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**INVESTIGATIONS AT HIGH TEMPERATURES:
CONDENSED-PHASE EQUILIBRIA AND VAPORIZATION STUDIES
WITH A MASS SPECTROMETER**

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(Ph. D. Thesis)

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PREFACE

Parts I and II of this thesis report the results of studies of condensed-phase equilibria in rare earth oxide and oxide-fluoride systems at temperatures above 1500°C. For Part I, I explored the Eu-Eu₂O₃ system in detail, determining the compositions and melting points of the stable phases. In the course of this study I investigated equilibria between compounds in the Eu-Pt system and europium oxides at 1500°C. Examinations of the Sm-Sm₂O₃ and Yb-Yb₂O₃ systems showed that previously reported reduced oxides were not stable at high temperatures. For Part II I studied ternary equilibria in the Eu-O-F system at 1500°C for oxidation states of europium between +2 and +3, and equilibria in the Eu-O-F and Sm-O-F systems from ~400 to 1500°C for Eu⁺³ and Sm⁺³.

Parts III and IV discuss the results of vaporization studies made with the use of a mass spectrometer. Part III presents the determination of equilibria for sublimation of the element hafnium. Data were analysed by both the second-law and third-law methods; zirconium present as a dilute solute in the hafnium was used as a reference. Part IV is an investigation of the vaporization kinetics of GaN. I established the composition of the vapor species from GaN surfaces and examined vapor from these surfaces for the possible presence of nitrogen gas in excited states.

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CONDENSED-PHASE EQUILIBRIA

Part I

AN INVESTIGATION OF THE Eu-Eu₂O₃ SYSTEM AND
THE EQUILIBRIA BETWEEN THE EUROPIUM OXIDES AND
THE Eu-Pt SYSTEM, WITH RELATED STUDIES OF THE
Sm-Sm₂O₃ AND THE Yb-Yb₂O₃ SYSTEMS

Abstract

The binary system Eu-Eu₂O₃ has been examined in detail over the composition range EuO to Eu₂O₃ at 1500°C. Only one intermediate oxide phase, Eu₃O₄, was found. Both EuO and Eu₃O₄ exhibit very narrow composition limits, while the monoclinic sesquioxide is stable over the composition range EuO_{1.45} to EuO_{1.50} at 1500°C. The melting points found for the three phases were 1900°C for EuO, 2000°C for Eu₃O₄ and 2300°C for Eu₂O₃. Europium was quantitatively extracted from EuO by reaction with platinum in sealed capsules at 1500°C, which resulted in the formation of an intermetallic phase plus a higher oxide of europium. The most europium-rich intermetallic phase found in these studies, EuPt_{2+x}, has the fcc MgCu₂ structure and is stable over the composition range EuPt_{2.0} to EuPt_{2.8} at 1500°C. There may be an additional phase besides the previously reported EuPt₅ at platinum-europium ratios above 3:1. No crystalline phases other than the sesquioxides were found in the Sm-Sm₂O₃ or the Yb-Yb₂O₃ systems.

Introduction

Brauer¹ has reviewed the structural and solid-state chemistry of the lanthanon oxides, and Westrum² has reviewed the thermodynamics and magnetic properties of the oxides and other chalcogenides.

When the work reported here began, the Eu-Eu₂O₃ system had not been clearly defined. Although the oxides Eu₂O₃, Eu₃O₄, and EuO had been reported and their structures described, the possibility of other intermediate phases in the system still remained.³⁻⁷ However, it has since been established⁸ that no other phases exist in this system. Significant ranges of stoichiometry have been reported for EuO⁹ and Eu₂O₃ (cubic).¹⁰ The results reported here confirm the findings of Ref. 8 and present new data on the composition ranges of these oxides.

Optical and x-ray examination of samples prepared by metathetical synthesis in sealed containers indicated that EuO, Eu₃O₄, and Eu₂O₃ were the only stable oxides in the Eu-Eu₂O₃ system. However, there had been some uncertainty about this conclusion because of interference by tantalum contamination in some of our early experiments. An investigation involving controlled quantitative extraction of Eu from EuO single crystals was devised, which unambiguously established the number of phases present in the range EuO-Eu₂O₃ and provided data on the stoichiometries of these phases. Europium was removed from EuO through the vapor phase by equilibration with platinum in sealed containers at 1500°C. These experiments also provided new information on the Eu-Pt system.

I applied the techniques and facilities previously used in studying the reduced europium oxides to investigate the possible stability of divalent or other reduced oxidation states of samarium or ytterbium in oxide systems. SmO, Sm₂O, and YbO had all been reported.¹¹⁻¹⁵ I was interested in characterizing these phases if possible and in comparing the samarium, europium, and ytterbium systems. Brauer et al. have reported that reduced oxidation states of Sm and Yb could not be prepared in binary oxides at temperatures up to 800°C and that the divalent ions could not be stabilized even in solution with SrO or CaO.¹⁶ Felmler and Eyring have reported that the substances previously identified as Sm₂O and SmO were actually SmH₂ and

$\text{SmN}_{1-x}\text{O}_x$.¹⁷ McCarthy et al. have also reported that divalent Sm can not be formed in titanates and is probably not stable in any oxide system.¹⁸ My results, which include observations from reactions carried out at temperatures up to 2100°C, confirm that in the binary oxide systems, reducing conditions lead to no new phases in which Sm or Yb are in reduced oxidation states. Reduced sesquioxides $\text{Sm}_2\text{O}_{3-x}$ and $\text{Yb}_2\text{O}_{3-x}$ were found. Similar reduced lanthanon sesquioxides have been reported and the oxygen deficiencies shown to be due to vacancies in the oxygen sublattice.¹⁹ My measurements show that the oxygen deficiency in $\text{Yb}_2\text{O}_{3-x}$ is approximately the same as that reported for the other reduced lanthanon sesquioxides.

Melting of Eu_2O_3

I melted Eu_2O_3 in both tungsten and iridium crucibles, using an induction furnace with a shielded tungsten susceptor. I measured temperatures with a disappearing-filament optical pyrometer sighted through a prism and window into a hole of 1 mm diameter in the lid and upper shields, and I applied prism and window corrections. The crucibles were not sealed, but they had close-fitting covers, and I used an argon atmosphere to repress vaporization. The starting material was nominally 99.9% Eu_2O_3 that had been previously heated in air for several hours at about 1200°C in a platinum crucible and then stored in a desiccator. The oxide is monoclinic, colorless, and highly birefringent.

On being heated to 2270°C in a tungsten container, the sample melted and reacted with the crucible, producing a noticeable recess in the wall at the meniscus. This behavior is typical for reactions involving a gaseous product of the container material such as WO_3 . The europium oxide product appeared dark in color and contained small red crystals of Eu_3O_4 uniformly dispersed throughout. A sample heated to 2280°C in an iridium crucible also melted. There was no evidence of reaction with the container; however, enough oxygen was lost (presumably by vaporization) to yield a product that contained a significant amount of Eu_3O_4 . Another sample heated in iridium to 2300°C appeared to have been only partly melted. Samples heated to

2250°C showed evidence of liquid formation only around the Eu_3O_4 inclusions. I maintained the samples at maximum temperature only for a few minutes because of rapid vaporization losses. This and the temperature gradients, which were unavoidable even in the well-shielded crucible used for a susceptor, leave some doubt about the accuracy of the melting point measurements. I can only estimate the melting point to be in the range 2250 to 2350°C.

My observations of the melting of Eu_2O_3 were therefore not precise enough to confirm either the value of $2240 \pm 10^\circ\text{C}$ given by Schneider²⁰ or of 2330°C by Foex,²¹ but agree with the values near 2300°C as opposed to 2000°C reported by Mordovin.²² Schneider determined the melting point in air, using an iridium container. Foex's measurement was also in air, using a solar furnace, and Mordovin's measurement was in argon under a pressure of 3 atm.

Except for the presence of Eu_3O_4 inclusions, the optical properties and x-ray diffraction results for the melted Eu_2O_3 were identical to those for the starting material. The x-ray powder patterns corresponded to the ASTM data.²³

Synthesis and Melting of EuO

The starting materials were Eu_2O_3 (described above) and nominally 99% europium metal in ingot form. The europium ingot was handled in a steel glove box that could be evacuated to 3×10^{-6} torr and filled with dry argon. A steel chisel was used to cut pieces of europium from the ingot as required, after the surface coating was scraped off. Normally, a clean europium surface would retain its shiny metallic appearance for several hours in the glove box before developing a noticeable tarnish.

Although a number of procedures have been reported for preparing EuO , most of them yield a product of questionable purity.^{6,12,24} I avoided methods for which a metal other than europium is used as a reducing agent, ones for which the stoichiometry could not be closely predetermined (such as reduction by carbon), and ones requiring difficult procedures or specialized equipment.

I prepared EuO by reducing Eu_2O_3 with europium metal in sealed, evacuated molybdenum crucibles. Reactions carried out even

at moderately low temperatures in silica yielded products contaminated with silicate. (See also Ref. 6.) Reactions carried out in tantalum containers at temperatures high enough to melt EuO ($\sim 1800^\circ\text{C}$) resulted in products which were contaminated by tantalum. The tantalum was found in two different forms. One was as an unidentified crystalline material thought to be a complex oxide, which was transparent, red or brownish in color, and birefringent. Tantalum was also found (by electron microprobe x-ray analysis) to be finely dispersed in the EuO, probably as precipitated metal that may have been in solution at higher temperatures. The occurrence of dispersed tantalum in EuO prepared in tantalum containers has also been reported by Guerri and Shafer.²⁵ Samples of EuO which had been heated to 1800°C in tantalum were found to have melted. Of two samples heated to 1800°C , one melted and one did not.

I prepared EuO without troublesome side reactions in molybdenum capsules, using an excess of europium metal. Samples were prepared by weighing the desired amounts of sesquioxide from the desiccator into capsules and transferring them into the glove box. The appropriate amount of metal was weighed on a torsion balance of ± 10 mg accuracy and added to each of the capsules. After the lids were pressed on, the capsules were placed in previously weighed bottles which were capped and removed from the box. The final weights of the filled capsules were then determined on an analytical balance without exposing the samples to the ambient environment. After being weighed, the capsules were placed in a vacuum system that was then pumped out to 10^{-5} torr. The capsules were left in the vacuum overnight to allow evacuation and then were sealed by electron-beam welding (EBW).

A sample heated to 1870°C resulted in a compact product of EuO that had not melted. The excess europium metal was found primarily at the bottom and sides of the capsules. Samples heated above 1990°C and cooled at about 70°C per hr resulted in EuO boules containing large crystals that had grown from a melt. Excess metal was found at the bottom and sides of the boule and in the grain boundaries.

Most of the EuO taken from several such preparations was then crushed, remelted in a sealed molybdenum container, and cooled slowly. About 1.5% Eu was added to ensure that the overall composition would remain on the metal-rich side of EuO. I estimate that the europium excess in the final product was from 1 to 5% by weight. From this preparation I obtained single crystals of approximately 1 cm^3 . There was no visible excess europium metal in this sample, but the surfaces of uncleaved crystals tarnished in air over a period of several months, probably because of the presence of europium metal in the grain boundaries.

These results are consistent with those of Guerci and Shafer.²⁵ However, I believe that as yet there is not enough evidence to conclude that EuO melts peritectically, as they suggest, rather than congruently. I estimate the melting point of EuO to be $1900^\circ \pm 50^\circ\text{C}$, in agreement with the value suggested by Shafer.⁹ X-ray powder diffraction analysis of this material gives a lattice parameter, $a = 5.14_4 \pm 0.005\text{\AA}$ for the NaCl type structure, in agreement with prior reports.

EuO crystals are dark reddish-violet in color and are opaque to visible light even in thin sections with the most intense illumination available on our microscope (a mercury discharge lamp).

Synthesis and Melting of Eu_3O_4

Attempts to prepare pure Eu_3O_4 from mixtures of EuO and Eu_2O_3 in sealed tantalum containers were unsuccessful. Extensive reduction occurred because of loss of oxygen by solution into the tantalum. This reduction resulted in products containing large excesses of EuO. A preparation heated to 1820°C had completely melted. The product was principally EuO, containing some Eu_3O_4 with minor amounts of two or three other unidentified phases. The latter were lightly colored, transparent, and birefringent. They were coprecipitated with the Eu_3O_4 in banded eutectic-like structures. These materials may have been complex europium-tantalum oxides.

A small sample of Eu_3O_4 (0.4 g) was prepared by heating an equimolar mixture of EuO and Eu_2O_3 (actual O/Eu = 1.331) to 2135°C in a sealed (by EBW) iridium crucible. I estimate the uncertainty in

the initial oxygen-to-europium ratio to be about one part per thousand, primarily because of the uncertain composition of starting materials. The product had melted completely. Examination with a polarizing microscope showed the product to consist primarily of transparent, very dark-red crystals that were birefringent, appearing bright red under crossed polarizers. A very few bright white birefringent crystals were also seen in the sample, indicating the presence of a trace of Eu_2O_3 . X-ray powder diffraction patterns agreed with the results reported by Bärnighausen and Brauer⁵ and Rau^{6,26} for Eu_3O_4 (orthorhombic).

A larger preparation (15 g) was made by heating a mixture of EuO and Eu_2O_3 ($\text{O}/\text{Eu} = 1.333$) to 2050°C in an iridium container and cooling at 40°C per hr. I was unable to make a leak-tight weld on this container, but the heating was done in an argon atmosphere to retard vaporization of the sample. The product completely melted. It consisted of relatively large Eu_3O_4 grains ($\sim 1 \text{ mm}^3$) with traces of Eu_2O_3 concentrated at the grain boundaries. Although there was no visible sign of reaction between the sample and the container, there may have been some loss of europium by vaporization, yielding a product slightly more oxygen-rich than the starting material. Part of the product was ground and reheated to 1920°C in a sealed iridium capsule; no sign of melting was observed. A portion of the product was heated to 2140°C in a sealed molybdenum capsule and cooled rapidly. The product, which had completely melted, consisted of Eu_3O_4 with traces of Eu_2O_3 , and was identical in appearance to the original material that had been cooled slowly. I could detect no sign of reaction with the container. Reheating in a sealed molybdenum container for 8 hr at 1625°C had no detectable effect on the sample. These observations indicate that the Eu_2O_3 resulted from a slight excess of oxygen in the sample rather than from disproportion by a peritectic reaction.

I estimate the melting point of Eu_3O_4 to be $2000 \pm 100^\circ\text{C}$. Part of the uncertainty in this figure is due to the fact that in some of the heatings the shielding was deliberately rearranged to establish a large temperature gradient ($\sim 80^\circ$ from top to bottom) to facilitate crystal growth. Results from preparations in tantalum indicate the possibility of peritectic melting. The experiments in iridium and molybdenum do

not support this conclusion, but neither do they provide direct contradictory evidence.

Investigation of Other Compositions Between EuO and Eu₂O₃

Several compositions between EuO and Eu₂O₃ were heated in sealed iridium or molybdenum containers in conjunction with the preparation and study of Eu₃O₄.

Mixtures with oxygen-to-europium ratios of 1.051, 1.093, and 1.401 that were prepared from EuO and Eu₂O₃ and then heated to 1970°C in EBW-sealed iridium capsules had completely melted. The samples with O/Eu = 1.051 and 1.093 showed evidence of reaction with the containers. The metallic reaction product was not identified but may have been EuIr₂ (see Ref. 27) or EuIr₅. The major oxide phase in the products was Eu₃O₄, with some opaque material (probably EuO) detectable by microscopic examination. X-ray diffraction analysis showed only Eu₃O₄. The sample with O/Eu = 1.401 apparently did not react with the container. The product in this case consisted of approximately equal amounts of Eu₂O₃ and Eu₃O₄ with no other phase detectable either by x-ray or optical analysis.

Samples with oxygen-to-europium ratios of 1.17 and 1.25, prepared from Eu₃O₄ and EuO, were heated to 2140°C in sealed molybdenum capsules and cooled rapidly. There was no indication of container reaction; Eu₃O₄ and EuO were the only phases detectable in the products by x-ray and optical analysis. The samples had been completely melted. The products were resealed in molybdenum capsules and heated to 1800°C for 8 hr without effect.

The x-ray powder diffraction patterns of Eu₃O₄ were identical within our precision for samples prepared with either excess oxygen or excess europium, as were the qualitative optical properties. The existence of Eu₃O₄ in the presence of either EuO or Eu₂O₃, and the failure to observe any other phases, are in agreement with other recent reports on this system.⁶⁻⁸

The presence of Eu₂O₃ in samples very close to the ideal composition for Eu₃O₄, and the concentration of the Eu₂O₃ in the grain boundaries of Eu₃O₄ preparations, indicate that the deviation from stoichiometry is very small on the oxygen-rich side. The

appearance of the crystallized samples indicated that the stable composition range for Eu_3O_4 is probably narrow even near the melting point. Even in rapidly cooled samples, the Eu_3O_4 crystals did not appear to contain inclusions of EuO or Eu_2O_3 .

Study of the $\text{EuO-Eu}_2\text{O}_3$ System by the Removal of Eu
from EuO at 1500°C by Platinum

To confirm the absence of compounds other than Eu_3O_4 between EuO and Eu_2O_3 , as well as to investigate in more detail the stoichiometry of these three oxides, I studied the distribution of europium between the oxide phases and intermetallic phases in the Eu-Pt system at 1500°C .

