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Technical Progress Report

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AN INVESTIGATION OF SOME LANTHANIDE BORON, CARBON, NITROGEN SILICON, CHALCOGEN AND HALOGEN SYSTEMS AT ELEVATED TEMPERATURES

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DISCLAIMER

TABLE OF CONTENTS

The following constitutes the technical progress report of work performed under Contract AT(11-1)-716 during the year 1971-72. The report is presented as a series of brief preprints, each bearing the name of the investigator. All documents produced since the last technical progress report have been submitted as separate items and are tabulated below. In addition six copies of reprints of manuscripts published since the last technical progress report are listed and are attached as a separate item.

The following papers were presented orally during the year:

1. "Vaporization Study of $EuCl_2$ and EuOCl" by Alleppey V. Hariharan. Presented at the Fourth Midwest High Temperature Conference, Rolla, Missouri, June, 1971.
2. "Vaporization Study of SmOBr" by Dale E. Work. Presented at the Fourth Midwest High Temperature Conference, Rolla, Missouri, June,1971.
3. "A Study of the Eu-O-F system" by S. L. Bacon and Harry A. Eick. Presented at the Fourth Midwest High Temperature Conference, Rolla, Missouri, June, 1971.
4. "Vaporization Thermodynamics of Europium(II) chloride and Europium(III) Oxidechloride" by Alleppey V. Hariharan and Harry A. Eick. Presented aththe Ninth Rare Earth Conference, Blacksburg, Virginia, October, 1971. (COO-716-068, COO-716-070)

For presentations numbers 1-3, abstracts were not required; hence document numbers are not assignable.

The following documents have been or will be submitted for publication:

1. "X-Ray Fluorescence Spectrometer Conversion Table for Graphite Crystals" by Robert L. Seiver, submission uncertain (COO-716-067).
2. "Vaporization Thermodynamics of $EuCl_2$" by Alleppey V. Hariharan and Harry A. Eick, submitted to High. Temp. Sci. (COO-716-069).
3. "On the Preparation of Condensed ScO" by Dale E. Work and Harry A. Eick, to be submitted to J. Less Common Metals (COO-716-071).

The following reprints are also appended:

1. "The Incongruent Vaporization of Nonstoichiometric $YbC_{1.25+y}$" by John M. Haschke and Harry A. Eick, High Temp. Sci., 2, 376 (1970) (COO-716-058).
2. "An Intermediate Phase in the $YbCl_2$-$YbCl_3$ System" by Norman A. Fishel and Harry A. Eick, J. Inorg. Nucl. Chem., 33, 1198 (1971) (COO-716-060).
3. "Vaporization Thermodynamics of Europium(II) Sulfide" by Alleppey V. Hariharan and Harry A. Eick, High Temp. Sci., 3, 123 (1971) (COO-716-061).
4. "Void Channels in the Nb_3Te_4, Ta_2S, and Nb_2Se Structure Types; The Structure of Nb_3Se_4" by John G. Smeggil, J. Solid State Chem., 3, 248 (1971) (COO-716-063).
5. "Vapor Pressure Measurements in the Samarium Dicarbide-Carbon and Thulium Dicarbide-Carbon Systems" by Robert L. Seiver and Harry A. Eick, High Temp. Sci., 3, 292 (1971) (COO-716-064).
6. "The Crystal Structure of Strontium Dibromide" by John G. Smeggil and Harry A. Eick, Inorg. Chem., 10, 1458 (1971) (COO-716-065).

The principal investigator has devoted twenty-five percent of his time to the research effort described in the report. He hopes to spend thirty-five percent of his effort on the work during the remainder of the contract year.

The present positions of doctoral students trained under this grant are:

1. Gordon L. Galloway, Ph.D., 1962, Associate Professor of Chemistry, Dennison University, Granville, Ohio.
2. Richard A. Kent, Ph.D., 1963; Staff Member, Los Alamos Scientific Laboratory, Los Alamos, New Mexico.
3. George D. Sturgeon, Ph.D., 1964, Associate Professor of Chemistry, University of Nebraska, Lincoln, Nebraska.
4. Robert E. Gebelt, Ph.D., 1965, Assistant Professor of Chemistry, Mankato State University, Mankato, Minnesota.
5. Philip A. Pilato, Ph.D., 1968, Xerox Corporation, Rochester, New York.
6. Dennis B. Shinn, Ph.D., 1968; Sylvania El. Prod. Co., Danvers, Massachusetts.
7. Kenneth J. Manske, Ph.D., 1969; Assistant Professor of Chemistry, Mars Hill College, Mars Hill, North Carolina.

8. A. Duane Butherus, Ph.D., 1969, Bell Telephone Laboratories, Murray Hill, New Jersey.
9. John J. Stezowski, Ph.D., 1969; Research Associate, Department of Chemistry, Cornell University, Ithaca, New York.
10. John M. Haschke, Ph.D., 1969; Assistant Professor of Chemistry, University of Michigan, Ann Arbor, Michigan.
11. Norman A. Fishel, Ph.D., 1970; Staff Chemist, Universal Oil Products, Chicago, Illinois.
12. Robert L. Seiver, Ph.D., 1971, Research Associate, Department of Chemistry, Michigan State University, East Lansing, Michigan.

The present position of postdoctoral associates trained under this grant are:

1. Dr. John Smeggil, 1970, General Electric Co., Schenectady, New York.

The Incongruent Vaporization of Europium(III) Oxidechloride

A. V. Hariharan

INTRODUCTION

Oxidechlorides of the type LnOCl have been characterized for all the trivalent lanthanides.[1] From vapor phase hydrolysis of the trihalides Koch, et al.[2-4] obtained the enthalpies of formation of LaOCl, PrOCl, NdOCl, SmOCl and GdOCl. Baev and Novikov[5] derived similar data for these oxidechlorides and for CeOCl from tensimetric equilibrium measurements. In the course of our work on the high temperature vaporization of $EuCl_2$,[6] we have investigated the incongruent vaporization behavior of europium(III) oxidechloride to provide pertinent thermochemical data.

EXPERIMENTAL SECTION

Pure EuOCl was prepared by the controlled thermal decomposition of Eu(III) chloride hydrate according to the method of Wendlandt.[7] A slow stream of air was passed over $EuCl_3 \cdot 6H_2O$ maintained at $\sim$ 500°, after which the product was cooled and removed into an argon-filled glove box. It was then outgassed in high vacuum at $\sim$ 700° to remove adsorbed moisture and air. Analytical.Calcd for EuOCl: Eu, 74.71%, Cl, 17.43%. Found: Eu, 75.02 $\pm$ 0.33%, Cl, 17.45 $\pm$ 0.04%. The X-ray diffraction pattern of the product EuOCl was in agreement with that reported[1] for the tetragonal PbFCl structure.

