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### Terbium Oxides. III. X-Ray Diffraction Studies of Several Stable Phases

BY N. C. BAENZIGER, H. A. EICK, H. S. SCHULDT AND L. EYRING

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A previous study<sup>1</sup> involving tensiometric measurements, differential thermal analysis and cursory X-ray diffraction analysis revealed intermediate stable phases in the terbium-oxygen system between the sesquioxide<sup>2,3</sup> and the dioxide.<sup>4</sup> Previously, many observations of a brown higher oxide of terbium had been made and the formula  $Tb_4O_7$  had been given to it.<sup>5-7</sup> Work done in these Laboratories,<sup>1,8</sup> however, failed to reveal any special stability for a composition  $TbO_{1.75}$ , and it is believed to arise from a slow oxidation of a lower oxide when the latter is cooled in air or oxygen. The present work was undertaken to clarify the various stable phases existing in this oxide system using previous work as a guide in sample preparation.

#### Experimental Part

**Materials.**—The terbium (99.9+ % pure) was obtained from Dr. F. H. Spedding, Ames Laboratory of the U.S.A.E. C., as oxide. Reagent grade chemicals were used in the dissolution of these oxides, precipitation of terbium as the oxalate and other procedures in the preparation of fresh oxides. Commercial tank oxygen was used to prepare the higher oxides.

**Preparation of Samples.**—Specimens with oxygen content not greater than  $TbO_{1.827}$  were made using molecular oxygen. Compositions between  $TbO_{1.827}$  and  $TbO_{1.81}$  were prepared in an autoclave operating under an oxygen pressure of up to 600 atmospheres and a temperature up to 425°. For compositions below  $TbO_{1.81}$ , the oxides were treated in a platinum lined reactor<sup>9</sup> capable of operation at 10 atmospheres at 1100° or in an apparatus<sup>10</sup> incorporating an automatic recording thermobalance.

Samples with oxygen content greater than  $TbO_{1.83}$  were made by treatment with atomic oxygen in a discharge tube.<sup>4,11</sup>

All samples were cooled as rapidly as the apparatus would permit after the desired composition had been reached. No appreciable weight change occurred in those experiments where analyses could be made. Previous observations<sup>1</sup>

imply that no new phases are introduced in this quenching procedure.

The composition of the oxides was always determined by observing the weight loss between the oxidized material exposed to oxygen as described above and the sesquioxide. The sesquioxide is formed by reduction of a higher oxide with hydrogen at 650° for 15 hr.

**X-Ray Analysis.**—Powder diagrams were obtained in a 114.6 mm. Norelco powder camera. Diffractometer traces were produced using a Norelco diffractometer. Iron radiation ( $\lambda_{\alpha_1} = 1.93597 \text{ \AA.}$ ,  $\lambda_{\alpha_2} = 1.93991 \text{ \AA.}$  and  $\lambda_{\beta} = 1.75654 \text{ \AA.}$ ) was produced by a General Electric XRD5 unit.

#### Results and Discussion

Figure 1 shows the phases which have been identified in the terbium-oxygen system in this study.  $TbO_{1.500}$  prepared by reduction in  $H_2$  as described above is a body-centered cubic structure ( $a = 10.7281 \pm 0.0005 \text{ \AA.}$ ) with only a small range of solid solution. It has the  $Mn_2O_3$  (bixbyite) structure and is isostructural with many other rare-earth sesquioxides. The bixbyite structure results from the ideal fluorite type structure upon the ordered removal of one-fourth of the oxygens from eight unit cells of the parent fluorite type. A sample melted on a tungsten strip in high vacuum was observed to be the monoclinic B type.

