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METALLURGY OF THE RARE EARTHS WITH PARTICULAR EMPHASIS ON CERIUM

by

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A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Major Subject: Physical Chemistry

Approved:

Signature was redacted for privacy.
In Charge of Major Work

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INTRODUCTION

The rare earth metals are so similar in electronic structures and properties that they offer an excellent opportunity for the evaluation of existing theories of metals and possibly for the establishment of a more precise explanation for the relationship of the properties of metals and their electronic structure. For example, as the atomic weights of the rare earth metals increase, there is a regular decrease in the atomic volume with the exceptions of europium, ytterbium and possibly samarium, which have a very high atomic volume in comparison to the other rare earth metals, and of cerium, praseodymium and terbium, which have atomic volumes lower than would be expected (1). By confirming these variations and comparing them with the differences of other measurable properties, such as metal-metal bond strengths, melting points and boiling points, some correlation of these properties with the electronic structure of the atoms might be made. The present investigation of the preparation and properties of the rare earth metals is the beginning of an overall program on this subject.

Pure salts for the preparation of pure rare earth metals were available as a result of the development of a method for the separation of rare earths by others at this laboratory (2). In producing metals, the metallothermic reduction process, a modification of the Goldschmidt reaction (3), was used exclusively, partly because an excellent procedure involving this principle was perfected for cerium at this laboratory during the war; it also lends itself to the preparation of very pure metals on a scale down to 25 grams. By controlling the purity of the reactants, metals free of all other impurities can be prepared. This is not true in the widely used method for preparing rare earth metals by electrolytic deposition from fused salt baths; in this procedure only very careful control will reduce the usual iron and silicon impurities to less than 0.5 per cent. Moreover, in the electrolytic method for producing rare earth metals, it has been found that the difficulty of preparation of the rare earth metals increases as atomic weight increases; this phenomenon is correlated with the increased volatility of the halide and the higher melting point of the metal. The higher melting point of the metal necessitates electrolysis at higher temperatures in order to obtain massive metal, but at these high temperatures there is an excessively large loss of the halide due to its high volatility. Although this difficulty has been partially solved by various schemes, a simpler procedure would involve the reduction of the halide in a refractory-lined, sealed steel tube in which the vapor pressure of the halide would aid rather than hinder reaction.

The physical properties of the more common rare earth metals might be expected to be rather well established since their preparation in the massive state was accomplished as early as 1902; however, due to the difficulty in obtaining pure salts of even the more abundant rare earths and to the reactivity of the metals when prepared, there is little agreement on even the melting point, the property usually determined first on a metal. In a review on rare earth metals published in 1946 (4) the melting point of cerium metal was reported as 645°C., whereas the temperatures between 775 and 815°C. are usually accepted (1). It is evident that a further investigation of this property was in order. Since the measurement of the density of the metal gives a good indication of its contamination by slag or gas pockets, this property was determined although the values in the literature are in agreement. Hardness measurements were also taken in conjunction with studies on the mechanical working of the metal.

The study of the vapor pressure of the rare earth metals is of interest on a practical and a theoretical basis. Practically, the feasability of the separation of the rare earth metals by distillation is of interest, since this procedure could be used in conjunction with other methods to separate some of the rare earth metals which, although having almost identical chemical properties, may have slightly different physical properties. Theoretically, the determination of the vapor pressure is quite useful in evaluating some of the basic constants of a metal. According to the Clausius-

Clapeyron equation, the plot of the logarithm of the vapor pressure against the reciprocal of the absolute temperature can be extrapolated as a straight line to establish the boiling point; also the heat of vaporization can be calculated from the slope. If the heat of fusion and the specific heat of the metal are known, the heat of vaporization can be used directly to obtain the heat of sublimation which is a measure of the metal-metal bond strength.

The effusion method for the measurement of vapor pressures, based on the work of Knudsen (5), was used for the determination of the vapor pressure of cerium metal. The particular procedure employed was a modification of that developed by Phipps and co-workers (6) who first applied the use of radioactive materials to this type of problem. In the effusion method the vapor pressures from 10^{-5} mm. to 10^{-2} mm. of Hg are determined. Work in this low pressure range is particularly useful for metals such as cerium whose vapor pressures are so low that measurement of vapor pressures from 10 to 760 mm. of Hg would require prohibitively high temperatures.

PREPARATION OF THE RARE EARTH METALS

Introduction

The preparation of cerium metal was first investigated in this laboratory in meeting a request for massive cerium metal to be used for experimental purposes at another laboratory. The metallothermic method of preparing cerium metal was studied and a process for the reduction of cerous chloride to metal was perfected (7); by this process approximately 1000 pounds of commercial grade metal (95 to 97 per cent cerium with the remaining impurities being other rare earths and calcium) were produced. Some reasonably pure cerium metal containing less than one per cent of impurities was also prepared and its melting point measured.

The metallothermic reduction of cerous chloride to metal is a modification of the Goldschmidt reaction (3) in which the chloride is reduced by calcium metal with an auxiliary "booster" to supply additional heat. The reactions are:

$$2\ CeCl_3 + 3\ Ca \longrightarrow 3\ CaCl_2 + 2\ Ce,$$

$$Ca + I_2 \longrightarrow CaI_2.$$

The reduction was effected in a bomb which consisted of a sealed steel tube lined with a refractory oxide such as lime, CaO, or magnesia, MgO. The reaction was initiated by heating the loaded bomb in a furnace. As the calcium reacts with the cerous chloride and the iodine, the outside of the bomb is heated to a cherry-red by the excess heat of the reaction. The bomb is then cooled and the metal ingot removed and cleaned. The excess calcium is eliminated by vacuum distillation.

In adapting this method to the preparation of rare earth metals of high purity, slight changes in the ratios of the reactants were necessary to obtain optimum yields. The purity of the starting rare earth halide was preserved by using very pure materials for the reduction, since any metallic impurity would collect in the reduced metal and thus contaminate the final product. By employing the best grade of calcium available, only magnesium was introduced as an impurity; the latter of course distilled with the excess calcium in casting. The crucibles were prepared from high grade dolomite or lime and were fired in a muffle to burn out any carbon impurity remaining from the fabrication process. Only resublimed iodine which has a negligible amount of metallic impurities was used as the "booster". By these precautions a better grade of ingot metal was obtained.

The development of spectrographic analytical procedures by Dr. V. A. Fassel of this laboratory was a considerable factor in the improvement of the finished metal since it permitted a better evaluation of the purification procedures used.

Historical

The metallothermic method of producing metals was the first used in attempts to prepare the metals of the rare earths. In 1826, Mosander (8) reduced cerous chloride by means of sodium to obtain powdered metal badly contaminated by sodium and sodium chloride and in poor yields. In 1842, Beringer (9) using the above method reported the preparation of a grey powder of cerium which burned in chlorine, bromine and sulfur. de Marignac in 1853 (10), and Wöhler in 1867 (11) employed sodium and the other alkali metals with a similar result. In 1925, Kremers (12) reported that he was unable to prepare any metal by the reaction of sodium on neodymium chloride, but in 1933, Zintl and Neumayr (13) were able to reduce cerous chloride by sodium or potassium vapors in high vacuum at 400°C.; however, they did report incomplete reaction and obtained a mixture of cerium metal powder and sodium or potassium chloride. The last reported use of the alkali metals to prepare the metals of the rare earths by reducing the anhydrous halides was published in 1937 by Klemm and Bommer (14). They prepared the metals of all the rare earths as powders by heating the chlorides and one of the alkali metals at temperatures from 200-400°C. They claimed partial success in reducing even the divalent rare earths: samarium, europium and ytterbium. The powdered metal was used as prepared, that is intermixed with the alkali chloride, for crystallographic and magnetic studies.

The metals, calcium, aluminum and magnesium, have also been used in attempts to prepare cerium metal by the reduction of the chloride or fluoride of cerium with somewhat greater success. Moldenhauer in 1914 (15) reduced cerous fluoride with calcium and obtained an alloy containing 12 per cent calcium; he also obtained an aluminum alloy with aluminum as the reductant. In 1934, Karl (16) produced cerium metal in 85 per cent yields by reacting cerous chloride in a molten bath of calcium in the presence of calcium chloride; however, the reductions were carried out in an iron vessel so that the average ingot contained 1.7 per cent of iron. The most recent work on the metallothermic preparation of the rare earth metals was published by Trombe and Mahn (17), in 1944, who were able to prepare alloys of several rare earth metals with magnesium by adding the rare earth halide to a bath of molten magnesium. They removed the magnesium by distillation and obtained what they describe as 99 per cent pure metal in yields of 50 per cent for cerium, neodymium and gadolinium.

A considerable number of attempts to prepare the rare earth metals from their oxides has been reported. In 1890, Winkler (18) heated the oxides of cerium, lanthanum and yttrium with magnesium in a vacuum and obtained a pyrophoric powder mixed with magnesium and rare earth oxide. Similar results were obtained by Holm (19) with magnesium on ceric oxide. Matignon (20) attempted the reduction of cerium oxide under an atmosphere of hydrogen and of nitrogen with both aluminum and calcium and obtained the hydride or nitride of the metal. Aluminum was heated with ceric oxide by Schiffer (21) to yield a pyrophoric powder. Hirsch (22) attempted reductions of ceric oxide with magnesium, calcium and aluminum and obtained pyrophoric alloys in each case; with carbon and silicon he obtained carbide, CeC_2, and the silicide, $CeSi_2$, respectively. A number of patents have been awarded for the preparation of cerium metal from the oxide. Kuhne (23) patented the reduction of ceric oxide to metal by the thermite process using chlorates as "boosters", Kuzel (24) was awarded a patent for the reduction of ceric oxide by calcium, and N. V. Philips Gloeilampenfabriek (25) obtained a patent for the preparation of pyrophoric metal by heating ceric oxide with zirconium. However, no metal was ever commercially produced by these methods and a number of papers stating that no metal could be produced by various reactions on ceric oxide have appeared. For example, Moldenhauer (15) reported that he could not prepare cerium by the thermite reaction with aluminum, calcium or magnesium as the reducing agent, and Karl (16) was unable to produce metal from ceric oxide with either silicon carbide or magnesium as reductants. Therefore at the present time, there appears to be no method of obtaining massive cerium metal from the oxides.

The only method by which rare earth metals have been produced in quantity and of sufficient purity to merit determining the physical properties is by electrolytic means. The most widely used process involves the electrolysis of the rare earth metal from a molten salt bath of the rare earth halide dissolved in a mixture of alkali metal halides. The first to use this procedure were Hillebrand and Norton (26, 27), in 1875, who prepared the metals: cerium, lanthanum and didymium in a coherent form by electrolysis of the fused chlorides covered by a layer of ammonium chloride and held in a porous cell surrounded by a sodium chloride-potassium chloride eutectic mixture in a porcelain crucible. They used iron sheet as the anode and iron or platinum wire as the cathode. The method used at the present time is essentially the same as that employed by the above authors, with refinements in electrodes and crucible to avoid contamination.

The first to prepare massive metal were Muthmann and his co-workers (28, 29, 30) who prepared cerium, lanthanum, neodymium and praseodymium and measured the melting points. Kremers (12, 31) has also produced a number of the rare earths by this method and has determined their properties. The most recent workers in this field are Trombe and co-workers (17, 32, 33) who have improved the electrolytic cells by using molybdenum electrodes and a water cooled copper crucible; they reported the production of metallic cerium, lanthanum, neodymium with a purity greater than 99.5 per cent and other rare earth metals slightly less pure. They were also able to prepare samarium by electrolyzing the metal on the cathode as the cadmium alloy and separated the alloying metal by distillation in high vacuum; however, they report no properties of the metal obtained by this procedure.

Another electrolytic method used successfully to prepare rare earth metals was investigated extensively by Audrieth, Hopkins and co-workers in 1933-35 (4, 34, 35); it consists of electrolyzing an alcoholic solution of the rare earth halide into a mercury cathode. The metal is recovered from the resulting three per cent amalgam by distilling the mercury in high vacuum. According to some experiments (1) it is very difficult to remove the last traces of mercury from the metal; also it is difficult to adapt the cell to produce more than a few grams of rare earth metals at a time. For these reasons the method has not been generally adopted.

Methods of Procedure

Purification of the rare earth salts

Cerium

The cerium salts used in this study were obtained from two sources. The Lindsay Light and Chemical Company of West Chicago, Illinois, supplied a commercial grade of cerium, as cerous chloride, containing 95-99 per cent cerium, the impurities being the other rare earths and thorium, and a specially purified grade of cerium in the form of the oxalate which, however, contained thorium and possibly traces of other rare earths. Cerium, spectrographically free of other rare earths and thorium, was purchased from the G. Frederick Smith Chemical Company of Columbus, Ohio, who supplied this rare earth as the chloride and as cerium ammonium nitrate $\left[(NH_4)_2\,Ce(NO_3)_6\right]$. A flocculent white precipitate, identified as silica, was observed when the chloride was dissolved. Evidently silica is introduced as a contaminant in their method of converting the cerium ammonium nitrate. The form in which the cerium is purified, to the chloride.

Separation of silica. The purification steps varied with the contamination of the starting material. In the case of the silica contamination in the chloride, the cerous chloride was dissolved in concentrated hydrochloric acid and evaporated to a syrup in order to partially dehydrate the silica. The solution was then diluted and filtered to remove the precipitate.

Separation of thorium. The purification procedure of the Lindsay material was considerably more tedious than was the case with the more pure cerium salts supplied by the G. Frederick Smith Chemical Company. The oxalate was destroyed by dissolving in hot nitric acid according to the probable reaction:

$$Ce_2(C_2O_4)_3 \cdot 9H_2O + 12HNO_3 \longrightarrow 2\ Ce(NO_3)_3 + 6CO_2 + 15H_2O + 6NO_2.$$

This step left the cerium in the proper form for separation of thorium by an iodate precipitation using a modification of the method of Meyer (36) and Speter (37) for the quantitative determination of thorium in the presence of cerium. In the procedure as described by the above authors, the thorium iodate is precipitated from a 6 normal nitric acid solution to effect a separation from the trivalent cerium. It has been found that, at the very high acid concentration recommended, there is incomplete precipitation of the thorium. By reducing the nitric acid concentration to 0.5 to 1 normal, the thorium iodate precipitates completely, but carries alohg a small amount of cerium. Since it was desired to insure thorium-free cerium, all thorium precipitations were made from the 1 normal acid concentration. After the thorium was removed, the excess iodic acid was destroyed by formic acid, and the most of the iodine was distilled.

<u>Separation of other rare earths</u>. The rare earth impurities were removed by utilizing one of the differences in the chemical properties of tetravalent cerium from those of the remaining trivalent rare earths by a method published by Smith, Sullivan and Frank (38). The

separation is accomplished by crystallizing the salt, cerium ammonium nitrate, from a concentrated nitric acid solution, the trivalent rare earths remaining in solution.

To prepare the filtrate from the thorium removal step for this purification, the trivalent cerium was electrolytically oxidized to the tetravalent state. Platinum electrodes were used for the oxidation; they consisted of an anode surrounded by a porous glass diaphram and of a cathode with an area three times that of the anode. Four moles of cerium were oxidized in each run by passing nine amperes through the solution for from 18 to 24 hours, thus supplying 6 to 7.5 faradays or a 50 to 88 per cent excess of the current required to oxidize the cerium. No analysis was made to check the efficiency of this oxidation, but other investigators (39) have shown it to be greater than 99 per cent and the 95 per cent yield in crystallization indicated that the oxidation was nearly complete.

The tetravalent cerium nitrate solution was concentrated by evaporation and was then crystallized as cerium ammonium nitrate by the addition of three moles of ammonium nitrate to each mole of cerium, a 50 per cent excess. The crystals were washed with concentrated nitric acid on a sintered glass filter and were partially dried by drawing air through the mass for several hours.

Other rare earths

The rare earths, neodymium, praseodymium, samarium and yttrium were obtained from another section of this laboratory, where they had been separated by elution through an Amberlite column with citrate solution (2).

Preparation of the anhydrous halides

After purification, the cerium salts were recovered as the chloride or as cerium ammonium nitrate. The nitrate was converted to the chloride by dissolving in concentrated hydrochloric acid, boiling until the evolution of nitrogen tetroxide fumes ceased and repeating this process. This treatment destroys a large proportion of the nitrate ion present, but does not produce a nitrate-free solution. To effect the complete conversion of nitrate to the chloride the mixture of cerous chloride and nitrate was crystallized by boiling off the water until the temperature reached 135°C. and cooling while stirring. The crystalline hydrate was then heated under an atmosphere of dry hydrogen chloride at reduced pressures. After the water of hydration had been removed by slowly raising the temperature of the mixture to 220°C., the temperature was increased to 450°C. Below this temperature any remaining nitrate will decompose to form the oxychloride; the remaining ammonium salt will be distilled over to the cold end of the drying tube as ammonium chloride.

The resulting mixture of cerous chloride and oxychloride was then dissolved by heating in concentrated hydrochloric acid and the solution treated as discussed below.

The chlorides of cerium or the oxides of the other rare earths studied which, in contrast to cerium, are readily soluble in acids were dissolved in concentrated hydrochloric acid. The solution was concentrated by boiling, until the boiling point rose to approximately 128-130°C., at which temperature it was cooled and crystallized to a fine powder by continuous stirring. The temperature required to drive off sufficient water to permit crystallization is approximately the same for all the rare earth halides, the value listed above being high enough to insure crystallization on cooling in practically all cases, but low enough to avoid the formation of oxychloride by the extensive decomposition of the hydrate. The hydrate contains seven waters of crystallization in the case of cerium and praseodymium and six waters of crystallization in the case of neodymium and samarium.

The procedure of Kleinheksel and Kremers (40) was used for the preparation of the anhydrous chloride. It consists of passing dry hydrogen chloride gas over the heated hydrate at reduced pressures. The method has been reported as being the most satisfactory for the preparation of very pure anhydrous halides (41, p. 29). The usual procedure used in the drying runs consisted of slowly raising the temperature of the hydrate from below 85°C. to above 400°C. while passing through hydrogen chloride gas at a pressure of 5 cm. of Hg. Completely anhydrous $CeCl_3$ was obtained in 10 to 24 hours; the chloride hydrate was not permitted to melt since this would cause the formation of the oxychloride. The salt produced is quite hygroscopic and must be handled in a dry atmosphere. The maximum temperature required to produce anhydrous chlorides according to the above authors is 250°C.; however, the higher temperature of 400°C. was used to insure the sublimation of any remaining ammonium chloride. This precaution was necessary because of the large pressures that could be generated in the reduction bomb by the gaseous byproducts of the reduction of ammonium chloride by calcium.

The anhydrous fluoride and iodide of samarium were also prepared in the attempts to obtain samarium metal. The fluoride was made by passing dry hydrogen fluoride over samarium oxalate $Sm_2(C_2O_4)_3 \cdot 10H_2O$ at 300-325°C. for six hours. The salt prepared was white and relatively non-hygroscopic; analysis indicated that its formula was SmF_3. Anhydrous samarium iodide was obtained by drying an intimate mixture of ammonium iodide and the hydrated samarium iodide under a stream of hydrogen iodide according to the method of Jantsch and Skalla (42) in a manner analogous to that used to prepare the chloride, although at atmospheric pressure. The gaseous hydrogen iodide was prepared according to a standard procedure (41, p. 159) by passing a mixture of hydrogen and iodine vapor over platinized asbestos at 600°C. The final temperature of the drying run was 500°C. to guarantee the sublimation of the ammonium iodide present. This salt was light green in color and was quite hygroscopic.

A fourth compound of samarium, the dichloride, was prepared for reduction attempts. This compound was synthesized by reducing the anhydrous trichloride, prepared as described above, by means of a mixture of hydrogen and dry ammonia passed over the heated chloride. The procedure, worked out by Jantsch, Rüping and Kunze (43), consisted of passing hydrogen over the chloride as the temperature was raised to 450°C., then to also add ammonia in the ratio of two moles of ammonia to each mole of hydrogen as the temperature was raised to 750°C. Complete reaction was obtained in 15 hours. The ammonia was dried by passing over potassium hydroxide and barium oxide, two very good dehydrating agents. The hydrogen was cleaned by passing over hot uranium metal powder at 600°C. At this temperature the uranium removes all the nitrogen and oxygen, but permits the hydrogen to pass through (44). By the above procedure 300 grams of samarous dichloride was obtained in two runs. Since the dichloride melts at 740°C., it had fused and was obtained as a caked, chocolate-brown mass in the silica trays. Although the original workers reported no reaction between the silica and the dichloride below 800°C., there was evidence of a slight reaction in these preparations. For this reason the layer of samarous chloride in immediate contact with the crucible was not used. The discarded samarous chloride was completely soluble in water which indicates that there was little or no silica or oxychloride in the salt since these are both insoluble. After grinding and screening, the samarous dichloride had the red-brown color described in the literature.

Reduction techniques

Bomb and liner

The bombs were constructed from standard black steel pipe by welding a bottom of ¼ in. steel plate on one end. The top of the bomb was threaded to receive a standard steel or cast iron pipe cap. Four sizes of bombs were used. The largest, 4 in. in diameter and 24 in. long, was utilized in the production of commercial grade cerium; it contained up to 1600 grams of cerous chloride from which 900 grams of metal were produced. The next size, constructed from 2½ in. pipe, 7½ in. long, and was used for the experimental reductions of the more abundant rare earths; it held 150 grams of charge and produced approximately 40 grams of metal. The smallest bomb was made from 1 in. pipe, was 5 in. long and yielded 10 grams of metal from 37 grams of charge.