Vaporization

In view of the anticipated incongruent vaporization of EuOCl, samples for Knudsen effusion measurements were contained in a secondary ThO_2 crucible fitted inside the regular graphite symmetric effusion cells. Total weight losses of EuOCl in two separate experiments from such an assembly at 1150° and 1250° gave, respectively, 98.9% and 100.8% of theoretical for conversion to Eu_2O_3, with no evidence of any interaction with the thoria crucible. Target collection effusion measurements for EuOCl were made over the temperature range 963°-1344° through use of the procedure very similar to that described previously for $EuCl_2$.[6] The effusion cell was supported symmetrically inside

a tungsten-molybdenum oven of 1.59 mm wall thickness which completely surrounded the effusion cell. The cover of the oven was designed such that it would not intercept the direct beam which would impinge on the target. The effusion cell was heated by radiation from the oven which was inductively heated. Such an arrangement provided very uniform temperature in the inner graphite effusion cells and prevented condensation of the effusing vapors experienced previously with $EuCl_2$.[6] Three different knife-edge orifices (11.4×10^{-4}, 54.8×10^{-4} and 73.7×10^{-4} cm^2) were used in the series of six experiments reported herein. Approximately 50-75% of the expected weight loss from the 0.13-0.16 g sample used in each vaporization experiment was incurred during a run. The targets were analyzed for Eu by X-ray fluorescence.[8]

RESULTS

The incongruent nature of the high temperature vaporization of EuOCl according to equation (1)

$$3\ EuOCl(s) \rightarrow Eu_2O_3(s) + EuCl_2(g) + 1/2\ Cl_2(g) \qquad (1)$$

was established by the combined weight-loss data and X-ray diffraction analysis of the vaporization residues and sublimate. Essentially monoclinic Eu_2O_3 was the condensed phase in the vaporization residues above 1050°, but traces of the cubic Eu_2O_3 phase were always detected. Calculations involving the isomolecular exchange reaction in the gas phase according to (2)

$$EuCl_2(g) + Cl_2(g) = EuCl_3(g) + Cl(g) \qquad (2)$$

which used derived thermal functions for $EuCl_3(g)$[9-12] and the equilibrium constant for the dissociation of Cl_2,[13] indicated negligible contribution from gaseous $EuCl_3$ and Cl.

The partial pressures of $EuCl_2(g)$ in equilibrium with EuOCl(s) and $Eu_2O_3(s)$ obtained in six independent experiments (52 data points) are represented by the unweighted linear least square equation (3),

$$2.303 \log P_{EuCl_2(g)atm} = -\frac{(424_{90} \pm 2_{14})}{T} + (19.6_2 \pm 0.1_5)(1236 - 1617\ K) \qquad (3)$$

The incongruent vaporization requires that the pressure of Cl_2 in the cell be related to $P_{EuCl_2(g)}$ according to (4),

$$P_{Cl_2(g)} = 1/2\ P_{EuCl_2(g)}[M_{Cl_2}/M_{EuCl_2}]^{1/2} \quad (4)$$

and accordingly the equilibrium constant for reaction (1) is computed as (5),

$$2.303 \log K = -\frac{(637_{35} \pm 3_{21})}{T} + (28.8_0 \pm 0.2_3) \quad (5)$$

At the median temperature (1427 K), $\Delta H°_{1427} = 126.6_6 \pm 0.6_4$ kcal/3 EuOCl; $\Delta S°_{1427} = 57.2_3 \pm 0.4_5$ eu. To reduce the 2nd law data to 298 K, the heat capacity of EuOCl(s) was approximated by a variation of Kopp's rule[14] according to equation (6)

$$Cp°\ EuOCl(s) = 1/2\ Cp°\ Eu_2O_3(s) + 3/2\ R \quad (6)$$

The standard entropy, [$S°_{298}$(EuOCl(s)) = 24.5 eu] was estimated according to the schemes of Latimer[15] and Westrum[16] and included 3.5 eu for the magnetic contribution of the Eu(III) ion. These data were utilized to derive the thermal functions for EuOCl(s) and were combined with the published data for Eu_2O_3 (monoclinic)[17] and Cl_2[13] and the functions obtained for $EuCl_2(g)$[18] to reduce the data to 298 K.For reaction (1): $\Delta H°_{298} = 135._4 \pm 2._4$ kcal/3 EuOCl; $\Delta S°_{298} = 68._9 \pm 1._9$ eu.

Combination of the experimental equilibrium constants with the free energy functions gave a 3rd law $\Delta H°_{298}$ for reaction (1) = $136._1 \pm 1._2$ kcal/3 EuOCl with no observable temperature trend. The standard entropy of EuOCl(s), $S°_{298}$, was computed from the 2nd law value and the entropies of Eu_2O_3 (monoclinic), $EuCl_2(g)$ and $Cl_2(g)$ as $24._7 \pm 1._0$ eu.

From the published enthalpies of formation of Eu_2O_3 (monoclinic),[17] $EuCl_2(s)$,[19] and the enthalpy of sublimation of $EuCl_2(s)$,[18] the enthalpy of formation of EuOCl(s), $\Delta H°_{f\ 298}$, is computed as $-213._9 \pm 3._3$ kcal/gfw.

DISCUSSION

The vaporization mode of EuOCl(s) to the gaseous $EuCl_2$ is not surprising in view of the stability of the Eu(II) species compared to that of $EuCl_3$. Contrary to this, the oxidechlorides whose thermal data were reported[2-5] and the rest of the series, except possibly YbOCl, would vaporize entirely to $LnCl_3(g)$ and $Ln_2O_3(s)$.

There are no pertinent thermodynamic data available for EuOCl and the present study contributes the only information on this phase. However the enthalpy and entropy of the incongruent vaporization of EuOCl(s) are in line with the values reported for EuOBr.[14] The $\Delta H^\circ_{f\ 298}$ EuOCl(s) is also consistent with the corresponding estimates for other lanthanide(III) oxidechlorides.[2-5] To this extent and the given agreement of the 2nd- and 3rd-law enthalpies, the approximations used in the data reduction seem valid.

