presence of ThI_2 means that ThO_2 is no longer a component of the system since the reaction

$$ThO_2(s) + 2ThI_2(s) = 2ThOI_2(s) + Th(s) \qquad (4)$$

is known to occur at these temperatures.[2] In this case the pressure of ThI_4 is larger and fixed by the disproportionation of ThI_2

$$2ThI_2(s) = Th(s) + ThI_4(g) \qquad (5)$$

The transport reaction now is probably governed by equilibria 5 and 6 in the hot zone followed by the same

$$ThOI_2(s) + H_2(g) = ThI_2(s) + H_2O(g) \qquad (6)$$

reverse of reaction 1 in the colder zone and at the metal

$$2HI(g) + Th(s) = ThI_2(s) + H_2(g) \qquad (7)$$

The necessary thermodynamic data for ThI_4 and ThI_2 are not available, but it will be noted that the value of K_{1000} for eq 6 will be less than the 10^{-17} calculated[9] for the couple $ThO_2(s)$–$Th(s)$. (It is assumed that neither thorium nor tantalum has a substantial effect on the hydrogen pressures in the above systems since neither absorbs hydrogen very strongly at these temperatures.) The very low P_{H_2O} so estimated is consistent with the markedly slower transport of $ThOI_2$ in the presence of thorium, the reverse of reaction 1 in the colder zone being controlling. In fact, one may question whether a different transport reaction may be involved which is insignificant in the absence of thorium. However, no direct evidence for such is available, and the addition of HI is clearly important in the presence of thorium as well.

The means by which the red and apparently slightly reduced form is colored during the transport process is by no means obvious. At the possible impurity levels indicated, a trace of a volatile, reduced thorium species could be involved although there is no direct evidence for such. No volatilization or transport of ThI_2 or ThI_3 has ever been noted in tantalum containers up to 850°.[2] The attack of these materials on glass becomes important above about 550°[2] and although vaporization of ThI_3 has been suggested to be responsible,[10] the possibility that conventional transport reactions may instead be involved has not been eliminated. On the other hand, the extremely high ratio of hydrogen to water indicated in the presence of thorium or ThI_2 suggests a slight reduction of $ThOI_2$ by very pure hydrogen. Obviously tank hydrogen is not likely to meet such a stringent water limit, but hydrogen generated from UH_3 and sealed with $ThOI_2$ in Vycor or tantalum containers which had first been baked out at 800° does not produce the coloration either. However, it is questionable whether a water content of the order of 10^{-11} ppm can be obtained in hydrogen handled under any conditions rather than generated within a closed system.

The red form of $ThOI_2$ may be compared with the blue crystals of ThO_2 which are obtained when the dioxide is heated to 1700° in hydrogen.[11] The fact that the transitions observed in ThO_2 are in part at lower energies (710 and 403 nm) than in red $ThOI_2$ suggests that the coloration mechanisms may not be very comparable. Subsequent oxidation of the blue dioxide in air at 1000° produces a tan sample with a new band at 306 nm.

Experimental Section

Materials, techniques, and analytical methods were similar to those employed earlier.[2] A reactive form of ThO_2 was prepared by heating the oxalate (a precursor of the high-purity metal) with a Meeker burner for several minutes. Reflectance spectra were secured with 100-mesh samples diluted with strongly ignited ThO_2. Data were taken from the cutoff at 216–218 nm to 1200 nm on a Beckman DU instrument with a no. 2580 reflectance attachment.

Gaseous HI for the transport studies was generated by the reaction of aqueous HI with P_4O_{10} at −78° and was further dried by condensation on P_4O_{10}. In order to avoid contamination or loss of HI during transfer to or evacuation in the tantalum welder, a 6-mm tantalum tube was electron-beam-welded to a Kovar-to-glass seal. This was then attached through a stopcock to the vacuum line for the introduction of HI and the inert atmosphere. The metal part was then crimped and the apparatus was transferred and welded while closed at the stopcock.