EuO single crystals weighing from 100 to 400 mg were sealed by EBW into molybdenum capsules, along with pieces of chemically pure platinum thermocouple wire weighing 6 mg to 1 g. The platinum wire was suspended from molybdenum wire holders to avoid physical contact between the platinum and the oxide. Subsequently, several runs were made with the configuration shown in Fig. I-1. A tungsten-lined molybdenum cup was used instead of the molybdenum wire to contain the platinum. Unfortunately, I did not have enough single crystals for these runs. I therefore used dense polycrystalline EuO from the same preparation used for the previous work. The sealed capsules were heated at 1500°C for about 5 hr and cooled quickly. About 1.5 min were required for the temperature to fall below 700°C . In the second series I did not use a quench gas, and the samples cooled more slowly, falling below incandescence in 5 to 10 min. After being cooled the capsules were broken open to recover the oxide and platinum samples.

The product oxide phases were recovered intact and had the same size and shape as the starting EuO crystals. There was no evidence of vapor transport of oxide within the capsules nor of mechanical losses of oxide in transfers or recovery. After being weighed and examined with a low-power microscope, the oxide products were cleaved and examined further. The two-phase oxide products consisted of a central core of the lower oxidation state phase surrounded by an outer shell of the higher oxidation state phase. The boundaries were very sharp with no gradation in properties detectable. Samples were taken

Fig. I-1. Sample configuration for extraction of europium from EuO by platinum. The protective cover prevents molybdenum particles from falling into the container when the capsule is opened. Early runs were made with platinum wire hung directly on the molybdenum wire stand.

from the inner and outer phases for x-ray diffraction and examination with the polarizing microscope. The x-ray and optical properties of the products of these experiments were identical to those described above for EuO , Eu_3O_4 and Eu_2O_3 . The results showed unambiguously that the only stable oxides in this system at 1500°C are the three mentioned above.

The samples changed as the initial ratio of platinum to EuO was progressively increased. At lower ratios ($\text{Pt}/\text{EuO} < 0.5$), not enough europium was extracted to increase the overall oxygen-to-europium ratio in the product oxide phase to $4/3$. In these samples a dense layer of polycrystalline Eu_3O_4 was formed on the external surfaces of the EuO crystal. Where the platinum-to- EuO ratio was further increased so that more than one-fourth of the europium was extracted from the oxide, the product was a homogeneous, dense, polycrystalline core of Eu_3O_4 with an outer layer of Eu_2O_3 . With continued Eu extraction from the oxide, the outer layer of Eu_2O_3 became progressively thicker. However, the outer layers were not pure Eu_2O_3 . Small red crystals of Eu_3O_4 were uniformly dispersed in these layers. When enough platinum was added to give an oxide product with an oxygen-to-europium ratio of 1.45 ± 0.01 or more, the Eu_3O_4 core was absent and the product was Eu_2O_3 containing small crystals of Eu_3O_4 uniformly dispersed throughout.

The metallic phase products were weighed and examined with a microscope and by x-ray diffraction. For runs in which the platinum-to-europium ratio of the product was $3.45:1$ or less, the surfaces of the products were very rough, and relatively large (0.05 mm) plate-like crystals had developed. There was no evidence of liquid formation, and the platinum-phase molybdenum or tungsten interfaces were sharp with the interaction confined to very small regions at the points of contact between the sample and holder. In most cases there was no mechanical bond or a very weak one between sample and holder. The samples with $\text{Pt}:\text{Eu}$ of 3.69 and 5.21 had completely melted. The platinum phase wetted the molybdenum and was strongly bound to it; however, the boundary observed under the microscope was very sharp with no evidence of reaction or corrosion of the original molybdenum surfaces. The samples with higher platinum-to-europium ratios were

similar but had only partly melted. They retained the basic form of the original wire, and were smooth with coils stuck together by the crystallized liquid phase. The liquid phase is probably due to a eutectic reaction below 1500°C between platinum and the platinum-rich intermetallic compound.

Although the solubility of molybdenum in platinum at 1500°C is about 40 at.% and there is a stable intermetallic compound of molybdenum and platinum,²⁸ I believe the interactions of platinum with the containers did not have an important effect in this experiment except for the samples where a liquid phase was formed. This judgment is reinforced by the agreement between the first runs and the later runs in which tungsten-lined containers were used for the platinum. The solubility of tungsten in platinum is about 50 at.% at 1500°C, but there is no platinum-tungsten intermetallic compound. The solubility of platinum in either molybdenum or tungsten is small.²⁸ Spectroscopic analysis of the $\text{EuPt}_{5.21}$ sample indicated that it was contaminated with about 200 ppm molybdenum. The presence of molybdenum may have influenced the form and structure of the platinum phases that were melted or partly melted, but I think that even in these samples the platinum-europium ratios are essentially the same as they would be in the pure equilibrium Eu-Pt phases. The molybdenum concentration on the products of runs for which tungsten-lined containers were used was about 30 ppm. Tungsten was not detected by either spectroscopic or x-ray fluorescence analysis in any of the products.

X-ray powder diffraction analysis of the platinum-phase products gave additional information. The most europium-rich phase formed in these experiments has the fcc MgCu_2 structure. The measured compositions of the products in equilibrium with two-phase mixtures of $\text{EuO} + \text{Eu}_3\text{O}_4$ ranged from $\text{EuPt}_{1.87}$ to $\text{EuPt}_{2.08}$. The lattice parameters of these samples were identical within the precision of our measurements ($\pm 0.005 \text{ \AA}$), with a value of $7.72_3 \text{ \AA}$. This indicates that the products were all of the same composition, which is required by the fact that they were all in equilibrium with the same two oxide phases at the same temperature. The variation in the measured compositions of the samples is significantly greater than can be explained by the $\pm 1\%$ uncertainties in weighing. Possible additional sources of

error that may have contributed to the spread in experimental values are the interaction between platinum and the containers and some vaporization process by which small amounts of platinum are lost from the wire or oxide is lost from the crystal. The weighted average of the compositions of the intermetallic phase in equilibrium with $\text{EuO} + \text{Eu}_3\text{O}_4$ is $\text{EuPt}_{2.021}$. The experimental compositions were weighted by the sample masses to account for differences in weighing precision. The lattice parameter reported for EuPt_2 by Elliott²⁷ is 7.731 Å. The lattice parameter of EuPt_{2+x} decreases linearly with increasing Pt concentration to a value of 7.620 Å for $\text{EuPt}_{2.8}$. The dependence of lattice parameter on composition for EuPt_{2+x} is shown in Fig. 1-2. The results of Harris²⁹ for EuPt_3 (MgCu₂ structure type) are inconsistent with mine, which indicate that the EuPt_{2+x} solid solution extends only to $\sim\text{EuPt}_{2.8\pm0.1}$.

X-ray diffraction results for samples with Pt:Eu ratios higher than 2.8 are inconclusive. The powder diagrams were either too poor in quality or too complicated for complete analysis. Compositions with Pt:Eu ratios of 3.17 and 3.45 appeared to be two-phase mixtures of $\text{EuPt}_{2.8}$ and another phase whose structure and stoichiometry are undetermined. Of the possible candidates for this phase, Eu_2Pt_7 seems to be the most reasonable. It is in agreement with our equilibration results, and preliminary single-crystal results on specimens from the $\text{EuPt}_{3.45}$ sample appear to be consistent with one of the Ln_2Ni_7 structure-types.³⁰⁻³³

Powder diagrams of the products with Pt:Eu ratios of 3.69 and 5.21 showed identical patterns corresponding to another unidentified phase plus some very weak Pt lines in the 5.21 pattern. The structure or stoichiometry of the phase producing these patterns has not been determined in this study, but it is probably EuPt_5 which has been prepared by Bronger.³⁴ Results from single-crystal studies of material from the samples with Pt:Eu ratios of 3.69 and 17.69 were consistent with single-crystal results for EuPt_5 reported by Bronger.³⁴ Although I do not have firm evidence, I believe that the reason the $\text{EuPt}_{3.69}$ sample appeared to be monophasic is that a EuPt_{5-x} solid solution is stable over a wide range of stoichiometries extending from the ideal Pt:Eu ratio of 5:1 to compositions which are substantially

Fig. I-2. The fcc lattice parameter of EuPt_{2+x} vs composition. Data obtained from measurements of back reflection lines of Debye-Scherrer powder patterns taken with $\text{CuK}\alpha$ radiation.

platinum-deficient, and that the concentration of Eu_2Pt_7 in the $\text{EuPt}_{3.69}$ was too low to observe by x-ray diffraction analysis. Products with Pt:Eu ratios of 9:1 and 17:1 contained mixtures of EuPt_5 and platinum. The platinum lines in these patterns were identical to those for pure Pt, with no detectable change in lattice parameter. Examples of x-ray powder patterns of selected products are shown in Fig. I-3. Table I-1 gives d-spacings taken from the patterns from the Pt:Eu = 3.45 and 5.21 samples. Professor Bronger kindly furnished a list of d-spacings for EuPt_5 to be compared with the unresolved patterns of this study. Neither of my unidentified phases produces a pattern that corresponds exactly to Prof. Bronger's EuPt_5 . EuPt_5 obtained in a study involving similar equilibrations between europium fluorides and europium-platinum phases at 1260°C produced patterns that corresponded to patterns from my products from the oxide equilibrations.³⁵ Inter-metallic products from the fluoride equilibrations with Pt:Eu ratios higher than 5:1 contained an unidentified phase not seen in the oxide experiments; Pt lines were not found in products from the fluoride experiments until the Pt:Eu ratio reached 95:1.

The results of the oxide-platinum equilibration experiments are summarized in Table I-2. I calculated the product compositions assuming that the weight loss of the oxide phase resulted only from europium loss and that all of this europium was transferred to the platinum phase. Ideally, the europium transfer could be measured both by the weight loss of the oxide and the weight gain of the platinum, which should be identical, but in my early experiments I was unable to accomplish this ideal mass balance. In many runs the platinum came in contact with the capsule and could not be quantitatively recovered. Even in those runs for which the recovery of the platinum phase seemed to be quantitative, and in the runs in which the platinum was placed in tungsten-lined cups, the weight gain of the platinum was always slightly less than the weight loss of the oxide. The discrepancy seemed to be the largest for the samples that contained the most platinum. Since the errors amounted to only 0.05 to 0.5 mg (a few tenths of a percent or less of the platinum weights) the discrepancies will not significantly alter the conclusions from these experiments. In the later runs the results indicated that the polycrystalline EuO

Pt/Eu = 2.02

Pt/Eu = 2.10

Pt/Eu = 2.75

Pt/Eu = 3.45

Pt/Eu = 5.21

↓ Platinum

Pt/Eu = 17.29

Fig. 1-3. Typical x-ray powder patterns of platinum-europium samples.

Table 1-1. d-Spacings for $\text{EuPt}_{3.45}$ and $\text{EuPt}_{5.21}$.

Pt:Eu = 3.45		Pt:Eu = 5.21	
d	I/I ₀	d	I/I ₀
4.55	15	4.57	10
4.40 ^a	10	2.66 ^a	15
2.83	5	2.5	--
2.69 ^a	10	2.42	--
2.53	5	2.26	65
2.40	--	2.19	100
2.31	60	2.14	--
2.29 ^a	100	2.06	--
2.22	15	1.96 ^b	--
2.18 ^a	70	1.69	5
2.15	75		
1.95	10	1.53	--
1.91 ^a	--		
1.75 ^a	7	1.45	10
1.69	5	1.38 ^b ₅	5
1.58	--	1.32 ₅	10
1.56 ^a	--	1.28 ₅	35
1.52	--	1.27	5
1.50	--	1.25 ₅	--
1.47	7	1.18 ^b	--
1.46	35	1.13 ^b ₈	10
1.43 ^a	10	1.10	15
1.42	--		
1.36	7		
1.34 ^a	30		
1.30 ₅	20		
1.28 ^a	15		
1.17 ₃	7		
1.14 ₅	40		

^aSpacings corresponding to fcc $\text{EuPt}_{2.8}$.^bSpacings corresponding to Pt.

Table I-2. Results from equilibration of samples in the Eu-Pt - Eu₂O₃ ternary system at 1500°C.

Composition of starting EuO-Pt mixture		Metallic phase product		Oxide phase product	
		X-ray analysis		X-ray analysis	
Mole fraction platinum	Composition Pt:Eu	Structure	Lattice parameters (Å)	Identification	Notes
Composition O:Eu	Analysis O:Eu	Structure	Lattice parameters (Å)	Identification	Notes
0.019 ₇	1.97 ₆ (1)	fcc	7.72 ₁	EuPt ₂₋₃ x	(8)
0.040 ₄	1.86 ₉ (2)	fcc	7.72 ₁	EuPt ₂₋₄ x	(8)
0.060 ₃	1.95 ₀ (2)	fcc	7.72 ₁	EuPt ₂₋₅ x	(6)
0.102 ₁	(2.59 ₀) (2,3)	fcc	7.72 ₁	EuPt ₂₋₁₂ x	(8)
0.143 ₇	1.83 ₃ (2)	fcc	7.72 ₁	EuPt ₂₋₁₂ x	(8)
0.180 ₉	2.03 ₂ (2)	fcc	7.72 ₁	EuPt ₂₋₁₂ x	(8)
0.212 ₅	2.04 ₉ (2)	fcc	7.72 ₁	EuPt ₂₋₁₂ x	(7)
0.252 ₀	2.03 ₀ (2)	fcc	7.72 ₁	EuPt ₂₋₁₂ x	(6)
0.289 ₈	2.03 ₁ (2)	fcc	7.72 ₁	EuPt ₂₋₁₂ x	(7)
0.317 ₀	2.07 ₈ (2)	fcc	7.72 ₁	EuPt ₂₋₁₂ x	(7)
0.318 ₈ (6)	1.98 ₈ (1)	fcc	7.72 ₁	EuPt ₂₋₁₂ x	(6)
0.353 ₇	2.13 ₅ (2)	fcc	7.71 ₅	EuPt ₂₋₁₂ x	(6)
0.356 ₁ (4)	2.06 ₀ (1)	fcc	7.71 ₅	EuPt ₂₋₁₂ x	(6)
0.382 ₄	2.13 ₁ (2)	fcc	7.71 ₅	EuPt ₂₋₁₂ x	(7)
0.396 ₈ (4)	2.03 ₇ (1)	fcc	7.71 ₅	EuPt ₂₋₁₂ x	(6)
0.417 ₃ (4)	2.19 ₁ (1)	fcc	7.69 ₁	EuPt ₂₋₁₂ x	(6)
0.452 ₇ (4)	2.62 ₄ (1)	fcc	7.63 ₉	EuPt ₂₋₁₂ x	(6)
0.467 ₄	2.75 ₂ (2)	fcc	7.64 ₂	EuPt ₂₋₁₂ x	(7)
0.484 ₁ (6)	2.61 ₈ (1)	fcc	Pattern too poor to measure		(6)
0.502 ₀ (4)	3.16 ₉ (1)	fcc + wk. lines	7.62	EuPt ₂₋₁₂ x (EuPt ₂₋₁₂) ¹²	(8)
0.531 ₂ (4)	3.44 ₅ (1)	(fcc) ¹² + unidentified	(7.62) ¹²	(EuPt ₂₋₁₂) ¹² (EuPt ₂₋₁₂) ¹²	(6)
0.545 ₀	3.68 ₇ (2)	unidentified		(EuPt ₂₋₁₂) ¹²	(8)
0.626 ₀	5.20 ₅ (2)	unidentified		(EuPt ₂₋₁₂) ¹²	(8)
0.748 ₀	9.13 ₄ (2)	unidentified + fcc	2.265	(EuPt ₂₋₁₂) ¹² Pt	(6)
0.848 ₄	17.29 ₁ (2)	unidentified + fcc	2.265	(EuPt ₂₋₁₂) ¹² Pt	(6)

NOTES:

- (1) Calculated from weight loss of oxide and weight gain of platinum phase.
- (2) Calculated from weight loss of oxide.
- (3) Value rejected, inconsistency between initial and final weights indicates weighing error.
- (4) Equilibrations done with configuration in Fig. 1, using tungsten liner in container for Pt.
- (5) EuO starting material was not single crystal and may have contained excess Eu, which would result in a high calculated experimental O:Eu ratio.
- (6) Wire intact, no melting, no container reaction, extensive recrystallization.
- (7) Wire stuck to capsule wall.
- (8) Completely melted, wet Mo capsule and formed strong bond. Boundary sharp with no evidence of extensive reaction. Analysis showed 200 ppm Mo.
- (9) Partly melted.
- (10) Inner core of EuO with dense outer layer of Eu₂O₃ which increases in thickness as the O:Eu ratio increases.
- (11) Inner core of dense polycrystalline Eu₂O₃ with outer layer of yellow material which increases in thickness with increasing O:Eu ratio. Yellow material is Eu₂O₃ with a small amount of Eu₂Si₂ uniformly dispersed in it.
- (12) Eu₂O₃ with uniformly dispersed second phase of Eu₂Si₂ identical to outer layer described in Note (11).

starting material may have contained excess Eu. For several of these runs the composition of the oxide phase product was determined by igniting the sample in air to constant weight (about 60 hr at 1200 to 1300°C) and measuring the weight gained on oxidizing to Eu_2O_3 . Weighings were made to ± 2 micrograms.

The quantitative results of the equilibrations are illustrated in Fig. 1-4, where the oxygen-to-europium ratios for the oxide phases are plotted against the platinum-to-europium ratios for the equilibrium metallic phases. The lines in Fig. 1-4 were drawn using the information from optical and structural (x-ray) examinations of the samples as well as the composition data. The graph represents the locus of the endpoint compositions of tie lines in the ternary diagram and facilitates finding the compositions of the binary compounds. Such a graph for a pair of binary systems with a common component, which form only binary compounds and no solid solutions or ternary compounds, would consist of vertical and horizontal line segments. Curved or sloped lines might be obtained where the equilibria involved solutions. These characteristics may be seen by comparing Fig. 1-4 with the derived ternary diagram shown in Fig. 1-5. The interpretation of results presented here is based on the following assumptions: (1) compounds and solid solutions may exist in either binary system but there are no ternary phases, (2) the solubility of either of the noncommon components in any phase of the other binary system is negligible, i.e., there is negligible solubility of platinum in any of the oxide phases or of oxygen in any of the platinum-containing phases.

