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The vapor pressures of lanthanum and praseodymium

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THE VAPOR PRESSURES OF LANTHANUM AND PRASEODYMIUM

by

Adrian Hill Daane

A Dissertation Submitted to the
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The Requirements for the Degree of

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INTRODUCTION

The rare earth elements form a unique group; while they numerically constitute over one-seventh of the elements in the periodic table, they have very similar chemical and physical properties. In the preface to their monograph on the rare earths (1), Yost, Russell and Garner state

> The discovery of most of the rare earth elements took place in the latter half of the 19th century, but the purely chemical methods of study available in that period and the monotonously similar chemical behavior of the members of this group of substances placed them for some time in the category of puzzling but rather dull mysteries.

The tremendous advances in chemistry and physics which took place between 1900 and 1920 greatly clarified the electronic structures of these elements and showed some of the reasons for their similar properties. It is now known that these fifteen elements, occupying the positions between barium and hafnium in the periodic table, all have their lower orbitals filled through the 4d level, and that the reasons for the differences among them lie mainly in the manner in which their 4f and 5d orbitals are populated. Between these orbitals lie the 5s and 5p orbitals which are filled in the rare earths, and partially shield the 4f level from external fields. Although the electronic configurations for the neutral states of the gaseous atoms have been determined for only 7 of the rare earths, Meggers (2) has postulated the configurations for the others; lanthanum, the first member of this group with an atomic number of 57, has the normal configuration $4f^0\ 5d^1\ 6s^2$, and as the atomic number is increased to 58 for cerium, the new electron is added to the 4f orbital and the one 5d electron in lanthanum drops back to the 4f orbital also, giving the normal configuration $4f^2\ 5d^0\ 6s^2$. Progressing through this group, the 4f orbital is gradually filled to its capacity of fourteen electrons, with gadolinium, terbium and luteoium having one 5d electron the same as with lanthanum. However, in the condensed phase, as well as in chemical compounds, the relative stabilities of the 4f and 5d orbitals are modified by external fields.

In chemical compounds the 5d and 6s electrons are involved in bonding orbitals, in ionic compounds they are held by the negative ions. In these cases, the relative stability of the 4f level is such that it is occupied by a regularly increasing number of electrons, from zero in the case of lanthanum on up to fourteen for luteoium, without the jumps evidenced in the normal gaseous atom. Since the differences among the rare earth ions are mainly in the 4f orbital which is screened by the completed 5s and 5p orbitals, it is evident that the chemical similarity of these elements is a consequence of their nearly identical outer electronic structures. Some physical properties however, are very much affected by these differences in the 4f orbital; for example, differences in the magnetic susceptibilities of the rare earth ions have been particularly helpful in determining their electronic structures (3).

In the case of the metals the valence electrons are in electronic conduction bands; as a result, the relative stability of the 4f and 5d electrons may also be modified somewhat giving rise to anomalies in physical properties such as densities and specific heats (4).

The filling of orbitals in lower shells also gives rise to the iron, palladium and platinum groups of transition elements, in which groups many similarities of properties are also found, although the degree of similarity is much less striking than in the case of the rare earths. Seaborg has pointed out that the recently enlarged actinium group of transition elements appears to be very closely related to the rare earth group (5), since it is formed by the filling in of the 5f orbital, starting with actinium. This group of elements is not an exact counterpart of the rare earths since the 5f electrons are bound less tightly than are the 4f electrons of the rare earths, but the similarities in properties within these two groups has prompted Seaborg to refer to the actinium group as the "type 5f rare earths".

In the rare earth group, the increasing nuclear charge with a relatively uniform outer electronic structure, results in a slight decrease in the atomic radius as the atomic number increases (6), and it is this gradually changing parameter in a group of otherwise very similar elements which makes them an extremely interesting and potentially useful group to study. An example of a field in which data concerning the rare earths should be of considerable assistance is in the correlation of various properties of metals with their atomic and molecular structure; because of their availability and the similarity of many of their properties, the alkali metals and the alkaline earth metals have been used in studies of this kind (7). However, even within these groups so many parameters are varying from element to element that correlation between experiment and theory is difficult and far from satisfactory. Since the rare earths offer such a large number of similar elements to work with in which there is such a gradual change in but one parameter, they should be particularly helpful in advancing theories concerning metals.

The problem of separating the rare earths has been such a difficult one that there has been little opportunity to study the fundamental properties of most of these elements. As stated by Yost, Russell and Garner (1),

> As further research on this unique group in many branches of chemistry and physics is greatly impeded by the scarcity of pure compounds, it is of considerable importance that any promising method of separation be fully utilized.

It has recently been found in this laboratory that, with improved techniques and newer ion exchange resins, separations of the rare earths may be effected in a high degree of purity (8,9). With many pure compounds of these elements now available through these new procedures, an intensive research program is in progress in these laboratories in which it is hoped to correlate some of the properties of the rare earths with each other and relate them to the electronic and molecular structures of these elements and their compounds.

In any study of the properties of metals, it is extremely important that very pure materials be used, since small amounts of impurities are known to greatly affect many of the properties of metals. As an example, small amounts of impurities are known to stabilize crystal structures of metals which are not characteristic of the pure metals under equilibrium conditions; the conflicting data concerning the structures and allotropy of some of the rare earths (4,10) is undoubtedly due to the presence of impurities in some of the samples. Consequently, the first metallurgical problem attacked in this program was that of devising a method of preparing very pure metals. Considerable progress has been made in this laboratory on this problem; the preparation of several rare earth metals in a higher degree of purity than has heretofore been available has already been described (11). Since, however, these metals contained small amounts of carbon, nitrogen and oxygen acquired in the metallurgical processing, one of the most important problems of the present study was that of devising metallurgical techniques which would greatly reduce the amounts of these impurities.

Since very pure rare earth metals have not been available in the past, their properties have not been determined with accuracy. Of the many properties of these metals that were unknown, the vapor pressures were chosen for the first work of this laboratory for several reasons: 1) any differences in this property among these elements could conceivably permit separations of them from their mixtures; 2) the heat of vaporization, obtained from the slope of the plot of the logarithm of the vapor pressure versus the reciprocal of the temperature, is an important thermodynamic quantity; 3) information concerning the behavior of component metals in metal-metal liquid solutions is rather meager since, in most cases, the temperatures involved would be so high as to make accurate measurements difficult; also, most of the metals available are of such different types that it would be difficult to work with combinations which did not involve intermetallic compounds. The rare earth metals, due to similarities in their external electronic structures, would be expected to form nearly perfect liquid solutions among themselves, and if this were the case, the vapor pressures over their alloys with each other should be proportional to their mole fractions. However, before this type of problem could be studied, it would be necessary to know the vapor pressures of the pure metals. The first step toward this end was accomplished in these laboratories by Ahmann (12); he determined the vapor pressure of cerium, utilizing the Knudsen method of molecular effusion (13) as modified by Phipps and others (14). In this method, the metal sample is radioactive, and the number of molecules escaping from the effusion vessel is determined by collecting a known fraction of the escaping molecules on a target. The quantity of material collected on the target is determined from the radioactivity of the deposit, based on the specific activity of the original sample. This appears to be one of the best techniques developed up to the present for measuring the vapor pressures of metals, although there are some general objections to this method; for example, the necessity of determining the accommodation coefficient of the metal vapor on the target. In the case of the rare earths, its use would be somewhat difficult in some cases due to the properties of the available radioactive isotopes (15).

The very reactive nature of the rare earth metals makes them quite subject to corrosive attack by air and moisture; therefore, the unmodified Knudsen (13) and Langmuir (16) vapor pressure methods are not well adapted for use with these metals since they involve transferring the sample from the furnace chamber to a balance and back again for each measurement. Protecting the sample from air and moisture during these operations would make the methods undesirably complex. As these two methods possess the advantages of being basically very simple and direct, a modification of one of them appeared to be best suited for work with the rare earth metals. Consequently, another aim of the present study was to devise a technique for measuring vapor pressures, having as its basis either the Knudsen or Langmuir methods, but designed particularly to permit its use with active metals such as the rare earths.

The correlation of physical properties of the rare earths with their atomic structures is a long range program requiring much preliminary work before sufficient data can be collected to show the quantitative relationships which must exist. The present thesis deals with the following contributions to this program:

1. The development of an improved method for preparing purer rare earth metals.
2. The development of an improved technique for measuring vapor pressures of metals; the testing of this technique with metals of known vapor pressure; and the measurement of the vapor pressures of lanthanum and praseodymium.

PREPARATION OF THE RARE EARTH METALS

Introduction

The highly electropositive nature of the rare earth metals has made their preparation difficult by limiting the methods which can be used. The only chemical reducing agents which have been successfully employed to prepare the pure rare earth metals from their compounds are the alkali metals and the alkaline earth metals. Electrolytic methods have also been used in the production of the rare earth metals. With few exceptions, the anhydrous halides have been employed in the preparation of the rare earth metals since the use of oxides, nitrates, sulfates etc., leads to contamination of the product with oxygen.

During the war this laboratory developed the bomb reduction technique for the production of metals. Any volatile impurities in the metal were removed by a vacuum casting process. The general method was so successful that it was utilized, with modifications for individual cases, in the preparation of electropositive metals including beryllium, cerium, lanthanum, titanium and zirconium (18). The utility of this method in the case of cerium is demonstrated by the fact that over 1000 pounds of 96% cerium, containing 4% of the more common rare earths, was prepared for use at this and other Manhattan Project sites (19). In the interests of rapid procurement, the purity requirements of the above grade of cerium were kept as lenient as was consistent with the program of intended use. As a result, it was necessary to modify the procedure when a purer grade of rare earth metals was desired for the investigation of properties such as neutron cross sections, heat capacities, melting points, vapor pressures etc. Typical modifications introduced were the use of higher vacua in the casting operations; the use of purer refractories and reactants; and the employment of more inert atmospheres in bomb-loading operations. This improved technique has been used to prepare very pure cerium, lanthanum, neodymium, praseodymium and didymium in 160 gram batches in yields of over 98% (11). The main objections to this method are: 1) yields were considerably lowered whem smaller batches were run; 2) recovery of rare earth salts from unsuccessful runs was difficult since much of the fused reaction mixture had soaked into the porous bomb liner; 3) the resulting rare earth metals were found to contain small but appreciable amounts of oxygen in the form of the particular rare earth oxide introduced by reaction of the rare earth metals with the refractory oxide crucibles. The amount of oxygen pick-up from these refractories was approximately the same for magnesium oxide, calcium oxide, dolomitic oxide, beryllium oxide and lanthanum oxide. Considerable experience proved the calcium oxide, dolomitic oxide and lanthanum oxide crucibles to be undesirable because of their tendency to air slake; beryllium oxide was rejected as a refractory because of the health hazard involved in its use. Consequently, magnesium oxide refractories were generally used in the rare earth studies.

While the presence of a small amount of oxygen in these metals was of little consequence in some cases, it was particularly undesirable in a study of the vapor pressures of the metals by the effusion technique, in which a surface film would prevent free molecular evaporation from the entire surface of the metal. If the oxygen were present in the form of a dissolved oxide, it would result in an observed vapor pressure not that of the pure metal. One of the first problems of the present study was to develop a method for preparing purer rare earth metals than were previously available. As will be shown, a solution to this problem was found in the fact that tantalum metal is not attacked by the reactants or products at the temperatures reached in the general rare earth metallurgy work to be described. Using all-tantalum equipment, pure rare earth metals were prepared using techniques which greatly reduced chances for oxygen contamination of the product metal. The overall modifications in technique introduced in this work resulted in an improved procedure for preparing the rare earth metals on a smaller scale with higher yields, and opened the way for practical application of rare earth metallurgy techniques to some rare earth separation problems.

