AN INVESTIGATION OF THE CERIUM OXYGEN NITROGEN SYSTEM

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This is to certify that the

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ABSTRACT

AN INVESTIGATION OF THE CERIUM OXYGEN NITROGEN SYSTEM

By

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The cerium oxygen nitrogen ternary phase diagram has been partially characterized from an examination of X-ray powder diffraction data of samples with various cerium oxygen nitrogen compositions. These samples were prepared by arc melting cerium dioxide and nitride, which was also prepared by the arc melting process. X-Ray powder diffraction patterns and micrographic examinations revealed the presence of four phases: cerium sesquioxide, cerium nitride, cerium metal, and a previously unreported cerium oxide nitride. Analysis of three different micrographically pure preparations of this cerium oxygen nitrogen phase gave the following weight percentages: cerium, 88.33 ± 1.11%; nitrogen, 4.84 ± 0.17%; oxygen (by difference), 6.83 ± 1.12% (composition $CeN_{0.55\pm0.02}O_{0.68\pm0.11}$). X-Ray powder diffraction photographs indexable on face-centered cubic symmetry, yielded a lattice parameter of $a_0 = 5.115 \pm 0.002$ Å.

Pulverized samples of this phase underwent no apparent reaction upon exposure to moist air for periods of up to two days. However, treatment with 6 *M* HCl yielded bubbles

of a gas thought to be hydrogen. When the phase was struck with a hard object it could be made to spark and immediately oxidize to CeO_2.

This oxide nitride phase upon heating to 1400° in vacuum lost nitrogen according to the following equation:

$$CeN_{0.55}O_{0.68}(s) \xrightarrow{1400^\circ} CeN_{(0.55-x)}O_{0.68}(s) + \frac{x}{2} N_2(g) \qquad (a)$$

As the phase became deficient in nitrogen, its lattice parameter decreased. Further decrease in the nitrogen content during heating yielded a two phase mixture of the nitrogen deficient oxide nitride ($\sim CeN_{0.42}O_{0.80}$) and the sesquioxide.

Cerium oxide nitride samples confined in a tungsten crucible and heated at 1200° in an ammonia atmosphere yielded the nitride and sesquioxide according to reaction b:

$$5.88\ CeN_{0.55}O_{0.68}(s) + 0.667NH_3(g) \longrightarrow 3.88\ CeN(s) + Ce_2O_3(s) + H_2O(g) \qquad (b)$$

whose validity was confirmed by calculation of the free energy at selected temperatures.

The properties of this oxide nitride are discussed in comparison with those of other metal oxide nitride phases.

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TABLE OF CONTENTS

TABLE OF CONTENTS (Cont.)

LIST OF TABLES

LIST OF FIGURES

I. INTRODUCTION

Information about the physical and chemical properties of lanthanon nitrides has, until recently, been very brief. Within the last ten years, however, information available concerning the lanthanon nitrides has increased. The semiconducting properties of some of these species and their potential application as semi-conductors has accounted for most of the current interest in these compounds.

Some workers who have investigated lanthanon-nitrogen systems have indicated the possibility of changes in the physical and chemical properties of lanthanon nitrides when oxygen is intentially or inadvertently introduced into these systems. A report has been made of a detailed investigation of the samarium oxygen nitrogen system and the existence of a gadolinium oxygen nitrogen phase has been demonstrated. Previous investigations performed at Michigan State University have indicated the existence of a cerium oxide nitride phase with physical properties different from those of cerium nitride. As a consequence of these previous observations, an investigation of the cerium oxygen nitrogen system was undertaken.

II. HISTORICAL

A. Literature Concerning the Lanthanon Nitrogen Systems

1. Preparation and Properties

The preparation of lanthanon nitrides were reported first by Magtinon (1) who prepared them by reduction of the oxides with magnesium or aluminum in a nitrogen atmosphere. Muthmann and Kraft (2) heated cerium metal in a nitrogen atmosphere and found that up to red heat cerium absorbs nitrogen slowly, but that at 850° the absorption increases sharply. If pure nitrogen is used, the authors claim pure CeN is obtained. Friederich and Sittig (3) attempted to prepare CeN by reduction of CeO_2 with carbon in a nitrogen atmosphere, but CeN was not formed at temperatures up to 1600°.

Fichter and Schöllig (4) report that CeN is formed also when cerium carbide is heated in a nitrogen or ammonia atmosphere at 1250°, the reaction being more rapid in nitrogen than in ammonia. These authors state that the reaction is greatly retarded by the formation of a nitride film.

Iandelli and Botti (5) in 1938 prepared the nitrides of lanthanum, cerium, praseodymium and neodymium. In 1956, Eick, *et al*. (6) and Klemm and Winkelmann (7) prepared the remainder of the lanthanon nitrides and reported their lattice parameters. Klemm and Winkelmann prepared the nitrides by passing ammonia over the powdered metal mixed with KCl contained in an alundum boat situated in a quartz tube. The reaction mixture was heated for 3 to 4 hours at 700°.

Gaume-Mahn (8) summarizes the properties of a number of lanthanon borides, carbides, nitrides, and sulfides. The data presented agree closely with data given by other authors.

In recent years, a number of investigators have prepared lanthanon nitrides by the reaction of the metal or the metal hydride with nitrogen or ammonia. Eick, et al. (6), Young and Ziegler (9), and Samsonov and Lyutaya (10) have prepared a number of these species by the action of nitrogen on the metal. Other investigators (11,12,13,14) have prepared the nitrides by the action of nitrogen or ammonia on the metal hydride.

Gambino and Cuomo (15) have reported the preparation of lanthanon nitrides by a reactive arc melting technique. The nitrides were prepared by arc melting ingots of the metal under a stream of nitrogen gas for periods of up to one minute three or four times in succession.

A number of studies have been made of the electric and magnetic properties of lanthanon nitrides. Von Essen and Klemm (16) have studied the magnetic susceptibility of LaN, CeN, PrN, and NdN. Their data indicate that in CeN most of the metal and in PrN a considerable amount of the metal is present in the +4 oxidation state. The per cent of +3 metal ions increases with temperature. Their X-ray diffraction data indicate that with increasing temperature (100-700°K) CeN expands considerably more and PrN somewhat more than LaN. From conductance data, the authors conclude that CeN, LaN, and PrN are metallic conductors.

Sclar (12) has studied the optical and electrical properties of lanthanon nitrides. The electrical properties from 80° to 1500°K were found to be comparable to those of a metallic substance; characteristic of those species exhibiting associated large concentrations of electron carriers.

Didchenko and Gortsema (11) determined the paramagnetic susceptibility and the specific resistivities of these nitrides. They noted that CeN, which is a p type conductor, displayed a very weak molar susceptibility. All of the other nitrides investigated showed electronic conductivity. The authors think that in the lanthanon nitrides a rather fine balance in the competition for electrons prevails between the 4f levels of the metals, the conduction band, and the nitrogen ions.

2. Crystal Structure of the Lanthanon Nitrides

Most of the authors previously cited give some structural data for the lanthanon nitrides. However, Klemm and Winkelmann (7) give the most complete listing of the lattice parameters. There is adequate agreement among the lattice parameters reported by the various investigators. A compilation of lattice parameters of lanthanon nitrides is presented in Table I.

Examination of these data reveals a regular decrease in lattice parameter with increasing atomic number in agreement with the lanthanide contraction. The lowering of the lattice parameter of CeN is generally attributed to the presence of the Ce^{+4} ion.

Iandelli and Botti (5) determined that lanthanon nitrides exhibited the face-centered cubic NaCl type crystal structure. Young and Ziegler (9) confirmed the earlier work of Iandelli and Botti by determining the crystal structure of LaN from intensity data. Young and Ziegler have also shown that powder X-ray diffraction patterns of LaN and face-centered cubic lanthanum metal are different, an indication that the fcc modification of lanthanum metal is not due to the formation of a surface coat of LaN on the metal.

Kempster, Krikorian, and McGuire (19) have determined the crystal structure of yttrium nitride and have found that it exhibited space group symmetry O_h^5 - Fm3m (NaCl structure type) with 4(YN) groups per unit cell.

3. Investigation of Thermodynamic Properties of Lanthanon Nitrides

Neuman, Kröger, and Kunz (20) calculated the heat of

Table I. Lattice parameters for the lanthanon nitrides

Metal	a_0 (Å) ± 0.001	Reference
La	5.295	(5,6,7,9)
Ce	5.021	(5)
Pr	5.155	(5)
Nd	5.151	(5,7)
Pm		
Sm	5.046	(7,17,18)
Eu	5.014	(7,18)
Gd	4.999	(6,7)
Tb	4.933	(7)
Dy	4.905	(6,7)
Ho	4.874	(6,7)
Er	4.839	(6,7)
Tm	4.809	(6,7)
Yb	4.785	(7,18)
Lu	4.766	(6,7)

formation of CeN as 78 kcal/mole. The authors determined calorimetrically the heats of solution of cerium and cerium nitride in HCl. From the following relations they calculated the heat of formation of CeN:

$$\mathrm{CeN} + 4\mathrm{HCl}\cdot \mathrm{aq} = \mathrm{CeCl_3}\cdot \mathrm{aq} + \mathrm{NH_4Cl}\cdot \mathrm{aq} \qquad [1]$$

$$\mathrm{Ce} + 3\mathrm{HCl}\cdot \mathrm{aq} = \mathrm{CeCl_3}\cdot \mathrm{aq} + 3\mathrm{H} \qquad [2]$$

$$\mathrm{N} + 3\mathrm{H} = \mathrm{NH_3} \qquad [3]$$

$$\mathrm{NH_3} + \mathrm{HCl}\cdot \mathrm{aq} = \mathrm{NH_4Cl}\cdot \mathrm{aq} \qquad [4]$$

The authors prepared CeN by heating finely divided cerium metal in nitrogen at 850° for many hours. They were never able to obtain the stoichiometric nitride, but obtained samples whose nitrogen content varied between 6.6 and 8.0% nitrogen (theoretical 9.08%). In a similar manner, the authors determined the heat of formation of LaN as 72.7 kcal/mole.

Brewer, et al. (21) have compiled ΔG, ΔH, and ΔS values for LaN and CeN from various sources and estimates.

There have been no high temperature vaporization studies performed on the lanthanon nitrides.

B. Literature Concerning Lanthanon Metal Oxide Nitride Phases

To date, there have been only two studies reported of the lanthanon oxygen nitrogen system.

Gambino and Cuomo (15) have reported the existence of a phase of the type $GdN_{1-x}O_x$. This phase was prepared by the reaction of Gd metal and Gd_2O_3 with nitrogen. The authors found that at 2000° oxygen could substitute for nitrogen up to an X value of 0.12. They also found that the lattice constant of the gadolinium oxygen nitrogen phase decreased from 4.99 to 4.96 Å as the oxygen content reached its maximum value.

Flemlee and Eyring (22) have reported an investigation of the samarium oxygen nitrogen system. They report the preparation of a number of compounds of the type $SmN_{1-x}O_x$ where $0<x<0.5$. They found that where $x = 0.5$, the oxide nitride phase has the same properties as a phase previously reported as SmO. The lattice parameter of $SmN_{1-x}O_x$, which has the NaCl structure, decreases continuously with an increase in x. The authors report that $SmN_{1-x}O_x$ undergoes hydrolysis on exposure to the atmosphere.

C. Reported Work on Other Metal Oxide Nitride Phases

A series of papers have appeared (23,24,25) in which the authors have prepared oxide nitride phases of aluminum, titanium, zirconium, vanadium and niobium.

Lejus (25) has prepared some aluminum oxide nitride phases by a solid state reaction between Al_2O_3 and AlN in an argon atmosphere. Aluminum nitride was prepared by the reaction:

$$\mathrm{Al_2O_3 + 3C + N_2 \longrightarrow 2AlN + 3CO}$$ [5]

The reacting mixture was placed in a graphite crucible and heated by induction at 1700° for several hours. No mention was made of the purity of the aluminum nitride formed.

To prepare the oxide nitrides, AlN and Al_2O_3 were mixed in various proportions, placed in a graphite crucible and heated at temperatures of 1400-1800°. No contamination of the sample by the graphite crucible was observed in the X-ray powder diffraction spectra.

Analysis of the mixtures by X-ray diffraction revealed no reaction between AlN and Al_2O_3 up to 1600°. At about 1600°, a reaction occurred and lines appeared in the diffraction spectrum corresponding to a new phase which was designated as phase γ. The phases observed when this system is heated to 1700° are indicated in Table II.

In the vicinity of fusion (about 2000°) the γ phase exists alone except for very high contents of Al_2O_3. The phases observed in this system at 2000° are indicated in Table III.

The γ phase was observed to have a cubic structure while the δ phase was tetragonal. It was noted by the author that the lattice parameter of the phase prepared at 1700° varies as a function of its composition from 7.950 Å at an Al_2O_3 content of 65% to 7.927 Å at an Al_2O_3 content

Table II. Phases observed in the Al_2O_3-AlN system at 1700°C

Composition of samples (mole per cent)	Phases observed
50 to 67% Al_2O_3 50 to 33% AlN	AlN + γ phase
67 to 84% Al_2O_3 33 to 16% AlN	γ phase alone
84 to 100% Al_2O_3 16 to 0% AlN	γ phase + αAl_2O_3

Table III. Phases observed in the Al_2O_3-AlN system at 2000°C

Composition of samples (mole per cent)	Phases observed
50 to 86% Al_2O_3 50 to 14% AlN	γ phase alone
86 to 98.5% Al_2O_3 14 to 1.5% AlN	γ phase and probably δ phase
98.5 to 100% Al_2O_3 1.5 to 0% AlN	δ phase + α Al_2O_3

of 85%.

Collongues, Gilles, and Lejus (23) have studied the action of ammonia on some refractory oxides. When these authors allowed ammonia to react with aluminum oxide, they observed results comparable to those obtained from the reaction of AlN and Al_2O_3 in a neutral atmosphere.

With the zirconium oxygen nitrogen system, they found that ZrO_2 powder was attacked by ammonia at 650°. Below 950° the reaction proceeded slowly. However, by heating ZrO_2 in a stream of ammonia at 950° for several hours, a new phase designated β was observed. If the sample was heated in ammonia at this temperature for several days, a different phase designated γ appeared. This phase decomposed at 1100° with loss of nitrogen producing the β phase and ZrN. If ZrO_2 was heated at this temperature in ammonia, the β phase was formed.

At temperatures in excess of 2000°, the β phase decomposed with loss of nitrogen to ZrN and a phase designated β' which exhibits a structure similar to that of the β phase. The β' phase was also prepared by the reaction of ammonia with ZrO_2 at temperatures above 2000°.

The β, β', and γ phases were stable at their temperature of formation only in the presence of a nitrogen or ammonia atmosphere. If the sample was heated in a neutral atmosphere such as argon, it decomposed into ZrO_2 and ZrN with loss of nitrogen.

