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.

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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

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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).

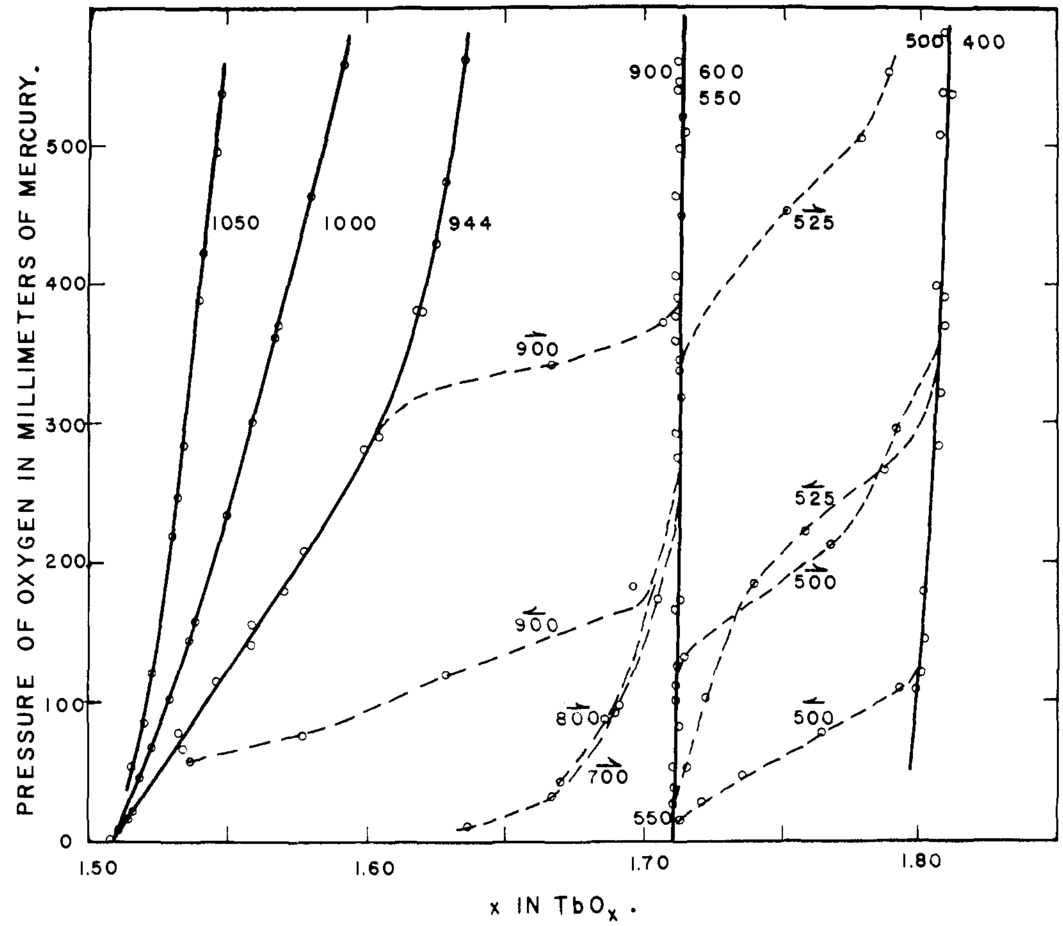

Fig. 1.—Pressure–composition diagram of the TbO$_x$–O$_2$ system.

enough points were obtained to define an isothermal curve of pressure *versus* composition. Curves were obtained at various temperatures.

The criteria for equilibrium were constant pressure and reproducibility. If the pressure was constant over the sample for one-half hour or more, it was tentatively labeled as the equilibrium pressure. If the points determined as the sample was reduced fell on the same smooth curve as those determined on oxidation, at the same temperature, the curve thus obtained was thought to represent equilibrium conditions.

X-Ray Experiments.—A standard 114.6-mm. powder camera was used to take pictures of quenched samples. The samples were prepared in the vacuum system mentioned above. The precise temperature and pressure, which were previously determined from the dissociation pressure curves (Fig. 1), were maintained until equilibrium was established.

