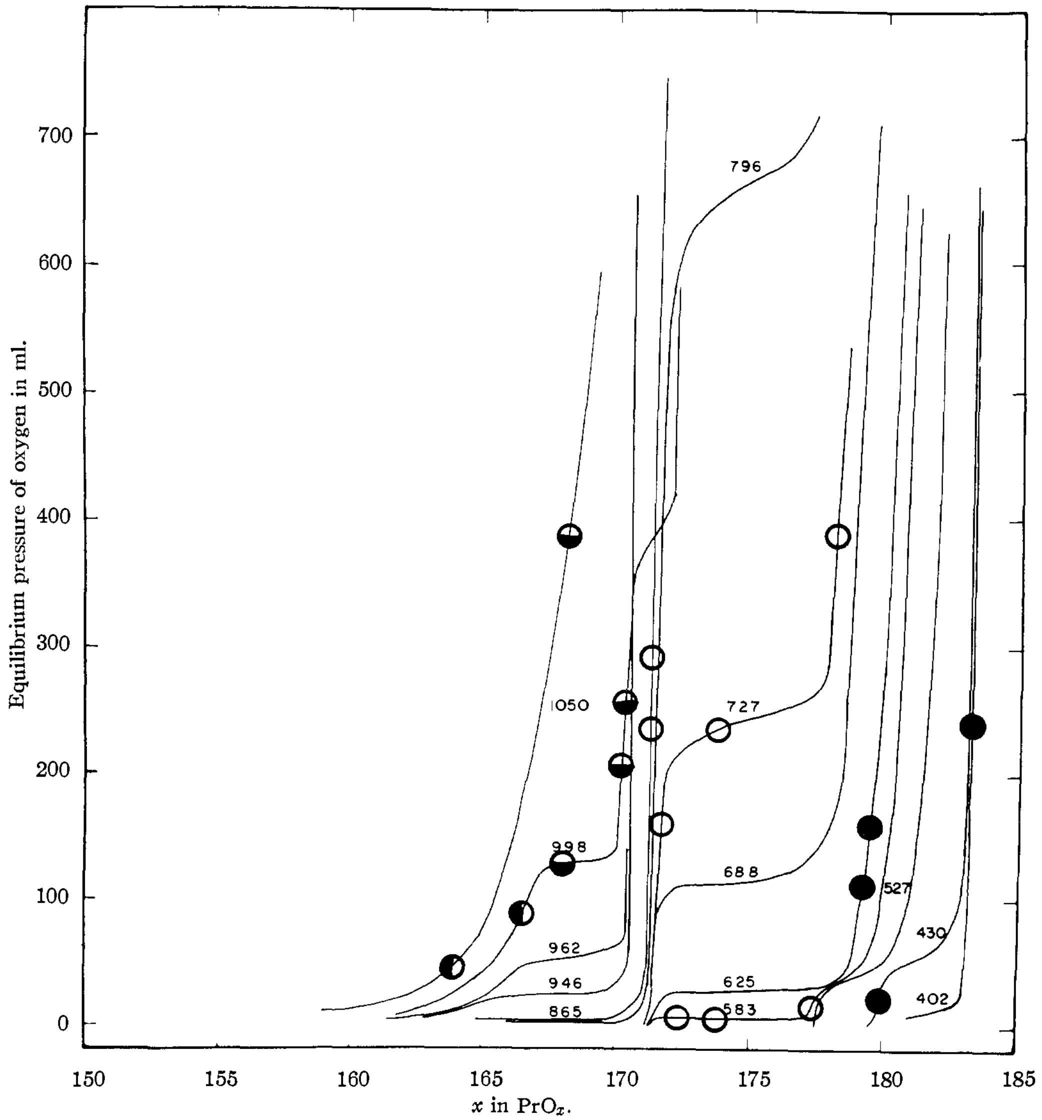

Fig. 1.—Composition of praseodymium oxide showing crystal lattice types: ●, face centered cubic; ○, rhombohedral; ⊖, body centered cubic; ◐, hexagonal.

Experimental Methods

Materials.—The $99.9^{+}\%$ Pr_6O_{11} used in these experiments, obtained from Prof. F. H. Spedding, Iowa State College, Ames, Iowa, contained no other rare earth cations in detectable amounts. The oxygen used in the preparation of quenched samples was generated from $KMnO_4$. Commercial oxygen and nitrogen were used in the differential thermal analyses.