Historical

Mosander (20), in 1826, was the first to report the production of a rare earth metal; cerium was prepared by the reduction of cerous chloride with potassium. The product of this reaction was an impure powder containing some oxide; however, it contained enough metal to permit a study of some of the reactions of cerium with various gases. In 1842 Beringer (21) used sodium to reduce cerous chloride; he found that the resulting cerium powder was similar to that described by Mosander. This same reaction was employed by de Marignac (22) in 1853 to prepare didymium metal powder, and by Wohler (23) in 1867 to produce cerium powder. In 1925, Kremers (24) reported that he was not able to prepare neodymium metal by the reaction of sodium with neodymium chloride. Zintl and Neumayr (25), in 1933, passed sodium vapor over hot cerous chloride to obtain cerium metal powder mixed with sodium chloride; the mixture was used for further experimentation without separating the products. In a very careful piece of work in 1937, Klemm and Bommer (6) prepared each of the rare earth metals except promethium by reducing the chlorides with sodium, potassium or caesium, obtaining a mixture containing the powdered rare earth metal and the alkali chloride which were not separated. The reaction was carried out in a resistance glass apparatus at 300°C; by using potassium as the reductant and not heating the reactants over 250°C, even samarium, europium and ytterbium metal could be prepared, although twenty hours were required to complete the reaction in the case of samarium. Since the objective of this work was the preparation of these metals for an x-ray study of their structures, the presence of the alkali metal halide was an advantage; its diffraction pattern provided a calibration of the x-ray film for each exposure. The scale on which this work was done was not indicated, but some of the samples appear to have weighed about 200 milligrams. The latest reported use of an alkali metal in an attempt to prepare rare earth metals was by Asprey, Eyring and Heppler (26) in 1948; they heated the trifluorides of europium, samarium, neodymium, gadolinium and lanthanum to 1200°C in sodium vapor, using beryllia crucibles. They reported obtaining a grey to black material which in each case possessed a cubic structure of the fluorite type, with a lattice constant which was too large to be the metal. The observed lattice constant of the europium product was very near that reported for europous fluoride by Beck and Nowacki (27), but since the rare earth oxyfluorides and solid solutions of the trifluorides in the oxyfluorides have cubic structures with lattice constants close to those observed in the above preparations, the presence of oxyfluorides was assumed. The product was obtained in the powdered form in all of the reported cases of the preparation of the r are earth metals by the reaction of a rare earth halide with an alkali metal.

The alkaline earth metals have generally proved to be much better reductants for the rare earth halides than are the alkali metals. Moldenhauer (28), in 1914, and Karl (29), in 1934, reduced cerous chloride by adding it to a molten bath of calcium. Although massive metal was obtained in each case, the conditions of the experiments were such that the products contained appreciable amounts of impurities; for example, Karl's product contained 12% calcium and 1.7% iron. Trombe and Mahn (30), in 1944, reported the preparation of cerium, neodymium and gadolinium 99% pure by adding the rare earth halide to a molten magnesium bath which resulted in magnesium alloys of the rare earth metals; they stated that the pure rare earth metal was obtained from this alloy by distilling off the magnesium in a vacuum. The above operations were carried out with the products in molybdenum equipment which prevented contamination of the product by crucible attack; however, an average of 1% magnesium remained in their samples.

Several reports in Manhattan Project literature contain brief statements concerning the preparation of rare earth metals using alkaline earth metals to reduce rare earth halides. Eyring and Cunningham (31) prepared praseodymium metal on a small scale by passing barium vapor over praseodymium fluoride at 1100°C in a vacuum. The quantities and yields obtained were not mentioned in their paper. Derge and Martin (32) prepared cerium metal in 1944 by reducing cerous chloride with calcium; they obtained yields of up to 81% and 87%, respectively, on 1 gram and 50 gram reductions. They also studied the ignition temperature of the reaction between calcium metal and cerous chloride and found it to be between 570 and 575°C, with only a 170°C temperature rise due to the heat of reaction. This latter statement is only qualitative since the scale of the reduction was not mentioned. The ignition temperature range reported above is higher than the value of about 400°C found in this laboratory (11), although this is very probably due to the triggering of the principal reaction at the lower temperature by a booster reaction employed for reasons to be discussed later. Derge and Martin (32) reported 61% yields on 1 gram scale reductions of cerous bromide with calcium. The poor results which were obtained in an attempted reduction of cerous chloride with barium were ascribed to the high melting point of the slag from this reaction; they reported no reaction between cerous chloride and magnesium. At 900°C, lanthanum bromide was reduced on a 1 gram scale with a 78% yield; lower yields were reported as the charge was heated above the optimum temperature of 996°C.

Partial reduction of some of the rare earth halides to metal by hydrogen has been reported by Jantsch, Skalla and Grubitsch (33), although the conversion was less than 50% in the best case; the metal was obtained in the form of a gold alloy since the reaction was carried out in a gold boat. Reduction of the trihalides of samarium, europium and ytterbium with hydrogen progresses only to the divalent halides, although these are reported by Jantsch and Skalla (34) to disproportionate on heating according to the reaction:

$$3MX_2 \longrightarrow 2MX_3 + M .$$

Brewer and others (35) have indicated that these reports are in contradiction to the existing thermodynamic data of the rare earth halides and that the relatively high heat of formation of the alloys or compounds which resulted in each case was responsible for the apparent disproportionation; in inert containers such as molybdenum the disproportionation does not take place (35).

Moldenhauer (28) obtained an alloy of cerium and aluminum by reacting cerous chloride with aluminum. The stable character of this alloy prevented the separation of these metals. Siebert and Korten (36) reported, in 1920, that they were able to prepare the rare earth metals by reducing the halides with carbon at high temperatures.

Due to the difficulty of preparing the anhydrous rare earth halides, many workers have attempted to produce the rare earth metals by reducing the oxides with various reducing agents; although some of the reactions can be effected, the extremely refractive and inert character of the resulting slag in each case prevents consolidation or separation of the metal. Winkler (37), in 1890, reduced the oxides of lanthanum, cerium and yttrium with magnesium and reported obtaining pyrophoric powder intermixed with excess magnesium and semi-fused oxides. Holm (38), in 1902, described the preparation of cerium metal powder by reducing the oxide with magnesium. Matignon (39), in 1900, Schiffer (40), in 1900, Muthmann and Weiss (41), in 1904, and Hirsch (42), in 1911, all reported the preparation of cerium by reducing the oxide with aluminum; however, in several cases the atmosphere in which the reaction was carried out lead to the formation of nitrides and hydrides as the end products. With praseodymium oxide, Matignon used magnesium to prepare the metal. Hirsch also found that the action of carbon, silicon or calcium on the rare earth oxides produced carbides, silicides or alloys of calcium. Kuhne (43), in 1904, was issued a patent for a method of preparing the rare earth metals which utilized the "thermite" method, modified by the addition of chlorates to the reaction mixture to provide a more exothermic reaction thereby promoting fusion of the reaction products with a resulting agglomeration of the rare earth metal. Patents have also been issued to Kuzel (44), N. V. Philips' Gloeilampenfabriek (45), and Siemens and Halske (46) for processes for the production of rare earth metals, using oxides, nitrides and other rare earth compounds as reactants, with aluminum, zirconium and elements of the nitrogen family serving as the reductants.

In rebuttal to the above claims of the preparation of rare earth metals from their oxides, Moldenhauer (28) reported that cerium could not be prepared by the "thermite" reaction with aluminum, calcium or magnesium as the reducing agent, and Karl (29) was not able to prepare cerium metal by reducing the oxide with silicon carbide or magnesium. In fact, there have been no reports of the industrial application of the "thermite" type of reaction for the preparation of rare earth metals, and at least one authoritative writer (47) has cast serious doubts on the reported successes of others.

Electrolytic methods have been used for the commercial preparation of the rare earth metals, particularly cerium and "misch metal". The first use of this technique with the rare earths was reported by Hillebrand and Norton (48), in 1875, who prepared lanthanum, cerium and didymium;

this latter mixture was considered an element at the time of this work. Their method utilized a porcelain crucible containing a molten mixture of sodium chloride and potassium chloride in eutectic proportions, in which was placed a porous cup containing the molten rare earth chloride covered with a layer of ammonium chloride. The anode was an iron sheet and the cathode was either iron or platinum wire on which the product was obtained as a mass of finely divided crystals. Muthmann and co-workers (49, 50, 51), in 1902, electrolyzed a molten cerous chloride bath which contained 10% of the sodium chloride-potassium chloride eutectic. A water-cooled copper vessel contained the electrolyte; no attack of the container was evidenced due to a thin layer of the salt which solidified on the walls of the vessel. The metal produced by this technique contained carbon introduced by the carbon cathodes. Muthmann's group was able to prepare cerium metal by the electrolysis of a molten bath of cerous fluoride to which had been added ceric oxide, although the current efficiency in this process was not high; it was also found that potassium fluoride, calcium fluoride or cryolite could not be successfully substituted for the cerous fluoride as the solvent for the ceric oxide. The presence of silicates in the electrolyte was found by Muthmann to seriously interfere with the electrolysis and to cause the formation of high melting silicides; carbon electrodes or crucibles were found to introduce relatively large amounts of carbon into the metal. Lanthanum, praseodymium and neodymium were also prepared by these workers; by adding to it one third its weight of barium chloride, a bath of samaric chloride was electrolyzed to prepare an impure grade of samarium metal. In this latter electrolysis, it was necessary to employ a high current density to obtain even low yields. Hirsch (42) employed an iron crucible as the cathode and a carbon anode to electrolyze a fused bath of cerous chloride, to which was added sodium chloride, potassium fluoride and barium chloride to increase the resistance of the melt and check its decomposition. The cerium metal prepared by this process contained carbon, oxygen and 2% iron. A purer metal was reported to be obtained by adding mercury to the impure product to form the dilute amalgam, skimming off the impurities, and then distilling off the mercury; however, as will be mentioned later, other workers have stated that considerable mercury remains in the rare earth metal after such treatment. Kremers and Stevens (52) electrolyzed lanthanum onto tungsten anodes and reported a pure product uncontaminated with tungsten. Trombe (53, 54) has recently published detailed accounts of the chemical and electrolytic methods which he has employed in his laboratory to prepare cerium, lanthanum, neodymium and praseodymium. By employing a molten cadmium anode, he was able to obtain samarium-cadmium alloys by the electrolysis of a fused bath of alkali halides containing samaric chloride. By distilling off the cadmium, a sample of samarium metal was obtained which Trombe estimated contained less than 0.01% cadmium. The same technique was used to obtain gadolinium metal of comparable purity.

Hopkins and his co-workers have electrolyzed non-aqueous solutions of some of the rare earth halides into mercury cathodes at room temperature, and have reported that the pure rare earth metals were obtained by distilling off the mercury from the resulting amalgams (55, 56, 57). The concentration of the lanthanum, neodymium and cerium in the amalgams was from 1 to 3% by weight, and 0.6% for yttrium; the concentration of the samarium amalgam was not given. However, Derge and Martin (32) have more recently attempted the preparation of pure rare earth metals by the removal of mercury from amalgams by vacuum distillation; it was found that, after heating to 1000°C in a high vacuum, the residual metal contained 5% mercury with lesser amounts of other impurities. These workers noted that massive rare earth metals are obtained in this process only when wet, dilute, well consolidated amalgams are used as starting materials; with dry, concentrated amalgams, a spongy product is obtained. However the technique of Hopkins and co-workers has not been a method of choice for the preparation of rare earth metals because of: 1) the low concentration of rare earth metal in the resulting amalgam; 2) the low solubility of the rare earth salts in the non-aqueous solvents; and 3) the inherent difficulty in removing all the mercury from the product.

Previous work in this laboratory (11) has shown that several of the rare earth metals may be produced by the reduction of the rare earth trichloride with calcium in refractory lined steel bombs. Since the heat of this reaction is not great enough to melt the reaction products and hold them in this condition long enough to permit agglomeration of the rare earth metal, iodine was added to the reaction mixture along with an additional amount of calcium to form calcium iodide. The heat from this side reaction provided sufficient heat to allow consolidation of the product metal; additional assistance was provided by the presence of the calcium iodide in the slag which lowered its melting point. The use of oxide refractories in this work, however, introduced undesirable amounts of oxygen into the product metal as will be shown later. Magnesium oxide, calcium oxide, dolomitic oxide, beryllium oxide and lanthanum oxide refractories were tested; however, in each case it was estimated that the resulting rare earth metal contained up to 1% rare earth or refractory oxide. The metallurgical work described in this thesis had as its aim the development of techniques which would permit the preparation of purer rare earth metals.

Methods of Procedure

Pure rare earths

The lanthanum was purchased from the Lindsay Light and Chemical Company as their "pure lanthanum oxalate, code 518". Analyses by the spectrochemical analytical group of the Ames Laboratory showed it to contain between 0.05 and 0.1% each of cerium, neodymium and praseodymium, no other rare earths or thorium, and about 0.01% calcium. The oxalate was calcined in a silica tube in a stream of air at 800°C to produce lanthanum oxide for the preparation of the anhydrous chloride.

Praseodymium, samarium and gadolinium oxides were produced in this laboratory (8, 9) by the recently developed techniques with ion exchange resins to effect the separations from other rare earths. The praseodymium was found to be free of other rare earths by spectrochemical analytical methods; the lower limit of detection for lanthanum, cerium and neodymium was 0.1%. Amalgam extractions of the gadolinium had reduced its samarium content to about 1.6%, with 0.26% europium being the only other contaminant detectable. The samarium contained 0.5% europium and about 0.2% each of neodymium, praseodymium and gadolinium.