Acknowledgment.—The authors are indebted to Dr. D. T. Peterson for the thorium metal and oxide and for discussions on their equilibrium properties.

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High-Pressure Polymorphism and Reactions of Dysprosium Sesquioxide

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The close relationship between ionic size and the structure type assumed by the rare earth sesquioxides was first pointed out by Goldschmidt, Barth, and Lunde.[1] Recent work has provided a more detailed description of the distribution of these oxides among the three structure types A, B, and C, as a function of temperature at atmospheric pressure[2–4] and, later, as a function of pressure and temperature.[5,6]

This work was directed toward determining the *p–t* dependence of the B–C polymorphism of one of these sesquioxides over as broad a range as possible. The specific goal was the establishment of the equilibrium boundary and the general one was to seek a cross comparison of performance of various high-pressure systems.

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Experimental Methods

Most runs were made in an opposed-anvil apparatus which is described elsewhere.[7] The starting material was pressed into nickel rings of 0.25-in. o.d., 0.16-in. i.d., and 0.01-in. thickness and then enclosed by two Pt–10% Rh foils. Anvils of Rene 41 or tungsten carbide–Rene 41 combination were used to contain the samples. For runs at temperatures below 300° a modified opposed-anvil apparatus was used to apply continuously oscillating shearing stresses on the samples during the runs.[7,8] By this means, it was possible to obtain the C → B transformation of Dy_2O_3 for temperatures as low as 200°. Pressures were controlled to 0.4 kbar. As the opposed-anvil devices are limited to temperatures of less than 750°, runs above that temperature were carried out in an internally heated pressure vessel. Temperatures were maintained within ±5° by a Honeywell controller and measured by chromel–alumel thermocouples which were placed just beside the sample. The duration of runs varied from 115 hr at 300° to 4 hr at 1100°. All runs were quenched under constant pressure and the reaction products were identified on a Norelco diffractometer. In all runs, Dy_2O_3 in the C form was used as the starting materials.

Results

Figure 1 summarizes results of the experiments. The boundary C–B is determined by the first appearance of B-Dy_2O_3 in the quenched reaction product, with the results obtained above 500° being given more weight than those at lower temperatures. This is consistent with our experience where the sluggishness of phase transitions of oxide or other systems tends to require higher than equilibrium pressures to cause noticeable reaction at lower temperatures. An example indicating relationships between the progress of reaction and excess pressure over equilibrium values is given elsewhere.[8] That the boundary approximates the equilibrium position is supported by (1) the reversal reaction experiments and (2) the fact that, on extrapolation to atmospheric pressure, the transition temperature of 2155° falls in with recently reported values. These are 1900,[3] 2000,[4] 2150,[2,9] and 2300°.[10] Obviously, experimental details are influencing the transition temperature so that at this time the true value is in doubt.

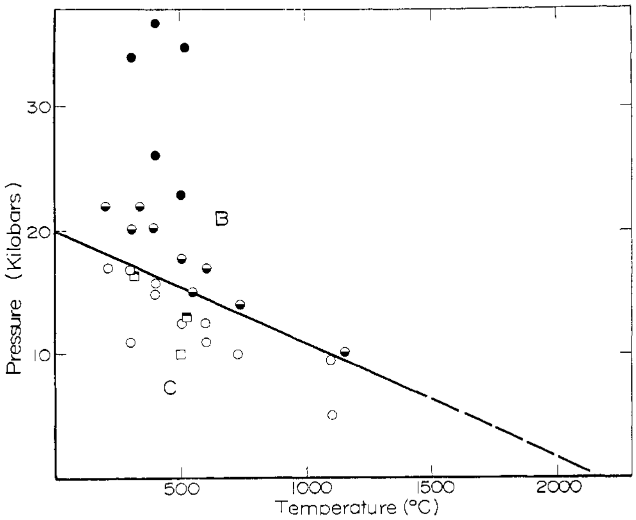

Figure 1.—The p–t equilibrium boundary between the B and C phases of Dy_2O_3. Open circles represent the C phase as product; filled circles, the B phase. Squares represent results of transition reversals. See text.

