whereas the error propagated by an uncertainty of ±1.0 Hz in $\delta\nu$ is 6.0%. The activation energies shown in Table VII were calculated from the first-order rate constants by assuming that the frequency factor is equal to the value obtained for *cis*-$(CH_3)_3Si(acac)$.

From the above data it may be concluded that there is a general increase in the rate of acetylacetonate methyl group exchange with increasing polarity of the substituents on silicon. For the *cis*-$R(CH_3)_2Si(acac)$ compounds, the rate increases in the order $R = n\text{-}C_4H_9 < C_2H_5 < CH_3 < CH_2{=}CH, C_6H_5 < CF_3CH_2CH_2$, and the lability of *cis*-$(C_6H_5)_2(CH_3)Si(acac)$ is comparable to that of $(CF_3CH_2CH_2)(CH_3)_2Si(acac)$. The dependence of the rates on the polarity of the silicon substituents is consistent with a mechanism involving formation of a five-coordinated silicon intermediate or transition state. Although several factors contribute to the energy required for such a bond-making activation process, as the electron-withdrawing ability of the substituents is increased, the resulting increase in positive charge on silicon should facilitate the use of a metal d orbital in achieving the transition state.[21] Relative to the alkyl-substituted silicon derivatives, the phenylsilyl derivatives are less labile than might be expected on the basis of σ inductive effects alone. However, the phenyl group has a greater steric requirement than the other substituents studied and, also, may participate in ligand→metal π bonding. Both of these latter factors would tend to lower the rearrangement rate. Since *cis*-$(C_6H_5)_2(CH_3)Si(acac)$ is more labile than *cis*-$(C_6H_5)(CH_3)_2Si(acac)$, however, σ inductive effects must play an important role in determining the *relative* labilities of these derivatives.

Acknowledgment. The support of this research by National Science Foundation Grant No. GP-9503 is gratefully acknowledged. We thank Mr. Ronald Robinson of the Dow Corning Corporation for providing the mass spectra.

[21] D. P. Craig and C. Zauli, *J. Chem. Phys.*, **37**, 609 (1962).

Preparation and Vaporization Thermodynamics of Europium Oxide Bromides

John M. Haschke[1a] **and Harry A. Eick**[1b]

Contribution from the Department of Chemistry, Michigan State University, East Lansing, Michigan 48823. *Received March 13, 1970*

Abstract: Orthorhombic trieuropium tetraoxide monobromide, Eu_3O_4Br, ($a = 11.98 \pm 0.03$, $b = 10.36 \pm 0.02$, $c = 5.92 \pm 0.01$ Å); tetragonal europium monoxide monobromide, EuOBr, ($a = 3.926 \pm 0.003$, $c = 8.019 \pm 0.008$ Å); and hexagonal trieuropium monoxide tetrabromide, Eu_3OBr_4 ($a = 9.825 \pm 0.004$, $c = 7.510 \pm 0.003$ Å) have been prepared and their incongruent vaporization reactions investigated. Single-crystal X-ray diffraction data for Eu_3O_4Br are consistent with space group Pmnm or $Pmn2_1$. Values of $\Delta H^\circ_{1399} = 129._0 \pm 1._1$ kcal/gram formula weight and $\Delta S^\circ_{1399} = 50.8_1 \pm 0.8_1$ eu were obtained from target-collection Knudsen effusion measurements of the equilibrium dibromide pressure according to the reaction $3Eu_3O_4Br(s) \rightarrow 4Eu_2O_3(s, \text{monoclinic}) + EuBr_2(g) + Br(g)$. For $Eu_3O_4Br(s)$ $\Delta H_f{}^\circ_{298} = -597._7 \pm 5._1$ kcal/gram formula weight, $\Delta G_f{}^\circ_{298} = -565._0 \pm 5._1$ kcal/gram formula weight, and $\Delta S^\circ_{298} = 64._5 \pm 3._1$ eu. Estimated thermodynamic data are presented for EuOBr ($\Delta H_f{}^\circ_{298} = 203._3 \pm 6._5$ kcal/gram formula weight).