Anhydrous rare earth chlorides

To prepare the rare earth chlorides, the oxides were dissolved in 6N. hydrochloric acid; the resulting solution was evaporated until its boiling point reached 130°C and then poured into a porcelain evaporating dish and stirred until crystallization to a sugar-like consistency was complete; the last trace of free water disappeared at about 90°C, which is the reported (58) melting point of the septahydrate. Analyses showed that this material had a rare earth chloride:water ratio of 1:5 in the case of lanthanum and praseodymium, although Ahmann (12) in his work with cerium has reported the product to be the septahydrate; data were not obtained for samarium and gadolinium. By stopping the evaporation at 125°C, the septahydrates were obtained in this present work, but the lower water content was preferred since it permitted more rapid dehydration in the subsequent step.

The anhydrous chlorides were prepared from the hydrates by the procedure of Kleinheksel and Kremers (58). In this method, the hydrates are gradually heated to 400°C in a stream of anhydrous hydrogen chloride at a pressure of about 40 mm Hg. For this drying operation, the hydrates were contained in a Pyrex tube 4 inches in diameter and 18 inches long, with 40/50 standard taper joints at each end to facilitate loading and unloading; the tube and its contents were heated in a chromel-wound resistance furnace which had a heating cavity 5 inches in diameter and 30 inches long.

The hydrogen chloride was purchased from the Matheson Company in No. 3 cylinders which contained 5 pounds of the gas. A stainless steel reducing valve on the tank permitted regulation of the flow of the gas into the drying apparatus with little corrosion. To remove hydrogen chloride from the effluent gas, a bubbler-trap combination was devised (59) consisting of a gas washing bottle with a layer of carbon tetrachloride covering the tip of the inlet tube, above which floated a solution of sodium hydroxide. The excess hydrogen chloride from the drying tube bubbled first into the carbon tetrachloride, and then rose to the sodium hydroxide layer where it reacted to be removed from the atmosphere of the apparatus. An ice bath around the bubbler-trap prevented excessive evaporation of the carbon tetrachloride. A glass water aspirator served to maintain the pressure in the apparatus at about 40 mm Hg.

The hydrogen chloride contained 0.2% acetylene and 0.3% chlorinated hydrocarbons as impurities (60), and it was found that, at the temperatures encountered in the drying runs, these organic compounds were decomposing to form a gray to black layer of finely divided carbon on the salt. This difficulty was circumvented by first passing the hydrogen chloride through a bed of hot anhydrous lanthanum chloride in which the organic compounds were pre-decomposed; the resulting carbon was filtered from the gas stream before it entered the drying furnace. This "pre-scrubber" tube of anhydrous lanthanum chloride was placed in a Vycor tube in a resistance furnace so that the center of the bed was maintained at 500°C while the two ends of the bed were outside of the furnace and remained at about 30°C. Most of the carbon resulting from the decomposition of these compounds was found to be deposited at the point where the "pre-scrubber" bed entered the heating furnace. In starting the drying runs, the temperature of the tube was kept below 90°C for several hours to permit any of the septahydrate which might be present to decompose to a higher melting hydrate instead of melting at this temperature. The temperature could subsequently be raised at the rate of about 25°C per hour which permitted a charge of 1 kilogram to be dried in about 16 hours. A typical analysis of a sample of lanthanum chloride prepared by this process was: Calculated for $LaCl_3$: La, 56.64%; Cl, 43.36%. Found: La, 56.60 ± 0.05%; Cl, 43.38% ± 0.04%.

Calcium

The calcium was prepared by another group in the Ames Laboratory. The crude calcium, obtained from Dominion Magnesium, Ltd., was redistilled, ground to size first in a Mitts and Merrill hog and then in a Sprout, Waldron and Company rotary knife mill (61). The ground calcium was passed over a Dings Company magnetic separator to remove any ferromagnetic contaminants and then sieved to remove the "fines" which included any loose calcium oxide powder. A typical analysis of the calcium from this process showed the presence of the following amounts of impurities, in parts per million: Fe, 40; Mn, 20; N, 50; B less than 1; Cd, less than 1; Al, 15; Mg, 400; C, 250; Na less than 50; K, less than 50; Li, less than 20. The freshly ground calcium was stored in an argon atmosphere until it was ready for use.

Reaction crucibles

A tantalum crucible in which the reaction between the rare earth chlorides and calcium was carried out on a 20 gram scale is shown in Figure 1. The tantalum crucible at the right of the figure, and all other tantalum equipment used in this work, was obtained from the Fansteel Metallurgical Corp., and had been cold drawn from 0.02-inch tantalum sheet. The crucible was 1 inch in diameter,

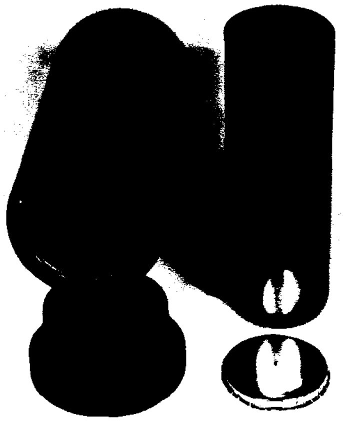


Figure 1. Tantalum crucible and lid, with graphite jacket.

3 inches high with 0.015 inch walls. The lid for the crucible was cold drawn in this laboratory from 0.001-inch tantalum sheet, using steel dies similar to those described by Ziegler, Speiser and Johnson (62), and was tapered slightly so that it fitted snugly in the crucible. The lid was held in position by placing the capped container inside of the graphite jacket shown at the left in Figure 1. Holes in both the tantalum and graphite lids allowed gases to escape and enter the tantalum crucible during the flushing operations.

The smaller tantalum crucible shown in Figure 2 was 10 mm high, 8 mm in diameter with 0.008 inch walls, and was the size used for two reductions of lanthanum chloride on a 250 milligram scale. These crucibles, obtained from the Eitel-McCullough Company, were cold drawn from 0.012-inch sheet. The lid, drawn from 0.001-inch tantalum sheet in this laboratory, was held in place by crimping it onto the 1.5 mm wide flange on the top of the crucible.

Since tantalum adsorbs large quantities of gases on its surface, it was necessary to degas the tantalum containers before use. This was accomplished by heating them to 1400°C in a vacuum by means of an Ajax-Northrup 6KVA high frequency converter equipped with a 3P2 furnace coil; the coil consisted of 26 turns of copper tubing, and was 3 inches in diameter and 3½ inches high. The vacuum

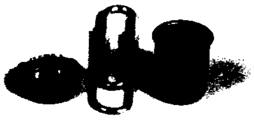


Figure 2. Small tantalum crucible and lid.

pumping line for this furnace consisted of a Welch Duo-Seal vacuum pump, Cat. No. 1405-J, obtained from the Welch Scientific Company, which served as the backing pump for a Martin No. M-40050 two stage, high speed mercury diffusion pump, purchased from the H. S. Martin Company; a cold trap between the pump and the furnace prevented mercury vapor from entering the furnace. In order to maintain a high pumping speed, 30 mm diameter glass tubing was the smallest used in the apparatus. A National Research Corporation type 507 ion gauge and a type 501 thermocouple gauge indicated the vacuum in the furnace. The crucibles were set in sintered magnesium oxide crucibles which served as radiation shields and eliminated the need for a packed granular or powdered insulation with an accompanying undesirable amount of degassing. A 50 mm diameter fused silica tube, closed at one end, served as the vacuum envelope for the furnace; this was attached to the Pyrex vacuum system by means of a 55/50 standard taper joint, the inner half of which was ground on the silica tube. Apiezon "W" high vacuum wax, purchased from the J. G. Biddle Company, effectively sealed the silica-Pyrex joint and permitted pressures lower than 10^{-5} mm Hg to be realized with this apparatus. A water jacket around the silica tube and joint prevented overheating the seal and the induction coil of the furnace. Since the smaller tantalum crucibles were not large enough in diameter to heat efficiently in the induction furnace, they were suspended in one of the larger tantalum crucibles for the degassing and firing operations. One atmosphere of argon was admitted to the apparatus before opening in order to reduce adsorption of reactive gases in the furnace.

Temperatures in the degassing and firing operations were measured by means of a disappearing filament type of optical pyrometer, Model No. 8622-C, obtained from the Leeds and Northrup Company. Although this instrument was not calibrated at the time it was used in this metallurgical work, a subsequent calibration, as will be discussed in the vapor pressure studies, showed that the upper half of each of the two lower scales of this instrument were not in serious disagreement with true temperature readings; these were the scales employed in the present work.

Techniques for loading and firing the crucibles

The reaction mixture in most of the reductions consisted of the rare earth chloride and calcium in the ratio to give the reaction

$$2\mathrm{RECl_3} + 3.3\ \mathrm{Ca} \longrightarrow 3\ \mathrm{CaCl_2} + 2\mathrm{RE} + 0.3\ \mathrm{Ca}.$$

In some of the experiments, the quantity of calcium varied slightly from this ratio.

The rare earth chloride for this reaction was placed in a "dry box" in an argon or nitrogen atmosphere, and a weighed sample was ground to a powder with a mortar and pestle. The calcium was added to the chloride and the two were mixed thoroughly by tumbling together in a sample bottle. The charge was then jolt-packed into the tantalum crucible which was capped and immediately loaded into the same vacuum apparatus used for the degassing operations. The apparatus was alternately evacuated and filled with purified argon several times, leaving one atmosphere of argon in the furnace. The argon was purified by passing it over uranium turnings held at 600°C as described by Newton (63). Recent studies in these laboratories by Svec (64), in which he employed the mass spectrometer to measure the amounts of impurities in the gas, have shown that the hot uranium removes all of the oxygen from the argon, but leaves 0.1% CO_2 and 0.5% N_2 in the gas. The charge was heated to the desired temperature in about two minutes, and for the larger crucibles this temperature was maintained for at least 13 minutes; agglomeration of the reacted charge was found to be complete in this time, but incomplete at 6 minutes. For the smaller charges, 5 minutes was found to be a sufficient holding time at the maximum temperature to permit consolidation of the product.

Since the rare earth metal was the highest melting material in the reaction, its melting point determined the temperature to which the crucible had to be heated to melt its contents; a holding temperature 100 to 200°C above the melting point of the metal product was chosen in each case. The temperature ranges were 975 - 1000°C for lanthanum, 1000 - 1050°C for praseodymium, 1375-1450°C for gadolinium, and 1375 - 1450°C for samarium.

On opening the crucibles, the products were found fused in the lower half of the container as shown in Figure 3. As the calcium chloride slag was leached off with water, the vigor of the resulting reaction and the quantity of hydrogen evolved indicated that a portion of the excess calcium was present in this layer; Cubicciotti's (65) description of the calcium-calcium chloride binary system is characteristic of this material. In the successful runs, removal of the slag revealed a slightly dished surface of the rare earth metal in the bottom of the crucible.

Vacuum melting and casting

Previous experience with rare earth metals, prepared by reducing the rare earth chlorides with calcium, had indicated that the product metal might contain from 1 to 5% calcium when an excess amount of this material was present

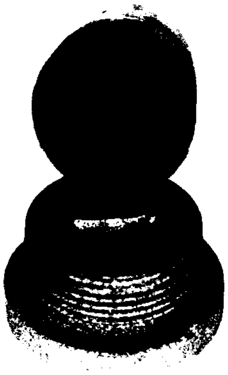


Figure 3. Fused reaction products in bottom of tantalum crucible.

in the reaction mixture. To remove this impurity from the rare earth metal, the leached reaction crucible and contents were reheated to 1400°C in the same furnace used to fire the charge, maintaining a vacuum of 10^{-5} mm of Hg or better during the run. Twenty minutes at this temperature was sufficient to reduce the calcium content to less than 150 ppm.

To remove the purified metal, the reaction crucible was inverted in the vacuum furnace at an angle of 10 degrees from the vertical over a tantalum mold as shown in Figure 4, and a vacuum of 10^{-5} mm Hg, or better, was pumped on the apparatus. The temperature of the furnace was then raised to 100°C above the melting point of the metal being cast; it was held at this temperature for 10 minutes permitting the metal to melt and then run down the side of the crucible into the mold. In cases where the mouth of the mold was small, a tantalum funnel directed the metal into the mold. Molds for the casting operation were formed by drawing or folding 0.001-inch to 0.005-inch tantalum sheet into the desired shape, with spot welds at strategic points to prevent the folded molds from collapsing from the hydrostatic pressure of the molten metal. Most of the mold could be peeled loose from the cast metal; any adhering tantalum was filed away.