As oxygen is added to the b.c.c. material, a second phase of composition  $TbO_{1.715}$  appears. There is a miscibility gap between these phases at temperatures as high as 750°. Neither phase shows an appreciable range of solid solution. The X-ray diffraction pattern of this phase is very similar to that for a face-centered cubic fluorite-type phase except that some of the lines have split into

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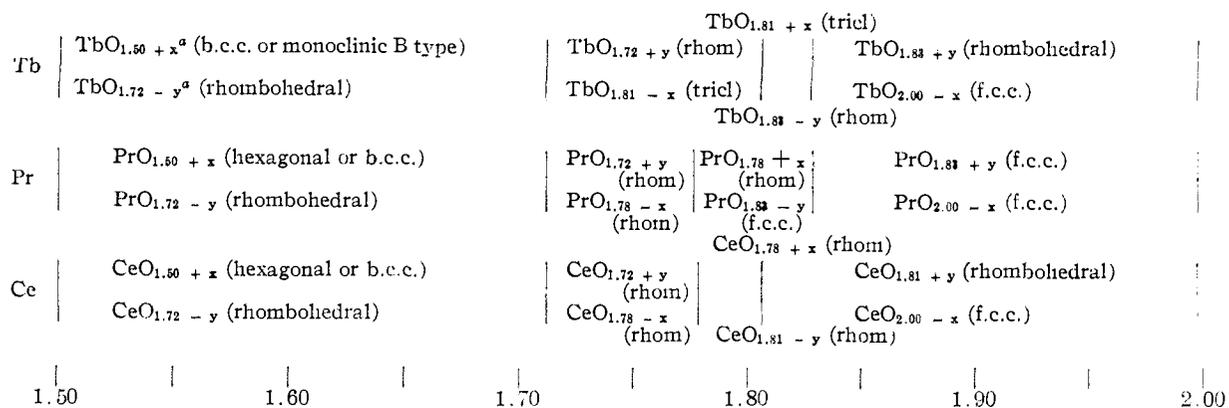


Fig. 1.—Schematic representation of the regions of stability in some rare earth-oxygen systems. The symbols  $x$  and  $y$  are to signify a range of composition which is dependent on both composition and temperature.

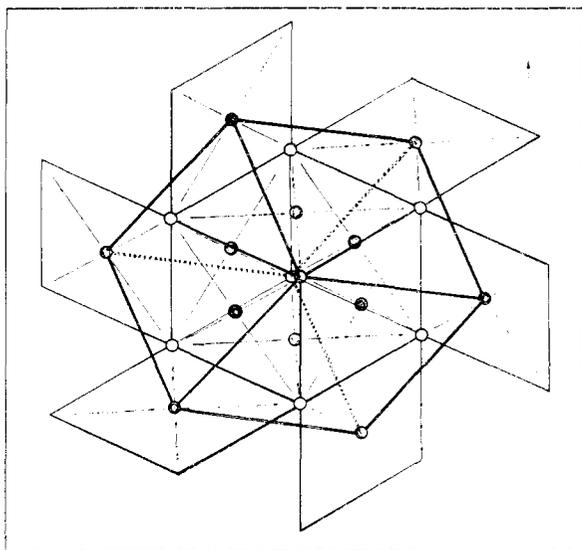


Fig. 2.—Rhomboidal cell of  $\text{Tb}_7\text{O}_{12}$ . The cell is outlined with rods; the shaded circles represent Tb atoms associated with the rhomb. cell.

doublets or triplets and a few additional weak lines occur. The splitting of the fluorite-type lines can be accounted for on the basis of a rhomboidal pseudo cell,  $a_0 = 5.319 \pm 0.001 \text{ \AA}$ ,  $\alpha = 89^\circ 41.2'$ , which is only a slight distortion of the ideal fluorite type cell. In order to account for the weak additional lines, the rhomboidal cells (and their related hexagonal cells) listed in Table I were considered. In this table, only the  $a'$  axis is given; the  $b'$  and  $c'$  axes may be obtained by cyclic permutation of  $a$ ,  $b$  and  $c$  in  $a'$ . The smallest cell which will explain the weak reflections has  $a' = a - b/2 + c/2$ ,  $b' = a/2 + b - c/2$ ,  $c' = -a/2 + b/2 + c$ , with a volume  $7/4$  times the fluorite unit cell. Table II shows the comparison of the observed  $1/d^2$  values with those calculated on the basis of this cell with  $a = 6.509 \pm 0.002 \text{ \AA}$ ,  $\alpha = 99^\circ 21' \pm 0.5'$ . The relationship of this unit cell to the fluorite cell is shown in Fig. 2. The ideal rhomboidal angle is  $99^\circ 36'$ .