The γ phase has a cubic Tl_2O_3 type structure whose formula was determined as Zr_2ON_2. The β phase exhibited rhombohedral symmetry and has a structure similar to the fluorite structure of ZrO_2. The formula attributed to this phase was $Zr_7O_8N_4$. Collongues, Gilles, and Lejus think that the β' phase was attained from the β phase by a slight deformation of the cell along the ternary axis. The three zirconium oxide nitride phases had approximately the same metallic conductance as ZrN.

These authors also present a study of the titanium oxygen nitrogen system. When mixtures of TiN and TiO_2 were heated in an argon atmosphere at temperatures between 1000 and 2000°, a series of oxide nitride phases whose structures are analogous to those of the intermediate phases between TiO and TiO_2 were obtained. The results obtained are presented in Table IV.

Roubin and Paris (26) have investigated the preparation of a chromium oxide nitride phase. This phase of face-centered cubic symmetry and composition $CrN_{0.96}O_{0.13}$ was prepared by heating the complex oxalate $(NH_4)_3[Cr(C_2O_4)_3] \cdot 3H_2O$ in a stream of ammonia and hydrogen for 20 hours at temperatures between 600 and 1000°. Heating this oxide nitride in hydrogen at 1000° for 100 hours produces chromium metal of 99% purity.

Gilles (27) has presented a thorough review of the chemistry of the oxide nitride phases known to 1966. Gilles, in his review, makes the following general statements about the reaction of metal oxides with

Table IV. Phases observed in the TiO_2-TiN system

Composition of sample(mole %)	Phases present	Sub-oxide of the same structure
80% TiN	2 cubic phases NaCl type	TiO
	C_1 more rich in nitrogen	
	C_2 less rich in nitrogen	
66% TiN	Same results	
50% TiN	3 phases	
	C_1	
	C_2	
	H hexagonal	
33% TiN	2 phases	
	C_2	
	H	
30% TiN	1 phase H	Ti_2O_3
25% TiN	2 phases	
	H	
	M monoclinic	
20% TiN	Same results	
15% TiN	1 phase M	Ti_3O_5
10% TiN	2 phases	
	M	
	T triclinic	Ti_5O_9

ammonia:

1. Many refractory or super refractory oxides are sensitive to the action of ammonia.
2. Depending upon the nature of the initial oxide, if reaction occurs, one obtains the corresponding nitride or the oxide nitride.
3. The oxide nitrides adopt the structures which are derived from the characteristic structures of the corresponding metal oxide.

D. This Research

A review of the lanthanon nitride literature at the time this work was started indicated neither the existence of any lanthanon oxide nitride phases nor any unassigned phases which might reasonably be expected to be such a species.

Since previous work by Eick (28) had indicated the possible presence of a cerium oxide nitride, an investigation of the cerium oxygen nitrogen system was undertaken. The general method of approach was to examine briefly the phase equilibria in the cerium oxygen nitrogen system and to ascertain the existence of any oxide nitride phases. Subsequently, if such a phase were observed, it was to be prepared in pure form and its thermodynamic properties were to be determined. In addition, the vaporization behaviour of cerium nitride was to be examined.

III. EXPERIMENTAL

A. Preparation of Cerium Nitride

1. Materials

Cerium metal of 99.9% purity was obtained from Research Chemicals Corporation, Phoenix, Arizona. Nitrogen gas (prepurified grade) and ammonia (C.P. grade) were obtained from The Matheson Company, Joliet, Illinois. Molybdenum rod for the reaction crucible was obtained from Sylvania Inc., Towanda, Pennsylvania.

2. Preparation by Induction Heating

Cerium nitride was prepared by heating cerium metal in ammonia at 850°.

Chunks of cerium metal were chipped in the laboratory air from a large ingot that previously had been buffed on a wire brush to remove the oxide coat present. The chips of cerium metal were immersed in benzene for storage. Subsequently they were removed from the solvent, dried, and placed in a molybdenum crucible that had been outgassed previously by heating under a vacuum of 10^{-5} torr at 1900°. The crucible, machined from 2.2cm molybdenum rod, was 2.8cm high and was bored with a cavity 1.6cm in diameter and 2.1cm deep. A molybdenum lid machined to fit on the crucible, was drilled through the center with a 1.4mm diameter orifice. To support the crucible, three 1.5mm tungsten legs 1.9cm in length were force-fitted at 120° intervals around the base into 0.5cm deep holes.

The crucible was arranged in a vacuum system (shown schematically in Figure 1) constructed almost entirely of glass except for areas adjacent to the diffusion pump and the absolute pressure gauge. A tubular Vycor post and boron nitride table supported the crucible.

The system was evacuated with a Consolidated Vacuum Corporation MCF-60 oil diffusion pump backed by a Cenco Hyvac-2 forepump. The residual pressure, measured with a vacuum ionization gauge (Veeco Type RG21A), was usually 1×10^{-4} torr after 1 hour of pumping. When ammonia was used in the system, the gas pressure was measured with a combination vacuum and pressure gauge.

The crucible was heated by a 20 kilowatt, variable output, Thermonic induction generator under vacuum to a dull red heat and maintained at this temperature for a few minutes while any residual gases were pumped off. The power was then turned off and after the crucible was cool, ammonia gas was admitted into the system to a pressure of approximately 500 torr. The crucible was then heated slowly. As the temperature of the crucible was increased, the pressure in the system decreased because of the

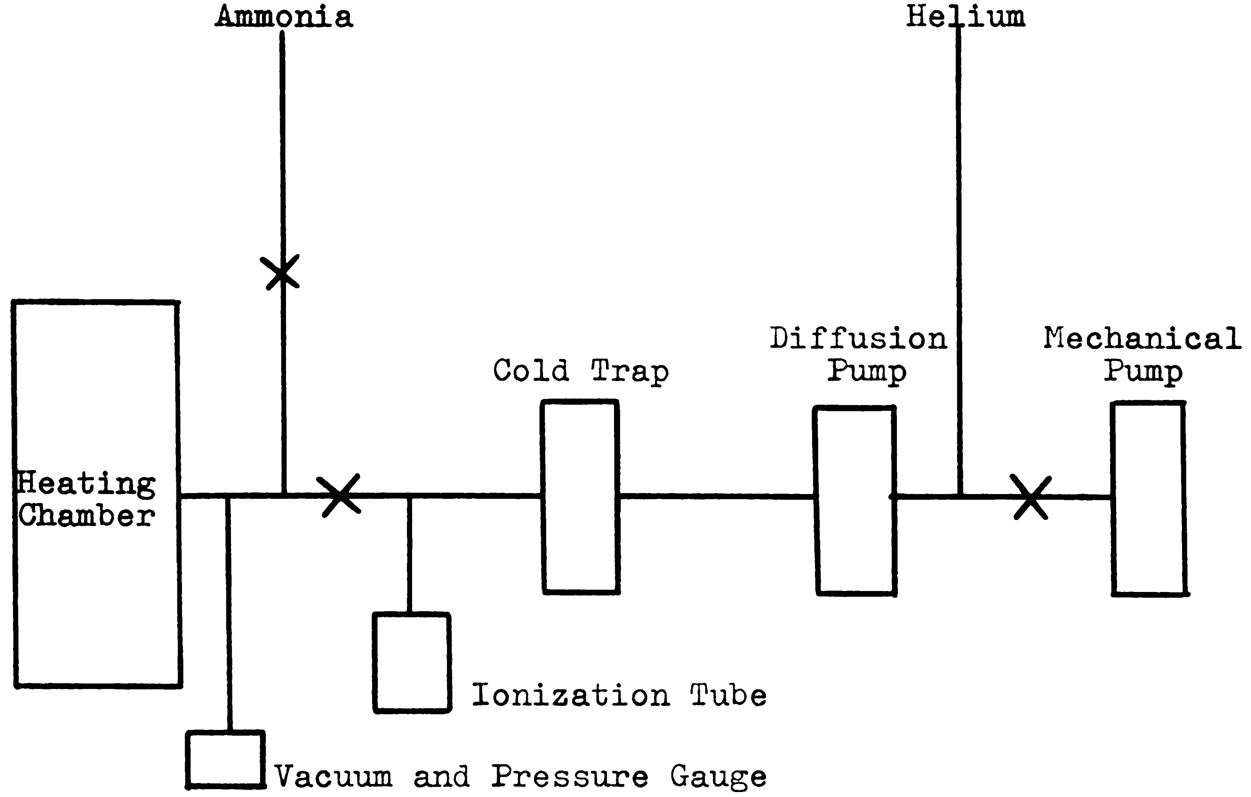


Figure 1. Schematic diagram of apparatus used to prepare cerium nitride

reactions:

$$2NH_3(g) \longrightarrow N_2(g) + 3H_2(g) \qquad [6]$$

$$2Ce(s) + 3H_2(g) \longrightarrow 2CeH_3(s) \qquad [7]$$

The magnitude of the pressure drop was obviously dependent upon the initial amount of sample, but if the pressure decreased below 250 torr, additional ammonia was admitted to maintain the pressure at about 500 torr. As the temperature of the crucible was elevated, the pressure in the system increased due to the release of hydrogen from the metal sample. The crucible was heated at a temperature of 950° for 30 minutes. Heating was terminated, and after the crucible had cooled to room temperature, the gases in the system were pumped off and ammonia was again admitted to a pressure of 500 torr. The crucible was next heated at 850° for one-half hour. After it had cooled, the system was evacuated again and the cycle repeated. After three or four cycles, the crucible was heated in vacuum to 850°. If gas was evolved, additional cycles were performed until the crucible could be heated to 850° under vacuum without appreciable gas evolution. Subsequently, ammonia was admitted into the cooled system to a pressure of 500 torr and the crucible was heated at 1150° for 3 hours. After the system had cooled, it was opened to the atmosphere and the crucible was placed in a glove box where the sample was removed from it.

3. Preparation by Arc Melting

Cerium nitride was also prepared by melting pieces of cerium metal in an arc melter equipped with a water-cooled holder into which a tungsten electrode was inserted and a water-cooled copper hearth. Metal chips, prepared as described previously, were transferred immediately after they had been dried to the vacuum chamber of the arc melter. The vacuum chamber was purged by successive evacuation and subsequent filling with nitrogen. During the arc melting, the chamber was filled with nitrogen to a pressure of 2-3p.s.i.g. An arc, first struck to a zirconium button, served as a getter to remove oxygen. The specimens, melted by the arc, reacted with nitrogen. The specimens were then turned over and melted again in nitrogen. After they had cooled, the nitrided specimens were transferred rapidly from the chamber to an inert atmosphere glove box. All subsequent operations such as weighing and the filling of X-ray capillaries were performed in the glove box.

B. Investigation of the Cerium Oxygen Nitrogen System

In the glove box, weighed amounts of the arc melted cerium nitride preparations and either previously calcined CeO_2 (99.9%, Lindsay Chemical Company, West Chicago, Illinois), or this dioxide and cerium metal were mixed together. Weighings were performed on a single pan balance situated in the glove box. The amounts of oxide, nitride, and metal were varied so that pre-selected compositions could be obtained. These mixtures were then arc melted and X-ray powder diffraction photographs[+] were taken of these and all other resultant products.

All X-ray photographs were examined for the presence of previously unreported phases. Those samples whose X-ray photographs indicated the possible presence of an unknown phase were annealed under vacuum at 1050-1300°.

The unknown cerium oxide nitride phase was prepared in pure form by mixing CeN and CeO_2 together in proportions corresponding to the composition where previous X-ray diffraction photographs had indicated the phase to be present in the largest quantity. Subsequent investigations have shown that this composition was approximately $1CeO_2 : 5CeN$ by weight. The samples were arc melted and X-ray diffraction photographs taken. The diffraction photographs were examined for the presence of the oxide nitride phase, and if the diffraction photographs indicated that the phase was pure, the sample was annealed by heating in a vacuum at 1200° for 4 hours. If the diffraction photographs indicated the sample was not pure but contained excess Ce_2O_3, additional cerium metal was added to the sample and the sample arc melted.

[+] Hereafter, the statement "X-ray photographs" can be taken to mean "X-ray powder diffraction photographs."

C. Methods of Analysis

1. X-Ray Analysis

X-Ray powder diffraction photographs of the samples were taken using Cu Kα radiation (λ_{α_m} = 1.5418 Å) and a Debye-Scherrer X-ray powder camera of 114.59mm diameter. The samples were ground to a fine powder in an inert atmosphere with a "Diamonite" (United States Ceramic Tile Company, Canton, Ohio) mortar and pestle, and loaded into 0.3mm diameter Pyrex capillary tubes.

Lattice parameters were obtained both by calculating the inter-planar d-spacings from the back reflection lines of the X-ray powder diffraction films and applying a Nelson-Riley extrapolation function (29), and by use of a computer program "HERTA" (obtained from the Los Alamos Scientific Laboratory, Los Alamos, New Mexico) with a CDC 3600 computer.

High temperature X-ray diffraction patterns were obtained with a Materials Research Corporation high temperature X-ray diffraction attachment (30) Model X-86-G, mounted on a Siemens diffractometer. A platinum-10% rhodium flat heater was generally used, but because of the poor adhesive qualities of some samples, dish-type platinum heaters were at times more satisfactory. Cerium oxide nitride samples were mixed with 325 mesh platinum powder to provide an internal standard for temperature measurements and ground in dry n-heptane. A few drops of the sample slurry were placed upon the heater surface. The mounted samples were then inserted in the attachment and the unit was evacuated. The pressure measured in the vacuum line was less than 5×10^{-6} torr.

A diffraction tracing was obtained at room temperature over the 2θ range of 29-106°. A range of the diffraction angle, which included both a suitable specimen and a platinum standard peak, was then chosen for scanning with increasing temperature. The temperature of the specimen could be calculated by combining the observed lattice parameter of the internal standard, platinum, with its known thermal coefficient of expansion.

2. Metallographic Analysis

To prepare specimens for metallographic analysis, fragments of a crushed arc melted preparation were removed before the sample was ground into a fine powder. These small pieces of ingot were mounted and subsequently rough-polished under a lubricant such as ethylene glycol or mineral spirits with progressively finer grits of metallographic abrasive paper. For the final polish, progressively finer grades of aluminum oxide powder suspended in ethylene glycol or mineral spirits were used on a vibrating type (A.B. Buehler Ltd., "Vibromet") polisher. The samples were examined immediately, for they tarnished rapidly. If the polished specimen was to be retained, its surface was covered with a layer of Canada balsam and a thin microscopic cover glass was applied.

The samples were examined with a Bausch and Lomb "Dynazoom" bench metallograph, primarily under polarized light. A Polaroid camera attachment fitted to the viewing body of the metallograph permitted the photographing of the specimen.

3. Chemical Analysis

Cerium metal analyses were gross analysis for cerium present in any form in the product. A sample of from 0.1 to 0.2g was dissolved in dilute nitric acid (3N) and digested on a hot plate. The solution was adjusted to pH 4-5 with ammonium hydroxide and excess saturated oxalic acid solution was added. The precipitate which formed was allowed to digest overnight on a hot plate, was collected in a tared alundum filter crucible, and was washed with saturated oxalic acid solution. The sample was dried in an oven at 110° and then ignited in a muffle furnace at 900° to convert it to the oxide.

