

INVESTIGATIONS INTO THE
PREPARATION AND DECOMPOSITION OF
SAMARIUM TETRABORIDE AND
SAMARIUM HEXABORIDE

Thesis for the Degree of Ph. D.
MICHIGAN STATE UNIVERSITY

Gordon L. Galloway
1961

THESIS

0.2

1.1

ABSTRACT

INVESTIGATIONS INTO THE PREPARATION AND DECOMPOSITION OF SAMARIUM TETRABORIDE AND SAMARIUM HEXABORIDE

by Gordon L. Galloway

Attempts to prepare pure samarium tetraboride either by the reaction between samarium sesquioxide and varying amounts of boron or by utilizing the direct reaction between the elements have been shown to result only in mixtures of the tetra- and hexaborides. No evidence whatsoever was obtained to suggest the stable existence of a lower boride such as samarium diboride or a higher one such as samarium dodecaboride.

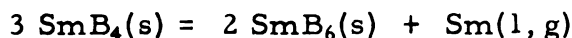
The extent of contamination of the products of any reaction used to prepare a preponderance of one or the other of the borides was shown to be a function of the starting composition of the reactants, the temperature and duration of the heating, and, in some cases, the nature of the heating cell used to confine the reactions.

Changing only the starting composition of mixtures of samarium sesquioxide and boron examined at 1650° in a crucible of boron nitride resulted in a smoothly continuous variation in the ratio of boron to oxygen lost on heating. This result, coupled with accompanying weight data, has been interpreted as evidence of the non-validity of any single equation to describe the reaction simply.

A survey was made of some of the materials suitable for use as crucibles at these high temperatures and details of this study are presented in the thesis.

The apparent stability of samarium tetraboride and samarium hexaboride at various temperatures was shown to be dependent upon the matrix material with which these borides were in contact.

The existence of the equilibrium:



was ultimately verified as a result of observations on the diffusion and evaporation phenomena occurring within the system.

When samarium tetraboride-hexaboride mixtures were heated in a crucible of boron nitride, the top surface of a sintered compact was observed to become depleted in samarium tetraboride and rich in samarium hexaboride; complete conversion was brought about by continued heating. However, when in contact with a matrix capable of absorbing boron into its interstices at a sufficiently high rate, a sintered mixture of samarium hexaboride was found to contain samarium tetraboride on its top surface after being heated at temperatures higher than those at which this tetraboride is normally unstable with respect to the hexaboride. These observations have been explained in terms of a competition between equilibrium, rates of evaporation of samarium from the heating cell and rates of diffusion of samarium to evaporation sites.

INVESTIGATIONS INTO THE PREPARATION AND DECOMPOSITION
OF SAMARIUM TETRABORIDE AND SAMARIUM HEXABORIDE

By

Gordon L. Galloway

A THESIS

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

Department of Chemistry

1961

ACKNOWLEDGEMENTS

The author wishes to express his sincere thanks and appreciation to Dr. Harry A. Eick for his guidance, encouragement, and cooperative tolerance throughout the course of these investigations.

Appreciation is also extended to my colleague, James J. Mattis, for his singular and devoted interest in a problem unrelated to his own work and for his many perceptive and worthwhile suggestions.

Thanks is also due to Mr. Gene Hood for all forms of his help, to Mr. Frank Betts for his advice and assistance in the machine shop, and to Mr. Paul Julien for the tedium of reading many x-ray films.

Finally a large token of gratitude is extended to the Atomic Energy Commission, to the Monsanto Chemical Company, and to the National Science Foundation for their generous financial support.

TABLE OF CONTENTS

	Page
I. INTRODUCTION	1
II. HISTORICAL	3
A. Preface	3
B. The hexaborides	3
C. The tetraborides	5
D. The dodecaborides	8
E. Other borides	11
F. Methods of preparation	11
1. Direct reaction of metal with boron	12
2. Reactions of rare earth sesquioxides with boron carbide	12
3. Reactions of rare earth sesquioxides with boron	13
4. Other methods of preparation	15
G. Properties of the rare earth borides	16
III. EXPERIMENTAL	19
A. Materials	19
B. Sample preparation	20
C. Analytical methods	24
1. Samarium	24
2. Boron	25
D. Reactions of samarium sesquioxide and boron in a molybdenum crucible	27
E. The samarium-boron system in a molybdenum crucible	33
F. The reaction between samarium sesquioxide and boron in a boron nitride liner	37
G. The reaction between samarium sesquioxide and boron in a zirconium diboride crucible	39
H. The heating of a sample of samarium hexaboride in a low-density tungsten cell	41
I. Miscellaneous experiments	45

TABLE OF CONTENTS - Continued

	Page
IV. DISCUSSION	48
A. Crucible materials	48
B. Results and conclusions	57
C. Proposals for future work	70
LITERATURE CITED	73
APPENDICES	77
A. Supplementary experimental data	78
B. Tabulation of physical constants	95

LIST OF TABLES

TABLE	Page
I. The samarium-boron system in a molybdenum crucible	36
II. The reaction between samarium sesquioxide and boron in a boron nitride liner	40
III. The reaction between samarium sesquioxide and boron in a zirconium diboride crucible	42
IV. The heating of a sample of samarium hexaboride in a low-density tungsten cell	44
V. Melting point and vapor pressure data for rare earth metals	96
VI. Metallic and trivalent ionic radii of the rare earth metals	97
VII. Lattice parameters of cubic rare earth hexaborides. .	98
VIII. Lattice parameters of tetragonal rare earth tetraborides	99
IX. Lattice parameters of some cubic dodecaborides . . .	100
X. Lattice parameters of tetragonal rare earth MB_x phase	100
XI. Comparison of the interatomic spacings of an experimental sample with those of the 1550° polymorph of samarium orthoborate	101
XII. Comparison of the interatomic spacings of two experimental samples with those of the delta polymorph of molybdenum boride	102
XIII. Raw data used for correcting observed temperatures to true temperatures	103

LIST OF FIGURES

FIGURE	Page
I. Radii of rare earth metal atoms and lattice parameters of rare earth hexaborides versus atomic number	6
II. The structure of a cubic hexaboride (MB_6)	6
III. The structure of a hexagonal diboride (MB_2)	7
IV. The structure of a tetragonal tetraboride (MB_4)	7
V. The structure of a cubic dodecaboride (MB_{12})	10
VI. Heating cell assembly	22
VII. Variation of pH in the vicinity of the end-point of mannitol titrations	28
VIII. Mole ratios of boron to oxygen and boron to samarium <u>versus</u> composition of starting materials heated in boron nitride	60
IX. Weight losses versus composition of starting materials heated in boron nitride	60
X. Mole ratios of boron to oxygen and boron to samarium <u>versus</u> composition of starting materials heated in zirconium diboride	62
XI. Weight losses versus composition of starting materials heated in zirconium diboride	62

I. INTRODUCTION

Although very little is known about the actual chemistry of the rare earth borides, they are nonetheless important from the standpoint of two potentially useful considerations. As a first instance, since both the rare earth elements and boron are individually effective neutron moderators, some attention has already been devoted to the possibility of combining these elements into control rods of refractory borides. However, there must first be a collection of sufficient information regarding the engineering involved in using the borides as well as an assimilation of more specific details about their behavior at high temperatures.

As a second instance, the trend toward higher and higher frequencies has confronted the tube designer with the need for larger current densities at the surfaces of cathode materials. By nature, metals such as cesium, barium, cerium, and thorium are not only the best electron emitters, but also evaporate most readily. Therefore, operation of these metals at sufficiently high temperatures to produce electron emission of high current density causes so rapid an evaporation rate that the cathode becomes useless in high vacuum devices.

Because of the unique nature of the bonding in rare earth hexaborides, these compounds have not only high electrical conductivity, but high thermal and chemical stability as well. If the borides can be heated to temperatures sufficiently high to cause evaporation of the metal atoms at the surface, and if these metal atoms can be replaced by diffusion from underlying cells without the destruction of the boron framework, then a mechanism is provided for constantly maintaining an active cathode surface. Such characteristics are ideal for cathode materials; thermionic

emission properties can be maintained without the loss of the very materials which contribute to their high thermionic activity. Lafferty (1) has performed an extensive investigation on the boride cathodes of calcium, strontium, barium, lanthanum, cerium, and thorium, with particular attention devoted to lanthanum hexaboride (LaB_6). He has convincingly demonstrated that when lanthanum hexaboride is heated in contact with a material capable of absorbing boron into its interstices, the lanthanum atoms which evaporate from the surface are replaced by diffusion of the metal atoms from underlying cells. This process continues without destruction of the boron framework until such time when the boride becomes so depleted in lanthanum that only a boron residue remains.

Even though there is a need for more efficient control rod materials as well as for cathodes for use in high vacuum devices, there is an equally severe need for thermodynamic data on rare earth borides. Once the formation and decomposition processes within the borides are understood, it should be possible to make precise measurements of the free energies of formation for these compounds. Any introduction to work of the sort contained in this thesis would be incomplete without the assertion that, ultimately, collection of these fundamental data is considered to be more important than the possible uses to be made from such measurements.

II. HISTORICAL

A. Preface

It is frequently suggested that the rare earth metals represent a class of elements whose chemistry is similar. While this is casually and quite generally true, any serious scrutiny of the lanthanides readily exposes the subtle, but definite, dissimilarities among them. One such fundamental difference is found in the vapor pressure of these elements in their free state, and for any given temperature, the vapor pressure of samarium, europium, and ytterbium is appreciably higher than it is for the other elements in this sub-group.

This study was undertaken initially to determine how the vapor pressure of the metal component would affect the high temperature behavior of the rare-earth boride. Specifically it was hoped that measurements could be made on the vapor pressure of samarium tetraboride; but in order to fully appreciate this most immediate and direct aim of the research, it is necessary to consider the preliminary work on the rare earth borides in general as well as a discussion of their properties and structures in particular.

B. The hexaborides

The first of the metal borides, categorically the hexaborides, were prepared as early as 1897 by Moissan and Williams (2) who synthesized calcium hexaboride, strontium hexaboride and barium hexaboride by aluminum reduction of the corresponding borates in an electric arc. Other workers (3-5) studied the calcium hexaboride preparation by melting together calcium carbide and boron sesquioxide, by the reaction of

calcium chloride or calcium fluoride with boron, or by the reaction of calcium metal with boron sesquioxide. However, with respect to yield and purity of product, probably the most satisfactory of these early preparative techniques was that used by Andrieux (6) who electrolyzed molten mixtures of borates and fluorides of the corresponding metals as well as mixtures of boron sesquioxide and the metal oxide or carbonate. Using carbon electrodes, the borides were produced as fine crystals at the cathode.

By the late 1920's, sufficient interest had developed in metal borides to warrant studies into the preparation, structure, and properties of the rare earth borides. In 1932, using the method of Andrieux, von Stackelberg and Neumann (7) prepared the hexaborides of lanthanum, cerium, praseodymium, neodymium, and erbium, and showed that these compounds were all isostructural with the simple cubic lattice of cesium chloride. Allard (8) duplicated some of von Neumann's work as well as extending its conclusions to include the hexaborides of yttrium, gadolinium, ytterbium, and thorium. The hexaboride structure was therefore firmly established as one in which the metal atom was centrally positioned and surrounded by a cage of boron atoms. The boron atoms are known to be B_6 octahedral units, with one such unit at each of the eight corners of the cell and resulting in one molecule of MB_6 per unit cell. The electrons of the metal atom are not directly used in the bonding and are therefore free to provide for the conductivity of the hexaborides. S. Flodmark (9) has since completed a theoretical study of bonding in the MB_6 compounds and concludes that conductivity should be expected since several strongly bonding orbitals are in the conduction band.

In view of the metallic nature of these compounds, it is therefore not surprising that the trend in their lattice parameters (see Appendix B) parallels the trend observed in the size of the rare earth metal atoms, that is, unusually high values are shown for europium and ytterbium.

Furthermore, the absence of any formal electron bonding between the central metal atom and the octahedral boron units strongly suggests the possibility of metal atom mobility in a situation where such mobility might be the easiest path to decomposition of the compound.

Figure I provides a graphical representation of how both the lattice parameters of the rare earth hexaborides and the radii of the rare earth metal atoms vary with atomic number. In Figure II, a diagram of the MB_6 lattice is presented. At any corner of the cube, only three of the six boron atoms comprising the B_6 octahedron are shown.

C. The tetraborides

For about twenty years subsequent to these early structure determinations, virtually no metal boride work was performed. Then, in 1951, Zalkin and Templeton (10) prepared the tetraborides of cerium, thorium, and uranium by heating the elements together in a vacuum at about 1500° . All three of these borides are isostructural and form a tetragonal lattice which is a combination of the structure of uranium diboride and that of calcium hexaboride. The boron atoms form a continuous three-dimensional network among the metal atoms. There are sixteen boron atoms in the unit cell, twelve of which are arranged in two identical octahedra and the remaining four of which are used to connect these octahedra in a continuous two-dimensional chain. The actual continuity of the entire network is sustained by the connection of atoms of the octahedra above and below the aforementioned chain with other boron atoms in neighboring cells. There are four molecules of MB_4 in each unit cell.

Figures III and IV represent, respectively, diagrams of the lattice of a metal diboride and a metal tetraboride. The diboride lattice is presented since the metal atom arrangement of MB_4 is intermediate between that of MB_6 and MB_2 .

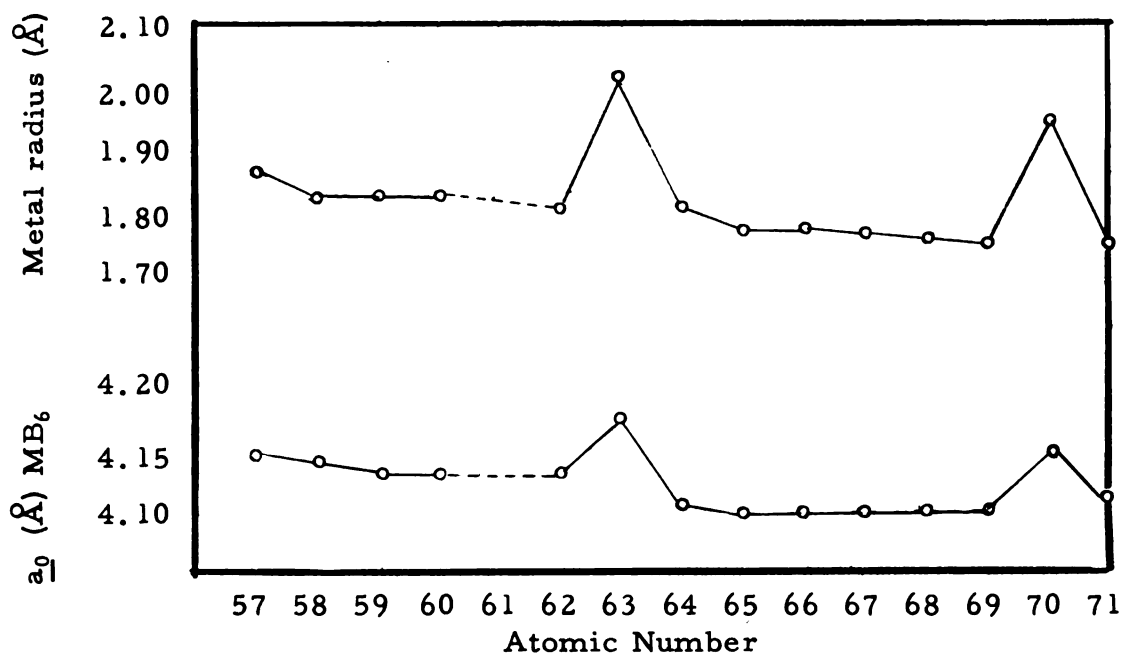


Figure I. Radii of rare earth metal atoms and lattice parameters of rare earth hexaborides versus atomic number.

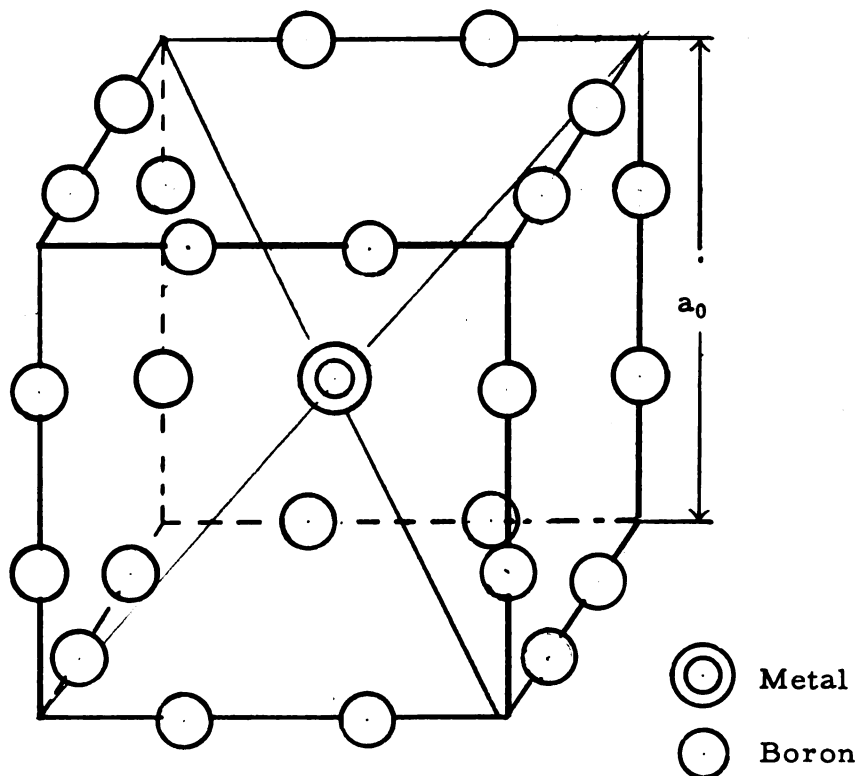


Figure II. The structure of a cubic hexaboride (MB_6).

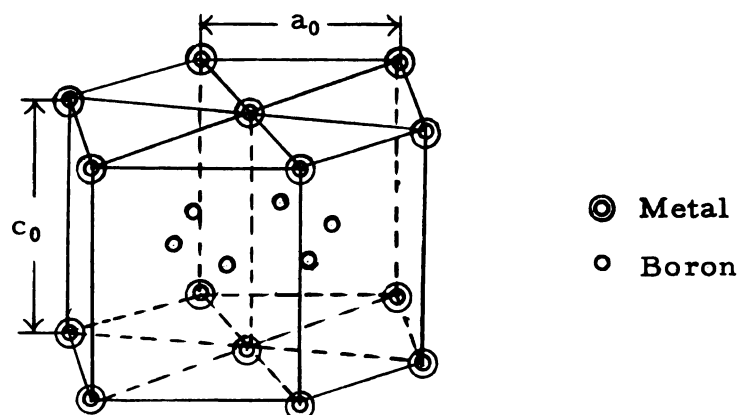


Figure III. The structure of a hexagonal diboride (MB_2).

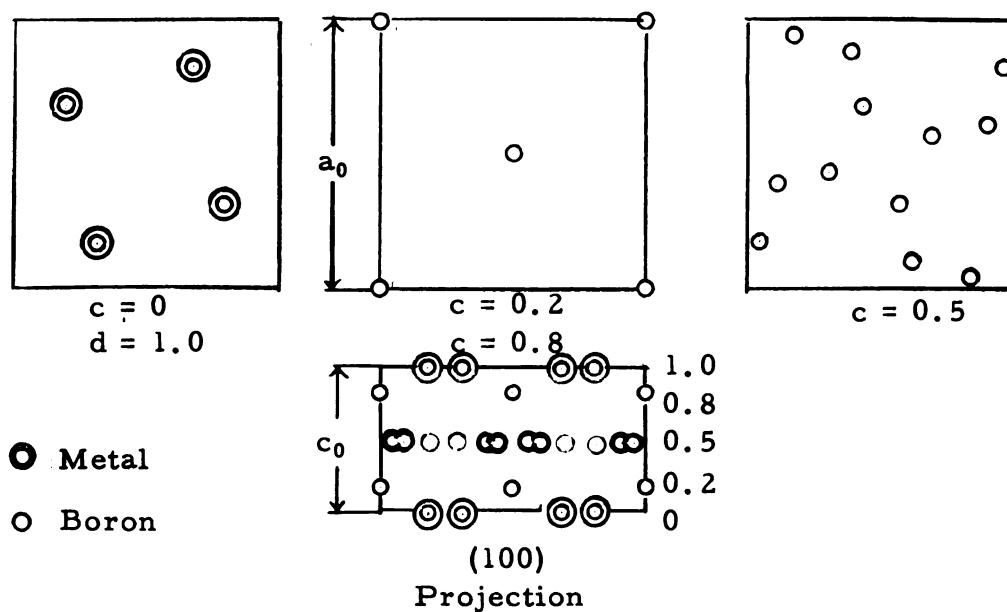


Figure IV. The structure of a tetragonal tetraboride (MB_4).