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The Vaporization of Europium Diiodide

A. V. Hariharan

INTRODUCTION

As a continuing part of our investigation of the vaporization thermodynamics of divalent europium compounds, the high temperature vaporization of europium(II) iodide has been studied. Preparative methods for EuI_2 are well established.[1,2,3] It is the only stable phase reported in the Eu-I binary series; the triiodide is thermodynamically unstable. Two modifications of the crystal structure of EuI_2 have been reported by Baernighausen.[3] However, thermochemical data on EuI_2 in particular, and the lanthanide iodides in general, are limited solely to the comprehensive estimates by Brewer et al.[4,5] Recently the vapor pressures in equilibrium with SmI_3 and NdI_3 and the heat capacities and enthalpies of fusion and transition of these and other lanthanide triiodides[7] have been reported.

The vapor pressures of $EuCl_2$ and $EuBr_2$ have been reported[8,9] and that of EuF_2 has been measured by Petzel and Greis.[10] This investigation was undertaken to complete vaporization studies of the divalent europium halides.

EXPERIMENTAL SECTION

Anhydrous EuI_2 was prepared by a modification of the method of Taylor and Carter.[11] The wet molecularly dispersed mixture of hydrated europium triiodide and ammonium iodide was dried over conc. H_2SO_4 in a vacuum dessicator. The dried cake, contained in a graphite boat and situated in a Vycor apparatus,was heated slowly in a stream of He dried by passage through P_2O_5 and liquid N_2 traps. During the heating schedule appreciable amounts of free iodine were liberated at temperatures below 150° - an indication of decomposition of $EuI_3 \cdot xH_2O$ to EuI_2 even at these low temperatures. Final heating to $\sim$ 650° provided complete removal of all excess NH_4I and the product melted into a greenish mass in the crucible. The sample was cooled under He and isolated into an argon-filled dry box. This crude EuI_2 was further purified by distillation from an outgassed graphite crucible heated by induction at $\sim$ 1200° in high vacuum. The distilled pale greenish

yellow crystals were analyzed for Eu and I by conventional analytical methods. Calcd. for EuI_2: Eu, 37.46%; found: Eu, $37.5_2 \pm 0.2_0$%, I, $62.3_7 \pm 0.0_6$%. Because of the extreme hygroscopicity of EuI_2, X-ray diffraction patterns of the polycrystalline samples and residues from the vaporizations were taken with a Haegg-type Guinier camera (Cu Kα radiation/Pt internal standard, a_o = 3.9237 ± 0.0003 Å) with the samples sealed in flat PVC bags. The lattice parameters and intensities of the diffraction lines were in agreement with those reported for the monoclinic form of EuI_2.[3]

Vaporization

Target collection Knudsen effusion measurements for liquid EuI_2 were made in the temperature range 813°-1122° by use of the procedures described previously.[12] Graphite effusion cells were found to be both satisfactory and nonreactive containers. Three different knife-edged orifices (10.7×10^{-4}, 44.5×10^{-4} and 58.8×10^{-4} cm^2), the areas of which were determined by planimeter measurements of photomicrographs, were used in the four vaporization experiments reported herein. Effusates were collected on liquid N_2-chilled copper targets and were analyzed for Eu by X-ray fluorescence.[13] Mass spectrometric investigation of the vapor species over liquid EuI_2 was also effected by use of a Bendix Model 12-107 time-of-flight mass spectrometer in the temperature range 964°-1072° with a 30 eV ionizing electron energy beam. Appearance potentials for the identified species, EuI_2^+, EuI^+ and Eu^+, were obtained by the linear extrapolation procedure with Hg, H_2O and N_2 as references.

RESULTS

The mass spectrometric data indicated the parent vapor species to be entirely $EuI_2(g)$ which then fragments to EuI^+ and Eu^+ in the ratio $EuI_2^+:EuI^+:Eu^+ \approx 34:100:81$. No $EuI_3(g)$ was observed. Moreover the fragmentation pattern with the highest intensity, that of EuI^+, is in conformity with results obtained for $EuCl_2$[14] and $EuBr_2$,[9] both of which are known to vaporize congruently. The ion intensities *vs* temperature data indicated that EuI_2^+, EuI^+ and Eu^+ all derived from the species having $\Delta H°_v(1291\ K) \approx$ 66 kcal/gfw. In addition, the invarient nature of the X-ray diffraction

patterns of the vaporization residues and total vaporization of a typical sample from a graphite cell confirm congruent vaporization according to equation (1). The appearance potentials for EuI_2^+, EuI^+ and Eu^+ were

$$EuI_2(\ell) \rightarrow EuI_2(g) \qquad (1)$$

established as 8.8_5 eV, 9.9_0 eV and 12.4_5 eV, respectively, with a possible uncertainty of $\pm$ 0.2 eV.

The vapor pressure data derived from the four independent vaporization experiments (40 data points) gave the unweighted linear least squares equation (2). At the median temperature (1241 K), $\Delta H°_{1241} = 62.7_0 \pm 0.3_4$ kcal/gfw

$$2.303 \log P_{EuI_2(g)} \text{ atm} = -(315_{52} \pm 1_{69})/T + (16.0_2 \pm 0.1_4) \qquad (1086 - 1395 \text{ K}) \qquad (2)$$

and $\Delta S°_{1241} = 31.8_3 \pm 0.2_7$ eu. By use of the estimates of Brewer et al.[4,5] for the heat capacity changes and enthalpy and entropy of fusion at the melting point, 853 K,[1] the median temperature data were reduced to 298 K to give for reaction (3)

$$EuI_2(s) \rightarrow EuI_2(g) \qquad (3)$$

$\Delta H°_{298} = 69._9 \pm 1._0$ kcal/gfw; $\Delta S°_{298} = 47._8 \pm 1._0$ eu. The free energy of vaporization for equation (1) may be represented by (4)

$$\Delta G°_T = (751_{11} \pm 3_{36}) - (113.0_7 \pm 0.2_7)T + 10T \ \ell n \ T \ (853 \text{ K} - \text{bpt}) \qquad (4)$$

At the extrapolated boiling point, 2037 $\pm$ 15 K, $\Delta H°_v = 54.7_4 \pm 0.3_4$ kcal/gfw and $\Delta S°_v = 26.8_8 \pm 0.2_7$ eu.

DISCUSSION

The general vaporization pattern of EuI_2 is in line with those observed for $EuCl_2$ and $EuBr_2$ and the tentative 2nd law thermodynamic data correspond to the trend in the Eu(II) halide series. The final third law data reduction is in progress.