Nitrogen analyses were performed by the Kjeldahl technique in an apparatus designed to allow for the rapid decomposition of the samples upon their contact with acid. A diagram of the apparatus is shown in Figure 2. All connections between various components of the apparatus

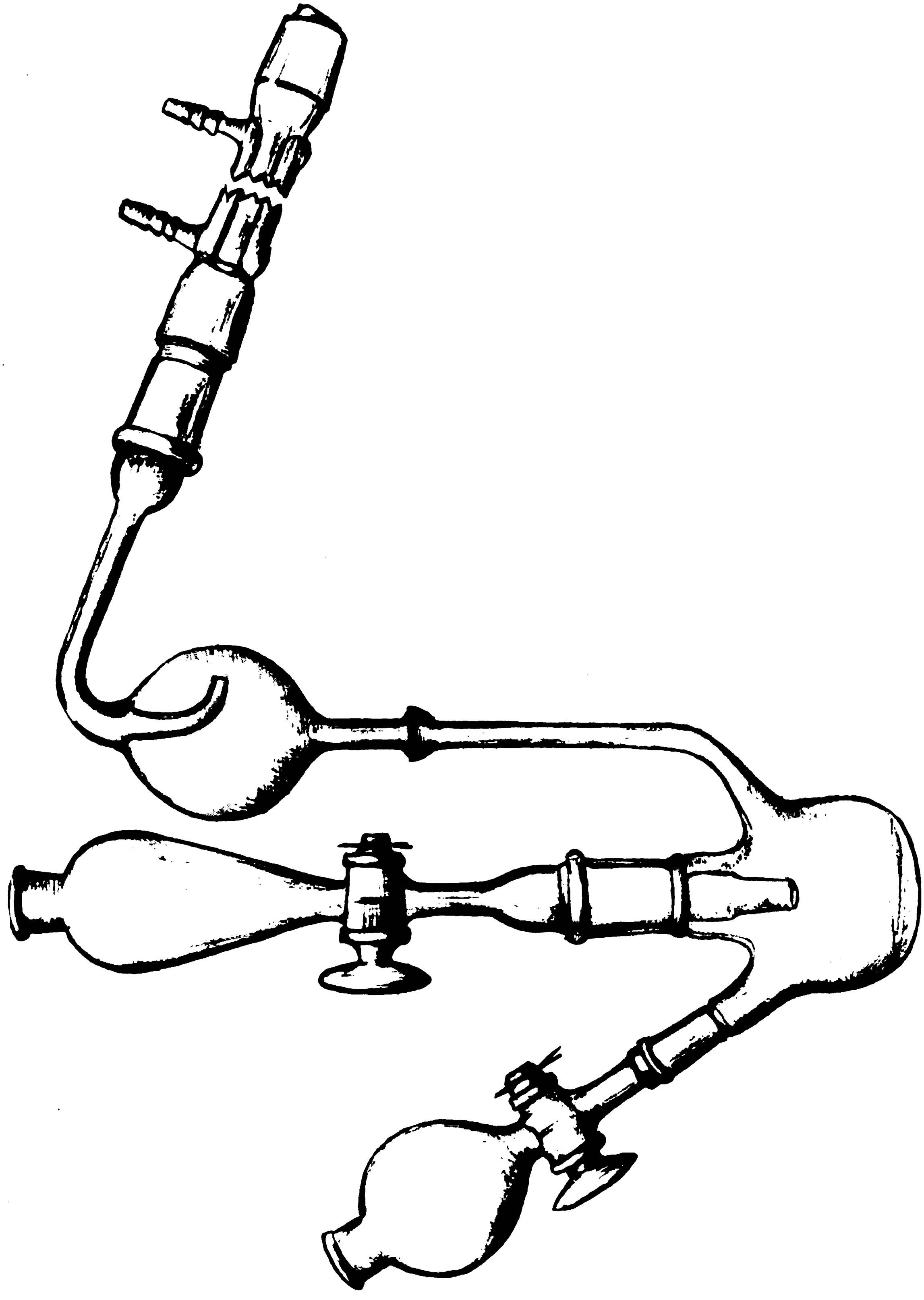


Figure 2. Apparatus for nitrogen analysis

were made with ground glass joints lubricated with silicone stopcock grease.

The apparatus consisted of a 100ml single neck round bottom boiling flask to which two small side inlet tubes had been added. A 60ml separatory funnel was connected to one inlet tube and a Kjeldahl distilling bulb to the other. A 60ml separatory funnel was connected to the center neck of the flask. The Kjeldahl connecting bulb was attached to a 300mm West condensor. An extension was attached to the end of a condensor adapter so that it easily reached the bottom of a 300ml Erlenmeyer flask used as a receiver.

The following procedure was used for an analysis. After the ground glass joints of the apparatus had been greased, a one dram vial was weighed in the glove box. Approximately 0.1 to 0.2g of the sample to be analyzed was placed in the vial, the vial reweighed, and the specimen weight thus determined. The vial was stored in a desiccator until use. Immediately before the sample was inserted into the analysis flask, 150ml of a 4 per cent boric acid solution was placed in the receiving flask and the receiver was put in place. Through the large ground glass joint, a few boiling chips were added to the flask, and the vial containing the sample was inserted as rapidly as possible with a long forceps. The separatory funnel was immediately replaced and 50ml of a dilute (2N) hydrochloric acid solution which contained a few drops of phenolphtalein indicator was added slowly to the flask through one of the separatory funnels. The heating mantle was turned on, and the solution was boiled for 5 to 10 minutes to insure decomposition of the sample. While the solution was boiling, a concentrated sodium hydroxide solution was prepared and placed in the empty separatory funnel. This solution was then added drop-wise until the contents of the flask were distinctly basic. Approximately 50ml of the now basic solution was then distilled into the receiver and titrated with a standardized hydrochloric acid solution (approximately 0.05N) using bromcresol green indicator. Blanks were periodically run and appropriate corrections were applied to the calculated results.

D. Vaporization Studies

1. Test for Congruent Vaporization

A tungsten crucible (Kulite Tungsten Company, Ridgefield, New Jersey) which had a height of 2.5cm and a diameter of 1.9cm, was used for the vaporization congruency studies. The cavity was 1.9cm in depth and 1.12cm in diameter. A loose-fitting lid which had a 1.4mm diameter centered orifice was provided to allow for escape of gases. The crucible was supported on three tungsten pins which protruded from a boron nitride table. The vaporization experiments were carried out in a vacuum system employing a current concentrator modeled after a design which has been described previously (31).

The congruency tests were performed as follows. The tungsten crucible was outgassed by heating under vacuum at 2000°. It was then weighed, charged with a sample, reweighed, and placed in the vacuum system which was immediately evacuated. The crucible was heated by induction until the maximum temperature of the vaporization run was attained and was maintained at this temperature for a period of time expected to cause significant evaporation of the sample. After it had cooled, the crucible was removed from the vacuum line, weighed, and a portion of the residue was taken for an X-ray powder diffraction analysis. Sometimes an additional portion of the residue was removed for nitrogen analysis. The remaining portion of the sample was recycled through this procedure several times.

2. Mass Spectrometric Study

A Bendix Time-of-Flight mass spectrometer which has been described in detail elsewhere (32), was used for this study and will be discussed only briefly. The instrument was designed to monitor two peaks independently or to scan two separate mass regions simultaneously. Their output was displayed on both an ammeter and a Bausch and Lomb Model VOM 5 strip chart recorder. The electron energy was monitored by a Digitec (United Systems Corporation, Model Z-200B) digital d.c. voltmeter. The mass spectrometer was equipped with a high temperature Knudsen cell inlet assembly heated by electron bombardment (33).

The crucible used in this work was machined from molybdenum rod and had an overall height of 2.1cm and a diameter of 1.6cm. The cavity was 1.15cm in depth and 1.0cm in diameter. A molybdenum lid drilled with a 1mm diameter knife-edged orifice was machined to fit tightly on the bottom portion of the crucible. The crucible and lid were simultaneously sealed together and outgassed by heating under vacuum at 2000°.

After outgassing, the cell was taken into the helium-filled glove box, weighed, and the sample loaded into the cell through the orifice as a finely ground powder. The cell was then reweighed, removed from the glove box, and placed in the electron bombardment heating assembly of the mass spectrometer. The assembly was attached to the instrument and evacuated immediately. After the pressure in the spectrometer had decreased to 10^{-6} torr, the cell was heated slowly by radiation to 800° to degas both it and the sample. A negative d.c. potential was then applied to the filament to cause the electrons emitted by it to go to the grounded crucible. By varying the d.c. potential, the energy of the electrons was either increased or decreased, and produced a corresponding increase or decrease in the temperature of the crucible.

Once temperature equilibrium had been established, the mass region of interest was scanned and recorded. Ion intensities were determined from the recorded peak heights. The ion intensity was also measured as a function of the energy of the electrons used to form the ions.

E. Temperature Measurement

Temperatures were measured with two different types of optical pyrometers. For most congruency of vaporization determinations, temperatures were measured with a two-color optical pyrometer, Model PC334 manufactured by Latronics Corporation, Latrobe, Pennsylvania.

Radiant energy (watts/cm^2) available for emission by an incandescent body is expressed by Planck's Law (34):

$$J_{\lambda_1, T} = C_1 \lambda_1^{-5} / (e^{-C_2/\lambda_1 T} - 1) \qquad [8]$$

where J_{λ_1} is the amount of energy radiated per unit area, per second, at wavelength λ_1, and T is the radiator's absolute temperature. C_1 and C_2 are the first and second radiation constants, respectively.

In the visible portion of the spectrum and for temperatures below 4000°K a simplification of the above law, known as Wien's equation, may be generally used:

$$J_{\lambda_1, T} \cong C_1 \lambda_1^{-5} \, e^{-C_2/\lambda_1 T} \qquad [9]$$

The diminuation of energy flux in passing through an intervening filter at a given wavelength is:

$$J_{\lambda_1, T_a} = J_{\lambda_1 T} \, e^{-k_1 x} \qquad [10]$$

where T_a is the apparent object temperature as observed through the filter, T is the true temperature, k_1 is the absorption coefficient in cm^{-1} at wavelength λ_1, and x is the absorbing path length in cm. Combining the two previous equations yields:

$$J_{\lambda_1, T_a} = C_1 \lambda_1^{-5} \, e^{-C_2/\lambda_1 T} \, e^{-k_1 x} \qquad [11]$$

If another wavelength of radiation (λ_2) is chosen, a similar equation results.

$$J_{\lambda_2, T_a} = C_1 \lambda_2^{-5} \, e^{-C_2/\lambda_2 T} \, e^{-k_2 x} \qquad [12]$$

The ratio (R) of the energies which pass through an intervening filter at two given wavelengths is:

$$R = \frac{J_{\lambda_1, T_a}}{J_{\lambda_2, T_a}}$$

$$= \frac{C_1 \lambda_1^{-5} \, e^{-C_2/\lambda_1 T} \, e^{-k_1 x}}{C_1 \lambda_2^{-5} \, e^{-C_2/\lambda_2 T} \, e^{-k_2 x}} \qquad [13]$$

The absorption coefficient for most substances varies only slowly with wavelength so that the ratio of the factors e^{-kx} is close to unity and thus the ratio of the intensities of the radiations becomes proportional to the temperature. The two color pyrometer used in this work measures with a photosensitive detector the intensities of two selected wave bands of the visible or near infrared spectrum emitted by the heated object. The ratio of the two wave bands is computed and converted into a linear temperature measurement on a direct-reading meter. Since the output of the pyrometer unit was a linear function of the temperature of the heated object, this output was used to run a proportional type control device for the induction generator. Whenever it was considered necessary, the instrument was calibrated with an internal tungsten calibration lamp.

Temperatures attained during the mass spectrometric and the cerium nitride preparatory studies were measured with a Leeds and Northrup Model No. 8622-C disappearing-filament type optical pyrometer which had been calibrated at the National Bureau of Standards. A graph of ($T°C_{NBS}$ minus $T°C_{scale}$) *versus* $T°C_{scale}$ was made for each temperature range and was used to correct the observed temperature.

Since this instrument measured the temperature of a heated object by comparing the brightness of light of a specific wavelength emitted by a heated object to the brightness of a heated filament contained within the instrument, correction for the absorption of light by any window and prism combination was necessary. Substitution of the value of J_{λ,T_a} obtained from equation [9] into equation [11] yields:

$$C_1 \lambda^{-5} e^{-C_2/\lambda T_a} = C_1 \lambda^{-5} e^{-C_2/\lambda T} e^{-kx} \qquad [14]$$

where λ is the wavelength of the radiation measured and the other quantities are as defined previously. Two equations which can then be obtained are:

$$\frac{-C_2}{\lambda T_a} = -kx - \frac{C_2}{\lambda T} \qquad [15a]$$

$$\frac{1}{T} - \frac{1}{T_a} = \frac{-kx\lambda}{C_2} \qquad [15b]$$

The term $\frac{kx\lambda}{C_2}$ may be evaluated by measuring how much the intensity of light radiated by a hot object is diminished by the filter (prism and/or window). Since Wien's law of radiation states that the energy radiated by a given substance is proportional to its temperature the magnitude of this term is obtained by:

$$K_i = \left(\frac{1}{T_f} - \frac{1}{T_L} \right) \qquad [15c]$$

where T_f is the temperature of a standard lamp read with the pyrometer sighted through the filter, T_L is the temperature of the standard lamp read with the pyrometer directly, and K_i is defined by equation [I5c]. The true temperature is then obtained by using equations [I5b] and [I5c] to give:

$$\frac{1}{T} = \frac{1}{T_a} - K_i \qquad [I5d]$$

To measure the transmissivity of the window and prism, the temperature of a closely regulated tungsten band lamp heated to a temperature near 1500° was read directly with the pyrometer and then through the window and prism.

IV. RESULTS

A. Preparation of Cerium Nitride

The two methods for the preparation of cerium nitride discussed in Chapter III yielded different results and will be discussed separately.

1. Preparation involving Induction Heating and Ammonia

Five separate preparations of cerium nitride were attempted. Three of the preparations were successful in that a single phase with both a satisfactory nitrogen content and a lattice parameter similar to that previously reported for CeN were obtained. The temperature, time of heating, and analytical data are summarized in Table V.