Since a tetraboride existed for cerium, the expectation that tetraborides of other rare earths could be prepared seemed reasonable. In 1956, by reacting unspecified amounts of rare earth oxides with boron and carbon black in graphite crucibles, Post, Moskowitz and Glaser (11), succeeded in preparing the tetraborides of praseodymium, samarium, gadolinium, and ytterbium. Lattice parameters were obtained for these compounds which were, as expected, completely isostructural with uranium tetraboride.

By 1959, lattice parameters had been obtained for all of the rare earth tetraborides with the exception of promethium, europium, and thulium. Examination of the a_0 values of the lattice parameter for these tetraborides (see Appendix B) shows a slow but regular decrease proceeding from lanthanum through lutetium, quite devoid of the irregular increases in size noted for europium hexaboride and ytterbium hexaboride. It was this fact that led Post and his co-workers (11) to make the observation that in the conducting hexaborides, the effective valence state of the metal was very much like that of the uncombined metal, whereas the non-conducting tetraborides, the metal atoms had much more of an "ionic" nature.

D. The Dodecaborides

The reported existence of uranium dodecaboride (12) and zirconium dodecaboride (13) provided ground for the speculation that the dodecaborides of the rare earths might be synthesized. Post and his co-workers (11) had been unsuccessful in their attempts to prepare any dodecaborides from the reaction of the sesquioxides of lanthanum, cerium, praseodymium, samarium, gadolinium, ytterbium, and/or thorium with boron. However, in 1959, Binder, LaPlaca and Post (14) did report such dodecaborides for yttrium, dysprosium, holmium, erbium, thulium, and lutetium. These compounds were prepared by heating 99.95% pure sesquioxides with

amorphous boron in vitrified alumina crucibles at 1400-1500° in a protective helium atmosphere.

It is not surprising that this later attempt proved successful since it involved the use of rare earth metals all of whose atomic radii are smaller than those initially used.* Furthermore, the conspicuous absence of ytterbium dodecaboride offers firm vindication to the argument that dodecaboride formation is size-controlled.

The cubic cell of the dodecaborides contains four molecules per unit cell, is isostructural with the phases ZrB_{12} and UB_{12} , and consists of a metal atom held in the center of a cage of 24 boron atoms. This cage, a regular polyhedron with square and hexagonal faces, shares its atoms with other similar cages to make a continuous three-dimensional network of boron atoms. A diagram of the cell is shown in Figure V.

The metallic atomic radius of the zirconium atom is reported by Sanderson (15) as 1.597 Å. Furthermore, Katz (16) reports that the α -uranium atom may be considered as a nonspherical ellipsoid with major and minor half-axes respectively 1.65 and 1.4 Å., and the cubic γ -uranium atom as a sphere of atomic radius 1.485 Å. The metallic atomic radius of dysprosium has been determined to be 1.770 Å (17) and no dodecaboride formation has been observed for any rare earth with a metallic radius larger than this value. It is of interest to note that the atomic radii of zirconium and either form of uranium are both well below the metallic radius of dysprosium, and that the size-controlled dodecaboride postulation withstands this additional test.

Not much more is known about this difficultly prepared phase, and it has been suggested that it can be prepared only by reaction of the sesquioxide with boron.

* See Appendix B for values.

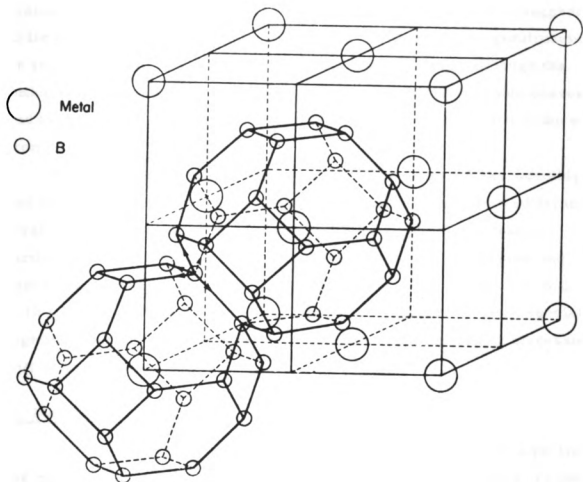


Figure V. The structure of a cubic dodecaboride (MB_{12}).

E. Other borides

In addition to the tetraborides of praseodymium, samarium, gadolinium, and ytterbium, Post, et al. (11) also have reported the preparation of a contamination phase, MB_x , where the value of x is suggested to lie between 3 and 4, M being lanthanum, praseodymium, gadolinium, or ytterbium. A set of lattice parameters was obtained, although the authors (11) suggest that the compounds are only boride-carbide phases and that their stabilization was effected by carbon impurities introduced from the graphite crucibles.

Nonetheless, the MB_x compounds could be prepared reproducibly and all are believed to be tetragonal even though no sophisticated structural data are available. Gilles and co-workers (18) have presented further evidence for these materials being boride-carbide phases and report the preparation of a GdB_x compound with atom ratios: $Gd:B:C :: 0.10 \pm 0.05 : 0.55 \pm 0.05 : 0.37 \pm 0.05$. There appears to be no special significance attached to this rare earth boride, and no further discussion will be presented.

F. Methods of preparation

If one is interested in the high temperature properties of a particular rare earth boride, or even in the room-temperature physical properties of such a compound, it becomes important to work with the purest material available. Since the initial goal of this study was an investigation of the vapor pressure of samarium tetraboride, the preparation of a pure phase was of enhanced significance.

This study has provided us with information regarding the variables involved in synthesizing a "pure" boride; it seems worthwhile to consider briefly the methods that have been employed previously. No attempt will be made here to evaluate the effectiveness of these methods.

1. Direct reaction of metal with boron

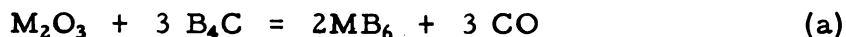
The most direct means of synthesizing rare earth borides is the reaction between the metal and elemental boron. Felten, et al. (19), have reported the preparation of LaB_4 "of a satisfactory purity" by reaction of lanthanum metal with boron at about 1500° . No details are given regarding the crucible material used to confine this reaction.

Post, et al. (11), reported the preparation of the MB_6 phase "when the appropriate amounts of boron and metal were caused to react." Using x-ray powder techniques, they also reported the detection of this phase when compositions were employed having a mole ratio of metal to boron other than 1:6. Although it is not completely clear from the literature, it appears that these workers used graphite crucibles even when the syntheses were performed using mixtures of metal and boron. Binder, et al. (14), have stated that it is impossible to prepare the dodecaboride by this means.

In this work, mixtures of samarium hexaboride and samarium tetraboride were prepared from the direct reaction of the elements. The important fact regarding this means of preparation, and one which is too frequently ignored, is that the product is not independent of the crucible material used to confine the reaction. This will be discussed later in more extensive detail.

2. Reaction of rare earth sesquioxides with boron carbide

A second method of preparation, and one that has received wide attention, is that described by the equations:



and employed by several Russian investigators (20-23) for the preparation of the hexaborides of yttrium, europium, holmium, and lutetium, and the

tetraborides of terbium, dysprosium, holmium, erbium, and lutetium. These reactions were carried out in vacuo at 1400-1600° with varying amounts of boron carbide. Samsanov (24) has reported the use of boron and carbon in any desired mole ratio; however, he has cautioned that if the starting oxide is of the formula, M_2O_3 , as are most of the rare earth oxides, then boron carbide of composition exactly B_4C must be used.

3. Reaction of rare earth sesquioxides with boron

Another method of synthesizing the borides is through the reaction between the metal sesquioxide and boron. First mention of this method was made by Post, et al. (11), who successfully used crucibles of graphite or zirconium diboride to contain the pressed pellets of sesquioxide and boron. The formation of the volatile species, B_2O_3 , was reported by Post, but no chemical proof was offered to substantiate the existence of this species. Margrave, et al. (25), have reported mass spectrometric evidence that between the limits of 1331 and 1808°K., the vaporization of boron sesquioxide is satisfactorily described as a monomeric vaporization shown simply as:

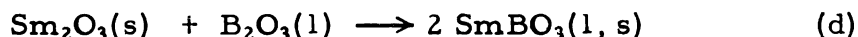


However, even if boron sesquioxide is formed in the reactions between boron and rare earth sesquioxides, one must allow for at least three possible occurrences subsequent to the formation of this oxide:

- 1) Vaporization as shown
- 2) Reaction with a rare earth sesquioxide to produce a rare earth borate
- 3) Reaction with excess boron to produce a lower boron oxide.

Enough has been said regarding the first of these possibilities.

Levin, et al. (26), have substantiated the possibility of the second occurrence cited above. They have synthesized rare earth borates by the reaction of boron sesquioxide with rare earth sesquioxides; their x-ray diffraction data for samarium orthoborate are shown in Appendix B. Since samarium orthoborate was encountered in this work, its formation as a result of the reaction:

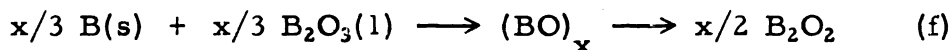
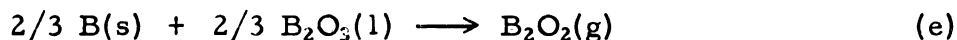


should not be excluded.

With respect to the third alternative, the existence of suboxides of boron is well established. Ray and Sinha (27) have reported the formation of the colorless oxide B_4O_5 from the decomposition of $(\text{NH}_4)_2\text{B}_4\text{O}_6$, and Kahlenberg (28) has presented considerable evidence for the existence of the suboxide, B_3O , which was prepared by the complete oxidation of B_7O with a 1% solution of potassium hydroxide. Kahlenberg has concluded further that B_7O and B_5O are only mixtures of B_3O and boron. However, the unequivocal existence of B_7O has been demonstrated recently by Pasternak (29) who has determined the crystal structure of this compound. This determination casts some doubt on the validity of Kahlenberg's conclusions.

Inghram, Porter, and Chupka (30) have examined the gaseous species effusing from an alumina Knudsen cell containing a mixture of solid boron and liquid boron sesquioxide. The major peaks observed on the mass spectrometer for the temperature range, 1300-1500°K., were B_2O_2^+ , B_2O_3^+ , BO^+ , and B^+ . However, these workers (30) attribute the latter two species only to dissociative ionization of $\text{B}_2\text{O}_2(\text{g})$ and $\text{B}_2\text{O}_3(\text{g})$. Scheer (31-32) has used a torsion effusion cell to substantiate the hypothesis of Inghram, et al.; his measurements have shown that, in the 1300-1500° K. temperature range, the major gaseous suboxide formed in the reaction between solid boron and liquid boron sesquioxide is gaseous B_2O_2 .

Scheer did not detect any gaseous BO; however, his data required the postulation of an intermediate condensed polymer, $(BO)_x$. Gaseous B_2O_2 can then be formed by two paths:



Kanda, et al. (33), have reported polymeric $(BO)_x$ prepared from a mixture of solid boron and liquid boron sesquioxide, but found that the yield of sublimed polymer depended on the atom ratio of boron to oxygen initially used. On the basis of Inghram's mass spectrometric study (30) and some x-ray diffraction data obtained in his own laboratory, Scheer has felt compelled to emphasize the complications of the system and the extent of possible interactions. He has written: "It is therefore suggested that equilibration between the condensed phases $[B(s), B_2O_3(l),$ and possibly $(BO)_x]$ and gaseous B_2O_2 is not readily achieved in such effusion measurements."

From this it would seem, that in any system where it is possible for oxides of boron to co-exist with boron itself, there is also the possibility of extensive interaction among the phases. This fact strongly suggest that, without a mass spectrometer, it is virtually impossible to study the mechanism by which a rare earth boride is formed from the reaction of the rare earth sesquioxide with boron.

4. Other methods of preparation

The three principal and most widely used means of synthesizing the rare earth borides have already been carefully outlined. Aside from the electrolysis of molten media, which was mentioned earlier, any other methods for successful preparation of the borides are merely combinations or modifications of the three principal methods. Assuming the need for starting with the rare earth metal oxide, the modifications

concern themselves with such questions as whether or not to use, additionally, boron sesquioxide and carbon, boron and carbon, boron carbide, or boron alone. [The reader is referred to Samsonov's extensive review (24) on the subject of rare earth metal borides if a more comprehensive outline of any of the methods of preparation for any particular boride is desired.] Each method used, however, is subject to possible crucible interaction and the selection of any one method demands prudent consideration of just how the vessel confining the reaction may affect the nature, yield, and purity of the products.

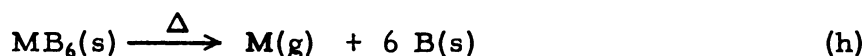
G. Properties of the rare earth borides

Most of the structural properties of these compounds have already been discussed in detail. However, since the keystone of this thesis was initially an attempt to measure the vapor pressure of samarium tetraboride, the decomposition of the borides must be considered.

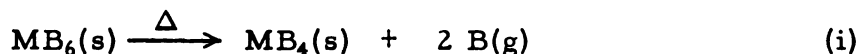
If a rare earth boride is heated to a sufficiently high temperature, two paths of decomposition are possible. The first involves the loss of metal atoms and the subsequent increase in boron content of the boride as shown:



which, of course, in the limiting case is merely:

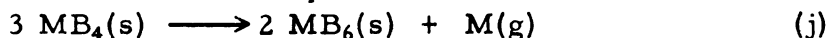


The second possibility is a disproportionation of the hexaboride to give a lower boride and free boron as shown:



Naturally, the thermal stability of any rare earth tetraboride is not independent of the stability of the corresponding hexaboride. And so, for those elements for which the tetraboride represents the more

stable phase, the tetraboride should be able to be heated to its melting point without appreciable decomposition. The other course is:



Consider the following hypothesis: that those rare earth metals with a high vapor pressure would show hexaboride decomposition according to equations (g, h), while those with low vapor pressure would follow the path shown in equation (i). Since a hexaboride decomposition according to equation (i) is incompatible with a tetraboride decomposition shown in equation (j), any tetraboride which decomposes according to path (j) should behave according to paths (g, h) on being heated to a higher temperature, providing that the rate of escape of M(g) is sufficiently high to bring about quantitatively measurable changes.

Since the hypothetical paths of decomposition are vapor pressure dependent, it was decided to initiate this study assuming the truth of the hypothesis that the high vapor pressure rare earth metals would show boride decomposition according to equations (g, h) and (j). With the acceptance of this hypothesis, the selection of samarium as the metal component was made merely on the basis that samarium was the first in line of the three rare earth metals which exhibited abnormally high vapor pressure.

It seems worthwhile to note here that Samsonov (24) had written prior to any of this work: "On the other hand, hexaboride phases are always more stable than tetra- or diboride ones, as experiments on heating the lower phases in vacuo show; in time they pass into hexaborides with simultaneous loss of the metallic component." Also, during the course of these investigations, Leitnaker, et al. (34), had written: "In view of the regularity of the heats of formation of the rare earth sesquioxides, one is tempted to estimate that the heat of formation of rare

earth hexaborides is -12 ± 2 kcal. per gram atom of boron, with the tetraborides perhaps 3 or 4 kcal. per gram atom of boron more stable."

In order to investigate the vapor pressure of samarium tetraboride, there were two fundamental requisites. The first was the preparation of pure samarium tetraboride; the second was to find an inert crucible material in which the boride could be decomposed.

This research, with all its experimental ramifications and, ultimately, its conclusions, is an outgrowth of the failure to satisfy the two requisites set forth above.

III. EXPERIMENTAL

A. Materials

Samarium sesquioxide of 99.9% total purity was obtained from the Michigan Chemical Company, St. Louis, Michigan. Similar purity samarium (> 99%) was obtained from the same source and also from Research Chemicals, Burbank, California. Crystalline boron (-100 mesh) of 99.2% purity and containing 0.4% iron and 0.4% carbon was purchased from the U. S. Borax and Chemical Corporation, New York, New York. Amorphous boron of 99% total purity was provided by the Fairmount Chemical Company of Newark, New Jersey. The molybdenum, as a powder (-325 mesh) or as stock used for machining crucibles, was obtained as 99.9% pure molybdenum from the Climax Molybdenum Company, New York, New York; boron nitride rods of 97.0% purity and containing 2.4% boron sesquioxide, 0.1% alkaline earth oxides, and 0.2% alumina and silica were purchased from The Carborundum Company, Latrobe, Pennsylvania. Machined crucibles and lids of zirconium diboride were obtained from the Borolite Corporation, Pittsburgh, Pennsylvania. No purity specifications are available for this material although the manufacturer does use an unspecified binder to bond the zirconium diboride. An experimental sample of tungsten-copper alloy was provided by Philips Electronics, Inc., Mount Vernon, New York, for use in fashioning a tungsten crucible. No purity specifications were available; the techniques of preparing this alloy for use are described in the next section of this thesis.

B. Sample preparation

For the reactions between samarium sesquioxide and boron, small amounts of these components were mixed in the desired mole proportions and carefully ground, to insure complete homogeneity, with alundum mortars and pestles. The mixtures were then pressed into pellet-wafers using a die of "carborized" steel with outside diameter of 2-1/2" and pellet bore of 5/16". Average sample size was from 0.5 to 0.7 g., and pressing at 4000 - 8000 p.s.i. resulted in pellets ranging in height from 3/16" to 5/16", depending upon the boron content.

These pellets were loaded directly into a molybdenum crucible fashioned from 7/8" molybdenum rod, 1 to 1-1/2" high, and bored with a reaction well of 1/2" diameter by 19/32" deep. The crucible was also provided with a lid of total thickness comparable to the wall thickness of the crucible and fashioned with a lip to fit snugly into the crucible well. Tantalum (0.005") spacer rings were used between lid and crucible body to prevent adherence of the lid to the crucible; these rings were especially necessary in studies of the reaction between samarium sesquioxide and boron.

In the series of reactions for which boron nitride was used as a liner inside a molybdenum crucible, the liners were machined from rods of boron nitride whose outside diameter was 1/2". They were about 5/8" in length and bored and milled with 3/8" tools to provide a bottom thickness of 1/8" to 1/16". Because of the fusion of a boron nitride lid to a boron nitride crucible as a result of decomposition and re-formation of the material at high temperatures, the heating cell was capped with a lid of molybdenum rather than one of boron nitride.

These molybdenum crucibles, used either directly as reaction vessels or as a means of heating boron nitride liners, were supported with three tantalum legs (0.060" in diameter), force-fitted at 120° intervals around the base into holes 1/4" deep. Each lid was also provided

with a hole of approximately 0.045" diameter to allow for escape of gases. A black body radiation hole, 1/16" x 10/16", was drilled into the base of the crucibles.

The low-density tungsten heating cell was fashioned from the tungsten-copper alloy by machining a crucible of 1" length and was bored with a well 5/16" in diameter and 3/8" deep. A lid was also machined with an edge of 1/32" and a lip of 1/16", providing a total thickness of 3/32", and drilled with a gas escape hole of approximately 0.040". Tungsten legs of 0.040" diameter were inserted into holes pre-drilled in the base of the crucible; a black-body hole was also provided. After machining this alloy into a crucible-lid combination, a tantalum spacer ring (0.005") was inserted between lid and crucible and the entire unit was heated with a magnetic field at temperatures high enough to cause expulsion of the copper from the alloy. Several heatings were necessary to remove all of the copper and care had to be taken not to raise the temperature too high too rapidly. Since the boiling point of copper is 2310° (35), it was felt that heating the alloy for a long time, and finally at the most extreme temperatures possible with the existing magnetic field ($\sim 2250^{\circ}$), would eventually remove all of the copper. The cell and lid were heated several times at the maximum attainable temperature until there was no further visible deposition on the Vycor tube confining this vacuum distillation of copper. Thus prepared, the cell was used to study the vaporization behavior of samarium hexaboride.