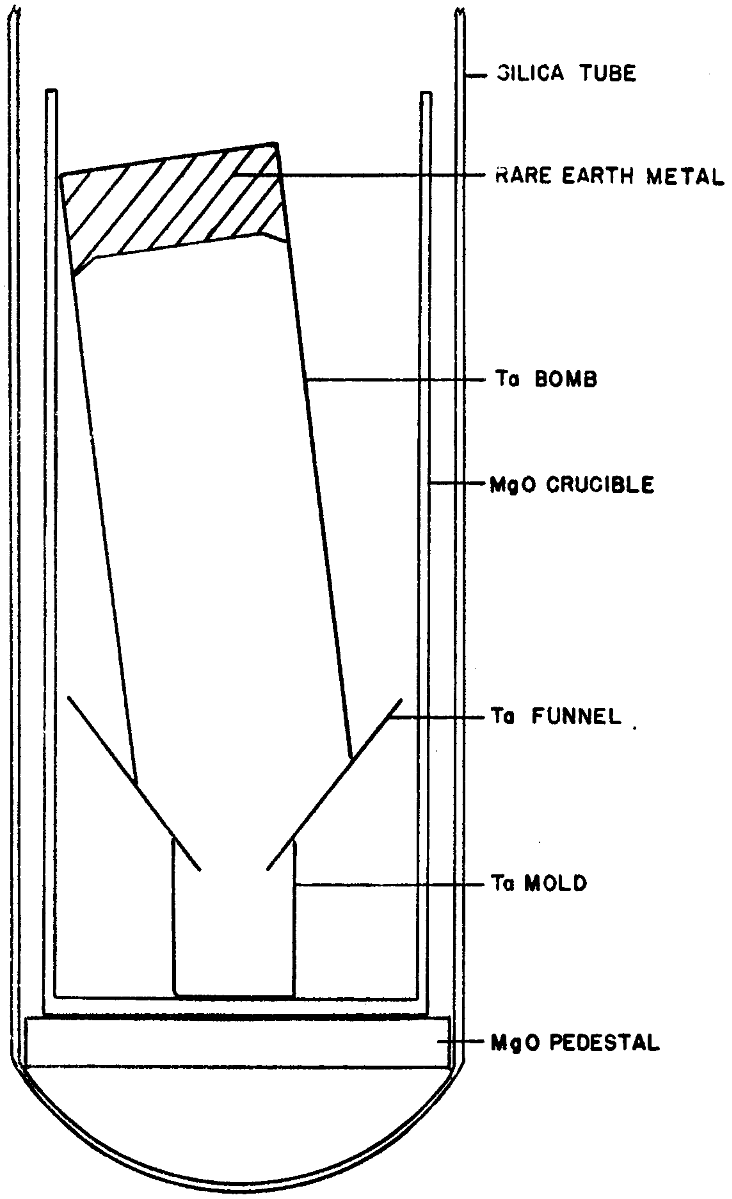


Figure 4. Assembly for casting rare earth metals.

Results

Lanthanum

The first attempt to prepare a rare earth metal in a tantalum crucible was a reduction of lanthanum chloride with calcium carried out on a scale to produce 10 grams of metal. A 5% excess amount of calcium was used in the charge to give the reaction:

$$2LaCl_3 + 3.15Ca \longrightarrow 2La + 3CaCl_2 + 0.15Ca.$$

The charge was placed in a tantalum crucible of the type shown at the right in Figure 1, but no cover was placed on the bomb and no graphite jacket was employed. After loading the degassed crucible in an argon atmosphere, the apparatus was evacuated for several hours and then fired in a vacuum of about 5 microns of Hg. Just as the crucible reached a barely discernable red color, the exothermic reaction took place with such violence that much of the contents was expelled from the crucible. However, after leaching away the slag, 1.5 grams of lanthanum remained as a thin layer on the bottom of the bomb. The temperature of the initiation of the reaction between the calcium and the lanthanum chloride is in qualitative agreement with the figure of 575°C reported by Derge and Martin (32) for the reaction between cerous chloride and calcium without a "booster" reaction.

To prevent loss of material from the bomb, the lid and graphite jacket shown at the left in Figure 1 were prepared. The first charge run in this assembly contained 33 grams of lanthanum chloride and 8 grams of calcium, representing a 10% excess amount of calcium. The loaded bomb was evacuated to 3×10^{-3} mm Hg; then filled to one atmosphere with purified argon; then heated to 950°C and held at this temperature for 15 minutes. After cooling for 3 hours, the bomb was opened and it was found that both the graphite jacket and the tantalum crucible were undamaged. The contents of the bomb were found to be fused in the lower half of the crucible with a light yellow layer of calcium chloride on top. This slag was leached away with water, revealing the smooth surface of the lanthanum metal. A yield of 20 grams of metal was obtained, representing an approximate 100% conversion of the chloride to the metal, within the limits of measurement. Using the technique described previously in this thesis, the metal was remelted and then cast in a circular tantalum mold.

Three additional reductions of lanthanum chloride, made using the same conditions as those of the above run, gave the same results. However, in trying to shorten the holding time of the bomb at the maximum temperature, one run was made in which the charge was held at 1000°C for 6 minutes. It was found in this case that although the reduction of the lanthanum chloride had been effected, the reaction products had not agglomerated. Two additional runs made with the bomb held at 1000°C for 13 minutes produced approximately 100% yields, so all subsequent reductions on this scale were held for this minimum time at the holding temperature.

To test the tantalum bomb technique on a smaller scale, the bomb and lid shown in Figure 2 were employed. A charge of 0.5 gram of lanthanum chloride with 10% excess calcium was loaded into the bomb and the lid, with a 1 mm diameter hole in the center, was crimped onto the vessel. A 5 minute holding time at 950°C was used to fire this bomb; during this period a considerable portion of the charge was expelled through the hole in the lid, partially accounting for a yield of lanthanum metal of only 40%. However, an identical charge was run under the same conditions, except that there was no hole in the lid; although there was some loss of the bomb contents by leakage through the crimped seal during the heating period, 255 milligrams of lanthanum metal were obtained, representing a 90% yield.

Analyses of lanthanum prepared by this technique show it to contain between 0.05% and 0.1% each of cerium, neodymium and praseodymium, no other rare earths or thorium and 150 ppm of calcium. Although no oxygen analyses have been made on this metal, Figures 5 and 6 indicate that it contains less oxygen than metal prepared using oxide refractories.

Praseodymium

One reduction of 33 grams of praseodymium chloride was carried out, employing the same conditions which were used with success with the lanthanum reductions, except that the bomb was heated to 1050°C for 13 minutes. After casting the resulting praseodymium into a tantalum mold, an over all yield of 99.5% was obtained. Analyses of this metal showed it to contain no detectable amounts of other rare earths or of tantalum and 150 ppm of calcium.

Gadolinium

Particularly interesting results were obtained in a reduction of gadolinium chloride containing 98% gadolinium, 1.7% samarium and 0.23% europium. Since attempts to prepare samarium metal by reducing samarium chloride with calcium have not been successful (11), it was of extreme interest in the present case to see if the samarium would be obtained as an alloy with the gadolinium or would be separated and remain in the slag. Due to the higher density of the gadolinium chloride, it was possible to

Figure 5. Cross-section of lanthanum cast in magnesium oxide crucible. La_2O_3 visible as needles. 7X

Figure 6. Cross-section of lanthanum cast in tantalum equipment. 7X

pack into the bomb a charge containing 42 grams of the chloride with the usual 10% excess amount of calcium. The bomb was heated to 1130°C for 15 minutes in the same manner as for the lanthanum reductions. After cooling, the slag was leached off, leaving 23.8 grams of metal in the bottom of the bomb, which represented a yield of 96%, based on the total amount of rare earth chloride in the bomb. Samples of the original rare earth chloride, the product metal and the slag were analyzed spectrophotometrically by the Analytical Section of the Ames Laboratory; the results are given in Table 1.

TABLE 1

RARE EARTH CONTENT OF PRODUCTS AND REACTANTS OF GADOLINIUM REDUCTION

	Sm/Gd ratio	Eu/Sm ratio
$GdCl_3$	1:50	1:100
Gd metal	*	*
Slag	1:1.2	1:100

* not detected.

Since the separation of small amounts of samarium from gadolinium is very tedious by the amalgam extraction process (66), this metallurgical method appears to be a more convenient method of obtaining pure gadolinium. Since europium follows along with the samarium in this process, this may provide a general method for separating these elements, and possibly ytterbium also, from the other rare earths.

Samarium

All of the reported attempts to prepare samarium metal by the reduction of samaric or samarous halides with calcium have been failures (11, 12). Since the reaction products from these experiments have not generally been well fused, the tantalum bomb technique offered an excellent opportunity to hold the bomb contents in a molten state long enough to attain a close approach to equilibrium conditions and to present a clearer picture of the reaction products. In an attempt to force the reduction of the samaric chloride with a large excess of calcium, 33 grams of the chloride were mixed with 9.3 grams of calcium to give the reaction:

$$2\ SmCl_3 + 3.6\ Ca \longrightarrow 3\ CaCl_2 + 2\ Sm + 0.6\ Ca.$$

A tantalum bomb was loaded with this charge and fired in the same manner as were the successful lanthanum reductions mentioned above, except that the bomb was held at 1290°C for 15 minutes. On opening the bomb, 85% of the reaction products were found to be in a fused condition at the bottom with the remainder present as semi-fused balls on the upper walls of the bomb. A very exothermic reaction, which began as soon as water was added to the bomb, became so violent as to expell the leaching solution from the bomb. The intensity of this reaction was probably due to the large amount of calcium metal which was dissolved in the slag. As leaching progressed, the solution became reddish-purple; the color, characteristic of the samarous ion, became very intense as the lower half of the bomb contents was dissolved in successive washings. Some of the dark red fused material in the bottom of the bomb was chipped out, and from its physical appearance, and the fact that the reddish color of its aqueous solution could be dispelled by the addition of hydrogen peroxide or acetone, it was apparent that it contained samarous chloride.

Discussion

The techniques described above for the preparation of lanthanum, praseodymium and gadolinium metals should be applicable to the preparation of other rare earth metals with only minor modifications for individual cases. For the smaller scale reductions, there is some chance that, unless a tightly fitting bomb cap were used, there would be a significant loss of the chloride before reduction has gone to completion. The fumes observed leaving the small-scale lanthanum bomb during firing are quite probably vapors of lanthanum chloride, as this material has an appreciable vapor pressure at the temperature employed (67). Since such losses would be very undesirable with the more scarce rare earths, a possible improvement in the technique would be to reduce rare earth fluorides instead of chlorides. The fluorides of the rare earths have much lower vapor pressures than do the other earth halides and, in addition, are not nearly as hygroscopic. The preparation of the fluorides may be accomplished by precipitation of the unhydrated salt from an aqueous solution followed by washing with absolute alcohol to remove adsorbed water (68), or preferably, by the hydrofluorination of the chlorides, hydroxides or carbonates (69). The melting points of these fluorides, as well as that of calcium fluoride, are higher than those of the chlorides; however, the higher melting points should not cause serious difficulty since they are within the range of temperatures used in some of the reductions already carried out.

The failure of calcium to reduce samaric or samarous chloride to metal reported in this thesis is in agreement with previous work (11, 12). In the light of the thermodynamic data on the halides of the elements which Brewer (35) has published since the work of this thesis began, the stability of the samarous chloride in the presence of calcium is not surprising. The free energy of formation of calcium chloride at 1500°K, as calculated from Brewer's data, is -143 Kcal. mole^{-1}, while that of samarous chloride at this same temperature is -149 Kcal. mole^{-1}; these data would not favor the reaction

$$SmCl_2 + Ca \longrightarrow CaCl_2 + Sm.$$

Brewer's free energy functions provide a basis on which to speculate about possible methods of preparing samarium metal; free energies of the samarous halides and the halides of lithium, sodium, potassium, calcium, magnesium and barium were calculated at 500°, 1000° and 1500°K, using Brewer's tables. Of all of the possible reactions involving the above temperatures and materials, only the reduction of samarous fluoride by lithium at 500°K and the reduction of samarous bromide by barium in the temperature range 500° to 1000°K show free energy changes favorable to the formation of samarium metal. However, the uncertainties in Brewer's data are so much larger than the free energy changes calculated for these reactions that the preparation of samarium metal in this manner does not appear too promising.

VAPOR PRESSURE STUDIES

Introduction

A search in the literature for data on the physical properties of the rare earth metals shows the lack of data in many cases; only estimates have been made of some properties, and for some others, discrepancies exist among the values reported. An example is the melting point of cerium; Ahmann's (12) value of 793°C taken on large samples of very pure metal is 18°C above that reported by Mazza (70) and 22°C below that given by Billy and Trombe (71); both of these other values were also taken on metals reported to be very pure. This situation is due not only to the lack of the pure metals but also to the reactive nature of these metals which makes it difficult to carry out accurate measurements on them with conventional apparatus. The metallurgical work described in the first part of this thesis has alleviated somewhat the lack of metals of high purity; this should permit more accurate determination of some of their physical properties.

As has been mentioned previously, the vapor pressures of metals is an important property from the practical as well as the theoretical standpoint. For the rare earths, any property which shows decided differences among these elements could conceivably be the basis for a method of separating these elements. Vapor pressure differences, should they exist among the rare earth metals, would provide a very direct way of effecting separations of mixtures of these elements. From the theoretical standpoint, the vapor pressures of the rare earth metals may allow a closer insight into the theory of metals as has been pointed out in the general introduction to this thesis. However, experimental methods in current use for measuring the vapor pressures of metals are not well adapted for use with the rare earths; the development and use of a technique for measuring the vapor pressures of metals, particularly the rare earth metals, is described in the following sections.