Attempts were made to analyze the vaporization targets for both Eu and I by X-ray fluorescence, but analysis of the latter has not been successful for reasons we do not yet understand.

The appearance potential for (Eu^+/EuI_2) was combined with the first IP of Eu (5.64 eV)[15] to derive the dissociation energy of $EuI_2(g)$; $D°_o = 157._0 \pm 4._6$ kcal/gfw. Combination of this datum (corrected to 298 K) with the 2nd law $\Delta H°_{298}$ sublimation of $EuI_2(s)$ (this work) and the enthalpy of vaporization of Eu(s)[16] and decomposition of $I_2(s)$[17] gives for $EuI_2(s)$, $\Delta H°_{f\ 298} = -138._4 \pm 5._0$ kcal/gfw. This value appears in reasonable agreement with that reported for SrI_2 ($135._5 \pm 5._0$ kcal/gfw, Ref. 18).

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The Thermal Decomposition of NdOBr

Dale E. Work

INTRODUCTION

A thorough understanding of the high-temperature decomposition modes of the lanthanide oxide halides must be based on reliable thermodynamic data; the present sketchy understanding of these processes attests to the lack of such data. In an effort to partially fill this void, a study of the SmOBr system was undertaken[1] and its decomposition mode in vacuo was determined. The thermodynamic characterization of this decomposition proved very complex, however, suggesting subtle complications in the process which were not observed in the Eu_3O_4Br system.[2] In order to isolate some of the parameters affecting the thermal decomposition of SmOBr and thus to provide a more satisfactory context in which to interpret the earlier data, and in order to further provide basic thermodynamic data for the oxide halides, an investigation of the NdOBr system was initiated.

EXPERIMENTAL SECTION

NdOBr was prepared by heating the sesquioxide at 800° for 3-5 hours in a stream of dried He saturated with bromine. Metal content was assayed by ignition to the sesquioxide; bromine content was determined by measuring the weight gain in the preparatory step (the gravimetric factor is 1.427). In addition, the sample was characterized by X-ray powder diffraction (Haegg Guinier camera, $t = 24 \pm 1°$, internal standard KCl, $a = 6.2930 \pm 0.0001$ Å).

The thermal decomposition of the monoxide monobromide was traced by a series of X-ray powder diffraction patterns as the decomposition progressed. The gaseous decomposition product was characterized by mass spectrometry and by X-ray powder diffraction of the condensed gaseous species. A Bendix Model 12-107 time-of-flight mass spectrometer was used. Appearance potentials were obtained by a linear extrapolation technique using mercury as a reference.

Equilibrium vapor pressures were determined as a function of temperature by the Knudsen effusion target collection technique. The effusate collected on the copper targets was assayed by X-ray fluorescence, by use of a previously

described collection and analytical technique.[3] Vapor pressures were measured over the temperature range 1194-1458° by use of outgassed molybdenum crucibles with orifice area ranging from 1 X 10^{-3} cm^2 to 1 X 10^{-2} cm^2. Both weight loss data and X-ray powder diffraction were used to check for crucible-sample interaction.

RESULTS

The preparatory method described above yielded essentially pure monoxide monobromide. Both metal and bromine contents were typically >99% of their theoretical values based on the stoichiometry NdOBr.

The decomposition trace *via* powder diffraction data clearly showed the monoxide monobromide to decompose to the tetraoxide monobromide, Nd_3O_4Br, which further decomposed to the sesquioxide. No other discrete solid phase was observed. The diffraction patterns of NdOBr and Nd_3O_4Br were in excellent agreement with published X-ray data.[4,5]

The mass spectrum of the gaseous decomposition product yielded an appearance potential of 11.8 eV for the $NdBr_2^+$ species. The fragmentation pattern showed the ions $NdBr_2^+$, Nd^+, and $NdBr^+$ present in the ratio 2.0:1.0:1.6. This pattern is very different from those resulting from the mass spectra of the Eu_3O_4Br[2] and SmOBr[1] decomposition reactions, and clearly shows the gaseous decomposition product to be the tribromide, $NdBr_3$. Accordingly, the decomposition reaction of NdOBr has been definitively characterized in the temperature range studied as:

$$4\ NdOBr(s) = Nd_3O_4Br(s) + NdBr_3(g) \qquad (1)$$

Based on 67 data points obtained for the equilibrium vapor pressure of $NdBr_3$ over a NdOBr-Nd_3O_4Br mixture, it is clear that the measured vapor pressure is a function not only of temperature, but also of orifice size. Using only those 23 data points obtained with orifice areas $\leq$ 1.1 X 10^{-3} cm^2, the thermodynamic data for reaction (1) are:

$$\Delta H^\circ_T \approx -105.3 \text{ kcal/gfw}$$

$$\Delta S^\circ_T \approx 45.72 \text{ eu}$$

These data have been reduced to 298 K values, and reasonable agreement between second and third-law calculations is obtained, though further refinements in the data reduction remain to be made. Absolutely no crucible-sample interaction was detected.

DISCUSSION

The significance of this research lies not only in the generation of fundamental thermodynamic data (this is the first such data for a lanthanide oxide-bromide which decomposes to a tribromide gaseous species), but also in the clarity it lends to the earlier vaporization study of SmOBr. Of crucial importance is the observation of a vaporization coefficient <1 (i.e., orifice effect) which, upon reviewing earlier data, is also detected in the vaporization of SmOBr. Thus the "subtle complications" in the SmOBr decomposition reaction, cited earlier, have been at least partially resolved.

Presumably, the vaporization coefficient <1 reflects a structurally-related kinetic restraint impressed on the system. The precise interpretation of the origin and significance of this orifice-size effect in the NdOBr system, and its effect on the vaporization thermodynamics, is yet to be formulated.

The thermodynamic data obtained should be particularly useful as a guide to estimating the high-temperature entropy values of other gaseous tribromides, and should provide a means for checking the validity of various heat capacity approximations required for data reduction in high-temperature lanthanide chemistry. Of particular importance there is the appearance potential of $NdBr_2^+$ from $NdBr_3$, this being the first such data obtained for any lanthanide trihalide other than fluorides.