Heatings were performed for varying amounts of time using a 20 kilowatt induction heating generator (Model 2000) supplied by the Induction Heating Corporation of Brooklyn, New York. The existing glass system used for containing the heatings is shown in Figure VI. Both the samarium sesquioxide-boron compacts and samples of samarium hexaboride were heated in a vacuum of 10^{-4} to 10^{-6} mm., while in the studies

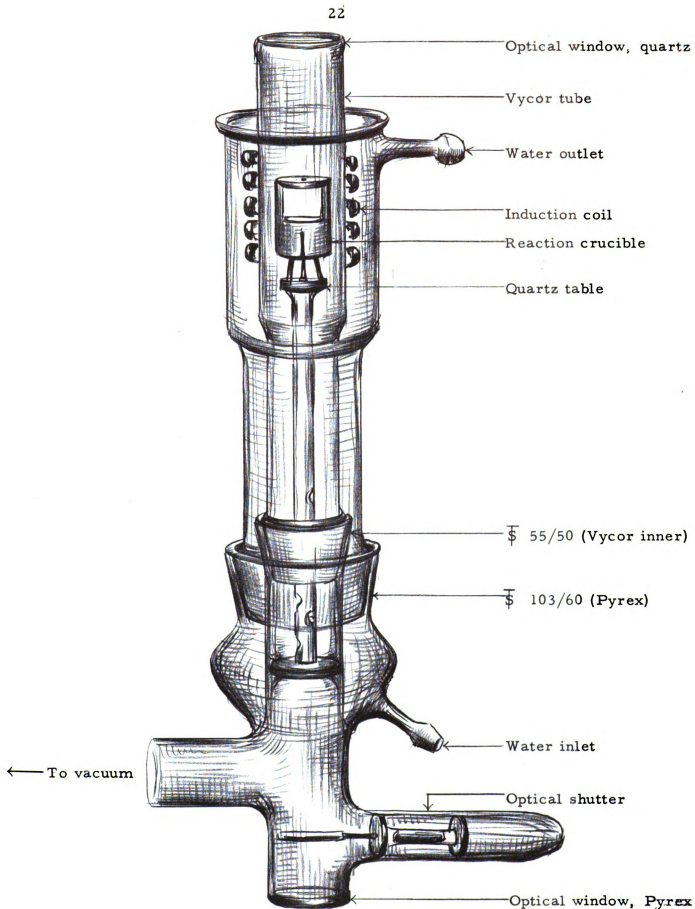


Figure VI. Heating cell assembly.

involving samarium metal and boron, heatings were performed in an atmosphere of helium equal to a vacuum of 100-125 mm.

The metal heating cells were outgassed for from 5 - 20 hours at 1800 - 2100° prior to heating and, according to directions from the manufacturer, the boron nitride was outgassed for at least two hours at 1600° to remove most, if not all, of the boron sesquioxide impurity. No evidence whatsoever was observed to suggest samarium nitride formation in studies using boron nitride, and in no instance involving the use of a boron nitride liner did the liner gain weight.

Temperatures were read with a Leeds and Northrup optical pyrometer (Serial No. 1524388) and unless otherwise noted are given in degrees centigrade. X-ray photographs were obtained using Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) and a Debye-Scherrer x-ray powder camera of 114.59 mm. diameter. Temperatures reported herein have been corrected for absorption due to the optical window and the prism when such corrections are applicable.

The reaction products in all cases were always in the form of sintered compacts regardless of how the samples were introduced into the crucibles. Pellets remained intact; mixtures of samarium metal and crystalline boron were introduced into the crucibles as a mound of boron with the samarium confined within this mound in the form of tiny chunks; these mixtures sintered on heating. The decomposition study in the tungsten cell involved the introduction of a non-compacted material; again sintering took place during heating.

The sample of samarium hexaboride used for the decomposition study was prepared by heating a mixture of samarium sesquioxide and crystalline boron (in a respective mole ratio of 1:12) in a crucible of zirconium diboride. The actual decomposition sample represented the compilation of the material prepared from nineteen successive preparations. This material was washed several times with concentrated

hydrochloric acid followed by massive amounts of water. Dried and photographed,* the x-ray powder pattern showed no phase other than samarium hexaboride although the a_0 lattice parameter of this cubic phase was measured to be $4.141 \pm 0.002 \text{ \AA}$, as opposed to the value of $4.1333 \pm 0.0005 \text{ \AA}$ reported consistently by other investigators (36).

Chemical analyses were performed whenever there was a sufficient amount of material for doing so and when it was felt that such analyses justified the time involved in performing them. Description of these analyses follows.

C. Analytical methods

1. Samarium

The samarium analyses were only gross analyses for samarium present in any form in the product. As a means of testing the analysis, samples of from 0.05 to 0.15 g. of freshly dried samarium sesquioxide were dissolved in 4.0 ml. of 6.0 M nitric acid and then diluted to 250 ml. with distilled water. To these solutions, now approximately 0.1 M in hydrogen ion, five to ten ml. of a saturated oxalic acid solution were added dropwise and with stirring. The precipitates which formed were allowed to digest overnight on a hot plate and then were filtered, washed, and ignited in platinum crucibles. Results obtained using the sesquioxide as described showed a consistent accuracy of $\pm 1\%$ or better.

It should be noted that samarium hexaboride is believed to be completely soluble in 6.0 M nitric acid. This is based on the observation that on dissolution of hexaboride samples, the less the residue which remains on treatment of a sample with nitric acid, the more nearly the samarium content approaches the percent samarium in samarium hexaboride. Some of the residues remaining from nitric acid treatment of the samples were collected, photographed, and found to be boron.

* In the entire text, "photograph" refers only to x-ray photographs.

It was therefore assumed that samarium in any form (metallic, as an oxide, or as a boride) would not escape dissolution on treatment with 6.0 M nitric acid. The tetraboride behaved similarly to the hexaboride on nitric acid treatment; in both cases a large amount of nitrogen(IV) oxide gas was liberated indicating the strongly reducing nature of the borides. In all cases, the samples were filtered subsequent to dissolution and prior to oxalic acid treatment. Analyses were run in duplicate wherever possible and agreement of results was always within 1%.

2. Boron

Boron analyses were performed essentially as described by Blumenthal (37). However, the modifications and elaborations which had to be added are presented below.

The mere mixing of a sample of the boride with sodium carbonate prior to the fusion is inadequate for the protection of the platinum crucible. Even though sodium nitrate was added after the initial carbonate fusion, total fusion was not effected rapidly enough to prevent the mixture from attacking the crucible. This was not a rapid attack, but one definite enough to cause tiny pits, and subsequently holes, in the platinum after any repetitious use. Such attack could not be prevented even by fusing the samples immediately with a sodium carbonate-sodium nitrate mixture. However, if the bottom of the platinum crucible was covered with sodium carbonate which was then fused prior to the addition of any sample, attack on the platinum became negligible. Samples were introduced onto the fused sodium carbonate; 0.05 to 0.15 g. of sodium nitrate was added, and the entire mixture was covered with a fine sprinkling of sodium carbonate sufficient to contain the vigor of the reaction that followed on heating.

The crucibles were heated in a very low Meeker flame. An initial and vigorously exothermic reaction occurred, but as long as the heating

was gentle and the sodium carbonate present in sufficient amount, no spattering losses were encountered. The fusions were continued at moderate heat for about one-half to three-quarters of an hour to insure complete decomposition of the sodium nitrate.

After fusion, the crucibles and contents were digested with 50 ml. of 6 M hydrochloric acid. Twenty milliliters of 12.5 m sodium hydroxide were added before slow addition of 8 g. of barium carbonate. The order of operations here is extremely critical and cannot be reversed.

The remaining operations were performed as described by Blumenthal (37). However, while he has offered the choice of determining the end points of the mannitol titrations using either a mixed indicator or a pH meter, this work has shown that the potentiometric titration is the only means of obtaining satisfactory results for samarium borides.

It was possible to use the prescribed mixed indicator successfully for standardizations of sodium hydroxide with re-crystallized orthoboric acid. Standardizations performed in this fashion with 0.1 g. samples of orthoboric acid showed an average deviation of from 0.2 to 0.4%. However, when samarium sesquioxide was added to the scheme as a control, and subsequently removed as a carbonate, the color changes in the boric acid titration were so gradual and subtle that results ranged from 2 to 10% high. (This must result from incomplete removal of the samarium(III) ion and resulting hydrolysis of that species.)

In view of this, the use of a potentiometric titration was chosen; excess hydrochloric acid was titrated with sodium hydroxide to a pH of 6.2 and the boric acid was titrated in the pH range of from 6.2 to 9.0. The standardization of sodium hydroxide was also performed in this fashion and the mixed indicator was completely abandoned. Using a Beckman Model G pH meter equipped with (large size) standard calomel and glass electrodes, the average deviation in standardizations ranged

from 0.2 to 0.5%. However, when a titration using a mixed indicator was compared to one using a pH meter, the difference in the value of the grams of orthoboric acid equivalent to one milliliter of sodium hydroxide was as much as 10%. Therefore, the sodium hydroxide was always standardized over the same range of pH as the samples, just as if it were a sample. Figure VII contains four curves showing pH plotted against milliliters of sodium hydroxide added in the region of the end point. The slope of these curves shows the necessity of standardizing the sodium hydroxide over precisely the same pH range as used for the samples.

Using the entire scheme of the method, beginning with fusion of samples of samarium sesquioxide and subsequent removal of the samarium carbonate, it was possible to account for no less than 98.9% of added orthoboric acid with no result being higher than 101.7%. The same general precision was obtained using samples whose x-ray photographs showed no phase other than samarium hexaboride. It is therefore believed that boron analyses performed in this fashion are accurate to within $\pm 2\%$, and that greater accuracy can only be obtained using some more elegant method at the expense of tediousness.

D. Reactions of samarium sesquioxide and boron in a molybdenum crucible*

The first set of reactions in this category involved samples of a composition of 1.00 mole of samarium sesquioxide for every 10.00 moles of boron. Using the same crucible for all experiments, investigations were made in the temperature range 1360 - 1830°. A summary of these

* In the experimental descriptions which follow, much of the rigorous detail associated with early preliminary experiments has been deleted for the sake of clarity. The data associated with these experiments are more completely and thoroughly presented in Appendix A under the same general headings as those listed in this section.

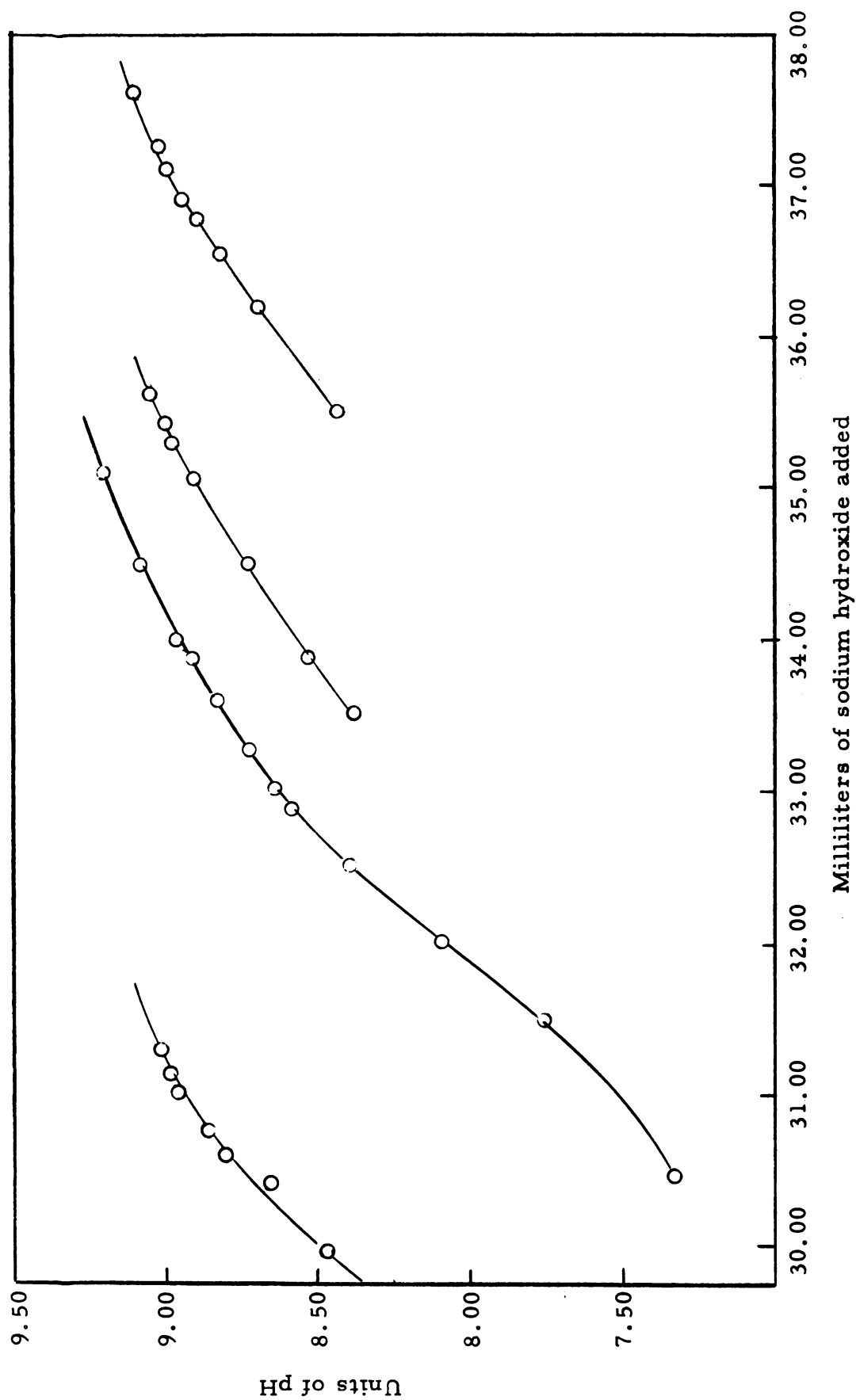


Figure VII. Variation of pH in the vicinity of the end-point of mannitol titrations.

experiments is presented below.

1. Low temperature heatings of these mixtures in the range of $1360 - 1405^{\circ}$ for periods of about an hour resulted in the formation of SmBO_3 on top and bottom surfaces of the pellets as well as on the molybdenum lid of the crucible.
2. Additional heating for one to two hours at temperatures of about 1600° resulted in the formation of SmB_4 on the surface of the pellets. The concurrent appearance of $\text{B-Sm}_2\text{O}_3$ (high temperature form) on the lip of the molybdenum crucible was also observed.
3. Continued heatings at 1800° for one hour subsequent to the heatings in (2) resulted in the continued existence of SmB_4 on the surface of the pellets, but caused the grow-in of some SmB_6 as well. A coating of what was principally $\text{B-Sm}_2\text{O}_3$ appeared on the inner walls of the crucible.
4. Adding small amounts ($\sim 0.05 - 0.07$ g.) of crystalline boron to the molybdenum crucible between some of the heatings resulted in the formation of SmB_6 on the surface of that boron when the crucible was heated to temperatures in the range of $1590 - 1750^{\circ}$.
5. Following one such use of boron to "clean" the crucible, a pellet heated for an hour in the range $1675 - 1810^{\circ}$ was severely diminished in size and showed only SmB_6 .
6. Another heating in the range $1675 - 1830^{\circ}$ over a 0.5 hour time span, again subsequent to "cleaning" the crucible with boron, caused the formation of a layer of $\delta\text{-MoB}$ midway up the crucible, blocking off the orifice in the lid. The lid of the crucible also contained $\delta\text{-MoB}$. X-ray photographs of both the top and the bottom of the pellet showed the presence of SmB_4 and SmB_6 .
7. Immediately subsequent to the phenomenon of the $\delta\text{-MoB}$ grow-in, the same crucible was used to heat a pellet for seven hours at 1460° . The top surface of the pellet contained SmB_4 and SmB_6 ,

but six hours of additional heating at 1440° , followed by two hours at 1650° , yielded a pellet principally SmB_4 but which did contain small amounts of SmB_6 .

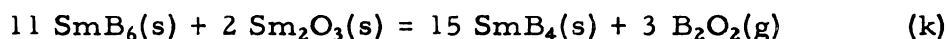
8. Finally, the crucible had to be abandoned since an attempt to clean it at $1900 - 1950^{\circ}$ resulted in its destruction. The destruction was a consequence of $\delta\text{-MoB}$ formation which had become a sufficiently intensive component of the crucible to cause interior melting.

The second set of experiments involving the molybdenum crucible and samarium sesquioxide-boron mixtures was performed with ratios other than one mole of sesquioxide for every ten moles of boron. In what follows, only a numerical ratio will be used to describe the starting composition of the materials, using numbers such as 1:10, 1:8, 1:6, 1:2, to describe the respective ratio of moles of sesquioxide to moles of boron present in the initial compacts. A new molybdenum crucible was used to begin this series, and the following salient facts are set forth as a consequence of these experiments:

9. A pellet of composition 1:6 was heated in an outgassed molybdenum crucible for ten hours at 1435° . X-ray examination showed the crushed pellet to contain SmB_4 and SmB_6 ; the lid of the crucible was coated with SmBO_3 . The crucible was subsequently treated with boron for one hour at 1750° .
10. The operations above were followed by heating a pellet of 1:8 composition in the same crucible for 12.5 hours at 1435° , this sample being 1.25x heavier. The x-ray photograph of the pellet showed the presence of SmB_4 and SmB_6 . Again, the crucible was treated with boron for an hour at 1700° , which treatment caused a small crack in the crucible. There was a concurrent deposition of $\text{B-Sm}_2\text{O}_3$ on the crucible.

11. A final 1:10 sample was heated for 12.0 hours at 1435° . Only SmB_6 was observed in the product.
12. Using the same crucible as in (3), a pellet of composition 1:6 was heated for two hours at 1435° . At the end of this heating, the surface of the pellet was found to contain SmBO_3 and the interior contained only SmB_6 . No SmB_4 could be detected by x-ray powder analysis.
13. An intermediate 1:10 run for 1.5 hours at 1435° and 1.5 hours at 1565° resulted in a homogeneously blue product of SmB_6 .
14. Invoking a more radical change of composition to 1:2 and heating the pellet for three hours at 1435° , resulted in a grey mixture whose x-ray photograph contained no lines of normally identifiable phases.
15. Heating a 1:2 mixture at 1540° for three hours again resulted only in the formation of yellow-white material which collected in the base of the crucible and which appeared to have once been a molten mass.
16. However, when a 1:2 mixture was heated for 12.0 hours at 1540° in the same crucible used for (6) and (7) and immediately subsequent to (7), the product x-ray showed the presence of SmB_6 and $\text{B-Sm}_2\text{O}_3$.
17. Heating a 1:1 mixture for three hours at 1435° resulted in a product whose x-ray showed no lines other than those ascribable to $\text{B-Sm}_2\text{O}_3$.
18. Another 1:10 pellet was heated for 1.5 hours at 1435° . Visual examination of its surface at this point showed it to be the same color normally associated with SmBO_3 . Without any further destruction of the pellet, it was returned to the molybdenum crucible and heated for 1.25 hours at 1540° . Only SmB_6 was found in the product after this secondary treatment.

19. Using a mixture of SmB_6 and Sm_2O_3 in a respective mole ratio of 11:2 and assuming the possibility of the reaction:



a pellet (≈ 0.15 g.) was pressed and heated in the molybdenum crucible for one hour at 1540° . At the completion of this run, the top surface of the pellet was found to contain SmB_4 and SmB_6 , while the interior was found to contain only SmB_6 .

No Sm_2O_3 was observed.

20. A new molybdenum crucible had to be fashioned for succeeding runs since the previously mentioned crack became intolerable. The new crucible was outgassed for several hours at 1850° and initiated by heating a pellet of -325 mesh molybdenum metal with Sm_2O_3 (prepared in a respective mole ratio of 3:1) at 1460° for 3.5 hours. No phases other than B- Sm_2O_3 and molybdenum were observed on the x-ray photograph.
21. A final heating of a 1:10 pellet was performed in the new molybdenum crucible for 14.5 hours at 1510° . Immersed in a shell of glassy-looking material, some of which had dispersed on all parts of the lid, the pellet was a silver-grey color. The material was exceedingly soft on crushing and the x-ray photograph showed no lines of SmB_6 . The principal phase was clearly SmB_4 , but there seemed to be a few lines of another unidentifiable phase.
22. Another 1:10 pellet was heated for 11.5 hours at 1505° in the same crucible used for (21). In this case, the pellet was totally nonhomogeneous on crushing and represented only a glassy kind of nondescript residue. No photograph was taken of the residue, but material scraped from the molybdenum lid was observed to be B- Sm_2O_3 .

23. The crucible was heated with boron for 5.5 hours at 1435° to "clean" it. At the conclusion of this heating, the Vycor tube was coated with a residue which looked like a metallic mirror and which, after dissolution with 6 M nitric acid diluted to pH = 1, formed a precipitate with a saturated oxalic acid solution.

E. The samarium-boron system in a molybdenum crucible

The general nature of these reactions is quite simple. The components were mixed on the assumption that samarium-boron^{*} homogeneity would result from the samarium becoming molten. Vacuum heating could not be used due to the high volatility of the samarium metal and therefore most of the reactions were performed in an atmosphere of helium (575-600 mm.), bled into the line directly from the tank with no pre-purification. Evacuation was used as a sort of purification technique for removing excess samarium after running the reactions. Since, at any temperature, the vapor pressure of the samarium borides appears to be quite small relative to that of samarium, it was possible to remove excess samarium in this manner. Using samples of from 0.5 - 1.0 g., all of these experiments led to essentially the same result; namely, success in the preparation of both borides of samarium. In all instances, the product material was light grey and in some instances the x-ray photographs were even devoid of any lines of the samarium hexaboride phase. But in no instance did analysis verify the preparation of pure samarium tetraboride. In most cases, the products had sintered to the shape of the crucible and all could easily be ground using only alundum mortars and pestles.