Historical

The methods which have been employed to measure the vapor pressures of metals have been discussed by Ditchburn and Gilmour (72) in their review, and by Speiser and Johnston (73) in a more recent paper. Of the many methods and techniques which have been devised, only two are in present use for materials of relatively low volatility; these are the Knudsen effusion method (13) and the Langmuir surface evaporation method (16).

Knudsen (13), in 1908, in his studies on the kinetic behavior of gases found that he was able to calculate the amount of gas flowing through tubes and orifices at low pressures by application of equations derived from the kinetic theory of gases. For very low pressures, he was able to formulate equations by which vapor pressures of the gas could be calculated if the rate of flow of gas through an orifice and the dimensions of the orifice were known. This molecular effusion method of determining the vapor pressures of materials was used in only a few studies in the period of about 10 years after Knudsen published his findings. This was in part due to the fact that the high vacuum necessary to use this method was not easily attained with the laboratory apparatus available at that time. Within the past thirty years, however, this method has been used widely to measure the vapor pressures of many materials, especially of metals. Harteck (74) used the method of molecular effusion to measure the vapor pressures of several metals including copper, silver and gold; in recent reviews (75) on vapor pressures of metals, his data are considered to be among the best.

One of the modifications of Knudsen's method which has been widely used is that in which a certain portion of the beam from the effusion vessel is collimated and condensed on a target. Knowing the geometry of the collimating system, the total amount of vapor leaving the sample vessel may be determined from the amount of material condensing on the target; the vapor pressure of the sample in the effusion vessel may be calculated from this information. The amount of material condensing on the target during exposures may be determined in several ways, including the following: 1) the weight gain of the target from an exposure is measured directly as in the work of Weber and Kirsch (76) on bismuth; 2) the original sample is made radioactive, and by measuring the radioactivity of the deposit on the target, the amount of the deposit is determined, as in the work of Phipps and co-workers (14), and in the study of the vapor pressure of silver by Schadel and Birchenall (77); 3) the deposit on the target is removed and its weight determined by chemical analysis, as in Rudberg's (78) work with calcium.

The principal advantage of this target technique is that a magazine can be placed in the apparatus to introduce new targets into the effusion beam without cooling down the furnace or breaking the vacuum; in the unmodified method as employed by Harteck (74) it was necessary to cool the apparatus to room temperature, remove the effusion vessel, weigh it and replace it in the apparatus for each exposure. Also, by placing a shutter in the beam, the time of the exposure in the target method can be measured accurately; in Harteck's studies it was necessary to apply corrections for the time required for the effusion vessel to reach the temperature of the exposure at the beginning of each run, and to cool down to room temperature again at its completion, since vapor was escaping from the vessel during these end periods.

Some of the objections which have been raised to the use of the target technique are; 1) an accommodation coefficient of one is assumed for the condensation of the vapor on the target; 2) much of the vapor pressure work with this method is done in temperature ranges in which an optical pyrometer is the best method of measuring the temperature, but to measure the temperature of the interior of an effusion vessel by this method, the target must have a hole in its center which introduces a possible source of error in an effort to compensate for the uncaptured portion of the collimated beam; 3) the construction of a collimating system and the determination of its geometry, allowing for any thermal expansion occurring during the exposures, introduces another possible source of error; 4) the radiochemical target assay technique is not always feasible due to unavailability of satisfactory radio isotopes of the sample material.

In 1913, Langmuir (16) published a paper on "The Vapor Pressure of Metallic Tungsten" in which he described a method of determining vapor pressures in which the rate of evaporation of material from a known surface area was the measured quantity. This method is particularly suitable for solids and has been widely used with the more refractory metals, since it is conveniently employed to vapor pressures as low as 10^{-8} mm Hg. Marshall and Norton (79) have recently determined the sublimation pressure of carbon by this method, and Speiser, Johnston and Blackburn (80) have employed it to study the vapor pressure of chromium. This last study illustrates one of the difficulties of the Langmuir method. In the liquid state, metals often wet their containers and creep outside of the space they would normally occupy thus presenting an inconstant surface area from which evaporation takes place with a corresponding uncertainty in the calculated vapor pressure. In this study of chromium, all of the data were taken below the melting point which limited the pressure range covered to 1.8×10^{-3} to 2.4×10^{-6} mm Hg. Another objection to the Langmuir method is that the accommodation coefficient of the vapor on its solid or liquid phase must be known.

The vapor pressures of copper and silver were first measured in the range below 10^{-2} mm Hg by Harteck (74) in 1928, employing the unmodified Knudsen technique. Although his results do not possess the precision shown in recent vapor pressure measurements, the heats of vaporization calculated from Harteck's data have been cited as being in excellent agreement with theory in Kelly's (75) review of thermodynamic properties of the elements. Marshall, Dornte and Norton (81) used the Langmuir method to determine the vapor pressure of copper; Brewer (82) has combined their data with those of Harteck to calculate the vapor pressure of copper which is in agreement with solid entropy data.

Mack, Osterhof and Kraner (83) obtained an approximate value for the vapor pressure of copper by measuring the amount of the metal transpired in a stream of nitrogen at 810°C; however, the uncertainty of this method of measuring vapor pressures at such low pressures, together with the fact that measurements were made at only one temperature have not warranted the inclusion of their data in an accurate evaluation of the vapor pressure data on copper.

Jones, Langmuir and Mackay (84) measured the evaporation rate of electrically heated filaments to calculate the vapor pressures of copper and silver; their vapor pressure figures are generally believed to be lower than the true vapor pressures of these metals.

In a recent study of the vapor pressure of silver by Schadel and Birchenall (77), the vapor pressure over both the liquid and solid phases of this metal were measured very accurately, and a plot of the logarithm of the pressure against the reciprocal of the temperature permitted the calculation of the heats of sublimation and vaporization with small probable errors. From these data, a calculation of a value of the heat of fusion of silver has been made which is in good agreement with that reported in literature. The technique employed was the radioactive sample-target modification of the Knudsen method; although the numerical data obtained are not given, the text and plots of data indicate that it is a very careful piece of work.

Ahmann (12) was the first to obtain experimental data on the vapor pressure of a rare earth metal; in his work with cerium, he employed the radioactive sample-target modification of Knudsen's method as described by Phipps and co-workers (14).

Brewer (82) in his compilation of the thermodynamic data of the elements, has given vapor pressure data for some of the rare earth metals, although only in the case of cerium was he able to base his figures on actual measurements; even these were indirect. With reference to the data for scandium, yttrium and lanthanum, Brewer states:

> No quantitative vapor pressure data are available and boiling points and vapor pressures were estimated. Although consistent with known thermodynamic data, all the temperatures . . . (corresponding to given vapor pressures) may be uniformly in error by several hundred degrees.

Theory and Method

According to kinetic theory, a gas consists of discrete particles moving in random straight paths until collision with other gas molecules or the walls of the container cause them to change the direction of their paths. If a thin-walled container filled with gas molecules is placed in a vacuum and a hole is cut in a side of the container, the gas molecules which are moving toward the hole will pass through it into the vacuum, unless they suffer collision inside the chamber before they reach the hole. The rate at which the molecules pass through an orifice is equal to the number of gas molecules, N, which in unit time strike an area of the vessel wall equal to the area of the orifice. The value of N may be calculated from the following equation developed from kinetic theory by Knudsen (85) and Loeb (86):

$$(1) \qquad N = 1/4\ n\bar{v} \text{ molecules per cm}^2 \text{ sec},$$

in which n is the number of molecules per cubic centimeter in the gaseous phase in the vessel and $\bar{v}$ is their arithmetical average velocity obtained from the Maxwellian distribution of velocities. Equation (1) may be converted to the more general weight-loss equation

$$(2) \qquad w = 1/4\ \frac{n\bar{v}Mat}{A},$$

in which M is the molecular weight, A is Avogadro's number, t is the time in which the weight loss, w, occurred and a is the orifice area. Since the gas in the vessel is at very low pressures in effusion studies, and in the case of most metals is also at very high temperatures, the value of n may be calculated from the perfect gas equation

$$(3) \qquad PV = RT$$

for one mole of gas. The relation is

$$(4) \qquad n = \frac{A}{V} = \frac{AP}{RT}$$

? in which A is Avogadro's number, V is 1 cubic centimeter, P is the pressure in millimeters of Hg and R is the gas constant in units of mm cm^3 mole^{-1} degree^{-1}. Substituting the numerical values in the above equation, it becomes

$$(5) \qquad n = 9.656 \times 10^{18} \frac{P}{T} .$$

The arithmetical average velocity $\bar{v}$ may be obtained directly from the Maxwell-Boltzman distribution of velocities as

$$(6) \qquad \bar{v} = \sqrt{\frac{8RT}{M}} = 14551 \sqrt{\frac{T}{M}} \text{ cm sec}^{-1} ,$$

in which M is the molecular weight of the gas. Combining equations (2), (5) and (6), we obtain for the equilibrium pressure of the gas in the effusion vessel

$$(7) \qquad P = 17.14 \frac{w}{at} \sqrt{\frac{T}{M}} .$$

In order for these equations to be valid, it is necessary that the molecules suffer no collisions among themselves as they pass through the orifice. This condition will be maintained if the mean free path of the molecules, $\underline{\lambda}$, is large compared with the diameter of the orifice, $\underline{d}$. By experiment, Knudsen (13) showed that if the ratio of $\frac{\lambda}{d}$ was greater than 10, the number of collisions between molecules was small enough to permit use of equation (7) to calculate the true vapor pressure of the material in the vessel. Schadel and Birchenall (77) have recently verified Knudsen's findings.

It is necessary to assume that the escape of the molecules from the effusion vessel will not disturb the equilibrium between the vapor and the condensed phase within the vessel. Speiser and Johnston (73) have examined the validity of this assumption with respect to the orifice size; they showed that if the ratio of the orifice area to the effective evaporating surface area is small compared to the accommodation coefficient, the number of molecules effusing does not seriously upset the equilibrium in the cell, and that the vapor pressure calculated from equation (7) is equal to the equilibrium pressure to a very close approximation.

Vacuum metallurgical operations with the rare earth metals had indicated that the vapor pressures of these metals were so low at their melting points that they would have to be heated well into their liquid range to develop pressures high enough to employ either the Knudsen effusion method or the Langmuir surface evaporation method to measure their vapor pressures. However, the Langmuir method would have been difficult to use with the rare earth metals, since in their liquid state they wet tantalum, molybdenum and other materials which might have been used to contain them in this work; this wetting presents an inconstant surface area from which evaporation would take place. Since it is necessary to know the effective evaporating surface in the Langmuir method, the above phenomenon introduces an undesirable uncertainty.

The more important techniques which have been employed to measure the vapor pressures of metals by the effusion method have been previously discussed in this thesis; all of them possessed some disadvantages which limited either their accuracy or their applicability in use with the rare earth metals. The radioactive tracer technique employed by Ahmann (12) to study the vapor pressure of cerium would have been inconvenient to use in the case of lanthanum, since the available radioisotope of this element required such radiation safeguards as to make the operations cumbersome; in addition, its relatively short half-life of forty hours would have permitted the samples to decay through several half-lives before the radiochemical assaying of the targets could be completed.

In any of the effusion methods which employ a collimating system and targets to obtain the sample, the view into the effusion vessel through the orifice is usually obstructed by part of the sample-taking apparatus. At the high temperatures of much of the vapor pressure work with metals, the optical pyrometer provides the best means for measuring the temperature of the effusion vessel. To obtain accurate readings with this instrument it is desirable to sight into the vessel through the orifice to take advantage of the near-black body conditions which prevails. This is not easily accomplished with a target and collimating system over the effusion vessel; however, Brewer and Mastick (87) have managed to overcome this difficulty by employing washer-shaped targets which provide a hole through which to sight the optical pyrometer. This requires a calculation to take into account the amount of effused vapor lost to the target through this hole. Another general objection to the target technique is the necessity of designing the apparatus to permit cooling of the targets to insure an accommodation coefficient of near unity.

The direct measurement of weight losses for each exposure is a highly desirable method of employing the effusion technique to measure the vapor pressures of metals;

as in the work of Harteck (74), the weight losses are obtained directly without employing collimating systems or analytical methods which introduce chances for errors. Also, the unobstructed view into the effusion vessel permits accurate temperature measurement by means of an optical pyrometer; since the methods did not measure a sample which had condensed on a target, the accommodation coefficient was not a factor in the calculation of the vapor pressure from the data. The one serious disadvantage of this procedure for the direct measurement of weight losses was that the apparatus must be opened and the vessel removed and weighed after each exposure; this was very time consuming since the apparatus had to be re-evacuated and degassed after opening for each measurement. Also, to employ this technique in the present work, it would have been necessary to protect the rare earth metals from attack by air and moisture during the weighing operations, a procedure requiring undesirably complex equipment and manipulations.