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The Crystal Structure of TmC_2

Robert L. Seiver

INTRODUCTION

In 1968 Krupka and co-workers[1] reported for thulium dicarbide a high-pressure, low-temperature crystal modification which previously had been observed, but not identified in this laboratory's vaporization study of $TmC_2(s)$. Earlier progress reports[2-3] described attempts to prepare single crystals of this phase and preliminary crystallographic examination of the product. The modification is actually a mixture of two phases, the structure of one of which is described herein.

EXPERIMENTAL SECTION

Stoichiometric amounts of thulium chips and outgassed graphite were placed into an outgassed tantalum ampoule which was sealed under argon by arc-welding. The ampoule was heated inductively to 1650° for 12 hours in vacuum, cooled, inverted, and heated again for 6 hours. It was then sealed into an evacuated quartz tube which was heated in a tube furnace at 1100° for 1000 hours and then cooled uniformly over a 500 hour period.

The ampoule was opened in an argon-filled dry-box and the bulk of the sample stored there. Small portions were removed under sodium-dried paraffin oil. The sample was analyzed by X-ray powder diffraction (Haegg-type focussing monochromator camera); microscopic examination; and Weissenberg and precession single crystal X-ray diffraction. Intensity data were collected using the multiple film Weissenberg technique and Cu $K\alpha$ radiation.

RESULTS

Guinier powder diffraction photographs showed mainly the pattern reported by Krupka. Traces of graphite, tetragonal TmC_2 and cubic TaC were also observed. The TaC was readily distinguished under the microscope by its gold color, while the bulk of the sample was black, with some silvery faces present.

Single crystal techniques showed two distinct phases, one orthorhombic and one hexagonal, on the basis of which the complex powder pattern could be indexed completely. The orthorhombic cell ($a = 3.68 \pm 0.01$, $b = 12.40 \pm 0.04$, $c = 13.58 \pm 0.03$ Å) is a subcell of the orthorhombic unit cell proposed by Krupka, with one-fourth the volume. All specimens of this type examined so far have been twinned badly.

One suitable crystal of the hexagonal phase ($a = 3.19 \pm 0.01$, $c = 16.74 \pm 0.07$ Å) has been found. The following conditions for reflection were observed: (1) 00ℓ for $\ell = 6n$, and (2) $hk\ell$ for $h = k \pm 3n$, $\ell = 6n$ or $h \neq k \pm 3n$, $\ell \neq 6n$. These restrictions and the geometry of the Weissenberg method allowed intensity measurements of only 56 independent observable reflections.

The metal positions were located by analogy with Ho_2C, which has similar lattice parameters and also shows the 00ℓ, $\ell = 6n$ restriction. This restriction is a result of a 6-fold packing sequence along the c-axis and is not symmetry-required in the space group, $P\bar{3}1c$. The metal atoms are located in position 2a, (0,0,1/4), and 4f, (1/3, 2/3, z), where z is very close to 1/6. A difference Fourier synthesis showed twelve maxima of an intensity close to that expected for carbon, corresponding to the formula TmC_2. Four of the twelve are clearly acetylenic, with a C-C distance of 1.3 Å. The other eight are individual peaks. All twelve show tetrahedral metal coordination at a distance of about 2.1 Å, a very reasonable environment for carbon.

DISCUSSION

Solution of the structure of the hexagonal crystal has been hampered by lack of an absorption correction. To prevent hydrolysis the crystal was sealed into a glass capillary. Refraction of the glass made it very difficult to obtain the accurate crystal dimensions. The present data have been corrected roughly by assuming the crystal to be spherical. It is believed that this approximation acounts for the failure of the structure to refine to an R value below 0.12. At present a search for another crystal is underway, and the intensity data will be recollected on a newly available Picker automated diffractometer with Mo Kα radiation. The extra reflections accessible by this technique and the accurate absorption correction attainable should permit further refinement of the structure and determination of accurate anionic sites.

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Ternary Systems of Lanthanide(III) Fluorides

Carol G. Biefeld

INTRODUCTION

Ternary systems of lanthanides and a nonmetal such as oxygen, sulfur, or selenium (i.e., $Ln_xLn_yY_z$) as well as alkali metal-lanthanide-fluoride systems are well known. The purpose of this research is to study the ternary systems consisting only of lanthanides and fluorine to determine if discreet, stable compounds can be isolated.

EXPERIMENTAL SECTION

Two methods were used for the production of mixed lanthanide fluorides. In the first method the two constituent fluorides were coprecipitated rapidly from an acidic solution of the corresponding lanthanide oxides. The resulting precipitate was mixed with an excess of ammonium fluoride and dehydrated at 350° under a continuous flow of helium. The second method involved mixing the desired lanthanide trifluorides and sealing the mixture, previously enclosed in platinum, in an outgassed, evacuated quartz ampoule. After the ampoule had been heated to 1200° for ca. one day, the sample was either quenched, annealed at a lower temperature and then quenched, or allowed to cool slowly to room temperature. The necessary lanthanide trifluorides were prepared in a manner similar to that used for the coprecipitation procedure or were used directly from a group of samples prepared by Shinn.[1]

Two methods were used for phase analysis. All samples were examined by X-ray diffraction with a Guinier-Haegg forward focussing powder camera (Cu $K\alpha_1$) in which platinum was used as an internal standard ($a = 3.9237 \pm 0.0001$ Å). A few samples were subjected to differential thermal analysis (DTA). The apparatus was essentially that described by Shinn[1] with the following modifications: both a stainless steel and nickel DTA cells were used, the differential signal was amplified through a Hewlett Packard voltmeter, then recorded on a Bausch and Lomb recorder. The sample and reference material (La_2O_3 in the stainless steel and CaF_2 in the nickel cell) were packed tightly into their respective wells. Heating and cooling cycles were both examined at a temperature change of ca. 5 to 6°/min, with a maximum of 1050° being reached.

RESULTS

Both X-ray powder diffraction results and the intensified color of all but the coprecipitated products indicated that some type of interaction occurred. Least squares fitted lattice parameters, based on an orthorhombic cell for the Gd-Er-F system and a hexagonal cell for all other systems, are presented in Table I along with several products which yielded unindexable powder patterns. Cell volume is a linear function of mole fraction for the La-Nd-F system (expt 18, 20 to 23), the Gd-Er-F system (expt 24 to 28), and those products of the La-Er-F system which were quenched and for which the mole fraction of ErF_3 was less than 0.500 (expt 2 to 4).

