COO-716-091

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

Final Report

Harry A. Eick
Principal Investigator

Michigan State University
East Lansing, Michigan 48824

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MASTER

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DISCLAIMER

The following constitutes the final report of work performed under Contract E(11-1)-716 during the period February 1, 1959 to March 31, 1976. The document consists of a narrative summary of the principal activities and, in addition, two brief sections on as yet unfinished projects, each section of which bears the name of the project investigator.

The following reprints are appended:

1. R. M. Biefeld and H. A. Eick, "Vaporization Reactions in the Ytterbium-Fluorine System," J. Chem. Phys., <u>63</u>, 1190 (1975), COO-716-086.

2. R. L. Seiver and H. A. Eick, "The Crystal Structure of Dilanthanum Dioxidedicarbide, $La_2O_2C_2$," J. Less-Common Metals, <u>44</u>, 1 (1976), COO-716-087.

Copies of the following manuscripts are enclosed or have been submitted together with appropriate transmittal form:

1. R. M. Biefeld and H. A. Eick. "Vaporization Reactions in the Thulium-Fluorine System," J. Less-Common Metals, 45, 117 (1976), COO-716-088.

2. R. M. Biefeld and H. A. Eick, "Vaporization Reactions in the Samarium-Fluorine System," COO-716-089.

3. H. Luke and H. A. Eick, "The Structure of the M_6X_{13} Phase, Yb_5ErCl_{13}," COO-716-090.

The present positions of doctoral students whose education/training was supported in part under this contract are:

1. Gordon L. Galloway, Ph.D., 1962, Professor of Chemistry, Denison 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, Associate 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, Associate 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, Associate Professor, Institute for Organic Chemistry and Biochemistry, University of Stuttgard, Germany.

10. John M. Haschke, Ph.D., 1969, Assistant Professor of Chemistry, University of Michigan, Ann Arbor, Michigan.

11. Norman A. Fishel, Ph.D., 1970, Monsanto Chemical Company, St. Louis, Missouri.

12. Robert L. Seiver, Ph.D., 1971, Esso Research and Development Corporation, Baton Rouge, Louisiana.

13. Dale E. Work, Ph.D., 1972, Sylvania El. Prod. Co., Danvers, Massachusetts.

14. Alleppey V. Hariharan, Ph.D., 1972, CEQ Institute de Energia Atomica, Sao Paulo, Brazil.

15. Carol G. Biefeld, Ph.D., 1973, Albuquerque National Bank, Albuquerque, New Mexico.

16. Robert M. Biefeld, Ph.D., 1974, Sandia Laboratories, Albuquerque, New Mexico.

The present positions of some of the students whose Master's degree training was supported in part under this contract are:

1. Sandra Leonard, M.S., 1971, unemployed.

2. John Richards, M.S., 1974, Eastman Kodak Corporation, Rochester, New York.

3. Beatrice Clink, M.S., 1974, Great Lakes Chemical Company, West Lafayette, Indiana.

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

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

2. Dr. Conrad Ayasse, 1972, Dow Canada, Sarnia, Ontario, Canada.

3. Dr. Heinrich Luke, 1975, Universitat Karlsruhe, Karlsruhe, West Germany.

FINAL TECHNICAL REPORT

The general theme throughout the entirety of the effort produced under this contract has been research into the properties of lanthanide binary and ternary phases. The initial research effort was addressed to achieve a better understanding of lanthanide borides and nitrides. We originally attempted to repeat some reported preparations for Er, Tm and Lu hexaboride phases--but were unable to prepare them. We postulated reasons for the non-existence of these phases. They were subsequently reported and our work seemed to be in error, but more recently, this initial work has been substantiated. It has been demonstrated that these hexaborides can be prepared only when an alkaline earth element, such as Ca, is a major contaminant in the phase.(1) The method of preparation used by others allowed the contaminant to enter the reaction mixture.