No chemical analyses were performed on the products of the early experiments involving samarium metal and boron. Once again the

* The ratio of moles is now expressed as samarium to boron respectively.

important aspects of these preliminary attempts to prepare pure samarium tetraboride may be summarized as follows:

1. A 1:4 mixture of samarium and crystalline boron was heated at 1045° in vacuo for only 5.0 minutes. The samarium effused so rapidly that helium was added to provide an inert atmosphere. The sample was reheated to 1365° for 10.0 minutes and an x-ray photograph of the product indicated SmB_4 and SmB_6 . (Helium was used in all successive experiments unless otherwise noted.)
2. Heating another 1:4 mixture to 1250° for one hour again yielded a product containing both borides of samarium.
3. Even when the composition of the samarium-boron mixture was raised to 1:10 and heated as low as 1100° for one hour, the product was observed to contain SmB_6 and SmB_4 .
4. Lowering the composition to 1:3.8 to compensate for samarium lost in vaporization still resulted in SmB_4 - SmB_6 mixtures after 1.5 hours at $1275 - 1300^{\circ}$.
5. Again using the molybdenum crucible and heating 1:4 mixtures of samarium with crystalline or amorphous boron at 1125° for 1.0 - 1.5 hours resulted only in unidentifiable phases. The same experiment, when performed for 11.5 hours, yielded a product containing SmB_4 , and a contamination phase, common to the heatings of short duration, but significantly devoid of SmB_6 .
6. Heating a 1:3.5 composition for 2.5 hours at $1100 - 1125^{\circ}$ and then in vacuo for 10.0 minutes at 1275° resulted in a product whose x-ray photograph showed SmB_4 with a trace of SmB_6 .
7. Finally, heating another 1:3.5 mixture for four hours at 1150° in helium and then for one hour at 1455° in vacuo resulted in a mixture of SmB_4 - SmB_6 . When the sintered cake was replaced

into the molybdenum crucible and heated in helium for an additional 8.0 hours at 1275° , no significant changes were observed. However, continued heating from 0.75 - 2.0 hours over the range $1390 - 1735^{\circ}$ finally resulted in a phase whose x-ray photograph showed only SmB_4 . The grow-in of the grey-colored SmB_4 as a consequence of the heatings began after a heating at 1585° and was visually observed to commence at the bottom of the sintered mass.

Additional experiments were performed to examine further the effects of varying the temperature, the duration of heating and the initial starting composition.

It was possible to prepare samarium tetraboride in a molybdenum crucible using the 1:3.5 starting composition even when the mixture was heated to as high as 1640° in a helium atmosphere. It was further observed that when the orifice in the molybdenum lid had become clogged, the x-ray photograph showed no phase other than samarium tetraboride, while an exact duplication of the experiment at 1615° (except for no orifice clogging) resulted in a product whose phases were samarium tetraboride and samarium hexaboride.

Thirteen final samarium-boron experiments were performed in the same crucible. The x-ray photographs of every product showed the presence of samarium tetraboride. Samples weighing from 0.50 - 0.52 g. were heated in helium at a pressure of approximately 600 mm. and chemical analyses of the products were performed in duplicate wherever possible. All data are tabulated in Table I on the following page; special notations have been made regarding the presence of samarium hexaboride in the products.

It should be noted that tiny bluish crystals were microscopically observed only in the runs numbered E-24, E-41, and E-43. They are

Table I. The samarium-boron system in a molybdenum crucible.

Run Number	Starting Composition	Sample Weight (g.)	Heating Description	Comments on X-Ray Photos	Δ Crucible (in mg.)	Δ Reactants (in mg.)	% Sm in Product	% Boron in product
E-13	1:3.5	0.51725	10.5h at 1590°	Shows only SmB ₄	+24.29	-142.49	77.2	22.6
E-14	1:3.5	0.51743	20.0h at 1590°	Shows only SmB ₄	+25.71	-134.42	76.3	24.0
E-15	1:3.5	0.52166	1.0h at 1175° 0.5h at 1555°	Minor SmB ₆	+61.72	-23.78	73.3	27.8
E-16	1:3.5	0.52737	1.0h at 1125° 1.0h at 1705°	Minor SmB ₆	+1.68	-108.30	76.0	23.1
E-17	1:5.0	0.50164	2.0h at 1540°	Minor SmB ₆	+13.48	-37.82	72.3	27.5
E-18	1:5.0	0.51153	0.5h at 1175° 1.5h at 1325°	Minor SmB ₆	+32.96	-8.26	70.3	27.0
E-19	1:5.0	0.51557	2.0h at 1695°	Trace SmB ₆	-9.97	-35.28	75.0	24.9
E-23	1:3.0	0.50635	1.0h at 1175° 1.0h at 1640°	Trace SmB ₆	+5.33	-137.30	75.8	25.4
E-24	1:3.0	0.50191	2.0h at 1620°	Minor SmB ₆	+3.41	-162.15	75.2	23.7
E-26	1:3.0	0.50410	1.0h at 1540°	Trace SmB ₆	+1.37	-152.18	76.5	23.1
E-41	1:2.5	0.51365	2.0h at 1545°	Minor SmB ₆	+9.51	-207.24	Insufficient sample	
E-42	Residue from E-41	0.27151	1.0h (Vacuum) 1735°	Trace SmB ₆	+6.47	-28.45	----	----
E-43	1:2.5	0.50172	2.0h at 1620°	Trace SmB ₆	+12.18	-238.77	77.7	22.7
E-44	1:2.5	0.48643	2.0h at 1365°	Trace SmB ₆	+10.59	-253.76	72.5	23.4

* These numbers are retained to refer to experiments described (with the same numbers) in Notebook B.

apparently not samarium hexaboride inasmuch as isolation of one of these led to a very complicated and unresolvable x-ray pattern.

Prior to initiation of the series of 1:2.5 composition, several attempts were made to heat phases rich in samarium tetraboride to a temperature high enough to convert them to samarium hexaboride in a molybdenum cell. A portion of the residue from E-16 was treated in just such a manner. At pressures of about 1.5×10^{-5} mm. and temperatures as high as 1750° , no conversion could be effected and SmB_4 - SmB_6 mixtures merely lost the SmB_6 phase and coated the Vycor confining tube with a heavy deposit of samarium containing material.

Subsequent to the series, E-41 - E-44, the molybdenum crucible and its lid were heated to 1960° . The lid fused to the body of the crucible and the bottom boiled up within the cell. The interior of the cell was determined once again to be principally δ -MoB, which is unaffected by dilute hydrochloric acid or dilute sulfuric acid, but which dissolves appreciably in concentrated nitric acid.

F. The reaction between samarium and boron in a boron nitride liner

By using a liner inert to boron, or at least one which showed far less reaction with boron than molybdenum, it was hoped to determine the mechanistic path by which SmB_6 or SmB_4 - SmB_6 mixtures were produced from heating pellet compacts of Sm_2O_3 and boron.

A general outline regarding the construction of these liners has already been provided. However a few more specific comments should be made.

Since it was necessary to select a temperature easily attained and one which would, at the same time, be high enough to prevent SmBO_3 formation but low enough to preserve the life of the boron nitride, 1650° was chosen as the temperature for this study. There is no doubt that

oxide-boron compacts will undergo reaction at this temperature, and it was hoped that boron deposition on the surface of the boron nitride (from heating) would lower its vapor pressure significantly enough to prevent rapid thermal destruction. Fortunately, it did. In no instance did the boron nitride liner gain weight. Using a liner weighing from 1.7 to 2.0 g. 10 - 20 mg. of weight were lost in every instance. It is also noteworthy that for all the runs performed, the interior of the liner remained white, even when the liner was heated devoid of contents. Only when the boron composition was very low relative to the amount of sesquioxide, did there appear to be any darkening whatsoever on the interior walls of the boron nitride, and in these cases, darkening was minor.

Each heating was performed for one hour because it was believed to represent an amount of time reasonable for the reaction to be complete. In one instance, an especially large pellet (0.92 g.) was heated for a second hour at 1650° . The weight loss at the end of one hour was equal to 16.0%. At the end of the second hour, the percent weight loss was 16.1.

Temperature measurements were made by sighting from above the heating cell into the hole in the molybdenum lid.

All samples described below were heated for one hour at $1650 \pm 10^{\circ}$. The pressure before heating was $< 10^{-3}$ mm and after about 15 to 20 minutes, the pressure had again dropped to $< 10^{-3}$ mm. The only variable was the starting composition. Samples were run in duplicate for the compositions 1:12.5 and 1:7.5, but all other samples were run in triplicate or quadruplicate. X-ray powder photographs were obtained for every product and all products were analyzed for boron and samarium. Sample weights of the pellets, all of which retained their shapes during the course of the reaction, ranged from 0.58 to 0.91 g.; sample weight was a function of the amount of material needed for analysis.

For all instances except those in which the starting ratio was 1:5, the only phase shown in the x-ray photographs of the product was SmB_6 .

In the case of the 1:5 mixtures, the products contained both SmB_6 and SmB_4 , with the former being the minor phase and the latter being the phase which the pellet visually appeared to be. In only one of the three 1:5 samples did the product appear totally grey; in the other two samples, the interior of the pellets was grey and only the top surfaces were blue.

Data regarding these experiments are summarized in Table II. the columns represent, from left to right:

1. The starting composition of the pellet.
2. The average percent weight loss of the sample.
3. The average value of the ratio of moles of samarium lost divided by the moles originally present.
4. The average value of $\bar{x}$, where $\bar{x}$ represents the number of moles of oxygen lost divided by the number of moles of boron lost as a consequence of the heating.
5. The average mole ratio of boron to samarium in the product as determined by analysis.
6. The average value of the percent samarium in the product.
7. The average value of the percent boron in the product.

G. The reaction between samarium sesquioxide and boron in a zirconium diboride crucible

This section of the experimental results is included for the sake of a more complete report of the investigation. However, because the zirconium diboride crucible and its lid were never subjected to very high extremes of temperature, there is some question as to whether or not the cell was properly outgassed before use. Outgassing of the crucible and lid was performed for two hours at 1750° ; the cell was then used for nine experiments exactly comparable to the more extensive investigation undertaken in boron nitride and reported in Part F of this experimental section.

Table II. The reaction between samarium sesquioxide and boron in a boron nitride liner.

Starting Composition	Av. % Wt. Loss	Av. % Sm Lost	Av. Value of $\bar{x}$ in BO_x	Mole Ratio B/Sm in Product	Average % Sm	Average % B
1:5.0	76.8	77	0.92	4.3	73.0	24.1
1:7.5	40.8	41	0.81	4.4	71.3	22.6
1:10.0	39.3	37	0.73	5.5	68.2	26.8
1:12.5	33.4	28	0.60	6.0	67.2	29.1
1:15.0	22.9	11	0.54	6.2	68.1	30.3
1:17.5	21.9	13	0.35	7.0	63.8	31.9
1:20.0	17.8	5	0.27	8.0	61.4	35.6

Once again each heating was performed for one hour at 1650° and again the temperature was read by sighting from above the heating cell into the hole in the lid. The emissivity of the lid was observed to be only minutely different from that of the crucible body.

Sample weights ranged from 0.60 to 0.90 g., heavier samples being used for compositions lower in boron. The compositions studied are shown in Table III. Three samples were run for the 1:20 composition, while only two samples were used for the other three compositions examined.

For all instances except those in which the starting ratio is 1:5, SmB_6 was observed to be the principal phase of the x-ray powder photograph of every reaction product. In no instance was SmB_4 observed, and for one 1:5 composition, no SmB_6 was observed either.

The zirconium diboride heating cell, weighing about 8.75 g., showed weight losses of from three to ten milligrams during the heating of the 1:20 samples, but subsequent to these three experiments, it showed consistent weight increases of from three to twenty-five milligrams. In the range of low compositions, the heatings were observed to produce perceptible blue color in the base of the crucible. Since the lower composition mixtures were heated after the ones of higher composition, the grow-in of this blue color may be partially a result of cumulative effects.

The data are presented in Table III, each column represents the same things that were presented in Table II, page 40, for which an explanation has already been presented.

H. The heating of a sample of samarium hexaboride in a low-density tungsten cell.

This portion of the investigation involved only seven experiments. The starting material was analyzed in triplicate for samarium and

Table III. The reaction between samarium sesquioxide and boron in zirconium diboride.

Starting Composition	Av. % Wt. Loss	Av. % Sm Lost	Av. Value of $\bar{x}$ in BO_x	Mole Ratio B/Sm in Product	Average % Sm	Average % B
1:5.0	21.7	16.0	2.3	2.6	80.1	14.9
1:10.0	14.5	9.0	0.45	4.3	69.9	21.7
1:15.0	20.5	11.6	0.37	6.1	65.4	28.9
1:20.0	18.3	9.6	0.20	8.3	59.7	33.6

boron and found to contain: Sm - 64.0%, B - 30.8%; the remainder is assumed to be oxygen.* Each of the runs cited in Table IV was performed in the order listed. The heating cell was heated for 1.0 hour at 2170° subsequent to each experiment. By the end of the experiments, both the lid and the base of the reaction well contained fissures and the lower portion of the crucible had swollen considerably. Cracking was noticed after the second experiment, and swelling in general was first noticed after the fourth experiment. In each instance, the Vycor tube confining the reaction at pressures of 10^{-5} to 10^{-6} mm. was coated with a deposit completely soluble in 6.0 M nitric acid. These acid solutions were collected as quantitatively as possible and analyzed for samarium content. Because all samples had sintered and were easily removed, it is believed that weight data on the crucible and the sample are quite meaningful. The weight of samarium in the Vycor deposit was added to the weight increase in crucible lid and body to determine what percent of the sample weight-change could be considered accountable. Limits of precision in the analyses were: Sm - $\pm 0.5\%$; B - $\pm 1.5\%$.

Powder photographs were taken in every instance, but only in the first two experiments was any SmB_4 detectable in these x-ray photographs. It is significant that a layer of SmB_4 was visually detectable on the top surface of the sintered compact after the first and second heatings, although in the second experiment the layer was much thicker than in the first. The data for these experiments are tabulated on the next page in Table IV.

*The excess oxygen is assumed to be in the form of amorphous material of a formula BO_x . While one might suspect the contamination to be samarium orthoborate, such contamination would tend to raise (rather than lower) the percent samarium above 69.9%, the percent samarium in SmB_6 .

Table IV. The heating of a sample of samarium hexaboride in a low-density tungsten cell.

Run No.	Time and Temp.	Δ Cruc. (in mg.)	Δ Lid (in mg.)	Sample Wt. (in g.)	% Δ Sample	Av. % Sm	Av. % B	% of Wt. Loss Accountable	General Remarks
H-1	1.5h at 1750°C	+71.62	+8.65	0.53969	-21.7	70.0	27.8	89.6	Crucible surface golden-brown after heating; heavy Vycor deposit.
H-2	4.0h at 1750°C	+71.61	+18.38	0.63106	-28.0	70.6	27.4	90.2	Cracks appear in heating cell; crucible bright.
H-3 ^a	4.0h at 1960°C	+66.97	+8.76	0.62293	-37.2	68.9	29.5	94.5	H-3 heated too rapidly; lid blew off; sample showed grey color; H-3' = new sample.
H-4	1.5h at 1960°C	+47.98	+8.55	0.64731	-22.8	68.9	30.0	89.6	Crucible swelling at base of reaction well.
H-5	4.0h at 1750°C	+49.85	+11.15	0.57080	-25.3	68.6	29.3	85.2	Lid shows cracks
H-6	4.0h at 1540°C	+38.76	+8.68	0.55365	-11.0	67.8	30.3	77.6 [†]	[†] Vycor residue lost.
H-7	1.5h at 2170°C	+124.64	+16.59	0.70309	-65.5	68.4	29.6	90.7	Massive Vycor deposition; sintered mass all blue.

I. Miscellaneous experiments

Some miscellaneous experiments which are of major importance to the conclusions of this study were performed and are summarized below:

- 1a. About 0.06 g. of samarium metal was heated for 0.5 hour at 1540° in boron nitride. Subsequent to this heating, the interior of the boron nitride was as white as before the heating was begun.
- 1b. A second heating of 0.07 g. of samarium in boron nitride was performed by raising the temperature slowly from 1020° to 1750° over a one hour period. Only when the temperature reached 1750° did the pressure within the system exceed 10^{-4} mm. The crucible showed some visible thermal decomposition and the internally coated with a thin layer of grey substance; however, not enough sample remained for a powder photograph. The samarium had volatilized without any apparent interaction (or reaction) with the crucible.
- 2a. A 0.1 g. mixture of (-325 mesh) molybdenum and SmB_6 was prepared in a mole ratio of 1:1 and heated in boron nitride for 1.5 hours at 1435° . The x-ray photograph of the product (A-711) contained lines of δ -MoB and SmB_6 . After the mixture was returned to the boron nitride crucible and heated for an additional hour at 1540° , the photograph (A-713) showed lines ascribable to MoB_2 and SmB_6 . No lines of SmB_4 were observed subsequent to the first or second heatings.
- 2b. Essentially the same experiment was performed using tungsten powder and SmB_6 in a respective mole ratio of 3:1. The duration of the heating was extended to 2.5 hours at 1615° . The x-ray photograph (A-719) revealed the presence of WB_2 ; a very faint pattern of SmB_6 remained, but no lines of SmB_4 were observed.

- 3a. A crucible and lid, both of boron nitride, were made for this experiment. The product from run E-19, a grey-colored mixture of principally SmB_4 with a trace of SmB_6 was placed into the freshly outgassed crucible and heated at 1450° at 10^{-4} mm. pressure for 0.5 hour. After heating, the material had sintered, but was visibly a two phase mixture with blue color confined to the top surface and to the sides of the wafer while the bottom was totally grey. The x-ray powder pattern (A-667) clearly revealed lines of SmB_4 and SmB_6 . Heating for an additional 1.5 hours at 1460° resulted in a totally blue product whose diffraction powder pattern (A-668) represented only SmB_6 .
- 3b. The residue from experiment 3a. was replaced into the same crucible and heated for one hour at 1540° . The pressure within the system remained essentially constant in the range of 10^{-4} mm., and no apparent deposition occurred on the walls of the Vycor confining tube. X-ray examination (A-669) of the product at this point showed only SmB_6 . The slightly sintered material was replaced into the boron nitride and heated for two more hours at 1750° . Since there was still no noticeable deposit on the walls of the Vycor tube, the temperature was raised to 1850° for a final 15 minutes, after which the crucible and contents were examined. The interior of the crucible was completely blue at this point, the color of SmB_6 , and the orifice of the lid had become partially blocked by a tiny cluster of blue crystals which were ground, photographed (A-670) as a powder pattern, and found to contain no phase other than SmB_6 .
4. A mixture of samarium metal and SmB_6 , weighing about 0.6 g., and prepared in a respective mole ratio of 1:2, was placed into a freshly outgassed crucible of boron nitride fitted with a molybdenum lid. The mixture was heated at 1380° for ten

minutes. At this point, the product was examined both visually and with x-rays (A-829) and found to contain SmB_4 and SmB_6 , the former on the bottom of the sintered mass, the latter confined principally to the top surface. An additional heating for ten minutes at 1485° produced no further observable change.

IV. DISCUSSION

The discussion section of this thesis is divided into three major sub-divisions. The first of these deals with the considerations to be made in the selection of a crucible material for use with borides or boron at high temperatures. Information has been presented regarding the actual empirical problems encountered in this work. However, considerable attention has also been devoted to work performed by others as it relates to the general problem of crucible selection.

The second sub-division of the discussion deals with the immediate results and conclusions of this thesis investigation.

In the third and final portion of the discussion are presented some proposals and recommendations for continuing work on the borides of samarium.

A. Crucible materials

There can be no doubt regarding the importance of selecting the proper container for studying high temperature reactions. Since magnetic induction offers a convenient means of heating in vacuo or in an inert atmosphere, the fundamental criterion governing crucible selection is electrical and/or thermal conductivity. Additionally, a reaction vessel must be able to be readily obtained (or the raw materials easily machined) and must be inert to the species being studied at any chosen temperature. Implicit in these restrictions is the restriction of a high melting temperature or decomposition point. It is difficult to meet all of these conditions, and it becomes especially difficult once the species to be studied contains free boron or boron available as a consequence of reaction.

In this study, a variety of materials was considered and ultimately employed, either directly as containers for the reactions, or indirectly as some part of the constructed system necessary to achieve the temperatures desired for reaction. Carbon, tantalum, tungsten, zirconium diboride, titanium diboride, and boron nitride were examined; none of these proved totally satisfactory for all investigations. A discussion of individual utility and limitations, as well as a summary conclusion, is presented herein.