In two of the preparations, N-1 and N-3, the heating procedure used differed somewhat from that described in Chapter III. Thus, these two experiments will be discussed first. In N-1, ammonia was admitted to the evacuated system containing the crucible at room temperature. Subsequently, the crucible was heated slowly to 600° and ammonia was admitted to keep the pressure at approximately 500 torr. After being heated, the crucible was placed in a desiccator which was set in the glove box. When the crucible was being transferred, its lid was

Table V. Data for cerium and ammonia experiments

Preparation Number	Maximum Temperature°C	Time at Maximum temp.	Per cent Nitrogen
N-1	600	3 hours	5.81
N-2	1200	1/2 hour	8.17
N-3	1200	4 hours	a
N-4	850	b	7.50
N-5	1200	3 hours	8.27

Notes:

a - sample was not analyzed since visual observation indicated a large amount of cerium metal was present.

b - sample heated for various intervals at maximum temperature.

inadvertently dislodged and the sample was exposed to air. A portion of the dark brown-black sample oxidized almost immediately to yellow CeO_2. Oxidation was so rapid that the sample ignited and burned momentarily. In the atmosphere of the glove box the portion of the sample that had oxidized was removed and discarded. The sample was then reheated in ammonia. An X-ray photograph taken subsequently indicated the presence of CeN and Ce_2O_3, CeN being the predominant phase. When this sample was removed from the preparatory system, it probably consisted of a mixture of the hydride and the nitride. The hydride, being very reactive, oxidized to form CeO_2 which was reduced subsequently to Ce_2O_3 by the heating in ammonia. Seemingly, the heating of cerium metal at 600° in an atmosphere of ammonia in a static type system is insufficient to cause complete decomposition of the hydride and formation of an active metal surface where nitriding can occur. The lattice parameter of CeN in this preparation was identical to that observed in the other successful preparations even though a substantial amount of Ce_2O_3 was present in the sample.

In experiment N-3, the crucible was heated rapidly to 1200° in an ammonia atmosphere, and during the heating no ammonia was added. While the sample was heated, a yellow gold powder seeped from the crucible into the space between the crucible body and its lid. Subsequent examination indicated that most of the sample had melted and stuck to the bottom of the crucible. The inhomogeneous sample evidenced two portions, one yellow gold colored and easily removable and the other, which portion was stuck to the bottom of the crucible, distinctly blue and metallic in appearance. X-Ray diffraction analysis of the metallic colored material indicated the presence of a small amount of Ce_2O_3 and a phase with a diffraction pattern similar to that of the nitride but with a larger lattice parameter. Apparently during nitriding the amount of nitrogen present for reaction was insufficient for complete formation of the nitride. As the hydride decomposed, the metal produced melted and flowed to the bottom of the crucible, leaving any nitride formed as the top portion of the sample.

The interplanar d-spacings calculated for these CeN preparations compared favorably with those reported by Iandelli and Botti (5). Comparison of the back reflection lines of the CeN preparations indicated no variation of the lattice parameter.

The theoretical nitrogen content for CeN (9.09%) was never attained in any preparation. An attempt to increase the nitrogen content of one of the samples, number N-4, was unsuccessful. This preparation was found by analysis to contain initially 7.77% nitrogen. It was then heated in ammonia at 850° until the pressure in the system ceased to rise. The sample was cooled, the system evacuated, and ammonia again admitted to yield a pressure of 500 torr.

The crucible and sample were then reheated to 850° until the pressure stabilized. This procedure was performed five times, after which a sample was removed for nitrogen analysis. The procedure was repeated again for the remaining portion of the sample with a temperature of 1200° being maintained for 3 hours. The nitrogen content of both portions (i.e. the one heated to 850° and the other to 1200°) decreased from 7.77 to 7.47%. A small increase in the lattice parameter was observed after the heating at 1200°, but not after the 850° heating.

2. Preparation by Arc Melting

All arc melted preparations of cerium nitride yielded essentially the same results. The preparations were inhomogeneous with portions of unreacted cerium metal dispersed throughout. This inhomogeneity was confirmed by both micrographic and X-ray powder diffraction analyses of the samples. However, the interplanar d-spacings of these preparations compared favorably with those reported by Iandelli and Botti (5). The back reflection X-ray diffraction lines of these preparations compared to within about 0.1mm both with each other and with those preparations described in Section 1, an observation indicative of no variation in lattice parameter.

B. Investigation of the Cerium Oxygen Nitrogen System

A rough characterization of the Ce-O-N ternary phase diagram was obtained from an examination of the X-ray photographs of the arc melted samples of various compositions. All of the cerium nitride used for investigation of the cerium oxygen nitrogen system was prepared by the arc melting technique. Because of the uncertainty in the composition of the cerium nitride, the composition of the arc melted oxide nitride mixtures could not be determined accurately by weighing the components prior to arc melting. Another factor which contributed to the inaccuracy of the method was spattering (especially prevalent among samples with a high oxide content) and resultant loss of portions of the sample during melting.

The X-ray powder diffraction patterns for the arc melted cerium nitride-cerium oxide-cerium metal mixtures revealed the presence of four phases. Reaction of a very small amount of cerium dioxide with cerium nitride ($CeN:CeO_2 \approx 15:1$, by weight) yielded no detectable change in the lattice parameter of the nitride. When the amount of cerium dioxide added to the nitride was increased ($CeN:CeO_2 \approx 10:1$, by weight), phase separation occurred. One of these phases was cerium nitride; the other which exhibits face-centered cubic symmetry has not been reported previously. This phase subsequently was observed in the X-ray diffraction films of a number of the samples prepared in the study of the cerium oxygen nitrogen system. Arc melted CeN-CeO_2 mixtures in the ratio of between one and eight grams CeN to one gram of CeO_2 (molar ratio CeN/$CeO_2 \approx$ 1.1 to 8.9) always yielded this phase as one of the components. As the relative amount of CeO_2 was increased, the diffraction lines for Ce_2O_3 were observed in the X-ray photographs. When the CeO_2/CeN molar ratio exceeded 1.8, Ce_2O_3 became the predominant phase. Because cerium metal is inherently present in the cerium nitride preparations and cerium dioxide is unstable with respect to intermediate oxides at high temperatures, the dioxide was never found in any of the arc melted samples. Addition of cerium metal did not alter the results described above. If an excess amount of CeO_2 were added to the preparation mixture, Ce_2O_3 appeared along with the oxide nitride phase. Since additional Ce_2O_3 corresponds to a composition richer in cerium and oxygen and poorer in nitrogen the oxidation state of cerium in the oxide nitride phase must become lower. A compilation of the phases observed for the various cerium nitride-cerium dioxide-cerium metal mixtures is presented in Table VI. The composition of the various mixtures is indicated in Figure 3 and the composition range within which the various phases occurred is presented in Figure 4.

Analysis of the X-ray pure cerium oxide nitride preparations for both cerium and nitrogen and the

Table VI. Compilation of composition (by weight) of reactants and products for the cerium oxygen nitrogen system

Point No. Figure 3	Reactants[a]	Products
1.	$1CeO_2:1CeN$	$+Ce_2O_3, Y^+$
2.	$1CeO_2:2CeN$	$+Y, Ce_2O_3$
3.	$1CeO_2:3CeN$	$+Y, Ce_2O_3$
4.	$1CeO_2:4CeN$	$+CeN, Y^+$
5.	$1CeO_2:5CeN$	Y
6.	$1CeO_2:7CeN$	Y
7.	$1CeO_2:8.7CeN$	CeN,Y
8.	$1CeO_2:18CeN$	CeN
9.	$1CeO_2:30CeN$	CeN
10.	$1CeO_2:1.5Ce:3.3CeN$	Y
11.	$1CeO_2:1.6Ce:6.6CeN$	Y
12.	$1CeO_2:2.6Ce:4.75CeN$	Y
13.	$1CeN:2CeO_2$	$+Ce_2O_3$, trY
14.	$1CeN:3CeO_2$	Ce_2O_3
15.	$1CeN:1.1CeO_2:2Ce$	$+Y, Ce_2O_3$
16.	$1Ce:1.4CeO_2:1.6CeN$	$+Y^+, Ce_2O_3$
17.	$1Ce:1.4CeO_2:3.5CeN$	Y
18.	$1Ce:2CeO_2:1.5CeN$	$+Ce_2O_3, Y^+$
19.	$1Ce:2.4CeO_2:3.5CeN$	$+Y, Ce_2O_3$

$^+$ indicates a change in lattice parameter

[a] CeN refers to CeN-metal mixture obtained from arc melting

+ indicates compound present in largest quantity. If no symbol is present and two compounds are listed, they are present in equal amounts.

Y cerium oxide nitride phase tr trace amount present

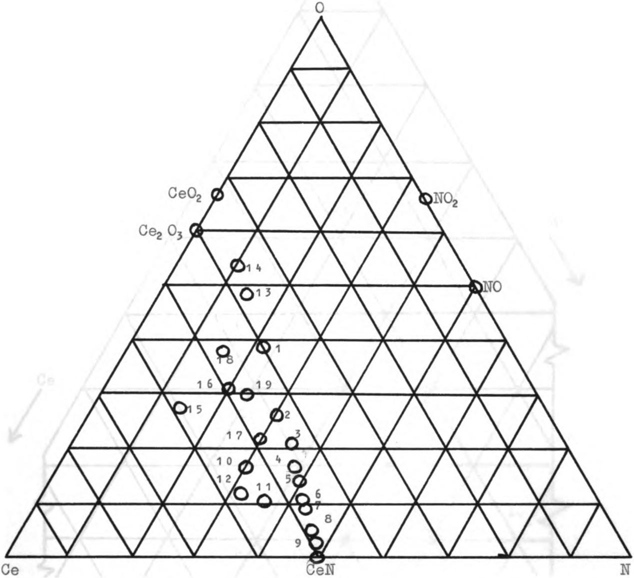


Figure 3. Composition of the reactants in the cerium oxygen nitrogen system. (Point numbers refer to Table VI).

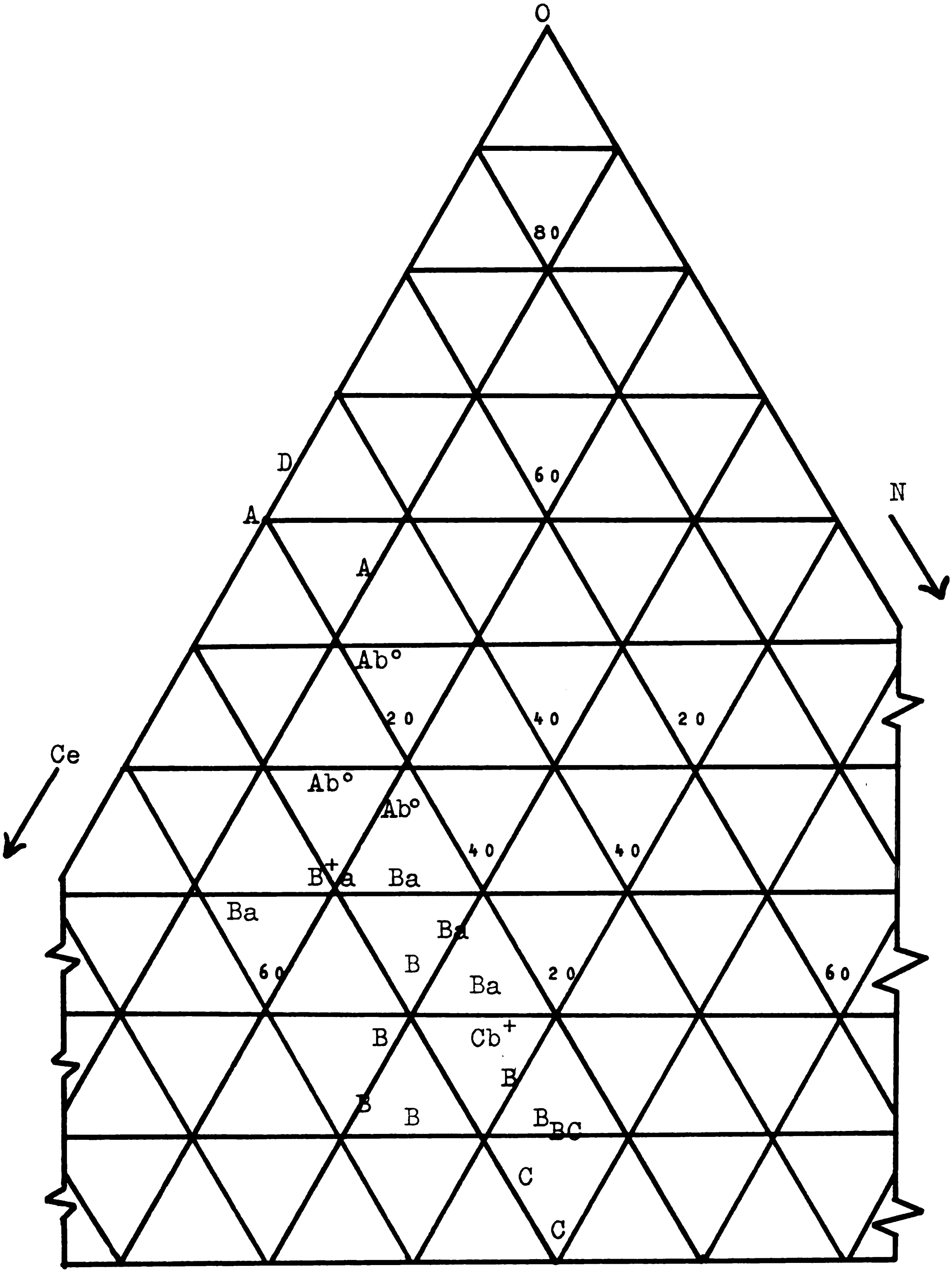


Figure 4. Phases observed versus composition in the cerium oxygen nitrogen system

Figure 4 (Cont'd)

Key:

A = Ce_2O_3
B = CeO_xN_y
C = CeN
D = CeO_2
$^{+}$ indicates a change in lattice parameter
$^{\circ}$ trace amount present

If an upper case letter is combined with a lower case letter, the compound in the upper case is present in the largest amount.

calculation of oxygen by difference yielded the following results: Ce:88.33 ± 1.11%, N:4.84 ± 0.17%, O:6.83 ± 1.12% where the errors reported are the standard deviations of the measurement. These data yield a composition of $CeN_{0.55 \pm 0.02}O_{0.68 \pm 0.11}$. A summary of the results obtained for each sample analyzed is given in Table VII. Micrographic analysis of the samples indicated that even at high magnification (800 x), any impurities present were dispersed throughout the sample. The presence of a common impurity, Ce_2O_3, could be detected readily because it exhibited a markedly different color from that of the oxide nitride. The cerium oxide nitride compound possessed a bronze color when in the arc melted ingot form, but a dark red-violet color when ground into a fine powder. When pulverized cerium oxide nitride specimens were treated with 6<u>M</u> HCl, only a portion of the sample would dissolve, and a yellow residue believed to be CeO_2 always formed. During the solution process bubbles of a gas thought to be hydrogen were evolved rapidly. The oxide nitride could be made to "spark" and immediately burn to CeO_2 upon striking the sample contained in a mortar by a hard object such as a file. However, X-ray diffraction photographs taken of samples exposed to moist air for two days indicated only the presence of the oxide nitride phase.