The sample was then exposed to the vacuum for five seconds to pump off most of the gaseous oxygen, isolated again and cooled. This quenching procedure was valid because: (a) high temperature X-ray pictures showed that the structure did not change on cooling, (b) the dissociation pressure measurements indicated that the reaction rates are slow, (c) several quenched samples prepared under the same conditions gave identical powder diagrams and (d) the composition of the quenched sample as determined by gravimetric means agreed with the predicted value. Filtered copper X-radiation was used to make the 16-hour exposures.

The high temperature X-ray camera[5] used in these experiments had a 114.6-mm. film holder. Two small Kanthal wound furnaces were used to heat the samples. The samples were left open to the air; thus, the pressure over them was about 150 mm. of oxygen.

Differential Thermal Analyses.—The apparatus for differential thermal analysis has been described previously.[5] A 120-mg. sample of terbium oxide was packed into a sample cavity drilled into a platinum block.[5] Aluminum oxide was packed into an identical cavity to act as an inert sample. The differential thermocouple was mounted so that the junctions were in the center of the cavities surrounded by the tightly packed samples. Another thermocouple was placed inside a hole near the center of the block between the sample cavities to measure the temperature of the block. Both thermocouples were made of Pt and Pt–10% Rh wires. The block was heated at a constant rate under a controlled, flowing atmosphere in a tube furnace. The differential e.m.f. and the temperature of the block were recorded automatically.[5] The heating and cooling curves shown in Fig. 2 were obtained.

Results and Discussion

Figure 1 is a plot of the dissociation pressure measurements. Equilibrium curves are represented with continuous lines. Non-equilibrium points are connected by broken lines.

At temperatures above 940° the curves are completely reproducible. Oxidation or reduction yields points which are on the same curve. The highest composition on this series of curves is $TbO_{1.60}$. The curve at 900° shows a different path on oxidation than on reduction. The points were taken when the pressure appeared to be constant, but samples followed for six or seven days showed that a slow but steady change was occurring. The composition $TbO_{1.71}$ shows stability at some pressure for temperatures between 550 and 900°. $TbO_{1.}$

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[5] E. Daniel Guth, J. R. Holden, N. C. Baenziger and L. Eyring, This Journal, **76**, 5239 (1954).

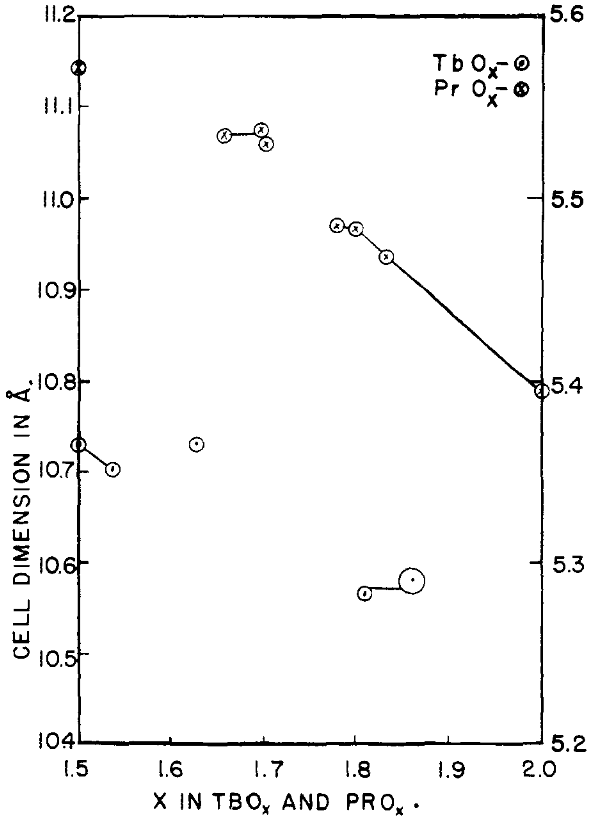

Fig. 2.—Cell dimension *vs.* composition.

is a stable composition and changes between that composition and $TbO_{1.71}$ are slow and irreversible. A slowly changing system was found to be the cause of this irreproducibility. $TbO_{1.81}$ was the highest oxide observed in these experiments.