The rhomboidal cell would contain 7 terbium atoms and 14 oxygen atoms if the composition were  $\text{TbO}_2$  and the structure were the ideal fluorite structure. Removal of two oxygen atoms along the three-fold axis of the cell would destroy the

cubic symmetry and allow the rhomboidal distortion which is observed. The cell contents now become  $\text{Tb}_7\text{O}_{12}$  or  $\text{TbO}_{1.714}$ , in excellent agreement with the analytical determination of the composition.

TABLE I

Cell axes <sup>a</sup> based on the cubic $\text{CaF}_2$ axes	Number of M atoms/cell	Cell axes <sup>a</sup> based on the cubic $\text{CaF}_2$ axes	Number of M atoms/cell
$a'$		$a'$	
$a/2 + b/2$	1	$a - b + c$	16
$a + b/2 + c/2$	2	$3a/2 - b + c/2$	19
$a$	4	$2a + b + 2c$	20
$3a/2 + b + 3c/2$	4	$2a - b/2 - c/2$	25
$2a + 3b/2 + 3c/2$	5	$3a/2 - b/2 + c$	26
$a - b/2 + c/2$	7	$5a/2 + 3b/2 + c$	26
$5a/2 + 5b/2 + 2c$	7	$2a + b/2 + c/2$	27
$a + b$	8	$3a/2 + 3c/2$	27
$3a + 5b/2 + 5c/2$	8	$3a/2 + b/2 + 2c$	28
$3a/2 + b + c/2$	9	$2a - b$	28
$5a/2 + 3b/2 + 2c$	9	$3a + 2b + 2c$	28
$3a/2 - b/2$	13	$a - 3b/2 + 3c/2$	31
$3a/2 + c/2$	14	$2a$	32
$2a + b + c$	16	$3a + 3b + 2c$	32

<sup>a</sup>  $b'$  and  $c'$  axes may be obtained by cyclic permutation of the  $a$ ,  $b$  and  $c$  of  $a'$ .

If monophasic  $\text{TbO}_{1.715}$  is further treated with oxygen, a new phase appears which becomes the only phase observed at a composition of  $\text{TbO}_{1.81}$ . A miscibility gap between  $\text{TbO}_{1.71}$  and  $\text{TbO}_{1.81}$  is present at temperatures below  $450^\circ$ . X-Ray diffractometer patterns show that the fluorite type lines are split in a different way. The fact that the cubic (111), (220) and (222) lines are split into three lines whereas (200) and (400) remain as single lines eliminates distorted cells based on the rhomboidal system or mixtures of rhomboidal phases with different cell dimensions. A possible triclinic cell which explains the splitting of the lines reasonably well, both in position and in a relative intensity (due to multiplicity alone), as shown in Table III, has the dimensions  $a = b = c = 5.286 \pm 0.001 \text{ \AA}$ ,  $\alpha = \beta = 89^\circ 25'$ ,  $\gamma = 90^\circ$ . (A tetragonal cell with  $a' = \sqrt{2} a/2$ ,  $c' \approx 98a$  or an end-centered monoclinic cell with  $a' = b + c$ ,  $b' = b - c$ ,  $c' = -a'$ , is equivalent to this triclinic cell.) Not all of the splitting is well resolved at higher angles in the diffractometer patterns. The triclinic cell

TABLE II  
OBSERVED AND CALCULATED  $1/d^2$  VALUES FOR  $Tb_7O_{12}$  ( $TbO_{1.714}$ )  
 $1/d^2 = 0.025197(h^2 + k^2 + l^2) + 0.009770(hk + kl + hl)$   
 $a_0 = 6.509 \pm 0.002 \text{ \AA.}, \alpha = 99^\circ 21' \pm 0.5'$