A vertical line is drawn in Fig. 1-4 at $\text{Pt:Eu} = 2.02$ corresponding to the composition of the platinum phase in equilibrium with two-phase mixtures of EuO and Eu_3O_4 . A limit to the range of stoichiometry for single-phase EuO at 1500°C can be established from the run with the lowest platinum-to- EuO ratio. The starting EuO crystals were prepared in excess Eu as described above. The run with $\text{Pt:EuO} = 0.02$ gave a product with a uniform layer of Eu_3O_4 covering the EuO crystal. The calculated overall composition of the oxide product (assuming a starting composition of $\text{EuO}_{1.000}$) is $\text{EuO}_{1.010}$. Therefore, the range of stoichiometry of EuO at 1500°C is < 0.01 . This result is contradictory to the findings of Shafer.⁹ The lattice

Fig. I-4. Oxygen-europium ratios vs platinum-europium ratios for samples equilibrated at 1500°C.

Fig. I-5. A portion of the Eu-Pt- Eu_2O_3 ternary diagram at 1500°C.

parameter of EuO in the equilibration products that were oxygen-rich was 5.14₄, identical to the parameter for europium-rich products. The color and appearance in bulk and under the microscope were also the same for hypo- and hyperstoichiometric EuO.

Another vertical line at Pt:Eu = 2.10 corresponds to the intermetallic phase in equilibrium with two-phase mixtures of Eu₃O₄ and oxygen-deficient Eu₂O_{3-x}. The limits for the stoichiometry of Eu₃O₄ provided by the samples with oxide products of O:Eu = 1.31 and 1.35 are far beyond the actual values. Both of the above samples contained substantial amounts of second-phase material (either EuO or Eu₂O_{3-x}). The range on the oxygen-rich side was shown to be very small by the synthetic work discussed previously. The absence of dispersed second-phase precipitates in the bulk material, after quenching from equilibrations at 1500°C either with EuO or with oxygen-deficient Eu₂O_{3-x}, indicates that the composition range is not significantly greater at temperatures up to 1500°C than it is at room temperatures. As with EuO, the hypo- and hyperstoichiometric materials have identical x-ray and optical properties. I conclude that at 1500°C the range of stoichiometry in Eu₃O₄ is very small, and a horizontal line is drawn at O:Eu = 1.333.

The sloped line from Pt/Eu = 2.10 to 2.8 corresponds to equilibria between EuPt_{2+x} and Eu₂O_{3-x}. Additional dashed lines are drawn to represent equilibria involving the unidentified phase found in this study (taken to be Eu₂Pt₇) and EuPt₅. The final horizontal line is drawn through the data at O:Eu = 1.48, which corresponds to the composition of oxide in equilibrium with two-phase mixtures of the platinum-rich intermetallic (assumed to be EuPt₅) and platinum saturated with europium.

The ternary diagram for part of the system, Pt-Eu₂O₃-Eu at 1500°C constructed using the above information and assumptions, is shown in Fig. I-5.

Limiting values for the free energies of formation at 1773°K of EuPt_{2+x} can be derived from observed equilibria with the europium oxides. We can get the partial molal free energy of europium in an intermetallic compound at a given temperature if we know the Eu(g) pressure in equilibrium with the compound. This gives a limiting

value for the free energy of formation. Consider the following reactions:

Equation I-4 defines the formation of $\text{EuPt}_{2.02}\text{(s)}$ from the elements in their standard states. For $\text{EuPt}_{2.02}\text{(s)}$, $\Delta G_{f,1773}^0 = \Delta G(1) + \Delta G(2) + \Delta G(3)$. Observed equilibria between the intermetallic compounds and the oxides show $\Delta G(1) < 0$. References 36 and 37 give free energies for Eqs. I-2 and I-3 of $\Delta G(2) = -25.1 \text{ kcal}$ and $\Delta G(3) = 1.8 \text{ kcal}$. Therefore for $\text{EuPt}_{2.02}\text{(s)}$ $\Delta G_{f,1773}^0 < -23.3 \text{ kcal/gfw}$. The value $-23.3 \text{ kcal/g-atom}$ also corresponds to the partial molal free energy of Eu in the intermetallic compound, with Eu(l) as the standard state. We also know how the partial molal free energy of europium in the intermetallic compound is changing with increasing platinum content. I determined that $\text{EuPt}_{2.10}\text{(s)}$ is in equilibrium with $\text{Eu}_3\text{O}_4\text{(s)} + \text{Eu}_2\text{O}_{3-x}\text{(s)}$ at 1773°K . Haschke and Eick determined the Eu(g) pressures for the coexistence of these two oxides.³⁸ Consideration of a set of reactions similar to those above gives a value of $-34.4 \text{ kcal/g-atom}$ for the partial molal free energy of Eu in $\text{EuPt}_{2.10}\text{(s)}$ at 1773°K .

The Sm-Sm₂O₃ and Yb-Yb₂O₃ Systems

I attempted to prepare Sm_2O_3 , SmO , Yb_2O_3 , YbO and other reduced oxides of Sm and Yb. The starting materials were nominally 99.9% Sm_2O_3 and Yb_2O_3 that had been fired in air at 1200°C , and corresponding metal chips that had been cut from ingots of nominal 99% purity with a tungsten carbide tool. The ingots were cut under dry hexane and the material from the first cut was discarded to reduce oxide contamination. The chips were transferred into the steel glove box and mixtures were prepared in the same way described above for EuO . The samples were sealed in molybdenum capsules by EBW.

The Sm samples were heated to 2100°C and cooled quickly, with He gas used as a quenching aid. The capsules were broken open and the products recovered without the use of the glove box. All samples

had been completely melted and cooled to a uniformly dark gray product. X-ray powder diffraction and microscopic analyses showed that the products, in all cases, were Sm_2O_3 with finely dispersed samarium metal. To check for the possible existence of Sm compounds stable only at lower temperatures, the samples were again sealed in molybdenum capsules and heated for 8 hr at 1500°C . The products of this run were identical to the starting material.

The results indicate that at temperatures above 2100°C , the system is one liquid phase for compositions from Sm metal to ones with O:Sm ratios of 1.33 or higher, and that no crystalline oxide of samarium other than Sm_2O_3 exists.

The Yb samples were heated for several hours at 1800°C in sealed molybdenum capsules and allowed to cool in the furnace under vacuum (about five min to cool to 700°C). The composition Yb_2O had completely melted and appeared to consist of a mixture of dark red crystals and excess metal. With the other two compositions, only the metal phase melted. In these samples the oxide sintered and consisted of very dark red crystals about 0.01 mm across.

Examination with the polarizing microscope showed the material to contain a mixture of dark red crystals and colorless crystals in addition to the excess metal. There was no birefringence. X-ray powder diffraction analysis showed only Yb_2O_3 (bcc) and Yb (fcc). By spectrographic analysis, the only metallic impurities detected in the products at levels greater than 15 ppm were La (3000 ppm) and Lu (2000 ppm).

The excess metal was dissolved from one sample with HCl as described by Miller and Daane.¹⁹ The loose crystalline powder from this treatment was washed in distilled water, transferred to a platinum dish, and dried in a vacuum oven at about 50°C . The weight gain of this sample, on ignition in air at 1200°C , was measured to assess the oxygen deficiency of $\text{Yb}_2\text{O}_{3-x}$ in equilibrium with Yb metal at 1800°C . The sample of 0.296211 g gained 112 μg on ignition. The composition of the reduced sesquioxide calculated from these data is $\text{YbO}_{1.495}$, which agrees well with the compositions of reduced sesquioxides of other rare earth elements reported by Miller and Daane.¹⁹

Since my products were obviously two-phase at room temperature, the reduced sesquioxide apparently disproportionated into $\text{Yb}_2\text{O}_3 + \text{Yb}$ as it cooled from 1800°C . I have assumed that the metal from this reaction is dispersed within the crystalline material and is not dissolved when the bulk excess metal is removed. If some of this metal was lost in the HCl treatment, then the oxygen deficiency in $\text{Yb}_2\text{O}_{3-x}$ at 1800°C is somewhat greater than the value I have reported.

Another sample of composition YbO was heated to 1450°C for 3 hr and cooled slowly (3 hr to 1000°C). The reaction temperature for this sample was in the range used by Achard for preparations of YbO.¹⁵ The product was a sintered pellet of oxide similar to the previous samples, but the excess metal was concentrated at the bottom of the capsule rather than dispersed through the oxide pellet.

I conclude that Yb_2O_3 is the only stable oxide of ytterbium and that the material Achard reported as YbO was probably a solid solution of oxygen in YbN similar to the samarium oxide-nitride that has been confused with SmO .¹⁷ Since Achard's preparations were made by reducing the sesquioxide with carbon, an oxide-carbide is also a possibility.

Conclusions

I have established that EuO and Eu_3O_4 are the only stable reduced oxides of europium and that they both have very narrow ranges of composition. I have also shown that oxygen-deficient $\text{Eu}_2\text{O}_{3-x}$ is stable to $\text{Eu}_2\text{O}_{2.90 \pm 0.02}$ at 1500°C . In the Eu-Pt system, the range of stoichiometry for the fcc (MgCu_2)-phase EuPt_{2+x} has been determined to be EuPt_2 to $\text{EuPt}_{2.8 \pm 0.1}$ at 1500°C , and two additional intermetallic phases were observed.

In contrast to the fluorides, for which there is rather close correspondence between the samarium, europium, and ytterbium systems,^{35,39} there are no stable oxides of samarium or ytterbium corresponding to EuO or Eu_3O_4 . This is a manifestation of the enhanced stability of the divalent oxidation states in the fluoride systems compared to the oxide systems. Results from two related investigations also show greater stability for divalent europium in the fluoride than in the oxides. In products from a study of the Eu-O-F ternary system

we found $\text{EuF}_{2.0}$ in equilibrium with oxygen-deficient $\text{Eu}_2\text{O}_{3-x}$ (Thesis, Part II). An investigation involving the equilibration of europium fluorides with platinum-europium phases was carried out at a lower temperature than that used for the oxide equilibrations, so the results cannot be compared directly. However, the fact that EuF_2 is in equilibrium with EuPt_5 at 1260°C ,³⁵ while EuO is in equilibrium with EuPt_2 at 1500°C , indicates that the divalent state is much more stable in the fluoride, since the activity ratio of europium between EuPt_2 and EuPt_5 is not expected to change much from 1260 to 1500°C . The factors that lead to the marked differences in stability of the divalent oxidation states of the lanthanum elements between the fluoride and the oxide systems are still not understood.

Part II

STUDIES OF THE Eu-O-F AND Sm-O-F SYSTEMS

Abstract

I investigated a portion of the ternary system Eu-Eu₂O₃-EuF₃ by equilibrating EuO-EuF₃ and EuO-EuF₂ mixtures at 1500°C and examining the products with a polarizing microscope and by x-ray diffraction. The composition at the liquid-solid boundary was not measured directly, but was estimated. A phase diagram is presented for that part of the system studied. No ternary compounds are formed with europium in an oxidation state lower than +3 in samples cooled from 1500°C.

I examined several compositions of the Eu₂O₃-EuF₃ and Sm₂O₃-SmF₃ binary systems, using differential thermal analysis and x-ray powder diffraction. In these systems, at least one intermediate phase (and probably two or more) in addition to LnOF is stable. These additional phases all lie on the fluoride side of LnOF. At temperatures above 600°C, solid solutions extend from approximately LnO_{0.8}F_{1.4} to LnO_{0.6}F_{1.8}.

Introduction

A few years ago, anomalous magnetic behavior in EuF₂ which was associated with trace impurities in the single crystals was observed.⁴⁰ The magnetic and optical properties of the inclusions in the EuF₂ crystals did not appear to correspond to any known europium compound. This prompted me to investigate the Eu-EuF₃-Eu₂O₃ system in an attempt to identify the impurity, since oxygen seemed to be the most probable contaminant. The EuF₂-EuF₃ and the EuO-Eu₂O₃ binary systems have been described in detail in Part I of this thesis and elsewhere.^{8,35,39}

Bevan et al.⁴¹ discussed the lanthanon oxyfluorides and reviewed the literature on these systems. Oxyfluorides have been reported for all the lanthanon (Ln) elements and yttrium, and the structures for the stoichiometric MOF compounds at room temperature for all but Ce, Tm, Yb, and Lu seem to be established as the rhombohedral LaOF-type

described by Zachariasen⁴² for LaOF and YOF.⁴¹⁻⁵⁰ For La and Y, Zachariasen found tetragonal solid solutions $\text{MO}_{1-x}\text{F}_{1+2x}$ ($0.0 < x < 0.3$) in addition to the stoichiometric rhombohedral LaOF and YOF.⁴² Bevan et al. showed that for the Y, Sm, Gd, and Er oxyfluorides, the composition region between the stoichiometric MOF and the trifluoride is much more complicated than previously assumed.⁴¹ The continuing investigation of the intermediate composition region and the transition of stoichiometric MOF from rhombohedral to cubic (fluorite) for La, Nd, Sm, and Gd was reported by Brauer and Roether.⁴⁹ Recently, Shinn and Eick published a paper on the rhombohedral-to-cubic transition for MOF compounds ($M = \text{La, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, and Y}$).⁵⁰

Detailed investigation of the phase relationships in the extremely complex oxyfluoride systems was not attempted here, because I was primarily interested in the possible existence of a compound containing europium in the divalent state. However, differential thermal analysis (DTA) and Debye-Scherrer x-ray powder diffraction studies were made for several compositions in the $\text{EuF}_3\text{-Eu}_2\text{O}_3$ system. These studies provide evidence for previously unknown oxyfluoride phases of Eu^{III} , supporting the findings of Bevan, Brauer and co-workers^{41,49} that the region between stoichiometric MOF and the trifluorides for lanthanon elements and yttrium is occupied by a number of discrete phases that undergo transitions or disproportionation reactions on heating. Similar studies were attempted with the analogous samarium system, but useful quantitative information was obtained only for stoichiometric SmOF.

The present study shows no ternary compounds in the $\text{Eu-EuF}_3\text{-Eu}_2\text{O}_3$ system with europium in an oxidation state lower than +3. The only phase in this system which resembles in any respect the impurities in the EuF_2 crystals of Ref. 40 is Eu_3O_4 . The color and structure of Eu_3O_4 are consistent, but the magnetic properties do not correspond to those of the impurity material. Recently, Shafer and Kuptsis published convincing evidence that the impurity in EuF_2 responsible for the anomalous magnetic behavior observed in Ref. 40 and other work was a sulfide of europium.⁵¹

The EuF_2 -EuO System

EuF_2 was prepared by hydrogen reduction of EuF_3 in a molybdenum container. EuO was made by reduction of Eu_2O_3 by Eu in a sealed Mo capsule. These materials are more fully described in Ref. 39 and Part I of this thesis.

Mixtures of EuO and EuF_2^* were sealed in molybdenum capsules by electron bombardment welding (EBW). The samples were heated to 1500°C in a vacuum induction furnace, held at that temperature for at least 2 hr, and cooled quickly by turning off the power and introducing argon or helium. About 2 min were required for the temperature to fall below 750°C . The resulting products were examined by x-ray powder diffraction and optical microscopy.

All the EuF_2 -EuO mixtures had completely melted. Microscopic examination of the products showed the composition 0.4 EuF_2 -0.6 EuO to be very near the eutectic. Samples with larger proportions of EuF_2 showed the eutectic structure in a matrix of EuF_2 . X-ray analysis showed the products of all of these runs to be EuO (cubic), $a = 5.14_4 \text{ \AA}$ and EuF_2 (fcc), $a = 5.84_3 \text{ \AA}$.

The EuF_3 - Eu_2O_3 and SmF_3 - Sm_2O_3 Systems

Mixtures of EuF_3 and Eu_2O_3 or SmF_3 and Sm_2O_3 were sealed in platinum-10% rhodium capsules by EBW and heated to 1500°C in an induction furnace. The products were crushed and resealed in Pt-10Rh capsules, again heated to 1500°C for 2 hr, and rapidly cooled by turning off the furnace power. Starting materials were nominal 99.9% oxides and trifluorides that had been heated in air or under HF to reduce contamination and stored in desiccators, as described in Ref. 39 and Part I of this thesis.

Samples from the above preparations were examined by x-ray powder diffraction, optical microscopy, and DTA. Samples of approximately 0.4 g for DTA were encapsulated in Pt-10Rh containers by EBW at $\sim 10^{-5}$ Torr. Measurements were made at heating rates of $10^\circ\text{C min}^{-1}$ from 200° to 1500°C .

*The compositions are plotted in Fig. II-1.

Fig. II-1. A section of the ternary system Eu-Eu₂O₃-EuF₃ at 1500°C. Data points correspond to the compositions listed in Table II-2 and sample EuO-EuF₂ mixtures.

My observations on EuF_3 - Eu_2O_3 and SmF_3 - Sm_2O_3 are insufficient to provide a complete understanding of these systems. Seven compositions in each system were studied. Optical examination did not provide useful information because of the similarity of the appearance of all phases under either unpolarized or polarized light. Refractive index measurements would be required to distinguish between the various phases. Since DTA measurements were limited to temperatures below 1500°C , melting was observed only for compositions rich in trifluorides. However, I did observe a number of effects that may help to provide a better understanding of these systems. A summary of my observations and interpretations is given in Table II-1, and a tentative phase diagram for the Eu_2O_3 - EuF_3 system is presented in Fig. II-2. Other possible phase diagrams are consistent with the observations. Figure II-2 is presented primarily to describe the general behavior of the binary system and to define assumptions used in interpreting the Eu - EuF_3 - Eu_2O_3 ternary system.