All of the pure cerium oxide nitride preparations gave identical diffraction powder patterns. The X-ray

Table VII. Summary of analytical results for cerium oxide nitride preparations

Sample No.	Weight per cent of element			Lattice parameter Å
	Ce	N	O (by difference)	
3-B	87.98 ± 1.40[+]	4.87 ± 0.14[+]	7.15 ± 1.50[+]	5.1174 ± 0.0015
4-B		4.77 ± 0.06		5.1183 ± 0.0003
3/9-1	88.16 ± 0.95	4.77 ± 0.15	7.07 ± 1.00	5.1165 ± 0.0003
3/10-1	88.95 ± 0.50	4.84 ± 0.23	6.21 ± 0.56	5.1134 ± 0.0005

[+] Standard deviation

All samples analyzed were X-ray pure; samples 3/9-1 and 3/10-1 were examined with a metallograph.

powder photographs were characteristic of the face-centered cubic structure and interplanar d-values together with their observed intensities are listed in Table VIII. The lattice parameter of this phase was determined from seven different preparations which contained either the pure oxide nitride or a mixture of the sesquioxide and the oxide nitride. No variation of the lattice parameter was observed unless the sample was deficient in nitrogen. The observed lattice parameter was: $a_0 = 5.115 \pm 0.002$ Å, where the error reported is the combined standard deviation.

Portions of cerium oxide nitride preparation 3/9 were examined in the high temperature X-ray diffraction camera and the elevated temperature spectrum was identical to that obtained by the film technique. As the temperature of the sample was increased, the diffraction angles changed slightly and the overall intensity of the spectrum diminished. When the sample temperature reached 600°, the intensity had almost decreased to background level. The sample was probably being oxidized by residual oxygen present in the camera to an amorphous, and hence nondiffracting, sesquioxide. Since a better vacuum and a higher pumping speed could only be attained with considerable camera modification, this aspect of the investigation was not pursued.

Table VIII. Interplanar d-spacings for cerium oxide nitride sample 3-B

Miller Indices (hkl)	d_{obs} Å	I_{rel}
111	2.937	72
200	2.547	100
220	1.804	60
311	1.539	48
222	1.474	16
400	1.278	12
331	1.173	16
420	1.143	18

C. Vaporization Studies on the Cerium Oxide Nitride Phase

The cerium oxide nitride phase was relatively nonvolatile since the temperature of the crucible was increased to about 1500° before any effusing vapors were detected by the mass spectrometer. As the temperature was increased above 1500°, effusate peaks became apparent. The sample was heated at temperatures in excess of 1600° for more than 2 hours and 1700° for more than 1 hour. During the course of the mass spectrometric investigation, the mass of the sample decreased 0.060 g from an initial mass of 0.160 g. Only $Ce^+(g)$ and $CeO^+(g)$ were observed in the spectrum. Nitrogen from the sample could not be observed because of the high nitrogen background in the spectrometer. That $Ce(g)$ and $CeO(g)$ were the primary effusing species was shown by varying the ionizing electron energy from 32 to 6 ev and observing the regular decrease in the intensity of the mass spectra peaks. A plot of intensity versus ionizing electron energy for $Ce^+(g)$ and $CeO^+(g)$ is shown in Figure 5.

A compacted pellet was obtained when a pure oxide nitride specimen was heated in a vacuum for at least 14 hours at 1400°. Two phases appeared to be present in this pellet. The exterior fraction, colored dull gold, completely surrounded the red gold interior. However, X-ray diffraction analysis revealed the presence of only the oxide nitride phase in both areas. Comparison of the back

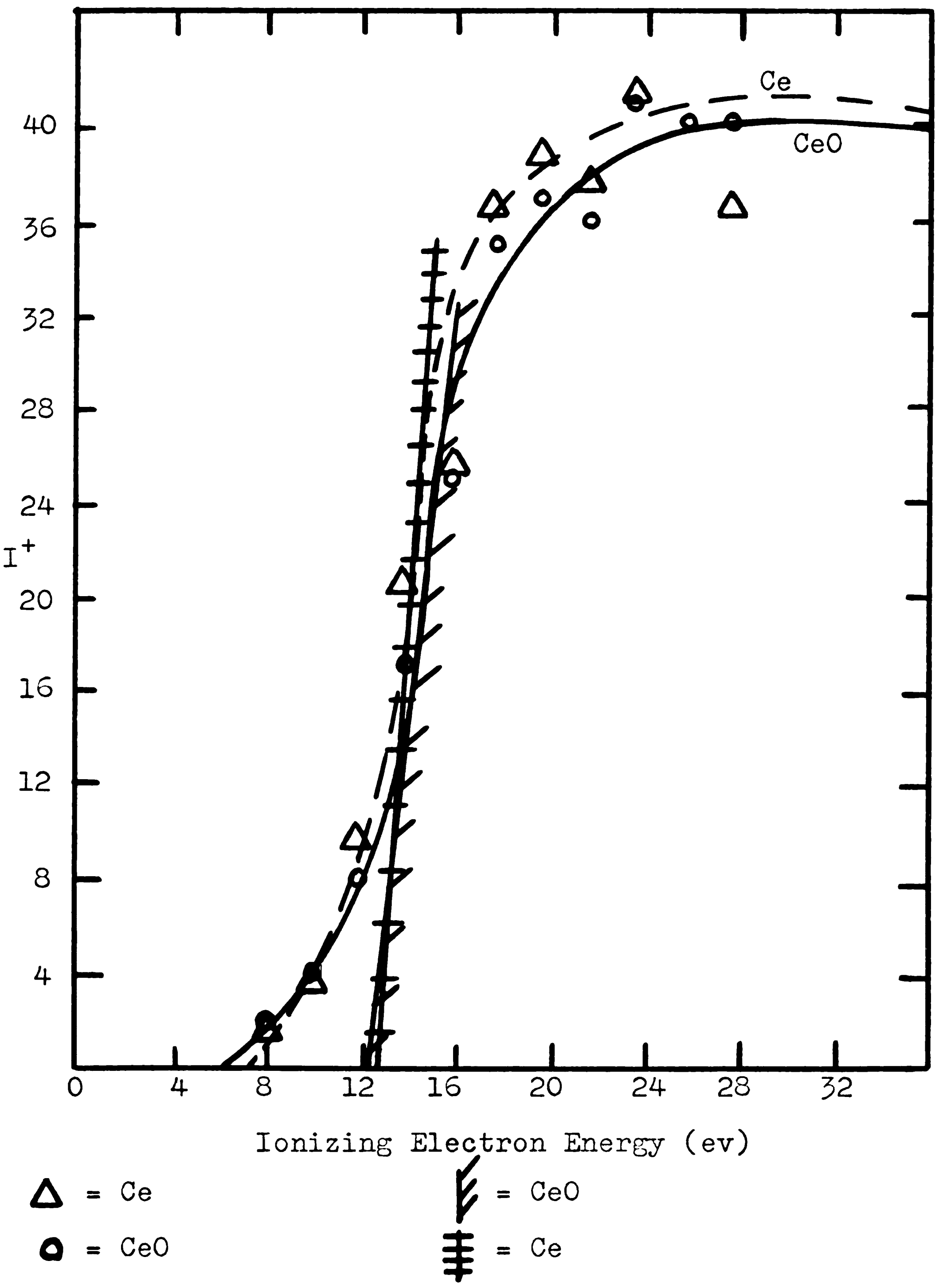


Figure 5. Ionization efficiency curves for Ce^+ and CeO^+

reflection lines of the two diffraction films indicated an identical lattice parameter for both portions of the sample but this parameter was smaller than that of the original oxide nitride specimen. None of the oxide nitride samples that had been heated for prolonged periods was analyzed for nitrogen. However, the diffraction photographs of these oxide nitrides compared favorably with those obtained from previously analyzed nitrogen deficient oxide nitride specimens which typically yielded a nitrogen content of 3.5 to 3.75%. Thus, it appears that the change in the lattice parameter of the oxide nitride after prolonged heating results from loss of nitrogen by the sample.

Results obtained during the vaporization of the cerium oxide nitride phase of composition $CeN_{0.55}O_{0.68}$ in the mass spectrometer indicate the following reactions:

$$\begin{aligned}(x+y)\ CeN_{0.55}O_{0.68} \xrightarrow{1500\text{-}1700^\circ}\ & x\ CeN_{(0.55-a)}O_{0.68}(s) + 0.68yCeO(g) \\ & + 0.32yCe(g) + (x\tfrac{a}{2} + 0.275y)N_2(g)\end{aligned} \qquad [16]$$

$$CeN_{0.55}O_{0.68}(s) \xrightarrow{1400^\circ} CeN_{(0.55-a)}O_{0.68}(s) + \tfrac{a}{2}\ N_2(g) \qquad [17]$$

The lattice parameter of the cerium oxide nitride phase was a maximum for the composition $CeN_{0.55}O_{0.68}$. For compositions richer in oxygen and poorer in nitrogen than this value - for which Ce_2O_3 was detected in X-ray photographs - the lattice parameter was the same or in some instances slightly smaller. As the composition of the oxide nitride phase became deficient in nitrogen, there was an apparent continuous decrease in the lattice parameter to the composition $CeN_{0.42}O_{0.80}$ - the lowest analyzed nitrogen composition. Further decrease in the nitrogen content upon vaporization yielded a two phase mixture of the nitrogen deficient cerium oxide nitride and the sesquioxide.

D. Reaction of Cerium Oxide Nitride with Ammonia

Cerium oxide nitride samples confined in a tungsten crucible were heated at 1200° in an ammonia atmosphere. X-Ray diffraction photographs taken of the resultant products indicated that the nitride and sesquioxide were formed according to reaction [18].

$$5.88\ CeN_{0.55}O_{0.68}(s) + 0.667\ NH_3(g) \longrightarrow 3.88CeN\ (s) + Ce_2O_3(s) + H_2O\ (g) \qquad [18]$$

The lattice parameter of the nitride thus formed was slightly larger than that of nitride formed by the heating of cerium metal with ammonia or by arc melting cerium in a nitrogen atmosphere.

E. Vaporization Studies on Cerium Nitride

Vaporization experiments were made on two different cerium nitride preparations. The data which are summarized in Table IX, indicate the residue of every vaporization contained cerium nitride. However, chemical analysis for nitrogen and comparison of the back reflection lines of the X-ray diffraction films indicated that the compositions of the nitride samples were changing as they were evaporated. The nitrogen content of each sample appeared to approach upon evaporation a certain limit which was dependent upon its initial nitrogen content. With sample N-4, the initial nitrogen content was 7.50 per cent and the final content was 6.08 per cent. With sample N-5, the initial content was 8.27 per cent and the final content was 7.10 per cent. The lattice parameter of each nitride sample increased as the amount of nitrogen present decreased, and did not appear to approach a limit as did the nitrogen content, but was still increasing when the vaporization experiments were terminated. The lattice parameter and corresponding nitrogen content of each sample are presented in Table X. These lattice parameters are plotted *versus* nitrogen content in Figure 6. The straight line drawn through the points has been extrapolated to the theoretical nitrogen content of CeN, 9.12%.

Table IX. Vaporization experiments with cerium nitride

Run No.	Initial Sample Wt.	Wt. Loss Evap.	Single Run Loss %	Time Heated	Temp.	X-ray Residue	Nitrogen % in Residue
N-4A	1.5816 g	0.0112 g	0.7	4 hurs.	1500°C	+	
N-4B	1.5704	0.0092	0.6	4	1600	+	
N-4C	1.5612	0.0228	1.5	4	1700	CeN	6.72
N-4D	1.1496	0.0520	4.5	12	1700	CeN	6.19
N-4E				13	1750	CeN	6.08
N-5A	2.8091	0.1385	4.9	14	1750	CeN	6.93
N-5B	1.4805	0.9662	65.3	16.5	1800	CeN	7.10

[+] The sample was only weighed - none of it was removed.

Table X. Lattice parameters during the vaporization of cerium nitride

Sample	Cerium %	Nitrogen %	Lattice parameter (Å)
N-4	86.41 ± 0.24	7.48 ± 0.07	5.0290 ± 0.0002
N-4C		6.72 ± 0.17	5.0382 ± 0.0002
N-4D		6.19 ± 0.24	5.0452 ± 0.0004
N-4E		6.08 ± 0.07	5.0502 ± 0.0004
N-5	86.79 ± 0.46	8.27 ± 0.19	5.0211 ± 0.0002
N-5A		6.93 ± 0.14	5.0250 ± 0.0004
N-5B		7.10 ± 0.05	5.0309 ± 0.0002

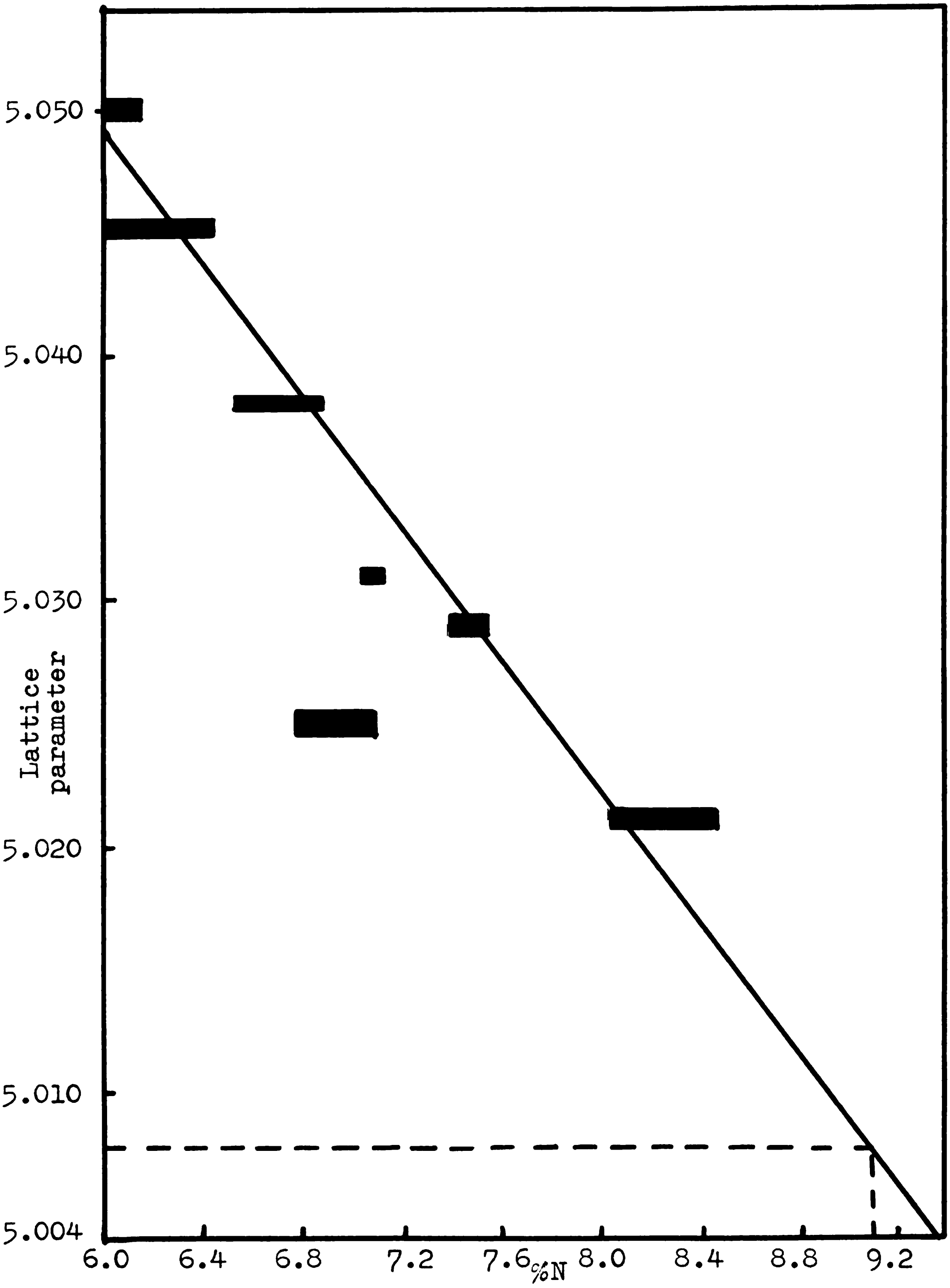


Figure 6. Lattice parameter of cerium nitride versus nitrogen content

V. DISCUSSION

A. Preparation of Cerium Nitride

1. Preparation involving Induction Heating and Ammonia

The lack of success in obtaining the theoretical nitrogen content in any of the cerium nitride preparations and the unsuccessful attempt to increase the nitrogen content in one of the samples indicates that in the case of cerium nitride grinding of the nitrided metal and subsequent reheating in ammonia does not increase further the nitrogen content of a sample formed by heating in ammonia at 850°.