Intensities <sup>a</sup>	Indices	$1/d^2$		Intensities <sup>a</sup>	Indices	$1/d^2$	
		Calcd.	Obsd.			Calcd.	Obsd.
	100	0.02520			4 $\bar{1}1$	0.44371	
	1 $\bar{1}0$	.04062		vw	321	.46022	0.45931
vw	110	.06015	0.06005		3 $\bar{3}2$	.46639	
	1 $\bar{1}1$	.06581			410	.46743	
	200	.10078			4 $\bar{2}1$	.47051	
	111	.10490			422	.48748	
s	2 $\bar{1}0$	.10644	.10656		33 $\bar{1}$	.50805	
	2 $\bar{1}1$	.12187			4 $\bar{3}0$	.51267	
m	2 $\bar{1}1$	.14141	.14143		33 $\bar{2}$	.52501	
vw	210	.14551	.14551		431	.52810	
	2 $\bar{2}0$	.16249			411	.54147	
vw	2 $\bar{2}1$	.18769	.18779		43 $\bar{1}$	.54764	
	211	.20004		vw	42 $\bar{1}$	.54866	.54823
	3 $\bar{1}0$	.22266		vw	422	.56563	.56590
	300, 22 $\bar{1}$	.22677			420	.58210	
	3 $\bar{1}1$	.22831			322	.58467	
	220	.24066		vw	5 $\bar{1}1, 333$	.59238	.59244
	2 $\bar{2}2$	.26327			432	.59392	
	3 $\bar{2}0$	.26893			510	.60626	
	3 $\bar{1}1$	.27805		vw	331	.62528	.62514
m	310	.28128	.28152		521	.62889	
m	3 $\bar{2}1$	.28436	.28461		500	.62991	
vw	3 $\bar{2}1$	.30389	.30365	vw	520, 432	.63300	.63303
	221	.30494			440	.64996	
	311	.34555			421	.66591	
	3 $\bar{2}2$	.35018		nw	5 $\bar{1}1$	.67054	.66990
	32 $\bar{1}$	.36252		mw	441	.67516	.67494
	330	.36561			521	.68750	
	411	.38515		mw	510	.70397	.70414
	320	.38617			530, 433	.71013	
m	410, 3 $\bar{2}2$	.38926	.38913	nw	432	.71117	.71066
m	331	.39081	.39057		531	.71578	
	400	.40315			430	.74715	
	222	.41959			531	.75486	
w	420	.42577	.42538				
vw	421	.43143	.43122				

<sup>a</sup> Symbols used (in decreasing intensity): s = strong, ms = medium strong, m = medium, mw = medium weak, w = weak, vw = very weak, vvw = very very weak.

permits additional weak reflections to occur (omitted for simplicity from Table III) which were not observed in the diffractometer patterns. Weak reflections were observed in Debye-Scherrer films but with insufficient accuracy to determine the true unit cell. On the premise that an ordered removal of oxygen atoms from the parent fluorite structure is responsible for this phase, the simplest stoichiometry corresponding to the triclinic phase is  $Tb_{16}O_{29}$  or  $TbO_{1.812}$ .

Oxides obtained by treatment in an autoclave were either a pseudo-triclinic  $TbO_{1.81}$  or a pseudo-rhombohedral phase depending on whether the resulting composition was less or greater than  $TbO_{1.82}$ . The absence of observations of two phases in any one sample must be due to the small composition change and the proximity of lines from each phase. The phase of highest oxygen composition obtained in these experiments with molecular oxygen is  $TbO_{1.827}$ . Diffractometer patterns

have been indexed as a rhombohedral pseudo cell with  $a = 5.283 \pm 0.001 \text{ \AA.}, \alpha = 89^\circ 41'$ . A comparison of calculated and observed  $1/d^2$  values is shown in Table IV. It is reasonable to expect that this cell is also associated with a specific stoichiometry, corresponding to the ordered removal of oxygen atoms from the ideal fluorite structure. Possible metal-oxygen ratios based on rhombohedral cells derived from the fluorite structure are listed in Table V. Although  $Tb_{28}O_{51}$  corresponds to the experimental composition, additional weak lines, absent in the diffractometer traces and extremely weak Debye-Scherrer films, could not be reliably explained by that unit cell.