Simultaneously, we began to probe into the chemistry of SmB_4 and SmB_6 and explored a number of ways to prepare these boride phases. We investigated the interaction of boride phases with molybdenum, tungsten, boron nitride, various refractories, and ultimately selected zirconium diboride as a suitable container material. In retrospect, it is apparent that this work could have been focused more directly to enable us to optimize return on time expended. As a result of this exploratory research, we undertook a project to determine the thermodynamic relationships between hexaborides and tetraborides, and studied the SmB_4-SmB_6 conversion via Knudsen effusion techniques. This was our first successful vaporization experiment. However, while we determined the enthalpy difference between the phases very accurately, the need to estimate thermal data for either terminal phase dictated that this approach was not too profitable. Furthermore, Smith and Gilles (2) developed a scheme whereby general stability trends could be established from inequalities. As a result, I discontinued further work on borides but they have remained a topic of great interest to me.

Because at that time there was great interest in and an apparent need for thermodynamic data on the uranium-carbon and plutonium-carbon systems, and the effects of oxygen contamination in directly measuring these thermodynamic properties had been identified, but not characterized, we decided to examine some carbides and oxide-carbides.

Our first effort was to determine the partial pressure of thorium in equilibrium with ThC_2 via the Knudsen effusion target collection technique. The very low partial pressure of thorium (and exceedingly high temperatures involved) forced us to utilize neutron activation with external standards for analysis of the planchet targets. Although we completed the measurements, the data did not seem consistent with values estimated from other data, and the results were never published in the open literature. Later research seemed to indicate that hydrolysis of the sample in the 10^{-6} torr vacuum of the system was the problem. For this research an ultra high vacuum ($\sim 10^{-10}$ torr) was required. We looked next at EuC_2, which at that time had not been prepared. We expected EuC_2 to bear some relationship to the actinide analogue, PuC_2. We could prepare the phase only under a mild (2-3 atm) pressure of Ar (i.e. in a sealed Mo container). We measured the vapor pressure of the EuC_2 phase we prepared--but that phase had extra lines in the powder diffraction pattern and consequently was characterized less satisfactorily than desirable.

Europium dicarbide has continued to be a topic of great research interest, and the vapor pressure work was repeated by Faircloth, et al.(3) at Harwell. He obtained somewhat different results and argued that our sample had contained some unreacted europium metal. These workers were unable to obtain satisfactory X-ray diffraction data however. More recently, Krikorian and Krupka(4) at Los Alamos and Greenwood and coworkers(5) again prepared EuC_2. These workers do not report consistent lattice parameters for the phase, and the latest report, that of

Greenwood has values which differ significantly from those reported by us and by Krikorian and Krupka. Since our phase was not characterized completely, it clearly could be in error but I do not believe the error could be as great as is indicated by their work. Furthermore, their method of preparation allowed the specimen to be contaminated with nitrogen; I am still not convinced that the EuC_2 phase is characterized properly.

A related aspect of this work involved equilibrium studies into oxide-carbide phases. The original effort was a repetition of research performed by Heusler(6) to equilibrate C with UO_2 and thereby determine thermodynamic properties of UC_2 from measurement of the partial pressure of CO as a function of temperature according to (1)

$$UO_2(s) + 4C(s) = UC_2(s) + 2CO(g) \qquad (1)$$

This research again was an attempt to characterize the elusive thermodynamic properties of UC_2. Our work reproduced very well that of Heusler, but uncertainties in the thermal functions of reactants and products prevented our data from solving the problem. We subsequently substituted La_2O_3 and Nd_2O_3 for UO_2. The results were most interesting, because from this study we did not obtain the expected MC_2 phase, but a phase which we characterized subsequently as $M_2O_2C_2$. The considerable effort spent on this phase over a ten-year period resulted not only in good thermodynamic data on the phase, but also a single crystal structural study of the $La_2O_2C_2$ member which I published only last year (after considerable checking to insure its accuracy). Essentially, we found that these phases contain an acetylide unit substituted for an oxygen atom in a lattice arrangement reminiscent of that of the sequioxide. We obtained equilibrium pressures of CO(g) according to reaction (2) rather than reaction (1)

$$M_2O_3(s) + 3C(s) = M_2O_2C_2(s) + CO(g) \qquad (2)$$

and from these partial pressures determined the thermodynamic data.