Although structural data for lanthanide monoxide monobromides (LnOBr) were reported by Zachariasen[2] in 1949, lanthanide–oxygen–bromine systems have been examined only recently. The thermogravimetric study of Zolotov and Mayer[3] indicated that the monoxide monobromides (LnOBr) were the only phases observed when Ln = La–Eu, but that an additional phase, $LnBr_3 \cdot LnOBr$, *i.e.*, Ln_2OBr_4, was present for the heavier analogs (Gd–Lu). Baernighausen, *et al.*,[4] confirmed the existence of the tetragonal, PbFCl-type monoxide monobromides and reported preparation of orthorhombic trilanthanide tetraoxide monobromides, Ln_3O_4Br (Ln = Sm, Eu, Yb). More recently Nd_3O_4Br has been reported.[5]

Thermodynamic data are not available for any of the europium–oxygen–bromine phases—the phase diagram has not been examined thoroughly—even though this is the best characterized lanthanide system. The preparative and thermodynamic data for both europium monoxide[6] and europium dibromide[7,8] suggest also that oxide bromides of Eu(II) should be stable. This work was initiated to examine the decomposition behavior of selected Eu–O–Br phases, to determine their thermodynamic stability, and to characterize more completely the ternary phase diagram.

Experimental Section

Samples of EuOBr were obtained only by direct bromination of the sesquioxide. A continuous helium flow which swept through a liquid bromine (technical grade, Dow Chemical Co., Midland, Mich.) reservoir carried the halogen vapor through a heated quartz

---

[1] (a) Abstracted in part from the Ph.D. Thesis of John M. Haschke, Michigan State University, 1969; (b) to whom correspondence should be addressed.

[2] W. H. Zachariasen, *Acta Crystallogr.*, **2**, 388 (1949).

[3] I. Mayer and S. Zolotov, *J. Inorg. Nucl. Chem.*, **27**, 1905 (1965).

[4] H. Baernighausen, G. Brauer, and N. Schultz, *Z. Anorg. Allg. Chem.*, **338**, 250 (1965).

[5] N. Schultz and G. Reiter, *Naturwissenschaften*, **54**, 469 (1967).

[6] J. M. Haschke and H. A. Eick, *J. Phys. Chem.*, **73**, 374 (1969).

[7] J. M. Haschke and H. A. Eick, *J. Inorg. Nucl. Chem.*, in press.

[8] J. M. Haschke and H. A. Eick, *J. Phys. Chem.*, **74**, 1806 (1970).

tube in which a sample of Eu_2O_3 was confined in a quartz boat. The 99.9% pure sesquioxide (American Potash and Chemical Corp., West Chicago, Ill.) contained, by spectrographic analysis, 0.05% La_2O_3, 0.02% Zn, and 0.01% Nd_2O_3; other lanthanides were below detectable limits. The oxide was heated first to 400° under a purge of helium and then to 750–800° for 8 hr under a helium–bromine stream.

Samples of Eu_3O_4Br were prepared by two procedures. Mixtures of EuOBr and Eu_2O_3 in 1:1 stoichiometric ratios were sealed in evacuated quartz ampoules and heated at 900–1050° for 12–15 hr. Single crystals were obtained if the mixture was heated at 1100–1200°. The tetraoxide monobromide was also prepared by the bromination procedure described above if the system was not purged initially with helium, and a higher partial pressure of oxygen was maintained by using a lower flow rate of inert gas.

Additional regions of the ternary system were examined as follows. The preparation of an Eu(III) oxide bromide phase more bromine rich than EuOBr was attempted by reaction of a 4:1 molar ratio of $EuBr_{3.009\pm0.012}$ and Eu_2O_3 ("Eu_2OBr_4" composition) in an evacuated quartz ampoule at 425° for 12 hr. Attempts to prepare Eu(II) oxide bromides were effected by heating mixtures of europium monoxide ($EuO_{1.010\pm0.031}$)[6] and europium dibromide ($EuBr_{2.006\pm0.017}$)[7] in the stoichiometric ratios of 1:3, 1:2, 2:2, and 1:1 in evacuated quartz ampoules at 650–700° for 5 hr. Some samples were annealed for 5–10 days at 400°.