A very desirable technique for measuring the vapor pressures of metals at high temperatures would be one in which the total amount of vapor escaping from an effusion vessel could be measured without removing the vessel from the vacuum apparatus or cooling the sample vessel. Such a technique was devised in the present work, employing a magnetically controlled quartz fiber microbalance of the type built originally by Dr. I. B. Johns at Iowa State College, and later further developed and described by Edwards and Baldwin (88). The construction, use and theory of this type of balance has been discussed in detail by the above authors; one of its features that is particularly pertinent to the present work is that it may be operated inside a closed apparatus, with the actual balancing operations and readings being made on equipment that is entirely external to the apparatus. The balance built for this work will be described later in this thesis; in use, an effusion vessel containing the sample was suspended in an induction furnace from one end of the balance beam which was counterbalanced by a tare weight on the other end of the beam as shown in Figure 7. The vessel was heated to the desired temperature and weighed; after a measured interval of time at this temperature, the vessel was weighted again; the weight difference represents the amount of vapor which had escaped from the vessel. From these data and the dimensions of the effusion orifice, the vapor pressure of the sample material was calculated from equation (7).

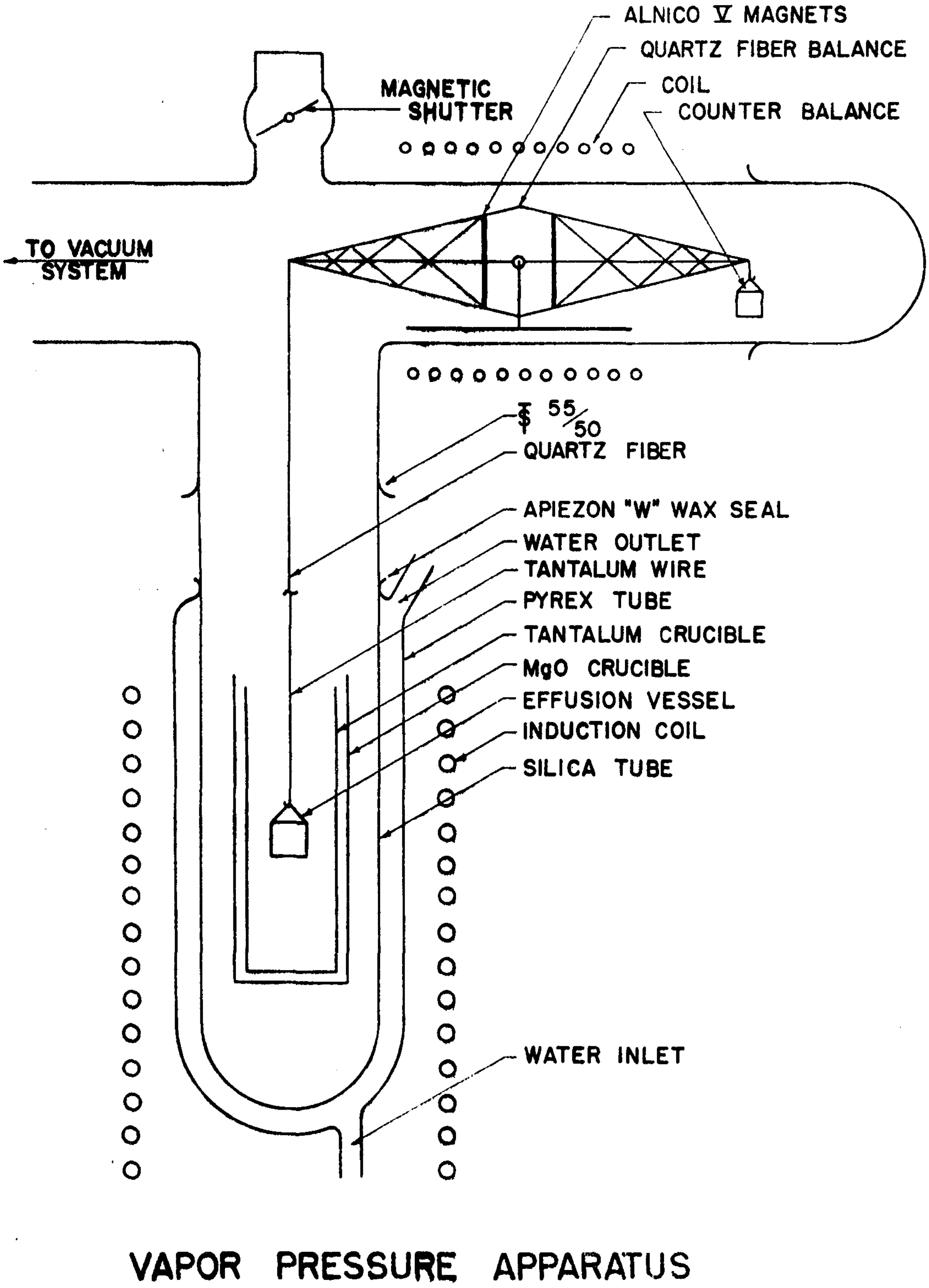


Figure 7. Vapor pressure apparatus.

Procedure

To prepare the vapor pressure apparatus for a run, a tare, weighing within 10 milligrams of the sample to be used, was placed in the empty effusion vessel which was counterbalanced so that nearly full current strength in the coil of the balance was required to hold the effusion vessel up in the furnace. During the actual runs, weight losses from the effusion vessel could be followed from full current down to zero coil current, and by reversing the polarity of the current, back to full current.

To degas the apparatus, the tare was removed from the effusion vessel, the apparatus was sealed and evacuated to a pressure of 10^{-4} mm Hg or less. The induction furnace was turned on and the temperature was gradually raised to 1500°C, with the pressure maintained at 10^{-4} mm Hg or lower. The temperature was held at 1500°C until the vacuum reached 10^{-6} mm Hg, when the furnace was turned off and allowed to cool to room temperature. Argon, purified as described in the metallurgical section of this thesis, was admitted to the apparatus to atmospheric pressure, the furnace was opened, the effusion vessel was removed, and the apparatus was re-sealed and re-evacuated while the effusion vessel was being loaded and sealed. About 10 minutes were required to load, seal and replace the effusion vessel in the apparatus; the metal sample was either in an argon atmosphere or in a vacuum over half of this time. With the loaded effusion vessel in place, a pressure of 5×10^{-5} mm Hg or lower was maintained on the apparatus as the furnace was degassed by a gradual warming; this was accomplished by applying power to the induction coil for slowly increasing periods of time as the degassing progressed. As soon as the furnace could be operated continuously in the desired temperature range, with the pressure still 5×10^{-5} mm Hg or lower, the balance was set at its null position and 10 milligrams of the sample was effused out of the vessel at a temperature about 50°C above the highest temperature at which data were to be taken. The above procedure served to remove any of the more volatile impurities in the sample, and also gave a rough check on the vapor pressure of the metal at the temperature employed. In addition, the apparatus was purged of adsorbed gases; after this treatment, the vacuum was maintained below 5×10^{-6} mm Hg for the vapor pressure runs.

To make a vapor pressure measurement, the temperature controller and furnace were adjusted to maintain the desired temperature. The furnace was turned off to set the balance, since the field from the induction coil disturbed the balance and prevented accurate readings being made of the null position. The balance was set by adjusting the current through the balance coil, which required from 30 to 60 seconds. In the meantime, the interior of the furnace had cooled several hundred degrees so that about 5 minutes were required to reheat it to the operating temperature. The furnace was then again turned off, the balance was reset and the furnace was turned on again, all within a period of about 10 seconds. The timing of the run was started when this second balance setting was made, and although the temperature dropped slightly during the resetting, no serious error was introduced since the desired temperature was reattained within 30 seconds. At the end of a run, the approximate balance setting was calculated from the vapor pressure equation (7), using the expected value of the vapor pressure; the balance could be set within 15 to 20 seconds after turning off the furnace.

In the work with copper and silver, the temperature in the furnace was recorded continuously on the chart of the temperature recorder-controller. The furnace temperature was checked with a precision potentiometer several times during each run. For the studies on the rare earth metals, optical pyrometer readings were made at no set intervals, although at least four readings were made during each run. The recorder on the temperature controller indicated whether or not prohibitively large power fluctuations had occurred between optical pyrometer readings; when such fluctuations were in evidence, the data from the run were rejected.

The quantity of metal effused in any series of runs was never more than 20% of the original sample, thus making certain that all of the measurements had been made on a sample of essentially the same composition.

Apparatus

Effusion vessels

Tantalum effusion vessels were employed in all of this work, since previous investigations in this laboratory have shown that the rare earth metals do not alloy with tantalum at temperatures up to 1500°C; tests made in the course of this work showed no tantalum detectable in lanthanum which had been held at 1650°C for several hours. Also, vapor pressure studies on cerium carried out in this laboratory by Ahmann (12) showed no tantalum contamination in the cerium. The preliminary work in which the apparatus and method were tested, by measuring the vapor pressures of copper and silver, utilized tantalum vessels obtained from the Eitel-McCullough Company. These vessels, shown in Figure 8, were cold-drawn from 0.006-inch sheet, and had a flange 1 mm wide on the top onto which the lid was crimped in a die. The lid was a shallow cup drawn from 0.003-inch tantalum sheet. Orifices of less than 0.75 mm diameter were made in these lids by first piercing the tantalum sheet with a tungsten point and then burnishing down any "dimpled" metal using #0 metallographic emery paper. The resulting hole was re-broached and re-burnished several times, producing a thin-walled orifice of very uniform diameter. Larger orifices were prepared by clamping

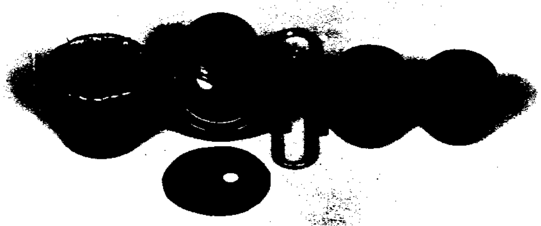


Figure 8. Tantalum effusion vessels.

the tantalum sheet between two pieces of ¼-inch brass sheet, and then drilling through the jig with a carbon steel drill of the desired size; the resulting hole was burnished to remove any burrs. A Bausch and Lomb monocular metallographic microscope with a filar eyepiece, calibrated with a stage micrometer, was used to measure the diameters of the smaller orifices. The larger orifices, which extended beyond the field of the microscope, were measured with a pair of "go -- not go" gauges turned from brass rod and measured to within 0.0005 inch with a Brown and Sharp micrometer caliper, Model 19.

The large effusion vessels shown in Figure 8 were used for the rare earth metals; they were obtained from the Fansteel Metallurgical Corporation. These had been cold-drawn and cupped from 0.010-inch sheet tantalum. Closure of the vessels was effected by placing the lid, made from 2 mil tantalum sheet, in the cupped flange, and crimping the edge down over the lid. It was found that this seal did not prevent creeping of the molten rare earth metals through it to the outside of the vessel, resulting in erroneous data. To close this seal effectively, the apparatus shown in Figures 9 and 10 was devised to electrically weld the lids onto the vessels. The vessel with the lid crimped on was placed in the lower half of the apparatus in the brass cup which was connected to the

Figure 9. Argon atmosphere welder
for tantalum vessels.

Figure 10. Argon atmosphere welder showing welded vessel in place. Connection for flushing with argon is at left.

positive terminal of a 250 volt DC source. The cap, containing a cored carbon electrode, was set in place on the apparatus which was then evacuated and flushed with argon several times, leaving one atmosphere of argon in the system. The cored carbon was connected to the negative terminal of the D.C. supply, which was set with a ballast to supply a current of 16 amperes. The arc was initiated by touching one of the electrical leads with a Tesla high frequency coil; the weld was then effected by rotating the cap containing the carbon electrode around the crimped seal. A weld made with this apparatus is shown at the left in Figure 8.

Furnace and vacuum apparatus

The effusion vessel was heated to the desired temperature by suspending it in an induction furnace shown diagrammatically in Figure 7. The heater in the furnace was a tantalum cylinder 27 mm in diameter, 76 mm high, with 0.40 mm walls, obtained from the Fansteel Metallurgical Corporation. This cylinder was contained in a sintered magnesium oxide crucible 35 mm inside diameter, 102 mm high with 1.6 mm walls, and covered with a lid containing a 10 mm diameter hole through which passed the 10 mil tantalum wire on which hung the effusion vessel. The space between the tantalum cylinder and the magnesium oxide crucible was packed with bubble zirconia D, size 36 F, obtained from the Norton Abrasive Company. This refractory was chosen for this purpose for its inertness, its low thermal conductivity and its observed tendency to degas easily in the vacuum system. The magnesium oxide crucible was suspended in the apparatus by two 20 mil tungsten wires which hung from two glass hooks in the upper portion of the vacuum chamber, allowing the furnace to be assembled with the effusion vessel in place, and the silica vacuum envelope to then be slipped into position.