Contact of the reaction mixture with the iron walls of the bomb was prevented by a smooth-surfaced lining of a refractory oxide 3/8 to 3/16 in. thick, depending on the size of the bomb. The loose packed liners were prepared by placing a mandrel inside the bomb and jolting loose calcium oxide powder, which was fine enough to pass a 200 mesh per inch sieve, into the annular space between the bomb wall and the cylindrical mandrel on a mechanical jolter. After thoroughly packing the calcium oxide by this means, the mandrel was carefully removed, leaving a firm and smooth surfaced liner (Figure 1). Although this type of container could be economically prepared and was adequate for the reduction of large amounts of cerous chloride in one charge, the porosity of the wall produced by this technique was high enough to permit soaking; the yields were reduced by the resultant adherence of the molten reaction mixture. This effect made the use of tamped liners impractical for small scale reductions. The more dense calcium oxide or dolomite ($MgO \cdot CaO$) crucibles were not wetted as badly by the slag and the metal, and therefore permitted a better collection of the metal after reaction. The bomb containing the sintered liner was prepared for reduction by inserting the crucible and by filling the narrow annular space between the crucible and the bomb walls with loose lime (Figure 2). The loose lime prevented leaks in case the liner cracked during the reaction.

The crucibles were made by jolting the lime or dolomite in a graphite crucible in a manner similar to that employed in preparing the loose packed liners, and then sintering by heating in an induction furnace to 1850°C. Crucibles so prepared are dense, smooth surfaced, mechanically strong and

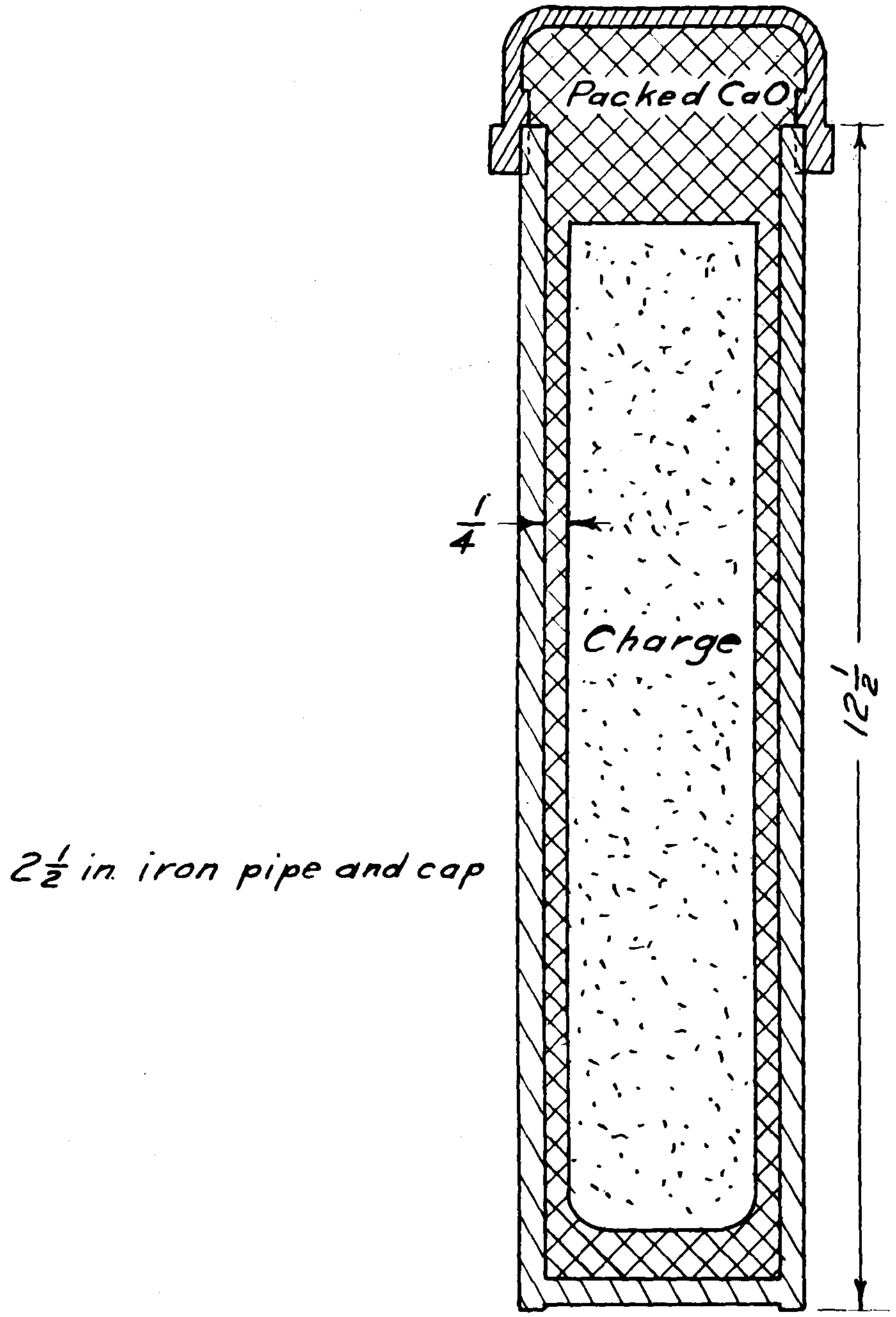

Figure 1. Cross Sectional View of Bomb with a Tamped Lime Liner.

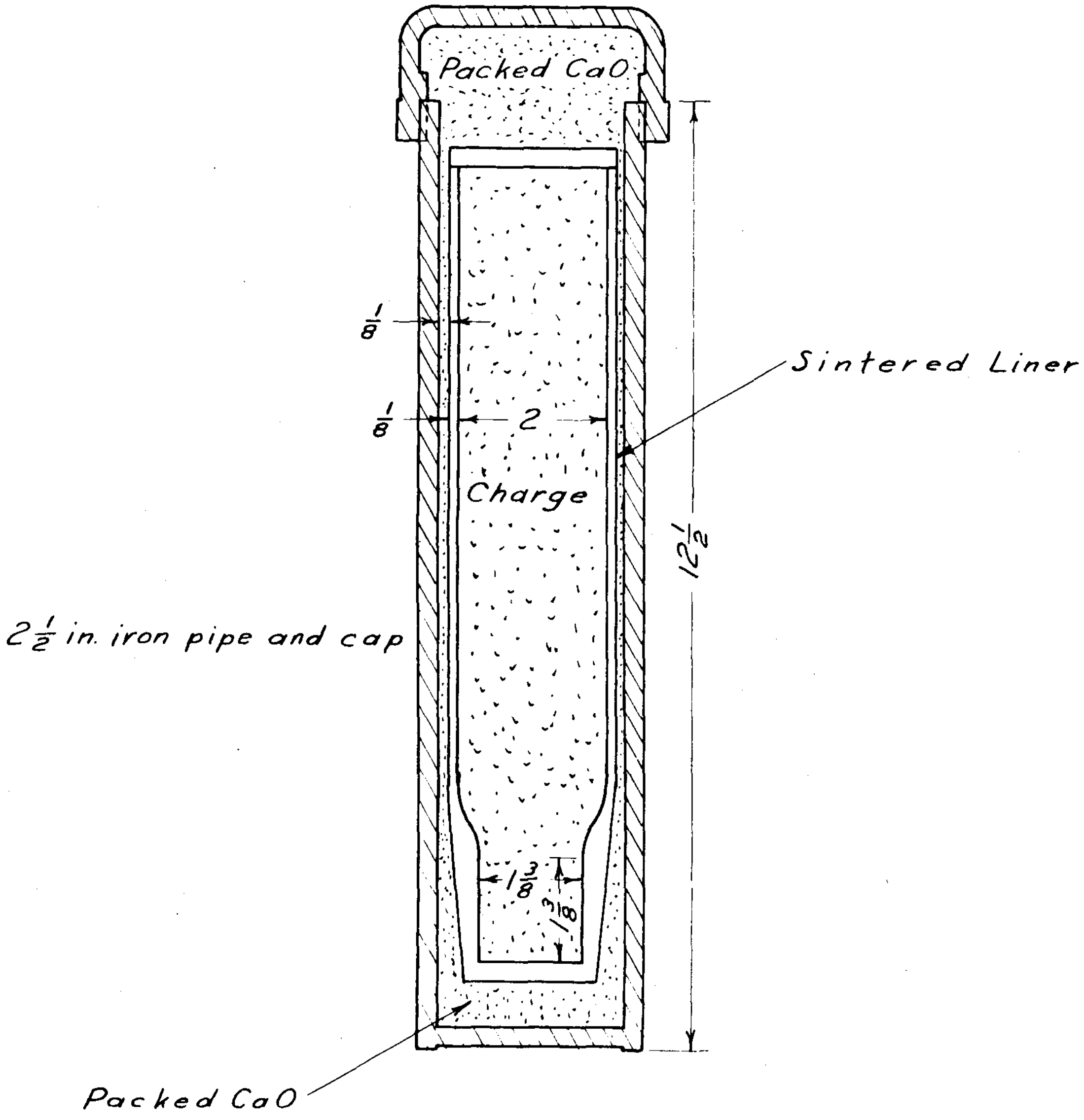

Figure 2. Cross Sectional View of Bomb with a Sintered Lime Liner.

fairly resistant to thermal shock. They do absorb water to some extent and hence must be stored in a dry atmosphere.

A layer of lime or dolomite was also tamped into the lid. To prevent the loose material from falling into the charge, the sintered crucible was covered with a beryllia (BeO) lid. To prevent the escape of any volatile components of the charge and to reduce losses by oxidation, the lid was sealed by means of plumber's seal (litharge and glycerine, or its equivalent) applied to the pipe threads. The success of this method was illustrated by the partial vacuum which was found to be still remaining in the bomb after cooling.

Reaction mixture and reduction

The reaction mixture for the preparation of rare earth metal consisted of the rare earth halide, a reductant such as calcium, and, in most cases, a "booster". The preparation of the rare earth halide was described above.

Calcium was selected as the reducing metal because of ease in handling, good storage stability, and the high heat of formation of its halides. The calcium was obtained as large aggregates from the Metal Hydrides, Inc., or the Electrometallurgical Company. It was of a very high grade of purity containing less than 5 ppm. of manganese, less than 5 ppm. of iron and less than 10 ppm. of aluminum. Its principal impurity was magnesium in amounts less than two per cent. The aggregates were reduced by a number of steps, to a size suitable for use in reduction. They were first broken up by a punch press; the pieces were then reduced in size in a hog manufactured by Mitts and Merrill. The hog was originally designed to pulverize wood chips for paper manufacture, but was also satisfactory for cutting calcium. The coarse calcium was cleaned by passing over a magnetic separator and then cut to final size by a rotary knife mill made by the Sprout, Waldron & Co., Inc. This size was such that the metal passed through a 10 mesh per inch screen, but was retained on a 50 mesh per inch screen. This treatment knocked off any loose calcium oxide coating, which was discarded in the "fines", and provided a very reactive, easily handled reductant.

In the first attempts at preparation of metal, the reduction of cerous chloride by calcium alone was used. Since insufficient heat was supplied by the primary reaction, the reaction mixture was externally heated to the necessary temperature to permit metal and slag separation. The limited success of this method made it necessary to include a side reaction of calcium and a "booster" such as iodine, sulfur, potassium chlorate or zinc chloride with the principal reduction reaction of cerous chloride and calcium. These materials all have the property of giving up a large amount of heat on reaction with calcium with a resultant rise in the temperature of the reaction mixture, thereby increasing its fluidity and permitting a more complete separation of the metal from the slag.

For the reasons discussed above, the primary function of a "booster" is to yield heat to the reaction; this means that it should react with calcium in a strongly exothermic reaction. Ordinarily "boosters" are oxidizing agents, however, compounds with a rather low heat of formation, for example zinc chloride, will also give up a large amount of heat when reduced by calcium. The efficiency of these materials in this respect can be calculated from heats of formation. A more intangible, but very important, effect of a "booster" is the impurity which is introduced into the reaction mixture. For example, during the reduction, iodine reacts to form calcium iodide which lowers the melting point of the calcium chloride slag, and thus lowers the temperature required for complete separation of the metal and slag; zinc chloride yields zinc which alloys with the metal being produced, thus lowering its melting point and permitting better agglomeration. A third consideration in choosing a "booster" is that it must not contaminate the metal. The materials discussed above all meet this requirement: the iodine collects in the slag, and the zinc is distilled out of the ingot with the calcium excess. Finally, ease in handling should be considered; it is desirable to have a material that can be intimately mixed with calcium and the rare earth halide, but will not react until heated in the firing furnace.

Iodine was the only oxidant which was troublesome in this respect; for after mixing with the reduction mixture its vapor slowly reacted with the calcium. This reaction would reduce yields if the bomb were not fired within 10 minutes after loading.

In preparation for a reduction, a bomb was lined and brought to the dry room. The charge of rare earth halide, calcium and "booster" was mixed in a MacLellan batch mixer in cases where the preparation of the metal has been reduced to a routine procedure and where large amounts of metal were to be prepared; otherwise it was adequately mixed by shaking in a more easily cleaned reagent jar. After thorough mixing, the charge was poured into the bomb and tamped in firmly; to avoid absorbing water from the air, these operations were carried out in a dry room or dry box. This precaution was found to be unnecessary for production runs in the large 4 in. bombs, provided that precautions were taken to limit the exposure of the anhydrous chloride to the air.

After tamping, the charge was covered by a firmly pressed layer of loose lime or by a refractory lid before the lined cap was screwed on. Use of a lid prevented any lime from entering the reaction mixture and increased the yield a few per cent. After covering, the cap was screwed down firmly.

To initiate reaction the loaded and sealed bomb was heated to 650 or 750°C. in a resistance furnace or a gas-heated soaking pit, or by a high frequency induction furnace. When the charge reaches the reaction temperature, about 400°C., the reduction is probably first initiated by reaction between the calcium and the oxidant. The excess heat of this reaction raises the temperature and induces the reduction of the rare earth halide by calcium. As the reaction proceeds, the interior of the bomb is heated to about 1400°C. as calculated from very approximate thermochemical data. At this temperature the entire reaction mixture is fluid and the heavier, molten metal agglomerates and collects in the bottom of the liner, with the slag of calcium chloride and the calcium salt resulting from the side reaction floating above it. In a successful reduction, a very sharp demarcation line exists between the metal and the slag; the metal ingot is usually smooth surfaced with even sides and bottom as shown in Figure 3. If only partial separation of the slag and metal takes place because of insufficient heat supplied by the "booster", small pellets of metal can be seen entrapped in the slag. In case a very poor reduction is obtained, no metal separates, but it remains as a fine powder evenly distributed throughout the reaction mixture.

After reaction, which could be detected by the sudden surge of the temperature of the bomb or by a dull rumble which could sometimes be heard at the moment of reaction, the bomb was cooled and opened. The contents were removed

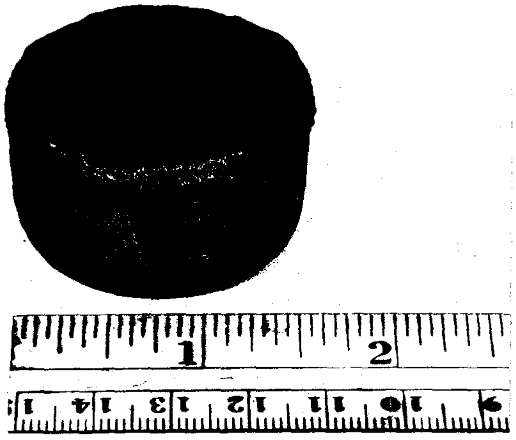

Figure 3. Typical Reduction Ingot.

by pounding on the side of the bomb to break up the liner and slag and thus permit the ingot to fall out. The slag and liner were set aside for recovery of residual rare earths and of iodine. The metal ingot was cleaned by chipping off the small pieces of clinging slag and was then washed in water to remove the layer of calcium which sometimes collected on the top of the ingot. After cleaning, it was weighed and then stored under mineral oil.

Iodine was recovered from the reaction products by passing oxygen through the crushed slag contained in a steel bomb heated to 300°C. At this temperature, the iodine was displaced by oxygen and was carried out of the mixture by the gas stream. The iodine vapor was led out of the bomb through a steel pipe and was condensed in a cooled flask. The iodine thus collected contained a small amount of water which was removed by fusion in a flask fitted with a water cooled condenser. Any iodine that was vaporized during the fusion collected in the condenser, from which it was later collected and recycled. Iodine recovered by this procedure was quite dry and relatively pure.

Casting materials and methods

The crude ingots of metal produced by the method described above contain varying amounts of calcium and adhering slag. Much of this contamination can be removed by leaching in hot water, but for production of pure metal the alloyed calcium must be removed by distillation through casting under a vacuum.

Since the rare earth metals are highly reactive, a number of crucibles were investigated for resistance to attack by the molten metal. These included beryllia (BeO), lime (CaO), magnesia (MgO), the rare earth oxides, metallic tantalum and metallic molybdenum. The crucibles of the refractory oxides were all prepared in the same manner. The fine oxide was tamped into the annulus between the graphite sintering crucible and a cylindrical mandrel. The mandrel was then removed and the crucible sintered by heating in an induction furnace. The temperatures which permit strong bonding between the refractory particles, but yet do not permit any reduction of the oxide, are: beryllia at 2100-2150°C.; lime at 1850°C.; magnesia at 1950°C.; and the rare earth oxides at lower temperatures. Of the above, the beryllia crucibles are the most resistant to thermal shock. All are quite dense and have smooth walls, although the magnesia crucibles after sintering at 1950°C. have an almost glazed surface. After sintering, the crucibles were cooled and fired in a muffle furnace to 900°C. to burn out any residual carbon. The metal crucibles of tantalum and molybdenum were fabricated from sheets of metal 0.005 in. thick. These crucibles were small, never exceeding 3/4 in. in diameter.

The first type tested was made by rolling the sheet of metal into a pipe and crimping the folded edges together in an interlocking bond. For further strength the bond was rolled once and creased. The bottom was made of a small circular piece with its edges crimped to fit over the end of the tube. The two pieces were held together by firmly packing beryllia powder around the crucible. The second type tested was prepared by folding a long strip of the sheet, sealing the sides by folding the edges over two or three times and then forcing the resulting envelope into a roughly cylindrical shape. In an effort to absolutely seal the edges against leaks, the folds were bonded by spotwelding.

In the purification procedure, the ingots were loaded into a refractory crucible which was then placed in a quartz sleeve with suitable insulating material. The insulation consisted either of loose packed beryllia or magnesia powder or simply of a large beryllia crucible with no other packing. To prevent contamination by carbon and to avoid the problem of degassing, no graphite or Norite insulation was used. A water-cooled brass lid provided with a glass sight hole was placed on the quartz sleeve, a seal being effected by a greased rubber gasket; the system was then evacuated to a pressure of 10 microns of mercury. The metal was melted by induction heating, using either self-induction with no heating crucible or a graphite heater which was separated from the molten metal by the refractory crucible. The temperature was raised slowly to permit a slow distillation of calcium which will distill at 750°C. under a pressure of 100 microns of mercury. The calcium distilled quickly to the equilibrium concentration retained by the alloy at that temperature and then evaporated more slowly as the temperature of the melt was raised. The vacuum above 100 microns was maintained during the distillation.

The induction furnace used for heating was a mercury arc, 20 kilowatt, 20,000 cycle oscillator produced by the Ajax Electrothermic Corporation of Trenton, N. J. The temperature was measured by means of a Leeds and Northrup optical pyrometer. The vacuum was determined by a Stokes McLeod Gauge, Flosdorf Type, manufactured by F. J. Stokes Machine Company, Philadelphia.

Experimental Results

Reductions

Cerium

Results of the first studies on the preparation of cerium metal by the metallothermic process, made at this laboratory (7), are being included in this thesis for the sake of completeness.

The first small scale reductions of cerium were made by heating an equimolar mixture of cerous chloride and calcium plus a 10 per cent excess of calcium in an induction furnace; upon completion of the reaction, the heating was continued until the bomb reached a temperature above the melting point of the cerium, on the assumption that such heating would melt the metal and slag and assure separation. It was found, however, that the prolonged heating produced a boiling action which resulted in the continued admixture of slag and metal as well as in greater melting and penetration of the liner by the metal. These conditions resulted in poor ingots which were highly contaminated with slag and lime, poorly formed and covered with a tightly adhering crust of slag on the top and sides.

In order to prevent this boiling action, a flux of potassium chloride was added to the reaction mixture to permit lower operating temperatures by lowering the melting point of the slag and thereby allowing separation of the slag and metal at lower temperatures. Twenty mole per cent of potassium chloride, as compared to the calcium chloride formed, was added and the holding temperature reduced to about 850°C. By this means, much cleaner metal was obtained in yields of from 50 to 80 per cent.

While this procedure was moderately successful, it appeared that, for large production, the unnecessarily high temperature of the post-heat was both tedious to maintain and difficult to control. It was decided to obtain the temperature necessary for melting the components of the system by the addition of an oxidant to supply the necessary heat.

Iodine was first investigated as a "booster". Charges of anhydrous cerous chloride and iodine, in the ratios of one mole of iodine per mole of cerous chloride, with a five per cent excess of calcium were heated in 2½ by 8 in. bombs with sintered lime crucibles as liners. Yields of 58 to 78 per cent of fairly clean castable metal were obtained with an average of 65 per cent for seven runs.

A study of the effect of the ratio of iodine to cerous chloride was then made with the results given in Table 1. This method was perfected to the stage that 85 to 95 per cent yields were consistently obtained with fully dried cerous chloride, dry iodine in the ratio of 0.5 moles of iodine to one mole of cerous chloride, and calcium in a five per cent excess, fired in sintered bomb liners, with graphite caps over the top of the liner. The reaction was carried out in a steel bomb 4 in. in diameter and 24 in. long. A charge of 1600 grams of cerous chloride was used, with the other components in the ratio indicated above.