The reaction products were analyzed chemically for europium by air ignition to the sesquioxide at 1000° and for bromine by either a gravimetric silver halide technique or by weight change during bromination. Oxygen content was determined by difference. Powder X-ray diffraction data were collected with a Guinier–Haegg camera using KCl (a = 6.29300 ± 0.00009 Å) and Pt (a = 3.9237 ± 0.0003 Å) as internal standards. Single-crystal X-ray diffraction data were collected using oscillation and equiinclination Weissenberg techniques. Air-sensitive samples were manipulated in the inert atmosphere glove box described previously.[7] Specimens prepared for X-ray analysis were coated with a thin layer of paraffin oil to prevent hydrolysis.

The decomposition reaction for Eu_3O_4Br was characterized by a combination of X-ray, mass spectrometric, weight loss, and effusate collection experiments. Residues were analyzed by powder X-ray diffraction and the equilibrium vapor emanating from a quartz-lined effusion cell was not only analyzed with a Bendix time-of-flight Model 12-107 mass spectrometer using a 10–70-eV ionizing electron beam, but also collected in a quartz cup which was inverted over the orifice of the cell. The effusate was analyzed subsequently both chemically and by X-ray diffraction. Appearance potential measurements were made by the linear extrapolation technique with mercury as a reference. A sample of Eu_3O_4Br confined in a quartz-lined graphite effusion cell was heated by induction to constant weight at 1000–1200°. The decomposition modes of EuOBr and Eu_3OBr_4 were determined also.

Target-collection Knudsen effusion measurements for the incongruent vaporization of Eu_3O_4Br were effected as described previously.[6] The effusates, which were condensed on copper targets, were analyzed for both europium and bromine by X-ray fluorescence. Symmetrical, quartz-lined, graphite effusion cells (knife edged orifice areas = 8.6×10^{-4} and 59.0×10^{-4} cm²) were employed in the temperature range 925–1327°. Cells were charged with 0.25–0.35 g of Eu_3O_4Br and 0.05–0.10 g of Eu_2O_3, and experiments were conducted to 95% sample depletion.

Results

Bromination of the sesquioxide *via* the flow procedure produced the tetragonal monoxide monobromide (a = 3.926 ± 0.003, c = 8.019 ± 0.008 Å); static bromination and reaction of sesquioxide with monoxide monobromide yielded the orthorhombic tetraoxide monobromide (a = 11.98 ± 0.03, b = 10.36 ± 0.02, c = 5.92 ± 0.01 Å). For Eu_3O_4Br the observed systematic extinctions, $h0l$ ($h00$, $00l$), with $h + l = 2n + 1$ absent, are consistent with space groups $Pmn2_1$ and Pmnm[9a] (No. 31 and 59, respectively).[9b]

Anal. Calcd for EuOBr: Eu, 61.31; Br, 32.63. Found: Eu, 61.37 ± 0.15; Br, 32.73 ± 0.30. Calcd for Eu_3O_4Br: Eu, 76.00; Br, 13.32. Found: Eu, 75.96 ± 0.10; Br, 13.38 ± 0.15.

No evidence was found for a phase more bromine rich than EuOBr. The various stoichiometric ratios of EuO and $EuBr_2$ produced a hexagonal phase (a = 9.825 ± 0.004, c = 7.510 ± 0.003 Å). X-Ray diffraction data showed, in addition to this hexagonal phase, $EuBr_2$ in the products which resulted from the EuO:$EuBr_2$ <1:2 reactants, and a third phase of unknown composition and symmetry, X, from the >1:2 reactants. Annealing of the >1:2 reactant products yielded two distinct portions, dark green and light brown. The green-colored portion exhibited X-ray diffraction lines characteristic of the 1:2 hexagonal phase. Metal analysis of the green-colored portion was consistent with the Eu_3OBr_4 stoichiometry (obsd wt % Eu, 57.42; calcd, 57.60). The identity of phase X was not determined. Although Eu_3O_4Br was stable in air, EuOBr hydrolyzed slowly, and Eu_3OBr_4 hydrolyzed rapidly.