Some publications unrelated to the goals of this contract resulted during the time period that the principal investigator was developing a better understanding of single crystal X-ray diffraction and structural analysis techniques. This work included structural studies on some vanadium-molybdenum oxides and on a lanthanum carbonate octahydrate. The principal investigator wanted to develop this technique to provide a broader base to which to relate the thermodynamic studies and did it during a sabbatical year.

Simultaneously with this effort to move more toward structural studies, we improved significantly our ability to effect Knudsen effusion studies by perfecting an X-ray fluorescent-based method of analysis suitable for the microgram quantities of effusate which condensed on planchets used in the Knudsen effusion experiments. The key to the success of this method was the availability of graphite monochronators which were appreciably more efficient than LiF for analyses. By fluorescence analysis we were able to detect efficiently and rapidly microgram amounts of lanthanide vapor deposited on the planchets. At about the same time the National Bureau of Standards undertook a project to establish vapor pressure standards. Our participation in the gold vapor pressure standardization experiments confirmed the reliability of the techniques we had developed, and we were able to determine in a systematic manner the vaporization behavior and from that the thermodynamic data for a number of lanthanide compounds. I chose to concentrate on the divalent lanthanide species--samarium, europium, and ytterbium.

The particular compounds to be studied were chosen according to the areas of interest as perceived by the principal investigator. They included EuO, Eu_3O_4, YbC_2, $EuBr_2$, EuOBr, SmOF, EuS, SmC_2, TmC_2, $EuCl_2$, EuI_2, $YbCl_2$, and EuSe.

While these vaporization studies were in progress, we examined some other interesting aspects of lanthanide systems. We noted that the chemistry of ytterbium was characterized the poorest of all the lanthanides, and decided to concentrate on that element for a few years. We determined that phases reported to be YbO were actually YbOC. As a result of this YbOC work, we characterized the phase diagram of the Yb-C binary system, and characterized the vaporization behavior of a phase entitled $YbC_{1.25 + \underline{y}}$. Thermodynamic predictions based on our EuO work indicated that YbO would be stable only at relatively low temperature. We therefore set about preparing it in liquid ammonia solutions, and from this effort began a study of the chemistry of ytterbium in liquid ammonia. Unfortunately, few publishable results came from this work, primarily because it was too far afield.

Another approach to obtaining thermodynamic data on some of the phases in which we were interested involved high temperature EMF cells. Such cells might allow an accurate characterization of species such as SmB_4 and SmB_6, for instance. We decided that fluoride solid state electrodes might perform satisfactorily for this task, and began an investigation of the samarium-fluorine phase diagram. Almost simultaneously, comparable work appeared on the europium-fluorine system.(7)

In our vaporization study of $EuBr_2$ we were unable to reproduce the structural data reported in the literature.(8) From powder intensity calculations we deduced the correct structure, but were unable to decide on the occupancy of certain sites. Rather than solve this structure, we chose to solve that of isostructural $SrBr_2$.

We also determined that previous reported preparatory schemes for $EuBr_3$ were erroneous. From the thermodynamic data obtained in our study of $EuBr_2$ we calculated that the trivalent compound could be prepared only under a pressure of bromine, and only at temperatures of a few hundred degrees centigrade. We established these conditions and prepared and characterized pure $EuBr_3$.

We decided to examine another oxide bromide system to obtain data to which to compare the results we obtained from our study of EuOBr. This study turned out to be most interesting, for in this work we encountered our first example of a severe vaporization coefficient problem. The results of this effort seemed to be characteristic of what we might expect from other oxide bromide phases. The EuOBr system was clearly atypical. We have investigated these systems no further even though they are very challenging and of theoretical interest.