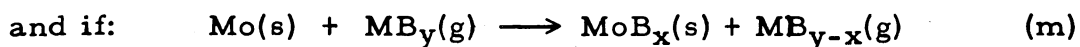
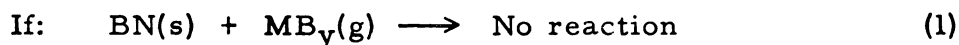
Since molybdenum was the first crucible to be used in this research, it will be the first to be discussed here. The choice of molybdenum was made for several reasons. It is a highly conducting, high melting, easily machinable material which was obtainable as a bar of high purity and which seemed to offer some promise of being inert. The fact that molybdenum would react with boron was well-known and has been investigated (38-40). However, it was hoped that although molybdenum was known to react with boron this would not mean that it would react with compressed pellets of samarium sesquioxide and boron, pellets which were pressed in the belief that the samarium sesquioxide was the ingredient in excess. In this belief, the molybdenum was used as the crucible material for containing the reactions between samarium sesquioxide and boron as well as reactions between samarium and boron. When it was discovered how actually non-inert molybdenum was, a change was made to boron nitride.

Of all the materials investigated, only the boron nitride (41) fails to meet the criterion of being an electrical conductor. This fact is particularly distressing since of the materials considered, boron nitride is easiest to machine and comes experimentally closest to being ideal for studies below 1550° . At higher temperatures, the decomposition of the nitride reduces the crucible life; cracks and fissures are produced from thermal decomposition, and there is a greater chance for chemical reaction between crucible and contents.

Since boron nitride cannot be heated by direct means, a radiation shield of material such as tantalum, carbon, or molybdenum must be used. These shields heat the material effectively, but make heating very cumbersome and clumsy. They are difficult to align, short-lived, and rather dangerous as a modification to a glass system not originally designed with shields in mind. An alternative is to use the poorer electrical conductors as liners in materials which are good conductors. If the liner is small relative to the containing body, temperatures of the containing body can be considered to be temperatures of the liner as well. The boron nitride was used in just this fashion--as a liner for a molybdenum heating cell.

Since boron nitride has an appreciable vapor pressure (42) at the desired reaction temperatures, one has the problem of finding a lid material (different from boron nitride) which can be heated to the proper temperature but which will not fuse to the crucible on decomposition and subsequent re-formation of the boron nitride. A lid of molybdenum was machined for this purpose. In using it, one must consider the possible temperature differential produced in heating the two different materials. Empirically, it was determined that if the main body of the boron nitride liner is confined completely within the molybdenum cell, the temperature difference between the lid and the bottom of the crucible liner was never greater than 50° , and in most cases less than that. It was necessary to prevent the molybdenum lid from coming into contact with the well confining the liner. For this purpose, a $1/32$ " clearance was allowed to prevent having to forcibly remove a lid from the main body of the crucible.

Additionally, the use of a molybdenum lid necessitates a consideration of the possible interactions induced within the system.



then one must not overlook the possibility of molybdenum interaction if MB_y or any portion of an MB_y decomposition (or formation) involves a gaseous molecule containing boron. Leitnaker (43) has asserted that there is no evidence whatsoever of any gaseous metal boride molecules, and thus far there has been no evidence to the contrary. In this work, both samarium orthoborate and samarium hexaboride were detected on the lid, but no sufficient amount of data was collected to assert that samarium hexaboride exists, or can exist, as a gaseous molecule.

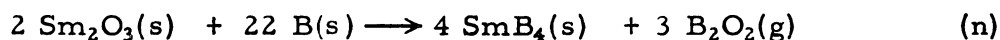
Finally, boron nitride does have the very useful quality of forming a protective layer of boron on its surface after initial use. This layer is thin enough so that interactions between sample and liner are negligible, but thick enough to radically inhibit later dissociation of the crucible, dissociation which is synonymous with self-destruction.

Besides molybdenum and boron nitride, the only other material used extensively in this study was a tungsten-copper alloy. As an alloy, the metal could be easily machined whereas this would have been an exceedingly laborious and time-consuming operation using tungsten alone. While the tungsten appears to be more inert to boron than molybdenum, it is still an essentially undesirable material. Brewer and Haraldsen (44) have reported that within their uncertainty, no difference could be distinguished between the thermodynamic stability of tungsten and molybdenum borides.

The three materials discussed above were actually the only materials to which any major attention was devoted in this research. The work comprising the largest portion of experimental data was performed in molybdenum or boron nitride, but heating samarium hexaboride in the tungsten cell was probably the most significant portion of the research in terms of useful material extracted from performing a minimum number of very careful experiments. Nonetheless, enough consideration was given to the use of other materials such as carbon,

tantalum, and zirconium and titanium diborides that they are deserving of inclusion in the discussion presented here. They are considered below.

Graphite is easy to obtain, to machine, and to heat. The principal reason for not using carbon as a crucible material was merely that its reducing properties were well-known with respect to boride preparation. Inasmuch as the equation:



was believed to represent a possible truth, it was necessary to avoid carbon in order to offer substantive proof that the reduction of the oxide was done by boron. Furthermore, the porosity of graphite would have provided an excellent route to rare earth carbide formation if any free rare earth metal were liberated in the gaseous state.

Tantalum was avoided because of its tremendously rapid reaction with boron. Leitnaker, et al. (45), have reported that amorphous boron and tantalum powder react rapidly at about 900° with the evolution of a great deal of heat. However, Johnson and Daane (46) have reported that as long as pure lanthanum was used, the addition of mixtures of lanthanum and LaB_4 to crucibles of tantalum resulted in no attack on the crucible. Brewer and Haraldsen (44) have estimated ΔH_{298}° for tantalum borides as < -26 kcal. per g. atom of boron, * and classify the tantalum borides as being more stable than the borides of either tungsten or molybdenum, whose ΔH_{298}° values are estimated to range from -5 to -25 kcal. per g. atom of boron. [There is the notable exception, W_2B , for which ΔH_{298}° has been estimated to be within the range -28 to -20 kcal. per g. atom of boron.]

* Brewer and Haraldsen (44) have asserted that because the entropy changes within these systems are small and because of the small changes in heat capacity with change in temperature, ΔH_{298}° is assumed to equal ΔF_f° at any temperature. This is an assumption, but presumably a valid one.

In 1951, Brewer, et al. (38) suggested that TaB offered considerable promise as a very refractory material if sufficiently high sintering temperatures were used to produce it in a compact and non-porous form. This fact, coupled with the information (45) regarding the surprisingly slow rates of reaction in the Ta-TaB system in the vicinity of 2000° , tempts one to suspect that TaB may be a good crucible material for examining the decomposition of rare earth borides even though tantalum itself is unsatisfactory.

Finally, the possibility of using the refractory materials, ZrB_2 and/or TiB_2 , was considered as a means of escaping the dilemma of boron diffusion into molybdenum and decomposition of boron nitride at high temperatures. Not enough work has been done with TiB_2 in this study to say anything extensive about it. However, the absence of the phase, TiB_{12} , and the stability estimate (44) of ΔH_{298}° for TiB_2 (about -36 kcal. per g. atom of boron), suggests that TiB_2 might serve as a crucible material for studying decomposition of rare earth borides. Brewer, et al. (38), have reported that when titanium was heated with more than 66 atomic percent boron, the metal was converted to pure hexagonal titanium diboride and any excess boron was lost. The titanium borides are estimated (44) to be slightly less stable than the corresponding borides of zirconium by about 3 kcal. per g. atom of boron.

The phase diagram for the zirconium-boron system has been reported by Post and Glaser (47) and shows that starting with material having a composition, ZrB_2 , at temperatures in the range of $1525 - 2320^{\circ}$, there exists the possibility of forming ZrB_{12} if boron can somehow be introduced into the ZrB_2 lattice. The value of ΔH_{298}° for ZrB_{12} has been estimated (44) to be about -10 kcal. per g. atom of boron, while the value estimated for zirconium diboride is approximately -30 kcal. per g. atom of boron.

There is some possibility for using crucibles of zirconium or titanium diboride, but only if these borides can be obtained in sufficiently pure form to assure that reactions which occur are not reactions between reactants and crucible impurities. There can be no doubt regarding their undesirability with respect to machining since only electro-machining can be used. In a magnetic field, these materials do not couple nearly as well as the metals, and while it is easy enough to attain temperatures of 1850° , in decomposition studies, the more important temperatures are higher ones. Using these materials, it is difficult to attain temperatures from $1850 - 2200^{\circ}$. Crucibles of zirconium diboride and titanium diboride have been used in our laboratory to confine liners of boron nitride and their utility for this purpose is excellent. Little more can be said except that these borides do warrant additional examination for use as containers which may be inert to boron, at least under special conditions.

The selection of crucible materials is therefore seen to be controlled by both kinetic and thermodynamic considerations. Boron is such a reactive element at high temperatures that it seems practically impossible to find a material completely satisfactory for confining syntheses of rare earth borides or for studying their decompositions. While a material may be essentially inert to a boride over a wide range of low temperatures, any boron produced in the thermal decomposition of that boride produces the instantaneous need for the crucible to be inert to boron as well.

It appears that diffusion processes are exceedingly important in high temperature boron chemistry, and in view of the small size of the boron atom relative to the size of the metal atoms within a matrix, this is not surprising.

The information obtained by workers at the Vallecitos Atomic Laboratory in Pleasanton, California, may also be ultimately useful in the selection of crucible materials. These workers have examined the

stability of metal borides relative to the metals which might be used to contain these borides as control rods. In one such study, Antony and Cummings (48) conclude that of the metallic-matrix-boride systems studied (matrices: titanium, zirconium, iron, nickel, copper, silver, aluminum, and stainless steel) only copper, silver and aluminum were determined to be compatible with boride compounds at elevated temperatures. The obvious difficulty with using materials of this sort is their low melting points. Unless a system can be engineered to produce high temperatures with rapid cooling, as in arc-melting, use of these metals becomes quite difficult. These workers also have reported that titanium and zirconium were found to be the least reactive of the refractory matrices; the diborides of hafnium, zirconium, and titanium were found to be the least reactive boron compounds regardless of the containing matrix.

Some additional conclusions of the work of Antony and Cummings (48) are cited below:

- a) The thermodynamic stability of metal borides appears to be partially dependent upon the boron density of the compound.
- b) If boron density is defined as:

$$\frac{\text{density of the compound}}{\text{molecular weight of the compound}} \times \frac{\text{grams of boron per mole of compound}}$$

- c) Then (b) implies high temperature reaction between a boride and a matrix if the matrix boride is of lower boron density than that of the boride to be dispersed.
- d) Diffusion of boron into the matrix is rate controlling, and reaction is more complete in matrices of a lower melting temperature.

The statements as presented are acceptable in those situations in which there is no interaction between any species other than boride and matrix. If the reaction between a species such as samarium hexaboride and

zirconium results in the release of samarium concurrently and if that samarium can possibly react with any of the boride species remaining or formed then the conclusions are invalid ones and cannot be employed. Samarium tetraboride has been found to be less stable than samarium hexaboride; but the boron densities for these compounds may be calculated to be 1.36 and 1.53 g./cc. respectively.

Aside from this sort of a qualification, the statements above are reasonably useful in evaluating crucible materials.

In summary conclusion, it appears that the use of any metal crucible for studying the chemistry of rare-earth borides is unacceptable unless plans are made to utilize the crucible's reactivity with boron as part of the synthesis or decomposition investigation.

Boron nitride seems suitable for inertness at lower temperatures as long as nitride formation is negligible, or at least minimal. The possibility of using refractory borides offers much hope if these materials can be conveniently sintered, machined, and heated to sufficiently high temperatures. Once the engineering difficulties are overcome, the rare earth borides themselves may be the materials in which to examine the decomposition and formation of other rare earth borides. In addition to zirconium and titanium diborides, tantalum boride in the form of TaB may be an excellent material for inclusion in this category.

Hoyt, et al. (49), have found that rare earth tetraborides and hexaborides react severely with carbon when hot-pressed in graphite dies, the products of the reaction being boron carbide and rare earth carbides. However, Lafferty (1) has noted that tantalum carbide is a surface impervious to boron. Tantalum may be carbonized by packing a crucible with sugared characoal and heating in a vacuum for one minute at 2300°. Lafferty has reported that this produces a carbonized surface about 0.002" thick which is not only extremely stable at 1500°, but which also prevents boron from diffusing into the tantalum.

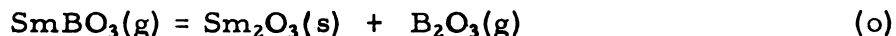
No discussion of this sort is ever complete; but its inclusion, however lengthy, is necessary to understand the scope of the problems besetting the individual who wishes to examine borides at high temperatures. The selection of a suitable crucible material is controlled by the chemistry of the materials under study. However, it is equally rigorously controlled by the power of the magnetic field used for heating, by the availability of facilities for machining and glass-blowing, and even by the sheer ingenuity of the experimenter. In an area of chemistry which is just beginning to expand, there remains much to be learned before the boride chemist can select a particular crucible to study a reaction involving boron and still be reasonably certain that it is the best crucible, best in the sense that it is capable of being heated to the desired temperatures, and best in being inert to reactants and reaction products at those temperatures.

B. Results and Conclusions

Every chemical reaction is dependent upon the thermodynamics and kinetics involved in going from a mixture of reactants to their existence as products. The very firm conclusion of this study is that the processes of the formation and decomposition of the borides of samarium are potentially capable of being more rigorously controlled by kinetic effects than by thermodynamic ones. It is further a conclusion of this work that the reaction between mixtures of samarium sesquioxide and boron is not described simply but that it is a very complicated process dependent not only upon the composition of the starting materials, but also upon the nature of the heating cell, the time allowed for reaching a temperature, the duration of maintaining that temperature, and the extent to which, and the rate at which, samarium escapes from the vicinity of the reaction. A more specific analysis follows.

In the first instance, it is believed that the failure of a molybdenum crucible to sustain long life when used for heating sesquioxide-boron compacts is principally the result of the formation of phases of the nature BO_x . When used in the studies involving just samarium and boron, the molybdenum crucible does not qualitatively appear to be attacked nearly as rapidly as when used for compacts of boron and samarium sesquioxide. The conclusions regarding rapid attack by a phase containing boron and oxygen is not unreasonable in light of the consideration that only a minimal amount of the boron content of the pellet is in direct contact with the crucible. Furthermore, the flow properties of oxides of boron are much more extensive than those for boron alone, and a considerable amount of evidence exists for concluding that the reaction of oxide-boron compacts involves a stage where molten phases containing boron and oxygen exist and/or volatilize. The importance of these BO_x phases should not be minimized. The mode by which they attack the crucible and the duration of that attack seems to influence the boride products resulting from heating various mixtures of samarium sesquioxide and boron in a molybdenum crucible.

The presence of samarium orthoborate detected on the surface of the pellets as well as on the molybdenum lid of the heating cells suggests that the orthoborate may be a volatile species. This provides a mechanism to account for the deposition of high temperature samarium sesquioxide on the sides and lids of the molybdenum crucible. Hot molybdenum may catalyze the decomposition of samarium orthoborate as follows:



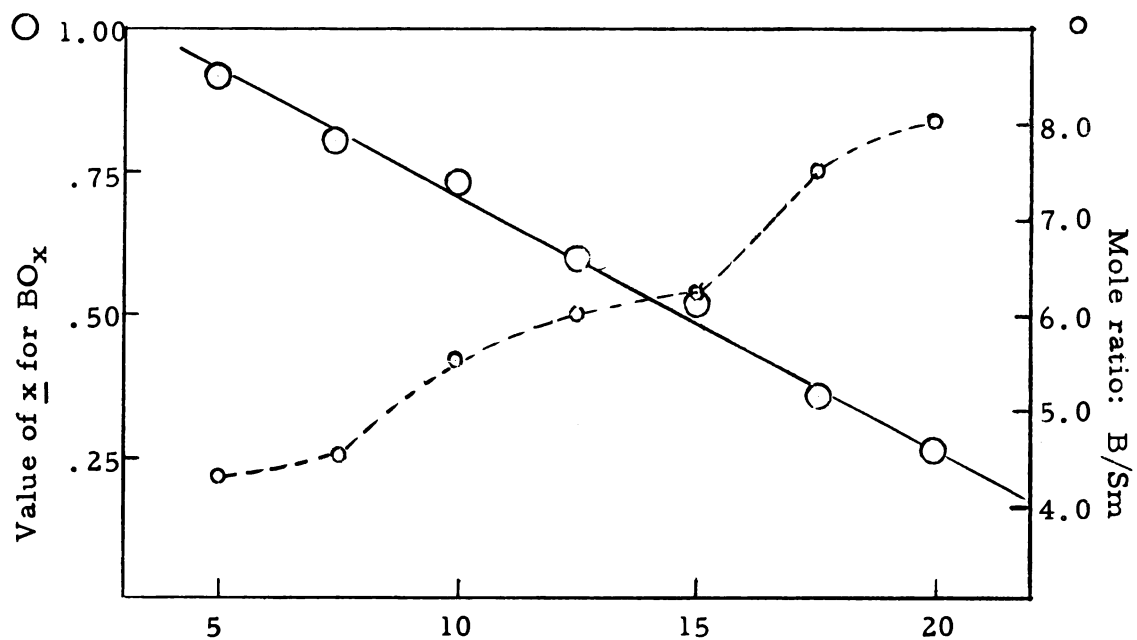
The samarium sesquioxide stays behind and the boron sesquioxide volatilizes if it can escape faster than it can undergo reaction with the lid or body of the heating cell. The Vycor tube confining the reaction always carries a white amorphous deposit early in the reactions which turns

brown as the reaction proceeds and which ultimately gives a positive methyl borate flame test. The Vycor appeared to collect more white material quite early in the reaction for those instances where the initial boron content of the sesquioxide-boron mixtures was high, rather than low. As long as any brown color was associated with the Vycor deposit, dissolution of it in 6 M nitric acid was always accompanied by the evolution of copious amounts of nitrogen(IV) oxide. (This result could be caused by samarium or suboxides of boron present in the deposit.)

At one point in the study, a sample of samarium sesquioxide was inadvertently heated in a crucible of boron nitride which had not been outgassed. The observation that most of the samarium sesquioxide was lost in the heating and the occurrence of tiny beads of material on the sides of the crucible is understandable if one considers that the principal impurity of the boron nitride was boron sesquioxide and that samarium orthoborate may be a volatile species.

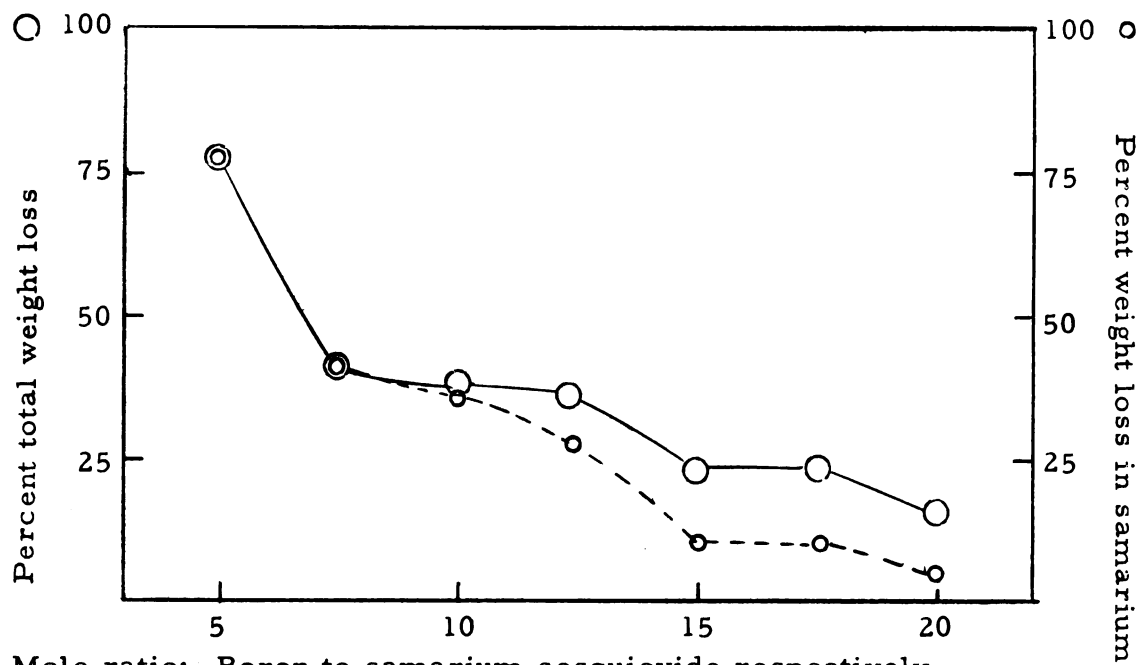
When pellets of samarium sesquioxide and boron were heated at 1650° in boron nitride (Experimental Section F), there were no indications of the complicating effects of borate phases.* In fact, if one plots the value of $\underline{x}$ for BO_x as a function of the starting composition of the pellet, the result is essentially a straight line with slope nowhere equal to zero. This result, shown in Figure VIII, suggests that the oxide of boron liberated from the reaction mixtures of samarium sesquioxide-boron pellets heated in boron nitride is not the same regardless of the starting composition and that since no plateau area is observed, one must conclude that no one simple equation can possibly describe the reaction. The greater the percentage of boron available for reaction with samarium sesquioxide, the more radical is the reduction in weight loss. Table II (and Figure IX) shows that the percent of overall weight-loss very closely

* Samarium orthoborate is never observed if the composition of the starting materials is greater than ten moles of boron for every one mole of samarium sesquioxide and the temperatures used are in excess of 1540°.