Anderson (35) in his investigation of the cerium nitrogen system found that even after he had carefully removed most of the oxygen present in the metal used as a reactant by melting it under an argon atmosphere and removing the skin of oxides which formed, he obtained at 900-950° a nitride of composition $CeN_{0.97}$ (8.84% nitrogen). He further indicated that preparation at either a lower or higher temperature would yield less nitrogen rich specimens. From these observations he concluded that this phase was definitely sub-stoichiometric.

The results presented in this thesis are consistent with those of Anderson if one assumes that the initial treatment of the metal with ammonia produced a nitride close to the equilibrium stoichiometry for the particular temperature used.

Since in this work the only precaution taken to remove dissolved oxygen was the heating of the metal under vacuum to outgas it, a significant amount of oxygen may possibly exist in the nitride samples. The presence of this oxygen may also explain why the percentage of nitrogen observed in this work is somewhat less than that reported by Anderson.

Previous investigators (36,37) have indicated the problem of attaining stoichiometric nitrides lies not with achieving complete reaction between the metal and the nitriding agent, but with securing very pure reactants so that impurities (principally oxygen) do not react with the metal in lieu of the nitriding agent. On the assumption that the difference in the total per cent of cerium and nitrogen present in the nitride and 100 per cent is due to oxygen impurity, calculations performed with these nitride preparations indicate that within the limits of error in the analyses, the amount of oxygen (present as CeO_2, the least favorable case in that it yields the lowest mole fraction of impurity) should be detectable by X-ray powder diffraction. The results obtained with a typical cerium nitride sample (preparation N-5) will serve to illustrate this point. This preparation contained 8.27% nitrogen and 88.16% cerium, and thus has an estimated 3.5% oxygen. On the assumption that all of this oxygen was present in combined form (CeO_2), of a hypothetical 100 g sample of original material, 15.3 g of Ce was used to form CeO_2. Of the 88.2 g of cerium originally present, 72.9 g are left to react with nitrogen to form CeN. According to the stoichiometry of the reaction, 0.52 mole of CeN will be produced. The 15.3 g of cerium metal used to form CeO_2 should produce 0.11 mole. Thus, the mole fraction of CeO_2 in this cerium nitride sample should be approximately 0.17 and therefore detectable. However, since no phase other than nitride was observed in the X-ray photographs, oxygen must be present in this phase.

2. Preparation by Arc Melting

The nitrogen content of samples prepared by arc melting cerium in a nitrogen atmosphere ($CeN_{0.65}$, 6.25%N) was similar to that reported by Gambino and Cuomo (15) and Anderson (35). Since the arc melted samples were observed to be inhomogeneous, the metal-nitrogen ratio of the nitride in these specimens must be closer to unity. Comparison of the X-ray photographs of arc melted and ammonia prepared nitrides as a means of estimating the stoichiometry is therefore of little value because the lattice parameters will be similar. As the ammonia prepared nitride specimens were vaporized, and therefore annealed, their lattice parameters increased. This apparently inconsistent observation may be rationalized by realizing that when the arc melted samples solidify, the nitride having the higher freezing point precipitates first. Ammonia prepared or vaporized samples, on the other hand, are never molten and upon quenching do not separate into phases. Thus, a nitrogen deficient sample must have a lattice parameter larger than that of the nearly stoichiometric nitride. This observation supports that of Gambino and Cuomo (15) that cerium nitride with a metal nitrogen ratio close to unity is crystallizing in the arc melting process from a nitrogen deficient melt and disagrees with Anderson's observation that as the nitrogen content is lowered, the lattice parameter decreases (35).

B. Vaporization of Cerium Nitride

A pure, single phase compound is said to vaporize congruently if, during the vaporization, the solid and the vapor phase have the same composition. If meaningful enthalpy and entropy determinations are to result from a vaporization process, the congruency of vaporization must be determined. To date, no vaporization studies have been reported for lanthanon nitrides so that no meaningful comparisons can be made.

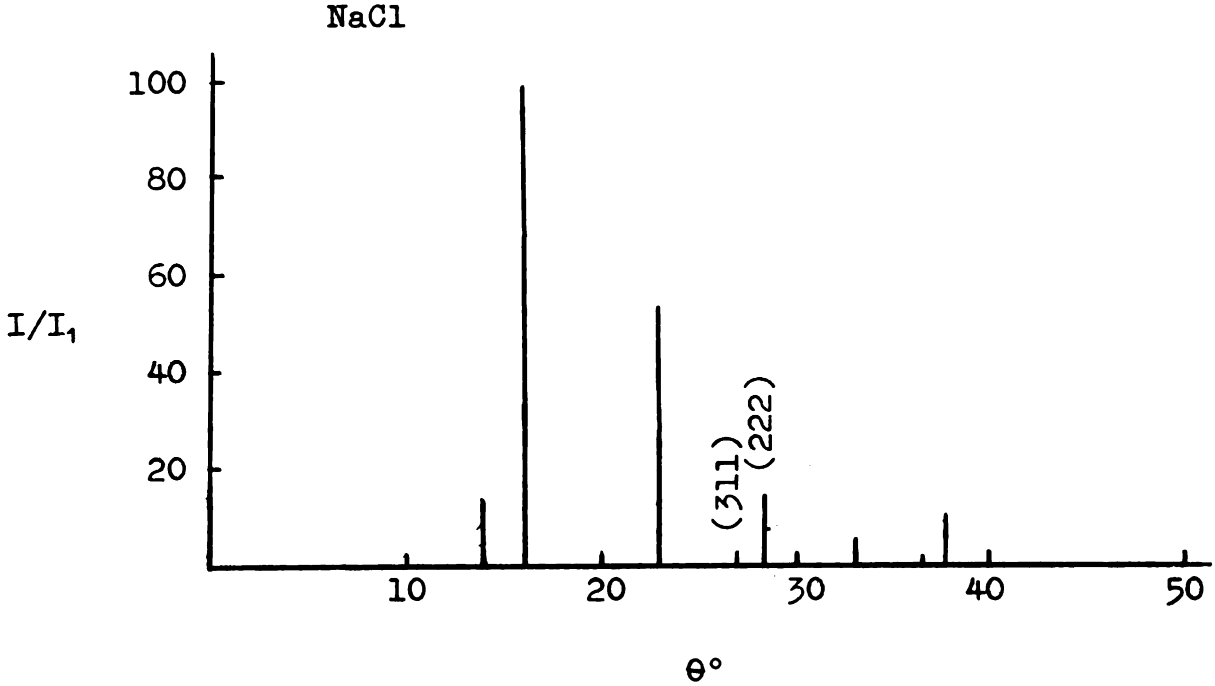
The observation that the lattice parameter of CeN continued to increase after the nitrogen content of the samples had approached what appeared to be a limiting value probably indicates that the cerium ions are being converted to an oxidation state of +3. Von Essen and Klemm (16) in their study of the magnetic susceptibility of cerium nitride indicate that at higher temperature the trivalent state of cerium becomes more predominant. Thus, in this system, there could be a change in lattice parameter after a congruent vaporization composition has been reached if cerium is still present in the quadrivalent state.

The results obtained in Figure 6 indicate a lattice parameter for CeN of 5.007_8 Å. This value is smaller than the reported lattice parameter of 5.021 Å (5) or 5.026_2 Å (35). Consequently, the extrapolated value probably would be the approximate lattice parameter of CeN were the cerium entirely in the +4 oxidation state.

C. The Cerium Oxygen Nitrogen System

Comparison of the relative intensities of the cerium oxide nitride X-ray diffraction lines with those of sodium chloride indicate that the oxide nitride probably exhibits the face-centered cubic sodium chloride lattice. The data shown in Figure 7 compare both the interplanar d-values and the relative intensities of the oxide nitride diffraction lines (Table VIII) with those of sodium chloride (ASTM X-ray powder diffraction card file).

One difference in the relative intensity pattern is noteworthy. The (311) plane of the oxide nitride exhibits



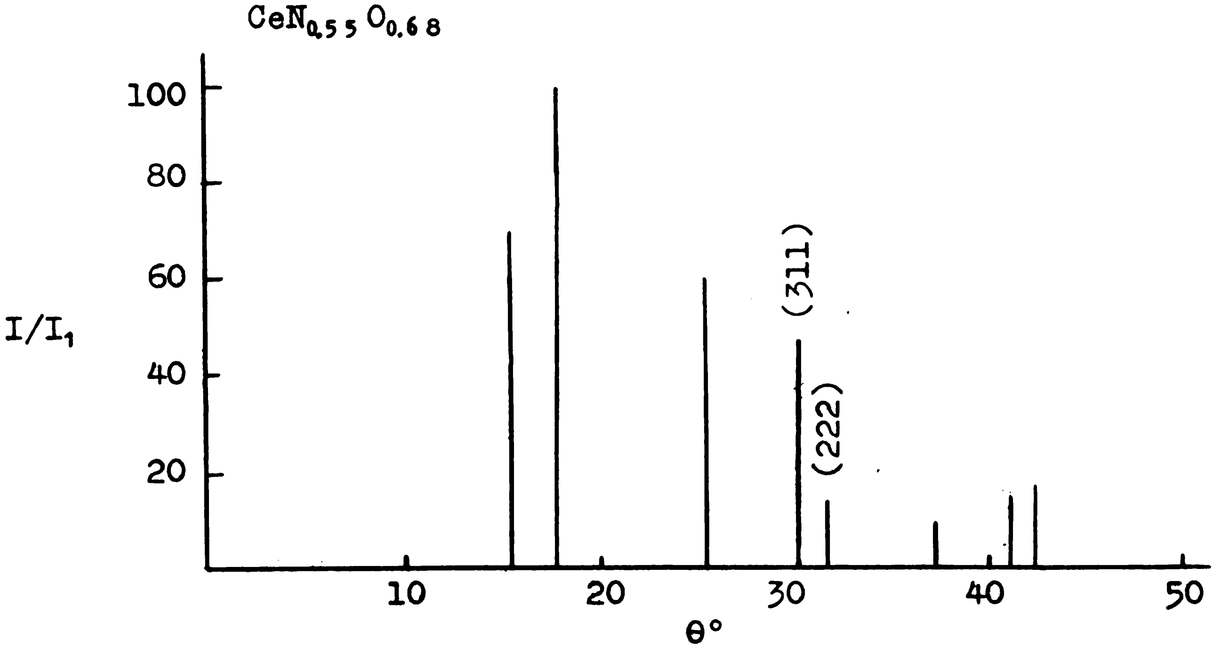


Figure 7. The relative intensities of the X-ray diffraction lines for cerium oxide nitride and sodium chloride versus θ.

a relative intensity greater than that of the (222) plane, while converse is and should be true in the sodium chloride structure. Because the structure is isotropic, preferred orientation would not be anticipated. However, the possibility of line overlap exists. Cerium nitride probably possesses a disordered face-centered arrangement (38); cerium dioxide has the fluorite type cubic structure (39), and cerium sesquioxide has the trigonal "A" type lanthanon sesquioxide arrangement (39). Since the most intense line of these diffraction patterns neither overlays this (311) line nor is present in the CeON pattern from which intensity data were collected, this possibility must be discounted. Thus, this intensity reversal must be interpreted as an indication either that additional atoms present in the structure alter the structure factor of this plane or that a considerable number of vacancies exist and cause the reversal.

The presence of additional atoms is consistent with the observed formula in that the ratio of the filled anion to cation sites is greater than unity, and sites other than the octahedral interstices thus must be occupied. Indeed, because the relative intensities are dominated by metal positions, the true symmetry may actually be considerably lower than cubic.

Although Anderson has indicated that CeN is probably highly disordered (35), the nitrogen atoms, or nitride ions, may be considered to occupy the octahedral holes while the metal ions are situated in the face-centered cubic sites. While the oxide nitride could be considered a solid solution of either "Ce_4O_7" or Ce_2O_3 in CeN, it is more probable that a new phase results from substitution in the nitride lattice of the oxide ion whose radius is 1.40 Å for the nitride ion whose effective radius in the lanthanon nitrides is 1.53 Å (11). The absence of a continuously variable lattice parameter between the nitride and oxide nitride supports this substitution hypothesis.

Two oxidation states of the metal in the oxide nitride were detected by the behavior of the compound in acid. Since cerium in the +3 oxidation state could be precipitated from the solution by oxalic acid, the metal in the oxide nitride exhibits the oxidation states of +3 and +4, a feature also observed in the nitride. The liberation of hydrogen upon solution may be interpreted as the interaction of free electrons, probably located in the conduction bands, with the acid, again indicative of cerium present in the +4 oxidation state.

The results obtained for the pure oxide nitride phase, reported in Section IV-B, yielded a composition of $CeN_{0.55}O_{0.68}$. This composition, represented in terms of integral numbers, becomes $Ce_4N_2O_3$, or $Ce_2O_3 \cdot 2CeN$. Although this 2:1 relationship may be coincidental, it does lead to the speculation that other similar relationships may exist, and indeed that the apparent composition variance evidenced by the variable lattice parameter may really result from an homologous series type of phases. Interestingly, the phase with the lowest analyzed nitrogen composition, $CeN_{0.40}O_{0.80}$, may be represented in terms of integral numbers as $Ce_5N_2O_4$ or $2CeN \cdot Ce_2O_3 \cdot CeO$.