Reversible thermal effects were observed beginning at 501°C for SmOF and at 503°C for EuOF (Table II-1). The temperatures for these effects are in good agreement with those reported by Brauer⁴⁹ for the rhombohedral-cubic transitions in oxyfluorides of La, Nd, Sm, and Gd. Brauer found these transitions in the range from 450° to 550°C with the value for SmOF close to 500°C . Shinn and Eick report rhombohedral-cubic transitions at 524°C for SmOF and 513°C for EuOF .⁵⁰ Shinn and Eick apparently reported peak maxima rather than temperatures corresponding to the initiation of transitions on heating, which may account for some of the discrepancy between my results and theirs. Despite the higher heating and cooling rates used in my experiments, the hysteresis I observed was only about 5° for SmOF and 10° for EuOF , compared with the 20° reported as typical by Shinn and Eick. The thermal effect beginning at 481°C in the sample with composition $\text{EuO}_{0.9}\text{F}_{1.2}$ is probably due to the rhombohedral-cubic transition in EuOF , lowered in temperature by solution of fluoride.

X-ray analyses indicated that except for the sample of stoichiometric SmOF , the samarium oxyfluoride mixtures did not reach equilibrium. Samples with compositions $\text{SmO}_{0.9}\text{F}_{1.2}$, $\text{SmO}_{0.8}\text{F}_{1.4}$ and

Table II-1. X-ray and DTA results for the Eu_2O_3 - EuF_3 system and SmOF .

Composition	X-ray powder diffraction analysis of products	DTA results	
		Temperature range-°C	Peak height ^a
EuOF	EuOF (rhomb)	503-505	5.3
$\text{EuO}_{0.9}\text{F}_{1.2}$	EuOF (rhomb) + wk lines	481-498	1.8
$\text{EuO}_{0.8}\text{F}_{1.4}$	EuOF (rhomb) + wk lines	718-734	1.5
$\text{EuO}_{0.7}\text{F}_{1.6}$	EuOF (rhomb) + EuF_3 (orth)	721-734	4.1
$\text{EuO}_{0.6}\text{F}_{1.8}$	EuOF (rhomb) + EuF_3 (orth) + wk lines	505-522	1.0
$\text{EuO}_{0.3}\text{F}_{2.4}$	EuF_3 (orth) + wk lines	553-578	0.7
		568-588	(0.5) ^b
		1293-1315	8.8
EuF_3	EuF_3 (orth)	776-806	~3
		1180-1258	21.9
SmOF	SmOF (rhomb)	501-508	7.7

^a Peak heights normalized to average sample size of 0.4 g. assuming peak height directly proportional to mass of sample.

^b Peak detectable only on cooling.

Fig. II-2. The binary system Eu_2O_3 - EuF_3 .

$\text{SmO}_{0.7}\text{F}_{1.6}$ appeared to be mixtures of SmOF (rhombohedral) + Sm_2O_3 (bcc) after heating at 1500°C as described above. Samples of $\text{SmO}_{0.6}\text{F}_{1.8}$ and $\text{SmO}_{0.3}\text{F}_{2.4}$ appeared to be mixtures of SmOF (rhombohedral) and SmF_3 (orthorhombic). I observed thermal effects in these samples that were similar to those seen in the europium oxyfluorides but with lower intensities, wider temperature ranges, and more hysteresis. In the samarium oxyfluoride mixtures, I did not observe an effect corresponding to the peaks at 720°C in $\text{EuO}_{0.9}\text{F}_{1.2}$ and $\text{EuO}_{0.8}\text{F}_{1.4}$. Failure to achieve equilibrium in the samarium oxyfluoride system is not surprising. Bevan et al. found that several hours of annealing were needed to prepare the fluorine-rich phases they identified.⁴¹

The europium oxyfluoride system was apparently better behaved than the corresponding samarium system, although it is possible that the effects observed in both systems correspond to metastable equilibria. Observation of the thermal effect at 720°C for $\text{EuO}_{0.9}\text{F}_{1.2}$ and $\text{EuO}_{0.8}\text{F}_{1.4}$ and the absence of the rhombohedral-cubic transition in $\text{EuO}_{0.8}\text{F}_{1.4}$ implies the existence of an intermediate compound such as that reported by Brauer⁴⁹ for the samarium oxyfluoride system. The thermal effect at 1293°C for $\text{EuO}_{0.3}\text{F}_{2.4}$ was due to melting, as confirmed by visual inspection of samples heated to 1500°C in sealed Pt-10 Rh containers before being loaded into the DTA capsules. The $\text{SmO}_{0.3}\text{F}_{2.4}$ sample also was completely melted at 1500°C . None of the other samples showed any evidence even of partial melting after being heated to 1500°C . The small temperature range of the thermal effect indicates that the eutectic composition lies very close to $\text{EuO}_{0.3}\text{F}_{2.4}$.

The disappearance of the thermal effect corresponding to the rhombohedral-to-cubic transitions of the stoichiometric oxyfluorides in samples of higher fluoride concentration is at variance with x-ray results indicating the presence of LnOF (rhombohedral) at room temperature for all compositions down to $\text{LnO}_{0.6}\text{F}_{1.8}$ in both the samarium and europium systems. A possible explanation for this discrepancy is that phases identified as SmOF (rhombohedral) and EuOF (rhombohedral) in the fluoride-rich samples were actually compounds with closely related structures in the composition range $\text{LnO}_{0.9}\text{F}_{1.2}$

to $\text{LnO}_{0.6}\text{F}_{1.8}$. The structures of all of these phases reported by Brauer⁴⁹ are closely related to the fluorite structure. My specimens could also be composed of phases quenched in from solid-solution regions at higher temperatures.

An attempt to prepare an oxyfluoride $\text{Eu}_3\text{O}_4\text{F}$ analogous to the phase $\text{Eu}_3\text{O}_4\text{Br}$ reported by Bärnighausen⁸ was unsuccessful. A sample of this composition prepared from EuF_3 plus Eu_2O_3 yielded EuOF (rhombohedral) plus Eu_2O_3 (bcc, $a = 10.86_9 \text{ \AA}$) when annealed at 1500°C and quickly cooled. In only four cases have I seen Eu_2O_3 in the cubic form after it was heated above 1300°C : in this preparation, in a ternary mixture described in Table II-2, and in the products of two preliminary runs in which mixtures of $\text{EuO} + \text{EuF}_3$ and $\text{EuF}_2 + \text{EuF}_3 + \text{Eu}_2\text{O}_3$ were heated to 1800° in tantalum containers, cooled slowly to 1500°C , and then quenched. The products of the runs in tantalum were $\text{EuF}_{2.26}$ (fcc, $a = 5.80_5 \text{ \AA}$) + Eu_2O_3 (bcc). These results have not been included in the discussion of the ternary system because the samples reacted with the tantalum containers.

The similarity between the oxyfluoride systems and the reduced fluoride systems is worthy of some attention. Solid solutions and nonstoichiometric compounds in both the $\text{LnO}_{1-x}\text{F}_{1+2x}$ ($0 \leq x \leq 0.4$) (see Refs. 41, 42, and 49) and the LnF_{2+x} ($0 \leq x \leq 0.45$) (see Refs. 35 and 39) systems have structures based on an fcc fluorite lattice. The predominant lattice defects in a number of nonstoichiometric oxides, fluorides, and oxyfluorides based on the fluorite structures are interstitial anions or anion vacancies.⁵² Interstitial anions have been shown to be the primary lattice defect in several such solid solutions involving a lanthanon trifluoride in a difluoride or an oxyfluoride.^{39,52-55} The cation sublattice in these systems is essentially ideal.

Because of the energy involved in anion-cation separation, it is unlikely that configurations that do not satisfy local charge compensation will be significant in these systems. In LnOF (fluorite), the oxide and fluoride ions are randomly distributed on the anion lattice sites, satisfying the condition that unit cells with excess oxide ions contain corresponding anion vacancies and cells with excess fluoride ions contain corresponding interstitial ions. For solid solutions containing

Table II-2. Analysis of compositions in the ternary system Eu-Eu₂O₃-EuF₃ prepared by equilibrating EuO-EuF₃ mixtures at 1500°C.

Mol ratio EuO/EuF ₃	Optical observations (transmitted light)	X-ray sample No.	X-ray powder pattern observations (with intensity and quality) ^o					Comments
			fcc fluoride phase [†]		Composition- EuF _{2+x}	Additional phases [‡]		
			Lattice parameter-Å	Pattern		Pattern	Composition	
2.70 ^{\$}	1st phase dark red, transparent, and brightly birefringent	1	5.84 ₀	s, g	EuF _{2.00}	s, g m, f	EuO Eu ₃ O ₄	—
	2nd phase colorless, transparent, and non-birefringent	2	5.80 ₅	m, p	EuF _{2.26}	s, g s, g	EuO Eu ₃ O ₄	—
	3rd phase opaque (1st phase is major component; 2nd phase minor; 3rd phase very small amounts.)							
2.33 ^{\$}	1st phase dark red, transparent, and brightly birefringent	1	5.83 ₈	s, g	EuF _{2.02}	w, p	Eu ₃ O ₄	—
	2nd phase colorless, transparent, and non-birefringent							
	3rd phase colorless, transparent, and brightly birefringent (1st and 2nd phases about equal in amount; 3rd phase very small amounts.)							
1.86 ^{\$}	Same as previous sample	1	5.83 ₈	s, g	EuF _{2.02}	m, f	Eu ₃ O ₄	—
1.50 ^{\$}	1st phase colorless, transparent, and non-birefringent	1	5.83 ₈	s, g	EuF _{2.02}	s, g	Eu ₂ O ₃ (monoclinic) + additional weak lines, possibly EuOF	—
	2nd phase light tan, transparent, with mosaic-like birefringence (Both phases about equal in amount.)	2	5.84 ₀	s, g	EuF _{2.00}	s, g	Eu ₂ O ₃ (monoclinic)	—
1.50 ^{\$\$}	1st phase light tan, transparent, and non-birefringent	1	5.80 ₅	s, g	EuF _{2.26}	m, f	Eu ₂ O ₃ (bcc)	Cooled slowly, see discussion under section 3.
	2nd phase colorless, transparent, and brightly birefringent (Both phases about equal in amount.)							
1.22 ^{\$}	1st phase light tan, transparent, with mosaic-like birefringence	1	5.83 ₈	s, g	EuF _{2.02}	w, p	EuOF + sev- eral extra weak lines	
	2nd phase colorless, transparent, and non-birefringent (1st phase is major component.)	2	5.80 ₅	s, g	EuF _{2.26}	s, g	EuOF + sev- eral extra weak lines	

Table II-2 (continued)

Mol ratio EuO/EuF ₃	Optical observations (transmitted light)	X-ray sample No.	X-ray powder pattern observations (with intensity and quality) [*]					
			fcc fluoride phase [†]			Additional phases [‡]		Comments
			Lattice parameter-Å	Pattern	Composition- EuF _{2+x}	Pattern	Composition	
1.00 [§]	1st phase tan, transparent, and none-birefringent	1	5.80 ₅	m, f	EuF _{2.28}	s, g	EuOF	—
	2nd phase colorless, transparent, and birefringent	2	5.83 ₀	s, g	EuF _{2.09}	w, p	EuOF	—
		3	5.81 ₄	s, g	EuF _{2.20}	s, g	EuOF	—
0.825 ^{§§}	1st phase colorless, transparent, and non-birefringent 2nd phase light tan, transparent, and birefringent (Both phases about equal in amount.)	1	5.79 ₅	s, g	EuF _{2.27}	s, g	EuOF	—
0.618 [§]	Same as previous sample but with opaque metallic inclusions (Mo contamination)	1	5.78 ₃	m, f	EuF _{2.28-2.43}	s, g	EuOF	Interior of crucible corroded
0.667 ^{§§}	1st phase colorless, transparent, and brightly birefringent 2nd phase tan, transparent with some optical density, and birefringent	1	5.78 ₃	s, g	EuF _{2.28-2.43}	(Patterns very similar to EuOF)		
0.667 [§]	Same as previous sample but with opaque metallic inclusions (Mo contamination)	1	5.78 ₃	m, f	EuF _{2.28-2.43}	m, f	EuOF	Interior of crucible corroded
0.400 ^{§§}	At least two colorless, transparent phases, with some birefringence	1	5.78 ₂	s, g	EuF _{2.28-2.43}	(Patterns similar to EuOF but with different lattice parameters.)		(Sample perhaps not completely melted)
0.389 ^{§§}	1st phase brown, transparent, and weakly birefringent 2nd phase colorless, transparent, and non-birefringent	1	5.78 ₃	s, g	EuF _{2.28-2.43}	(Several unidentified lines)†		Cooled slowly

^{*} Powder pattern observations rated as follows:
s - strong; m - medium; w - weak; g - good; f - fair; p - poor

[†] EuF_{2+x} solid solution; compositions derived from lattice parameter, Ref. [2].

[‡] Phases identified from patterns corresponding to the following structures:

EuO (fcc)—a = 5.14₅ Å

Eu₃O₄ (orthorhombic)—a = 10.09 Å; b = 12.07 Å; c = 3.50 Å

Eu₂O₃ (monoclinic)—a = 14.04 Å; b = 3.68 Å; c = 8.74 Å; β = 100° 7'

Eu₂O₃ (bcc)—a = 10.86₉ Å

EuOF (rhombohedral, hexagonal representation)—a = 3.88₄ Å; c = 19.34₅ Å

[§] Container: Mo

^{§§} Container: Pt-10%Rh

excess LnF_3 that have either the fluorite or a closely related structure, the extra fluoride ions are introduced as pairs, one substituting for an oxide ion and the other as an associated interstitial ion. Changes in structure involving ordering of these "defects" require interdiffusion of the anions. As pointed out by Brauer,⁴⁹ dimorphic transitions become more difficult in these systems as the interstitial sites are filled.

In the reduced fluoride systems with compositions LnF_{2+x} , the excess F^- ions are introduced as associated pairs of interstitial F^- ions and trivalent cations. Phase changes in these systems should occur more readily because they require only local rearrangements of anions and electron transfers. In fact, the manifestation of this behavior is observed in the difference between DTA thermograms for the difluoride-trifluoride,³⁵ and the oxide-fluoride systems. The hysteresis for nonstoichiometric samples is much more pronounced for the oxyfluoride material.

The Ternary System in the Region Bounded by the Composition EuF_2 - EuF_3 - Eu_2O_3 - EuO

Compositions within the ternary field were prepared by equilibrating mixtures of EuF_3 and EuO . The mixtures were encapsulated in either Mo or Pt-10Rh crucibles and sealed by ERW. Starting materials were the EuF_3 and EuO already described. Molybdenum crucibles were used for mixtures for which the EuO/EuF_3 mole ratio exceeded 0.67 and Pt-10Rh crucibles for mixtures with $\text{EuO}/\text{EuF}_3 \leq 1.50$. Several intermediate compositions were heated in both kinds of containers. The samples were held at 1500°C in an induction furnace for at least 2 hr before being cooled rapidly. Two samples were cooled slowly after annealing at 1500°C .

The products of the equilibrated mixtures of EuF_3 and EuO were examined by x-ray powder diffraction and optical microscopic techniques. (See Table II-2.)

Optical identification of EuO and Eu_3O_4 is unambiguous because no other phases in this system appear similar to either of these materials. Fluorides on the divalent side of $\text{EuF}_{2.1}$ are transparent, nearly

colorless, and nonbirefringent. Fluorides from $\text{EuF}_{2.1}$ to $\text{EuF}_{2.3}$ are transparent, light brownish-yellow, and weakly birefringent. Compositions from $\text{EuF}_{2.3}$ to EuF_3 are transparent, nearly colorless, and brightly birefringent.³⁹ It is difficult to detect small concentrations of EuO in Eu_3O_4 or of EuF_{2+x} in one of the other transparent colorless phases. It is not possible to distinguish between EuF_3 , EuOF , and Eu_2O_3 without using more sophisticated techniques than those applied in this study. However, very small amounts of EuO can be detected in phases other than Eu_3O_4 . It is also easy to detect very small amounts of one of the trivalent species or of Eu_3O_4 in any of the other phases.

The compositions of the fluorides found in the products were obtained from x-ray lattice parameters by using data reported in Ref. 39. In a number of runs, microscopic examination indicated the presence of more than one fluoride composition. For these cases, x-ray powder diffraction patterns were taken for several samples. The x-ray data confirmed that two different fluoride compositions were present in some of the products, and three fluoride compositions were found in one sample. The composition of crystalline products in rapidly cooled samples depends upon the phase boundary surfaces in the system and the crystallization paths. Since my samples were cooled rapidly, equilibrium was not necessarily maintained, and more than three phases were found in some of the products.

The interpretation most consistent with the ternary equilibration data, the Eu_2O_3 - EuF_3 pseudo-binary shown in Fig. II-2, and the EuO - Eu_2O_3 binary system (see Ref. 8 and Part I of this thesis) is illustrated in Fig. II-1.

Conclusions

The ternary equilibria in the Eu-O-F systems are well established at 1500°C , with the following exceptions. The number, compositions, and structures of the oxyfluoride phases in the range $\sim\text{EuO}_{0.6}\text{F}_{1.8}$ to $\text{EuO}_{0.8}\text{F}_{1.2}$ are uncertain. The phase diagram (Fig. II-1) is drawn on the assumption that the EuF_3 - Eu_2O_3 system is binary and correctly represented in Fig. II-2. The liquidus points on

the EuF_3 - Eu_2O_3 and EuF_2 - EuO joins can be estimated with fair reliability, but the liquid-solid phase boundaries in the intermediate region are pure speculation. The products of the EuF_3 - EuO reactions all appeared to have been completely melted; but since the samples were not crushed and reheated nor analyzed by DTA, the possibility that some of these compositions could have been only partially liquid at 1500°C cannot be excluded. The diagram in Fig. 11-1 is drawn as if there were only one liquid phase, but there is no direct evidence for this interpretation. A miscibility gap may exist between anion-rich and metal-rich liquids similar to the gaps found in other lanthanon-lanthanon-halide systems.⁵⁶⁻⁶² The region of the system on the metal-rich side of EuO - EuF_2 has not been investigated.