Mole ratio: Boron to samarium sesquioxide respectively.

Figure VIII. Mole ratios of boron to oxygen and boron to samarium versus composition of starting materials heated in boron nitride.



Mole ratio: Boron to samarium sesquioxide respectively.

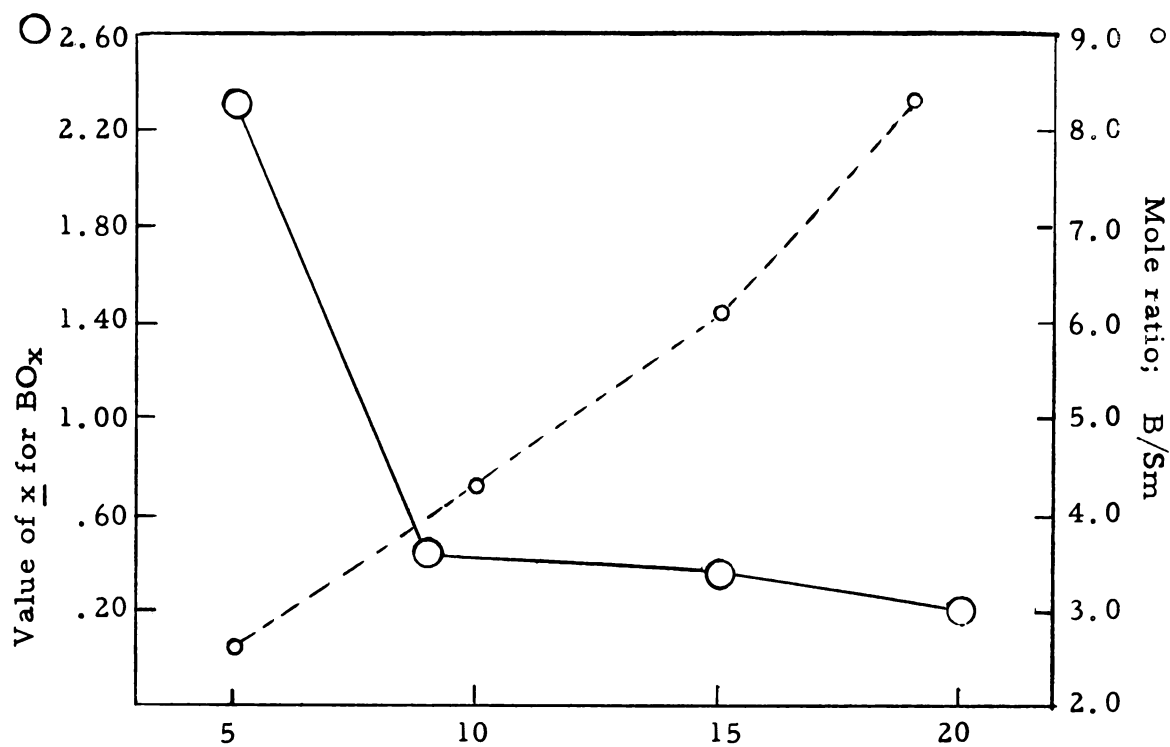
Figure IX. Weight losses versus composition of starting materials heated in boron nitride.

parallels the percent loss in samarium in the range of low boron composition. One may therefore conclude that if the percentage of boron in the starting materials is increased, the samarium losses are sharply diminished concomitant with a marked increase in the amount of weight loss ascribable to oxides of boron. Since this is true and since for the material lost oxygen ratios are not reflective of simple species such as $B_2O_2(g)$ or $B_2O_3(g)$, it appears that changing the composition of starting materials results in a change in the ratio of two or more competing reactions rather than a change in merely the actual oxide of boron lost. Yet in view of the complex chemistry of this system, one must not exclude the possibility of species such as B_3O or B_7O being volatile at the temperature of the investigations.

In the above discussion, no consideration was given to oxygen lost in the form of SmO or O_2 . There should be no difficulty in accepting the absence of any appreciable amounts of molecular oxygen, but even if all the samarium lost were accompanied by an equimolar amount of oxygen, the boron to oxygen ratio would still show the same trend even though the slope of the curve would be lessened.

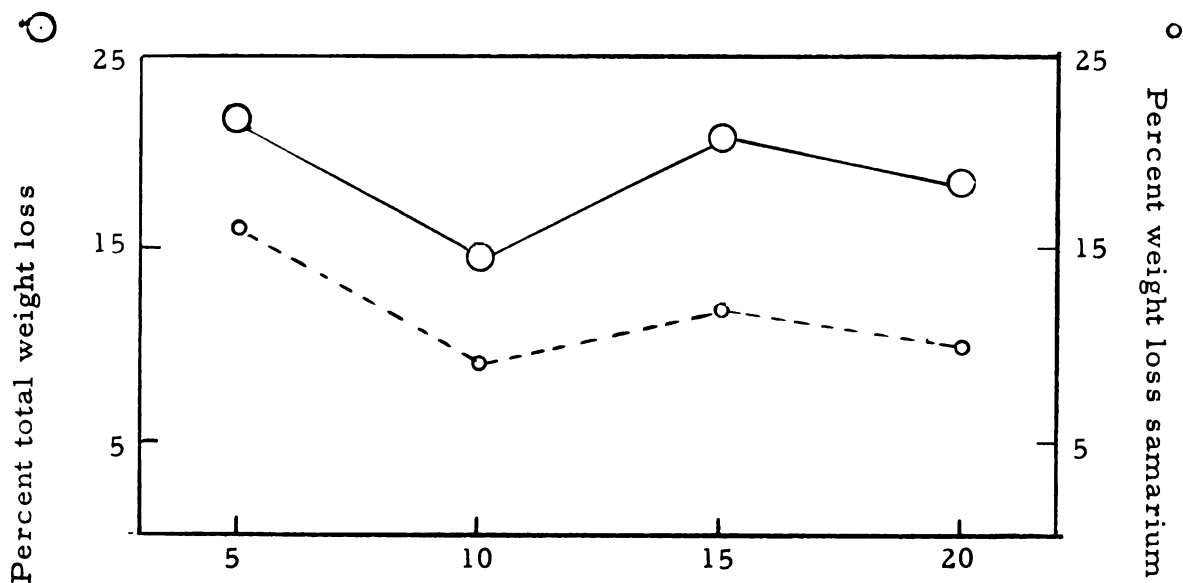
The same general results were observed for the work done using zirconium diboride except that here the conclusions seem less certain. The ratio of boron to oxygen lost was more closely constant, as seen in Figure X, but the value of x in BO_x still increased with a decrease in the boron content of the starting composition. Aside from the series using a 1:5.0 starting mixture, the value of x was less than for comparable compositions examined in boron nitride.

The most striking fact about the studies performed in zirconium diboride was the low percentages of samarium lost on heating (Table III, and Figure XI). Coupled with the observed weight increases in the crucible and the grow-in of the blue color in the base of that crucible, the low percentages of samarium lost may reflect the formation of samarium



Mole ratio: Boron to samarium sesquioxide, respectively.

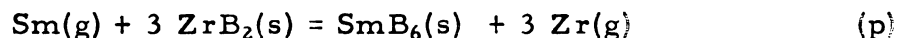
Figure X. Mole ratios of boron to oxygen and boron to samarium versus composition of starting materials heated in zirconium diboride.



Mole ratio: Boron to samarium sesquioxide, respectively.

Figure XI. Weight losses versus composition of starting materials heated in zirconium diboride.

hexaboride if samarium could be released from the pellet of boron and samarium sesquioxide, and if any excess boron were present in the zirconium diboride. The reaction:



is not likely either thermodynamically or in light of the observations made on boron density (48). However, since no analysis of ZrB_2 was performed or provided, the first possibility is not to be excluded.

Data presented in Table I for the "E" series also shows the marked effect of the boron concentration of starting materials upon the weight losses within a system, even over a variety of temperatures. The weight loss of samples having compositions of 1.0 mole of samarium for every 5.0 moles of boron is about one-eighth of the weight loss of samples one-half as rich in boron.

Before leaving the discussion of the studies performed in zirconium diboride and in boron nitride, mention should be made regarding the implications of the variation in the ratio of moles of samarium to boron observed in the products. Two assertions are worthwhile.

No phase higher than samarium hexaboride was observed in the x-ray powder photographs, and no boron was ever detected in any of the photographs obtained in these two series of reactions. The first assertion is neither surprising nor exceptionally significant since samarium dodecaboride was never knowingly obtained at any time. However, the second assertion is important since it demonstrates the difficulty in detecting free boron with x-ray analysis. Even when powder photographs were made of boron-samarium sesquioxide starting mixtures of 1:10 composition, no boron could be detected, although boron was observed on the powder photograph of a sample whose starting composition was 1:20.

Returning to the reactions occurring in molybdenum, it may be asserted that the longer the extent of heating of an oxide-boron compact

in molybdenum, the greater the chance of obtaining a product rich in samarium tetraboride. In the early work, a mixture of the two borides, prepared in seven hours, was observed to become depleted in samarium hexaboride as a consequence of eight hours of additional heating. Even a 1:10 starting composition resulted in the preparation of samarium tetraboride with no detectable samarium hexaboride when a 14.5 hour heating was employed at temperatures as low as 1510° .

The general observation that long duration heatings in molybdenum favor production of the tetraboride is borne out clearly in experiments E-13 and E-14. X-ray photographs of the products showed no phase other than samarium tetraboride when heatings were 10.5 and 20.0 hours respectively.

This particular generalization cannot be extended directly to the study performed in the tungsten cell since none of these heatings was longer than 4.0 hours. However, it is noteworthy that the amount of samarium tetraboride produced in the 4.0 hour heating at 1750° (H-2) was ostensibly greater than that amount produced in the 1.5 hour heating at the same temperature, and that in none of the instances to follow (H-3 through H-7) was any tetraboride detected either visibly or in the diffraction powder patterns of the products.

At this point, an analysis of diffusion phenomena seems necessary and pertinent. The data of Tables I and IV show that in every instance but one (E-19) where weight data were recorded for the molybdenum or tungsten crucibles, the crucibles gained weight. It is primarily significant that for the one instance where an overall weight loss was recorded, the heating represented the longest time a reaction of the "E" series was held at a temperature as high as 1695° . If boron is the element responsible for these weight gains, then it seems plausible to suggest that in the instance where a weight loss was recorded for the crucible, the conditions of time, temperature, and previous treatment were all favorable for this result. The molybdenum borides are capable of decomposing in this

temperature range, and a proper set of conditions could easily result in loss in crucible weight as boron diffuses from the crucible into the contents.

For the studies performed in the tungsten crucible, the greatest mass gain in crucible and lid (under 2170°) was observed for the 4.0 hour run, H-2, an experiment performed at a full 200° less than two other comparable (4.0 hour) experiments. Since the product of experiment H-2 contained the highest percent samarium and the lowest percent boron of any of the tungsten heatings, the high weight gain in crucible and lid for this experiment seems to be more a consequence of being the second experiment performed in this heating cell than as a consequence of being at 1750° . Since the crucible is still close to being "new", boron can diffuse into the cell at a very rapid rate. The crucible weight gain observed in experiment H-1 is about the same as that observed in H-2 even though there is a 2.5 hour difference in the duration of heating. Yet under the same conditions of time and temperature as those employed for experiment H-2, the total weight gain observed in H-5 was only about seven-ninths of the amount observed in H-2; furthermore, there was a marked difference between the two experiments in the percent samarium in the product.

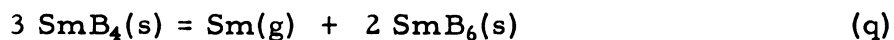
It should be noted that the data in Table IV do assert that an increase in weight gain is favored by either higher temperatures or increased duration of heating and that increase in both of these variables has an associative effect.

The H-6 experiment clearly represents the low extreme of the study. The total weight gain in crucible and lid is lowest; the percent loss in sample weight is the lowest; the percent samarium in the product is lowest, and the percent boron is the highest. It is of interest to note that for the two instances where samarium tetraboride was observed in the products

after heating (H-1 and H-2), the percent samarium in the products was the highest for any of the seven heatings.

Regardless of how many numbers are associated with an experiment, they are of essentially no value unless they can be interpreted meaningfully and with internal consistency. In attaching a finalizing significance to these experiments, the two most pressing questions are: Why does samarium tetraboride decompose in boron nitride at temperatures far lower than those at which it exists stably in molybdenum? Why is samarium tetraboride observed as a constituent of the upper surfaces of several pellets of boron and samarium sesquioxide heated in molybdenum, of some samples of samarium hexaboride heated in tungsten, and, indeed, of some of the sesquioxide-boron pellets heated in boron nitride, while samarium hexaboride is clearly the top surface component after a sample of samarium tetraboride has been heated in boron nitride? There is also a need to justify why samarium hexaboride is the only boride of samarium present in addition to borides of molybdenum or tungsten after heating a mixture of samarium hexaboride and molybdenum or tungsten powder in a crucible of boron nitride. [Similar phenomena are independently reported by Antony and Cummings (48).]

In answer to these questions and in view of the experimental results, samarium tetraboride must be thermodynamically less stable than samarium hexaboride; but the following equilibrium exists:



It is suggested that the mutual existence of samarium tetra- and hexaboride is possible not only as a consequence of equilibrium but also because of the inter-relating effects of diffusion and surface evaporation. It has been noted that the reaction between samarium metal and samarium hexaboride does, indeed, result in the formation of some samarium tetraboride at temperatures as low as 1435⁰.

Lafferty (1) has shown that heating lanthanum hexaboride in contact with a base material capable of absorbing boron by diffusion into its interstices can effectively permit the evaporation of lanthanum atoms. The mechanism is simply that the base material will absorb boron from the lattice of the hexaboride and that as the boron framework of the hexaboride collapses, the metal atoms are released.

The conclusion of this work is that exactly the same phenomenon is demonstrated by samarium hexaboride. If heating samarium hexaboride in tungsten results in the production of the less stable samarium tetraboride on the surface of the sintered product, and if this process ceases to be observable as the crucible material is used again, even though the crucible weight gains continue, then it seems reasonable to suggest that the gains in crucible weight are due to boron diffusion and that the observation of samarium tetraboride on the surface is only a consequence of the diffusion of samarium atoms to the surface at a rate faster than they can actually evaporate. In boron nitride, samarium tetraboride only partially decomposed to the hexaboride after 0.5 hour and in this case, the top surface was blue (SmB_6) rather than grey (SmB_4). Clearly then, evaporation of samarium from samarium tetraboride heated in boron nitride is primarily a surface phenomenon whereas in the tungsten heatings, samarium released from the hexaboride lattice-collapse must diffuse to an area of evaporation faster than it can actually evaporate. When the temperature is very high, e. g. H-7, large weight gains in the crucible may occur without observing any tetraboride on the surface of the "product" since now the evaporation rate equals the rate of diffusion.

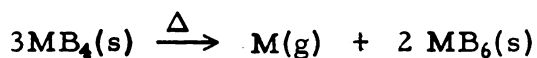
Some discussion should be devoted to the ease with which samarium tetraboride can remain the principal phase of mixtures prepared from heating samarium and boron (even at a variety of temperatures and compositions) in a molybdenum crucible. Since the tetraboride is less stable than the hexaboride, then subjecting samarium tetraboride to high

temperatures should result in conversion to samarium hexaboride unless some mechanism exists for preventing tetraboride decomposition. The only instances for which samarium tetraboride appears to remain stable when heated in molybdenum are those in which the material was prepared from a direct reaction of the elements under a helium pressure of about 600 mm. or those in which a very long duration of heating was employed. Since an equilibrium exists between the two borides, the effect of the helium inhibiting the vaporization of samarium may be responsible for the ease with which samarium tetraboride is prepared in molybdenum from a direct reaction of the elements. Heating these same mixtures of tetraboride in vacuo results in their conversion to hexaboride unless boron diffusion into molybdenum becomes so great that the tetraboride appears to reduce its weight without changing phase.

The absence on the powder patterns of lines of a lower boride of samarium after samarium hexaboride was heated with molybdenum and/or tungsten, and the continued presence of lines of SmB_6 in these same powder patterns that show MoB or WB_2 , demands that the rate of evaporation of samarium from the areas of its production equals the rate of diffusion of the gaseous atoms through the solid compacts.

It must be recognized and appreciated that the ultimate result of any of these experiments says nothing about the time dependence of the rates of diffusion and/or evaporation, but merely reflects the gross amount of change that occurs in a given amount of time at a given temperature.

The hypothesis present in Part I of this thesis must now be recalled. It was suggested that rare earth metals possessing a high vapor pressure would show a tetraboride decomposition according to the path:



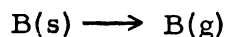
and a hexaboride decomposition at a higher temperature according to the path:



It is easy to see, now, the complications involved in proving or disproving this hypothesis. There must exist a container inert to the borides and to boron at temperatures sufficiently high to permit observation of the overall sum of the reactions:



Yet at the temperatures needed for this, we are faced with another possible reaction:



whose rate will determine not only the remaining product to be examined after materials are subjected to high temperatures but will also determine the extent of possible recombination between $\text{M}(\text{g})$ and $\text{B}(\text{g})$ in a cooler area such as a lid orifice. It may be that this is the process which led to the formation of crystals of samarium hexaboride in the orifice of the boron nitride crucible (as described in Part III). One is faced with choosing between a gaseous metal boride molecule, a recombination of gaseous boron and samarium, or the reaction between gaseous samarium and solid boron produced in the decomposition of the boron nitride. Considering the extent of the crystal growth in the orifice, the perfection of the crystals themselves, and the heretofore absence of gaseous metal boride molecules, the recombination process seems the most likely one.

Nonetheless, no absolute assertion can be made without a mass spectrometer and the need for this kind of examination should be obvious.

The decomposition of samarium tetraboride into samarium hexaboride when the former is heated in a cell of boron nitride and the formation of the hexaboride when samarium and boron are caused to react directly in boron nitride offers substantial proof to the notion that samarium tetraboride is the less stable of the two borides and that its decomposition

product is the hexaboride. Unfortunately, the existence of the tetraboride-hexaboride equilibrium, the lack of a mass spectrometer, and the absence of a container totally inert to boron at the high temperatures necessary to decompose samarium hexaboride, whose melting point has been estimated to be about 2800°K (49), make proof of the second decomposition path a rather severe problem.

Daane and Johnson (46) have reported the partial conversion of lanthanum tetraboride to lanthanum hexaboride when the tetraboride was heated for fifteen minutes in vacuo in a tantalum crucible. They observed a surface layer of lanthanum hexaboride, just as we observed a surface layer of samarium hexaboride. Complete conversion to lanthanum hexaboride could be affected when a pressed mixture of boron and lanthanum tetraboride was heated in vacuo for fifteen minutes at 1500° .

It is both interesting and satisfying to note the consistency between the work of Lafferty (1) in 1951 and the work of Daane and Johnson (47) in 1961. Without evidence to the contrary, the samarium-boron system appears to behave quite similarly. Yet no definite proof has been obtained to justify the assertion that its particular behavior is an immediate consequence of the high vapor pressure of samarium metal relative to the vapor pressure of other rare earth metals.

C. Proposals for future work

1. Not enough attention has been devoted to the crucible materials for use in high temperature studies of the rare earth borides. There is a severe need for quantitative measurements on boron and rare earth interaction with a variety of crucible materials. Until these fundamental investigations are made, crucible materials will continue to be a variable with effects of undetermined magnitude.

2. With particular reference to the samarium-boron system, the gases evolving from the reactions between various mixtures of samarium sesquioxide and boron should be examined with a mass spectrometer if any unequivocal conclusions are to be made regarding the mechanism by which samarium tetra- or hexaboride is formed.

3. A thorough examination should be made of mixtures of samarium hexaboride and boron. One could compare the lattice parameters of pure and impure samarium hexaboride and determine the relationship between the parameters and the percent boron in the materials. Since boron seems so insensitive to powder diffraction detection, it would be of interest to know what percent of boron could be added to a sample of pure samarium hexaboride before detection of the boron could be made. The compilation of these data might result in a more complete characterization of the nature of samples whose x-ray powder photographs show only samarium hexaboride. There is still uncertainty regarding the form of sample impurity and its effect on sample behavior. Such fine points could be carefully and neatly examined and should prove quite useful towards preventing future misinterpretations.

4. If a truly inert crucible can be obtained, then studies should be performed aimed at measuring the equilibrium constant of the samarium-boron system. These studies might be approached using a Knudsen cell to measure the vapor pressure of samarium escaping from a sample of samarium tetraboride. Of course, the use of this method is precluded by a need to know the exact molecular weight of the vaporizing species.

There is a possibility that the equilibrium constant might be more easily measured by quenching a series of samples heated in a closed system. Since the crystal structure of the two borides is different, perhaps an x-ray diffractometer could be used to quantitatively analyze the composition of the quenched phases.