In an effort to find a substitute for the expensive, and at that time not readily available iodine, other "boosters" were investigated. Sulfur was tried in the range of one-half to two moles of sulfur per mole of cerous chloride. Although sufficient heat was generated, as evidenced by the outside temperature of the bomb, no separation of the metal and slag

TABLE 1

EFFECT OF IODINE ON THE PRODUCTION YIELD OF CERIUM

Charge gms.	Moles I_2 per mole of $CeCl_3$	Calcium excess %	Yield range %	Yield average %
150	1.0	5	48-78	65
150	0.75	10	62-65	64
300	0.75	10	73-88	84
420	0.625	10	70-91	82
1600	0.625	5	76-91	84
1800	0.5	5	90-97	94

occurred. Apparently the sulfides are miscible with the metals present.

Potassium chlorate was next tested as an auxiliary oxidant with more satisfactory results. The range from 0.10 to 0.16 moles of potassium chlorate per mole of cerous chloride was investigated. An optimum yield of 83 per cent was obtained with 0.11 moles of potassium chlorate per mole of cerous chloride. Even under the best conditions the use of potassium chlorate did not produce cerium metal in yields comparable to those produced by use of iodine, neither externally with respect to adhering slag nor internally with respect to inclusions.

In view of these facts nearly all the metal produced was prepared using the iodine "booster". In a period of a year, nearly a thousand pounds of the commercial grade cerium was prepared by this method and sent to other laboratories.

In the present investigation essentially the same ratio of reactants used in the large scale production of cerium was successfully adopted for the production of very pure cerium. However, since the smaller bomb, 2½ in. in diameter and 12 in. long, was used, a greater heat loss from the reaction mixture occurred and a small adjustment of the ratios of the reactants was necessary to obtain optimum yields. A ratio of 0.62 moles of iodine per mole of cerous chloride with a 10 per cent excess of calcium was adopted for a charge of 312 grams of cerous chloride. The calcium excess was later increased to 15 per cent with an attendant increase in yield.

In the production of four kilograms of cerium an average overall yield of 90.4 per cent was obtained with yields varying from 79 to 100 per cent as illustrated in Table 2. By raising the calcium excess to 15 per cent, the yield was increased to 93.5 per cent. The yield was based on the gross weight of the ingot produced; however, since the ingot contained approximately three per cent of calcium and magnesium impurities, the actual yield was lower, amounting to 87.8 per cent for the average overall yield and 90.8 per cent for the reductions carried out with a 15 per cent excess of calcium. The size of the charge in the reductions tabulated in Table 2 varied slightly because of the varying capacity of the sintered liners.

The ingots obtained were almost invariably very clean with smooth sides and top as illustrated in Figure 3. The cerium metal thus produced contained from 0.5 to three per cent calcium and 0.5 to two per cent magnesium.

The main causes for low yields were attributed to contamination of the cerous chloride by cerium oxy-chloride during the drying run and to moisture absorbed on the calcium oxide liners. As discussed previously, oxychloride formation was caused by melting the hydrate while removing the water. Portions of the molten hydrate were protected

TABLE 2

RESULTS OF CERIUM REDUCTIONS*

Weight of ingot produced gms.	Calcium excess %	Yield %
175	10	98.8
150	10	94.2
144	10	81.4
141	10	79.8
167	10	94.5
165	10	93.4
140	10	80.0
148	10	83.5
148	10	83.5
140	10	79.0
140	10	79.0
178	15	100.2
169	15	95.4
148	15	83.6
169	15	95.4
173	15	97.7
163	15	92.2
181	15	102.1
179	15	100.7
174	15	98.3
175	15	98.8
164	15	92.6
140	15	79.0
140	15	79.0
153	15	86.4
148	15	102.0
Average 158		90.4

* Total metal produced was 4100 grams.

from the contact with the hydrogen chloride gas, and, as the water was removed, this portion had a tendency to react with the water forming the oxychloride and hydrogen chloride gas by the probable equation:

$$CeCl_3 \cdot H_2O \longrightarrow CeOCl + 2\ HCl.$$

Cerium oxychloride will not be reduced completely by the calcium but will yield a mixture of oxide and metal. The resulting mixture does not agglomerate well and consequently low yields result.

A similar reaction may occur in the bomb if the liner and the reactants are not completely anhydrous; however, it is more likely that the water vapor will combine with the calcium reductant forming an oxide layer and thereby retarding the slower reaction with the iodine and cerous chloride. If the water contamination is high, there is danger of explosion due to the hydrogen pressure produced in the reaction:

$$H_2O + Ca \longrightarrow CaO + H_2.$$

Therefore, it is necessary to have completely anhydrous conditions.

Neodymium

The successful production of cerium metal by reduction of the chloride with 0.63 moles of iodine per mole of cerous chloride, using a 10 per cent excess of calcium, indicated that most of the other rare earth metals could also be prepared by this or a very similar method since, according to the available thermochemical data (45), the heat of formation of cerous chloride, 261.5 kilocalories, was higher than those of the other common rare earth chlorides. This assumption was confirmed in the first reduction attempt. A charge of 246 grams of neodymium chloride, containing 10 per cent of praseodymium, with 0.63 moles of iodine per mole of neodymium chloride was reduced by calcium in 10 per cent excess to yield 138.3 grams of neodymium metal for a 97.5 per cent yield.

As a result of the success of this first reduction the ratio of rare earth chloride, iodine and calcium used in the preparation of cerium, was adopted for the reduction of neodymium chloride. Check reductions on 98 per cent neodymium chloride, containing two per cent praseodymium, in the same ratio of reactants but in a 1½ in. bomb, gave an average yield of 86.6 per cent for two reductions (Table 3). This result is better than that obtained for cerium on a comparable scale. More reductions were made in preparing pure neodymium metal for a melting point determination. The average yield obtained for neodymium reductions in the 2½ in. bomb is 91 per cent, which is comparable to the reduction yields for cerium.

TABLE 3

RESULTS OF NEODYMIUM REDUCTIONS

Weight of $NdCl_3$ gms.	Impurity in Nd %	Weight of ingot gms.	Calcium excess %	Yield %
246	10 Pr	138.3	10	97.5
69.4	2 Pr	32.3	10	88.6
64.5	2 Pr	31.5	10	85
289	2 Sm	150	10	91
326	pure	162	19	89
326	pure	182	19	97
130	pure	32	19	86
60	pure	13	19	77
			Average	91

Samarium

Extension of the reduction method to the production of samarium metal was not as successful as with the other rare earths studied. The stability of the samarium salts could not be predicted from the heat of formation of 240 kilocalories for the trichloride, a value below that of any of the other rare earth chlorides studied. However, the difficulty in reducing samarium chloride to metal is in agreement with previous findings (14) that all the rare earths could be readily reduced to metal with the exceptions of those having a stable divalent state, namely samarium, europium, and ytterbium.

Attempted reductions of samarium trifluoride, samarium triiodide, and samarium trichloride with an iodine "booster" in the ratio of 0.628 moles per mole of halide were failures, the dihalide being formed in each case. The reaction between the calcium and iodine and the one available halide of the samarium salt proceeded quite vigorously as evidenced by the heat generated in the bomb at the time of reaction and the complete collection of reaction products in the bottom of the liner; however, no metal was obtained by this method.

Use of potassium chlorate as a "booster" was also tested in the reduction of samarium trichloride. In the two runs in a one inch bomb using 25 grams of samarium trichloride with 0.1 and 0.167 moles of potassium chlorate per mole of samarium trichloride, the bombs were heated to a bright red heat by the reaction; the reaction products were completely fused, but only the dichloride was formed.

Since the dihalide was formed in each reduction, it was decided to start with this material and check the results. Samarium dichloride was prepared and the reduction attempts were made. The results obtained are listed in Table 4. No metal was found when iodine was used as a "booster" in the one reduction attempted. Since this reaction was approximated by the reduction of the samarium trichloride and iodine by calcium, if one considered the loosely held third chlorine atom as an additional "booster", and since the more promising results obtained with the mixture of the dichloride and calcium merited further work, no further reductions of the dichloride were attempted with an iodine oxidant present. In the reduction of samarous chloride by calcium without an iodine oxidant, there was evidence of a reaction since a network of metal containing some samarium had formed in the slag in some cases. The metal could not be recovered from the slag; it was difficult to break out since the pieces were small, and it could not be cleaned by washing because of the reactivity of the calcium present. Attempts to recast the reduction products did not accomplish separation and a casting attempt on some of the partially separated metal failed because of the extensive oxidation of the alloy in washing away the unreacted samarous chloride.

TABLE 4

RESULTS OF THE REDUCTIONS OF SAMARIUM DICHLORIDE

Weight of charge gms.	$SmCl_2$ to Iodine ratio	Calcium excess %	Results
18	1:0.63	10	No metal formed
22.1	none	10	Network of metal (small amt.)
33	none	10	Network of 12 gms. of metal
47.5	none	10	No metal formed
33	none	10	No metal formed
136	none	10	Network of 25 gms. of metal
33	none	10	No metal formed

The possibility of obtaining samarium as a more stable alloy of another metal was next investigated. A mixture of magnesium and calcium in large excess with 10.9 grams of samarium trichloride was heated to 1000°C. The samarium trichloride was reduced to the dichloride which, when cooled, was found to be intermixed with a network of very dilute alloy of samarium with magnesium and calcium. Evidently the samarium dichloride is relatively stable to magnesium and calcium at this temperature.

Zinc chloride which combines the properties of an alloying agent and a "booster", was next investigated for the reduction of samarium compounds. The results are given in Table 5. In all the experiments, with the exception of the one sample lost during reaction, an alloy of zinc, samarium and calcium was obtained in low yields. Since the alloy was quite brittle and reacted quite rapidly with water, it was necessary to remove the metal from the slag, piece by piece, to obtain a sufficient amount for recasting. The reductions were only partially complete and much samarium dichloride remained. Ten grams of alloy, the result of the last three reductions, intermixed with several grams of slag, was heated to 900°C. The zinc was distilled, leaving approximately two grams of a hard metal which showed no signs of having been molten at this temperature. Analysis showed that the metal contained at least 50 per cent samarium.

TABLE 5

RESULTS IN THE PREPARATION OF SAMARIUM-ZINC ALLOYS BY REDUCTION

Weight of halide gms.	Molar ratios used					Calcium excess %	Weight of alloy gms.
	$SmCl_3$	$SmCl_2$	SmF_3	$ZnCl_2$	ZnF_2		
15.4	1			1		20	?
18.0		1		1		20	1
11.4	1			2.3		10	6
27.4*			1		6	5	--
22.6			1		2.5	12	2
15.0	1			1.5		5	2.5
61.6	1			1.5		10	10

* Lid was blown off the bomb.

In summary, the reduction of the trihalides by calcium with an iodine oxidant to increase the reaction temperature was a failure. Judging from the appearance of the reaction products, the reduction of the fluoride proceeded more vigorously than the chloride and iodide, but in all three cases the dihalide was obtained as the final product. The potassium chlorate, although supplying considerable heat in the reaction with calcium, did not aid in producing metal since only a mixture of well fused slag and dichloride was obtained. Of the reduction methods for the preparation of samarium metal, the most successful was by using an alloying agent to reduce the melting point of samarium metal and perhaps to lower the reduction potential of the samarium salt by solution in much the same way that the samarium ion is removed from aqeous solution by a sodium amalgam. The recovery of a small amount of samarium-rich alloy by use of a zinc chloride "booster" indicates that this procedure may be successful.

Didymium

After the first successful reductions of neodymium, a need arose for a cheap rare earth metal to be used for testing crucible materials as a standin for neodymium, praseodymium, and samarium; this was necessary since crucibles that would not be wetted by cerium would be eroded considerably by neodymium. The possibility of producing samarium metal by preparing it in solution in the other rare earth metals and then perhaps distilling them out was also considered.

For these reasons and to fill requests from other laboratories, 1850 grams of didymium metal were prepared; the mixture contained 80 per cent neodymium, 10 per cent samarium, eight per cent praseodymium, and one or two per cent gadolinium. The metal was produced by the same ratio found successful for neodymium, namely with 0.63 moles of iodine per mole of didymium chloride reduced by calcium in 10 per cent excess.

From the results of these reductions listed in Table 6 it is apparent that the yields are considerably below those obtained for cerium or neodymium. The main cause of the decrease is attributed to the deleterious effect of the samarium present. This is confirmed by the definite enrichment of samarium in the slag, while the samarium content dropped from the original 10 per cent in the starting material to about three per cent in the metal. Due to the lower melting point of the hydrated didymium chloride some trouble was encountered in preventing the chloride from melting during the first drying runs. For this reason, three to five per cent of oxychloride, according to analysis, was formed. The effect of this contamination reduced the yield in the first series of reductions to 77.6 per cent as compared to 83.5 per cent obtained reducing charges of oxychloride-free didymium chloride.

TABLE 6

RESULTS OF DIDYMIUM REDUCTIONS

Weight of $DiCl_3$ gms.	Drying run	Calcium excess %	Weight of ingot gms.	Yield %
69.8	1	10	22	58
65.4	1	10	35	91
276	1	10	112	78.9
307	1	10	125	70.7
318	1	10	137	75.0
318	1	10	128	70.0
318	1	10	135	73.8
318	1	10	133	72.5
155	1	10	70	78.7
318	2	10	156	85.3
318	2	10	147	80.4
276	2	10	131	82.3
318	2	20	143	78.1
318	2	20	156	85.2
318	2	20	164	89.6
158	2	20	67	72.8
Total 1858				Average 77.6

In the runs in which calcium excess was increased to 20 per cent, no definite increase was found that could be ascribed to the increased calcium content.

Praseodymium

According to thermochemical data (45), the reduction of praseodymium to metal should proceed with the same success as in the case of cerium, since the heat of formation of the chloride is 254.9 kilocalories, 6.5 kilocalories less than for cerous chloride, a factor that is counterbalanced by the slightly higher melting point of praseodymium metal.

One reduction of praseodymium was attempted. Seventy-two grams of praseodymium chloride, containing 10 per cent neodymium with an iodine "booster" in the ratio of 0.63 moles of iodine per mole of chloride, was reduced by calcium in 10 per cent excess. A very clean, well shaped ingot weighing 33.2 grams was obtained for a yield of 78 per cent. The yield was slightly lower than expected, but compares with the results obtained for cerium, namely, 76.6 to 86 per cent, for the same scale reduction. It is probable, therefore, that the same high yields as obtained for cerium and neodymium will be obtained for praseodymium when a charge is used large enough to fill a 2½ in. bomb.

Yttrium

Since the heat of formation of yttrium chloride is 240 kilocalories, or 21 kilocalories below that of cerous chloride and 6 kilocalories below that of neodymium chloride, the chloride should be more readily reduced to the metal than any of the rare earths studied; however, due to the high melting point of the metal some difficulty could be expected in fusing the reaction mixture of a reduction, and consequently in obtaining a good collection of metal.

The first experimental reduction of yttrium chloride was carried out on a 70 per cent yttrium chloride sample containing 18 per cent neodymium, 10 per cent samarium, and two per cent gadolinium as impurities. Using a ratio of 0.63 moles of iodine to one mole of yttrium chloride, with a 10 per cent excess of calcium, 58 grams of this salt were reduced to give 29.2 grams of metal for a 79 per cent yield. After the successful preparation of metal from the rather impure yttrium chloride, reductions were carried out on the anhydrous chloride of 90 per cent yttrium, containing six per cent dysprosium, two per cent gadolinium and two per cent of other rare earths. In two trials with the same ratio of iodine and calcium as used in the first reduction, no massive metal was obtained. In these latter reductions the metallic yttrium produced by the reduction was intimately mixed with the slag. Apparently there was not enough heat generated to fuse the yttrium metal, although the reaction proceeded vigorously enough to permit complete slag collection.

Casting

The rare earth metal produced by reduction must be recast to remove the alloyed calcium and to convert the ingots into usable shapes. The casting can be made under any inert atmosphere such as that provided by a vacuum, an inert gas or a flux. In the work described in this thesis, all castings were made in a vacuum to permit distillation of the excess calcium at lower temperatures. A vacuum of less than 100 microns of Hg was maintained for these castings to prevent the formation of a very tenacious oxide layer which formed on the metal at higher pressures. This oxide "skin" prevented the flow of the metals at temperatures as much as 200°C. above the melting point. The same phenomenon explains the difficulty in casting the rare earth metals through small holes or into small crucibles (less than $\frac{1}{2}$ in. diameter) of refractory oxide. It is probable that a slight reaction occurs between the metal and the oxide crucible thus producing the thin oxide coating which prevents flow of the metal and hinders the complete filling of a small crucible. The effect of the oxide coating was especially noticeable with small pieces of metal. For example: a bar of neodymium metal, suspended on two knife edges, was heated to 1100°C., or 270 degrees above its melting point, before collapsing.

Recasting of the ingots produced by reduction has been quite successful in removing calcium. In many cases the calcium content can be reduced to 0.2 per cent by heating the metal to 1000°C.; however, a much higher temperature, 1300-1400°C., is required to remove the last traces. The results in calcium removal have been rather irregular, apparently depending on the history of the metal ingot, the size of the casting and the vacuum obtained during the decontamination run. As a general rule, practically all the calcium can be removed from cerium ingots weighing less than 100 grams by heating to 1250°C.; however, if a casting of 1000 grams is heated to this temperature, 0.1 to 0.2 per cent calcium still remains.

A number of refractory oxides were tested for resistance to attack by the molten rare earth metals at the temperatures required to remove calcium. It had been reported (1) that the oxides of aluminum, beryllium, zirconium, and thorium as well as quartz are strongly attacked by the rare earth metals at the temperatures necessary for melting the metal; only magnesium oxide and fluorite (CaF_2) of the refractory salts and molybdenum and tungsten of the refractory metals were found to be resistant to attack by the rare earth metals. Of those listed as being attacked, only beryllia was rechecked because of the excellent results obtained in work in this laboratory with similar metals. Magnesium oxide, calcium oxide, and several rare earth oxides were also investigated as crucible materials, since, if reaction occurred, only oxygen would be introduced as a new contaminant. Fluorite was not tested because of its low melting point (1360°C.). The refractory metals, molybdenum and tantalum were also used as crucible materials.

Considerable variation in results was found in studying the resistance of the refractory oxides to attack by the molten metals. For example, in a test run cerium metal was heated to 1250°C. in a calcium oxide crucible without wetting the walls, but in a large casting the metal extensively wetted the walls and soaked into the crucible at 1150°C. This irregularity is explained on the basis that the oxide coating on the metal prevented any wetting of the walls when the weight of the metal was small, but was ineffective when a larger amount of metal was used. It is evident that specific examples are somewhat misleading, although the general trend can be observed.

Both cerium and neodymium were melted in beryllia crucibles with the following results: cerium heated to 1000°C. dissolved less than 400 ppm. of beryllium, while the calcium and magnesium content was reduced to 0.2 per cent for both metals; at 1250°C., the cerium extensively attacked the crucible. Neodymium could be heated to 900°C. without any extensive pickup of beryllium, but at 1150°C. 0.4 per cent beryllium was introduced.

Calcium oxide was somewhat more stable in the presence of molten rare earth metals than was beryllia. Cerium could be heated to 1150°C. without reacting with the crucible, but above this temperature an agitation of the metal was observed and later correlated with the following reaction:

$$2\ Ce + 3CaO \longrightarrow Ce_2O_3 + 3Ca$$

The calcium metal formed by the reduction of the oxide by cerium immediately distilled and caused an apparent boiling of the metal. By casting 300 grams of cerium in calcium oxide at 1150°C., the residual calcium was reduced to 0.1 or 0.2 per cent, and the magnesium was removed to amounts less than 0.025 per cent, the lower limit of analysis. A casting of one kilogram of cerium is illustrated in Figure 4. Didymium and neodymium attacked calcium oxide crucibles at 1000°C. Below this temperature the calcium oxide appeared to be fairly stable to these metals; however, under these conditions one per cent calcium and 0.5 per cent magnesium remained in these rare earths after casting.

The magnesia crucibles, as previously noted, are the most resistant to attack by the lighter rare earth metals particularly in the case of neodymium and praseodymium. Didymium, neodymium, praseodymium, and yttrium can be heated at 1150°C. in this type crucible without wetting the crucible walls. The residual calcium and magnesium contents are listed

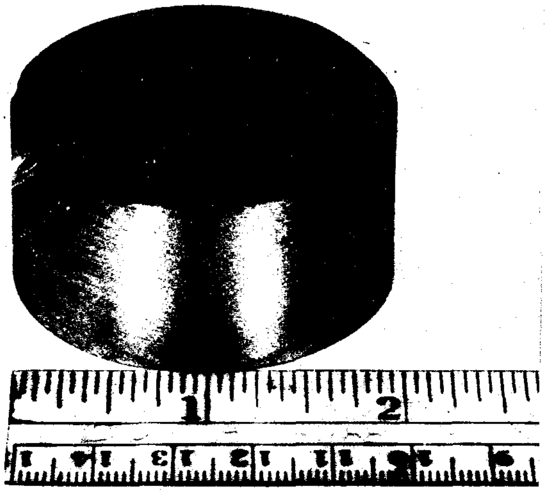

Figure 4. Typical Casting of Cerium.

in Table 7. The lower temperatures were used for praseodymium and yttrium because an agitation of the neodymium metal was observed at 1200°C. Since this effect has previously indicated attack of the crucible by the reaction,

$$2Nd + 3MgO \longrightarrow Nd_2O_3 + 3\ Mg\ ,$$

a lower casting temperature was used to insure against loss of the more scarce metals. The very high calcium content of the yttrium is not too surprising since the metal was not heated to its reported melting point; however, this alloy was molten at temperatures above 900°C. The results in Table 7 were obtained for 30 gram samples, so a higher temperature would be required to obtain an equivalent purity on larger samples. This fact is aptly illustrated by a casting experiment in which 350 grams of neodymium metal were heated to 1200°C. in magnesia but still contained one-half per cent calcium and one per cent magnesium.