There is clearly no evidence for a ternary compound in this system other than those between EuF_3 and Eu_2O_3 . It is possible that one or more other ternary compounds may exist; but I think this unlikely, as no such phase was evidenced in any of the preparations — neither in those cooled rapidly nor in those cooled slowly.

The optical and x-ray properties of the three oxide phases prepared in the presence of fluorides are identical to those observed for samples in which no fluoride was present. Also, the properties of the fluorides formed in the presence of oxides or oxyfluorides are identical to those of fluorides for which analysis indicates negligible oxygen content. Therefore, I believe that the solubility of fluorides in any of the oxide phases or of oxide in the fluorides is very small in the crystalline state. Since there were no color changes in the oxyfluoride samples equilibrated with reduced fluorides similar to the color changes observed when lanthanon sesquioxides are partially reduced (see Ref. 19 and Part I of this thesis), partially reduced or anion-deficient lanthanon oxyfluorides may not be stable. One would have expected to observe partially reduced solid solutions based on the fluorite structure with anion vacancies, particularly in the europium oxyfluoride system.

VAPORIZATION STUDIES

Part III

A MASS SPECTROMETRIC INVESTIGATION OF THE SUBLIMATION OF HAFNIUM AND ZIRCONIUM FROM A DILUTE HAFNIUM ALLOY

Abstract

The vaporization of hafnium and zirconium from a hafnium alloy filament with an initial zirconium content of 5 at.% was studied over the temperature interval 1800 to 2300°K, using a mass spectrometer. Least-squares analyses of hafnium ion intensity vs temperature data by the second-law method gave a standard enthalpy of sublimation at 298.15°K, ΔH_{298}^0 , of 153.6 ± 3.0 kcal/g atom. Similar analyses of zirconium ion intensity data gave a standard partial molar enthalpy of sublimation, $\overline{\Delta H}_{298}^0$, of 148.8 ± 3.4 kcal/g atom, which is in agreement within the estimated experimental errors with the standard enthalpy of sublimation of pure zirconium. The hafnium data were also analysed by the second-law and the third-law methods, with zirconium used as a reference, assuming the alloy to be an ideal solution. Second-law evaluation of the intensity ratio data gave $\Delta H_{298}^0 = 150.04 \pm 2.3$ kcal/g atom, and the third-law treatment gave an average value of 148.5 ± 2.5 kcal/g atom, for the enthalpy of sublimation of hafnium.

Introduction

Experimental values for the enthalpy of sublimation of hafnium were unavailable when this investigation was started. Stull and Sinke⁶³ estimated $\Delta H_{298}^0 = 168$ kcal/g atom, using a reported normal boiling point, and Krikorian⁶⁴ estimated $\Delta H_{298}^0 = 145$ kcal/g atom by correlating properties of neighboring elements of the periodic table.

Subsequently, the vaporization of hafnium was studied by several investigators using Langmuir vaporization techniques⁶⁵⁻⁶⁸ and a mass-spectrometric Knudsen vaporization method.⁶⁹ The results of these investigations were evaluated and reduced by use of a consistent set of thermodynamic functions.^{68, 70} The value recommended by Hultgren et al.,⁷⁰ based on Refs. 65-67, is $\Delta H_{298}^0 = 148.0 \pm 1.0$ kcal/g atom, and the results of Koch et al.⁶⁸ for liquid hafnium are in

agreement with that value. My results are slightly higher than these and are in accordance with Blackburn⁶⁷ and Trulsen and Goldstein's⁶⁹ results.

Longfellow and Wood⁷¹ reported the results of an investigation on the cohesive energy of hafnium in which they compare the cohesive energies of two materials by measuring the wear-rate ratios of the materials during a spark erosion process. Their result for hafnium was 185.5 ± 8.5 kcal/g atom. Longfellow and Wood expressed concern about uncertainties in the thermodynamic properties of hafnium. Certainly, the properties must be reliably known in order to properly assess the significance of the anomalous wear-rate ratios observed with this element.

Work described in this thesis confirms the previously reported experimental determinations of the enthalpy of sublimation of hafnium and introduces a somewhat novel technique for using mass spectrometry to study vaporization phenomena.

A sensitive technique is required to study the vaporization of solid hafnium, since it has such a low vapor pressure (about 10^{-6} atm at the melting point, 2500°K). The evaporation process may be complicated by reaction of hafnium with oxygen, in the environment or dissolved in the metal, to form a volatile oxide, even at low oxygen activities. A mass spectrometer is both sensitive and selective. With such an instrument one can study individually each of the species vaporizing from a sample. And they can be studied even at very low partial pressures. Vapor species could be detected at vaporization rates corresponding to pressures as low as 10^{-12} atm in the system used for these experiments. This sensitivity refers to condensible species; the sensitivity for noncondensable gases is greater because of multiple passes through the ionizing region of the ion source made by noncondensable gas molecules. This high sensitivity permitted measurements to be made over a temperature range greater than 500°K, with a corresponding range in hafnium vapor pressure of four orders of magnitude from $\sim 10^{-11}$ atm at 1800°K, to $\sim 10^{-7}$ atm at 2300°K. The only detectable hafnium-containing species in the vapor emanating from the hafnium-zirconium alloy filaments were Hf(g) and HfO(g). The other important vapor species observed were Zr(g) and ZrO(g).

In my experiments I used a metal filament inside the ion source, heated by self-resistance, as a vaporizing sample in order to obtain higher sensitivities than are ordinarily available with furnace sources.

I used a novel technique for determining the relationship between experimental ion intensities and vapor concentrations in which the reference element is dissolved in the sample material. This guarantees that geometrical effects will not introduce errors, since both reference and sample species originate at the same place.

My results indicate that the assumption of an ideal solution for the alloy is valid. Kubaschewski⁷² has also shown that the experimental phase diagram for the hafnium-zirconium system is consistent with the assumption of ideal solutions for both the solid and liquid phases.

Equipment

The mass spectrometer used was a 60-deg sector magnetic deflection instrument with a radius of curvature of 30.5 cm. The instrument was described in a previous publication.⁷³ A fast magnetic sweep⁷⁴ was used in these studies rather than the ion-accelerating voltage sweep. The magnetic field was swept in synchronization with a 256-channel, multichannel scaler, and signals were accumulated as described in Refs. 73-75 to obtain signal-to-noise enhancement. The field sweep was linear over the portion of the spectrum used for quantitative measurements.⁷⁴ An ion-accelerating potential of 10,000 V was used for all measurements. An additional 4000-V accelerating potential was provided between the analyser exit slit and the Dumont SP-172 electron multiplier used as an ion detector. The window of the photo multiplier was removed, and a nickel wire grid of about 97% transmission mounted over the first dynode was used as an electrostatic shield. The ion source is illustrated in Fig. III-1. The electron beam ionizer and sample filament were mounted inside a stainless steel box that was supported by a fused silica insulator plate in a carriage of an airlock system similar to the one described by Stevens.⁷⁶ Electrical leads were brought into the vacuum system through tungsten-in-glass seals in the core of the carriage. Components of the ion source were supported on nickel-through-alumina feedthroughs to which the electrical connections were made. A rhenium filament was

Fig. III-1. Schematic diagram of ion source.

used as a cathode. Magnetic field and electrostatic field shielding was provided by a sheet of an iron alloy (μ -metal) wrapped around the outside of the source box. Tungsten or nickel mesh of about 97% transmittance was used for the grids and over all openings to the ion source, except for apertures used for temperature measurement. The cathode potential was adjustable from -5 to -80 V, and the collector was operated at +75 V, relative to the steel box. The control grid voltage was determined by the collector current to $\pm 0.3\%$. A potential of +10,000 V was applied to the ion source. Molecules and atoms in the molecular beam were ionized by electron bombardment. Positive ions were extracted from the source box by the field that "leaked" through the source ion slit and then were accelerated into the analyser. The ion beam was aligned and focused by rotating the carriage and adjusting the potentials on a set of crossed field electrostatic alignment and focus plates in front of the analyser entrance slit.

Samples used were in the form of filaments spot-welded to 0.1-by 10-mm tantalum electrodes that were folded to put the sample under slight tension in order to maintain alignment as the filament expanded on heating. The filaments were heated resistively with a 12-V, 20-A, regulated d. c. power supply. Preliminary measurements with zirconium and hafnium filaments and the first series of data reported for hafnium were made without using the molecular beam slit plate shown in Fig. III-1 to isolate the sample from the ionizing region.

An ion-pump vacuum system maintained the residual gas pressure at 2×10^{-8} to 1×10^{-7} Torr in the ion source region during the measurements. Temperatures were measured with a disappearing filament optical pyrometer that had been calibrated to the International Practical Temperature Scale of 1948. Pyrometric lamps calibrated by the National Bureau of Standards were used as secondary standards. The specimen was observed through a 0.5- by 1.0-cm slot in the ion source box and a window in the vacuum chamber from a distance of 15 cm. A correction factor for absorption and reflection by the window was determined before it was installed on the spectrometer. The window was protected by a shutter except during observations.

Since this was the first investigation of this nature conducted with this apparatus, a preliminary experiment was carried out with zirconium, an element similar to hafnium, for which the enthalpy of sublimation was known.

Zirconium

Experimental

The zirconium filament was made from a strip of foil 45 by 7 by 0.025 mm. The principal impurities determined by spectrographic analysis were 5000 ppm iron and 200 ppm chromium. No other metallic impurity exceeded 20 ppm. This strip was folded into a tube of triangular cross section 2.5 mm on a side. A gap was left between the edges of the strip, forming a slit down the center of one side of the tube about 0.3 mm wide. This sample filament was spot-welded to the tantalum electrodes in the ion source so that one flat side faced the ion slit and the side with the 0.3-mm gap faced the window of the vacuum system.

After the system was degassed for several hours with the sample at about 1350°C, the temperature was increased to about 1600°C and the spectrum was surveyed by sweeping the magnetic field slowly while observing the ion intensities with a count-rate meter and oscilloscope as described in Ref. 73. Peaks from the sample were found only at mass-to-charge ratios, m/e , corresponding to Zr, ZrO, and alkali metal ions. Peaks from residual gases and organic materials were also present. The ionization voltage for the survey was 30 V.

The magnetic field sweep was then set to give a spectrum including $m/e = 89$ to 91 in the linear range. The slits were adjusted and the instrument tuned to give trapezoidal-shaped mass peaks with half widths of about 20 channels on the 256-channel scaler. Resolving power was about 200, giving separations between adjacent mass peaks about equal to the peak widths. The spectrum for increasing magnetic field was collected in the first 128 channels and that for decreasing field in the remaining 128 channels of the scaler. Spectra were accumulated at a sweep frequency of about 2 sweeps per second for

times from about 1 to 20 min. Intensities were normalized to 1.92 min, the summing time used for most of the measurements.

The emission regulator was set for an ionizing voltage of 11.5 V and a collector current of 25 μ A. Ion intensities were measured with the filament at temperature and the electron bombardment current turned off, to determine the background due to thermal ions from the sample filament. Intensities were measured with the electron-bombardment ionizer on immediately after turning the sample temperature down to obtain the background due to residual vapors in the system.

Temperature measurements were made by observing the 0.3-mm slit and the surface next to the slit. Temperatures used were the average of three measurements, one each before and after counting the gross intensities and one after the thermal-background determination. The spread between extremes for a given run was usually less than 5°C.

Intensity measurements were also made for $m/e = 105$ to 107, corresponding to ZrO^+ , at an ionizing voltage of 17.5 V.

Calculations

Ion intensity data were printed out as sums of accumulated counts in the multichannel scaler over a number of channels fewer than the number across the flat tops of the peaks. The gross observed intensity of a given ion was taken as the largest sum of counts in the channels across the tops of the increasing magnetic field peak and the decreasing field peak, and was normalized to 1.92 min. For the zirconium experiments, the data were printed out as running sums of 8 channels, so the intensities are the total number of counts accumulated in 16 channels corresponding to the tops of the peaks in 1.92 min. The gross observed intensity for m/e is referred to as N_o^m . The corresponding thermal ion background (B_t^m) was taken as the sum of counts in the same channels with the bombardment current off, and the sum in these channels with the sample cool and the bombardment current on was used for the background due to residual vapors (B_r^m). The positions of the background peaks were generally displaced from the principal spectra, so the background values did not usually correspond to the tops of the background peaks.

Coincidence corrections were applied as described in Ref. 73. The "saturation counting rate" (N_s), an instrumental constant, was determined by plotting the N_O^{185}/N_O^{187} ratio vs N_O^{185} for several spectra from a thermal ionization source with a rhenium filament. At this mass with a thermal source, the background was negligible. N^{185}/N^{187} is a linear function of N^{185} , and N_s is the intercept on the N^{185} axis where N^{185}/N^{187} extrapolates to 1.0. The intensity of a given peak due to neutral atoms or molecules evaporating from the sample is

$$I^m = N_O^m / (1 - N_O^m / N_s) - B_t^m / (1 - B_t^m / N_s) - B_r^m / (1 - B_r^m / N_s). \quad (\text{III-1})$$

A CDC-6600 computer was used to calculate standard enthalpies of sublimation, ΔH_{298}^0 , from the intensity-vs-temperature data by the method of least-squares, using the second law of thermodynamics. If one has pressure-vs-temperature data, it can be analysed by the second-law and third-law methods, both, using the equation

$$-R \ln P^0 - \Delta \left(\frac{G_T^0 - H_{298}^0}{T} \right) = \Delta H_{298}^0 / T + \delta, \quad (\text{III-2})$$

where R is the gas constant, 1.98717 gibbs/mole. P^0 is the pressure of the pure substance in atmosphere at temperature $T^\circ\text{K}$;

$$\Delta \left(\frac{G_{11}^0 - H_{298}^0}{T} \right)$$

is the difference between the free energy functions (fef) for the gas and condensed phases, and δ is the difference between the entropy of sublimation implicit in the free energy functions and the value consistent with the temperature dependence of the vapor pressure. In third law calculations, δ is taken to be 0.

The mass spectrometry data do not give pressures directly, but the intensity of a given ion is proportional to the concentration of the species from which it was formed, $C^z = F^z I^m$, where C^z is the concentration of atoms or molecules from which ions of m/e are formed and F^z is the sensitivity factor of the mass spectrometer for species z , including isotope abundance, ionization efficiency, ion extraction

efficiency, transmission and detector efficiency. We can then relate ion intensity to pressure by using the ideal gas law:

$$P_{(z)} = RC^z T = RF^z I^m T. \quad (\text{III-3})$$

Our mass spectrometric data were analysed by using a variation of Eq. III-2 in the form

$$\text{SIGMA} = -R \ln I^m T - \Delta \left(\frac{G_T^0 - H_{298}^0}{T} \right) = \Delta H_{298}^0 1/T + K, \quad (\text{III-4})$$

where $K = \delta + R \ln RF^z$. The free energy functions were taken from Hultgren et al.⁷⁷

Results

Emittances for the zirconium filament were calculated from the temperature observations of the slit and surface adjacent to the slit, assuming the slit to be a blackbody. The effective wavelength for the pyrometer was assumed to be 0.65×10^{-4} cm, and $1.4380 \text{ cm}^2\text{K}$ was used for the radiation constant, C_2 . The results are listed in Table III-1. The average value for the emittance of βZr , $\epsilon_{0.65}$, over the temperature range 1660° to 2040°K was 0.439 ± 0.024 . The emittance was independent of temperature within our precision. These results are in agreement with published values for the emissivity of zirconium. Bradshaw reports $\epsilon_{0.655} = 0.426 \pm 0.013$ for βZr , essentially independent of temperature from 1300 to 1810°K .⁷⁸ Zwicker gives $\epsilon_{0.65} = 0.43$ for βZr .⁷⁹ Our results might be expected to be high because the surface was not polished and the slit might not have been a perfect blackbody. Color matching of the zirconium filament or blackbody slit to the pyrometer filament was poor because of interference by grid wires of the electrostatic shield, which extended across the observation slot and were too closely spaced. This problem was eliminated by cutting away part of the grid before starting the hafnium studies.

The ion intensities vs temperature are listed in Table III-1 and graphs of $-\text{sigma}$ vs $1/T$ are shown in Fig. III-2. Residual gas

Table III-1. The sublimation of zirconium as a function of temperature measured by ion intensity, using a mass spectrometer, and the spectral emittance of a zirconium filament.