The vacuum pumping equipment consisted of a Welch Duo-Seal pump, Model #1405H serving as the forepump for a 3 stage all-glass oil diffusion pump, model #GF-25W, operating with Octoil S as the pumping fluid. A National Research Corporation thermocouple gauge, Model No. 501, between these pumps indicated when the forepump had the system sufficiently evacuated to permit operation of the oil diffusion pump. This pump as supplied by the manufacturer was modified in that the 28 mm diameter high-vacuum line and water cooled trap were replaced by a 80 mm diameter pumping line, 66.0 cm long, including a total obstruction cold trap. From Dushman's (89) calculations this change would serve to increase the pumping capacity of the apparatus to permit nearly full use of the 23 liter per second pumping speed of the oil diffusion pump at 10^{-3} mm.

A National Research Corporation type 507 ion gauge on the furnace side of the cold trap indicated the pressure in the main body of the apparatus.

The silica tube containing the furnace was connected to the Pyrex portion of the apparatus by means of a 55/50 standard taper joint. The inner joint of this connection was ground on the silica tube by means of a bronze sleeve in which an outer half of a 55/50 standard taper had been turned in a lathe. The grinding compounds employed in this work were the Carborundum Company's grades R7, R5 and H440.

As shown in Figure 7, a pyrex envelope sealed around the silica furnace tube with Apiezon "W" vacuum wax allowed a heavy stream of water to run through the annulus between these tubes, to prevent both the vacuum seal and the induction coil from overheating.

A 6 killowatt Ajax-Northrup high frequency converter of the tilting arc pot type supplied the power to the furnace coil in use, which was either a 3P1, 3P2 or 3P4 furnace as designated by the Ajax Electrothermic Corporation.

Balance

The balance used to measure the weight changes of the effusion vessel was a magnetically controlled quartz fiber balance of the type described by Edwards and Baldwin (88), except that it was made larger to handle the relatively heavy load of approximately 4 grams; it was correspondingly more rugged and less sensitive. The beam of the balance was constructed of 0.8 mm quartz rod which was drawn from 3 mm rod in an oxygen-gas flame; two Alnico V magnets 1.6 mm in diameter and 19.2 mm long were mounted on the beam in quartz tubes as shown in Figure 11. In sealing the magnets to the balance beam, they became heated enough to demagnetize them slightly. To restore them to their original strength, the assembled balance, with the beam welded to the supporting cradle by 2 mm quartz rods, was placed between the poles of an electromagnet, and a magnetizing force of 10,000 ampere turns was applied across the balance. This was considerably more magnetizing force than the 4000 to 6000 ampere turns per linear inch recommended by Sanford (90) for these magnets. Stabilization of the magnet was accomplished by aging the balance several hours in a demagnetizing field of about 300 ampere turns. The main suspension fiber and two terminal suspension fibers, not shown in Figure 11, were 80 microns in diameter and were attached to the balance using an oxygen-gas microtorch similar to that described by Strong (91).

The coil which was used to restore the balance to its null position consisted of 3000 turns of #24 B&S gauge Formvar insulated copper wire wound on a soft brass spool

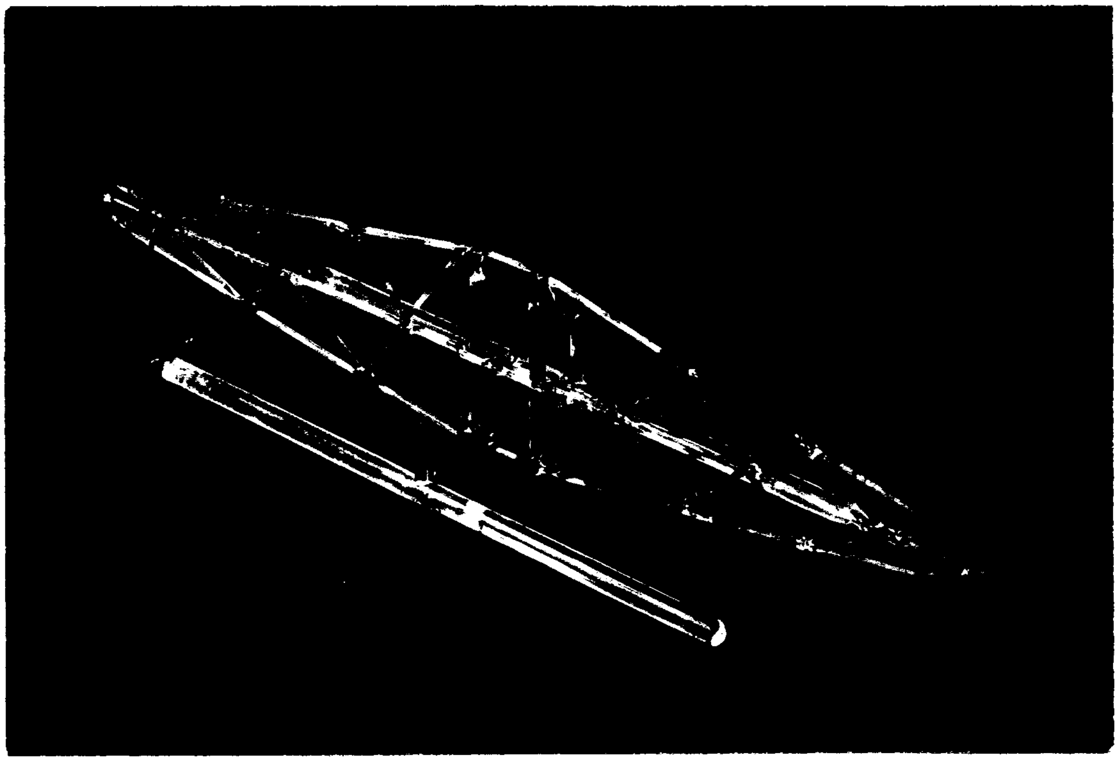


Figure 11. Quartz beam of balance. Alnico V magnets are in vertical quartz tubes at the center of the beam.

80 mm long and 47 mm in diameter. This coil was positioned on a 42 mm diameter arm of the vacuum envelope so that when the balance was placed in the center of the coil, one bow of the balance was directly over the center of the furnace as indicated in Figure 7. The current controlling and measuring circuit for this coil contained, in series, a 0-200 DC milliammeter, a reversing switch with a dead center position, a Marma decade resistance box, a 50 ohm Helipot potentiometer, a 6 volt battery and a standard resistor consisting of 370 cm. of #22 B&S gauge constantin wire. Constantin wire was used for this resistor since it has such a low temperature coefficient of resistance that fluctuations in room temperature would not affect the balance readings to a measurable extent. The balance was brought to a null position, as observed by means of a Gaertner Scientific Company microscope, Model No. M101, with a 10x eyepiece and 38 mm objective, by adjusting the decade resistance box and Helipot to pass the proper current. The current was determined by measuring the potential drop across the constantin resistor, using the same potentiometer and auxiliary equipment as was employed to calibrate the optical pyrometer.

The balance was calibrated by observing the change in coil current required to restore the balance to a null position after adding a platinum weight to one side of the balance. The weights used for this work were from a set of No. 1000 assay weights obtained from the W. M. Ainsworth and Sons. The sensitivity of the balance in terms of milliamperes/milligram was constant within 1% for a range of pan loads from 0 to 4 grams. The volt-weight factors for converting potentiometer readings directly into weight readings varied from 1.01 millivolts per milligram to 1.06 millivolts per milligram, depending on the particular suspension fiber being used. By varying the coil current from full strength (about 120 milliamperes) to zero, and then reversing the current direction and increasing it again to full strength, a weight change of over 0.5 gram could be determined without adding any weights to the balance. The sensitivity of the balance was $\pm 2 \times 10^{-5}$ gm.

Temperature measurement and control

For the studies on copper and silver, the temperature of the furnace chamber was first measured with a platinum/platinum-13% rhodium thermocouple which had been calibrated before use by observing the emf of the couple at the melting points of pure copper, pure silver and the 28% copper-72% silver eutectic. It was found however that the thermocouple became contaminated in the furnace even when it was protected by both ceramic and metal thermocouple protection tubes, so that calibrations made after the couple had been used only a short time in the copper or silver studies showed that the temperature-emf curve of the couple had shifted as much as 130°C. Fortunately, it was found that chromel-alumel thermocouples were not seriously affected by the above conditions; the calibration curves shifted less than 4 degrees after 1 week of continuous use.

Precautions were taken to be certain that the thermocouple indicated the true temperature of the effusion vessel. Two thermocouples were placed in the furnace cavity on the axis of the inductor tube with their junctions about 1.5 cm apart, and their position as a unit was varied up and down in the inductor until a location was established where the two couples indicated the same temperature over a range of furnace temperatures. Then a dummy effusion vessel with a thermocouple junction inside was substituted for the upper thermocouple junction; it was found that the two thermocouples still indicated the same temperature to within 2°C. This same position of vessel and thermocouple was maintained throughout the copper and silver studies. The emf from the thermocouples was measured with a Rubicon portable precision potentiometer, model No. 2702.

Since the temperatures encountered in the work with the rare earth metals were generally above the range of the chromel-alumel thermocouple, and since the platinum/platinum-13% rhodium couple had proved to be too easily contaminated by metal vapors to be reliable, an optical pyrometer was used to measure the temperature of the effusion vessel in these studies. The instrument employed for this work was a Leeds and Northrup disappearing filament type optical pyrometer, Model No. 8622-C, possessing three ranges. All of the temperature measurements in the rare earth studies were made on the middle, or "High" scale, which covered the indicated range of 1075°C to 1750°C. This instrument was calibrated by reading the brightness temperature of a standard tungsten ribbon filament lamp supplied and calibrated by the standards department of the General Electric Company. The lamp operated off of a 6 volt battery; to determine its temperature, the current through the bulb was measured to within 1 part in 6000 by observing the potential drop across a standard 0.001 ohm resistor placed in series with the standard lamp. This resistor was held at 25°C ± 0.25°C by immersing it in a mineral oil bath thermostated by means of a Precision Merc-merc thermoregulator and a Precision Scientific Company relay and heater, catalog No. 6535. The potential drop across the 0.001 ohm resistor was measured with a Rubicon Type B high precision potentiometer whose slide wire had been standardized against a standard cell, which in turn had been compared with a standard cell whose emf had been certified by the U. S. Bureau of Standards. A Rubicon Model No. 3402 galvanometer was used with the potentiometer.

A magnetically controlled shutter covered the optical pyrometer observation window when no temperature readings were being made; this procedure prevented fogging of the window by the molecular beam from the effusion vessel. Temperature readings were taken on the bottom of the effusion vessel by sighting through the orifice, thus insuring a close approach to black-body conditions.

The temperature controlling apparatus consisted of a Brown mechanical potentiometer, model 113661x29, and a solenoid which was actuated by the "on-off" controlling portion of the potentiometer. The solenoid was connected to the output control mechanism of the high frequency oscillator, as shown in Figure 12, and was set with the limit screws so that when the solenoid was not actuated, the output control arm was pulled to the left by the retractor spring, thereby decreasing the output of the oscillator, and causing the temperature of the furnace to fall slightly below the desired setting. When the solenoid was energized, the output of the oscillator was increased and the tempera-

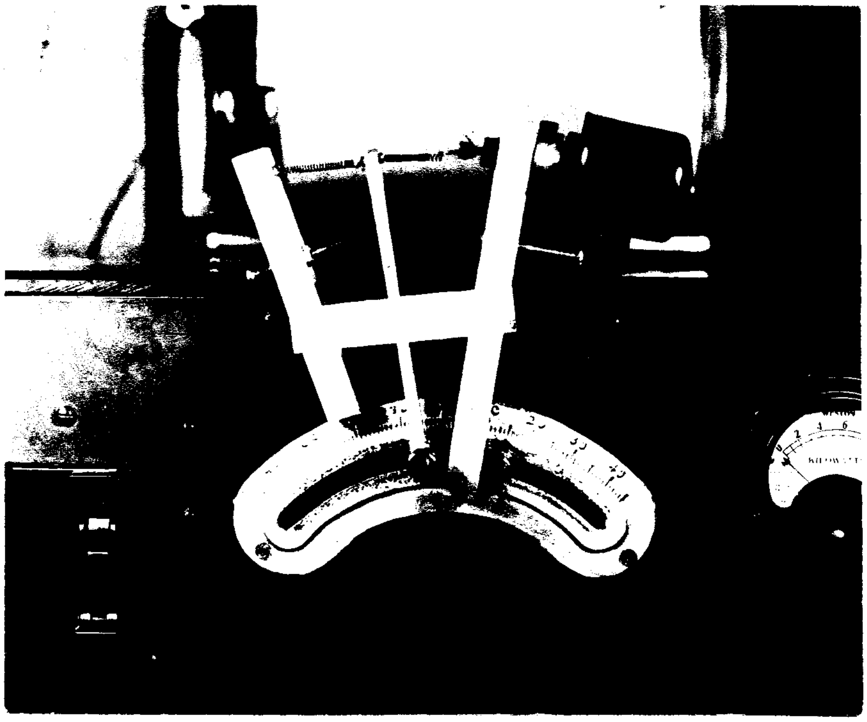


Figure 12. Temperature regulator in place on power source for induction heater.

ture of the furnace increased to slightly above the desired setting. In the copper and silver studies, a thermocouple in the furnace was connected to the mechanical potentiometer to provide direct temperature control of ± 3°C. Since the temperatures required for the work with the rare earth metals were above the temperature range of the chromel-alumel thermocouple, indirect control of the furnace was maintained by placing a second induction coil in series with the furnace coil. A small platinum crucible was placed inside of a magnesium oxide crucible in this second coil; by adjusting the position of the platinum crucible along the axis of the coil, it could be held in the temperature range 600° to 1000°C with the vapor pressure furnace operating at 1300° to 1700°C. The chromel-alumel thermocouple of the recorder-controller was placed in this second reference coil, and, by controlling the temperature in this smaller furnace, the temperature of the vapor pressure furnace was controlled to ± 5°C.