The rare earth oxides had been used as refractories in other laboratories (34). They were considered because the very tenacious oxide coatings on molten metal suggested a very low solubility of the oxide in the metal. This fact was confirmed by tracer studies in the case of lanthanum oxide in lanthanum at temperatures up to 1200°C. by another member of this laboratory (46); however, by metallographic techniques it was shown that at 1450°C. there was considerable solution of the oxide in the lanthanum. Several didymium

TABLE 7

IMPURITIES REMAINING AFTER CASTING IN MAGNESIA CRUCIBLES

Metal	Temperature °C.	Calcium %	Magnesium %
Ce	1200 - 1250	< 0.05	0.025 - 0.25
Di	1150 - 1200	0.13	< 0.025
Nd	1200 - 1250	< 0.05	< 0.025
Pr	1125	0.13	< 0.025
Y	1125	2.1	0.25 - 0.50

oxide crucibles were prepared and several castings of didymium were made, but since the metal wetted the crucible considerably, it followed that only oxide of the same purity as the metal could be used if the tedious separation procedures of the rare earths were to be avoided. For these reasons crucibles of rare earth oxides were not further investigated.

Since the rare earth metals appear to attack all the refractory oxides to some extent, the refractory metals, tantalum and molybdenum, were tested. Crucibles were fabricated from sheets of metal 0.005 in. thick. The castings were all carried out on a small scale to conserve crucible material and metal. The first castings were made in the "stove pipe" crucibles, which did not leak up to 1350°C. Above this temperature the metal leaked through the cracks and reacted with the beryllia packing. The envelope type crucibles were tight up to 1400°C., but at this temperature or above, the rare earth metal, which wetted both molybdenum or tantalum, seeped through the folded edges and soaked into the insulation. By spot welding the sides of the envelope type crucible, a tantalum crucible sufficiently tight to hold cerium metal at 1700°C. was obtained. Even at this high temperature no tantalum could be detected in the cerium by chemical or spectroscopic analysis. Didymium was heated in tantalum to 1350°C. and in molybdenum to 1350°C.; no contamination by the crucible material was detected by spectroscopic methods in either case.

A summary of the temperatures at which the various refractories studied are stable to the rare earth metals is given in Table 8.

Many of the temperatures are based on experiments which showed that a slight reaction between the metal and the crucible occurred one hundred degrees above the temperature listed; it is assumed that by lowering the temperature this amount, reaction will become negligible. The estimates are based on the behavior of molten didymium or neodymium on the refractory material, since all the rare earth metals studied, with the exception of cerium, appear to have about the same reactivity.

TABLE 8

TEMPERATURES AT WHICH REFRACTORIES ARE STABLE TO RARE EARTH METALS

(Temp. in °C.)

Metals	BeO	CaO	MgO	Rare earth oxide	Ta	Mo
Ce	1000	1150	1200	1200*	>1700	>1400
Di	900*	900*	1200	1200	>1350	>1350
Nd	900*	900*	1175	1200*	>1350*	>1350*
Pr	900*	900*	1175	1200*	>1350*	>1350*
Y (70%)	---	---	1175	---	---	---

* Estimated.

GENERAL PROPERTIES OF CERIUM AND NEODYMIUM METALS

Introduction and Historical

Many of the physical properties of the rare earth metals are still not definitely established. The best agreement among investigators is on the crystal structure, the atomic radii, the atomic volume, and consequently the calculated density of the common rare earth metals, that is: lanthanum, cerium, praseodymium and neodymium. Using a method of producing powdered metal, which gave agreement with other crystallographic work on the common rare earth metals, Klemm and Bommer (14) were able to obtain the metal and determine the crystal structure and the associated properties of the other rare earths, with the exception of samarium, whose structure was too complicated to be analyzed. The above authors also measured the magnetic properties of metals of all the rare earths and obtained dependable results that compared well with the best measurements so far obtained in the case of the more common metals. Other properties that have been determined but on which there is not too good agreement or which have been reported by only one investigator are: the melting point, the hardness, the electrical conductivity, the specific heat and the compressability.

Of these the melting point and the density measurements will be reviewed completely. The hardness values which can be compared with those obtained in this investigation will also be reported. Unfortunately, in the early work hardness was measured by such qualitative or arbitrary scales as the Moh scale and the scleroscope hardness test which can not be compared to our measurements.

The melting point of cerium as determined by a number of investigators is given in Table 9 with the listed impurities. The low temperatures obtained in the early work can be explained on the basis of iron contamination since iron forms a eutectic with cerium, at a concentration of 4.5 per cent iron, with a melting point of 633 - 640°C. Considering the metals of 99 per cent purity, there is fair agreement in the melting points reported. The data of Billy and Trombe are considered by some authorities (1) to be the most satisfactory of those listed. The analysis of the metal in this case is the only complete one reported with the maximum limit of impurities listed. One difficulty with this measurement is that the melting point was determined by supporting a cerium wire as the junction between the two wires of a platinum-90 per cent platinum 10 per cent rhodium thermocouple. The temperature was recorded when the wire melted. Since even a slight oxide coating could prevent the molten metal from parting at temperatures as much as 20 degrees

TABLE 9

MELTING POINT OF CERIUM AS REPORTED BY VARIOUS INVESTIGATORS

Melting point °C.	Cerium %	Impurities %	Author
622	?		Muthmann and Weiss (30)
635	93.6	4.5 Fe	Hirsch (22)
720	96.7	0.5 Fe 2.5 other rare earths	Hanaman (47)
775	95.6	no Pr, Nd 4.3 other rare earths	Vogel (48)
815 ± 5	99.8 - 99.9	0.08 Si 0.05 Fe	Billy and Trombe (49)
775	99.8 - 99.9	traces of C, Si, Fe	Mazza (50)
777	98 - 99	0.14 Fe 0.14 Mg 0.02 Si	Rolla and others (51)
780	99.3	0.15 Ca 0.12 C 0.4 other rare earths	Petersen, Lyon and Keller (52)

above the melting point, considerable error could be introduced by having a slight contamination in the atmosphere for the experiment.

Densities reported for cerium are listed in Table 10. The density calculated from crystal structure is included for purposes of comparison. Of the densities determined experimentally, the results of Trombe, on cerium metal prepared by electrolysis (density 6.75) and remelted to remove alkali impurities (density 6.89), appear to be the most nearly correct.

Although neodymium has been prepared by a number of investigators, its melting point has been reported only by Muthmann and Weiss (30) in 1904. The melting point of 840 ± 10°C. which they reported was determined using a platinum - 90 per cent platinum 10 per cent rhodium thermocouple, whose electromotive force was measured on a millivoltmeter. The inaccuracy in reading the millivoltmeter introduced the possible error of 10 degrees, since the melting point was obtained by observing the temperature at the moment a weighted rod suspended in a bar of the metal sank into the bar, as the metal melted. No analysis of the neodymium metal was given.

The density of neodymium has been measured by several investigators and is given, together with listed impurities, in Table 11. Two of these densities, those by Muthmann and

TABLE 10

DENSITY OF CERIUM AS REPORTED BY VARIOUS INVESTIGATORS

Density gm./cc.	Cerium %	Impurities %	Investigator
6.810*		No other rare earths	Klemm and Bommer (14)
6.73		No analysis given	Hillebrand and Norton (26)
7.04		No analysis given	Muthmann and Weiss (30)
6.92	93.6	4.5 Fe 2.5 other rare earths	Hirsch (22)
6.61	94	0.5 Si 0.7 Fe 0.3 Al	Blitz and Pieper (53)
6.77	99		Kremers and Beuker (31)
6.734	94.9	4.2 other rare earths 0.35 Fe 0.27 Si	Sieverts and Gotta (54)
6.75	99.8 - 99.9	0.05 Fe 0.08 Si	Billy and Trombe (49)
6.789	99.8 - 99.9	0.05 Fe 0.08 Si	Trombe (55)
6.78	99.8 - 99.9	Traces of C, Si, Fe	Mazza (50)

* Calculated from crystallographic data.

TABLE 11

DENSITY OF NEODYMIUM METAL AS REPORTED BY OTHER INVESTIGATORS

Density gm./cc.	Neodymium %	Impurities %	Author
6.998*		No other rare earths	Klemm and Bommer (14)
6.956		No analysis given	Muthmann and Weiss (30)
7.05		No analysis given	Kremers (12)
6.94	99.4	0.6 Si 0.02 Fe	Trombe (56)

* Calculated from crystallographic data.

by Trombe, approach the calculated density. However, the analysis shows that no metal of high purity has yet been prepared.

The hardness values for cerium and neodymium reported on a scale that is comparable to those obtained on the instruments available at this laboratory are given in Table 12. There is general agreement that cerium is a soft malleable metal, slightly harder than lead, but soft enough to cut with a knife, and that neodymium is somewhat harder than cerium, and compares approximately to that of brass.

No investigation of the vapor pressure of cerium or of any of the rare earth metals has been reported. The boiling point of 1400°C. that is frequently listed for cerium is based on an estimate by Mott (57) who calculated the boiling point using the observation that the ratio of the absolute boiling temperature to the absolute freezing temperature of most elements is approximately 1.8. Moreover, 640°C. was used in the calculation as the melting point of cerium; since it is now known that the melting point of cerium metal is 790°C., the higher boiling point of 1650°C. would result from the formula. The above relation gives approximate agreement for several elements but cannot be considered as giving even an estimate of the boiling point in many cases; for example, it is in error by 650°C. by predicting the boiling point of aluminum at 1400°C.

TABLE 12

BRINELL HARDNESS VALUES REPORTED FOR CERIUM AND NEODYMIUM

Element	Hardness Brinell scale*	Investigator
Ce	28	F. Hanaman (47)
	21	Kremers and Beuker (31)
	42.5	Billy and Trombe (49)
Nd	70	Kremers (12)
	60	Trombe (56)

* 500 kg. load, 10 mm. standard steel ball.

Density, Hardness and General Characteristics of Cerium and Neodymium Metal

Density

The density of cast cerium and neodymium metal was determined by measuring the loss in weight of the metal on immersion in carbon tetrachloride at a known temperature. The specific gravity of the carbon tetrachloride was measured by weighing in a pycnometer. Water could not be used for the density determination because its immediate, although slow, reaction with cerium produced gas bubbles on the surface of the metal and consequently caused erratic results.

The density of cast cerium metal containing 0.2 per cent calcium, as determined on turnings and pieces of cast metal, has a density of 6.739 ± 0.003 grams per cubic centimeter at 24°C. A portion of this metal was recast in magnesia at 1100°C. The density of the resulting metal, now containing 0.1 per cent calcium, was increased to 6.747 ± 0.003 grams per cubic centimeter at 23°C.; this value is 0.04 grams per cubic centimeter below the density calculated from crystallographic data as shown in Table 10. The lower density found for the cerium produced by the metallothermic process is caused by the residual calcium remaining in the metal and by the small amount of oxide contamination introduced in casting.

Neodymium metal, containing one-half per cent calcium and one per cent magnesium, has a density of 6.999 grams per cubic centimeter at 25°C. according to the density measurement on a 100 gram cylinder of cast metal. This high density equals the theoretical density listed in Table 9. The results are surprising since the impurities present would be expected to reduce the density considerably; for this reason it is possible that the density reported from x-ray data may be low because of dissolved impurities.

Hardness

The hardnesses of cerium and neodymium were measured on two hardness testers: the Tukon Hardness Tester which gives hardness values in terms of Knoop Hardness Numbers; and the Rockwell Hardness Tester which gives hardness in Rockwell numbers. Both machines are manufactured by the Wilson Mechanical Instrument Company, Inc. Earlier measurements on a cerium-calcium reduction ingot were made with the Rockwell machine and the Vicker's Hardness Tester, which gives hardnesses in units of Diamond Pyramid Hardness. The latter machine is manufactured by Vickers, Ltd. and is distributed by the Riehle Testing Machine Company. For purposes of comparison the Brinell Hardness number was considered to be equivalent to the Diamond Pyramid hardness number to which it corresponds closely. For cerium and neodymium, the hardness values on the Knoop and Rockwell scales were converted to the Diamond Pyramid hardness number using the calibrations made by Brodie (58); it must be emphasized that these conversions are approximate since a conversion curve must be found by empirical measurement for each different metal.

The hardness values, determined by the various procedures, are listed in Table 13. By comparison with Table 12, it is apparent that the hardness values of the two metals tested are somewhat less than those previously reported. Since the other metals were all prepared by electrolysis, their greater hardness could be attributed to the silica contamination that usually occurs in that preparation.

The different hardnesses of the cerium reduction ingot are of interest. Two different layers are visible in a cross section of the reduction ingot. The top layer contains more calcium, about three per cent, and is relatively hard; the bottom layer contains less calcium and is considerably softer. On the basis of this difference which could have been caused by the formation of an intermetallic compound, the preparation of cerium-calcium alloys was attempted. No alloys could be prepared and, according to x-ray analysis, no compound was formed between the two metals; therefore the greater hardness of the upper layer is probably due to intimately mixed calcium that was entrapped by the metal as the ingot froze.

TABLE 13

HARDNESS VALUES FOR CERIUM AND NEODYMIUM

		Knoop hardness number	Rockwell H hardness	Diamond pyramid hardness	Brinell hardness scale*
Ce-Ca ingot	Top	--	96	88	ca. 88
	Bottom	--	59	46	ca. 46
Ce		25	39	--	ca. 19
Nd		47	60	--	ca. 33

* 500 kg. load, 10 mm. standard steel ball.

General characteristics

The general characteristics of cerium metal prepared by the metallothermic reduction method are almost identical with the descriptions published previously (1). Fresh cut cerium has a silver-gray color that tarnishes immediately in air. The metal will oxidize slowly in air and consequently must be stored under mineral oil in closed bottles. This reactivity was quite apparent in the casting experiments discussed earlier; in the reaction with crucible materials, the oxide produced was included in the metal as thin shells. These oxide inclusions have a considerable effect on the mechanical properties. For example, metal which has been heated without reaction with the crucible can be cold rolled into thin sheets with little tearing or cracking; however, if much oxide is introduced during the purification casting, the metal loses its malleability and will crack slightly and tear on as little as a 25 per cent reduction by cold rolling. A similar effect is observed in cutting cerium metal. If the metal is free from inclusions, it can be turned or sawed without burning; however, if, as is generally the case, the metal does contain oxide, the heat or sparks caused by these inclusions will ignite the cuttings. For this reason, most of the pure samples of cerium prepared by casting at high temperatures are inferior in mechanical properties to metal prepared by electrolysis where it is not necessary to distill impurities.

Certain differences between neodymium metal and cerium metal are pertinent to this discussion. Although when molten, neodymium attacks most oxides at a lower temperature than cerium, it is more stable in air. The silver-white color does not tarnish quickly, and all samples of the metal can be cut without burning. No tests of the mechanical properties of neodymium were made.

Melting Points of Cerium and Neodymium

The melting points of cerium and neodymium were determined by means of thermal analysis. The temperature was measured by a chromel-alumel thermocouple, calibrated before and after the melting point measurement by the freezing points of the three standards, aluminum, silver and the copper-silver eutectic mixture.

Apparatus

The resistance furnace used to provide controlled heating and cooling rates was 24 in. high, 14 in. in overall diameter with a heating element 4 in. in inside diameter, as illustrated in Figure 5. The heating element consisted of No. 12 chromel resistance wire imbedded in Sillimanite, an aluminum silicate cement, and was capable of producing temperatures up to 1000°C. Four and one-half inches of Dicalite,

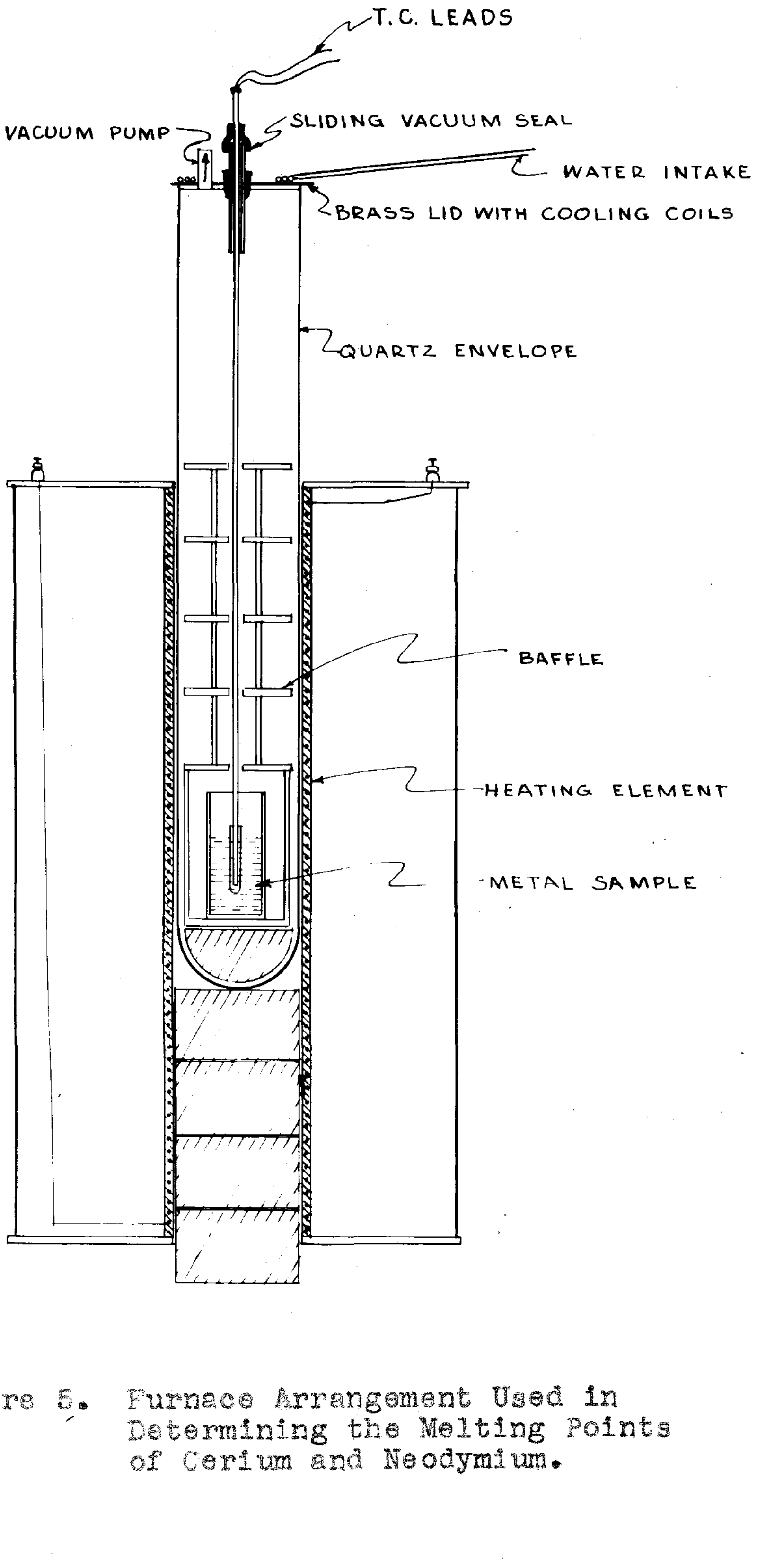

Figure 5. Furnace Arrangement Used in Determining the Melting Points of Cerium and Neodymium.

a commercial insulator composed of diatomaceous earth, reduced the heat loss through the walls of the furnace sufficiently to provide very slow cooling rates. The outside shell of the furnace consisted of a sheet iron cylinder inserted into grooves of cut transite which served as the furnace ends.

The furnace had a maximum heating and cooling rate of three degrees a minute in the temperature region of the melting points of the metals studied. Both rates could be varied by altering the amount of electrical current passing into the furnace. In practice, heating and cooling rates from three degrees to one-half degree per minute were used. The thermal gradient of the center of the furnace, the region in which the samples were placed, was low. When the baffles were inserted to reduce radiation losses, there was a one or two degree temperature variation in the center 6 in. of the heating element.

The samples were heated in an evacuated quartz envelope. As illustrated in Figure 5, the sample was placed inside a larger crucible, above which was a series of baffles prepared from refractory oxides. The extra crucible and the baffles were designed to reduce the heat loss by radiation up the quartz tube, and thereby to assist in obtaining an even heat loss in all directions from the metal sample. The quartz tube was sealed by waxing on a water cooled brass lid which contained the vacuum and thermocouple outlets.

The thermocouple was inserted into the furnace through the lid by means of a sliding vacuum seal which consisted of two concentric pieces of glass tubing; the outside tube was waxed into the lid and was sealed to the longer inside piece by a piece of rubber tubing heavily greased with Celvacene vacuum grease. This sliding seal permitted quick and certain adjustment of the thermocouple. The thermocouple passed down through the baffles and into the sample; it was protected from the molten metal by a thin protection tube of beryllia or magnesia, which was prepared in the same manner as the crucibles discussed earlier. Beryllia was used as the protection tube for the first melting point determination of cerium because at the low temperatures attained no detectable amounts of beryllium dissolved in molten cerium.

The thermocouples were prepared from chromel P and alumel No. 18 gauge wire manufactured by the Hoskins Manufacturing Company of Detroit, Michigan. The hot junction was made by welding the two wires in an oxy-acetylene flame. The cold junction was obtained by immersing the connections with the potentiometer leads in separate dry mercury baths contained in test tubes which were suspended in an ice bath. The mercury served as a heat exchange medium between the cold junction and the bath.