Run No.	Temperature (°K)	Emittance (0.65×10^{-4} cm)	- R ln(IT) gibbs/mole (m/e = 90)	- R ln(IT) gibbs/mole (m/e = 91)	-Δ (fef) gibbs/mole
353	1662	0.436	-29.110		33.164
350	1714	0.443	-31.647	-28.745	33.121
358	1751	0.459	-33.192	-30.310	33.093
361	1780	0.456	-35.317	-32.400	33.070
366	1817	0.430	-36.281	-33.277	33.045
369	1818	0.439	-36.877		33.045
374	1838	0.454	-37.935	-34.964	33.033
377	1865	0.445	-39.197	-36.203	33.017
382	1899	0.437	-40.082	-37.091	32.997
385	1935	0.416	-41.480	-36.455	32.969
391	1955	0.436	-42.386	-39.370	32.953
394	2004	0.424	-43.925	-40.892	32.914
399	2043	0.430	-45.350	-42.325	32.891

Fig. III-2. Sigma plot for the sublimation of zirconium. $-\Sigma = R \ln (IT) + \Delta \left(\frac{G_T^0 - H_{298}^0}{T} \right)$.

backgrounds, B_r^m , were 283 for $m/e = 90$ and 140 for $m/e = 91$. B_t^m ranged from 2.2×10^2 to 7.974×10^4 for $m/e = 91$ and from 4.0×10^2 to 1.368×10^5 for $m/e = 90$. At temperatures above 1900°K the experimental isotope ratios I^{90}/I^{91} agreed within 1% with the literature value of 4.582.⁸⁰ The apparent isotope ratios decreased with decreasing temperature to a value of 4.30 at 1714°K, indicating a systematic error in background corrections. The results are represented by the equations

$$\text{Sigma (90)} = (148.2 \pm 5.0) \times 10^3/T - 85.1 \pm 2.8$$

and

$$\text{Sigma (91)} = (146.6 \pm 6.6) \times 10^3/T - 81.3 \pm 3.6,$$

where the uncertainties include only the statistical variations in the intensity vs temperature data. Throughout this report uncertainties indicated that $\pm$ represent two standard deviations as recommended by Rossini.⁸¹ The value for ΔH_{298}^0 obtained by combining the two results, weighting them inversely as their variances, as described in Ref. 81, is 147.6 ± 4.0 kcal/g atom. Hultgren et al. list $\Delta H_{298}^0 = 145.5 \pm 1.0$ kcal/g atom.⁷⁷

Conclusions

The enthalpy of sublimation measured in the preliminary study was slightly higher than the accepted value for zirconium, and the precision was not as good as hoped. However, the shortcomings seemed to result from three sources that could be corrected: the partial collimation of the optical path for temperature measurements; background errors mentioned previously; and a problem in the ion source, described below. The background errors could be reduced by more extensive baking of the ion source before the measurements are made, in order to decrease the total background corrections.

After completing the ion intensity-vs-temperature measurements, I observed that the ion intensity of a given species was a linear function of the collector current only up to a critical value that depended on the ionization voltage. At 11.5 V, the voltage used for these measurements, the ion intensities were linear functions of collector current

only up to about $10\ \mu\text{A}$. I believe that the nonlinearity is a result of electron-beam geometry changes with field variations within the source, as the control-grid potential changes. In the nonlinear region, the electron-beam geometry is likely to be more susceptible to variations in magnetic field resulting from changes in current through the sample filament. This problem was alleviated by installing the drawing-out grid. Placing a positive voltage on this grid allowed me to achieve ion intensities that were linear functions of collector current to collector currents of $20\ \mu\text{A}$ at $11.5\ \text{V}$. All intensity measurements for the subsequent studies were made under conditions where the ion intensities were linear with collector current.

Since I believed that the problems discussed above accounted for the excessive scatter and any major systematic errors, the hafnium experiments were started without further preliminary tests with zirconium.

Hafnium

Experimental

The hafnium filaments were made from 0.25- by 2.54-mm ribbon (obtained from the Wah Chang Corporation, Albany, Oregon, in 1961).*

The ion source was modified as discussed in the previous section and, in addition, after the first run with hafnium the molecular beam slit shown in Fig. III-1 was added. This allowed a bias voltage to be applied to the sample, reducing the thermal ion background substantially.

The data register and sweep signal systems were modified to compensate for the dead time by extending the counting time in each channel by an appropriate amount. Each time a pulse was counted, the pulses that drive the multichannel scaler were gated-off for a period of time equal to the dead time of the system. Data were taken for a fixed number of sweeps rather than for a constant total elapsed time. Since the magnet sweep signal was generated by the same pulses that stepped the

* This was part of the same material used in the high-temperature electrical resistivity and allotropic transformation studies reported in Ref. 82.

scaler, the field was still a linear function of channel position, and the position of the spectral features were not affected by intensity changes. The gate time could not be adjusted to completely eliminate the dead time corrections. For the first few runs the delay was too short, and for the subsequent runs it was too long, leading to negative effective dead times. The coincidence correction factor was measured each day a run was made, either by using the rhenium filament thermal ion source or by plotting ion intensity ratios from the hafnium filament, I^{180}/I^{179} vs I^{180} . When both methods were used, they were in agreement. Although modifying the system did not entirely eliminate the necessity for coincidence corrections, the magnitude of the corrections was reduced by factors of 0.1 to 0.01.

After the system was baked-out with the sample at about 1500°C for several days, a survey of the spectrum was made with an ionizing voltage of 20 V and the sample at about 1650°C. The only important vapor species from the sample were Hf(g), HfO(g), Zr(g), ZrO(g) and alkali metals. The intensity ratios of mass peaks for each species were determined by sweeping the appropriate mass ranges. Corrected relative intensities agreed with the isotope ratios given by Strominger et al.⁸⁰

Several attempts were made to relate the intensity ratios of HfO^+/Hf^+ , ZrO^+/Zr , and $\text{HfO}^+/\text{ZrO}^+$ to temperature and oxygen partial pressure. Only approximate values were obtained, because constant oxygen pressures could not be maintained in the system long enough to achieve steady state. The magnitude of the MO^+ intensities are of interest, as they indicate the extent of the reaction between the filament and oxygen in the system. With the filament heated to about 2000°K, the I^{196}/I^{180} ratio was 0.015 when the total pressure in the source region of the spectrometer was 3×10^{-8} Torr. The residual gas spectra indicated the presence of CO and N_2 , H_2O , and Ar in order of decreasing importance with traces of other species. At a source manifold pressure of 1×10^{-7} Torr, with residual gases N_2 and CO, H_2O , O_2 , Ar, and CO_2 , plus traces of other species, the I^{196}/I^{180} ratio was 0.5. The I^{106} intensities from ZrO were too low and variable to be even qualitatively useful at a source pressure of 3×10^{-8} Torr. At $\sim 1 \times 10^{-7}$ Torr, the I^{106}/I^{90} ratio seemed to be somewhat greater than

the I^{196}/I^{180} ratio. The data were taken with an ionizing energy of 12.5 V. Studies of this type with a reliable oxygen gas inlet system could yield interesting results concerning the thermodynamics and kinetics of reactions involving hafnium, zirconium, and oxygen, or similar systems.

During the course of these experiments and some ionization efficiency measurements to be discussed later in the paper, the Zr^+/Hf^+ , I^{90}/I^{180} , ratio had decreased significantly. Before the experiments were continued, the filament was replaced by a new one and instrumental adjustments were made to obtain optimum sensitivity and resolution.

Specimens cut from the ends of the sample filaments during fabrication and from the center section of the used filament were analysed by the chemical methods described in Ref. 82; they contained 2.25 ± 0.1 and 1.70 ± 0.1 wt% zirconium, respectively. The filament used for the remaining experiments also exhibited a decreasing I^{90}/I^{180} ratio as the studies progressed. The filament burned out at the end of the final experiments, so a post-mortem analysis of the center section was impossible. The residue from the ends of this filament was analysed and found to contain 2.9 wt% zirconium. These results indicate that zirconium depletion of the sample occurs primarily due to diffusion of zirconium to the cooler ends of the filament. From the analytical results on the first filament, I was able to estimate the rate of zirconium depletion of the samples and found that they were in agreement, within random errors to the changes in intensity ratios.

After the system was baked again for several days to reduce the residual gas background, measurements of intensity as a function of temperature were made for Hf^+ ($m/e = 179$ to 181) at 11.0 V ionization energy and for Zr^+ ($m/e = 89$ to 91) at 12.0 V. The energy used for Zr^+ was as high as possible to give maximum sensitivity. The energy was maintained below the second ionization potential of hafnium to eliminate the contribution of $Hf^{++}(180)$ to the $m/e = 90$ peak. The second ionization potential of hafnium is estimated to be about the same as for Zr, 13.13 V.⁸³ Intensities of HfO^+ ($m/e = 195$ to 197) and ZrO^+ ($m/e = 105$ to 107) were measured at an ionizing energy of 17.5 V, to establish that the gaseous oxide concentrations were not high enough to interfere with

the metal ion intensity measurements. The maximum intensity ratios observed during any of the vaporization measurements were $I^{196}/I^{180} \sim 0.015$, and for most runs the ratio was less than 10^{-3} .

All intensities are given as the sum of counts in a selected number of channels—constant throughout a given series and fewer than the number across the flat tops of the peaks—for 100 sweeps, and increasing and decreasing field scans were added together. In different series of measurements, data were summed over 4 to 16 channels. In series 540, all data were summed over 8 channels. In subsequent runs, twice as many channels were used in peaks for m/e in the range 180 to 200 as for $m/e = 90$ to 110, because of the increase in peak width with m/e . This gave sums over corresponding parts of the peaks. The intensities were normalized to equivalent counting times.

Ionization efficiencies as functions of ionizing energy were determined for Hf, Zr, and HfO. The measurements were made at different times and under a variety of conditions. The results normalized to maximum net intensities are shown in Figs. III-3 through III-5. Voltages were read from a 1% meter on the emission regulator, which had been standardized with a calibrated meter. Readings were corrected for voltage drops across the current-carrying conductors between the points of meter connections and the center of the filament. The voltage scale was checked by measuring the ionization efficiency curve of argon, $m/e = 40$, and no normalization factor was necessary. The energy distribution of the electron beam was the normal thermal distribution at about 2200°K, plus a linear gradient of about 1 eV across the ionization region due to the voltage drop across the effective part of the cathode. The appearance potential obtained for Zr^+ of 7.0 ± 0.8 V agrees with the spectroscopic ionization potential given by Moore.⁸³ My appearance potential of 6.0 ± 0.8 V for Hf^+ is somewhat lower than Moore's estimate of 7.0 V. The appearance potential of HfO^+ was found to be 6.3 ± 0.8 V.

Most of the ionization efficiency measurements were made by scanning three adjacent peaks, as in the intensity-vs-temperature experiments. A number of spectra were taken at different ionizing voltages, holding the sample temperature and electron beam collector current constant. Intensity ratios were compared to isotope

Fig. III-3. ionization efficiency vs ionizing voltage for hafnium.

Fig. III-4. Ionization efficiency vs ionizing voltage for zirconium.

Fig. III-5. Ionization efficiency vs ionizing voltage for HfO.

abundances, and data that did not agree within statistical limits with Ref. 80 were discarded.

The final two runs for zirconium, for which a zirconium metal filament was placed in the source after the hafnium runs were finished, were done by a different technique. After several preliminary scans at different voltages to confirm that the relative ion intensities corresponded to the isotope abundances of zirconium, i.e., residual background was low enough, the magnetic field was locked at a value that focused $m/e = 90$ on the detector slit.

The multichannel scaler was stepped at a rate of about 256 channels per 5 to 10 min for one sweep, while the ionizing voltage was changed manually to a new value every 10 channels. The data were printed out digitally; no running sum was made. Intensities were taken as the average number of counts per channel in consecutive channels for which the data were fairly constant, usually 7 or 8 channels. Thermal ion background corrections were applied, and residual gas backgrounds were negligible. There was generally good agreement between the ionization efficiency curves for Zr taken from the hafnium alloy filament and those taken from a zirconium metal filament after the final hafnium experiments. We could not resolve an effect due to the second ionization potential of hafnium. The peculiar hump in the curve that we at first attributed to that effect was also seen in runs with the zirconium filament.

Measurements of ion intensity as a function of collector current were made for Hf^+ . The spectrum from $m/e = 179$ to 181 was counted for each value of the current at constant sample temperature and ionizing voltage. Some of the results are illustrated in Fig. III-6. The deviation from linearity of these curves of ion intensity vs collector current must result from changes in the ionization efficiency, the ion extraction efficiency, or the transmission. The deviations from linearity occurred when the control grid potential approached the electron acceleration voltage. Changes in control grid potential would be expected to change the electron beam geometry and therefore to alter the spatial distribution of the ions produced. As a result, the ion extraction efficiency would change, and small changes in transmission could occur because of variations in ion focusing. Changes in the field

Fig. III-6. Ion intensity vs collector current at constant ionizing voltage and sample temperature.

distribution within the ionization region as the control grid voltage changes could lead to variations in the effective ionization energy and thereby to variations in ionization efficiency. When the drawing-out grid was used, the control grid potential required to regulate at a given collector current and ionization voltage was lowered, thus allowing higher collector currents before deviations from linearity occurred. All measurements of ionization efficiencies and of ion intensities vs temperature were made at collector currents within the linear range for all voltages used.

Temperature Measurement

The corrections applied to the observed brightness temperatures of the hafnium filament included an emittance term in addition to the window correction factor. A value of 0.43 independent of temperature was used for emissivity, $\epsilon_{0.65}$, based on the data for βZr . The emissivities of the neighboring transition elements are not much different at the temperatures of our experiments. There appear to be general trends in $\epsilon_{0.65}$ at high temperature, decreasing with increasing atomic number in a given row of the periodic chart from group IVB to group VIB (from the titanium to the chromium subgroups) and increasing with increasing atomic weight within a given column or group. Since the trends are irregular and information is incomplete, and because of the close similarities in other properties of zirconium and hafnium, the emissivity of zirconium is probably the best estimate for that of hafnium. In general, $\epsilon_{0.65}$ decreases with increasing temperature; but since the temperature dependence for the neighboring elements is small in this temperature range and $\epsilon_{0.65}$ for βZr is reported to be independent of temperature⁷⁸ and was found to be independent of temperature within our precision, $\epsilon_{0.65}$ for hafnium was assumed to be constant within the temperature range of my experiments. Bradshaw⁷⁸ reports $\epsilon_{0.65} = 0.436$ for αZr , 0.01 greater than his value for βZr ; but since emissivity variations tend to become smaller at higher temperatures, the difference in emissivity between αHf and βHf is probably less than 0.01 and has been assumed to be negligible.

Background Corrections to Intensity Measurements

The residual gas backgrounds, B_r^m , were determined from the observed intensities at $m/e = 89$ for Zr^+ and at $m/e = 181$ for Hf^+ . Background intensities at 90 and 180, etc., were calculated from B_r^{89} and B_r^{181} by using peak intensity ratios from spectra obtained with the sample filament off. Extensive baking reduced these background corrections to values ranging from 10 at the lower temperatures to about 70 at the highest temperatures. In all cases, these backgrounds were much smaller than the uncertainties due to counting statistics.

In series 120, the thermal ion background, B_t^m , varied from 0.5 to 0.2 of the gross intensity as the temperature increased. In subsequent runs with the molecular beam slit, B_t^m ran from ranges of 0.2 to 0.1 of the gross intensity to 0.01 to 0.001 of the gross intensity. Net ion intensities were calculated by use of Eq. III-1. Good agreement between results from runs in which the magnitude of thermal background corrections varied by several orders of magnitude indicates that the corrections are reliable and valid.

In runs made before the molecular beam slit was used and in runs with the slit in which no bias voltage was applied, I accumulated quite a bit of thermal ion intensity-vs-temperature data. I attempted to correlate these data with the enthalpy of sublimation and the work function of hafnium without success; the calculated total activation energies were always less than the enthalpies of sublimation calculated from net intensities of ions formed by electron bombardment of neutral atoms in the vapor. The problem in this procedure may have resulted from the effect of the magnetic field due to the filament-heating current on the thermal ions. The technique is sound in principle and should be an effective method of obtaining sublimation and work-function data if a noninductive heating arrangement is used. The magnetic field from the filament current may also produce a systematic error in the results if net intensities are used; but the effect of the field on the ions produced by electron bombardment is much smaller, as they are formed at a distance from the filament and close to the ion exit slit. The ion source regulator parameters were unaffected by changes in filament heating current within our ability to observe them.

Results

Hafnium ion intensity vs temperature data were analysed by the second-law method, using Eq. III-4. Free energy functions tabulated by Hultgren et al.⁷⁰ were used. The data are given in Tables III-2 through III-7 and in Figs. III-7 through III-12. Results are listed in Table III-8.

The partial molal enthalpy of sublimation of zirconium from the alloy was determined by analysis of the data for $m/e = 90$ by using free energy functions extrapolated from those given in Hultgren's⁷⁷ compilation. Values extrapolated from αZr data were used below 2013°K, the transition temperature of hafnium, and values for βZr were used above 2013°K. These data are given in Tables III-3 through III-7 and Figs. III-13 through III-18, and results are listed in Table III-9. The value obtained by combining the results, weighting each by the reciprocal of its variance, is $\Delta H_{298}^0 = 148.8 \pm 2.0$ kcal/g atom, which is slightly higher than the standard enthalpy of sublimation of pure zirconium, 145.5 ± 1.0 kcal/g atom, given by Hultgren et al.⁷⁷ The uncertainty given for our results represents only the statistical variations in the final results assuming a random distribution of errors. Estimated systematic errors in both temperature and intensity measurements add another 1 or 2 kcal/g atom uncertainty, and place my result for the standard partial molal enthalpy of sublimation of zirconium from a dilute solid solution in hafnium within the errors equal to the standard enthalpy of sublimation of pure zirconium, i. e., the solution is ideal.

Absolute Hf(g) pressures at each temperature were calculated from the experimental ion intensity ratios and estimated Zr(g) pressures. If we assume that there was no significant mass discrimination in our instrument, i. e., the ion extraction efficiency and transmission were independent of mass, we can obtain the Hf(g) pressures from the equation

$$P^0(\text{Hf}) = P^0(\text{Zr}) (X_{\text{Zr}}/X_{\text{Hf}}) (I^{180}/I^{90}) (f^{90}/f^{180}) (\sigma_{\text{Zr}}/\sigma_{\text{Hf}}) (r_{\text{Zr}}/r_{\text{Hf}}) (d^{90}/d^{180}), \quad (\text{III-5})$$

Table III-2. The sublimation of hafnium by mass spectrometry for Series 120.