DTA experiments on products of the LaF_3-ErF_3 equimolar mixtures confined in a stainless steel cell gave an enormous peak which commenced at ca. 700° and increased as the temperature was elevated. Examination of the platinum liners by X-ray fluorescence indicated that the sample had interacted with the cell, and the results were thus questionable. When a nickel cell was employed, no peak was obtained in three heating and cooling cycles. Thus, pertinent information about a possible phase transformation temperature was not obtained.

DISCUSSION

The La-Nd-F and Gd-Er-F systems exhibit a continuous series of solid solutions between the respective terminal phases. The powder pattern for each mixture always consisted of lines belonging to only one phase, i.e., no lines belonging to either constituent trifluoride were ever observed, and cell volume is a linear function of mole fraction. Product color intensification would be expected of a solid solution which randomized the structure, i.e., made it less symmetrical and caused the f-f transitions to be "less" forbidden. Finally, the structure of the solid solution was apparently the same as that of its components since the relative intensities of the powder pattern lines of all were the same. We believe that the solid solution behavior extends over the entire temperature range since an annealed equimolar mixture of NdF_3 and LaF_3 (expt 19) showed no change from the quenched sample; however, further annealed samples of differing mole fractions for both the Nd-La-F and Gd-Er-F must be examined to substantiate this belief.

The behavior of the La-Er-F system is less easily explained. At high temperatures the system behaves analogously to those described above as long as the mole fraction of ErF_3 is less than 0.50. At low temperatures our present limited data indicates that either several phases are present or a phase which has a very large cell (cf., $Na_5Er_9F_{32}$, a = 5.514, b = 38.99, c = 7.798[2]) or one of low symmetry (cf., β-$3NaF \cdot ScF_3$ monoclinic[3]). Since the DTA experiments provided no information on the transformation between the high and low temperature forms, the transition must be slow. This conclusion is reinforced by the fact that lines attributable to the solid solution phase were present, though broadened, in powder patterns of samples which had been annealed for more than 12 days. The high temperature behavior of the ErF_3-rich samples remains unexplained. There is no indication of solid solution behavior and the powder patterns are complex.

The following general conclusions relate to mixed lanthanide fluoride systems. As long as two trifluorides of the same structure type, either the LaF_3-[4] or the YF_3-type,[5] are combined, only solid solutions of the same structure type will be produced both at high and low temperatures. However, if trifluorides of different structure types are combined, a system of different characteristics results. Single crystals of the low temperature phase and of the high temperature phase of a composition rich in the YF_3 structure type will be needed to characterize these phases.

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Table I. Results of X-Ray Analysis of Samples

	System	Treatment	Mole Fraction	Lattice Parameters
1	La-Er-F	unquenched	X_{ErF_3} = 0.5019	?
2	La-Er-F	quenched	X_{ErF_3} = 0.4304	a = 7.109 ± 0.002 c = 7.273 ± 0.003
3	La-Er-F	quenched	X_{ErF_3} = 0.3319	a = 7.112 ± 0.002 c = 7.275 ± 0.003
4	La-Er-F	quenched	X_{ErF_3} = 0.1995	a = 7.155 ± 0.004 c = 7.318 ± 0.005
5	La-Er-F	quenched	X_{ErF_3} = 0.6665	?
6	La-Er-F	quenched	X_{ErF_3} = 0.8135	?
7	La-Er-F	annealed 689°	X_{ErF_3} = 0.3319	appeared to be same as 3 but 2nd phase starting to grow in
8	La-Er-F	annealed 700°	X_{ErF_3} = 0.5019	a = 7.121 ± 0.002 c = 7.272 ± 0.003 plus another phase
9	La-Er-F	annealed 700°	X_{ErF_3} = 0.8135	?
10	La-Er-F	annealed 700°	X_{ErF_3} = 0.1995	a = 7.130 ± 0.002 c = 7.291 ± 0.002 plus 2nd phase
11	La-Er-F	never heated above 500° annealed 500°	Coppt. prep X_{ErF_3} = ca. 0.5	?
12	La-Er-F	annealed 630° 12 days	X_{ErF_3} = 0.8135	?
13	La-Y-F	quenched	X_{YF_3} = 0.4983	a = 7.108 ± 0.004 c = 7.268 ± 0.003
14	La-Y-F	annealed 700°	X_{YF_3} = 0.4983	a = 7.095 ± 0.002 c = 7.254 ± 0.003
15	La-Gd-F	quenched	X_{GdF_3} = 0.4542	a = 7.039 ± 0.002 c = 7.198 ± 0.002

Table I (Continued)

	System	Treatment	Mole Fraction	Lattice Parameters
16	La-Gd-F	annealed 700°	$X_{GdF_3} = 0.4542$	a = 7.042 ± 0.001 c = 7.210 ± 0.001
17	Nd-Er-F	quenched or annealed		?
18	La-Nd-F	quenched	$X_{NdF_3} = 0.4836$	a = 7.110 ± 0.002 c = 7.272 ± 0.003
19	La-Nd-F	annealed 700°	$X_{NdF_3} = 0.4836$	a = 7.109 ± 0.002 c = 7.275 ± 0.003
20	La-Nd-F	quenched	$X_{NdF_3} = 0.811$	a = 7.057 ± 0.002 c = 7.222 ± 0.002
21	La-Nd-F	quenched	$X_{NdF_3} = 0.7955$	a = 7.060 ± 0.001 c = 7.224 ± 0.001
22	La-Nd-F	quenched	$X_{NdF_3} = 0.197$	a = 7.155 ± 0.001 c = 7.318 ± 0.001
23	La-Nd-F	quenched	$X_{NdF_3} = 0.126$	a = 7.165 ± 0.003 c = 7.332 ± 0.005
24	Gd-Er-F	quenched	$X_{GdF_3} = 0.204$	a = 6.399 ± 0.003 b = 6.896 ± 0.003 c = 4.385 ± 0.002
25	Gd-Er-F	quenched	$X_{GdF_3} = 0.5000$	a = 6.465 ± 0.003 b = 6.911 ± 0.004 c = 4.383 ± 0.002
26	Gd-Er-F	quenched	$X_{GdF_3} = 0.126$	a = 6.378 ± 0.002 b = 6.861 ± 0.002 c = 4.382 ± 0.002
27	Gd-Er-F	quenched	$X_{GdF_3} = 0.792$	a = 6.527 ± 0.011* b = 6.939 ± 0.007 c = 4.382 ± 0.003
28	Gd-Er-F	quenched	$X_{GdF_3} = 0.859$	a = 6.551 ± 0.008* b = 6.968 ± 0.009 c = 4.391 ± 0.004