Calibration of the thermocouples was made against the freezing points of the three standards, aluminum, silver, and the copper-silver eutectic mixture. These metals were contained in graphite crucibles, approximating the shape and dimensions recommended by the Bureau of Standards (59) for the determination of the melting points, as shown in Figure 6. The standards were 4 cm. in diameter, 8 cm. long and were contained in a crucible 4½ cm. in outside diameter and 12 cm. high. Oxidation was eliminated by spreading loose graphite over the standard sample and by fitting the crucible with a tight graphite lid.

The electromotive force generated by the thermocouple was measured on a Leeds & Northrup Portable Precision potentiometer. The voltage of a standard cell included in the potentiometer was corrected against that of a calibrated standard cell manufactured by The Eppley Laboratory of New Port, Rhode Island. Time intervals were determined by means of an electric timer.

The vacuum attained during these runs varied from 5 to 200 microns of Hg. In the first runs, an oil diffusion pump, Model MC 275, manufactured by the Distillation Products Company, was used, backed by a Cenco Hyvac 20 mechanical pump. However, the vacuum obtained during the runs was approximately the same whether or not the diffusion pump was employed, and for this reason the mechanical pump was used alone in later runs.

In determinations 1 and 2 on cerium, the sample used was a cylinder, 5 cm. in diameter, 6 cm. high, with the thermo-

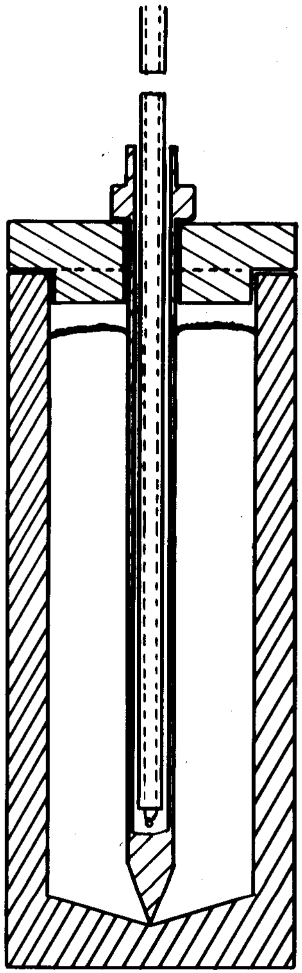

Figure 6. Crucible Recommended by the Bureau of Standards for the Determination of the Melting Point of Aluminum.

couple inserted 4 cm. into the sample to a point somewhat below the center of the mass as illustrated in Figure 7a. The crucibles used were calcium oxide and the thermocouple protection tubes were beryllia. In the third measurement of melting point, an attempt was made to approximate the ideal conditions recommended by the Bureau of Standards for the determination of melting points. In this case, the sample was 3 cm. in diameter, 15 cm. tall, with the thermocouple inserted 9 or 10 cm. into the sample (Figure 7b). In each case, the samples weighed more than a kilogram.

A 350 gram cylinder, 3 cm. in diameter and 6 cm. high, was used to determine the melting point of neodymium. The thermocouple was inserted 4.2 cm. into the billet or 1.8 cm. above the bottom. The crucible and protection tube were prepared from magnesia.

Procedure

The first step adopted for the determination of the melting point of the rare earth metals was a preliminary calibration of the chromel-alumel thermocouple by the determination of the melting point of the copper-silver eutectic. This precaution was taken to detect any variation in the electromotive force of the thermocouple that might be caused by contamination of the couple by possible vapors rising

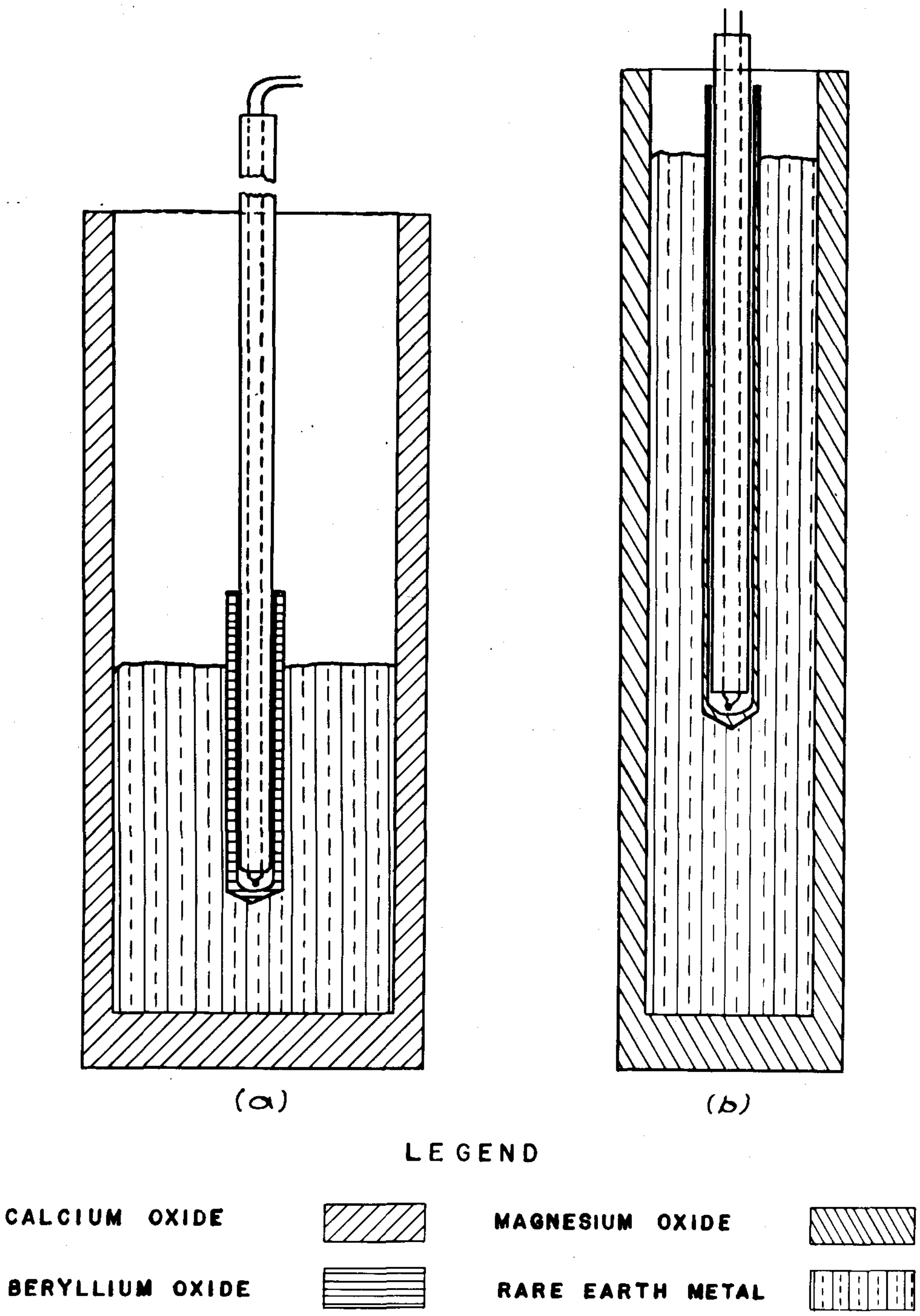

Figure 7. Crucibles Used for the Determination of the Melting Point of Cerium.

from the rare earth metal. The copper-silver eutectic was chosen since its melting point was believed to be within a few degrees of the melting point of cerium. In the melting point determinations only one change in the electromotive force corresponding to a change greater than one degree centigrade was ever observed. In this one case the upper portion of the thermocouple was attacked by calcium vapors from the cerium-calcium alloy, causing embrittlement and subsequent breaking; however, the junction was evidently shielded by the protection tube because only a one degree centigrade or 0.06 millivolt change in the electromotive force was detected.

As a preliminary step in the determination of the melting points of cerium, the cerium-calcium alloy and neodymium, a cooling curve of a sample of each metal was taken on a recording potentiometer, a Micromax Recorder, Model S, manufactured by the Leeds & Northrup Company. This recording gave an accurate indication of the number and temperature of the thermal arrests. These temperature regions were then carefully investigated using the precision potentiometer. The electromotive force of the thermocouple was read at one-half or one minute intervals; the data obtained were used to construct the heating and cooling curves. If the arrests were sharp, as in the case of the standards, the temperatures could be determined by visual inspection; otherwise the limits of the break were established graphically. For example, the upper limit of an arrest found in a cooling curve was established by extrapolating the curve beyond the temperature of the break, extending the flattest portion of the break to intersect the extrapolated curve, and taking the point of intersection as the upper limit of the arrest. Two or three measurements of the temperature of the thermal arrest were made for each sample, including the standard calibration metals. There was usually no change detected between the measurements, except in the case of the cerium-calcium alloy where the temperature changed slightly with each run because of loss of calcium by evaporation.

After the melting point measurement, the thermocouple was calibrated in a similar manner against the freezing points of the three standard samples, aluminum, silver and the copper-silver eutectic mixture, which are 660.1, 960.5, and 778.8°C. respectively.

The temperature correction of the thermocouple was calculated by means of difference curves. A typical example as used in Run 1 for cerium is illustrated in Table 14. The differences are then plotted against the observed electromotive force as shown in Figure 8. The electromotive force correction for a particular reading can be read from the graph with an accuracy of 1°C. By this means the temperatures of the thermal arrests were calculated.

TABLE 14

DATA FOR THE CONSTRUCTION OF A TYPICAL DIFFERENCE CURVE

Temperature °C	Observed emf E(mv)	Emf values from table E_{t}(mv)	Difference ($\Delta E = E - E_t$) mv
0	0	0	0
660.1	27.33	27.45	-0.12
778.8	32.20	32.42	-0.22
960.5	39.40	39.80	-0.40

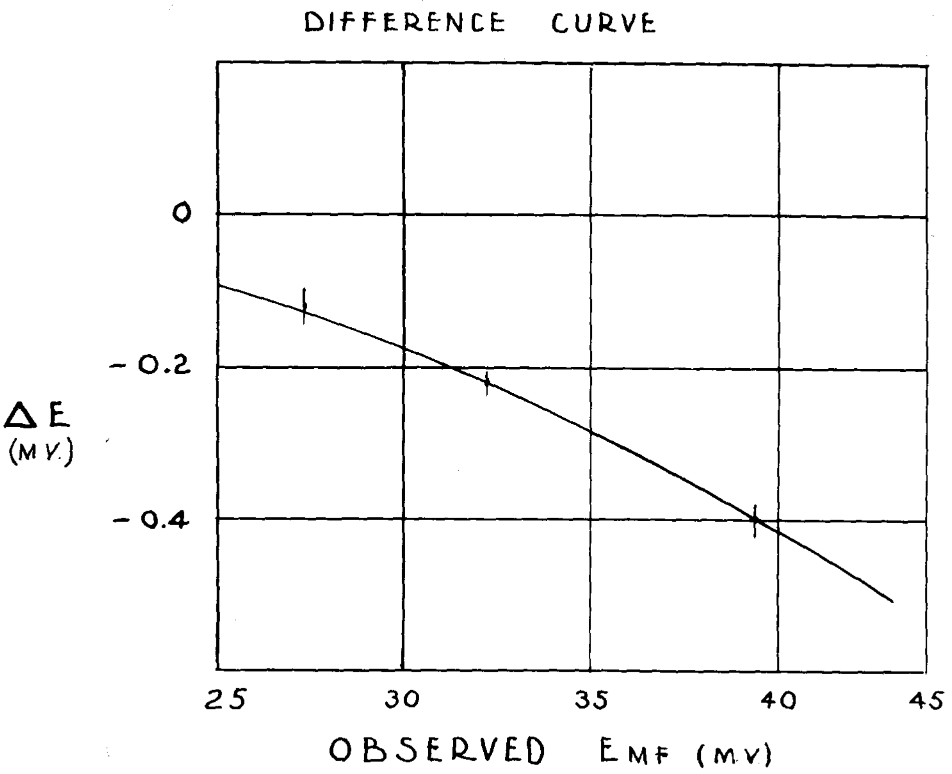

Figure 8. Difference Curve for the Correction of Chromel-alumel Thermocouple used in Run 1 for the Determination of the Melting Point of Cerium.

Results and discussion

The temperature limits of the thermal arrests as determined in this investigation are listed in Table 15. The temperatures are averages of two or more measurements.

From these data, the melting point of cerium metal for these runs was 788, 796 and 790°C. with a second arrest at 709, 705, and 693°C. respectively. In view of the fact that the effect of residual calcium and magnesium would tend to lower the melting point a few degrees, as illustrated by the cerium-magnesium system worked out by Vogel (60), the melting point of cerium is taken to be 793 ± 5°C. The solid transformation is evidently affected by impurities more than is the melting point and is taken to be 703 ± 10°C. A closer correlation between the amount of impurities and the melting point or transformation temperatures is not possible because of the limits of accuracy of the calcium and magnesium analysis. The melting point as determined by this work is 18 degrees above the 775°C. found by Mazza (50) on cerium of equivalent purity, and 22 degrees below that reported by Billy and Trombe (49). The temperature of the solid transformation agrees within the limit of error with one of the three high temperature transformations found in cerium by Loriers (61) using heating and cooling curves. Besides the transformation at 710°C., Loriers found others at 740°C. and at 640°C. in 99.6 per cent cerium containing 0.0005 to 0.03

TABLE 15

MELTING POINTS OF CERIUM AND NEODYMIUM

Metal	Run	Impurities		Melting point		Other arrests	
		Ca %	Mg %	Heating	Cooling	Heating	Cooling
Ce	1	0.2	0.02	788	788	709	709
	2	0.1	0.2	790-796	797-796	701-706	706-704
	3	0.1	0.2	799*	792-789	---	696-690
Ce-Ca-Mg		2.	2.	779-788	792-789	not detected	613-608
						505-507	494-493
Nd		0.5	1.	802-831	819-804		

* Sample superheated each time.

per cent iron with the remainder of the contamination being silicon. The transformation which he reports at 740°C. could not be detected and only a very slight inflection in the heating curve could be found at 640°C., the other reported transformation.

In the cerium-magnesium-calcium alloy, the melting point is about the same as the pure metal, namely 789°C., but the solid transformation at 703°C. had completely disappeared. Instead a very small arrest at 610°C. and a larger break at 497°C. were found. Comparing these results with those of Vogel (60) for the cerium-magnesium system, a very good correlation between the arrests of the cerium-magnesium-calcium alloy and those of a dilute magnesium alloy are found. The first arrest at 610°C. corresponds roughly to the eutectic temperature of 632°C. of a cerium-rich magnesium alloy, and the second arrest at 497°C. agrees exactly with the solid transformation at 497°C. of the magnesium alloy. Vogel reported a liquidus temperature of 710°C. for a two per cent magnesium in cerium alloy, while a liquidus at 788°C. was found in the cerium-two per cent magnesium-two per cent calcium alloy. Whether this means that calcium raises the liquidus, or whether there was less magnesium than the analysis indicated is not certain; however, since the cerium used by him contained 6.5 per cent of other rare earths, his data in the cerium-rich alloys may be in error.

The melting point arrest of neodymium was very gradual, as is illustrated by the temperature range of 21 degrees. For this reason the melting point is rather difficult to locate, but is considered to be 820 ± 10°C. No solid transformations were detected. Since the sample contained one per cent magnesium, it is probable that this amount of impurity will increase the melting range in the same manner as observed for cerium. As discussed previously, the excess magnesium was not removed by heating to 1200°C., the limit of stability of the magnesia toward molten neodymium.

Vapor Pressure of Cerium

Method and theory

The method used in the determination of the vapor pressure of cerium was suggested by a publication on the measurement of the vapor pressure of radioactive metals and their compounds by Phipps, Seifert, Simpson and their co-workers (6). Their paper outlined a procedure for determining vapor pressures at temperatures considerably above 1000°C. for metals that did not alloy with tantalum. As discussed previously, it has been found that cerium, didymium and probably the other rare earths do not alloy with tantalum and consequently could be studied by the method. The apparatus employed in this investigation was considerably modified from that described by the above authors and resembles more closely the less elaborate units used by Rudberg (62) and others (63, 64). By reducing the complexity of the apparatus, some loss in convenience and versatility and a small increase in error were incurred; however, the unit thereby obtained was much simpler to construct, easier to maintain, and did not require as much expensive auxiliary equipment.

The vapor pressures of cerium presented in this thesis were determined by the method of molecular effusion, in which radioactive cerium was vaporized from a crucible through a small orifice; a portion of the molecular beam produced was condensed on the target. From the rate of accumulation of the metal on the target, the geometry of the system, the temperature of the oven and the molecular weight of the vapor molecule, the vapor pressure may be calculated.

The basic assumption in this method is that the molecules effuse through the orifice and travel out into the chamber in a predictable manner. This means that while the motion of the vapor molecules in the crucible is chaotic, only those molecules having a definite velocity-direction pass through the aperture until they hit the walls. The motion of the molecules outside the crucible is no longer chaotic. According to the findings of various investigators (65), the effusion will be accomplished (a) if the mean free path of the molecules in the crucible is greater than three times the diameter of the orifice, (b) if the mean free path of the molecules in the chamber outside the crucible is greater than the distance to be traversed by the molecule before reaching the target, and (c) if the molecules striking the walls are not reflected. These and other supplementary conditions will be considered in detail after the derivation below.

The rate of effusion is readily calculated by equations based on the kinetic theory. The number of molecules effusing per second into an evacuated space through an aperture, a, is simply the number of moles, Q, of molecules which strikes that area of the containing wall per second:

$$(1)\quad Q = \tfrac{1}{4}\, n\, \bar{c}\, a$$

in which n is the number of moles of gas per cubic centimeter and $\bar{c}$ is the mean velocity. This equation assumes (a) that all the molecules striking the area will pass through the orifice and (b) that the uniform distribution of the molecules and their velocity directions are not disturbed by the act of effusion. In condition (a), since the intensity of the beam passing through the orifice is decreased 32 per cent if the thickness of the edge is equal to the diameter (66), the ratio of the thickness of the edge of the orifice to the diameter is important. The condition necessary for stringent fulfillment of requirement (b) is that the aperture dimensions shall be small in comparison with the mean free path of the molecules in the source. If this condition is not fulfilled, there will be a tendency to have cloud formation outside the orifice. Substituting P/RT for n, as obtained from the perfect gas law which holds for the low pressures and high temperatures used, and $\sqrt{\frac{8RT}{\pi n}}$ for $\bar{c}$, as calculated from the kinetic theory, equation (1) becomes: M

$$(2) \quad Q = pa/\sqrt{2\pi MRT}$$

in which p is the pressure in cgs units, M is the molecular weight of the vapor molecule, R is the gas constant and T is the absolute temperature.

The variation of Q with the change in direction of the solid angle was first proven experimentally by Knudsen (5) and is given in the law of cosines:

$$(3) \quad dQ = (Q/\pi)\cos\theta \, d\Omega$$

which simply states that the intensity (moles per second per unit solid angle) of vapor beam in an increment of solid angle varies in proportion to the cosine of the angle with the normal to the orifice. An illustration of this relation is shown by Figure 9 in which the intensity of the beam in any direction is proportional to the distance from the orifice to the tangent circle. Equation (3) will hold only if the orifice is thin edged, that is, if the thickness of the orifice edge is small compared to the diameter of the orifice. The dotted line in Figure 9 illustrates the distribution if a canal-like orifice is used.

To find a relation representing the rate of collection

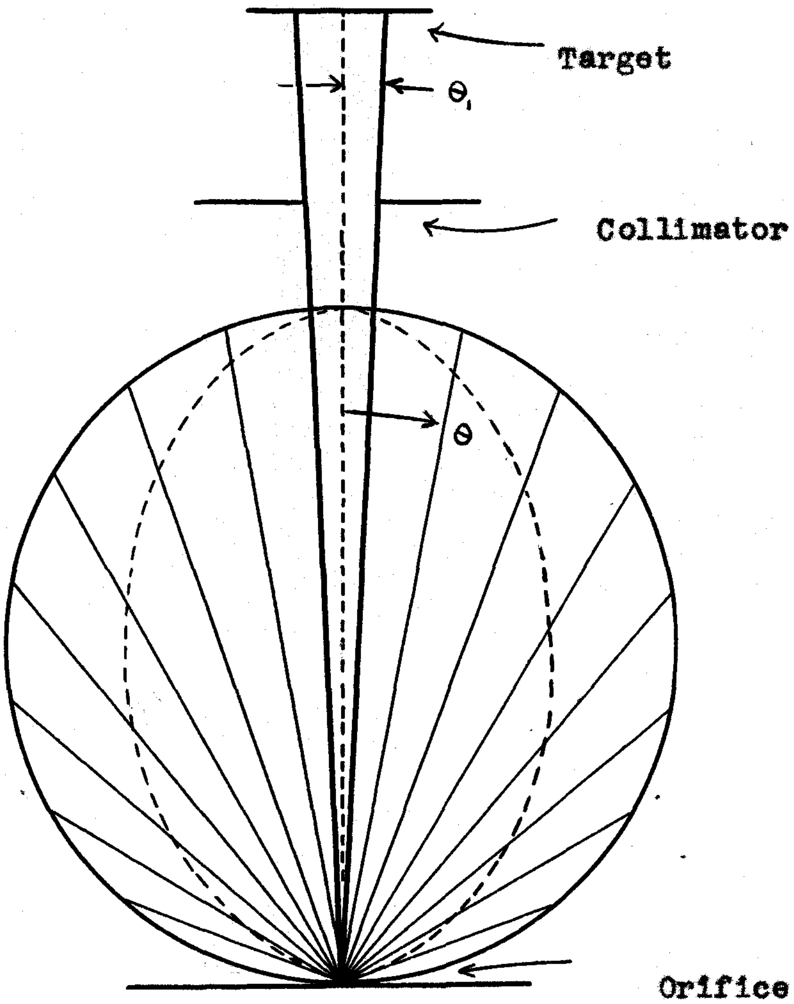

Figure 9. The Angular Distribution of Molecules Effusing from a Circular Orifice.

of the vapor on the target, the differential equation is integrated over the solid angle of the beam subtended by the collimator. Substituting for $d\Omega$ and integrating, the following equation is obtained:

$$(4) \qquad N = \int_0^{\theta_1} 2Q \cos\theta \sin\theta \, d\theta$$

$$= Q \sin^2 \theta_1$$

in which N represents the moles per second passing through the collimator. Evaluating $\sin\theta_1$ in terms of the distance, d, of the orifice to the collimator and of radius, ρ, of the collimator and substituting for Q from equation (2) the relation becomes:

$$(5) \qquad N = \frac{pa}{\sqrt{2\pi MRT}} \, \frac{\rho^2}{(d^2 + \rho^2)}$$

The amount of material condensed per second on the foil can also be evaluated from the activity of the sample by the relation:

$$(6) \qquad N = \frac{C}{60 \tau S M}$$

in which C is the counts per minute of the sample, τ is the exposure time in minutes, S is the apparent specific activity of the active cerium metal determined on a known weight of cerium in the same manner as the sample and M is the molecular weight.