Run No.	Temperature (°K)	$-R \ln (IT)$ (gibbs/mole)	$-\Delta (f_{ef})$ (gibbs/mole)
136	1828	-26.798	32.947
135	1835	-27.711	32.942
134	1869	-30.008	32.919
138	1891	-30.289	32.904
137	1914	-31.809	32.890
133	1923	-31.564	32.885
132	1990	-34.233	32.848
139	2016	-35.201	32.835
131	2069	-36.765	32.786
130	2106	-38.722	32.751
129	2148	-40.166	32.712
128	2178	-41.449	32.684
127	2179	-41.657	32.683
126	2217	-42.618	32.649
125	2267	-44.229	32.609
124	2309	-44.920	32.575
123	2337	-45.434	32.553
122	2366	-46.176	32.531
121	2372	-46.430	32.526

Table III-3. The sublimation of hafnium by mass spectrometry for Series 540.

$(X_{\text{Zr}}/X_{\text{Hf}} = 0.0543)$			$-R \ln (IT)$ (m/e = 180) (gibbs/ mole)	$-R \ln (IT)$ (m/e = 90) (gibbs/ mole)	Pressure for Zr (atm)	Pressure for Hf (atm)	$-\Delta$ (fef) for Hf (gibbs/ mole)	$-\Delta$ (fef) for Zr (gibbs/ mole)	ΔH_{298}^0 for Hf (kcal/ atom)
Run Hf	No. Zr	Tempera- ture ($^{\circ}\text{K}$)							
564		1770	-26.676				32.984		
563	562	1802	-28.252	-25.228	3.667×10^{-11}	1.291×10^{-11}	32.965	32.987	149.20
560	561	1878	-31.413	-28.543	1.846×10^{-10}	6.016×10^{-11}	32.913	32.939	149.64
565		1915	-33.109				32.889		
559	558	1927	-33.702	-30.578	5.127×10^{-10}	1.898×10^{-10}	32.883	32.989	149.10
556	557	2009	-37.014	-33.777	2.358×10^{-9}	9.241×10^{-10}	32.839	32.965	148.99
555	554	2058	-38.976	-35.602	5.324×10^{-9}	2.236×10^{-9}	32.795	32.832	148.97
566	567	2087	-39.882	-36.508	8.574×10^{-9}	3.600×10^{-9}	32.769	32.812	149.01
552	553	2120	-41.077	-37.543	1.472×10^{-8}	6.700×10^{-9}	32.738	32.790	148.71
569	568	2136	-41.437	-37.862	1.882×10^{-8}	8.742×10^{-9}	32.723	32.779	148.64
551	550	2178	-42.769	-39.134	3.586×10^{-8}	1.717×10^{-8}	32.684	32.750	148.54
548	549	2212	-43.702	-40.030	6.007×10^{-8}	2.930×10^{-8}	32.653	32.724	148.50
546	547	2252	-44.549	-40.801	1.059×10^{-7}	5.364×10^{-8}	32.621	32.690	148.39

Table III-4. The sublimation of hafnium by mass spectrometry for Series 570.

$(X_{\text{Zr}}/X_{\text{Hf}} = 0.0461)$									
Run Hf	No. Zr	Tempera- ture (°K)	$-R \ln (IT)$ (m/e = 180) (gibbs/ mole)	$-R \ln (IT)$ (m/e = 90) (gibbs/ mole)	Pressure for Zr (atm)	Pressure for Hf (atm)	$-\Delta$ (fef) for Hf (gibbs/ mole)	$-\Delta$ (fef) for Zr (gibbs/ mole)	ΔH_{298}^0 for Hf (kcal/ atom)
582	581	1933	-34.421	-30.678	5.794×10^{-10}	2.376×10^{-10}	32.879	33.003	148.69
579	580	1980	-35.888	-32.455	1.508×10^{-9}	5.533×10^{-10}	32.853	33.113	143.93
578	577	2071	-37.689	-35.268	6.634×10^{-9}	1.462×10^{-9}	32.783	32.823	151.64
583		2108	-40.364				32.749		
575	576	2143	-41.978	-37.570	2.105×10^{-8}	1.262×10^{-8}	32.717	32.774	147.56
574	573	2202	-43.462	-39.116	5.130×10^{-8}	2.979×10^{-8}	32.662	32.734	147.72
571	572	2248	-44.602	-40.284	1.006×10^{-7}	5.764×10^{-8}	32.624	32.693	147.83
		2271	-45.045				32.605		

Table III-5. The sublimation of hafnium by mass spectrometry for Series 540.

$(X_{\text{Zr}}/X_{\text{Hf}} = 0.0389)$									
Run Hf	No. Zr	Tempera- ture (°K)	-R ln (IT) (m/e = 180) (gibbs/ mole)	-R ln (IT) (m/e = 90) (gibbs/ mole)	Pressure for Zr (atm)	Pressure for Hf (atm)	-Δ (fef) for Hf (gibbs/ mole)	-Δ (fef) for Zr (gibbs/ mole)	ΔH ₂₉₈ ⁰ for Hf (kcal/ atom)
678		1800	-28.898				32.966		
677		1830	-30.216				32.946		
679		1887	-32.285				32.907		
676	675	1928	-33.902	-29.843	5.254×10^{-10}	2.231×10^{-10}	32.882	32.992	148.57
673	674	1986	-36.216	-32.017	1.695×10^{-9}	7.728×10^{-10}	32.850	33.127	148.05
672	671	2031	-37.641	-33.449	3.333×10^{-9}	1.514×10^{-9}	32.820	32.851	148.63
680		2041	-37.993				32.812		
669	670	2071	-39.500	-36.210	6.634×10^{-9}	1.913×10^{-9}	32.783	32.823	150.54
667	666	2114	-40.755	-36.501	1.338×10^{-8}	6.271×10^{-9}	32.744	32.794	148.58
647	648	2131	-41.425	-37.327	1.745×10^{-8}	7.559×10^{-9}	32.728	32.782	148.93
663	664	2167	-42.552	-37.824	3.045×10^{-8}	1.811×10^{-8}	32.694	32.758	147.60
644	642	2191	-43.469	-39.174	4.371×10^{-8}	2.090×10^{-8}	32.672	32.741	148.60
652	651	2198	-43.525	-39.140	4.865×10^{-8}	2.434×10^{-8}	32.665	32.736	148.37
660	659	2238	-44.828	-40.381	8.634×10^{-8}	4.458×10^{-8}	32.633	32.703	148.28
655	656	2274	-45.645	-41.246	1.430×10^{-7}	7.211×10^{-8}	32.603	32.672	148.44

Table III-6. The sublimation of hafnium by mass spectrometry for Series 680.

 $(X_{\text{Zr}}/X_{\text{Hf}} = 0.0330)$

Run Hf	No. Zr	Tempera- ture (°K)	-R ln (IT) (m/e = 180) (gibbs/ mole)	-R ln (IT) (m/e = 90) (gibbs/ mole)	Pressure for Zr (atm)	Pressure for Hf (atm)	-Δ (fef) for Hf (gibbs/ mole)	-Δ (fef) for Zr (gibbs/ mole)	ΔH_{298}^0 for Hf (kcal/ atom)
681	682	1971	-35.421	-31.545	1.249×10^{-9}	4.108×10^{-10}	32,858	33,091	149.40
684	683	2074	-39.101	-34.834	6.902×10^{-9}	2.763×10^{-9}	32,731	32,821	149.19
685	687	2229	-44.080	-39.617	7.657×10^{-8}	3.382×10^{-8}	32,639	32,710	148.96
691	690	2296	-47.474	-41.762	1.923×10^{-7}	1.593×10^{-7}	32,586	32,653	146.20

Table III-7. The sublimation of hafnium by mass spectrometry for Series 740 and 750.

(Hf intensity data treated as a single series)

Hf	Run No. Zr	Temperature (°K)	-R ln (IT) (m/e = 180) (gibbs/ mole)	-R ln (IT) (m/e = 90) (gibbs/ mole)	Pressure for Zr (atm)	Pressure for Hf (atm)	-Δ (fef) for Hf (gibbs/ mole)	-Δ (fef) for Zr (gibbs/ mole)	ΔH ₂₉₈ ⁰ for Hf (kcal/ atom)
Series 740 ($X_{Zr}/X_{Hf} = 0.0312$)									
752	751	2062	-37.720	-32.911	5.655×10^{-9}	2.810×10^{-9}	32.792	32.830	148.29
749	750	2142	-40.501	-35.566	2.066×10^{-8}	1.094×10^{-8}	32.718	32.775	148.09
748	747	2205	-42.426	-37.448	5.408×10^{-8}	2.926×10^{-8}	32.659	32.731	148.03
745	746	2273	-44.450	-39.416	1.407×10^{-7}	7.830×10^{-8}	32.604	32.673	147.99
743	744	2315	-45.828	-40.813	2.491×10^{-7}	1.373×10^{-7}	32.570	32.637	148.09
Series 750 ($X_{Zr}/X_{Hf} = 0.0264$)									
782		1839	-28.688				32.939		
781		1873	-30.197				32.916		
754		1879	-30.593				32.912		
783		1898	-31.188				32.899		
784		1926	-32.238				32.883		
778		1968	-33.823				32.860		
753		1988	-35.240				32.848		
785	786	2023	-36.177	-31.358	2.884×10^{-9}	1.217×10^{-9}	32.828	32.856	148.91
774	775	2050	-37.187	-32.145	4.623×10^{-9}	2.183×10^{-9}	32.803	32.838	148.49
779	776	2054	-37.221	-32.133	4.912×10^{-9}	2.373×10^{-9}	32.800	32.835	148.40
779	780	2054	-37.221	-32.287	4.912×10^{-9}	2.197×10^{-9}	32.800	32.835	148.71
773	772	2124	-39.071	-34.867	1.558×10^{-8}	7.218×10^{-9}	32.735	32.787	148.64
755	757	2166	-41.399	-36.337	2.890×10^{-8}	1.412×10^{-8}	32.695	32.759	148.59
770	771	2205	-42.359	-37.164	5.408×10^{-8}	2.758×10^{-8}	32.659	32.731	148.29
788	787	2223	-42.970	-37.764	7.024×10^{-8}	3.602×10^{-8}	32.644	32.715	148.29
760	759	2235	-43.182	-38.113	8.343×10^{-8}	3.993×10^{-8}	32.634	32.705	148.62
768	767	2282	-44.609	-39.410	1.606×10^{-7}	8.203×10^{-8}	32.596	32.664	148.39
763	764	2319	-45.547	-40.428	2.613×10^{-7}	1.283×10^{-7}	32.568	32.634	148.62
789	790	2319	-45.596	-40.435	2.613×10^{-7}	1.310×10^{-7}	32.568	32.634	148.53

Table III-8. Results of least-squares analyses of hafnium vaporization data by use of Eq. III-4.

Series	No. points	ΔH_{298}^0 (kcal/g atom)	K	
120	19	156.71 ± 4.52^a	$-80.3 \pm$	2.18
540	13	154.19 ± 2.93	$-80.8 \pm$	1.46
570	7	145.57 ± 7.10	$-76.8 \pm$	2.35
640	15	150.52 ± 3.06	$-79.3 \pm$	1.50
680	4	166.51 ± 24.2^a	$-86.8 \pm$	11.3
740	23	155.01 ± 1.80	$-80.0 \pm$	0.86
Weighted average		153.62 ± 1.34		

^a Not included in composite results.

Table III-9. Results of least-squares analyses of zirconium vaporization from hafnium alloy by use of Eq. III-4.

Series	No. points	ΔH_{298}^0 (kcal/g atom)	K
540	11	145.76 ± 4.09	-73.3 ± 2.00
570	6	136.77 ± 2.81^a	-68.5 ± 1.34
640	10	151.75 ± 4.52	-74.1 ± 2.60
680	4	147.42 ± 5.82	-71.8 ± 2.73
740	5	151.03 ± 4.97	-71.9 ± 2.26
750	12	149.42 ± 3.72	-70.9 ± 1.72
Weighted average		148.84 ± 2.06	

^aNot included in composite results.

Fig. III-7. Sigma plot for the sublimation of hafnium, series 120, $m/e = 178$.

Fig. III-8. Sigma plot for the sublimation of hafnium, series 540. $m/e = 180$.

Fig. III-9. Sigma plot for the sublimation of hafnium, series 570. $m/e = 180$.

Fig. III-10. Sigma plot for the sublimation of hafnium, series 640. $m/e = 180$.

Fig. III-11. Sigma plot for the sublimation of hafnium, series 680, $m/e = 180$.

Fig. III-12. Sigma plot for the sublimation of hafnium, series 740. $m/e = 180$.

Fig. III-13. Sigma plot for the sublimation of zirconium from a hafnium alloy, series 540. $m/e = 90$.

Fig. III-14. Sigma plot for the sublimation of zirconium from a hafnium alloy, series 570. $m/e = 90$.

Fig. III-15. Sigma plot for the sublimation of zirconium from a hafnium alloy, series 640. $m/e = 90$.

Fig. III-16. Sigma plot for the sublimation of zirconium from a hafnium alloy, series 680, $m/e = 90$.

Fig. III-17. Sigma plot for the sublimation of zirconium from a hafnium alloy, series 740. $m/e = 90$.

Fig. III-18. Sigma plot for the sublimation of zirconium from a hafnium alloy, series 750. $m/e = 90$.

where $P^0(A)$ is the vapor pressure of the pure substance, X_A is the mole fraction of the substance in the sample, I^m is the net intensity for m/e , f^m is the isotopic abundance of the ion measured, σ_A is the relative ionization cross section at high voltage (70 V), r_A is the ratio of ionization efficiency at the voltage of the experiment to that at 70 V, and d^m is the detector efficiency.

Intensity ratios I^{180}/I^{90} at comparable temperatures during the series of experiments showed that zirconium depletion of the sample occurred at a significant rate only when the sample was above about 2200°K. From the analytical results on the first filament and the number of runs made at high temperatures, I estimated that the average depletion rate was 3 to 5% for each normal run above 2200°K. In the calculations I used a constant concentration for each run and adjusted the value for each run for the estimated depletion that occurred during the previous run and during any intervening experiments, such as ionization efficiency measurements, in which the sample was heated hotter than 2200°K.

Isotope abundances were taken from Strominger et al.⁸⁰

Because zirconium and hafnium have similar electronic configurations and nearly equal atomic radii, their ionization cross sections at high voltage were assumed to be equal. The ratios of cross sections at the voltages used for measurements to the cross sections at high voltage were taken from the results shown in Figs. III-3 and III-4.

Detector efficiency corrections were taken from data furnished by R. Newbury⁸⁴; these data were obtained on another mass spectrometer in our laboratory with an identical detector. The dependence of detector efficiency on mass for mono-atomic metallic elements was found to obey the equation $d^m = 114.6 - 2.71(m)^{1/2}$, from $m = 40$ to $m = 238$.

The factors used in Eq. III-5 to calculate $Hf(g)$ pressures were

$$(f^{90}/f^{180}) = 1.461,$$

$$(\sigma_{Zr}/\sigma_{Hf}) = 1.00,$$

$$\left[r_{Zr}(12.0 \text{ V})/r_{Hf}(11.0 \text{ V}) \right] = 0.85,$$

and $(d^{90}/d^{180}) = 1.14.$

Values of $(X_{\text{Zr}}/X_{\text{Hf}})$ used for each series are listed in Tables III-3 to III-7. The data were analysed by the second-law and third-law methods by use of Eq. III-2. The third law results are listed in Tables III-3 to III-7. The pressure-vs-temperature data are shown graphically in Figs. III-19 to III-24, and the second-law results are listed in Table III-10.

Analysis of Errors

The most significant uncertainty in temperature arises from the uncertainty in emittance of the hafnium filament surface. It seems unlikely that the true emissivity of hafnium differs from my estimated value by as much as 0.02. An error of that magnitude independent of temperature would introduce an uncertainty corresponding to a standard deviation of about 0.5% or 0.7 kcal/g atom in the third-law results and would not affect the second-law values. The results of Bradshaw⁷⁸ for zirconium, and data for other refractory metals in this temperature range, suggest that the emissivity of hafnium probably changes less than 0.02 over the 500° temperature interval of the experiments. Such a variation would lead to errors of less than 2% in the second-law results. I believe an estimated error of 1% or a standard deviation of 1.5 kcal/g atom is more realistic. Since a temperature trend would probably be in the direction of decreasing emissivity with increasing temperature, the error would be positive, i.e., second-law results would be too high.

Additional temperature errors arise from difficulties in reproducing the temperature scale. These uncertainties are small, compared to uncertainties in emissivity corrections for the hafnium measurements, but are significant for the zirconium measurements because of the color matching difficulties mentioned earlier.

For the zirconium vaporization measurements from the zirconium filament, I estimate an additional uncertainty corresponding to a standard deviation of 1 kcal/g atom, because of difficulties in achieving the temperature scale.

Systematic trends in intensity measurements are difficult to evaluate. Since total residual gas background corrections were less

Fig. III-19. Sigma plots for the sublimation of hafnium, using Eq. 2. Pressures calculated using zirconium reference, Series 540. $-\text{Sigma} = R \ln P^0 + \Delta \left[\left(G_T^0 - H_{298}^0 \right) / T \right]$.

Fig. III-20. Sigma plot for the sublimation of hafnium, using Eq. 2. Pressures calculated using zirconium reference, Series 570.

Fig. III-21. Sigma plot for the sublimation of hafnium, using Eq. 2. Pressures calculated using zirconium reference, Series 640.

Fig. III-22. Sigma plot for the sublimation of hafnium, using Eq. 2. Pressures calculated using zirconium reference. Series 680.

Fig. III-23. Sigma plot for the sublimation of hafnium, using Eq. 2. Pressures calculated using zirconium reference. Series 740.

Fig. III-24. Sigma plot for the sublimation of hafnium, using Eq. 2. Pressures calculated using zirconium reference. Series 750.