Specimens obtained from treatment with atomic oxygen show a fluorite lattice with an average composition of  $TbO_{1.95}$  and  $a = 5.220 \pm 0.001 \text{ \AA.}$

Table VI summarizes the results of the X-ray analyses. Five distinct phases of considerable stability and with only limited solid solution have

TABLE III

OBSERVED AND CALCULATED  $1/d^2$  VALUES FOR  $TbO_{1.809}$   
 $1/d^2 = (h^2 + k^2 + l^2)(0.035785) + (2kl + 2hl)(0.000358)$   
 $a = b = c = 5.286 \pm 0.001 \text{ \AA.}, \alpha = \beta = 89^\circ 25', \gamma = 90^\circ$

Intensities <sup>a</sup>	Cubic indices	Triclinic indices	$1/d^2$ Calcd.	$1/d^2$ Obsd.
ms		11 $\bar{1}$	0.10592	0.10580
s	111	1 $\bar{1}$ 1, 111	.10736	.10720
ms		111	.10879	.10866
ms	200	200	.14314	.14314
111		20 $\bar{2}$ , 02 $\bar{2}$	.28341	.28313
ms	220	220, 220	.28628	.28618
111		202, 022	.28915	.28898
		11 $\bar{3}$	.38933	
		31 $\bar{1}$ , 13 $\bar{1}$	.39077	
111		3 $\bar{1}$ 1, 13 $\bar{1}$	.39220	.39246
	311	1 $\bar{1}$ 3, 11 $\bar{3}$	.39363	
m		3 $\bar{1}$ 1, 131	.39507	.39461
		311, 131	.39650	
		113	.39793	
w		22 $\bar{2}$	.42369	.42337
mw	222	222, 222	.42942	.42939
w		222	.43515	.43524
m	400	400	.57256	.57254
w		13 $\bar{3}$ , 31 $\bar{3}$	.67132	.67065
mw		33 $\bar{1}$ , 133, 313	.67561	.67549
	331	331, 331	.67991	
mw		133, 331, 313	.68422	.68380
		133, 313	.68851	
mw		042, 024, 402, 204	.70997	.70973
m	420	420, 240, 420, 240	.71570	.71568
mw		402, 042, 204, 024	.72143	.72056

<sup>a</sup> Symbols used same as in Table II.

TABLE IV

OBSERVED AND CALCULATED  $1/d^2$  VALUES FOR  $TbO_{1.823}$   
 $1/d^2 = 0.35838(h^2 + k^2 + l^2) - 0.0004023(hk + kl + hl)$   
 $a = 5.283 \pm 0.001 \text{ \AA.}, \alpha = 89^\circ 41'$

Intensities <sup>a</sup>	Indices	$1/d^2$		Intensities <sup>a</sup>	Indices	$1/d^2$	
		Calcd.	Obsd.			Calcd.	Obsd.
ms	111	0.10631	0.10613	mw	33 $\bar{1}$	0.67972	0.67862
s	111	.10774	.10768	m	331	.68453	.68363
ms	200	.14335	.14310	mw	420	.71355	.71281
m	220	.28510	.28512	mw	420	.71999	.71935
m	220	.28832	.28838	w	422	.85209	.85115
mw	311	.39142	.39165	m	422	.86173	.86128
m	311	.39462	.39521	m	422	.86495	.86392
	311	.39623			333	.95679	
w	222	.42524	.42547	w	511	.96323	.96304
w	222	.43167	.43131	m	511	.96804	.96713
m	400	.57342	.57326	m	333, 311	.97126	.97022
mw	331	.67493	.67441				

<sup>a</sup> Symbols same as in Table II.

been observed in the terbium-oxygen system. They are  $TbO_{1.500}$ ,  $TbO_{1.715}$ ,  $TbO_{1.81}$ ,  $TbO_{1.83}$  and  $TbO_{2.0}$ . In addition, monoclinic B type  $TbO_{1.5}$  has been observed in a melted sample. The phases at the extremes in composition have structures of high symmetry, the intermediate phases show lower symmetry with the least symmetrical phase having the composition  $TbO_{1.81}$ . Miscibility gaps are observed in the lower composition range and are implied at higher compositions.