Quenched Samples for X-Ray Analysis.—These samples were prepared in a vacuum system[3] which had a provision for maintaining oxygen over the sample at a given pressure. After degassing the sample it was heated to a given temperature which was controlled to ±0.2°. Oxygen was then admitted over the sample and the pressure adjusted to a given value. The pressure varied with time while the sample was oxidizing or reducing, but when equilibrium was reached no further change in pressure was found. After it reached equilibrium, the sample was opened to the vacuum for five seconds to pump off the gaseous oxygen. The sample was then isolated and allowed to cool to room temperature. The composition of the sample was taken as that indicated from the dissociation pressure curves.[3]

This quenching technique was justified by further experiments. The high temperature X-ray diagrams when compared to those made at low temperature showed that the structure had not changed in cooling. Gravimetric determinations of the compositions of several samples agreed excellently with the results obtained from the dissociation pressure data. Finally, X-ray powder diagrams of several samples expected to be the same structure were identical.

The X-ray diagrams were taken in a 114.6 mm. diameter camera using exposure times of about 16 hours.

High Temperature X-Ray Analyses.—The film holder of the high temperature camera was 114.6 mm. in diameter and was water-cooled by several turns of copper tubing. The collimator and exit tubes were made from stainless steel, and the slit system was made of silver. The heating was done by two hemispherical furnaces 15 mm. in internal diameter. They were wound internally with a helix of No. 26 Kanthal wire. The series connected furnaces, the resistance of which was 30 ohms, were mounted with alundum cement in short sections of alundum tube. These alundum cylinders were clamped in stainless steel collars, which were joined by a stainless steel rod, giving a gap of 7 mm. between them. This heater, the over-all height of which was six cm. was in the center of the camera. A hole through the top furnace allowed the sample to be mounted from above, and a hole through the bottom furnace allowed insertion of a Pt, Pt–10% Rh thermocouple, which had a ring of platinum welded to the junction to give a more accurate temperature indication. The thermocouple was positioned around the sample just below the X-ray beam.

The temperature was controlled to ±2°, and the uncertainty of the true sample temperature was about ten degrees.

The sample in a quartz capillary was mounted from above in such a way that it was open to the atmosphere. The pressure was therefore constant in these runs at about 150 mm. of oxygen. Pictures were taken at various temperatures up to 1050°. Exposure times up to 16 hours were used. This length of time insured equilibrium.[3] The results of these experiments were reproducible.

Differential Thermal Analyses.[4]—The Kanthal-wound furnace was a heavily insulated tube 30 cm. long and 4 cm. inside diameter. The sample block was machined from a platinum rod $^5/_8$ in. long and $^5/_8$ in. in diameter. Two parallel faces were milled on opposite sides of the cylinder. Two holes for sample wells were drilled symmetrically in one face. Perpendicular to these holes and to the axis of the cylinder two holes were drilled into the sample wells to carry the differential thermocouple which was placed so the junctions were in the center of the samples. A third hole was made above and between these to hold the control thermocouple. The thermocouples were made of Pt, and Pt–10% Rh wires. Good results were obtained when 125-mg. samples were tightly packed in the wells. The sample block was mounted at the end of an alundum tube two centimeters in diameter which could be moved in or out of the furnace without disturbing the sample. A provision was made to allow mixtures of nitrogen and oxygen to be passed through the furnace. In this way atmospheres of any partial pressure of oxygen up to one atmosphere could easily be produced.

The heating rate was controlled by an electronic controller-recorder purchased from Minneapolis-Honeywell. The output of the differential thermocouple was fed into a d.c. amplifier, and the output of this activated a Leeds and Northrup amplifier–recorder.

Several runs were made in each atmosphere to ensure reproducibility. A cooling curve was made following each heating curve in the normal heating, soaking and cooling cycle of the instrument, which operated without attention during the runs.

Results and Discussion

Figure 1 and Table I show the results of the X-ray powder diagrams on quenched samples. All cell dimensions reported here are in Å. units based on the wave lengths Cu Kα_1 = 1.5405 Å. and Cu Kα_2 = 1.5443 Å.

TABLE I

PRASEODYMIUM OXIDES, X-RAY RESULTS ON QUENCHED SAMPLES

Lattice	Temp. of preparation	Pressure of preparation, mm.	Composition (gravimetric anal.	Composition from pressure–temp.	Lattice constants, Å.
Face centered cubic	400	227		1.833	5.468 ± 0.002
	430	33	1.801	1.800	5.482 ± .003
Rhombohedral	530	21		1.780	
Rhombohedral	585	6		1.77	
Rhombohedral	585	6		1.74	
Face centered cubic	585	176		1.800	5.485 ± .002
Rhombohedral	727	199	1.717	1.715	
Rhombohedral	727	235		1.743	
Rhombohedral	727	426		1.774	
Rhombohedral	796	102		1.714	
Rhombohedral	796	141		1.714	11.02[a] α = 89°40′
Body centered cubic	998	71		1.700	11.071 ± 0.005
	998	190	1.703	1.702	11.055 ± .005
Hexagonal	998	8		1.625	a = 3.852 ± 0.002 c = 6.019 ± .003
Hexagonal	1050	47		1.640	

[a] Cell dimension not determined by analytical extrapolation method.