The figure shows that to convert C completely to the B form it was necessary to apply pressures at least 6–8 kbars higher than indicated by the transition boundary. A similar finding with other rare earth sesquioxides has been reported.[5] The reversal reactions were done by completely converting C-Dy_2O_3 into the B form at about 500° and 30 kbars and subsequently by changing conditions to a point below the phase boundary whereupon complete or almost complete conversion of B to C took place depending on the time allowed for the reaction.

As indicated above, the C–B boundary shows the consistency of results obtained with three methods necessary to cover a temperature range of almost 2200°. Further, a 1000° isotherm, determined in a large tetrahedral press utilizing solid pressure media, places the equilibrium pressure for the C–B transformation of Dy_2O_3 at slightly more than 10 kbars.[5] This is in good agreement with the boundary plotted from our data which gives a pressure of 10.8 kbars at 1000°.

The potential usefulness of p–t equilibrium data of materials such as Dy_2O_3 if utilized as internal calibrants in complex and varied high-pressure systems is to be noted.

High-Pressure Phases Encountered.—The d spacings and relative intensities obtained from the X-ray powder diffractometer traces for B-Dy_2O_3 are given in Table I. All but three of the d values could be indexed on a monoclinic cell with the use of a computer program. The lattice parameters determined from these data are $a = 13.97_2$, $b = 3.51_2$, and $c = 8.65_7$ Å and $\beta = 99° 54'$, in close agreement with the values given by Hoekstra.[5]

During an early stage of this study, many runs were carried out with the addition of water or solutions of NH_4Cl. Two new phases were prepared. The d spacings and relative intensities of their X-ray diffraction lines are also given in Table I.

In the system Dy_2O_3–H_2O, DyOOH was crystallized over a broad p–t range. At 5 kbars DyOOH appeared to be stable to temperatures as high as 1100°. The evidence that it is DyOOH lies in the very close agreement of its X-ray powder diffraction pattern with that of YOOH.[11]

The addition of NH_4Cl to the system Dy_2O_3–H_2O resulted in the crystallization of a phase (or mixture of phases) which has not been identified.

Thermochemical Considerations.—Dy_2O_3 displays the not uncommon condition that a denser modification is stable at higher temperatures than that with lower density, which results in a negative dp/dt slope for the

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TABLE I

HIGH-PRESSURE PHASES

B-Dy_2O_3		DyOOH		Crystallized in NH_4Cl soln[a]	
d, Å	I/I_0	*d*, Å	I/I_0	*d*, Å	I/I_0
3.115	75	5.68	100	5.47	25
3.076	45	4.067	30	3.985	10
2.998	85	3.978	50	3.907	10
2.935	75	3.904	15	3.203	100
2.842	70	3.076	95	3.078	20
2.788	100	2.894	80	2.987	15
2.720	80	2.862	05	2.884	10
2.172	20	2.837	65	2.850	10
2.104	35	2.792	65	2.792	60
1.899	45	2.724	30	2.726	25
1.760	20	2.698	50	2.694	10
1.738	20	2.244	60	2.272	15
1.679	30	2.202	10	2.245	35
1.631	30	2.152	30	1.975	25
		2.036	20	1.953	30
		1.891	55	1.778	10
		1.867	15	1.762	10
		1.782	55	1.681	30
		1.748	25	1.653	10
		1.741	45	1.597	10
		1.683	10		
		1.577	20		
		1.556	20		

[a] See text.

equilibrium curve. This has been noted generally for the rare earth sesquioxides.[5] Figure 1 shows that the equilibrium curve for the C–B transformation of Dy_2O_3 is a straight line within the experimental error. The equilibrium pressure is lowered by slightly less than 9.3 bars/deg. The calculated molar volume difference of the two phases at room conditions is 3.66 cm^3. If constancy of ΔV is assumed over the p–t range in question ΔH must vary considerably with temperature in accordance with the Clapeyron equation. At atmospheric pressure, the phase change takes place at about 2150° with a calculated ΔH of almost 2 kcal/mol and an entropy change of 0.8 eu.