It should be understood that the terbium-oxygen system is quite sluggish, and hence true equilibrium probably has not often been achieved in these

TABLE V

STOICHIOMETRIES BASED ON RHOMBOHEDRAL UNIT CELLS

Metal	Oxygen	Ratio	Metal	Oxygen	Ratio
4	7	1.750	25	43	1.720
5	9	1.800	25	44	1.760
7	12	1.714	25	46	1.840
7	13	1.857	26	45	1.731
8	13	1.625	26	47	1.808
8	15	1.875	27	46	1.704
9	16	1.778	27	47	1.741
9	17	1.889	27	49	1.815
13	22	1.692	27	50	1.852
13	23	1.769	28	51	1.821
13	24	1.846	31	53	1.710
14	25	1.786	31	54	1.742
16	27	1.687	31	55	1.774
16	29	1.812	31	56	1.806
19	33	1.737	31	57	1.839
19	34	1.789	32	55	1.719
19	35	1.842	32	57	1.781
20	34	1.700	32	59	1.844
20	37	1.850			

TABLE VI

SUMMARY OF CRYSTALLOGRAPHIC RESULTS ON THE TERBIUM-OXYGEN SYSTEM

Com-position	Major phase	Minor phase
$TbO_{1.500}$	Body centered cubic $a = 10.7281 \pm 0.0005 \text{ \AA.}$	
$TbO_{1.601}$	Body centered cubic $a = 10.7281 \pm 0.0005 \text{ \AA.}$	Rhombohedral $a' = 6.509 \pm 0.002 \text{ \AA.}$ $\alpha = 99^\circ 21' \pm 0.5'$
		Pseudo-cell $a = 5.319 \pm 0.001 \text{ \AA.}$ $\alpha = 89^\circ 41.2'$
$TbO_{1.715}$	Rhombohedral $a' = 6.509 \pm 0.002 \text{ \AA.}$ $\alpha = 99^\circ 21' \pm 0.5'$	
	Pseudo-cell $a = 89^\circ 41.2'$	
$TbO_{1.760}$	$TbO_{1.715}$ (rhombohedral)	$TbO_{1.81}$ (triclinic)
$TbO_{1.809}$	Pseudo-cell Triclinic $a = b = c = 5.286 \pm 0.001 \text{ \AA.}$ $\alpha = \beta = 89^\circ 25', \gamma = 90^\circ$	
$TbO_{1.823}$	Pseudo-cell Rhombohedral $a = 5.283 \pm 0.001 \text{ \AA.}$ $\alpha = 89^\circ 41'$	
$TbO_{1.95}$	Face centered cubic $a = 5.220 \pm 0.001 \text{ \AA.}$	

studies. Temperatures in excess of  $1100^\circ$  probably would be required to obtain rapid equilibrium and then an enormous oxygen pressure would be needed to observe the higher oxides.

Figure 1 shows the interrelation of the phases found in the terbium, praseodymium<sup>9,12,13</sup> and the cerium oxide<sup>13,14</sup> systems. Although this may not show all the intermediate phases in the latter two systems, the appearance of the  $MO_{1.715}$  phase in all three is striking. It has been determined<sup>15</sup> that the  $PrO_{1.715}$  phase is isostructural with  $TbO_{1.715}$ . It is also notable that a  $MO_{1.78}$  phase has been observed in the praseodymium and cerium-oxygen

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(13) G. Brauer and H. Gradinger, *Z. anorg. u. allgem. Chem.*, **277**, 89 (1954).

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systems. (This rhombohedral phase probably has the formula  $M_9O_{16}$ , as suggested by the possible values in Table V.) A  $MO_{1.81}$  phase occurs in the terbium and cerium oxygen systems, and a  $MO_{1.83}$  phase is found in the terbium and praseodymium systems. The latter phases are not isostructural. The  $TbO_{1.83}$  phase has a rhombohedral cell and the  $PrO_{1.83}$  has a face-centered-cubic unit cell. Whether or not there are miscibility gaps between the various phases or homogeneous ranges of composition depends primarily upon the temperature and the oxygen pressure.