Equating equations (5) and (6) and solving for p, the following equation is obtained with the pressure expressed in dynes per square centimeter:

$$(7) \quad P_{(\text{dynes/cm.}^2)} = \frac{C\sqrt{T}}{\tau}\,\frac{d^2}{\rho^2 r^2 S}\,(1 + \rho^2/d^2)\,\frac{1}{60}\,\sqrt{\frac{2R}{\pi M}}$$

Converting p to units of mm. of Hg, the working equation (8) results:

$$(8) \quad P_{(\text{mm. Hg})} = \frac{C\sqrt{T}}{\tau}\,\frac{d^2}{\rho^2 r^2 S}\,(1 + \rho^2/d^2)\,\frac{1}{(60)(1.328 \times 10^3)}\sqrt{\frac{2R}{\pi M}}$$

Evaluating the constants, and calculating the term, $(1 + \rho^2/d^2)$, which is equal to 1.002 within 0.03 per cent since the ratio of ρ^2 to d^2 is approximately constant in all the runs made, equation (8) reduces to:

$$(9) \quad P_{(\text{mm. Hg})} = \frac{C\sqrt{T}}{\tau}\,\frac{d^2}{\rho^2 r^2 S}\;7.726 \times 10^{-3}$$

which is the standard equation used in all the calculations on the data obtained for cerium.

The assumptions made in deriving the above equation are listed below:

(a) The mean free path of the molecules in the crucible is greater than 3 times the diameter of the orifice.

(b) The mean free path of the molecules in the chamber outside the crucible is greater than the distance to be traversed by the molecule before reaching the target.

(c) The vapor molecules are condensed by the walls.

(d) The orifice is thin edged; that is, its depth is negligibly small compared with its smallest diameter.

(e) The effective evaporating surface is large compared to the area of the orifice.

(f) There is no appreciable reaction between the cerium and the tantalum crucible.

(g) The temperature of the crucible is even throughout.

(h) Every vapor molecule arriving at the target is condensed.

(i) The molecular weight of the vapor is known.

Finally, to agree with the assumptions made concerning the geometry of the apparatus:

(j) The orifice and collimator are both circular.

(k) The plane of the collimator is parallel to the plane of the orifice, the circles being co-axial.

(l) The amount of the material on the target can be determined by counting methods.

These conditions appear to set up a stringent mode of procedure, but in practice many of the factors are not too critical or can be approached quite closely. Each of the conditions will be considered in detail and an attempt will be made to evaluate the errors occasioned by failure to completely fill the requirements.

(a) If the mean free path of the vapor molecules in the crucible is greater than the diameter of the orifice, there will be a quasi-hydrodynamic flow at the aperture and a turbulent gas jet instead of a molecular ray is produced. Apparently collisions of a fraction of the effusing molecules in or immediately in front of the orifice has the effect of damming them up just outside the crucible to form a vapor cloud. This causes a lessening of intensity and a weakening of the beam. According to Knauer and Stern (67) this effect is very minute for $\lambda > 6r$ (λ is the mean free path of atoms in a gas) if their work on slits can be extrapolated to a circular orifice. A rough expression for the mean free path in mercury vapor is:

$$(10) \quad \lambda_{(\text{mm.})} = 6.9 \times 10^{-5}\ T/P_{(\text{mm. Hg})}$$

If the mean free path of cerium vapor is approximately that of mercury, and assuming that the work by Knauer and Stern is applicable, the aperture size used in these experiments was always less than one-half the maximum size allowed.

(b) The mean free path of cerium vapor maintained at a pressure of 2×10^{-5} mm. of Hg is one meter (equation 10). This is more than 10 times the orifice-collimator distance, so no error should be introduced.

(c) As a check against reflection of vapor molecules from the walls, every fifth foil was left unexposed to be used as a blank. These blanks had an average activity of five counts per minute or about three per cent of the activity on the foils. The average of these blanks was used to correct the readings; so an error of ± 3 per cent could be introduced from this factor.

(d) If the orifice is not thin edged, but instead is a short circular canal, the distribution of the effusing particles no longer obeys the cosine law. For example, the dotted line in Figure 9 is an illustration of the decrease in intensity if the thickness of the orifice equals twice the radius as calculated by Clausing (68). In the cerium studies the ratio between the orifice edge and the diameter was less than 1 to 10; according to Clausing's findings (66) this would reduce the beam intensity less than five per cent as compared to the 32 per cent reduction for a 1 to 1 ratio. From Figure 9, the intensity loss is greatest at large values of the angle θ, so it is apparent that a small solid angle subtended will reduce the error associated with this effect. In the work done on cerium, the half angle $\underline{\theta}_1$ is never larger than 2.5 degrees; it follows that the error due to orifice depth is less than one per cent.

(e) If the effective evaporating surface is small compared to the area of the orifice, unsaturation exists in the crucible and the pressure measured would not be the equilibrium vapor pressure. According to Fraser (65), the effective evaporating surface should be at least ten times that of the orifice. In work with molten metals it seems best to make this area ratio 1 to 100 to compensate for any oxide coating floating on the surface. In this investigation, the ratio of the orifice area to the area of the bottom of the crucible was greater than 1 to 100; also, since cerium wets tantalum, the crucible material, it has a tendency to creep, thus aiding in obtaining a large clean metal surface. However, since the first exposures (to be discussed in the results) indicate temporary unsaturation, this error is assumed to be ± 5 per cent.

(f) No evidence of cerium alloying with tantalum was found by chemical or spectrographic analysis, or by visual or microscopic examination. A piece of cerium heated to a maximum of 1700°C. and held above 1500°C. for 30 minutes had not dissolved any tantalum according to chemical and spectrographic analysis. Metallographic examination of a cerium-tantalum interface showed no evidence of alloying between the two metals, and no change in the surface of a tantalum crucible was caused by cerium at 1450°C.

(g) An attempt was made to obtain a uniform temperature throughout the crucible by placing it inside a coiled tungsten heater extending 2½ cm. above and below the crucible and surrounding the heater by a reflector. The walls of the crucible were made as massive as possible to assist in decreasing heat gradients; however, this correction was limited by the size of the tantalum bar available. Since the vapor pressure is determined by the coldest wall temperature, the temperature was measured at the coldest point by placing the thermocouple in a well extending deep into the base of the crucible within 1 mm. of the charge and fairly near the supporting stem which acted as a heat leak. The temperature read is believed to give a very good representation of the temperature of the charge.

A possible error of one-half per cent in the temperature recorded may have been introduced due to the gradient between the bottom and top of the crucible, assuming a gradient of 20°C. at a temperature of 1500°C.

(h) Since cerium is extremely non volatile at room temperature, it is reasonable to assume that it would condense on water-cooled targets, especially since the reflection for the glass walls, which were at 400°C., is so low. Since it is a well known fact that condensation of metal atoms is more easily accomplished on metal surfaces, metal targets of aluminum were used to condense the cerium beam.

In experiments where condensation is known to be incomplete (69), it has been found that the fraction sticking depends upon the intensity of the beam of vapor molecules. In the measurements on cerium, the intensity of the beam varied by a factor of 10^3. If incomplete condensation did occur, the marked change in the amount of condensation should produce a non-linear plot of log $\underline{P}$ against $1/\underline{T}$. No such effect was observed.

(i) The cerium vapor is assumed to be monatomic, an assumption which is in agreement with observations on all but the alkali metals (70). Moreover, any association of cerium atoms would probably show up as a non-linear effect in the log $\underline{P}$ versus 1/$\underline{T}$ plots. This non-linearity was not observed. The work of King (71) who obtained the atomic spectra of cerium by vaporizing cerium in an electric furnace at temperatures of from 2000 to 3500°C., also gives corroborative evidence in favor of this assumption, since he reports no band spectra which would indicate association of the cerium atoms into molecules. While the temperatures used were somewhat above those used in the vapor pressure measurement, it does give evidence that cerium vapor is not associated at this higher temperature.

(j) The collimator was round within 0.5 per cent, while the orifice was round within one per cent. Any possible error was minimized by taking an average diameter.

(k) Since the cosine is a slowly varying function at small angles, a slight misalignment or non-parallelism of the orifice and the collimator would cause only small errors; however, there will be an error due to the variation of the crucible position on the tungsten support. This error is estimated at two per cent.

The errors enumerated above due to failure to meet the ideal conditions, will all affect the accuracy of the absolute value of the vapor pressure, but only a few will affect the slope of the plot of log $\underline{P}$ against 1/$\underline{T}$ and consequently the calculated value of the heat of vaporization. These errors will be discussed further with the presentation of data.

Apparatus

Effusion vessel

Tantalum was chosen as the material for the effusion vessel primarily because tests showed it tobe highly resistant to alloying with cerium. Other properties which favored its use are its high melting point, its reasonably good machinability and its property of adhering strongly to itself at a tantalum-tantalum interface when heated in a vacuum. Due to this property of cohesion, a threaded-lid gasket closure was impractical since the threads froze on the first run (6); instead, a tapered lid pressure closure was necessary, the cohesion preventing any leakage.

Among other factors that were considered in designing the crucible was the desirability of uniform temperature distribution. This suggested the use of massive crucibles; however, since the only tantalum available was $\frac{1}{2}$ in. rod, the crucibles were necessarily rather thin walled, having a thickness of 3/64 in. The wetting and consequent spreading of cerium on tantalum was quite useful in causing a large surface area of clean metal; however, this also caused failure in two runs because of seepage of the cerium through a slight leak in the pressure closure. The fact that tantalum can be spotwelded quite readily under carbon tetrachloride permitted the easy attachment of an accurately prepared orifice.

In the design of the crucible one of the primary considerations was in obtaining an orifice approximating the ideal conditions. Following the procedure of Phipps and his co-workers (6), a disc of tantalum 0.005 in. thick and the same diameter as the crucible, was dimpled at its exact center by pressure with a honed point of a short piece of tool steel. The dimple was ground off on a piece of Behr-Manning Polishing Paper, Grit No. 3/0. In this manner an approximately round hole with very thin edges was obtained. The hole was then burnished by a tapered tungsten point which had been formed by heating and partially dissolving on sodium nitrite. The grinding and burnishing were repeated until a round hole of the proper size was obtained. To measure the diameter of the hole, the drum of a Bausch & Lomb screw micrometer eyepiece was calibrated against a Bausch & Lomb standard 10 mm. micrometer scale having 0.1 and 0.01 mm. divisions; the number of revolutions of the drum required for the traversal of a diameter was then determined for each of at least four diameters of the hole. Unless these values agreed within one per cent the disc was rejected.

The effusion vessel or crucible was made of tantalum rod ½ in. in diameter. It was approximately 3/4 in. high with a bottom 1/4 in. in thickness. The crucible was supported by a 0.060 in. tungsten wire which fit snugly in a hole in the bottom of the crucible, as shown in Figure 10. The

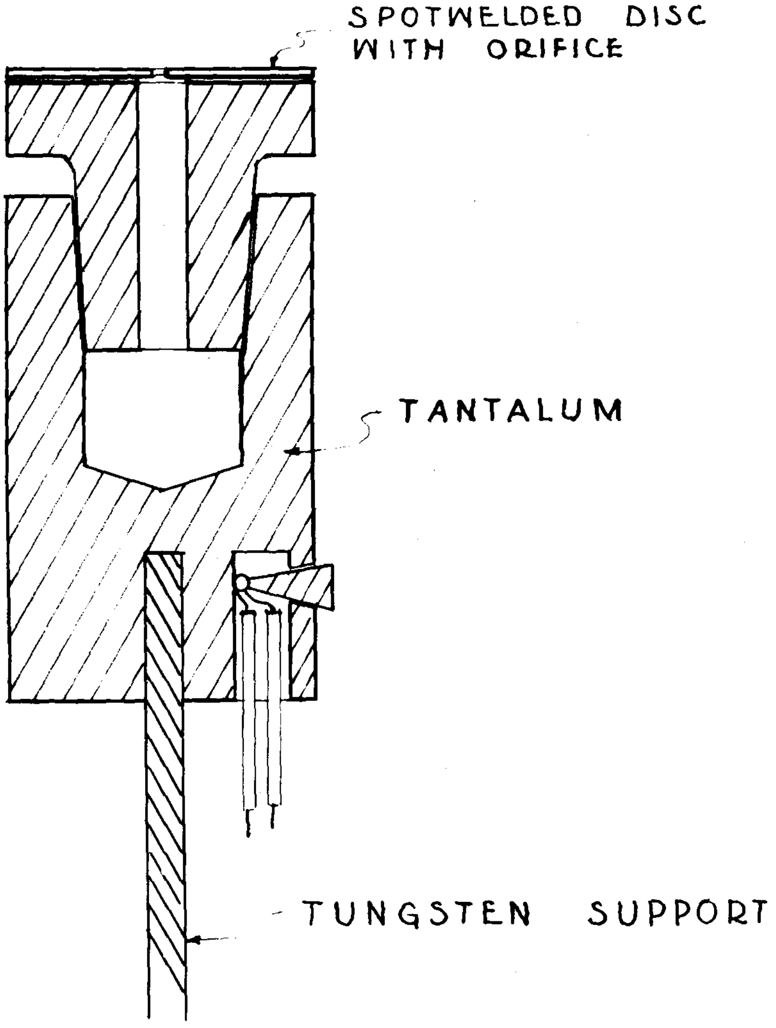

Figure 10. Design of Effusion Crucible.

tungsten wire held the crucible quite firmly and showed no signs of sagging or bending when heated. The crucible was closed by a lid having a male 4 or 5 degree taper.

The thermocouple was inserted into a well drilled in the bottom of the crucible and fastened by means of a tantalum wedge which was forced through a hole in the side of the well to push the thermocouple firmly against the opposite wall. The thermocouple wires were insulated by means of thin, single-holed porcelain insulators capable of withstanding a temperature of 1500°C. The junction was protected against contact with tantalum by a small piece of platinum foil. The thermocouple used was platinum - 87 per cent platinum 13 per cent rhodium; the size of wire used was B & S gauge No. 24.

Heating element and radiation shield

The heating element was a helix prepared by winding 0.032 in. tungsten wire on a threaded brass mandrel, with both at a red heat. The spiral formed was 2½ in. high, 9/16 in. in diameter with approximately sixteen regularly spaced turns to the inch. The lead wires were reinforced by 0.040 in. tungsten wire firmly attached by wrapping with 0.005 in. tungsten or 0.010 in. molybdenum wire. The leads were welded to a short length of 0.062 in. nickel wire which in turn was welded to the 0.060 in. tungsten wire passing through the glass. The short length of nickel wire gave a measure of pliability to the leads and aided in aligning the heating unit. Before installation the tungsten spiral was annealed by heating to a temperature greater than 1000°C. on a beryllia form. A progressive sagging of the coils of the heating element was noted as the coil was maintained at high temperatures. To avoid setting up any thermal gradients due to uneven heating, the coil was replaced after each run.

The reflector was made from 0.005 in. tantalum sheet rolled into a cylinder 5 in. long and 1 3/4 in. in diameter. The meeting edges were crimped together and spotwelded. Two nickel supports were spot welded to the sides. A removable lid of tantalum sheet with a hole of approximately the same size as the crucible together with a bottom shield with holes cut for the support and the electrical leads were also used to reduce radiation losses and to assist in reducing any possible thermal gradient.

Shutter

The shutter consisted of a portion of glass tubing of the proper size to fit the inside curvature of the 60 mm. tube containing the slide. The shutter was attached by glass rod to a sealed glass tube containing a piece of mild steel. It was operated by a permanent magnet outside the vacuum and could be opened or closed in less than two seconds. No guides were required, nor was there any tendency to wander or rotate when the shutter was opened or closed.

Collimator

The collimator was prepared from flat rolled brass stock 1½ in. wide and 3/8 in. thick. The collimator hole was cut with a 45 degree taper in the walls. The unit was held firmly against the underside of the water cooled slide support.

Collector

Flat rolled brass stock of the same kind as used to make the collimator was employed in fabricating the target holder. The slide holder was 24 in. long with twenty 3/4 in. holes drilled through at equally spaced intervals. A shoulder around each hole, to provide a seat for each target, was cut by a flat-cutting 1 in. drill. A winch operated from outside the vacuum through a greased standard taper joint was used to pull the slide by means of a No. 34 B & S gauge chromel wire. While the motion of the slide could not be reversed, it could be easily and accurately stopped at a given mark.

The targets were 1 in. discs cut from aluminum sheet 0.010 in. thick which fitted into the recesses of the slide holder described above.

Vacuum apparatus

The apparatus used in the measurement of the vapor pressure of cerium is illustrated in Figure 11. The system was evacuated and the vacuum maintained by a glass three-stage

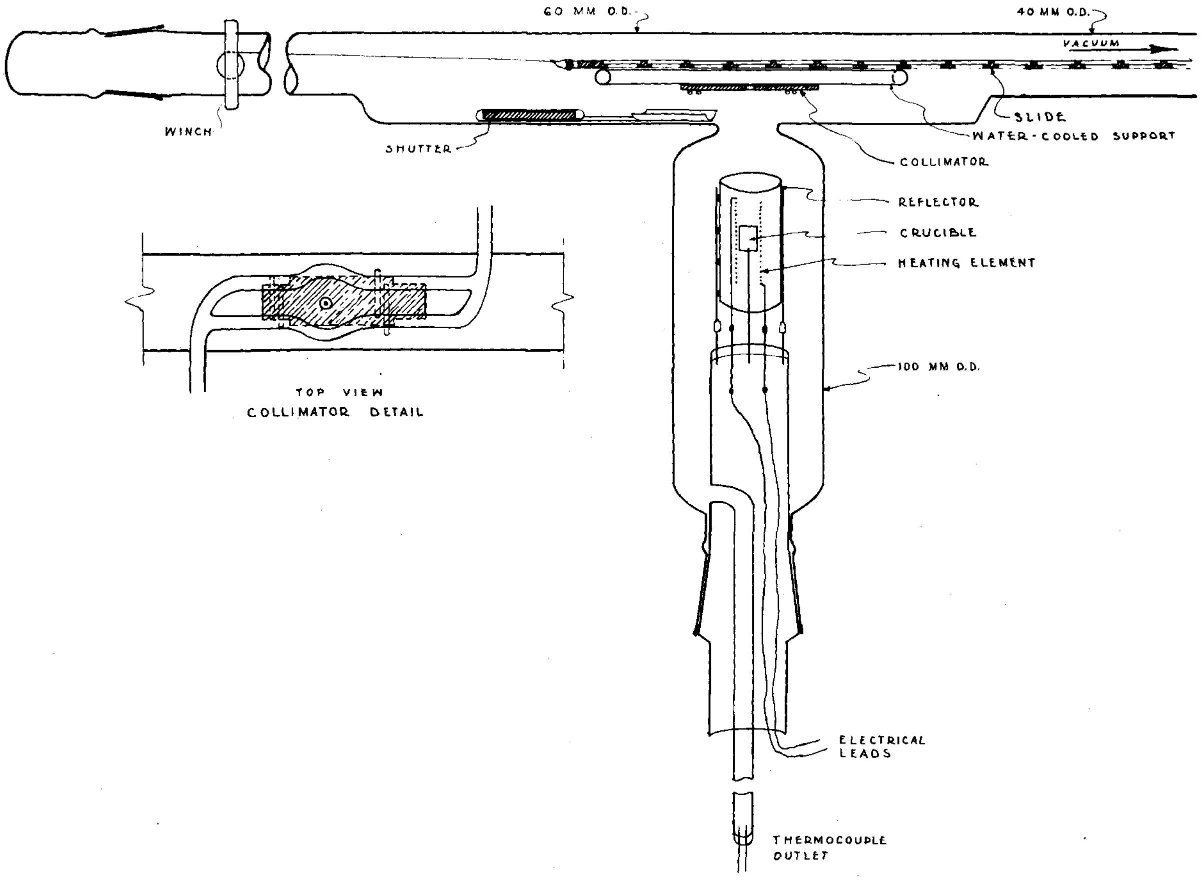

Figure 11. Apparatus for the Measurement of the Vapor Pressure.

fractionating oil pump, Type GF25W manufactured by Distillation Products, Inc. The diffusion pump had a rated capacity of 25 liters per second at 10^{-5} mm. of pressure and had an ultimate vacuum of 5×10^{-8} mm. at 25°C. A Welch DuoSeal mechanical pump was used as a backing pump. Vacuums of 10^{-5} mm. of Hg or better were obtained after outgassing. The operating range was below 2×10^{-5} mm. of Hg except at the very beginning of each run. Vacuum measurements were made with an ionization gauge, Type 507, manufactured by the National Research Corporation. A thermocouple vacuum gauge also made by this company was used to measure the vacuum down to the working pressures of the ionization gauge. The gauges were sealed into the system at a point between the trap and the system.