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Kinetics of the Incorporation of Copper(II) into a Water-Soluble Porphyrin

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Kinetic studies of the incorporation of divalent metal ions (M(II)) into porphyrin molecules (PH_2) to form metalloporphyrins ($M^{II}P$) (reaction 1) have shown that

$$M(II) + PH_2 \longrightarrow M^{II}P + 2H^+ \qquad (1)$$

a multiplicity of factors determines the rates and rate laws observed. In general, increasing the basicity of the porphyrin,[1] substituting anionic for cationic or neutral detergents,[2] and increasing the number of ionized carboxylic acid functions on the porphyrin[3] increase the rate of metal ion incorporation. The effects of complexing[4] M(II) and changing its geometry have been investigated.[5]

Four types of rate laws have been observed: R_1[2] $= k_1(M)(PH_2)$, R_2[5] $= k_2(M)(PH_2)/(H^+)$, R_3[6] $= k_3(M)^2 \cdot (PH_2)/(H^+)$, and R_4[7] $= [k_4(PH_2)/(H^+)] + [k_4'(M) \cdot (PH_2)(\text{pyridine})/(H^+)]$. Although R_1 may be a special case of R_2, the aims of a particular investigation have precluded a demonstration that this is true for most porphyrins. R_3 involves a "sitting atop" mechanism and has only appeared with *meso*-tetrapyridylporphine in aqueous solution.[6] (The addition of acetic acid to this porphyrin solution gives rise to R_2 behavior.) R_4 involves a pyridine catalysis of Mg(II) incorporation into deuteroporphyrin in buffered methanol solutions. A central problem is the origin of the 1/(H) terms in R_2, R_3, and R_4. Porphyrins can formally exist in diacid (PH_4^{2+}), monocation (PH_3^+), free base (PH_2), and monoanion (PH^-) forms. In R_2 and R_3, there is no evidence for PH_3^+ or PH^-; thus the $1/(H^+)$ term was tenatively ascribed[5,6] to either a metal ion hydrolysis or an unspecified porphyrin–proton preequilibrium. In R_4, the reactant was stated to be the free base (PH_2), with the rate-determining step involving either PH_2 or PH^-, which were kinetically indistinguishable.[7]

We report the kinetics of the incorporation of Cu(II) into deuteroporphyrin IX 2,4-disulfonic acid dimethyl ester[8] in buffered aqueous solutions. Neuberger and Scott[9] have shown this porphyrin to be monomeric and to exist as PH_4^{2+}, PH_3^+, and PH_2. We present evidence that the $1/(H^+)$ term in this reaction arises from a porphyrin rather than from a metal ion preequilibrium, with the rate-determining step involving the free base (PH_2).

Experimental Section

Deuteroporphyrin IX 2,4-disulfonic acid dimethyl ester[10] was prepared from deuteroporphyrin IX dimethyl ester[11] and N-pyridinium sulfonic acid and purified by column chromatography.[12] The extinction coefficients agreed with literature values.[12] The kinetics were followed at 625.6 mμ at 25° on a Cary Model 14 recording spectrophotometer with a thermostated cell compartment. The ionic strength was maintained at 0.5 with sodium perchlorate using $\mu = 0.1$ acetic acid–sodium acetate to adjust the pH. The reactions were run with an excess amount of metal ion to porphyrin. The pseudo-first-order rate constant k_{obsd} was obtained from ln ($D_t - D_\infty$) *vs.* time plots. D_∞

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