A notable omission is a stable  $M_4O_7$  phase in any of the three systems. This phase frequently has been reported for the terbium and cerium systems, but the studies reported and summarized have not given any evidence of special significance for such a stable solid phase. An important group of mixed oxides of formula  $M_4O_7$  recently have been described and named for the mineral Pyrochlore.<sup>16,17</sup>

Many studies have been made during the last decade<sup>18-20</sup> on mixed oxide phases of fluorite type with oxygen vacancies. It is not at present clear how the truly binary oxides discussed above compare with the pseudo binary mixed oxides. It will be important to know if the mixed oxides reported as solid solutions of the fluorite type are really that or if, when properly annealed, they show a tendency toward ordering of oxygen vacancies as demonstrated in the true binary oxide phases reported here. In this respect, it will be necessary to carry out the studies at temperatures where cation mobility is appreciable. Cation mobility is not required in the truly binary systems since electron movement will accomplish the same effect.

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(20) G. Brauer and H. Gradinger, *Z. anorg. u. allgem. Chem.*, **276**, 209 (1954).

In all these systems, anion mobility is very high at the temperatures at which the experiments were carried out but cation mobility very low.

It seems apparent that there are many ways of ordering vacancies in these materials and simple analogy will not be enough to be sure in any particular case. In some cases, the vacancies are reported as randomly arranged.<sup>21-23</sup> In these, it would be particularly important to study the electrical properties of the solids.

It has been suggested<sup>24</sup> that the oxygen deficiency in structures such as these may result from the formation of surfaces of discontinuity by a shear mechanism. In this way, the oxygen loss would be accommodated without the appearance of vacancies, as such, in the lattice. Structures of this type already have been solved, for example, in the  $(Mo, W)_nO_{2n-1}$ ,<sup>25</sup>  $Ti_nO_{2n-1}$ <sup>26</sup> and  $TiVO_x$ <sup>27</sup> systems. An alternative suggestion for the structure of bixbyite recently has been suggested<sup>28</sup> in which the oxygen lattice is changed to give a rather more octohedral arrangement around the metal atoms without the vacancies previously proposed.

This large set of anion defect structures related to the fluorite structure is at once one of the simplest and yet most beautifully intricate systems. A detailed elaboration of them would go far in advancing an understanding of the relationship between ordered intermediate phases and non-stoichiometry in chemical compounds.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME, NOTRE DAME, INDIANA]

## Chelate Stabilities of Certain Oxine-type Compounds. II. 4-Hydroxybenzothiazoles<sup>1</sup>

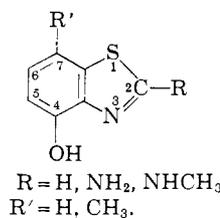
BY T. J. LANE, C.S.C., AND A. SAM

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The acid dissociation constants of 4-hydroxybenzothiazole, 2-amino-4-hydroxybenzothiazole, 2-methylamino-4-hydroxybenzothiazole and 2-amino-4-hydroxy-7-methylbenzothiazole were determined in 50% v./v. *p*-dioxane at 25° and the chelate stability constants of the ligands with Cu(II), Pb(II), Ni(II), Co(II), Zn(II) and Cd(II) were obtained by Calvin-Bjerrum potentiometric titration technique. The results were compared with those previously reported for 8-hydroxyquinoline, 4-hydroxybenzimidazole and 4-hydroxybenzoxazole. The stability constants of the 4-hydroxybenzothiazole chelates are lower than those of the corresponding 8-hydroxyquinolines. This is explained by larger nitrogen-oxygen distance and by unfavorable electron orientation on the donor nitrogen atom. The stability values are higher than those of 4-hydroxybenzimidazoles and 4-hydroxybenzoxazoles and this is attributed to the influence of the larger sulfur atom in the 1-position.

In the previous paper<sup>2</sup> the chelate stabilities of 4-hydroxybenzimidazoles and of 4-hydroxybenzoxazoles with divalent ions have been reported. In the present paper are presented and discussed the values obtained for the metal chelates of the 4-hydroxybenzothiazoles, represented by the

formula



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