In the temperature range investigated, trieuropium tetraoxide monobromide was found to vaporize incongruently according to reaction 1. Powder X-ray diffraction analysis of the vaporization residues indicated the presence of only Eu_3O_4Br and Eu_2O_3.

$$3Eu_3O_4Br(s) \longrightarrow 4Eu_2O_3(s, \text{monoclinic}) + EuBr_2(g) + Br(g) \quad (1)$$

Traces of the cubic modification of the sesquioxide were observed. The mass spectrometric analysis of the effusate indicated Br^+, $EuBr^+$, Eu^+, $EuBr_2^+$, and Br_2^+ in the respective ratio 1000:100:50:15:5. The fragmentation pattern of europium-containing species and the appearance potential of $EuBr^+$ (10.4 eV) agree with those reported for the dibromide.[8] The weight-loss experiment indicated 99.4% of theoretical according to reaction 1. Refractory metal (Mo, W) and thoria-lined cells yielded weight losses of 105–120% of the theoretical, and produced crucible or liner material oxide contamination. The quartz liners appeared satisfactory even though they acquired a greenish color at the highest temperatures (1300°). Chemical and X-ray analysis of the samples obtained in the effusate collection experiments confirmed that $EuBr_2$ was a vapor species.

The experimental data showed that the vapor contained both $EuBr_2(g)$ and an Eu:Br ratio of 1:3, but did not indicate whether the equilibrium bromine species was the monatomic or diatomic gas. By consideration of reaction 2, Br(g) can be proven the vapor species.

$$^1/_2Br_2(g) \longrightarrow Br(g) \quad (2)$$

Use of the Knudsen equation and the two possible vaporization reactions yields in one case $P_{Br} = 0.506(P_{EuBr_2})$, and in the other, $P_{Br_2} = 0.358(P_{EuBr_2})$. In either case, P_t, the total bromine pressure, is of the order of magnitude of the europium dibromide pressure. If experimental values for P_{EuBr_2} for reaction 2 at the maximum and minimum experimental temperatures are substituted for P_t in the equilibrium expression $K(2) = 2\alpha[P_t/(1 - \alpha^2)]^{1/2}$ (1600°K, $P_{EuBr_2} = 6 \times 10^{-4}$ atm, $K(2) = 0.496$;[10] 1200°K, $P_{EuBr_2} = 8 \times 10^{-7}$ atm, $K(2) = 0.042$[10]), the degree of dissocia-

---

[9] (a) Nonstandard setting; (b) N. F. M. Henry and K. Lonsdale, Ed., "International Tables of X-Ray Crystallography," Vol. 1, Kynoch Press, Birmingham, England, 1952.

[10] D. R. Stull, Ed., "JANAF Interim Thermochemical Tables," Dow Chemical Co., Midland, Mich., 1960 and Supplements.