We decided to follow up on the samarium fluoride study by measuring thermodynamic properties of other divalent fluorides to see if these properties could be related to the structural details.

The work on the Yb-F system was most interesting. I initially expected YbF_2 to vaporize congruently, as do $YbCl_2$ and $YbBr_2$, and initial measurements could be interpreted in that vein. However, through collaboration with T. Petzel,(9) we became convinced that the vaporization mode was indeed incongruent. Once this point had been established we were able to unravel the system--and eventually grow some excellent single crystals of fluorides of intermediate composition. That YbF_2 upon heating lost Yb(g) to yield a congruently varporizing phase of intermediate composition ($YbF_{2.4}$) was a most unexpected result!

To establish trends, we examined the vaporization behavior of the Tm-F and Sm-F systems; we found that samarium behaves like ytterbium and loses metal preferentially if one starts heating the MF_2 composition. Thulum behaves in a manner expected of a regular trivalent lanthanide, and loses metal preferentially to yield the trifluoride, which then vaporizes congruently. The samarium and ytterbium fluoride vaporization results correlated well with our previous phase studies of the Sm(II)-Sm(III) - fluoride system.

In the course of our vaporization studies we continually seemed to encounter problems when a ytterbium compound was being investigated. In the $YbCl_2$ work we found condensation of the underside of the orifice. The extra effort expended to achieve isothermal conditions was most helpful in assuring that the derived thermodynamic values were <u>really</u> accurate. We also found preparatory efforts required to make Yb(II) compounds much more stringent than those required for the preparation of Eu(II) compounds.

A comparison of ionic/covalent radii suggested that some aspects of the chemistry of zinc might be related rather closely to those of Yb. We pursued this idea to the extent of determining precisely the vaporization behavior ZnF_2. Unfortunately our results indicated absolutely no analogy between the compounds. Further analogies were not sought.

During vaporization and structural studies on $YbCl_2$ we continually encountered a phase intermediate between $YbCl_2$ and $YbCl_3$. Attempts to prepare this phase in pure form led to the production of $Yb_3(SiO_4)_2Cl$, the structure of which we determined by single crystal techniques. Further efforts at preparing a specimen of this phase led to the scheme of substituting another lanthanide--Er(III)--for the trivalent Yb(III). These attempts were successful, and we succeeded in preparing a single crystal of a heavy lanthanide intermediate halide. This crystal was found to be of the Vernier structure type (10) and its solution has opened the door to an understanding of the structural interrelationships of the heavier lanthanide halides, phase studies of which have been known for some time as a result of the work of Corbett.(11) The structural details of the crystal Yb_5ErCl_3 are described in a cursory manner in document COO-716-090.

Our interest in the heavy metal halides led us to consider the affect of two different halides in a lanthanide metal halide lattice. Our first look at this arrangement with docile europium proved that we could make a phase of the composition $EuCl_{2-\underline{x}}Br_{\underline{x}}$, where $\underline{x} \approx 1.55$,(12) and demonstrated that Br would preferentially occupy entirely the larger holes in the halide lattice and some of the smaller holes. This latter apparently random partial bromide occupancy is of concern, since it seems inconsistent with our previous observations on the highly ordered Vernier-type structures.

We are currently investigating the Gd(III)Cl-I system, and preliminary results of this study are attached. Also included are preliminary results on a vaporization study of $YbBr_2$.

Publications which were in part supported by this contract are listed in Table I. As a result of the support provided under this contract, our understanding of the chemistry of the divalent lanthanides has increased significantly.

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Preparation of Gadolinium(III) Chloride-Iodide Phases

Laura Seidemann

The goal of this research is to prepare and characterize a mixed gadolinium(III) chloride iodide phase.