In Fig. 1 the large circles represent the structure of samples quenched from the conditions indicated by their position. The isothermal curves in this figure were previously reported.[3] As Pr_6O_{11} is reduced it maintains the face-centered cubic lattice to a composition $PrO_{1.78}$. From $PrO_{1.77}$ to $PrO_{1.71}$ the rhombohedral lattice is observed. There is stability at the compositions $PrO_{1.71}$ and $PrO_{1.77}$ with reversible transitions between. At temperatures near 600° $PrO_{1.77}$ is stable on reduction until low pressures are reached, and then transitions occur rapidly for small changes in the pressure. At temperatures up to 800° the transitions occur more slowly with changes in pressure, and $PrO_{1.71}$ is stable to higher and higher pressures.

The rhombohedral lattice was identified from powder diagrams. Powder diagrams of the cubic praseodymium oxides have a characteristic set of strong powder lines which arise from a basic cell of about 5.5 Å. In the rhombohedral type samples these strong powder lines were split into several closely adjacent lines which corresponded to a rhombohedral cell with a = 5.5 Å., α = 89° 40′. In addition to these stronger lines, about a dozen additional weaker lines occurred in the X-ray diagram. The weak lines could not be explained using this rhombohedral lattice nor with the lattice type for LaOF.[5] Doubling the dimensions of the cell, giving a = 11.02 Å., α = 89° 40′ permits these additional reflections to be explained. Since the cell is large and the number of weak reflections requiring this cell is small, more data are required to establish this larger cell with certainty.

The reduction of $PrO_{1.71}$ results in a change in composition to $PrO_{1.70}$ and a change in lattice from

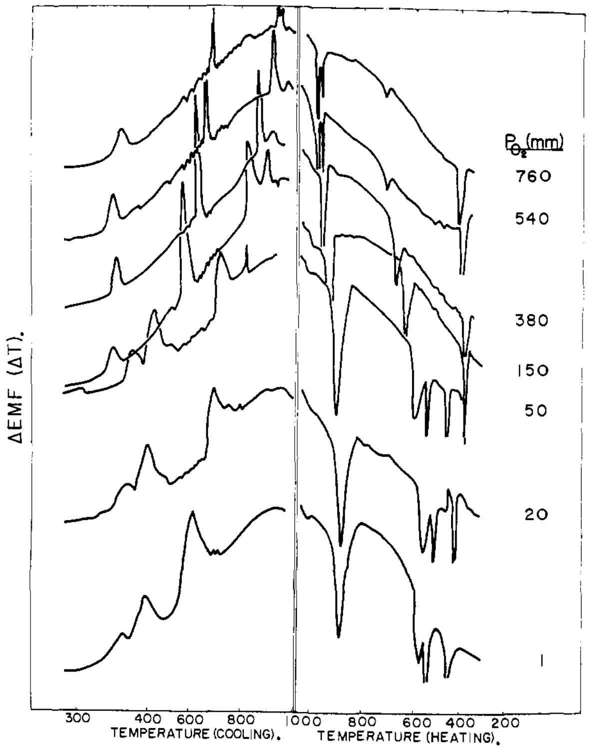

Fig. 2.—Differential thermal analysis of $PrO_{1.62-1.83}$.

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(4) L. Berkelhamer, U. S. Bureau of Mines, Technical Papers, No. 664, p. 38.

(5) W. H. Zachariasen, *Acta Cryst.*, 4, 231 (1951).

rhombohedral to body-centered cubic. At temperatures up to 1000° $PrO_{1.70}$ is stable at pressures above 120 mm. The change that occurs at lower pressures is to $PrO_{1.66}$, body-centered cubic. Further reduction results in a change to the hexagonal form at about $PrO_{1.65}$. The 1050° curve is smooth which indicates that the hexagonal form, which results at low pressures, shows no great tendency to reduce.

On the curves between 946 and 998° it is noted that the body-centered cubic structure is stable toward lower compositions at lower temperatures. Since this structure is known to be that obtained on low temperature reduction to the sesquioxide it is believed that at lower pressures, one millimeter or less, this structure is stable over to Pr_2O_3.

The values for the cell dimensions reported in Table I are calculated by an analytical extrapolation of the back reflection data.[6]

Table II is a compilation of the high temperature X-ray results.[7] It is seen that these results are completely consistent with those on quenched samples. The highest temperature attained with this apparatus was 1050° where the hexagonal phase was not observed. This structure is known to be the high temperature form of the sesquioxide and there is little doubt as to its range of stability as established by the quenched samples.