The ultimate goal in equilibrium and vapor pressure studies would naturally be to obtain values for the free energy of formation of the borides.

5. Finally, the use of an appropriately balanced magnetic field and the consequent levitation of a sample of material offers exciting possibilities for a rigorous examination of the decomposition of rare earth borides without the problem of crucible interaction. However the experimental details of this sort of technique are not simple and a levitation approach to the problem is probably still only a distant possibility.

LITERATURE CITED

1. J. M. Lafferty, J. Appl. Phys., 22, 299 (1951).
2. H. Moissan and P. Williams, Compt. rend., 125, 629 (1897).
3. M. Geelmuyden, Compt. rend., 130, 1026 (1900).
4. E. Jungst and R. Meines, Chem. Zentr., I, 195 (1905).
5. A. Stock and W. Holle, Ber. deut. chem. Ges., 41, 2095 (1908).
6. L. Andrieux, Compt. rend., 182, 126 (1926).
7. S. M. von Stackelberg and F. Neumann, Z. physik. Chem., 19B, 314 (1932).
8. G. Allard, Bull. soc. chim. France, 51, 1213 (1932).
9. S. Flodmark, Arkiv Fysik, 14, 513 (1959).
10. A. Zalkin and D. H. Templeton, Acta Cryst., 6, 269 (1953).
11. B. Post, D. Moskowitz, and F. W. Glaser, J. Am. Chem. Soc., 78, 1800 (1956).
12. F. Bertaut and P. Blum, Compt. rend., 229, 666 (1949).
13. B. Post and F. W. Glaser, J. Metals, 4, 631 (1952).
14. I. Binder, S. La Placa, and B. Post, Proceedings of the Conference on Boron, Plenum Press, Inc., New York, New York (1960). Also, private communication.
15. R. T. Sanderson, Chemical Periodicity, Reinhold Publishing Corporation, New York, New York (1960).
16. J. J. Katz and E. Rabinowitch, The Chemistry of Uranium, Part I, McGraw-Hill Book Company, Inc., New York, New York (1951).
17. F. H. Ellinger and W. H. Zacharaisen, J. Am. Chem. Soc., 75, 5650 (1953).

18. P. W. Gilles, Private Communication.
19. E. J. Felten, I. Binder, and B. Post, J. Am. Chem. Soc., 80, 3479 (1958).
20. G. V. Samasonov, V. P. Dzeganovskii, and I. A. Semashko, Kristallografiya 4, 119, (1959); C. A. 55, 7125g (1961); also Doklady Akad. Nauk S.S.S.R., Ural. Filial 119, 506 (1958); C. A. 53, 3962a (1959).
21. G. A. Kudintseva, M. D. Polyakova, G. V. Samsonov, and B. M. Tsarev, Fiz. Metal' I. Metalloved., 6, 272 (1958); C. A. 53, 9871i (1959).
22. V. S. Neshpor and G. V. Samsonov, Zhur. Fiz. Khim. 32, 1328 (1958); C. A. 52, 4370h (1958); C. A. 53, 953e (1959).
23. Yu. B. Paderno, T. I. Serebryakova, and G. V. Samsonov, Doklady Akad. Nauk. S.S.S.R., 125, 317 (1959); C. A. 55, 11159h (1961).
24. G. V. Samsonov, Uspekhi Khim., 28, 189 (1959). (Translated by F. Hilton.)
25. J. L. Margrave, J. R. Soulen, and D. Sthapitanonder, J. Phys. Chem., 59, 132 (1955).
26. E. M. Levin, R. S. Roth, and J. B. Martin, Am. Mineralogist, (1961, to be published).
27. R. Ray and P. Sinha, J. Chem. Soc., 742 (1941).
28. H. H. Kahlenberg, Trans. Am. Electrochem. Soc., 47, 23 (1925).
29. R. A. Pasternak, Acta Cryst., 12, 612 (1959).
30. M. G. Inghram, R. F. Porter, and W. A. Chupka, J. Chem. Phys., 25, 498 (1956).
31. M. D. Scheer, J. Phys. Chem., 61, 1184 (1957).
32. M. D. Scheer, J. Phys. Chem., 62, 490 (1958).
33. F. A. Kanda, A. J. King, V. A. Russell, and W. Katz, J. Am. Chem. Soc., 78, 1509 (1956).

34. J. M. Letinaker, N. H. Krikorian, and M. G. Bowman, Los Alamos Scientific Laboratory, Los Alamos, New Mexico. Paper presented at a Symposium on High Temperature Poisons, Albuquerque, New Mexico. February 1961.
35. N. V. Sidgwick, The Chemical Elements and Their Compounds, Clarendon Press, Oxford, England (1950).
36. H. A. Eick and P. W. Gilles, J. Am. Chem. Soc., 81, 5030 (1959).
37. H. Blumenthal, Anal. Chem., 23, 992 (1951).
38. L. Brewer, D. L. Sawyer, D. H. Templeton, and C. H. Dauben, J. Am. Ceram. Soc., 34, 173 (1951).
39. Climax Molybdenum Company Bulletin Cdb-8, March 1956. Available from the Climax Molybdenum Company, 500 Fifth Avenue, New York 36, New York.
40. A. Chrétien and J. Helgorsky, Compt. rend., 252, 742 (1961).
41. A. A. Giardini, Boron Nitride, a review; Bureau of Mines Information Circular 7664 (1953).
42. R. Lorenz and J. Woolcock, Z. anorg. Chem., 176, 289 (1928).
43. J. M. Leitnaker, Los Alamos Scientific Laboratory, Los Alamos, New Mexico. Technical Report No. LA-2402 (1960).
44. L. Brewer and H. Haraldsen, J. Electrochem. Soc., 102, 399 (1955).
45. J. M. Leitnaker, M. G. Bowman, and P. W. Gilles, J. Electrochem. Soc., 108, 568 (1961).
46. R. W. Johnson and A. H. Daane, J. Phys. Chem., 65, 909 (1961). Also, private communication.
47. F. W. Glaser and B. Post, AIME Trans., 197, 1117 (1953).
48. K. C. Antony and W. V. Cummings, Vallecitos Atomic Laboratory, Pleasanton, California. AEC Research and Development Report GEAP-3530.
49. E. W. Hoyt, J. Chorné, and W. V. Cummings, Vallecitos Atomic Laboratory, Pleasanton, California. AEC Research and Development Report GEAP-3548.

50. F. H. Spedding and A. H. Daane, The Rare Earths, John Wiley and Sons, Inc., New York, New York (1961).
51. J. O'M. Bockris, J. L. White, and J. D. Mackenzie, Physico-Chemical Measurements at High Temperatures, Butterworth Scientific Publications, London (1959).
52. D. H. Templeton and C. H. Dauben, J. Am. Chem. Soc., 76, 5237 (1954).
53. N. N. Tvorogov, Zhur. Neorg. Khim., 4, 1961 (1959); C. A. 54, 11788a (1960).
54. I. Binder, J. Am. Ceram. Soc., 43, 287 (1960).
55. S. La Placa, I. Binder, and B. Post, J. Inorg. & Nuclear Chem., 18, 113 (1961).
56. X-Ray Powder Data File, American Society for Testing Materials, Philadelphia, Pennsylvania (1961).

APPENDICES

APPENDIX A

SUPPLEMENTARY EXPERIMENTAL DATA

The series of experiments that are subsequently discussed represent attempts to prepare pure samarium tetraboride. Because of the importance of maintaining the identification of the various phases observed in these experiments, the original numbers assigned to the x-ray powder photographs have been retained. An A-number associated with a phase implies that the x-ray photograph has been taken for that phase even though direct mention of the photograph may have been avoided. In all context, the word photograph is to be understood to be associated only with x-ray powder diffraction photographs; no other kind of photography was employed.

Although compositions are casually referred to as 1:10, 1:8, 1:6, etc., in all cases they represent mixtures of samarium sesquioxide and boron carefully prepared in respective mole ratios of 1.00:10.00, 1.00:8.00, 1.00:6.00, etc., and weighed to the nearest one-tenth of a milligram.

D. Reactions of samarium sesquioxide and boron in a molybdenum crucible

1. A 1:10 pellet-mixture (0.29711 g.) of samarium sesquioxide and crystalline boron was placed into a freshly outgassed molybdenum crucible. (This crucible had been used only once prior to this run and only for an experiment in which the temperature of reaction was too low to result in any identifiable phases.) The crucible was equipped with a strip of tantalum foil (0.005") between its lid and the main body of the crucible. The temperature was slowly increased over an interval of 15 minutes to

1400° and maintained at that temperature for an additional 45 minutes. Subsequent to this heating, the pellet appeared light grey on its top surface which was scraped and photographed (A-342). The lid orifice of the crucible had clogged with a slight amount of yellow white material (A-343). Both of these photographs show the same phase, samarium orthoborate, but the photographs also show the absence of SmB_4 , SmB_6 , and $\delta\text{-MoB}$. X-ray data for SmBO_3 and $\delta\text{-MoB}$ is supplied in Appendix B. It is interesting to note that the phase of samarium orthoborate observed was the "1550° form" as recorded by Levin et al. (26).

Since the mixture was only light grey, it was reheated in the same crucible at 1540° for one hour. The pellet had darkened considerably and a photograph of the top surface (A-349) showed the principal phase to be SmB_4 . (The photograph leaves some question as to whether or not there was any SmB_6 present, and if there was it must have been in very small amounts; the cubic SmB_6 phase is much more sensitive to x-ray detection than the tetragonal SmB_4 phase.) The pellet was returned to the crucible and was heated for a third time for slightly under one hour at 1580°. The lid had become stuck to the crucible by a ring of light yellow material (A-345); the pellet itself was removed and the surface photographed (A-346). Photograph A-345 appears to contain some lines of $\text{B-Sm}_2\text{O}_3$ (high temperature form). However, photograph A-346 shows almost completely SmB_4 ; only the slightest trace of SmB_6 can be detected.

Still a fourth heating was performed by returning the pellet to the heating cell and heating for 1.5 hours at 1780°. The pellet was again scraped for x-ray analysis (A-348) and enough of the dark deposit from the walls of the Vycor containing-tube was removed for a photograph (A-347). The pellet had diminished in size ostensibly. Examination of A-348 showed a faint trace of SmB_6 contaminating the principal phase, SmB_4 ; however, A-347 could not be classified from the phases shown on the photograph.

2. The molybdenum crucible used above was heated with 0.07 g. of boron at 1425° for one hour. The crucible and contents experienced a weight loss of 0.00086 g., and the boron had become coated with a dark blue layer; a second heating for another hour at 1590° produced some additional blue on the surface of the boron and a flaky transparent deposit on the lid of the crucible. The lid deposit was photographed (A-351) but the very few lines on that photograph are unidentifiable.

Still a third heating was performed for one hour at 1880° . At the end of this third heating, the inside of the crucible had become quite bright; the dull film, which had coated the innards of the reaction well prior to the heating, was gone. The residual boron had turned blue, and the photograph (A-352) of some of the material from the surface of this residue showed only lines of SmB_6 . There was additionally a bit of white-yellow deposit at the top of the crucible (A-353); this material was mostly $\text{B-Sm}_2\text{O}_3$.

3. Using the crucible pre-treated as outlined in (2), a 1:10 mixture of (0.21337 g.) of Sm_2O_3 and crystalline boron was pressed into a pellet and heated (without opening the system between heatings) as follows: 10.0 minutes at 1480° ; 10.0 minutes at 1565° ; 15.0 minutes at 1675° ; 20.0 minutes at 1735° ; 20.0 minutes at 1765° ; and 10.0 minutes at 1810° . The deposit on the Vycor tube at the end of this series was very thin. What remained of the pellet resided at the bottom of the crucible in a snowflake-like disk and was photographed as A-367. The only phase shown in this photograph is SmB_6 . There were three additional photographs associated with this experiment: a crystalline deposit on the inside of the Vycor tube (A-366) showing no identifiable lines, and A-368 and A-369 which represent respectively the deposits on the inside surface and lip of the molybdenum lid. Both A-368 and A-369 are devoid of the $\text{B-Sm}_2\text{O}_3$ pattern, but otherwise cannot be identified.

4. Once again the crucible was heated with 0.06 g. of boron. Heatings were performed for 30 minutes at 1435° and 30 minutes at 1780° . The surface of the boron powder had become coated with a blue color, presumably SmB_6 , but the interior of this partially sintered mound of boron was distinctly black and merely boron.

5. Another 1:10 pellet (0.18466 g.) of Sm_2O_3 and boron was prepared for heating in the same molybdenum crucible used above, but this time at lower temperatures.

The first heating was performed for 20 minutes at 1360° and the second for 30 minutes at 1405° . The Vycor tube had become coated with a barely discernible white deposit which was not removed prior to the second heating. When the system was opened to the atmosphere, the inside of the crucible lid was observed to be coated with a glassy material which looked as if it may have been molten at one time. The lid, still warm, was a bit sticky, with an amount of yellow material clogging the orifice. The pellet was grey on top, the color of SmB_4 , but tan-white on the bottom. Material was scraped from both the top (A-371) and the bottom (A-372) of the pellet. Both A-371 and A-372 show the same phase, the 1550° form of SmBO_3 , although A-371 appears to contain a few more lines of this phase than A-372. Both of these photographs represent the same phase that appeared in A-342, described in (1).

The crucible and pellet were again returned to the line and heated for one hour at 1570° ; the white deposit on the Vycor tube had become thicker and had turned to a golden brown. The pellet appeared black on both the top and bottom surfaces. The only difference between the surfaces was that the bottom was flaky and contained blue specks, while the top appeared more homogeneous. The top of the pellet was scraped and photographed (A-373) showing the presence of both SmB_6 and SmB_4 .

Once more the same pellet was returned to the vacuum line and heated in 15 minutes to 1790° . Examination of the material subsequent

to this brief heating revealed the presence of grey color in the pellet and a deposit (A-376), principally SmBO_3 , on the lid of the crucible. The inside of the crucible was coated with material photographed as A-377. The pellet proper was photographed as A-374 which shows the presence of both borides, but in which the SmB_6 lines appear weaker than they do in photograph A-373. The photograph (A-377) of the material coating the innards of the crucible shows only lines accountable as $\text{B-Sm}_2\text{O}_3$.

6. Another 1:10 pellet (0.02955 g.) was prepared and initially heated for 45 minutes at 1550° in the same molybdenum crucible used above. On examination, the pellet was observed to be stuck to the bottom of the crucible with material which appeared to have oozed out of the reaction mixture. The lid was coated with a flaky, glassy-looking material, and a white sandy residue was on the bottom of the crucible. The following photographs were prepared: A-388, from the material which comprised the lid deposit; A-389, from the material with which the pellet was stuck to the crucible; and A-390, comprising the sandy residue. Photograph A-388 shows exactly the same phase as that previously recorded for A-376. Photograph A-389 and A-390 have not been characterized but do not appear to contain any lines of $\text{B-Sm}_2\text{O}_3$.

The pellet was returned to the line and heated from 1715° to 1830° in about 30 minutes. At the end of this heating, the molybdenum lid orifice had clogged with the yellow material previously encountered. Much deposit had lined the inside of the Vycor; this was scraped, ground, and photographed as A-394. Most striking of all developments was the inside of the crucible. While the lid was again coated with a deposit, a layer of crystalline material had grown across the entire interior of the crucible proper, completely closing off the path of any exit material. Nonetheless, there was still enough of the pellet at the bottom of the crucible from which to prepare a powder photograph. Four photographs were taken of the components of the reaction: A-397, representing the

top of the pellet; A-400, using scrapings from the bottom of the pellet; A-401 and A-402, from what appeared to be two different phases deposited on the lid of the crucible. The layer of deposit that had formed midway up the crucible was later identified as δ -MoB (A-410).

Characterization of A-394 was never accomplished; the photographs A-397 and A-400 both show the presence of SmB_6 , SmB_4 , and a few lines from another unidentifiable phase. The materials photographed as A-401 and A-402 both contained δ -MoB, but A-402 shows the additional presence of another contaminating phase. Subsequent to this run, the crucible was heated for a total time of about four hours, two of which were at 1435° - 1705° , one at 1745° , and one at 1900° - 1950° . The crucible was bright and shiny after this treatment, but a portion of the lid had cracked and was photographed as A-411. This photograph shows only lines accountable as δ -MoB.

7. Still another 1:10 pellet (0.14985 g.) was heated in the same crucible for seven hours at 1465° . The top surface of the resulting pellet was photographed at A-457 which shows a mixture of SmB_4 and SmB_6 . The material was returned to the crucible for another heating at 1440° for six hours; the temperature was then raised to 1640° for an additional two hours after which the heating was stopped. This time, the photograph (A-456) shows only lines of SmB_4 with a minute trace of SmB_6 .

8. The crucible was returned to the vacuum line and heated (without boron) to a temperature of approximately 1850° . At about 1640° , a deposit began to collect on the Vycor confining-tube. After about 0.5 hour at this temperature, the cleaning operation was stopped and the Vycor was scraped for enough material to photograph as A-486, material whose photograph shows the presence of some C- Sm_2O_3 (cubic low-temperature modification).

9. Subsequent to this cleaning, another 1:10 pellet (0.28048 g.) was prepared and heated for 2.5 hours at 1435° . No x-ray photograph was

made of this material for it appeared to be SmB_6 . The crucible was immediately re-heated for 20 minutes at temperatures of 1900-1960°.

This time however, heating caused the crucible to begin melting.

Apparently the boron concentration of the crucible had become sufficiently high to cause the molybdenum boride to begin flowing. Some material on the lid was scraped and photographed as A-491. This photograph shows lines of what is principally Mo_2B . The crucible had deteriorated to the extent that it could no longer be used and therefore was abandoned.

D₂. Use of other compositions of samarium sesquioxide and boron

10. A new crucible was machined and outgassed for two hours at 1850° to initiate these studies. Control x-ray photographs: A-495, A-497, A-498, A-499 and A-500 were prepared for comparison purposes and refer to, respectively, molybdenum metal, compositions of samarium sesquioxide and boron in mole ratios of 1.00:8.00, 1.00:6.00, and 1.00:10.00, and C- Sm_2O_3 .

11. A 1:6 pellet (0.19870 g.) was prepared and heated at 1440° for 10 hours. This pellet, removed with reasonable ease, appeared dark with no visible traces of blue. The inside of the crucible was coated with a very light grey material, not uniformly, although the lid bore a uniform coating of what appeared to be this same material. It is suspected that this grey material is the same that precedes any evolution of black Vycor deposits; the pellet was crushed and photographed as A-501. The lid was scraped and photographed as A-502. Photograph A-501 shows a mixture of SmB_4 and SmB_6 while A-502 contains lines of the same phase of SmBO_3 as shown A-342, A-371, A-376, A-388, and A-508.

Subsequent to this first heating, crystalline boron was added to the crucible which was then heated to 1750° in an attempt to clean it. At the end of this operation, the crucible looked bright; a mild deposit on the lid was discarded; the blue SmB_6 had formed in small measure on the surface of the boron inside.

12. Subsequent to the "cleansing" operation described above, a 1:8 sample (0.24424 g.) was prepared and heated for 12.6 hours at 1435° . Since the sample was 1.26x larger than in (11), heating was done for 1.26x as long as in (11). After the heating, the Vycor tube carried a mild cloudy grey film with no black deposit at all. The pellet from this experiment (A-503) seemed to be more full of blue specks this time than the last time. The photograph shows a mixture of SmB_4 and SmB_6 .

The crucible was treated with boron again for one hour at 1700° and, after cooling, was observed to be cracked. It not only had cracked but also had undergone some sort of reaction with the material which it had contained. Some of the exterior of the crucible was scraped and photographed as A-504. The photograph of these crucible scrapings shows lines ascribable to molybdenum metal and what appears to be $\text{B-Sm}_2\text{O}_3$.

13. As the end of a natural sequence to the 1:6 and 1:8 experiments, a 1:10 mixture (0.24915 g.) was heated at 1435° for 12 hours. At the end of this run, no visible deposit appeared on the Vycor although washing the tube with 0.5 M hydrochloric acid did produce bubbles. The pellet was brittle, containing irregular blue blotches on the surface; on crushing, the blue color was observed to be present throughout most of the interior. The photograph (A-506) shows only lines of SmB_6 .

14. Since the heating time of the experiments described in (11), (12) and (13) is long, in this experiment, a 1:6 pellet (0.23863 g.) was heated for only two hours at 1435° . At the end of this heating, the pellet was coated with a grey-white material on its top surface which was scraped for a photograph (A-508), while the remainder of the pellet was crushed completely and representatively photographed as A-509. After the top layer of white material had been scraped from the surface, the pellet was observed to be a dark color underneath. The principal phase observable on A-508 is SmBO_3 . In A-509, the lines are principally ones of SmB_6 ; there are a few lines of the A-508 phase, but none of SmB_4 .

15. An intermediate run was performed using a 1:10 mixture and heating the pellet at 1435° for 1.5 hours and at 1565° for an additional 1.5 hours. At the end of this heating, visual examination of the product revealed only a homogeneously blue material of a color normally associated with SmB_6 . No powder photograph was obtained.