Experimental

Anhydrous gadolinium trichloride and triiodide were prepared by the method described by Carter and Murray.(1) A 1:4 molar ratio of Gd:$HgCl_2$ was used for the preparation of $GdCl_3$ and a 1:3 molar ratio of Gd:HgI_2 for the preparation of GdI_3. The reactants were transferred to an outgassed quartz tube which was sealed under vacuum. This ampoule was heated overnight at a temperature of 300° to minimize the danger of explosion from excessive internal pressures. As pointed out by Carter and Murray, an excess of mercuric halide was found to be essential. The crude product was purified by distillation under high vacuum.

X-Ray powder diffraction patterns were taken of the distilled product with a Guinier camera and CuKα radiation. Theoretical powder diffraction patterns were determined by computer analysis with published or estimated atomic coordinates and thermal parameters with the program ANIFAC written by Larson, et. al.(2)

In the first attempt to prepare single crystals of the title compound the $GdCl_3$ and GdI_3 were mixed in predetermined molar ratios and confined under vacuum in an outgassed quartz ampoule. The ampoule was heated to approximately 700°C to form a liquid melt, and subsequently was cooled slowly to 400°C at a rate of 20°C per hour.

In the second attempt a method similar to that described by Taylor and Carter for the preparation of anhydrous trihalides was used.(3) One mole of Gd_2O_3 was dissolved in 4 moles HCl(aq) and two moles of NH_4I(aq). This mixture was evaporated to dryness and then transferred to a carbon boat and under vacuum was heated by increasing the temperature from 50°C to 550°C in increments of 50°/15 min. to remove excess water. This latter method was related closely to the successful preparatory work by B. Clink.(4)

In the third attempt Gd°, $HgCl_2$ and HgI_2 were sealed under vacuum into a degassed quartz ampoule and heated overnight at 300°C. The crude produce from the preparation was transferred to a carbon boat and heated at 450°C under high vacuum to remove excess reactants. A series of reactions were effected using one mole of Gd°, one-half mole of $HgCl_2$, and varying concentrations of HgI_2.

Far IR studies were also carried out on $GdCl_3$, GdI_3 and a few of the products obtained from the Gd° + $HgCl_2$ preparations (the third attempt). The mull technique and fluorolube were used to prepare the paste. Sample preparation was effected in a glove box and the sample was transferred to the instrument in a dessicator filled with Argon.

Results and Discussion

The crystals obtained from the first attempt appeared to be two dimensional, high disordered arrays. Meaningful data could not be obtained, and powder diffraction data indicated the presence of only the reactants. X-Ray powder diffraction patterns also indicated the product of the second attempt to be GdOCl. An attempt to use $GdCl_3$ instead of Gd_2O_3 also yielded GdOCl. A mixed halide phase may have resulted from the third attempt. The X-ray diffraction patterns of the reactions in which a concentration of 1, 1.5, 2.0, 2.5, and 3.0 moles of HgI_2 were employed indicate only the $GdCl_3$ lattice. The diffraction patterns of products from mixtures with 5.0, 5.6, and 6.0 moles of HgI_2 indicate a GdI_3-like lattice, but certain lines in the powder diffraction patterns are displaced from the normal GdI_3 line positions, indicative of a possible change in a lattice parameter of the powder. Qualitative analyses of each product indicate both chloride and iodide in every preparation.

Definite peaks were observed in the spectra of the $GdCl_3$ and GdI_3. A far IR spectrum taken of the product formed by a 5.6 molar excess of HgI_2 shows peaks for Gd-I and Gd-Cl which correspond to the frequencies of these interactions in the pure compounds, but in addition the peaks in the product are split. This splitting is indicative of interaction between the Cl and I in a mixed halide lattice. A quantitative analysis of the halides is being carried out by potentiometric methods.