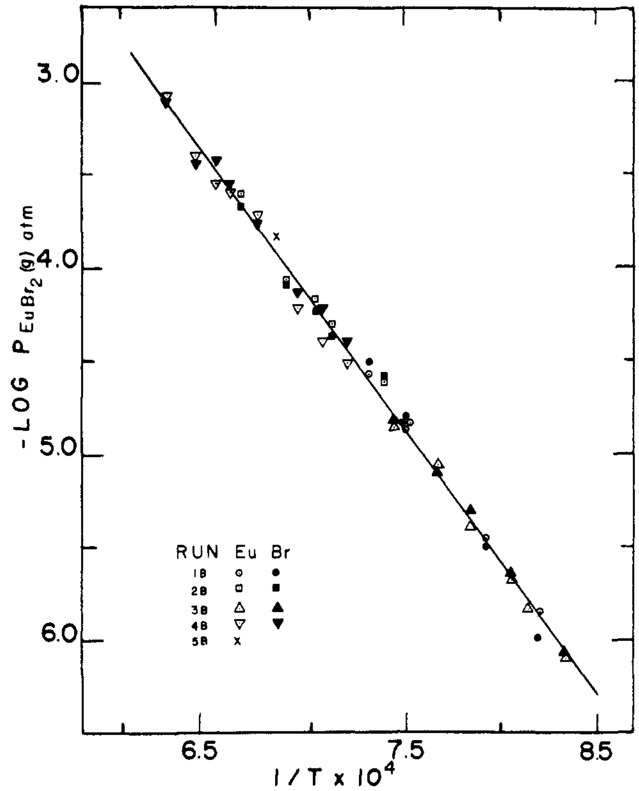

Figure 1. Graph of the logarithm of the pressure of gaseous $EuBr_2$ in equilibrium with condensed Eu_3O_4Br and Eu_2O_3 and gaseous Br.

tion, α_{1600}, is 0.995, and α_{1200} is 0.999. The diatomic bromine observed in the mass spectrum apparently resulted from recombination of the monatomic gas in the cooler portions of the heater assembly outside the Knudsen cell.

X-Ray diffraction analysis of the residue (EuOBr + Eu_3O_4Br) and the collected effusate ($EuBr_2$) indicates that EuOBr vaporizes incongruently according to reaction 3. The presence of monatomic bromine is assumed by analogy.

$$4EuOBr(s) \longrightarrow Eu_3O_4Br(s) + EuBr_2(g) + Br(g) \quad (3)$$

The collected effusate from Eu_3OBr_4 was also identified as the dibromide, and the phase therefore must vaporize incongruently according to reaction 4.

$$Eu_3OBr_4(s,l) \longrightarrow Eu_{3-y}OBr_{4-2y}(s,l) + yEuBr_2(g) \quad (4)$$

A value was not determined for y, but X-ray analysis of the fused, brown-colored residue gave a complex pattern whose lines were not assignable to condensed Eu_3OBr_4, phase X, or EuO. The results suggest that during the collection experiment the bulk composition shifted to a stoichiometry more oxygen rich than that of phase X, and that additional oxide bromides of Eu(II) exist.

Eu_3O_4Br(s). The log P_{EuBr_2} *vs.* $1/T$ ($1198 < T < 1600$°K) results presented in Figure 1 for reaction 1 are described by the least-squares equation

$$\log P_{EuBr_2} = -[(1.410 \pm 0.017) \times 10^4/T] + (5.70 \pm 0.12) \quad (5)$$

The sticking coefficient of the dibromide on copper has been shown to be unity[8] within experimental error. Combination of the equilibrium constant expressed in terms of the dibromide pressure with eq 5 yields

$$\log K(1) = -[(2.819 \pm 0.024) \times 10^4/T] + (11.10 \pm 0.18) \quad (6)$$

At the median temperature, $\Delta H°_{1399} = 129.0 \pm 1.1$ kcal/gram formula weight and $\Delta S°_{1399} = 50.81 \pm 0.81$ eu.

The second-law vaporization results, when reduced to 298°K with published data for the sesquioxide[11] and bromine[10] and estimated values for the dibromide[8] and tetraoxide monobromide,[12] yield $\Delta H°_{298} = 137.6 \pm 2.0$ kcal/gram formula weight, $\Delta S°_{298} = 64.7 \pm 2.9$ eu, and $\Delta G°_{298} = 118.3 \pm 2.0$ kcal/gram formula weight. The reported errors include an estimated ±20% error in the data reduction.

The third-law enthalpy of vaporization was calculated using published Gibbs free-energy functions for Br(g)[10] and those estimated for Eu_2O_3(s),[13] $EuBr_2$(g),[8] and Eu_3O_4Br(s). Values for the oxide bromide were obtained from the approximated heat capacity and an estimated $S°_{298}$ (63.8 eu) calculated by the scheme of Latimer[14] with the magnetic contribution of Eu(III) proposed by Westrum.[15] A temperature-independent $\Delta H°_{298} = 139.47 \pm 0.92$ kcal/gram formula weight was obtained.