*Large uncertainties due to the diffuse lines in the Guinier photographs

The Vaporization Thermodynamics of ZnF_2

Robert M. Biefeld

INTRODUCTION

An investigation of the vaporization thermodynamics of ZnF_2 is being undertaken to determine if a correlation exists in the relevant thermodynamic values of YbF_2,[1] CdF_2,[2] and ZnF_2. The possibility of a correlation is being considered because all of the M^{+2} ions have completely filled electronic subshells, i.e., the 4f, 4d, and 3d respectively. A linear relationship does exist between the atomic numbers of the three elements and the standard enthalpy of sublimation of the chlorides.[3,4] In 1934 Ruff and LeBoucher[5] carried out vaporization measurementson ZnF_2 in the temperature range of 1503 to 1738 K. However, this temperature range corresponds to a much higher pressure range, 0.04 to 0.78 atm, than that of interest in this study, 10^{-7} to 10^{-3} atm. Since extrapolation of their data would introduce considerable uncertainty, the present study was undertaken.

EXPERIMENTAL SECTION

Anhydrous ZnF_2 was obtained from Research Organic/Inorganic Chemical Corp., Sun Valley, California. Chemical analysis[6] for Zn indicated considerable impurity. Calcd for Zn: 63.24%. Found: $61.5_1 \pm 0.1_5$%. The ZnF_2 was purified subsequently in the temperature range 800 to 1000 K by high vacuum sublimation from an outgassed graphite crucible. Chemical analysis then gave for Zn $62.6_4 \pm 0.1_0$%. X-Ray diffraction patterns taken on a Haegg-type Guinier camera with an internal Pt standard ($a = 3.9238 \pm 0.0001$ Å) and Cu $K\alpha_1$ radiation yielded lattice parameters in agreement with the reported values ($a = 4.7034$, $c = 3.1335$ Å).[7]

The high temperature sublimation of $ZnF_2(s)$ was studied by a target collection Knudsen effusion technique. The sample was confined in symmetrical graphite effusion cells fitted with knife-edged orifices. Analytical procedures utilized included X-ray fluorescence analysis of the effusates and X-ray diffraction analysis of the residues. Complete sublimation of $ZnF_2(s)$ from an outgassed crucible revealed no sample-crucible reaction. The targets on

which the ZnF_2 vapor was condensed were liquid nitrogen chilled, aluminum-backed, platinum plates. The temperature of the graphite crucible, which was heated by radiation from an inductively heated outer oven of either graphite or a W-Mo alloy, was measured by an iron-constantan thermocouple which was in physical contact with the crucible. The heating rate was controlled by a Leeds and Northrup #10877 control system, the input of which was the millivoltage output of the thermocouple.

RESULTS

The conclusion that $ZnF_2(s)$ sublimes congruently according to reaction (1)

$$ZnF_2(s) = ZnF_2(g) \qquad (1)$$

is supported by the analogous vaporization modes of the other Zn and Cd halides,[2,8,9] the matrix isolation study by Margrave and coworkers,[10] and the X-ray diffraction patterns of the sublimation effusates and residues.

Due to possible temperature gradients inside the graphite crucible and interaction of $ZnF_2(g)$ with the W-Mo oven reproducible vapor pressure measurements have not been obtained.

DISCUSSION

To obtain consistent vapor pressure measurements temperature gradients must be eliminated and the sublimation reaction,(1), must be isolated from interfering reactions. In an attempt to attain this goal a nickel oven is being machined and a completely sealed graphite crucible with a channel orifice may be used to eliminate excess scattering of the $ZnF_2(g)$ inside the oven. In addition, the thermocouples will be calibrated externally in the presence of the high frequency field to insure either the absence of or allow correction for induction effects.

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The Crystal Structure Determination of a Ytterbium Carbide

Robert L. Seiver

INTRODUCTION

Workers in this laboratory[1] have determined the phase diagram and thermodynamic relationships in the ytterbium carbon system. However, attempts to prepare single crystals of these phases for structural studies have resulted in the formation of a previously unreported ytterbium carbide. An investigation of this compound by X-ray crystallographic techniques is currently in progress.

EXPERIMENTAL SECTION

The preparation was carried out by Dr. John Smeggil, who combined elemental ytterbium, graphite and a small amount of copper in a sealed tantalum ampoule. Neither copper nor tantalum reacts readily with graphite at the temperatures of interest, and the copper forms a molten alloy with the ytterbium, greatly enhancing atomic mobility. The ampoule was heated by induction for two hours at about 500° and two hours at around 1100°, then cooled and opened in an argon-filled glove box. To prevent hydrolysis, the sample was examined under oil and crystals were sealed inside glass capillary tubes for X-ray examination. Not enough product was available for elemental analysis. X-Ray analysis has been carried out by Weissenberg and precession techniques, and intensities of 781 reflections have been measured using a Picker automated diffractometer and Mo Kα radiation.

RESULTS AND DISCUSSION

The product has an orthorhombic unit cell ($a = 4.284 \pm 0.002$, $b = 7.365 \pm 0.004$, $c = 6.885 \pm 0.004$ Å) and single crystals show Imma diffraction symmetry. Results of a Patterson synthesis indicate that the space group is Ima2, with metals in the 4b special positions.

Identification of a new ytterbium carbide could necessitate a major reevaluation of the phase relationships in the ytterbium carbon system. It is possible that the phase will be found to be a mixed ytterbium-copper carbide or a ytterbium-copper alloy.

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An Investigation of the Europium Oxidefluoride-Europium Sesquioxide System

Sandra Leonard Bacon

INTRODUCTION

Of the existing lanthanide oxidefluorides, the vaporization thermodynamics have been determined only for samarium oxidefluoride,[1] although Shinn[2] did examine neodymium oxidefluoride to determine the mode of decomposition at high temperatures. Both these oxidefluorides decompose to the respective sesquioxide and the gaseous trifluoride. The high temperature vaporization behavior of europium oxidefluoride is of particular interest since europium has a greater tendency to form divalent compounds than either neodymium or samarium. Thus, the purpose of this investigation was to characterize the EuOF decomposition reaction with respect to the vaporization mode and the associated thermodynamic changes to establish clearer relationships among analogous lanthanide species and establish needed thermodynamic data.