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Vaporization Thermodynamics of $YbBr_2$

Michael Gebler

Experimentally determined values for such thermodynamic parameters as enthalpies of fusion, vaporization and formation, as well as for heat capacities are not available for many of the lanthanide halides. Indeed, as late as 1964 Novikov and Polychenok[1] observed the lack of experimental conformation for many values found in tables of estimates such as those by Brewer et al.[2,3] especially for divalent compounds. Since then much interest has centered around the trivalent state. Vapor pressure values and sublimation thermodynamics for most of the lanthanide(III) fluorides have been established,[4-10] and some vapor pressure values are known for lanthanide trichlorides and tribromides.[11-15]

For lanthanide halides in the less common divalent state Polychenok and Novikov[16] have reported values of $SmCl_2$, $EuCl_2$, and $YbCl_2$ but they assert that the "boiling point" method they used tends to be inherently inaccurate. Haschke and Eick[17] and Hariharan[18] have used the Knudsen effusion method to determine the vaporization thermodynamics of $EuCl_2$, EuI_2, and $EuBr_2$ and Hariharan, Fischel, and Eick[19] used the same technique to describe the $YbCl_2$ system.

The goal of this work was to measure values of the enthalpy and entropy of vaporization of $YbBr_2$ by the use of Knudsen effusen target collection technique.

The vaporization thermodynamics of the reaction

$$YbBr_2(\ell) \rightarrow YbBr_2(g)$$

were described over the temperature range 1190-1514 K. The microgram quantities of effusate which plated onto targets were analyzed with X-ray fluorescence by use of an external calibration procedure.

From a plot of the logarithm of partial pressures due to $YbBr_2$ versus reciprocal temperature the second law derived enthalpy and entropy at the median temperature were obtained as: $\Delta H^\circ(1360) = (66._9 \pm 3._5)$ kcal/mole, $\Delta S^\circ(1360) = (30._0 \pm 2._6)$ eu. To reduce these data to 298 K $HgBr_2$ was chosen as a model, since thermodynamic parameters for it would seem to be close to those of $YbBr_2$.

Free energy functions were determined from the $HgBr_2$ data and an estimated absolute entropy for $YbBr_2$. By use of these functions an entropy at the reference temperature was calculated by the third-law procedure. The second and third law values so obtained were:

$\Delta H^\circ(298)$ (2nd law) = $(79._8 \pm 4._4)$ kcal/mole,

$\Delta S^\circ(298) = (47._5 \pm 3._9)$ eu; $\Delta H^\circ(298)$ (3rd law) = $(72._3 \pm 1._5)$ kcal/mole.

The third law derived $\Delta H^\circ(298)$ values appeared temperature independent. From the reduced second law enthalpy and entropy values and literature data, free energies of formation were calculated as: $\Delta H^\circ(f,298,YbBr_2,g) = -(90.2 \pm 0.2)$ kcal/mole, $\Delta H^\circ(f,298,YbBr_2,s) = -(170._0 \pm 4._4)$ kcal/mole. The second law absolute entropy was determined from the entropy of vaporization and entropy of $YbBr_2$ gas (estimated from $HgBr_2$ values) as: $\Delta S^\circ(298,YbBr_2,s) = (29._0 \pm 3._9)$ eu. which combined with literature values of the entropy for Yb(s) and $Br_2(\ell)$ allows calculation of $\Delta S^\circ(f,298,YbBr_2,s) = -(21._7 \pm 3._9)$ eu. Values of $\Delta G^\circ(f,298,YbBr_2,s) = -(163._5 \pm 4._6)$ kcal/mole and $\Delta S^\circ(f,298,YbBr_2,g) = (25._8 \pm 3._9)$ eu. were determined and subsequently $\Delta G^\circ(f,298,YbBr_2,s) = -(97._9 \pm 1._2)$kcal/mole was estimated. By resorting to a $PbBr_2$ model system to obtain thermodynamic functions for $YbBr_2(\ell)$ calculation of $\Delta H^\circ_v = (58._7 \pm 4._4)$ kcal/mole was made at the normal boiling point of $(2.0_3 \pm 0.1_1) \times 10^3$ K. The ΔS°_v was then calculated to be $(28._9 \pm 2._2)$ eu.

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Table I

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