The second-law enthalpy of vaporization and the enthalpies of formation of Eu_2O_3(s),[16] $EuBr_2$(g),[8] and Br(g)[10] were combined to give $\Delta H_f°[Eu_3O_4Br(s)] = -597.7 \pm 5.1$ kcal/gram formula weight. From the Gibbs energies of formation of Eu_2O_3(s) (−370.9 kcal/gram formula weight, calculated from published data[10,15–17]), $EuBr_2$(g),[8] and Br(g)[10] and those of vaporization, $\Delta G_f°_{298}[Eu_3O_4Br(s)] = 565.0 \pm 5.1$ kcal/gram formula weight. Similarly, $S°_{298}[Eu_3O_4Br(s)] = 64.5 \pm 3.1$ eu was obtained.

EuOBr(s). Decomposition of EuOBr according to reaction 3 requires that the dibromide pressure be greater than that in equilibrium with Eu_3O_4Br(s), but less than that in equilibrium with $EuBr_2$(l), and therefore permits estimation of the vaporization thermodynamics. If the $S°_{298}$ data for Eu_3O_4Br(s), $EuBr_2$(g),[8] and Br(g)[10] are combined with that estimated for EuOBr (29.0 eu), a $\Delta S°_{298}$ (65.9 eu) may be approximated for reaction 3. An entropy correction employing estimated heat capacities gives $\Delta S°_{1400} = 56.7$ eu at the median temperature of the Eu_3O_4Br and $EuBr_2$[8] equilibrium measurements. Combination of this entropy with the median pressure of $EuBr_2$(g) in equilibrium with Eu_3O_4Br(s) and $EuBr_2$(l) at 1400° yields, for reaction 3, $\Delta H°_{1400} = 128.5$ kcal/gram formula weight ($\Delta H°_{298} = 135.5$ kcal/gram formula weight); and from this value, for EuOBr(s), $\Delta H_f°_{298} = -203.3 \pm 6.5$ kcal/gram formula weight and $\Delta G_f°_{298} = -193.4 \pm 6.5$ kcal/gram formula weight. The estimated error was calculated with the equilibrium

(11) L. B. Pankratz, E. G. King, and K. K. Kelley, U. S. Bureau of Mines Report of Investigation 6033, U. S. Government Printing Office, Washington, D. C., Jan 1962.

(12) J. M. Haschke and H. A. Eick, *Inorg. Chem.*, **9**, 851 (1970).

(13) J. M. Haschke and H. A. Eick, *J. Phys. Chem.*, 72, 4235 (1968).

(14) W. M. Latimer, "Oxidation Potentials," 2nd ed, Prentice-Hall, Englewood Cliffs, N. J., 1952, Appendix III.

(15) E. F. Westrum, Jr., *Advan. Chem. Ser.*, No. 71, 25 (1967).

(16) E. J. Huber, Jr., G. C. Fitzgibbon, and C. E. Holley, Jr., *J. Phys. Chem.*, **68**, 2720 (1964).

(17) R. Hultgren, private communication.

dibromide pressures for condensed Eu_3O_4Br and $EuBr_2$ as limiting parameters for the enthalpy of vaporization.

Discussion

The high-temperature europium oxide bromide phases which we observed are consistent with those reported formerly,[4] but the phase diagram is more complex than previous work has indicated. The single-crystal results show that the face-centered orthorhombic structure and space groups proposed previously for the Ln_3O_4Br phases[4] are incorrect. Lattice parameters recalculated for these phases[4,5] from the published data are presented in Table I. Although the powder diffraction data can be explained on the basis of orthorhombic symmetry, the preparations contained a few single crystals which exhibited only triclinic symmetry. No evidence for additional oxide bromide phases of trivalent europium has been observed, but one phase of the divalent metal has been characterized, and the existence of additional phases has been indicated. The hexagonal monoxide tetrabromide appears to be isostructural with the phases reported recently for the oxide halides of strontium and barium.[18,19] The lattice parameters of Eu_3OBr_4 are almost identical with those of the strontium phase (a = 9.82 ± 0.01, c = 7.51 ± 0.01 Å), for which the composition Sr_4OBr_6 is reported. Since this value is apparently based only on miscibility observations and X-ray data, the composition of the alkaline earth phases is probably M_3OX_4 instead of M_4OX_6.