16. Since decreasing the time of heating produced no marked changes in the product other than the undesirable absence of pure SmB_4 , a more radical change in composition was invoked.

A 1:2 pellet (0.51223 g.) was heated in the molybdenum crucible for three hours at 1435° . At the end of the heating, the color of the pellet was not uniform on the surface, but on crushing in a diamond mortar, the powder was a light grey throughout. The photograph of a portion of this material shows no identifiable lines other than those believed to be due to $\text{B-Sm}_2\text{O}_3$.

Immediately subsequent to this experiment, another 1:2 mixture (0.23726 g.) was heated for three hours at 1540° . This time there was no homogeneity whatsoever in the reaction product, which in fact was fixed as a gooey mass in the base of the crucible; no x-ray photographs were obtained.

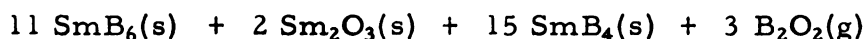
17. In view of the results of (16), it was decided to extend the heating time of a 1:2 mixture (0.97571 g.) to 12 hours at 1330° . The product was crushed and photographed as A-512 which shows the presence of SmB_6 and $\text{B-Sm}_2\text{O}_3$. Using a 60x microscope, it was possible to observe tiny blue flecks of material against a background of grey-white material.

Another pellet (0.22867 g.), inadvertently prepared in a ratio of 1:1 rather than 1:2, was heated for three hours at 1435° . The resultant x-ray powder pattern (A-513) shows only lines of $\text{B-Sm}_2\text{O}_3$.

18. A 1:10 pellet (0.20651 g.) was prepared and heated in the molybdenum crucible for 1.5 hours at 1435° ; both the top and the bottom of the pellet were a grey-white color at the end of the heating, the same

color normally associated with SmBO_3 . The pellet was returned to the vacuum line directly without crushing and re-heated for an additional 1.25 hours at 1540° . At the end of this second heating, the pellet was entirely blue-black in appearance save for one light grey spot on the edge of the top surface. Crushing, followed by x-ray examination (A-514), showed no phase other than SmB_6 .

19. Inasmuch as all previous attempts to prepare pure SmB_4 had proven futile, it was decided to make a change in experimental approach. The product of the experiment described in (13), whose photograph shows only SmB_6 , was mixed with Sm_2O_3 in a respective mole ratio of 11.00:2.00. The assumption was that:



might conceivably represent a reaction which would occur.

A pellet (0.15713 g.) was pressed from this mixture and placed in the molybdenum crucible for heating at 1540° for one hour. At the completion of this experiment, the sample had been reduced in weight to 0.13323 g. and both the top and bottom surfaces were coated with a blue-black layer photographed as A-515. The blue interior was photographed as A-516. Examination of both of these photographs showed that in the case of A-515, SmB_4 is a contamination phase of the principal SmB_6 phase. In A-516, no SmB_4 is discernible and the phase appears to be all SmB_6 .

20. Subsequent to the experiment described in (19), the crack first noted in (12) became intolerable and a new crucible had to be fashioned. This crucible was again fashioned of molybdenum, outgassed for several hours at about 1850° , and initiated as described in (21).

21. A pellet was prepared using 0.13137 g. of (-325 mesh) molybdenum and 0.15915 g. of Sm_2O_3 (a respective mole ratio of 1:3). The pellet was heated at 1460° for 3.5 hours and later photographed as A-521. The photograph shows only lines of molybdenum and B- Sm_2O_3 .

22. By now it was not believed possible to prepare pure SmB_4 from any mixture of Sm_2O_3 and boron in a molybdenum crucible. However it was decided to attempt this once more in a fresh crucible.

A 1:10 pellet (0.38543 g.) was prepared and heated for four hours at 1510° . The blue-black product was weighed, replaced in the line, and heated for an additional 10.5 hours at 1510° . The appearance of the product subsequent to this treatment was not at all what was expected. Immersed in a shell of glassy-looking yellow material, some of which seemed to have been dispersed on all parts of the lid, the pellet was a silver-grey color. The core-material (A-523) was soft on crushing, hinting of SmB_4 ; the x-ray photograph showed lines of this phase and of another unidentifiable phase, not SmB_6 . Total weight loss in crucible and pellet was 0.01081 g.

Immediately subsequent to the run described above, the experiment was repeated in the same crucible for 11.5 hours at 1505° . The total weight loss for this heating was 0.03410 g., roughly three times the weight loss encountered before; however, the pellet was silver grey only on its underside. A large amount of yellow material had collected on the base of the crucible and the pellet appeared totally non-homogeneous. The yellow material which had dispersed on the lid was photographed as A-524. The only identifiable lines in this photograph are some which may be attributed to B- Sm_2O_3 .

23. The crucible was heated for 3.25 hours at 1800° ; this resulted in the deposition of a large amount of black metallic material on the Vycor confining-tube. Some boron was added to the now-bright crucible and heating was performed at 1440° for 5.5 hours. A small amount of SmB_6 had formed on the surface of the boron; the crucible and boron were heated to 1800° for an additional hour with no results other than the production of a thin layer of deposit on the Vycor. The mixtures of Sm_2O_3 and boron were abandoned in favor of a system of boron and samarium.

E. The samarium-boron system in a molybdenum crucible

Again it should be noted that although mixtures are referred to as 1:3.8, 1:4, 1:5, etc., all mixtures have been carefully prepared weighing each component to the nearest one-tenth of a milligram.

1. The first of the experiments using samarium and crystalline boron was performed in the same molybdenum crucible used for the last experiment of the sesquioxide-boron work. Initial heating of the first 1:4 mixture of samarium and boron (0.48300 g.) was done in a vacuum of 10^{-4} mm. for only five minutes at 1045° . The rapid vaporization of samarium was observed immediately and the final heating of this first mixture was done at temperatures no higher than 1365° for only ten minutes. The product of the reaction was a sintered cake but quite soft to grinding. The x-ray photograph (A-530) of this product shows SmB_4 as the principal phase, with SmB_6 contamination.

2. Using another 1:4 mixture (0.52498 g.), but in this case using amorphous boron, a second heating was performed over an interim of one hour at a helium pressure of about 600 mm. (Unless otherwise noted, this is the pressure of the helium in all successive experiments described.) The temperature was raised quite slowly in an effort to ascertain at what temperature the Vycor deposit would begin to show a condensate. Only after 0.5 hour at 1150° did any appreciable deposit appear on the walls of the confining reaction tube. The maximum recorded temperature between the first half hour and the end of the one hour heating was 1250° .

Examination of the products suggests that the material inside the crucible never underwent any definite melting. However, the same grey substance which had caked into the shape of the crucible proper in a previous run came out of the crucible again as a single piece. It was very soft to grind and contained some specks of a clearly discernible blue material although the blue material was present in very small amount.

The photograph of the sample (A-533) shows principally SmB_4 with some SmB_6 contamination. There appears to be another phase present in A-533, but there are not sufficient lines on the film for any genuine characterization.

4. The mole ratio of samarium metal to boron was increased to 1:10 and a reaction mixture (0.71494 g.) of this ratio was heated in helium at $1075 - 1125^\circ$. The experiment was carried out for just under one hour. The product of the reaction was a non-homogeneous blob of material which nonetheless was observed to contain three distinct phases: a powder surrounding a central core and a silver material which stood out from the rest of the agglomerate.

The powder was photographed (A-540) and observed to contain SmB_4 and SmB_6 . However, the silver material (A-536) and the core (A-541) represent phases which could not be characterized, although neither appear to contain any SmB_4 .

5. In an attempt to compensate for samarium losses, a 1:3.8 mixture (0.50369 g.) was prepared. The mixture was heated in a helium atmosphere in the molybdenum crucible for 1.5 hours at 1275° . The x-ray photograph of the product (A-542) shows only SmB_4 with a trace of SmB_6 .

After an intermediate treatment with boron (45 minutes at 1800°), another 1:3.8 mixture (0.49466 g.) was added to the crucible and heated in an atmosphere of helium for 1.5 hours at $1300 - 1315^\circ$. Once again, the product (A-543) proved to be SmB_4 with a trace of SmB_6 .

6. Lowering the temperature of 1125° and returning to a 1:4 composition a mixture of samarium and amorphous boron (0.56244 g.) was heated in an atmosphere of helium for 1.2 hours. At 1125° , the product of the reaction was principally grey, but contained clusters of blue, flaky crystals throughout. An attempt was made to isolate one of these crystals and photograph it as A-546. This photograph shows the same phase(s) as A-548

which is the photograph of another "isolated" crystal of the blue material. In neither case was it possible to make any phase assignments. The gross material proper was photographed as A-552 which does not show any SmB_4 or SmB_6 .

7. Returning to crystalline boron, a repeat (0.56331 g.) was made of the experiment described in (6). Again the product appeared grey to the naked eye, but microscopic examination once more revealed the presence of the blue crystals (A-548). The material proper was photographed as A-549, but the only thing that can be said of it is that it looks the same as A-552 and is equally unidentifiable.

8. Another 1:4 mixture (0.51309 g.) was heated in the molybdenum crucible for 11.5 hours at 1125° in a helium atmosphere. The product of this reaction appeared lumpy and non-homogeneous at the end of the reaction and the x-ray photograph (A-554) shows the presence of SmB_4 with contamination by the phase common to A-549 and A-552.

9. This experiment is the initial one on the idea of attempting to prepare pure SmB_4 by heating a 1:3.5 mixture (0.53818 g.) in a helium atmosphere and then "cleaning up" the sample of excess samarium by heating for a time in a vacuum. The run was performed for 2.5 hours at $1100 - 1125^\circ$, followed by ten minutes at 1275° (in vacuo). The composition of the product was principally a black grey material with a few of the blue crystals again present. However, the photograph of the product (A-557) shows only a faint amount of SmB_6 within the principal phase of SmB_4 .

A portion of the above sample showed violent reaction with nitric acid resulting in an undissolved residue (A-558) which turned out to be boron.

10. This experiment represents a crucial one with respect to the work done using samarium and boron for it is the experiment in which, for the first time, a sample of SmB_4 was prepared for which the photograph showed no SmB_6 .

A 1:3.5 mixture (0.42576 g.) of samarium and crystalline boron was prepared and placed into the molybdenum crucible for heating in an atmosphere of helium. The mixture was maintained at 1150° for four hours. It was then evacuated to a pressure of 10^{-5} mm. and heated for an additional hour at 1450° . The bottom surface of the reaction mixture was devoid of blue after this treatment, but the interior was filled with blue crystals. The photograph of the material proper (A-559) shows a mixture of SmB_4 and SmB_6 with no predominance of either phase. The material was placed back into the crucible and heated once more in helium for eight hours at 1275° . After this heating, a portion was photographed as A-560. It is difficult to decide whether SmB_4 or SmB_6 is the principal phase of this photograph, but it seems safe to assert that the heating had caused some change.

The sample was returned to the furnace line and heated once more in helium for two hours at 1385° ; the x-ray photograph of the resultant product (A-567) shows the SmB_6 phase as the more predominant one. The material seemed homogeneous and was a dark blue-black color although a few isolated lighter blue crystals could be observed microscopically. The sample was ground easily and was reheated for another 1.5 hours at about 1480° . The orifice was allowed to remain partially clogged with what was believed to be Sm_2O_3 . (Actually, the orifice had been clogged with blue needles of a material which turned white on standing. Such needles were observed earlier in some of this work, but their photograph (A-555) is believed to represent SmO .)

A fourth heating was undertaken for two additional hours at 1480° . A portion of the resultant sample was photographed as A-568 which shows both boride phases and seems no different from A-560.

Again the mixture was returned to heat for 1.25 hours at 1585° . Examination of the product (A-569) revealed that much of the blue color had diminished and that a good deal of grey color had suddenly developed in the mixture although the grey was clearly confined to the lower regions of the sintered mass. The photograph shows a mixture of SmB_4 and SmB_6 .

Two final heatings were performed. The first of these was done at 1700° for 1.5 hours and led to a mixture (A-570) totally devoid of blue color although the x-ray photograph shows SmB_4 as the major and SmB_6 as the minor phase. The final heating was performed for 0.75 hour at 1750° and resulted in a completely grey product (A-571) showing only lines of SmB_4 in the x-ray photograph. However, the presence of tiny blue crystallites could be observed microscopically in spite of the x-ray detection of only SmB_4 .

No additional details are provided in the appendix for the remainder of the experiments (Sections E, F, G, H, and I) described in Part III of this thesis. However, in keeping with the policy of presenting A-numbers for x-ray photographs associated with particular experiments, a compilation of such numbers is presented below under a letter-heading corresponding to the headings in Part III.

E. The samarium-boron system in a molybdenum crucible

E-13	A-636	E-23	A-642
E-14	A- ⁶³⁷ ₆₃₈	E-24	A-644
E-15	A-640	E-26	A-647
E-16	A-641	E-41	A-657
E-17	A-643	E-42	A-658
E-18	A-645	E-43	A-659
E-19	A-646	E-44	A-660

F. The reaction between samarium sesquioxide and boron in a boron nitride liner

<u>Compositions</u>	<u>Photographs</u>
1:5.0	A-751, 752, 753, 759
1:7.5	A-773, 774
1:10.0	A-734, 737, 739
1:12.5	A-769, 770
1:15.0	A-730, 732, 733
1:17.5	A-762, 764, 765
1:20.0	A-742, 743, 745

G. The reaction between samarium sesquioxide and boron in zirconium diboride

<u>Compositions</u>	<u>Photographs</u>
1:5.0	A-780, 788
1:10.0	A-783, 784
1:15.0	A-779, 781
1:20.0	A-775, 776, 778

H. The heating of a sample of samarium hexaboride in a low-density tungsten cell

<u>Experiment</u>	<u>Photograph</u>
H-1	A-802
H-2	A-803
H-3'	A-804
H-4	A-805
H-5	A-807
H-6	A-808
H-7	A-809

APPENDIX B

TABULATION OF PHYSICAL CONSTANTS

Table V. Melting point and vapor pressure data for rare earth metals
(50, 51)

Element	Melting point at 1 atm.	Temperatures in °K for vapor pressures in mm. Hg		
	°C	1 mm	100 mm	760 mm.
La	920	2420	3180	3742
Ce	795	2430	3219	3741
Pr	935	2120	2820	3400
Nd	1024	2050	2800	3300
Pm	(1027)	----	----	(3000)
Sm	1072	1225	1580	2173
Eu	826	1100	1455	1712
Gd	1312	(1960)	(2580)	3273
Tb	1356	2290	2940	3073
Dy	1407	1680	2140	2873
Ho	1461	(1655)	(2215)	2873
Er	1497	(1872)	(2480)	3173
Tm	1545	1368	1749	2000
Yb	824	(1095)	(1500)	1700
Lu	1652	(2380)	(3010)	3600

Table VI. Metallic and trivalent ionic radii of the rare earth metals
(17, 52)

Element	Metallic radius ($\text{\AA}$)	Trivalent ionic radius ($\text{\AA}$)
La	1.871	1.061
Ce	1.818	1.034
Pr	1.824	1.013
Nd	1.818	0.995
Pm	-----	0.979
Sm	1.804	0.964
Eu	2.084	0.950
Gd	1.795	0.938
Tb	1.773	0.923
Dy	1.770	0.908
Ho	1.761	0.894
Er	1.748	0.881
Tm	1.743	0.869
Yb	1.933	0.858
Lu	1.738	0.848

Table VII. Lattice parameters of cubic rare earth hexaborides

Element	a_0 in Ångströms	Respective references
Y	4.128, 4.126, 4.08	53, 21, 54
La	4.153	54 and 53
Ce	4.141	53 and 54
Pr	4.130, 4.132	54, 53
Nd	4.1260, 4.128	36 and 53, 54
Pm	- - - - -	- - - - -
Sm	4.1333, 4.129	36 and 53, 54
Eu	4.178, 4.169	19 and 53, 24
Gd	4.1078, 4.121, 4.14	36 and 54, 53, 24
Tb	4.1020, 4.092, 4.13	36, 53, 24
Dy	4.0976, 4.407, 4.13	36, 54, 24
Ho	4.096, 4.12	36 and 53, 24
Er	4.101, 4.110	53, 54 and 24
Tm	4.10	53
Yb	4.1468, 4.140	36, 53, 54 and 24
Lu	4.11	24

Table VIII. . Lattice parameters of tetragonal rare earth tetraborides

Element	$\underline{a}_0$ in Ångströms	$\underline{c}_0$ in Ångströms	References
Y	7.09	4.01	54
La	7.30	4.17	54
Ce	7.205	4.090	10
Pr	7.20	4.11	54
Nd	7.219	4.1020	36
Pm	-----	-----	--
Sm	7.174	4.0696	36
Eu	-----	-----	--
Gd	7.144	4.0479	36, 53, 54
Tb	7.118	4.0286	36, 53
Dy	7.101	4.0174	36, 54
Ho	7.086	4.0079	36, 53
Er	7.071	3.9972	36, 54
Tm	-----	-----	--
Yb	7.01	4.00	11
Lu	6.98	3.93	24

Table IX. . Lattice parameters of some cubic dodecaborides (55)

Element	$\underline{a}_0$ in Ångströms
Zr	7.408
Y	7.500
Dy	7.501
Ho	7.492
Er	7.484
Tm	7.476
Lu	7.464
U	7.473

Table X. . Lattice parameters of tetragonal rare earth MB_x phase (14)

Element	$\underline{a}_0$ in Ångströms	$\underline{c}_0$ in Ångströms
La	3.82	3.96
Pr	3.81	3.81 (?)
Gd	3.79	3.63
Er	3.77 ₉	3.51 ₅

Table XI. Comparison of the interatomic spacings of an experimental sample with those of the 1550° polymorph of samarium orthoborate (26).

$d_{hkl}(\text{\AA})$ SmBO ₃	I^*	$d_{hkl}(\text{\AA})$ A-342	I	$d_{hkl}(\text{\AA})$ SmBO ₃	I	$d_{hkl}(\text{\AA})$ A-342	I
6.07	13	-----	--	2.356	15	2.36	VW
5.06	11	-----	--	2.264	15	2.25	VW
4.26	56	4.24	M	2.158	26	2.16	M
3.60	72	3.58	M	2.131	8	-----	--
3.56	28	-----	--	2.070	12	2.08	VW
3.15	13	-----	--	2.026	20	2.03	W
3.044	100	3.03	S	1.997	23	2.00	W
2.944	27	-----	--	1.953	21	1.96	VW
2.926	29	2.92	MW	1.873	21	1.87	W
2.832	20	-----	--	1.837	20	1.84	VW
2.789	34	2.78	M	1.801	20	1.81	W
2.715	10	-----	--	1.779	21	1.78	VW
2.556	30	-----	--	1.728	24	1.73	MW
2.531	43	2.530	MW	1.697	12	1.70	MW
2.490	9	-----	--	1.613	17	1.62	MW

*I = the intensity of each peak relative to the strongest peak.

Table XII. Comparison of the interatomic spacings of two experimental samples with those of the delta polymorph of molybdenum boride, δ -MoB (56)

$d_{hkl}(\text{\AA})$ δ -MoB	$d_{hkl}(\text{\AA})$ A-410	$d_{hkl}(\text{\AA})$ A-411
1.20	1.20	1.20
1.21	----	----
1.25	1.25	1.25
1.28	1.28	1.28
1.34	1.34	1.35
1.35	----	----
1.38	1.38	1.38
1.41	1.41, 1.45	1.41, 1.45
1.56	1.55	1.55
1.73	1.73	1.73
1.91	1.91	1.90
2.12	2.12	2.11
2.28	2.28	2.28
2.72	2.71	2.70
3.06	3.04	3.03
4.2	4.23	----

Table XIII. Raw data used for correcting observed temperatures to true temperatures.

Observed temperature °Centigrade	Observed temperature expressed as $1/^\circ K \times 10^{+4}$	Corrected to $1/K_{wo} \times 10^{+4}$	True temperature °Centigrade
1000	7.855	7.737	1019
1100	7.283	7.165	1123
1200	6.789	6.671	1226
1300	6.357	6.239	1330
1400	5.978	5.860	1434
1500	5.640	5.522	1538
1600	5.339	5.221	1642
1700	5.068	4.950	1747
1800	4.824	4.706	1852
1900	4.602	4.484	1957
2000	4.399	4.281	2063
2100	4.214	4.096	2168

Tungsten lamp temperature as a direct sighting: $1810^\circ K = K_{wo}$

Tungsten lamp temperature with prism and window: $1772^\circ K = K_w$

Since the theory of pyrometry demands that $1/K_w - 1/K_{wo}$ be constant over all range of temperatures, the corrections are made using the constant obtained from the value of K_w and K_{wo} . Specifically:

$$(5.643 \times 10^{-4} - 5.525 \times 10^{-4}) = 1.18 \times 10^{-5}$$

INDUSTRY LIBRARY

INDUSTRY LIBRARY

MICHIGAN STATE UNIVERSITY LIBRARIES



3 1293 03064 8042