These homologous series generally arise from combination of a cation in two different oxidation states, for example, $Ti_2O_3 \cdot TiO_2$ or $Ti_2O_3 \cdot 2TiO_2$. As has been indicated, the nitride might meet the requirements of the +4 cation while the sesquioxide meets the requirement for the +3 cation. In light of this observation, the plausibility of an homologous series does not seem unreasonable.

If oxidation states of minus three and minus two are assumed for the nitride ion and oxide ion, respectively, the oxidation state of cerium in this oxide nitride phase is 3.05. By neglecting the presence of Ce^{+4}, the effective radius of the nitride ion in this phase can be calculated from the radii of the oxide and the Ce^{+3} ions. If contact of the cation and the anion is assumed along the cell edge instead of through its body, the lattice parameter, a_0, may be expressed as:

$$a_0 = 2r_c + 2r_a \qquad [19]$$

where r_c is the radius of the cation and r_a is the radius of the anion. Substitution for a_0 and r_c (40) yields a

r_a value of 1.53 Å. This value of r_a may be considered the weighted mean radii of the oxide and nitride ions in cerium oxide nitride. The following equation is then valid for this system:

$$r_0 X_0 + r_n X_n = 1.53 \qquad [20]$$

where r_0 is the radius of the oxide ion and r_n is the effective radius of the nitride ion. X_0 and X_n are the respective mole fractions of the oxide and nitride ions. The insertion of the value of r_0 (41) and the appropriate values of X_0 and X_n calculated for $CeN_{0.55}O_{0.68}$ into equation [20] yields $r_n = 1.70$ Å. This value of r_n which compares favorably, although possibly fortuitously, with the effective ionic radius of the nitride ion (1.71 Å) reported by Pauling (42) is considerably larger than the effective radius of nitrogen in the lanthanon nitrides. Even though this size alteration may indicate that nitrogen is present as the N^{-3} ion, it could simply indicate that this phase contains fewer vacancies than the nitride. Flemlee and Eyring (22) conclude that in the samarium oxygen nitrogen system the nitride ion does not attain a charge of -3, but attains a charge closer to -2 and should therefore have a smaller radius than that given by Pauling.

Flemlee and Eyring in their investigation of the samarium nitrogen oxygen system also found that the lattice parameter of the samarium oxide nitride phase decreased with an increase in oxygen content. This same effect has been observed in the gadolinium oxygen nitrogen system (15). The opposite trend is observed in the cerium oxygen nitrogen system. The decrease in lattice parameter with increasing oxygen content would be the expected trend if an oxide ion of radius 1.40 Å substituted for a nitride ion of radius 1.53 Å and no other effect took place. Flemlee and Eyring conclude that in the samarium oxygen nitrogen system, samarium remains in the trivalent oxidation state as oxygen substitutes for nitrogen and they cite evidence to support their conclusion. The increase in the lattice parameter in the cerium oxygen nitrogen system as oxygen is substituted for nitrogen indicates that the ratio of cerium in the trivalent state to that in the quadravalent state is increasing.

Previous investigators (23,27) working with zirconium oxide nitride phases have noted that with long heating (100 hours) in a vacuum or argon atmosphere, zirconium oxide nitride decomposes to ZrO_2, ZrN and nitrogen. The formation of cerium nitride has not been observed in any of the cerium oxide nitride heatings, but the heating was never performed at a temperature high enough to cause a significant amount of evaporation. It should be noted that the decrease of the lattice parameter of cerium oxide nitride upon heating brings it closer to, but never in agreement with that of the nitride.

Flemlee and Eyring (22) found that the samarium oxide nitride phase undergoes hydrolysis on exposure to air producing ammonia that was detectable by moist litmus after approximately five minutes. In contrast, the cerium oxide nitride phase was fairly unreactive in air and retained its dark red violet color upon standing in air for periods of up to two days.

To test the validity of reaction [18] its equilibrium constant was calculated at 298, 600, 1000, and 1400°K using the equation $\Delta G^{\circ}_{T} = -RT\ln K$. The standard free energies of formation of the various species in equation [18] were either calculated from previously known thermodynamic data or were approximated. The free energy of formation of $CeN_{0.55}O_{0.68}$ was approximated as:

$$\Delta G^{\circ}_{T}\ CeN_{0.55}O_{0.68}(s) = 0.55\Delta G^{\circ}_{T}\ CeN(s) + 0.226\Delta G^{\circ}_{T}\ Ce_2O_3(s)$$

The free energy of formation of CeN(s) at these temperatures was approximated from the enthalpy of formation at 298°K and the variation of the free energy of formation of ZrN(s) with temperature. A compilation of the thermodynamic quantities, the sources of reference and the calculated values of the equilibrium constants are given in Tables XI and XII. The results of these calculations show that in going from 600°K to 1000°K the equilibrium constant increases by a factor of $10^{7.4}$. If the reaction indicated by equation [18] is carried out in a large excess of

Table XI. Free energies of formation

T, °K	ΔG°_T, kcal/mole				
	Ce_2O_3(s)	H_2O (g)	NH_3(g)	CeN (s)	$CeN_{0.55}O_{0.68}$(s)
298	-407.4	-54.51	-3.98	-78.1	-134.9
600	-386.2	-51.7	+4.0	-73	-127.5
1000	-359.0	-45.4	+15.3	-64	-114.2
1400	-332.0	-40.2	+26.0	-55	-105.2
Ref.	(43)	(44)	(45)	est'd	calc'd

Table XII. Equilibrium constant for reaction [18] as a function of temperature

T, °K	ΔG°_{rxn} kcal/mole	log K
298	+54.6	-43.8
600	+26.4	-9.63
1000	+10.4	-2.26
1400	+15.5	-2.41

ammonia as was done in this work, the free energy change, ΔG_T, at temperatures of 1000°K and above is sufficiently negative to result in the formation of CeN and Ce_2O_3. As the reaction proceeds, the increase in the concentration of water causes ΔG_T to become equal to zero and the system attains an equilibrium state.

Extrapolation of the straight line portion of the ionization efficiency plots for Ce^+ and CeO^+ to zero intensity indicates that the appearance potential of Ce^+ is probably slightly greater than that of CeO^+. This observation compares favorably with the results obtained for Nd^+ and NdO^+ by other investigators (46,47).

Flemlee and Eyring have indicated that a phase previously reported by Eick, *et al*. (6) to be SmO is actually a samarium oxide nitride phase. Gschneidner and Waber (48) have reported the existence of CeO. Their phase, which appears when cerium is heated at about 550° in silica containers, exhibits face-centered cubic symmetry with the lattice parameter $a_0 = 5.1186 - 5.1347$ Å. Although this lattice parameter is somewhat larger than that obtained for the cerium oxide nitride phase, there is a distinct possibility that the cerium reduced the silica and simultaneously reacted with a nitrogen impurity commonly present in vacuum systems, and that these two phases are identical.

VI. SUGGESTIONS FOR FURTHER RESEARCH

Studies should be performed on the cerium oxide nitride phase to determine as a function of temperature the relative amounts of cerium present in the +3 and +4 oxidation states.

Studies on mixtures of cerium nitride and oxide nitride should be made with a high temperature X-ray diffraction camera to determine both the nature of the transition between nitride and oxide nitride and thermal expansion data.

Investigations should be made with other lanthanon nitrides to determine the elements for which the oxide nitride phase exists.

Oxygen in cerium oxide nitride preparations should be determined directly to obtain more accurate measure of the amount present.

Further investigation should be undertaken to confirm the postulated congruent vaporization of cerium nitride. Subsequent to confirmation of congruent vaporization, the vapor pressure of cerium in equilibrium with solid cerium nitride could be measured by the Knudsen effusion technique.

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APPENDICES

APPENDIX A

Investigation of the Lanthanum-Oxygen Nitrogen System

1. Experimental

Lanthanum nitride was prepared by arc melting chips of lanthanum metal in a nitrogen atmosphere. After the nitrided specimens had cooled, they were transferred to a helium filled glove box where they were crushed in an iron mortar and pulverized in a "Diamonite" mortar. All subsequent operations such as weighing and filling of X-ray capillaries were performed in the glove box.

Weighed amounts of lanthanum nitride and previously calcined La_2O_3 were mixed together. These mixtures were subsequently arc melted, and X-ray diffraction photographs taken of the resultant products were examined for the presence of any unreported phases.

2. Results

The nitrides prepared by this method were inhomogenous with portions of unreacted lanthanum dispersed throughout the sample. The samples crushed with difficulty in the iron mortar, breaking into chunks which tended to smear. Nitrogen analysis of one of the arc melted ingots yielded an average nitrogen content of 6.18%. As is to be expected, the interplanar d-spacings for arc melted lanthanum nitride compared favorably with those reported by Iandelli and Botti. Furthermore, comparison of the back reflection lines of the various preparations indicated no variation in lattice parameter. Five different mixtures of La_2O_3 and lanthanum nitride were arc melted. The weight ratios varied from 3 parts lanthanum nitride:1 part La_2O_3 to 1 part lanthanum nitride:3 parts La_2O_3. The X-ray diffraction photographs of two of the mixtures indicated the presence of a phase whose lattice parameter was different from that of lanthanum nitride. The mixtures were of the ratio 2 parts lanthanum nitride:1 part La_2O_3 and 1 part lanthanum nitride:1 part La_2O_3. In the mixture 1 "LaN":1La_2O_3, La_2O_3 and the "extra" phase were present in equal amounts while in the 2 "LaN":1La_2O_3, the "extra" phase was present in the greater amount. The lattice parameter of this new phase, which is probably an oxide nitride, was the same in both mixtures.

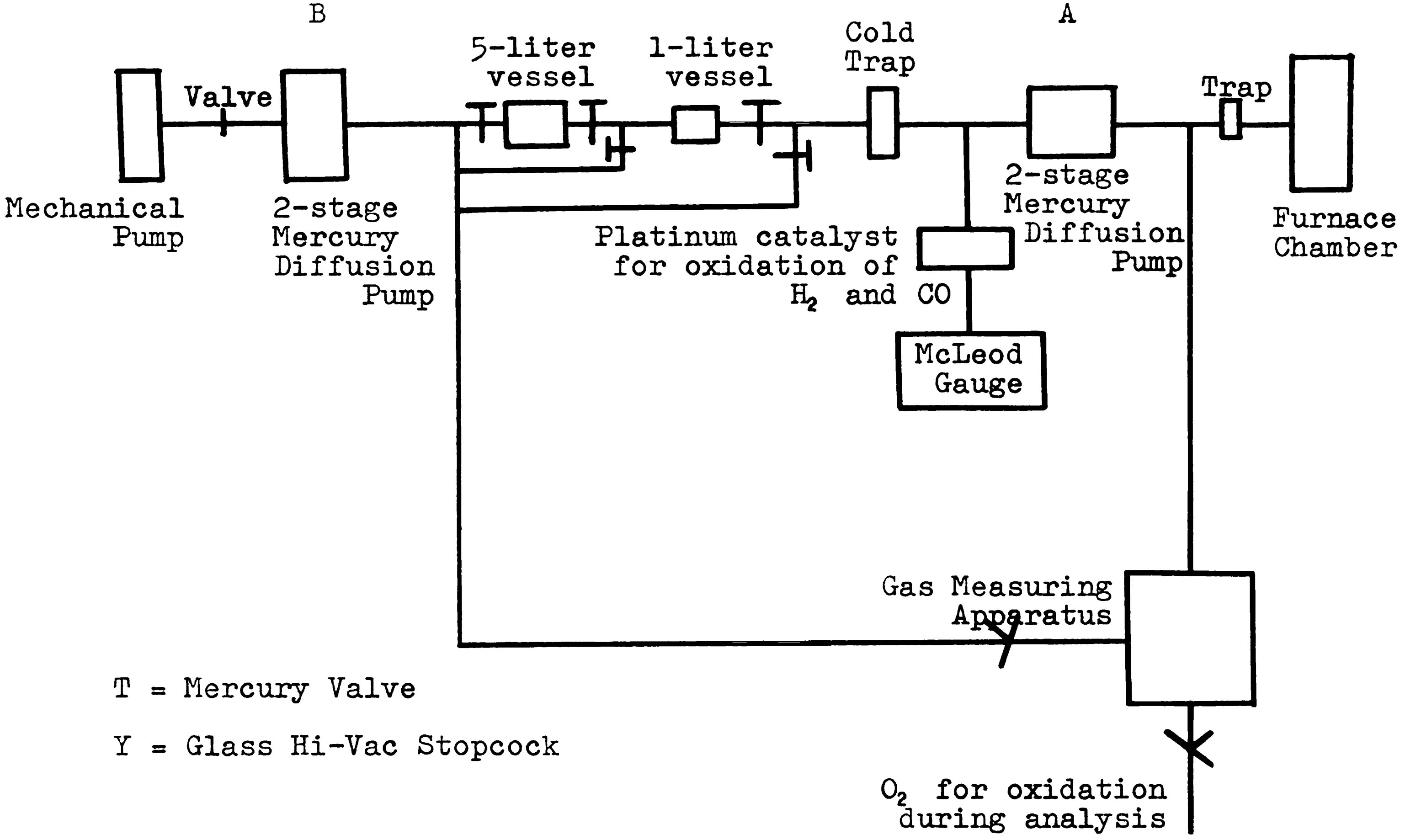
Further studies should be made to determine the composition and properties of this oxide nitride phase.

APPENDIX B

Analysis of Oxygen in the Lanthanon Oxide Nitrides

In the oxide nitride phase prepared in this work, the oxygen present was determined by difference. Since a determination by difference is dependent upon the accuracy with which the other components in a phase are known, direct determination is usually more desirable. This appendix describes an apparatus constructed for direct determination of oxygen in lanthanon oxide nitrides and the problems associated with its operation.

A review of the various methods used to determine oxygen indicated that the best method for lanthanon compounds would be one utilizing carbon fusion techniques. I chose the vacuum fusion method employing a molten platinum bath. A block diagram of the apparatus is shown in Figure B-1. The analysis system is similar to that described previously by Gregory and Mapper (49). In this method the sample is introduced into a graphite crucible supported in a furnace chamber. Oxygen present in the sample reacts with the graphite crucible to form carbon monoxide, and nitrogen present as nitride is released as nitrogen gas. The CO and N_2 so formed are pumped out of the furnace chamber of diffusion pump A into the analysis part of the system. In this part of the system, the carbon monoxide is oxidized to carbon dioxide catalytically



T = Mercury Valve

Y = Glass Hi-Vac Stopcock

Figure B-1. Block diagram of vacuum fusion apparatus with a platinum filament by an added measured excess of oxygen. The CO_2 formed can be separated from the nitrogen by condensing the CO_2 into a cold trap. The pressure of each component (CO_2, N_2, excess O_2) can be measured and the amount of nitrogen and oxygen originally present in the sample can be calculated. The volume of the analysis system is determined with the volumetric McLeod gauge (Delmar Scientific Laboratories, Maywood, Illinois, Model DS-7092) by admitting measured amounts of helium into the system and measuring the resultant pressure change. All pressure measurements are made on a double-scale McLeod gauge (Kontes Glass Company, Model K-92350, Size E).