TABLE II

PRASEODYMIUM OXIDES, HIGH TEMPERATURE X-RAY RESULTS

Sample	Temp., °C.	Lattice	Cell constant
PrO 1.833	400 ± 10°	Face centered cubic	5.486 ± 0.005
PrO 1.781	688	Face centered cubic	5.526 ± 0.003
PrO 1.776	700	Face centered cubic	
PrO 1.770	720	Rhombohedral	
PrO 1.714	770	Rhombohedral	
PrO 1.700	960	Body centered cubic	11.30 ± 0.05
PrO 1.661	1050	Body centered cubic	

Pantograph reproductions of the differential thermal analysis curves are presented in Fig. 2. The main feature of these curves is the clear demonstration they give of the stepwise nature of oxidations and reductions. The curves are reproducible. The peaks corresponding to a given transition moved toward higher temperatures at higher partial pressures of oxygen. This was expected for reductions on heating and oxidations on cooling. These results agree with those obtained from the dissociation measurements.

Acknowledgment.—The authors wish to thank the Atomic Energy Commission for financial support of this work.

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[6] F. Jette and E. Foote, *J. Chem. Phys.*, **13**, 605 (1935).

[7] Some films with poor back reflection were analyzed by a graphical extrapolation method relying more heavily on forward reflection data. The uncertainties were of the same order as by the other method when they were calculated from a least squares fit of the data.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY OF IOWA]

The Terbium Oxides. I. Dissociation Pressure Measurements: X-Ray and Differential Thermal Analyses[1]

BY E. DANIEL GUTH[2] AND L. EYRING

RECEIVED MAY 24, 1954

Some oxides of terbium were investigated by dissociation pressure studies, differential thermal analyses, X-ray analyses on quenched samples and high temperature X-ray powder diagrams. It was found that the only oxides to show stability in the range $TbO_{1.5}$ to $TbO_{1.81}$ were $TbO_{1.5}$, $TbO_{1.71}$ and $TbO_{1.81}$. The body centered cubic lattice which was observed for $TbO_{1.5}$ was found to take up oxygen to about $TbO_{1.60}$. $TbO_{1.71}$ had a rhombohedral lattice, and $TbO_{1.81}$ had the CaF_2 type lattice. The changes in composition, from $TbO_{1.60}$ to $TbO_{1.71}$ and from $TbO_{1.71}$ to $TbO_{1.81}$, could not be observed at equilibrium due to the extremely slow reaction rates. No evidence was found of a stable oxide "Tb_4O_7."

Prandtl and Rieder[3] reported the preparation of $TbO_{1.81}$ by treatment of the sesquioxide with oxygen at one atmosphere pressure between 285 and 390°. Tb_4O_7 (or $TbO_{1.75}$) was reported on the basis of gravimetric data obtained on ignition in air followed by reduction of four samples. Calculations from their data show a composition varying from $TbO_{1.750}$–$TbO_{1.764}$ with an average of $TbO_{1.76}$ for these four samples. It is believed that this variation of composition is significant.

This work was undertaken to elucidate the nature of the higher oxides of terbium in view of the scant information available on this subject.

Experimental Methods

Materials.—The terbium oxide used in these experiments was purchased from the Johnson, Matthey Co., Ltd., London, as spectrographically standardized "Tb_4O_7" (Catalogue No. J. M. 314) at least 98% pure. The lines of Y, Dy, Ca, Na and Si were faintly visible and the principal impurity was gadolinium. As a preliminary treatment samples were dissolved in HNO_3, precipitated as the oxalate, ignited at 650° in air, and reduced by H_2 at 650°. The sesquioxide resulting from this treatment was used as the weighing form.

Oxygen used in the dissociation pressure studies was generated from $KMnO_4$. Tank oxygen and tank nitrogen were used in the differential thermal analyses.

Dissociation Pressure Measurements.—The method and apparatus previously described[4] were used to make these measurements. A sample, in an alundum crucible, was placed in a quartz tube which was connected to a vacuum system. The temperature of the sample was controlled at some value between 400 and 1050°. Oxygen was admitted to one part of the system and the initial pressure measured. The stopcock to the part of the system containing the sample was opened and the final pressure was measured when it was apparently constant with time. The final composition was calculated from the known volumes of the two parts of the system, the initial and final pressures, the weight of the sample, the initial composition and the ideal gas law. This procedure was repeated until

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[1] From a dissertation submitted by E. D. Guth to the Graduate College, State University of Iowa, in partial fulfillment of the requirements for the Ph.D. degree.

[2] Research Division, Phillips Petroleum Co., Bartlesville, Okla.

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

[4] R. Ferguson, E. Daniel Guth and L. Eyring, THIS JOURNAL, **76**, 3890 (1954).