EXPERIMENTAL SECTION

EuOF was prepared[3] by mixing stoichiometric amounts of europium trifluoride and either the monoclinic or cubic form of the sesquioxide and by heating the resulting mixture to 600° under a flow of dried helium. The cubic sesquioxide was prepared by calcining in air the oxide (900°) obtained by thermal decomposition of europium oxalate. The monoclinic modification was obtained by heating the cubic form to 1200°. Europium trifluoride[4] was prepared either by fluorination of Eu_2O_3 with ammonium bifluoride or by dehydration (at 600° under dried helium) of hydrated europium trifluoride precipitated from an acid solution of the oxide.

Samples of EuOF were analyzed chemically for europium by standard analytical methods. Calcd. for Eu: 81.28%. Found: 81.1 $\pm$ 0.5%. X-Ray diffraction patterns of the sample taken on a Haegg-type Guinier camera with an internal Pt standard (a = 3.9238 $\pm$ 0.0001 Å) and copper $K\alpha_1$ radiation yielded lattice parameters in agreement with the reported values[5] (a = 6.827 Å, α = 33.05°) with the only impurity lines found being due to C-Eu_2O_3.

The high temperature vaporization of EuOF(s) was studied by the target collection Knudsen effusion technique described previously.[6] Symmetrical molybdenum effusion cells with knife-edged orifices were used in the majority of the experiments after a variety of materials including platinum, tungsten, and thoria in a molybdenum oven were found to interact with the sample. Effusates from vaporization experiments were collected on liquid nitrogen-cooled copper targets since previous experiments have shown that the sticking coefficient of europium species on copper is approximately unity.[6] The quantity of effusate on each target was determined by X-ray fluorescence spectroscopy.[7] X-Ray powder diffraction examination of the effusate and residue, weight loss experiments, and mass spectrometry were used to characterize the mode of vaporization.

RESULTS

All samples of europium oxidefluoride prepared by mixing the trifluoride with the cubic form of the sesquioxide contained sesquioxide impurities; however, when the trifluoride was mixed with monoclinic sesquioxide, pure oxidefluoride was obtained.

Efforts to characterize the mode of vaporization were inconclusive. The condensed effusate always appeared as a fcc phase with $\underline{a} \sim 5.78$ Å. Mass spectrometric measurements done in molybdenum effusion cells gave no evidence for EuF_3. The following species with their relative intensities were found: Eu^+:EuF^+:EuF_2^+, 33:100:24. The residue composition depended on the extent of loss of fluoride in the original sample. If 100% of the fluoride by weight was lost, the residue was B-Eu_2O_3. Residues which had lost $\geq$ 90% fluoride by weight contained C-Eu_2O_3 and another cubic phase, whereas, residues losing < 90% fluoride showed rhombohedral EuOF and C-Eu_2O_3. Checking for possible effusion cell-sample interaction from residue analysis via X-ray fluorescence and powder diffraction revealed that molybdenum, tungsten, thoria, and platinum all apparently had reacted.

A pressure equation based on reaction (1) could not be established

$$3\ Eu_2O_3(s) \rightarrow Eu_2O_3(g) + EuF_2(g) + F(g) \qquad (1)$$

primarily because pressure did not remain constant with temperature. Vaporization experiments done at a constant temperature established that there was a continuous decrease in pressure with time.

Several interesting phases which apparently resulted from crucible interaction were found. A cubic phase found in the residue from a vaporization experiment performed in tungsten was cubic, $\underline{a}$ = 10.760 Å. A similar phase was found in several molybdenum cell residues. A hexagonal compound ($\underline{a}$ = 9.590 ± 0.002, $\underline{c}$ = 7.065 ± 0.009 Å) was found in a residue from a thoria cell.

DISCUSSION

The full significance of a 1:1 mixture of B-Eu_2O_3 and EuF_3 producing pure EuOF while the same mixture of C-Eu_2O_3 and EuF_3 always showed excess C-Eu_2O_3 in the final product is not yet clearly understood, but this behavior could be due to the formation of a solid solution between the cubic oxide and EuOF.

Mass spectrometry results indicate conclusively that EuF_2 is one of the vapor species (at least from molybdenum effusion cells). This conclusion is supported by comparing the experimental appearance potentials (12.5 ± 1 eV, EuF^+; 10.5 ± 2 eV, EuF_2^+) with those generated by electron bombardment from EuF_3[8] (13.5 ± 0.7 eV, EuF_2^+; 19.5 ± 0.7 eV, EuF^+; and 27.0 ± 0.7 eV Eu^+) and also with those of Group II fluorides[9-11] (~ 12-13 eV for MF_2^+ and MF^+). The X-ray diffraction data of the effusate are not so conclusive. The lattice parameters of the cubic pattern which appears regardless of temperature or cell material do not coincide with those ($\underline{a}$ = 5.480 Å) reported for $EuF_{2.00}$.[12] Catalano and Bedford[12] report a composition region from $EuF_{2.29}$-$EuF_{2.44}$ which has an unsolved structure, but its strongest lines can be indexed on a fcc cell with $\underline{a}$ = 5.78 Å. Thus,it is believed the effusate corresponds to this intermediate fluoride and results from interaction of EuF_2 and F as they hit the collection surface. The analysis of the residue proved that the oxidefluoride decomposes to the cubic sesquioxide.

The exponetial type drop in pressure with time at constant temperature, may be explained either by a diffusion controlled process or by a reaction with more than one degree of freedom. Cooling and reheating the sample produces an increase in pressure when no change should be observed if diffusion problems are being encountered. All evidence points toward solid solution formation between EuOF and Eu_2O_3, a case in which F = 2 (C = 2 and P = 2).

As the solution is formed the vapor pressure is lowered, and as the sample under study becomes depleted in fluoride, the pressure falls off even more. Formation of a solid solution is reasonable since Catalano and Bedford[13] point out the availability of interstial holes in the EuOF fluorite lattice. The solid solution is definitely temperature dependent, probably due to the stability of rhombohedral EuOF at room temperature.

Investigations into the reactions of molybdenum and platinum with $EuF_3(s)$ revealed that some reduction occurs in the solid state during vaporization at 1500° in both cases. Thus the EuF_2 may result from reduction of the cell material.

The brown material found when a thoria effusion cell was used yielded a hexagonal pattern. On the basis of the X-ray diffraction pattern and some single crystal data, the structure appears to belong to the apatite family. The formula $Eu_3Th_2(EuO_4)_3O$ was deduced from the observed intensities and by analogy to compounds which exhibit the apatite-type structure.

Many unanswered questions remain concerning this system.

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