Table I. Recalculated Lattice Parameters of Orthorhombic Ln_3O_4Br Phases[a]

Phases	a, Å	b, Å	c, Å
Nd_3O_4Br	12.31 ± 0.05	10.55 ± 0.03	6.03 ± 0.02
Sm_3O_4Br	12.04 ± 0.03	10.46 ± 0.02	5.94 ± 0.01
Eu_3O_4Br	11.98 ± 0.03	10.38 ± 0.02	5.92 ± 0.01
Yb_3O_4Br	11.56 ± 0.03	9.98 ± 0.02	5.72 ± 0.01

[a] See ref 4 and 5.

The decomposition reactions of the oxide bromides are consistent with the trends observed previously for condensed Eu_3O_4,[13] EuO,[6] and $EuBr_2$.[8] The flow of reaction observed for all oxygen-containing europium phases is toward a more oxygen-rich condensed phase, ultimately the congruently vaporizing sesquioxide. In the europium–bromine system, the composition shifts to the congruently vaporizing dibromide; thus, gaseous dibromide is an anticipated oxide bromide decomposition product. The stoichiometry of the vapor is fixed by the composition change of the solid phases, and the vapor species are determined by the instability of the tribromide at elevated temperatures.[7] The same general behavior is expected for the oxide halides of all lanthanides. They should vaporize incongruently to give a more oxygen-rich condensed phase plus the gaseous trihalide. This behavior, which has been observed for NdOF,[20] however, may not occur for the oxide halides of europium and ytterbium, since the dihalides of these species may be the most stable gases. The stabilities of the lanthanide oxides and the relatively high volatilities of the halides prevent the appearance of gaseous lanthanide oxide halides analogous to those reported recently for other transition metals.[21]

Since no previous thermochemical measurement has been described for any of the lanthanide oxide bromides, evaluation of these results is difficult, but they may be compared with those obtained for the LnOCl phases.[22] The estimated enthalpy of formation of EuOBr (−203 kcal/gram formula weight) is consistent with the more negative values (−230 to −245 kcal/gram formula weight) observed for the oxide chlorides. The enthalpy of bromination of a divalent europium phase should be essentially constant; the differences between the enthalpies of formation of $Eu_3O_4(s)$[13] and $Eu_3O_4Br(s)$ and those of EuO(s)[6] and EuOBr(s) are 55.1 and 58.1 kcal/gram formula weight, respectively.

Although the Eu(II) and mixed Eu(II)–Eu(III) oxide bromides have not been characterized completely, the complexity of the europium–oxygen–bromine phase diagram is evident. The results for this system should be helpful in the elucidation of the phase diagrams and vaporization reactions of other lanthanide oxide halides.

Acknowledgment. Partial support of the U. S. Atomic Energy Commission (Contract No. AT(11-1)-716) and a National Science Foundation Fellowship to J. M. H. are gratefully acknowledged. The assistance of Mr. Donald Werner in mass spectrometric analyses is appreciated.

---

(18) B. Frit, B. Fanguy, and P. Hagenmuller, *Bull. Soc. Chim. Fr.*, 2190 (1966).

(19) B. Frit, M. M. Chbany, and P. Hagenmuller, *ibid.*, 127 (1968).

(20) D. B. Shinn and H. A. Eick, *Inorg. Chem.*, **8**, 231 (1969).

(21) C. O. Schulz and F. E. Stafford, *J. Phys. Chem.*, **72**, 4686 (1968).

(22) A. K. Baev and G. I. Novikov, *Zh. Neorg. Khim.*, 10, 2457 (1965); *Russ. J. Inorg. Chem.*, **10**, 1337 (1965).