Table III-10. Results of least-squares analyses of hafnium vaporization data by use of Eq. III-2 and the second-law method.

Series	No. points	ΔH_{298}^0 (kcal/g atom)	δ
540	11	153.52 ± 1.60^a	-2.25 ± 0.78
570	6	158.23 ± 22.6^a	-4.53 ± 11.3
640	11	150.80 ± 8.14	-1.04 ± 4.45
680	4	164.55 ± 18.4^a	-7.52 ± 8.67
740	5	150.08 ± 1.82	-0.90 ± 0.83
750	12	149.95 ± 2.14	-0.65 ± 0.99
Weighted average		150.04 ± 1.38	-0.80 ± 0.64

^aNot included in composite results.

than 1% of gross intensities at all temperatures, errors in their magnitude could not have affected the results. In Series 120, thermal backgrounds ran from 0.5 to 0.2 of gross intensities. Subsequent runs had thermal backgrounds from 10^{-1} to 10^{-4} of gross intensities, and there did not seem to be a correlation between runs with larger background corrections and higher or lower final results. Intensity ratios for the species observed agreed with the natural isotope abundances in all of the hafnium filament runs except for one case that was discarded for that reason. The background errors were more important in runs with the zirconium filament, as was discussed earlier, and the background contribution to the uncertainty in those results is estimated to correspond to a standard deviation of 2% or 3 kcal/g atom. There may have been an intensity effect related indirectly to sample temperature, such as one related to the magnetic field of the heating current mentioned above or to a shift in geometrical position due to thermal expansion effects. These would affect the second-law results, second-law results from intensity ratio, and third-law results, in different ways. The agreement between the different methods and the validity of the zirconium results allows us to place an upper limit on such effects, and we estimate that such systematic intensity errors contribute standard deviations of 2% to the second-law and third-law results, and 1% to the second-law results from ratio results.

Errors in concentration ratio, X_{Zr}/X_{Hf} , are estimated to be less than 25% and introduce uncertainties of 1 kcal/g atom standard deviation in the third-law results. Errors in the other factors in the pressure calibration, ionization efficiency ratios, transmission ratio, and detector efficiency ratios are believed to be less than 10%, and the combined contribution to the overall uncertainty is estimated to be 0.5 kcal/g atom standard deviation.

For second-law calculations, the uncertainties in results due to uncertainties in free-energy functions is estimated to be one half of the uncertainty listed by Hultgren et al.^{70,77} in the standard enthalpy of vaporization, or 0.5 kcal/g atom. The contribution of uncertainties in the thermodynamic functions to the uncertainty in our third-law results is assumed to be equal to the uncertainties in ΔH_{298}^0 listed by Hultgren et al.^{70,77} Small discrepancies between the tabulated

free-energy functions and the true values for hafnium do not affect the comparison between the results obtained from independent experiments when all are evaluated by using the same functions.

Except for Series 540, which yielded the highest values of enthalpy both from second- and third-law treatments, there was no significant temperature dependence of derived third-law enthalpies. In Series 540, the third-law results decreased systematically by about 1 kcal/g atom from the lowest to the highest temperature. For that reason, the second-law results from that series have not been included in the composite results.

Conclusions

Results derived for the enthalpy of sublimation of zirconium, the partial molal enthalpy of sublimation of zirconium from a dilute solution in hafnium, and the standard enthalpy of hafnium from combined results by the three methods are listed with estimated uncertainties corresponding to two standard deviations from the mean in Tables III-11 and III-12.

Data for zirconium from pure zirconium and from hafnium alloy filaments yield standard enthalpies of sublimation in agreement with the accepted value for zirconium metal. This is evidence that I have avoided large systematic errors and that the dilute solid solution of zirconium in hafnium is ideal.

Because the wide temperature interval yielded relatively precise second-law results while the pressure calibration for hafnium required somewhat uncertain approximations, the second-law results are probably as reliable as the third-law values. The second-law calculation in which intensity ratios are used is probably the most reliable, as it tends to provide cancellation of systematic errors. The fact that the third-law results did not show a temperature trend and were in good agreement with the second-law results is additional evidence that significant systematic errors were absent. The value chosen as the best representation of the results of my measurements

Table III-11. Standard enthalpy of sublimation for zirconium with estimated errors.

Source	ΔH_{298}^0 (kcal/g atom)	Random errors (σ)	Estimated systematic errors (σ)	Estimated total errors (2σ)
Composite results from m/e = 90 and 91 from zirconium fila- ment	147.6	2.0	2.5	± 6.4
Composite results from hafnium filament second law, Eq. III-4	148.84	1.03	1.34	± 3.4
Hultgren et al. ⁷⁷	145.5	0.00		± 1.00

Table III-12. Standard enthalpy of sublimation of hafnium with estimated errors.

Source	ΔH_{298}^0 (kcal/g atom)	Random errors (σ)	Estimated systematic errors (σ)	Estimated total errors (2σ)
Composite results, second law, Eq. III-4	153.62	0.67	1.34	± 3.0
Composite results, second law, Eq. III-4	150.04	0.69	1.03	± 2.48
Average third-law results, Eq. III-2	148.59	0.05	1.50	$\pm 2.50^a$
Average second- and third-law results, Eq. III-2	149.30	0.7	1.0	± 2.5
Panish and Reif ⁶⁵	145.59			± 2.0
Kibbler et al. ⁶⁶	148.08			$\pm 0.4^a$
Blackburn ⁶⁷	149.18			$\pm 0.75^a$
Koch et al. ⁶⁸	148.3			± 1.2
Trulson and Goldstein ⁶⁹	149.6			$\pm 2.0^a$

^a Relative errors are estimated to be about ± 0.5 kcal/g atom.

is the average of the second-law and third-law calculations for which Eq. III-2 was used, which is

$$\Delta H_{298}^0 = 149.30 \pm 2.5 \text{ kcal/g atom.}$$

Results from independent investigations of the vaporization of hafnium are listed in Table III-12. All data were reduced by using the thermodynamic functions given by Hultgren et al.⁷⁰ The results of Panish and Reif⁶⁵ are significantly lower than the other results. My observations indicate that reactions producing HfO(g) may have contributed to the weight losses of all the investigations in which the conventional Langmuir technique was used, and that the effects would have been most pronounced under the conditions used by Panish and Reif. It is significant that the two mass spectrometric studies that are not susceptible to interference by such side reactions yield the higher results. The standard entropy of sublimation derived from my second-law results for which Eq. III-2 was used is $\Delta S_{298}^0 = 35.03 \pm 0.64$ gibbs/mole, which compares to values of 34.23 ± 0.05 gibbs/mole given by Hultgren,⁷⁰ and 33.56 ± 0.44 gibbs/mole derived from the second-law results of Koch et al. The deviations between my results or those of Koch et al. and Hultgren's value arise from differences in experimental entropies of sublimation at the temperatures of the experiments and from uncertainties in the corrections to 298° and imply inconsistencies in the integrated ΔC_p terms rather than in the ΔS_{298}^0 . The lower entropy found by Koch et al. is associated with the lower enthalpy. However, the discrepancy among our results may not be as significant as it appears, since their measurements were made at much higher temperature on the liquid, and acceptable experimental heat content data on the condensed phase are not available above 1350°K.⁷⁰

Part IV

THE KINETICS OF SUBLIMATION OF GaN AND THE COMPOSITION OF ITS VAPOR

Abstract

High concentrations of gaseous GaN and $(\text{GaN})_x$ molecules in the vapor from gallium nitride sublimation have been reported by others. My observations indicate that the ion peaks that were believed to have originated from stable $(\text{GaN})_x$ gaseous molecules in the previous work probably resulted from ion-molecule reactions. I attempted to establish the nature of the activated complex involved in the sublimation of gallium nitride by observing the gaseous products of the decomposition reaction with a mass spectrometer. The kinetics study was inconclusive, but observations indicated that the N_2 molecules that leave the gallium nitride surface may contain excess internal energy because the fragmentation pattern for N_2 molecules from a gallium nitride surface is enriched in N^+ ions.

Introduction

The reaction $\text{GaN(s)} = \text{Ga(g)} + \frac{1}{2} \text{N}_2(\text{g})$ has a large activation energy. The experimental nitrogen pressures determined from Knudsen vaporization experiments are several orders of magnitude below the calculated equilibrium values.⁸⁵ The apparent enthalpy of activation for free surface sublimation under Langmuir conditions measured by Munir and Searcy⁸⁵ is about 39 kcal/mole higher than the equilibrium value calculated from calorimetric data of Hahn and Juza.⁸⁶ Lorenz and Binkowski⁸⁷ report that the equilibrium nitrogen pressure above GaN(s) at 800°C is greater than 0.5 atm, which is consistent with the enthalpy of formation given by Hahn and Juza. It is of interest to determine if the excess energy of sublimation appears as internal energy in the products. Measurements by Mar and Searcy indicate excess kinetic energy to be negligible.⁸⁸

Excess internal energy could be incorporated in the N_2 gas produced as excess vibrational or rotational energy. I investigated these possibilities by measuring the appearance potentials of N_2^+ and N^+ ions

produced from a molecular beam of nitrogen gas subliming from GaN(s) and by comparing the ratio of N^+ to N_2^+ ions obtained by electron bombardment of nitrogen vaporized from GaN to the ratio from bombardment of residual nitrogen in the spectrometer.

It has been reported that GaN and polymers of GaN are important species in the vapor of GaN(s).⁸⁹ I searched the mass spectrum in an attempt to confirm the reports.

Experimental

GaN(s) powder was prepared by the reaction of $Ga_2O_3(s)$ with flowing anhydrous $NH_3(g)$ in a tube furnace at $900^\circ C$. Our observations of this reaction were in agreement with those of Lorenz and Binkowski.⁸⁷ Depending on the temperature and time of reaction, products range in color from bright orange through light yellow to grey. Measurements of the degree of reaction showed that the orange and yellow products were incompletely converted and contained as much as 20 wt% unreacted Ga_2O_3 , even though all products had identical x-ray powder diffraction patterns, except that patterns for samples with large excesses of oxygen were less sharp. The patterns corresponded to the hexagonal structure previously reported for GaN ($a = 3.180 \text{ \AA}$, $c = 5.166 \text{ \AA}$).⁹⁰ The very light yellow and grey materials were $Ga_{0.98}N_{0.02}O_{0.02}$ and $Ga_{1.002}N$, as determined by the loss in weight of the starting materials.

The mass spectrometry experiments were carried out with an instrument similar to the one described in the previous section of this thesis. The source was modified to regulate by control of the cathode temperature⁹¹ and was attached to a flange rather than a removable carriage. The beam was focused by means of electrostatic deflection plates rather than by rotation of the ion source.

Several experiments were made with GaN(s) (~1 at.% O) subliming from rhenium boats that were heated by self-resistance in the ion source, as described in Ref. 91 and this thesis. With the configuration used, I was unable to view the rhenium boat and could not measure the temperature. Furthermore, the gallium corroded the rhenium and limited the time of experiments to less than an hour. In most of

these experiments, I observed only Ga^+ , N_2^+ , and Ga_2O^+ ions. The Ga_2O^+ peak intensities approached 50% of the Ga^+ peak intensities when some of the samples were first heated, but in all cases decayed completely away. In two cases I was able to observe Ga_2^+ , GaN^+ , and smaller peaks that may have corresponded to Ga_2N_2^+ . This was possible only at the maximum temperature, and the filaments lasted only a few minutes under these conditions. Vaporization was very erratic, and only crude values of intensity ratio could be obtained.

I also observed mass spectra from samples of GaN evaporated from a tungsten crucible at 900° to 1250°K . The crucible was 1.9 cm in diameter and 1.4 cm high, with an orifice in the lid 3 mm in diameter, and was placed in a tungsten holder. Temperatures were measured with a platinum-vs-platinum-10% rhodium thermocouple between the bottom of the cell and the cell holder. The furnace was mounted 11 cm beneath the ion source, with tungsten radiation shields and a water-cooled copper jacket surrounding the furnace. A tungsten helix resistance element was used as a heater. A manually operated shutter above the molecular beam hole in the furnace assembly permitted the determination of the signal from material originating in the furnace. In these experiments I could measure and control the temperature, but without a gas inlet tube into the furnace I could not control the nitrogen pressures independently or observe nitrogen gas from the furnace independently of the vaporization of a sample. The only ion peaks detected from samples heated in the furnace were Ga^+ , N_2^+ , N^+ , and Ga_2^+ .

Ionization efficiency curves for Ga^+ , N_2^+ , and N^+ were measured, using the furnace molecular beam source, by the methods described in the previous section of this thesis. The electron energy distribution in the new ion source is due primarily to potential gradients within the source and is estimated to be 0.5 V. Voltages were recorded to ± 0.05 V by using a voltage-to-frequency converter and pulse transformer system. The voltage scale was normalized by determining the appearance potential of $\text{Ar}^+(40)$. Checks of the appearance potentials

of Ag^+ (107), H_2O^+ (18), and O_2^+ (32) agreed with accepted values of ± 0.3 V.⁹²

Discussion

My results contradict the findings of Gordienko et al.,⁸⁹ who observed $\text{I}(\text{GaN}^+)/\text{I}(\text{Ga}^+)$ ratios from 0.6 to 2.0 and $\text{I}(\text{Ga}_2\text{N}_2^+)/\text{I}(\text{Ga}^+)$ ratios from 0.1 to 0.3 at temperatures from 1000 to 1150°K. The maximum $\text{I}(\text{GaN}^+)/\text{I}(\text{Ga}^+)$ ratio I saw was 0.1 from samples sublimed from the rhenium filaments. The nitrogen pressure in the manifold at that time was 10^{-5} Torr, and nitrogen pressure in the source probably was at least 1 order of magnitude higher. I attempted to achieve high source pressures of $\text{N}_2(\text{g})$ during the tungsten furnace experiments by throttling the pump. Runs with manifold pressures of 2×10^{-5} Torr did not produce GaN^+ peaks, although the Ga^+ intensities were as high as those for the previous experiments, where GaN^+ ions were seen.

Although I was not able to make measurements relating GaN^+ intensity to $\text{Ga}(\text{g})$ and $\text{N}_2(\text{g})$ concentrations and Ga^+ and N_2^+ intensities in order to show the occurrence of an ion-molecule reaction, I believe that the failure to find GaN^+ except under conditions of very high $\text{N}_2(\text{g})$ and $\text{Ga}(\text{g})$ concentrations and high N_2^+ and Ga^+ ion intensities indicates that the GaN^+ ions were produced by ion-molecule reactions. Appearance potentials measured for Ga^+ were the same, within the precision of our measurements (± 0.2 V), for experiments with $\text{GaN}(\text{s})$ or $\text{Ga}(\text{l})$ in the crucible. When the shutter was closed, the Ga^+ intensity was reduced to zero. The N_2^+ and N^+ appearance potentials were the same for runs with $\text{GaN}(\text{s})$ in the furnace and for runs with $\text{N}_2(\text{g})$ leaked into the spectrometer with the pump valve partially closed. All results agreed with values listed in Ref. 92. Since only a few percent of the nitrogen reached the detector from the sample without undergoing collisions, however, a difference in appearance potentials might not be observed even if all the N_2 molecules from the cell contained significant excess energy.

The ion ratios N^+/N_2^+ were distinctly higher when the shutter above the heated cell was open than when it was closed or when background gases were measured (Tables IV-1 and IV-2). The maximum possible partial pressure for nitrogen atoms can be calculated to be of

Table IV-1. Typical intensity measurements taken with powder GaN in a tungsten cell.^a

Sample temperature (°C)	Shutter open		Shutter closed		N^+/N_2^+ from cell	N^+/N_2^+ outside cell	$\frac{N^+/N_2^+ \text{ (cell)}}{N^+/N_2^+ \text{ (outside)}}$
	N_2^+	N^+	N_2^+	N^+			
907	70,863	4,505	48,835	3,003	0.0682	0.0615	1.11
941	180,331	12,240	123,009	8,144	0.0715	0.0662	1.08
962	259,701	19,157	181,516	12,529	0.0848	0.0690	1.23
979	368,068	30,284	259,400	19,583	0.0985	0.0755	1.30
1004	529,989	52,307	393,682	33,683	0.1266	0.0856	1.60

^aOrifice diameter 3.0 mm, N_2^+ data taken at 27 V, N^+ data at 38 V.

Table IV-2. Ratios from residual gases in spectrometer with furnace cold.

Manifold pressure	N_2^+	N^+	N^+/N_2^+
3.5×10^{-8} Torr	17,385	1049	0.0603
9.0×10^{-8} Torr	55,011	2556	0.0465
3.3×10^{-7} Torr (pump valve closed)	210,135	8155	0.0388
<u>Leaking N_2 in from manifold</u>			
1.4×10^{-8} Torr	10,092	507	0.0502
4.4×10^{-8} Torr	42,068	1844	0.0438
8.4×10^{-7} Torr	119,862	4271	0.0356

the order of 10^{-10} atm at 1300°K, from the equilibrium data for gallium nitride and for the elements. Free surface fluxes corresponding to pressures of 10^{-5} atm were observed by Munir and Searcy. The increase of the N^+/N_2^+ ratio when molecules from the cell were studied probably reflects, therefore, a higher fragmentation probability for N_2 molecules from the gallium nitride surface. This change in fragmentation behavior would be reasonable if the N_2 molecules were not at internal equilibrium. However, simple thermal excitation to about 1000°C produces higher populations of vibrationally and rotationally excited states, which might greatly change the fragmentation probability from that characteristic of N_2 at ambient temperatures. Proof of excess energy in N_2 molecules originating from a gallium nitride surface would require comparison of the fragmentation patterns of N_2 vaporized from GaN to patterns of N_2 thermally excited to a corresponding temperature, about 1000°C.

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