One and five liter vessels are integrated into the system to accomodate any large amounts of gas which may be produced during reaction. The analysis portion of the system is considered to be that portion between the diffusion pump and the one and five liter volumes. Diffusion pump A, a diffusion ejector pump (Consolidated Vacuum Corp., Model GHG-10), is capable of operating under a forepressure of 2mm Hg. Mercury float type stopcocks are used in the analysis portion of the system to eliminate stopcock grease contamination of the gas sample.

The furnace chamber used for fusion of the sample is similar to that described by Guldner and Beach (50). A diagram of it is shown in Figure B-2. Minor alterations have been effected to make it more usable. Generally the sample is introduced into the system in the form of a

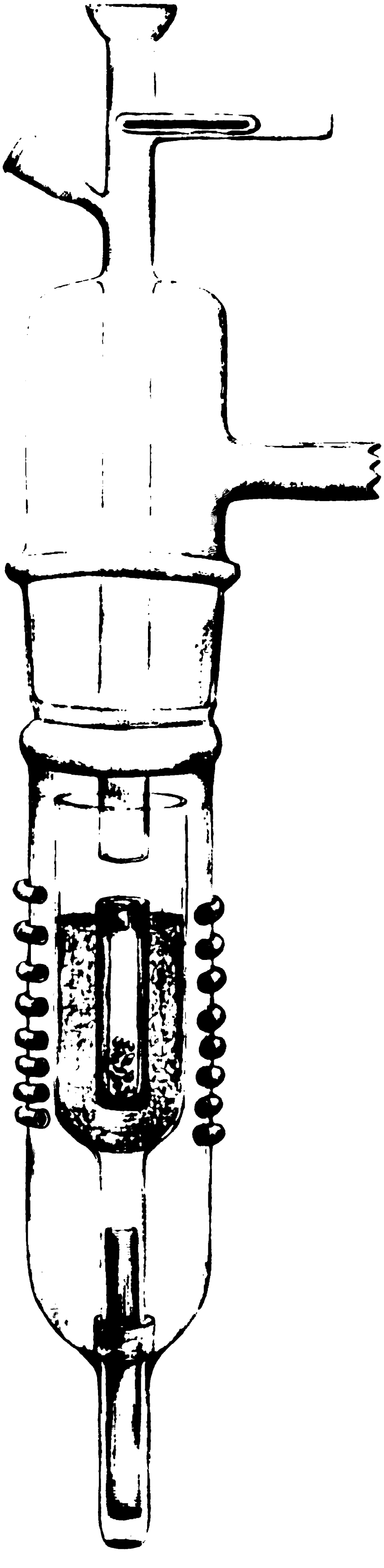


Figure B-2. Diagram of furnace chamber.

pellet. To eliminate this need and with it the possibility of contamination, powdered samples are used. The powder is placed in 0.001" platinum foil previously outgassed by heating at 1200° until a vacuum of 10^{-6} torr has been attained. The foil is subsequently folded and shaped spherically. The platinum-clad sample is confined in the sample holder which is fitted to the furnace chamber with a ground glass joint.

The glass furnace chamber contains a graphite crucible which is heated by induction with a 20KVA Thermonic high-frequency induction generator. This chamber is air-cooled with a 150cfm blower designed to direct a concentrated stream of air around the glass chamber.

A typical analysis is performed as follows. Graphite powder (Acheson grade No. 38) is placed in the quartz holder to a depth of approximately 2.5cm. A graphite fusion crucible (grade UF-4-S, Model A-2887, Ultra Carbon Corp., Bay City, Michigan) is set on the graphite powder and centered in the quartz holder. Graphite powder is packed loosely around the crucible until it is within 3mm of the top. A graphite funnel, slit to minimize coupling with the electric field, is placed on the crucible. Graphite powder is then packed loosely to the top edge of the funnel. A small tube is placed in the crucible and any graphite powder that inadvertently has fallen into it is blown out with a gentle stream of air. This graphite powder must be removed from the crucible in order to obtain a steady or negligible "blank" rate from the system. The quartz holder is now placed on a graphite post machined to fit inside the small tubing of the holder and the entire assembly is inserted into the Pyrex furnace chamber.

This chamber which now contains the crucible assembly is fitted to the top portion of the furnace assembly. (A high temperature - high vacuum grease is used for the ground glass joint since it is heated by radiation during the analysis). The long vertical tube running down the center of the top portion of the furnace tube through which the sample falls before dropping into the crucible should come within 2cm of the top of the crucible funnel. The center alignment of the crucible in the furnace tube is checked by sighting through the optical window in the top of the furnace tube. Care must be taken to insure that the cavity of the crucible appears to be in the center of the tube. Improper centering may cause the sample to fall into the graphite powder surrounding the crucible. This area is not hot enough to reduce the sample within a reasonable period of time but is hot enough to cause it to outgas at a rate sufficient to render the blank rate data meaningless. When this happens, the system must be shut down, the samples removed, and the entire analysis procedure restarted.

When the crucible is centered properly, the bottom tube is clamped in place while the sample holder is loaded. The sample holder is shown in Figure B-3.

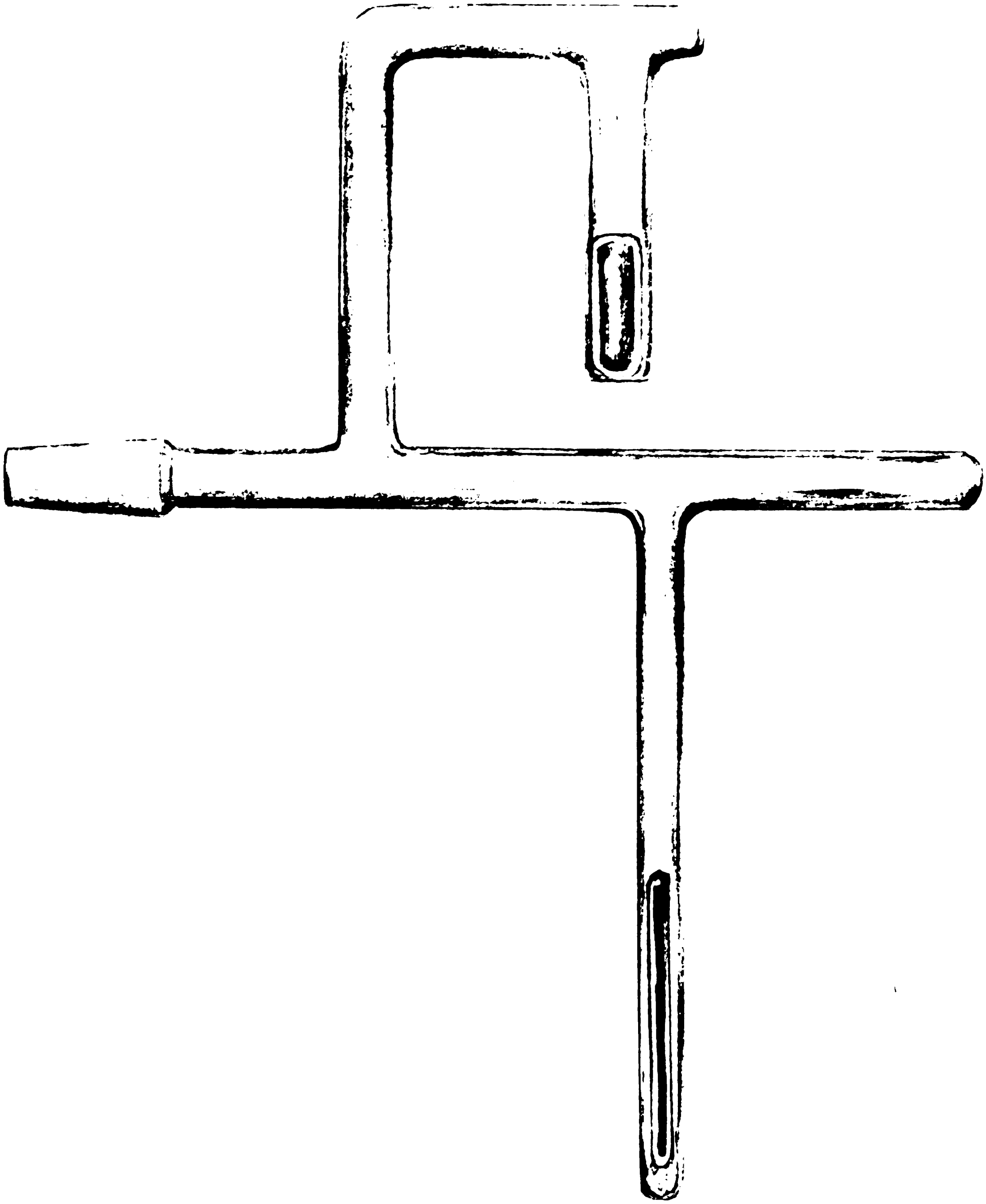


Figure B-3. Diagram of sample holder.

Since the quantity of gas evolved must not exceed the pressure-volume limitation of the equipment, the approximate amount of sample required is calculated before the specimens are weighed out. Assuming a total volume of the analysis system of seven liters and a pressure of 0.5 torr at the end of the gas extraction from the sample, the approximate weight of a pure lanthanon sesquioxide required would be 0.025g. The same weight was used for the lanthanon oxide-nitride preparations.

Determinations made with spherically folded foil of the same size as the foil used to wrap the samples have demonstrated that the blank gases from the foil are negligible when it has been outgassed as described previously. All sample manipulations are completed in a helium filled glove box. Also, about 10 grams of pure platinum for the bath is placed in the sample holder in such a manner that it will be ejected first. Platinum rod, 0.060" in diameter, cut into 1cm lengths is suitable for the bath. The sample holder is placed on the furnace chamber and the system is evacuated. The rough pump is allowed to evacuate the system slowly since rapid evacuation causes the violent release of air entrapped in the loosely packed graphite confined in the crucible holder and results in powdered graphite being thrown around the crucible holder. After the system is evacuated, the two diffusion pumps are turned on. When a pressure in the system is approximately 10^{-5} torr, the crucible is heated. The temperature is

increased slowly, all the time keeping the vacuum less than 10^{-4} torr. The temperature is increased to 2100° where the crucible is outgassed by heating for 10 hours or until the blank rate becomes negligible. During the outgassing procedure, the analysis portion of the system is warmed by heating tapes to outgas the glass tubing and further decrease the blank rate.

The much discussed "blank" rate is determined as follows. The crucible temperature is lowered to 1800° and the heating tapes are turned off. After the tapes have cooled, the analysis portion of the system is confined by closing the mercury valves, and the pressure is measured with the McLeod gauge. It should be in the range of 10^{-5} - 10^{-6} torr. After the system has sat for about 15 minutes, the pressure is again measured. If the pressure is below 5×10^{-4} torr, the blank rate is satisfactory and may be neglected during an analysis. If it is greater than 5×10^{-4} torr, outgassing must continue.

If the blank rate is satisfactory, the analysis system is opened to the diffusion pump and the crucible temperature is lowered to 1200°. The platinum for the bath is dropped into the crucible and the temperature is raised again to 2100°. The temperature is maintained there for about 10 minutes to outgas the platinum. Subsequently, the crucible is cooled to 1200°, and the mercury valves are adjusted so that the entire volume of the system is shut off from the main diffusion pump and can absorb the gases from the furnace chamber. The initial pressure inside the system is measured - it should be 5×10^{-6} torr or less. If the pressure is satisfactory, a sample to be analyzed is dropped into the crucible and the crucible temperature is raised to 1800° to extract the gas from the sample. Five to ten minutes are required for the extraction. Progress of the reaction may be followed by measuring the pressure. When the pressure has stabilized, the extraction is assumed to be complete. The crucible temperature is decreased to 1200° and the final pressure in the system is recorded. Should the crucible temperature decrease below 1200° at any time during an analysis, a steady blank rate will not be obtained. If the gas sample need not be analyzed, the data obtained as described above will yield the amount of oxygen. If a gas analysis is necessary, the pressure in the analysis system is reduced to approximately 10^{-2} torr by successively evacuating and expanding the gas into the one and five liter flasks.

From a lanthanon oxide nitride, three different gases usually will be obtained: carbon monoxide, nitrogen, and a small amount of carbon dioxide. The carbon dioxide can be determined by immersing a cold finger on the analysis part of the system into liquid nitrogen. Since the CO_2 will condense, the pressure before and after can be used to calculate the amount of this gas present. Carbon monoxide is determined by catalytic oxidation to carbon dioxide as described previously and subsequent condensation in liquid nitrogen. The nitrogen content of the gas sample is determined by difference.

Several difficulties have been encountered. In fact, the problems associated with this method eventually led to its abandonment. A discussion of some of these difficulties might prove useful for future work. The control of the filament temperature is critical. It must be heated only to a dull red - just detectable by the eye. Temperatures lower than this result in the incomplete oxidation of the gas sample or no oxidation at all - the latter being the more likely case. Temperatures higher than this result in a reaction, which eventually consumes much more oxygen than the theoretical amount required to oxidize all of the carbon monoxide to dioxide. It was thought initially that the oxygen gas contained impurities. A cylinder of research grade gas was used as the source of oxygen, and all stopcocks in the oxygen supply line but one were eliminated. This one was greased with Dow-Corning silicone high vacuum stopcock grease. The analysis system was filled with the pure oxygen - no other gas was present. Even under these conditions at filament temperatures higher than a visible dull red, there was a large decrease in the pressure within the system. This reaction product condenses from the gaseous phase at liquid nitrogen temperatures, but does not condense in a dry ice-acetone bath. Since all apparent possibilities of contamination had been removed, the oxygen seemed to be reacting with itself.

It is possible that ozone is being formed under these conditions; however, no mention of this occurrence has appeared in the literature.

The size of the platinum filament is another factor which limits the accuracy of the method. Initially a 3cm piece of 24 gauge platinum thermocouple wire was used. Unsatisfactory oxidation was obtained and a 3cm length of 0.005" platinum wire was substituted for the heavier gauge wire. Later experiments showed that this latter wire worked more satisfactorily.

Great difficulty was experienced in maintaining the oxidizing efficiency of the filament. It was invariably found that after a few oxidations, a higher filament temperature had to be used to obtain complete oxidation--or any oxidation at all. Heating the filament to orange red in vacua to outgas it after each sample did little to improve its efficiency. Heating it in pure hydrogen restored the efficiency somewhat, but the oxidizing ability again deteriorated with use.

When the filament was working properly, analysis of samples of pure carbon monoxide gas was satisfactory. However, the filament soon lost its efficiency and the analysis results were inconsistent. A range of filament temperature had to be selected within which the carbon monoxide would be oxidized completely and yet the oxygen would not react to give undesirable products. Unfortunately, such a middle range could not be selected since it was not known when complete oxidation had taken place on an unknown gas sample.

Quantitative extraction of gas occurred from specimens which fell into the crucible. Thus, the overall system can be used if a gas analysis is not required. The gas analysis portion of the system was considered too unreliable for our purpose and was abandoned. Some more reliable means of analyzing the gas will have to be devised.