The apparatus itself consisted of two arms to contain the collector, shutter, collimator and cooling unit, and of a shorter vertical barrel containing the furnace as shown in Figure 11. No guides were necessary in the outside arms because some part of the slide always rested on the water-cooled support and prevented rotation. Lateral displacement was avoided by having a close fit between the slide and the containing arms.

The furnace, consisting of crucible, heating element and reflector was supported by five 0.060 in. tungsten wires that were sealed into a post extending up into the vertical barrel.

A press seal of pyrex to the five tungsten wires, covered at the interface with a thin layer of uranium glass, gave a sturdy, vacuum tight seal that did not crack in four months of continuous use. The inside of the post was open to the atmosphere and contained the electrical leads and the thermocouple outlet. The post was sealed into the system by means of a lapped standard taper $\overline{\$}$ 55/50 joint. The joint was waxed shut with Pyseal or Apiezon wax. Some trouble was encountered due to softening of the wax when the furnace was at high temperatures. This difficulty was corrected by attaching copper cooling fins around the taper and cooling with a strong blast of air. The outlet of the thermocouple consisted of a glass tube sealed into the center post and extending down the center of the post into an ice bath. The thermocouple voltage was brought out through two 0.040 in. tungsten wires sealed in the tip. The thermocouple was attached to the tungsten by small brass clips which fit snugly over the tungsten wire. The entire junction was kept at 0°C. to avoid any electromotive force effects due to contact of the different metals.

<u>Auxiliary equipment</u>

The auxiliary instruments and apparatus may be classified according to use: (a) for regulating the heating current, (b) for temperature measurement, (c) for measurement of vacuum, (d) for measurement of distances, (e) for measurement of the radioactivity of the sample.

The heating current was varied by a large Variac, Type 50A, capable of delivering up to 50 amperes. The fluctuation of the primary voltage was reduced by a Sorensen voltage regulator, Model 1750.

The electromotive force of the platinum - 87 per cent platinum 13 per cent rhodium thermocouple was measured by a Rubicon portable precision potentiometer which had been checked by another precision potentiometer and found to agree within 0.005 millivolts. The temperatures corresponding to the millivolts measured were obtained from tables.

The vacuum was determined by measuring the output in micro-amperes of the ionization gauge, and in milliamperes for the thermocouple gauge. These currents were measured on a Thermocouple-Ionization Gauge Control, Type 706, manufactured by the National Research Corporation; their calibrations were used in converting microamperes to the corresponding vacuum.

The orifice-collimator distance was found by measuring the support-collimator distance and from this subtracting the effective height of the crucible. The support-collimator distance could be measured with an accuracy of 0.05 mm. by means of a cathetometer obtained from the Gaertner Scientific Corporation, but since this distance was varied by the amount of wax used in the standard taper seal, the distance was only known with an accuracy of 1 mm. The value of the effective height of the crucible was obtained by measuring the overall height of the crucible by means of a micrometer and subtracting the depth of the support hole.

A Geiger-Muller counter tube with a mica window produced by the Victoreen Instrument Company of Cleveland, Ohio, was used for the measurement of the radioactivity of the targets. The window had a thickness of 3 mg. per square cm. The pulses were amplified and counted by a Geiger-Muller Scaler (scale of 64) manufactured by the Instruments Development Laboratory.

Procedure

Preparation of radioactive cerium metal

The active cerium was prepared by irradiating 1.2 grams of cerium metal in the Oak Ridge reactor. The metal was quite pure, containing less than 0.1 per cent calcium and less than 0.025 per cent magnesium. The radioactive cerium was produced by neutron bombardment according to the following nuclear reactions (72):

$$Ce^{140} \xrightarrow{(n,\gamma)} Ce^{141} \xrightarrow[t_{\frac{1}{2}} = 29d]{\beta^-} Pr^{141} \text{ (stable)}$$

$$Ce^{142} \xrightarrow{(n,\gamma)} Ce^{143} \xrightarrow[t_{\frac{1}{2}} = 33h]{\beta^-} Pr^{143} \xrightarrow[t_{\frac{1}{2}} = 13.5d]{\beta^-} Nd^{143} \text{(stable)}$$

The energies of the radioactive disintegrations are given in Table 16. From the table, the praseodymium activ-

TABLE 16

ENERGIES OF RADIOACTIVE DISINTEGRATIONS OF THE ISOTOPES FORMED

Isotope	Half life $t_{\frac{1}{2}}$	β^- mev	γ mev	Ratio of activities (73)
Ce^{141}	29d	0.65	0.2	50
Ce^{143}	33h	1.03	0.5	12
Pr^{143}	13.5d	1.0	none	3

ity is seen to be about 6 per cent of that of the long lived cerium isotope at the time the cerium is removed from the reactor. It can be shown by calculations on the basis of half-lives that after 120 days, the time the final count was made this activity had decayed to 0.3 per cent of that of the long-lived cerium isotope. The low activity of the praseodymium isotope in the cerium was confirmed by a careful determination of the specific activity of the cerium.

The active sample was allowed to decay for 120 days before making the final count of the targets for the calculation of the vapor pressure. The specific activity of the radioactive cerium was determined at this time both from samples still containing the residual praseodymium activity and from praseodymium-free samples. Two samples containing the residual praseodymium activity were used: the first was weighed as metal and then dissolved in dilute nitric acid and diluted to a known concentration; the second was weighed as ceric oxide (CeO_2) which was dissolved in a hydrochloric-hydroiodic acid mixture and then diluted to a known volume. Three separate samples of praseodymium-free cerium were prepared by three successive iodate precipitations of the tetravalent cerium ion. According to Boldridge and Hume (74), who adapted this separation for tracer work, these precipitations remove 99 per cent of the activity due to trivalent rare earths. After the purification cycle, these samples were precipitated as the oxalate and in one case weighed as (i.e. $Ce_2(C_2O_4)_3 \cdot 9H_2O$), and in the other cases converted to the oxide for weighing. These samples were dissolved as oxides in a hydrochloric-hydroiodic acid mixture and diluted to known concentrations.

Aliquots from the standard solutions of the samples were taken with a micropipet, and transferred to the aluminum targets, rinsing the pipet three times after each transfer. The aliquot and washings were evaporated to dryness. There was a slight corrosion of the aluminum by the weakly-acid cerium solution; however, the activity of a sample prepared in this manner did not differ appreciably from the activity of a sample evaporated to dryness on aluminum which had been protected by a thin zapon film. The standard samples so prepared were counted in the same way as the targets from the vapor pressure measurement. Of the five samples prepared, an agreement within 2 per cent was obtained for the specific activity of cerium. This agreement indicates that by decaying through nine half-lives the praseodymium activity was reduced to negligible amounts.

For purposes of comparison, a standard comparison sample was counted with the targets obtained in each run. The decrease in activity of this sample was used to calculate the decrease in the specific activity of the cerium. Use of this standard also corrected for any variation in the counting rate of the instrument.

Manipulative methods

The entire setup was degassed before each run to reduce the possibility of oxidizing the reactive cerium by gases diffusing from the crucible, heating element and shield. The crucible and lid were first cleaned by boiling in *aqua regia* for several hours, and then rinsed carefully with water and acetone. The thermocouple was then attached and the crucible was mounted on the tungsten support. To prevent adhesion of the lid to the crucible, it was supported by a cone of molybdenum sheet or by tungsten wires slipped over the edge of the crucible. The lid of the reflecting shield was then placed in position, the furnace unit inserted into the apparatus and the standard taper waxed shut. The targets and slide holder were also loaded before degassing. These were first cleaned and then washed in distilled water, benzene and acetone. The grease free slide was then placed in the apparatus.

After evacuating, the heating element was heated to approximately 1000°C. and the entire unit excepting the waxed joints was torched. The furnace was then held above 1000°C. overnight. The temperature of the crucible was then raised to 1400°C. and held until the pressure dropped to 2×10^{-5} mm. of Hg. The apparatus was allowed to cool and the vacuum was broken by nitrogen dried by a long column of Drierite. The furnace was removed by melting the wax seal, and placed under a stream of dried air outside the apparatus. The lid and crucible were removed to a desiccator and the furnace returned to the unit. A continuous stream of nitrogen was passed through the apparatus during the period that it was open to the atmosphere.

The orifice was remeasured to detect any change in the diameter. The crucible was then removed from the desiccator to the stream of dry air from an inverted funnel. The metal pellet which had been cleaned by scraping and washing in benzene, was quickly loaded into the crucible and the lid was tapped into place. The crucible and lid were removed from the dry atmosphere and the oven top was pressed into the base with a hydraulic press at a pressure of 1500-2000 pounds per square in. The loaded crucible replaced on its support, the thermocouple was threaded into the outlet tube and attached to the tungsten lead outs and the furnace unit was slipped into the apparatus and waxed into place. After evacuation of the apparatus, the slide loaded with the foils was brought into position for the first exposure.

After again torching the apparatus, the furnace was heated to temperature for the first exposure. In the first heating, the sample was brought to temperature very slowly in an effort to remove any gases or vapors that might have been occluded on the surface of the crucible. In this step, the vacuum sometimes fell to 1 x 10^{-4} mm. of Hg momentarily, but in a few minutes was at 3×10^{-5} mm. of Hg. After the first exposure the vacuum was below 2×10^{-5}. When the temperature became constant, usually in five minutes if the temperature change was small, the timer was started and the shutter opened. The temperature fluctuated as much as 20 degrees during the long exposures, although for short exposures it held constant within several degrees. The variation was corrected for by taking regular temperature readings and averaging them. When the exposure was complete, the timer was shut off and the shutter closed. The slide was moved to a new position, the temperature changed and the process repeated. Three of the targets spaced at regular intervals were not exposed for use as blanks.

Standard counting procedure was followed with respect to corrections for background and for counter resolution loss. Each exposure was counted until 10,000 counts had been recorded.

The thermocouple was calibrated by thermal analysis against the melting points of copper, silver and nickel. The copper and silver were melted in a tantalum crucible under the same conditions used in determining the vapor pressure. It has been reported (75) that silver does not alloy with tantalum, and there also was no indication of alloying with copper; however, a gold standard melted in the same manner gave definite indications of dissolving tantalum and consequently the arrests for this sample were discounted although they fell on the difference line within the experimental error. A beryllia crucible was used for the melting point determination of nickel; the thermocouple was thrust down into the metal a short distance to assure good thermal contact. By experimentally determining the power settings required to permit the metals to just melt and to just freeze, the furnace temperature could be adjusted so as to obtain arrests of 10 minutes in duration. The correction of the thermocouple is listed in Table 17 and the true temperature is obtained from the difference curve, Figure 12, plotted from these data.

Results

Measurement of the vapor pressure of cerium metal was attempted on six samples from a 1.2 gram piece of cerium which had been cast in a calcium oxide crucible, recast in a tantalum crucible and swaged into a 3/8 in. rod; the cerium had been irradiated in the Oak Ridge pile for 30 days. The amount of cerium used in each run amounted to approximately 100 milligrams, the exact weights were: (1) 0.110 grams, (2) 0.1545 grams, (3) 0.1555 grams, (4) 0.0877 grams, (5) .0905 grams, and (6) 0.125 grams. The samples were cut from the rod by a pair of side-cutters; they were single pieces, but with small surface cracks due to the swaging operation. The samples were cleaned by scraping with a sharp

TABLE 17

DATA FOR CONSTRUCTION OF THE DIFFERENCE CURVE

Element	Melting point actual °C	Melting point observed °C	Temperature correction °C
--	0	0	0
Ag	960.5	955	5.5
Au*	1063	1057	7.0
Cu	1083	1073	10
Ni	1454	1443	11

* Sample alloyed with crucible.

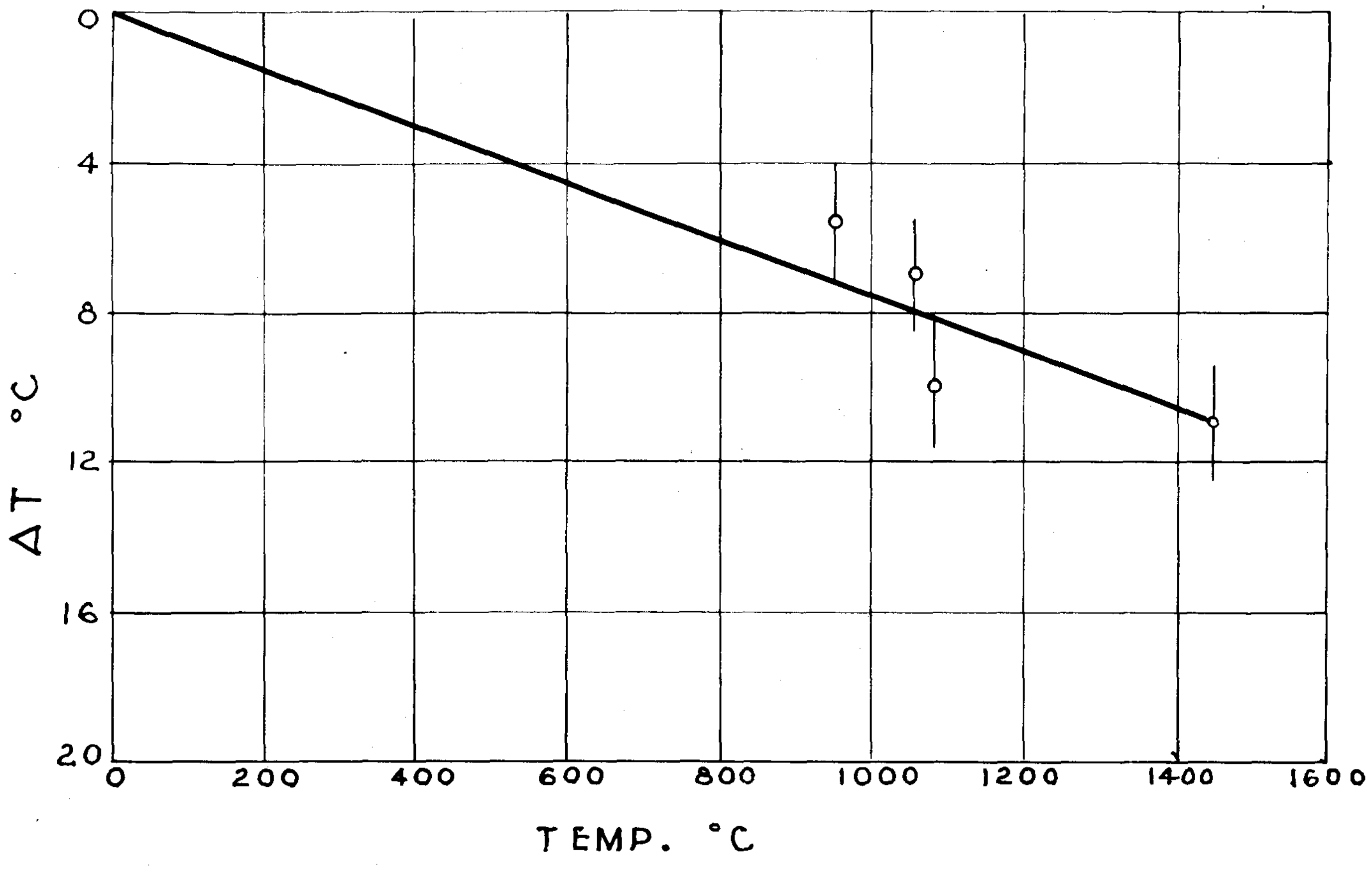

Figure 12. Difference Curve for the Correction of the Platinum-87 per cent Platinum 13 per cent Rhodium Thermocouple.

knife until the entire surface of the pellet was the silvery gray color of fresh cut cerium; they were washed in benzene to remove any oxide dust and the sample was then placed in a desiccator from which it was loaded into a crucible within an hour after cleaning.

In the vapor pressure measurements made, samples (3), (4), and (5) yielded values that were in essential agreement with each other. Samples (1) and (6) showed vapor pressures that were at first of the same order of magnitude as those of samples (3), (4), and (5), but which decreased very quickly to a negligible value. In both of these determinations, the vacuum had been partially destroyed by minute leaks which had developed, and the sample had been slowly oxidized. The run with sample (2) gave vapor pressure values which increased regularly with the temperature but which were greater by a factor of two than those obtained for later runs. At the close of the run it was observed that a large amount of the sample had leaked, by capillary action, through the pressure closure between the lid and crucible and had thereby increased the area of the vapor source and consequently, the apparent pressure.

The data and calculations for the s~~ix~~eventeen exposures made in Run A on sample (3) are given in Table 11. The orifice diameter, $\underline{2r}$, was 0.0786 cm., the collimator diameter, $\underline{2\rho}$, was 0.7938 cm., and the orifice-collimator distance, $\underline{d}$, was 8.75 cm. For these dimensions, the general vapor equation becomes:

$$(11) \qquad P_{(\text{mm. Hg})} = \frac{C\sqrt{T}}{\tau} \quad \frac{2178.5}{S}$$

The specific activity of the cerium was 3.10×10^8 counts per minute per gram when the first half of the foils were counted, and 3.06×10^8 counts per minute per gram when the second half of the foils were counted. The equations used for calculation of the vapor pressure are given in Table 18.

In the calculation of the vapor pressure temperature relation, the four starred samples in Table 18 were not included. The vapor pressures, as calculated from the activity on these foils, which were the first four exposed, amount to one third the pressures extrapolated from the least square line calculated from the other exposures. This phenomenon was observed in all of the runs made. However, once the sample was heated above approximately 1350°C., consistent vapor pressures, as calculated from the activity of the target, are obtained. The sample can be cooled to room temperature, and then reheated to any temperature, and the vapor pressure determined will be in agreement with the least squares line determined from the preceding consistent measurements.

Before considering an explanation of this discrepancy, a general review of the exposure procedure will be helpful. After torching the apparatus, the sample was heated very slowly to the first exposure temperature on the low temperature

TABLE 18

THE VAPOR PRESSURE OF CERIUM METAL

RUN A

Target	Exposure time τ(min.)	Counts per min. $\underline{C}$	Temperature T°K.	Vapor pressure $\log_{10} P_{mm.}$	Reciprocal temperature $1/T \times 10^{+4}$
$P_{(mm.\ Hg)} = \frac{C\sqrt{T}}{\tau} 7.85 \times 10^{-6}$					
A6	75	555.5	1623	$\underline{3}.369$	6.161
A7	60	1167.9	1650	$\underline{3}.793$	6.062
A8	30	653.1	1675	$\underline{3}.845$	5.970
A9	20	554.2	1694	$\underline{3}.952$	5.903
A11	15	553.8	1711	$\underline{2}.079$	5.845
A12	60	771.3	1655	$\underline{3}.614$	6.042
A13	75	626.2	1636	$\underline{3}.423$	6.112
A14	100	588.8	1599	$\underline{3}.267$	6.254
A15	100	316.3	1577	4.994	6.341
$P_{(mm.\ Hg)} = \frac{C\sqrt{T}}{\tau} 7.97 \times 10^{-6}$					
A1*	125	26.1	1494	$\bar{5}.81$	6.693
A2*	120	28.3	1539	$\bar{5}.87$	6.497
A3*	150	40.9	1557	$\bar{5}.93$	6.423
A4*	100	43.4	1582	$\bar{4}.14$	6.321
A17	120	146.4	1544	$\bar{4}.582$	6.477
A18	120	97.1	1511	$\bar{4}.400$	6.618
A19	120	42.6	1473	$\bar{4}.037$	6.789
A20	150	27.6	1453	$\bar{5}.747$	6.882

* Omitted from calculation of least square line.

end of the vapor pressure scale, and held there for the first exposure. By this means, the adsorbed vapors on the furnace, crucible and cerium slowly diffused out of the materials without increasing the pressure in the apparatus sufficiently to cause oxidation of the cerium. After the first exposure, exposure temperatures were increased in steps of 50 degrees until the maximum temperature was attained. Exposures were then made at temperature intervals down to the original starting temperature. At least twice during each run, the sample was permitted to return to room temperature.

The low results can be logically explained by the assumption that a slight oxide layer, probably from oxide entrapped in the swaged metal, had collected on the surface of the molten metal, thereby producing unsaturation of cerium vapor in the crucible as discussed in assumption (e). If this reasoning is accepted, the rather regular increase of the apparent vapor pressure with temperature would be explained, for if the unsaturating condition remains, the pressure will increase in proportion to the temperature. Also, since it is known that the solubility of the oxides of the rare earths in metal, as judged from lanthanum, increases markedly above 1200°C., the solution of the oxide layer and subsequent removal of the unsaturating influence would account for the sudden disappearance of this effect, since a clean metal surface would then be exposed for evaporation. On these bases, the four samples were rejected.

Since a slight amount of oxide is assumed to be in the cerium, the vapor pressure of a dilute solution of cerous oxide in cerium has been measured, but this pressure should agree within a few per cent with the vapor pressure of pure cerium.

From a least squares line computed for Run A on sample (3) the following equation is obtained relating the pressure and the temperature:

$$(12) \quad \log_{10} P_{(\text{mm. Hg})} = -\frac{2.245 \times 10^4}{T} + 11.25$$

from which the heat of vaporization is evaluated at 103.3 kilocalories per mole, and from which the boiling point at atmospheric pressure is 2690°K.