All computations ignored the less than 2% gadolinium in the sample. If it were assumed that there was 2% of unoxidizable impurity the composition calculated would not be significantly different than given. For example, $TbO_{1.71}$ would become $TbO_{1.714}$.

The presence of less than 2% gadolinium is not believed to have a marked effect upon the extent to which the terbium is oxidized.

The X-rays results on quenched samples are listed in Table I. All cell dimensions reported here are in Å. units based on the wave lengths: Cu $K\alpha_1$ = 1.5405 Å. and Cu $K\alpha_2$ = 1.5443 Å. The results show that $TbO_{1.81}$ has the CaF_2 type lattice, $TbO_{1.71}$ has a rhombohedral lattice, and $TbO_{1.50}$ has the body centered cubic lattice. The rhombohedral lattice which was indicated on the X-ray powder diagrams of $TbO_{1.71}$ was not indexed, but is analogous to the same phase in the PrO_x system.[5] High temperature X-ray measurements were made on terbium oxides with the camera already described.[5] These experiments show that: at 400°, $TbO_{1.813}$ has a face centered cubic lattice with a = 5.368 ± 0.003 Å.; $TbO_{1.810}$ has a face centered cubic lattice with a = 5.380 ± 0.003 Å. at 550°; and at 700°, $TbO_{1.712}$ has a rhombohedral lattice. These results indicate that as $TbO_{1.81}$ is heated it retains the face centered cubic lattice up to about 525°. Above this temperature it changes to the rhombohedral lattice This change is reversible.

TABLE I

TERBIUM OXIDE, X-RAY RESULTS ON QUENCHED SAMPLES

Lattice	Composition	Lattice constant, Å.	Remarks
Body centered cubic	1.500	10.729 ± 0.006	
Body centered cubic	1.541	10.704 ± .006	Oxidized sample (non-equilibrium)
Rhombohedral	1.66		Reduced sample (non-equilibrium)
Rhombohedral	1.714		
Rhombohedral	1.74		Oxidized sample (non-equilibrium)
Rhombohedral	1.76		Reduced sample (non-equilibrium)
Face centered cubic	1.810	5.286 ± .003	

Differential thermal analyses were made on the terbium oxides at oxygen pressures of 760, 380, 150, 76 and 1 mm. The curves, although they were not as reproducible as those for the PrO_x system,[5] did show distinct peaks corresponding to the stepwise reduction and oxidation of the terbium oxide as the temperature was increased and decreased in the range 0–1050°.

Two higher oxides of terbium (rhombohedral $TbO_{1.71}$ and face centered cubic $TbO_{1.81}$) were observed under conditions where they were in equilibrium with oxygen. No evidence was found for Tb_4O_7 which has been reported by other workers. It is believed that the approximate compound, Tb_4O_7, is formed when $TbO_{1.71}$ is cooled slowly in air. The very slow reaction rate usually prevents oxidation all the way to $TbO_{1.81}$.

Figure 2 shows variation of the lattice constants of the oxides of praseodymium and terbium as the oxygen content is varied. It is composed of data reported here and data previously published.[5,6] The diameter of the circles indicates the uncertainty in the lattice constants. These parameters cannot be represented by a single smooth curve from the sesquioxide to the dioxide. There are significant changes in slope at several points. This plot does not give unambiguous compositions from measured cell dimensions.

Linear coefficients of thermal expansion have been calculated from X-ray data obtained on the praseodymium and terbium oxides. The values of $C[1_t = 1_0(1 + ct)]$ multiplied by 10^6 and considered accurate ±25% are as follows: $PrO_{1.83}$, c = 8; $PrO_{1.78}$, 11; $PrO_{1.70}$, 22; and $TbO_{1.81}$, 3.

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[6] The value for PrO_2 was reported by J. D. McCullough, THIS JOURNAL, **72**, 1386 (1950).