The results of this first run are comparable with those obtained in Runs B and C, but the actual vapor pressure measured is slightly higher. This is attributed to a very slight leak in the pressure closure, as evidenced by a small amount of cerium metal in a several millimeter length of the crevice formed between lid and crucible. This area was not directly exposed to the collimator, so the effect should have been very small.

The results of Run B are included in Table 19 for the s~~ix~~even?teen exposures made. In this run the orifice-collimator distance was 8.76 cm., the orifice diameter was 0.0775 cm., and the collimator diameter was 0.7938 cm. At the time of

TABLE 19

THE VAPOR PRESSURE OF CERIUM METAL

RUN B

Target	Exposure time $\underline{\tau}$(min.)	Counts per min. $\underline{C}$	Temperature $\underline{T}$°K.	Vapor pressure $\log_{10} P_{mm.}$	Reciprocal temperature $1/T \times 10^{+4}$
			$P_{(\text{mm. Hg})} = \frac{C\sqrt{T}}{\tau} 7.61 \times 10^{-6}$		
B6	75	1077.	1644	$\bar{3}.646$	6.082
B7	50	743.6	1663	$\bar{3}.664$	6.012
B8	30	463.5	1677	$\bar{3}.682$	5.963
B9	20	365.0	1694	$\bar{3}.757$	5.903
B11	15	323.3	1702	$\bar{3}.831$	5.875
B12	10	346.2	1712	$\bar{2}.037$	5.841
B13	60	554.5	1655	$\bar{3}.456$	6.042
B14	75	306.0	1623	$\bar{3}.097$	6.161
B15	100	155.9	1581	$\bar{4}.674$	6.325
			$P_{(\text{mm. Hg})} = \frac{C\sqrt{T}}{\tau} 7.94 \times 10^{-6}$		
B1	120	20.7	1461	$\bar{5}.719$	6.844
B2*	120	16.7	1507	$\bar{5}.631$	6.636
B3*	120	45.5	1569	$\bar{4}.076$	6.373
B4*	100	69.4	1607	$\bar{4}.344$	6.223
B17	125	96.1	1552	$\bar{4}.382$	6.443
B18	125	78.0	1531	$\bar{4}.288$	6.531
B19	120	57.4	1520	$\bar{4}.170$	6.579
B20	150	43.5	1487	$\bar{5}.948$	6.725

* Omitted in calculation of least square line.

counting, the specific activity of the cerium was: for the first eight samples, 3.29×10^8 counts per minute per gram and for the second eight samples, 3.15×10^8 counts per minute per gram. The least squares equation relating the logarithm of the vapor pressure to the reciprocal temperature is:

$$(13) \quad \log_{10} P_{(\text{mm. Hg})} = -\frac{23{,}660 \pm 620}{T} + 11.78 \pm 0.40$$

from which the heat of vaporization is 104.9 ± 2.8 kilocalories per mole, and the boiling point at atmospheric pressure is 2660 ± 90°K. The probable errors are evaluated from the errors in the constants of the least squares equation.

Similarly, Table 20 gives the data and calculations for Run C. In this case, the diameter of the orifice, 2r, was 0.0834 cm., the diameter of the collimator was 0.7938 cm., and the orifice-collimator distance was 8.79 cm. The specific activity of the cerium at the time of counting was: 2.90×10^8 counts per minute per gram for the first set, 2.81×10^8 counts per minute per gram for the second set, and 2.70×10^8 counts per minute per gram for the third set. The equation representing the least squares line that was calculated for these points, with the exception of these starred, is:

$$(14) \quad \log_{10} P_{\text{mm}} = -\frac{22{,}790 \pm 372}{T} + 11.14 \pm 0.24$$

TABLE 20

THE VAPOR PRESSURE OF CERIUM METAL

RUN C

Target	Exposure time τ (min.)	Counts per min. $\underline{C}$	Temperature T°K.	Vapor pressure $\log_{10} P_{mm.}$	Reciprocal temperature $1/T \times 10^{+4}$
$P_{(\text{mm. Hg})} = \frac{C\sqrt{T}}{\tau} 7.51 \times 10^{-6}$					
C1	150	8.7	1433	$\bar{5}.218$	6.978
C2*	125	4.6	1499	$\bar{5}.029$	6.671
C13	120	178.9	1568	$\bar{4}.646$	6.378
C14	120	231.7	1591	$\bar{4}.762$	6.285
C17	120	67.4	1532	$\bar{4}.218$	6.527
C20	120	120.4	1546	$\bar{4}.471$	6.468
$P_{(\text{mm. Hg})} = \frac{C\sqrt{T}}{\tau} 7.75 \times 10^{-6}$					
C3*	120	17.5	1563	$\bar{5}.650$	6.398
C4*	100	27.0	1598	$\bar{5}.922$	6.258
C6*	76	52.5	1642	$\bar{4}.336$	6.090
C7	30	283.3	1686	$\bar{3}.477$	5.931
C8	15	296.4	1706	$\bar{3}.801$	5.862
C9	10	214.5	1712	$\bar{3}.838$	5.841
$P_{(\text{mm. Hg})} = \frac{C\sqrt{T}}{\tau} 8.07 \times 10^{-6}$					
C11	52	434.7	1657	$\bar{3}.439$	6.035
C12	100	446.0	1618	$\bar{3}.161$	6.180
C16	230	27.0	1459	$\bar{5}.559$	6.854
C18	120	37.7	1514	$\bar{5}.994$	6.605

* Omitted in calculation of least square line.

from which, the heat of vaporization is 108.9 ± 1.7 kilocalories per mole. The boiling point at atmospheric pressure is found to be at 2759 ± 59°K.

Combining the results of Runs B and C, which are the two successful experiments, the least squares line of the vapor pressure as determined in this investigation was calculated, with the result listed below:

$$\log_{10} P_{mm} = -\frac{23,400 \pm 440}{T} + 11.58 \pm 0.27 \tag{15}$$

from which the heat of vaporization is 107.7 ± 2.0 kilocalories per mole and the boiling temperature at atmospheric pressure is 2690 ± 70°K. The probable errors are calculated from the least squares method. A plot of the points obtained in Runs B and C compared to the least squares line is given in Figure 13. The points, not used in the calculation, were included for purposes of comparison.

Discussion of errors

In considering the errors in measuring the vapor pressure of cerium, it is convenient to rearrange the components of equation (8) and to consider them under the types of errors they might introduce. In equation (8^1)

$$P_{(\mathrm{mm.\ Hg})} = \left[\frac{C\sqrt{T}}{\tau}\right]\left[\frac{d^2(1+\rho^2/d^2)}{\rho^2 r^2}\right]\left[\sqrt{\frac{2R}{\pi M}}\ \frac{1}{S}\right] \tag{8^1}$$

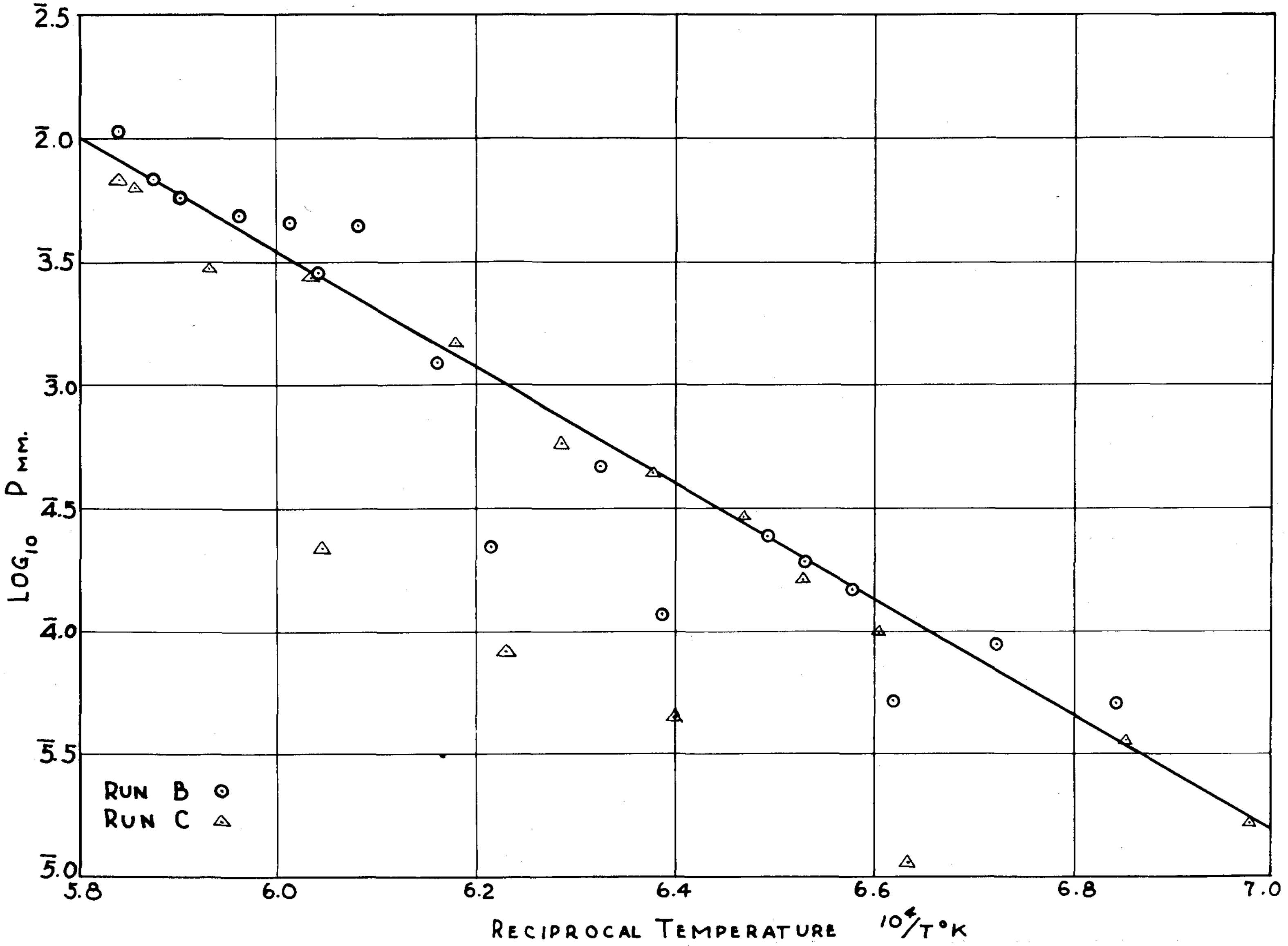

Figure 13. The Vapor Pressure of Cerium Metal. The Data are Given in Tables 19 and 20.

the truly statistical errors are assembled in the first group, the errors due to variations in the geometry which contribute a constant error to P for each run are contained in the middle portion, and the errors in the constants are grouped in the last section. Since the results of two runs were used, a more or less statistical variation due to all these factors will occur.

Errors of a statistical nature enter into the first terms of equation (8^1), namely C, τ, and T. Considering the high and low regions of vapor pressure, at 1700 and 1500°K. exposures of 15 and 120 minutes respectively were used. The error due to opening the shutter is ± 0.03 minutes, and to closing the shutter is ± 0.03 minutes. Taking the probable error in τ as the root mean square of these errors, the error is ± 0.042 minutes. Then at 1700°K., the error introduced to τ is ± 0.3 per cent and 1500°K., ± 0.05 per cent which introduces an error to P of the same magnitude. The error in measuring T is assumed to be ± 3°, which would introduce an error in T of ± 0.18 per cent at 1700°K. and ± 0.2 per cent at 1500°K. The uncertainty in C is determined by (a) the statistical fluctuation in counting which, for 10,000 counts, is 1 per cent (b) the uncertainty in counting time, which was negligible for the reasonably long counts required, (c) the uncertainty in resolutional losses, which is also slight in the counting range used, and (d) the uncertainty in obtaining the exact geometry to reproduce the counting procedure for $\underline{S}$, which is assumed to be ± 3 per cent because of the uncertainty of the exact position of the deposit. The uncertainty in $\underline{C}$ then is approximately ± 4 per cent.

The quantities related to geometry that introduce the systematic errors are grouped in the middle bracket of equation (8^1). For all the data involved, the term $(1 + \rho^2/d^2)$, does not change appreciably, so this term may be considered constant. The per cent error in the measurement of $\underline{d}$ and the radii, $\underline{r}$ and $\underline{\rho}$ are estimated as follows: $\delta d/d = \pm 0.01$; $\delta r/r = 0.005$; and $\delta\rho/\rho = 0.005$. These relations lead to corresponding probable errors of ± 2 per cent; ± 1 per cent, and ± 0.6 per cent.

Errors in the above quantities due to the assumption that no change occurs while the furnace is heated are caused by: the change in $\underline{d}$ resulting from the expansion of the tungsten support and the crucible, thereby shortening the collimator-orifice distance and an increase in $\underline{r}$, the radius of the orifice, due to the expansion of the oven. The variation in $\underline{d}$ may be calculated approximately by assuming that the mean temperature of the furnace was about 1650°K., that a one inch length of tungsten was at crucible temperature with the remainder at room temperature, and that a crucible 3/4 in. in length was used. Considering the coefficient of expansion of tungsten as 4.4×10^{-6} per degree C. at all temperatures, the increase in length of the support would be 0.02 cm. for an average correction in length of + 0.16 per cent. Taking 6.5×10^{-6} per degree C. at all temperatures for the coefficient of expansion for the tantalum crucible, the correction would be + 0.18 per cent. Combining the errors, a total correction of - 0.34 per cent in the collimator-orifice distance or a correction of - 0.7 per cent in the pressure is obtained. In calculating the error in $\underline{P}$ from the change in radius, $\underline{r}$, of the orifice, the correction to the radius is - 0.08 per cent which gives a correction to the pressure of - 0.2 per cent.

Considering the inherent errors, the value of $\underline{R}$ and $\underline{M}$ are known with much greater accuracy than that of the experiment. Of course $\underline{M}$ was obtained by assuming the vapor to be mono-atomic, but this is not likely to introduce an error for the reasons discussed in assumption (i). In the determination of $\underline{S}$, the specific activity of the cerium used, the highest accuracy which can be expected by taking 10,000 counts is a ± 1 per cent statistical accuracy and a ± 1 per cent geometrical accuracy by exact centering of the foils. It is probable that, while a ± 2 per cent reproducibility was observed in comparing the counts of the comparison standard of cerium, a maximum accuracy of ± 3 per cent is the best that can be claimed in this standard. This introduces an equal uncertainty in P.

Other errors that were discussed in the assumptions are those due to a variation in the position of the crucible which may introduce an error of ± 2 per cent, and those due to unsaturation efffects which were estimated at ± 5 per cent, and finally those that might be caused by the correction of background counts on the blanks which were ± 3 per cent.

The treatment above also does not include the error introduced to P by the variation of 1/T, for in that treatment it was assumed that there was no error in the measurement of 1/T. However, since the probable error in T was ± 3 degrees or about a ± 0.2 per cent variation in the value of T, it can be shown from equation 15 that the corresponding error reflected in P is ± 7 per cent.

A summary of the errors is given in Table 21 and indicates a maximum uncertainty of ± 28 per cent in the determination of the vapor pressures. The root mean square average of the errors in Table 21, which would give the most probable error if all the errors were statistical in nature, is ± 11 per cent. From the least squares treatment which gave equation 15, it can be shown from the consistency of the measurements that the probable error of a single value of P is ± 15 per cent. The difference between the predicted and the actual error can be explained on the basis that some

TABLE 21

SUMMARY OF ERRORS IN THE VAPOR PRESSURE MEASUREMENTS

Nature of error	Quantity whose error is involved	Probable error in P %
Inherent	S	± 3
Systematic		
(a) In measurements	d^2	± 2
	r^2	± 1
	ρ^2	± 0.6
(b) In neglect of changes caused by heating	d^2	+ 0.7
	r^2	- 0.15
	ρ^2	negligible
(c) Variation of orifice position		± 2
Statistical	τ	± 0.2
	T	± 0.2
	C	± 4
Other errors		
Unsaturation		± 5
Variation of background		± 3
In temperature measurement	1/T	± 7
Maximum total error		± 28
Root mean square error		± 11

of the errors are systematic in nature and vary only between the two runs and that the predicted probable error is slightly larger than ± 11 per cent.

SUMMARY AND CONCLUSIONS

The production of the light rare earth metals, neodymium and praseodymium, was found to be possible by the metallothermic method first perfected for the preparation of cerium at this laboratory. The metals were formed by the reduction of the anhydrous trichlorides of the rare earths by calcium in 10% excess with a "booster" of iodine in the ratio of 0.63 moles to one mole of the chloride; the iodine provided the excess heat required to completely melt the reaction products and thereby to permit the metal to separate. The reductions were carried out in a steel bomb lined with a sintered lime crucible. Four kilograms of pure cerium metal and 1.8 kilograms of didymium metal (80% Nd, 10% Sm, 8% Pr, and 2% other rare earths) were also prepared by this method. The reduction method for the preparation of these metals was completely reliable with no failures in any reduction attempt. An average of the apparent yields obtained for each of these metals is: 90.4 per cent for cerium; 91 per cent for neodymium; 76 per cent for praseodymium (on small scale where yields are low); and 83.5 per cent for didymium. The ingot metal produced in the reduction is well formed, with smooth sides and top, and free of occluded slag. Impurities introduced are magnesium and calcium which were removed by vacuum distillation.

An ingot of impure yttrium (70% Y, 18% Nd, 10% Sm, and 2% Gd) was prepared by the same process; however, the procedure did not yield metal with the chloride of more pure yttrium (90% Y, 2% Gd, 6% Dy, and 1.5% Sm). The failure is attributed to the high melting point of yttrium which prevented the fusion and, consequently, the collection of the metal.

An extrapolation of this method to the preparation of samarium metal from the halide was unsuccessful. No metal could be obtained by reduction of the trichloride, trifluoride, or triiodide of samarium by calcium, with either iodine or potassium chlorate as "boosters". A small amount of metal was prepared as a calcium alloy by the reduction of samarium dichloride by calcium; however, it could not be recovered for recasting. A zinc alloy of samarium was produced and separated in low yields by the reduction of the samarium trichloride or trifluoride by calcium with zinc chloride as a "booster". Ten grams of this alloy were removed from the slag and recast to give 2 grams of a samarium-rich metal containing greater than 50 per cent samarium. The preparation of samarium metal by the metallothermic process was not perfected, but proof was established that metal could be obtained by use of an alloying agent.

In studies on the purification of the metals, cerium, neodymium, praseodymium, and didymium, considerable differences were found between the reactivity on ceramic crucibles of molten cerium metal and that of the other metals investigated. Neodymium, praseodymium and didymium attack refractory oxides at temperatures more than 100 degrees below the temperature at which the same oxide is stable to molten cerium. In agreement with published work it was found that magnesium oxide was the most satisfactory refractory oxide for casting the rare earth metals. Beryllium oxide was attacked by cerium at 1000°C.; calcium oxide was stable to cerium at 1150°C., but was badly eroded at 1000°C. by the other three metals studied. The refractory oxide most suited for purification distillations is magnesium oxide which is stable in the presence of the rare earth metals up to 1200°C. By heating neodymium and cerium in magnesia, the calcium content was reduced to 0.05 per cent and the magnesium content to less than 0.025 per cent for neodymium and 0.25 to 0.025 per cent for cerium. The metals, molybdenum and tantalum, were investigated as crucible materials, and found to be insoluble in the rare earth metals. Cerium was heated to 1700°C. in tantalum with no solution of tantalum and to 1400°C. in molybdenum with no molybdenum contamination. These metals are apparently very resistant to alloying with the rare earths. Tantalum crucibles were not used for the purification of cerium because of the limited amount of crucible material available, but they were superior to any of the oxide refractories on the basis of the small scale castings made.

The density of cerium metal containing 0.1 per cent calcium is 6.747 grams per cubic centimeter at 23°C., which is 0.04 grams per cubic centimeter less than the theoretical density of pure cerium; its hardness on the Knoop Hardness Scale is 25 which corresponds roughly to 19 on the Brinell Hardness Scale. While the hardness is slightly less than that found by others (Table 10), the workability of the metal appears to be less. It can be cold rolled in the impure state (0.2% Ca, and 0.2% Mg), but when more of the impurities are removed the malleability decreases. The difference is attributed to oxide impurity introduced by reaction with the crucible.

Neodymium metal with 0.5 per cent calcium and one per cent magnesium has density of 6.999 which is equal to the theoretical density reported for pure neodymium (14). This result indicates that the theoretical density may be low, since the impurities in the neodymium should reduce its density considerably. The hardness of neodymium is 47 on the Knoop Scale which is approximately 33 on the Brinell Hardness Scale.

The melting points of cerium and neodymium metal were determined. Cerium, containing 0.1 to 0.2 per cent calcium and 0.05 to 0.2 per cent magnesium, melted at 793 ± 5°C.

with a solid transformation at 703 ± 10°C. A melting point of 820 ± 10°C. was found for neodymium metal containing 0.5 per cent calcium and one per cent magnesium.

The vapor pressure of cerium metal, from 10^{-5} to 10^{-2} mm. of Hg, was determined in the temperature range from 1460 to 1720°K. by a modification of the effusion method in which the amount of metal condensed was measured by use of radioactive cerium tracer. The vapor pressure was calculated from the temperature of the sample, the geometry of the system and the quantity of metal condensed. The relation between the pressure and temperature was found to be:

$$\log_{10} P_{(\text{mm. Hg})} = -\frac{23{,}400 \pm 440}{T} + 11.58 \pm 0.27.$$

From this equation, the heat of vaporization is 107.7 ± 2.0 kilocalories and the boiling point at atmospheric pressure is 2690 ± 70°K.

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