Results

The vapor pressures of silver and copper were measured in order to test the vapor pressure apparatus and method described in previous sections of this thesis. These metals were chosen for several reasons: 1) agreement is generally good among the various literature values of the vapor pressures of these elements; 2) their vapor pressures are reasonably close to those of the rare earth metals as reported in literature; 3) the metals are relatively easily obtained in the pure state; 4) the metals do not alloy with tantalum at the temperatures at which the vapor pressures are measured. To increase the rigor of the test, orifices of different sizes were employed.

Copper

Data obtained in the vapor pressure studies on copper are given in Table 2. For the E series of experiments, the sample was 0.5 gram of pure electrolytic copper obtained from the J. T. Baker Chemical Company; the orifice of the effusion vessel was 0.203 cm in diameter.

Evaluating the constants in the vapor pressure equation

$$(7) \qquad P = 17.14 \frac{w}{ta} \sqrt{\frac{T}{M}} ,$$

TABLE 2

VAPOR PRESSURE OF SILVER

Run	Temperature °K	Time Secs.	Wt. loss Mg.	$\frac{1}{T^{\circ}_K} \times 10^{-4}$	-log P
D1	1312	3600	13.37	7.62	2.16
D2	1275	12420	21.37	7.84	2.50
D3	1238	2250	2.32	8.08	2.73
D6	1187	7200	2.34	8.43	3.24
E1	1313	1980	1.74	7.62	2.10
E3	1215	33120	5.32	8.23	2.85
F1	1334	3780	2.11	7.50	2.07
F3	1277	3900	1.03	7.84	2.41

TABLE 3

VAPOR PRESSURE OF COPPER

Run	Temperature °K	Time Secs.	Wt. loss Mg.	$\frac{1}{T^{\circ}_K} \times 10^{-4}$	-log P
F1	1477	10800	2.53	6.77	2.66
E2	1383	25740	4.26	7.24	3.36
E3	1393	3180	0.75	7.19	3.24
E4	1416	3960	1.39	7.06	3.09
E5	1436	6000	2.74	6.96	2.94
E6	1456	7080	5.92	6.87	2.67
E7	1478	5760	5.34	6.77	2.63

the particular equation for this series of exposures is

$$P = 5.297 \times 10^{2} \frac{w}{t}\sqrt{\frac{T}{M}}.$$

The ratio of the mean free path of copper atoms to the orifice diameter in these exposures was never less than 18, which is well over the value of 10 which Knudsen (13) found to be the minimum allowable to prevent hydrodynamic flow of gas at the orifice instead of true effusion. However, to be certain that a variation in the orifice area would not affect the results, one exposure, F1, was made with a 0.092 cm diameter orifice, using 0.5 gram of pure electrolytic copper as the sample. The vapor pressure equation for this exposure is

$$P = 2.58 \times 10^{4} \frac{w}{t}\sqrt{\frac{T}{M}}.$$

The logarithm of the calculated vapor pressure values for the above experiments are plotted against the reciprocal of the absolute temperature in Figure 13; the continuous straight line through the points is based on the following equation calculated by the method of least squares

$$\log P = \frac{-15441}{T} \pm \frac{655}{T} + 7.835 \pm 0.453.$$

Included in the figure are the data of Harteck (74), and of Marshall, Dornte and Norton (81) for the same temperature range used in this thesis; the broken line represents the data presented by Brewer (35) and Dushman (89) in their

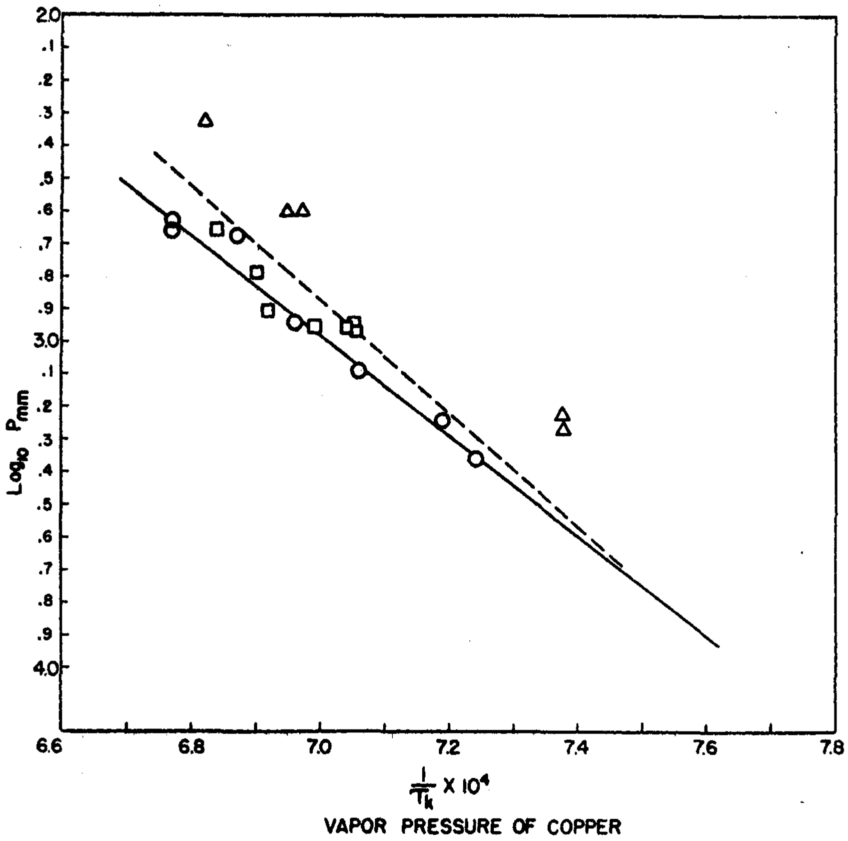


Figure 13. ○ This thesis.
◻ Harteck (74).
△ Marshall, Dornte and Norton (81).

reviews on the vapor pressures of metals. The heat of vaporization of copper calculated from the slope of the continuous line, is -70.6 ± 3 Kcal. $mole^{-1}$; the extrapolated normal boiling point is 3116 ± 300°K.

Silver

Pure silver was prepared by precipitation from a solution of silver nitrate, reagent grade of the General Chemical Company, by the addition of a solution of reagent grade ammonium formate, also obtained from the General Chemical Company; the procedure followed was that of Briscoe and Robinson (92). In each of the experiments on silver, 0.5 gram of metal was placed in the effusion vessel. Orifices of 3 different sizes were employed in these silver studies; the equations for the exposures are:

Series D, orifice diameter 0.203 cm,

$$P = 5.297 \times 10^2 \frac{W}{t} \sqrt{\frac{T}{M}} ;$$

Series E, orifice diameter 0.0919 cm,

$$P = 2.59 \times 10^3 \frac{W}{t} \sqrt{\frac{T}{M}} ;$$

Series F, orifice diameter 0.0739 cm,

$$P = 4.010 \times 10^3 \frac{W}{t} \sqrt{\frac{T}{M}} .$$

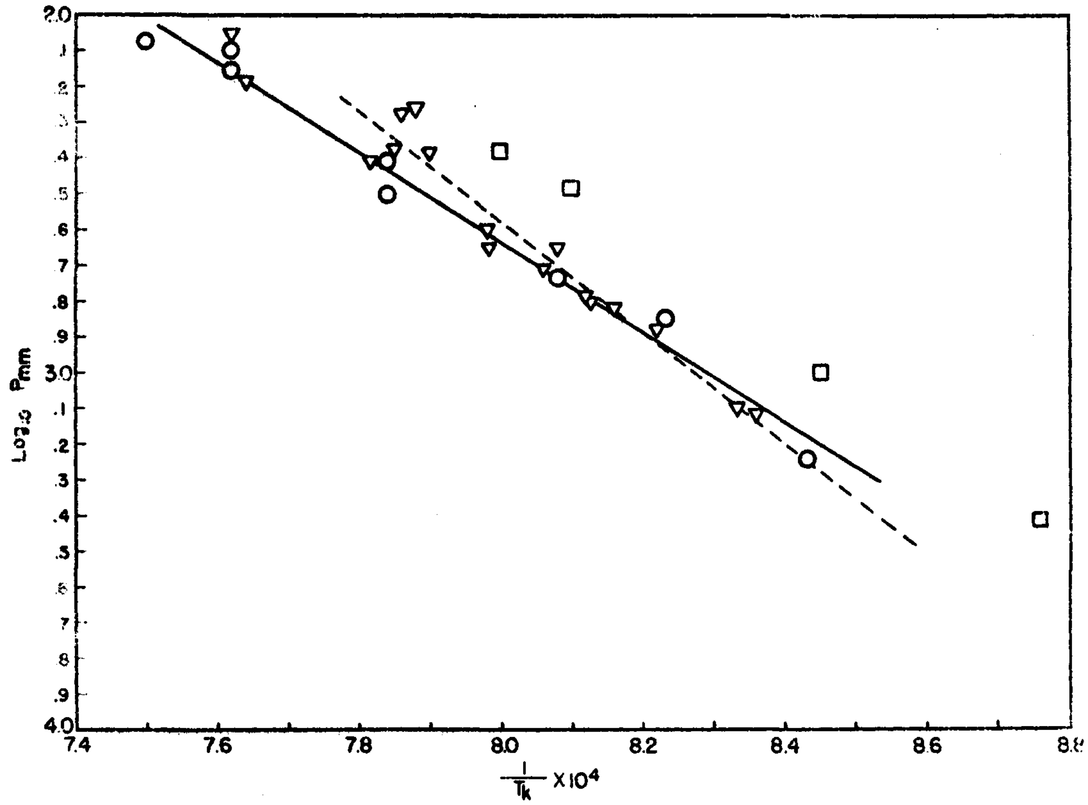
The data obtained in these experiments are given in Table 3. The logarithm of the calculated vapor pressure values are plotted against the reciprocal of the absolute temperature in Figure 14; the continuous straight line through the points is based on the following equation calculated by the method of least squares

$$\log P = \frac{-12493}{T} \pm \frac{652}{T} + 7.355 \pm 0.514 .$$

Included in Figure 14 are the data of Harteck (74) and of Schadel and Birchenall (77) for the same temperature range covered in this thesis. The broken line represents the data presented by Brewer (35) and Dushman (89) in their reviews on the vapor pressures of metals. The heat of vaporization of silver calculated from the slope of the continuous line is -57.2 ± 3.0 Kcal. mole^{-1}; the normal boiling point is 2790 ± 290°K.

Lanthanum

Samples of lanthanum were prepared by the technique described in the first section of this thesis. Considerable difficulty was experienced in obtaining a satisfactory arrangement of the furnace coil and the effusion vessel. In some preliminary experiments, the lid of the vessel was about 5°C cooler than the bottom; as a consequence, some of the sample condensed on the under side of the lid, partially covering the orifice and creeping onto the top of the lid to produce erroneous data. By lowering the effusion vessel in the furnace, a position was found at which the tempera-



VAPOR PRESSURE OF SILVER

Figure 14. ○ This thesis.
▽ Harteck (74).
□ Schadel and Birchenall (77).

ture of the bottom of the vessel was one or two degrees cooler than the top; this arrangement was used to obtain the data given in Table 4. The series of exposures A, B, C and F were all made with 0.243 cm diameter orifices for which the vapor pressure equation is

$$P = 3.745 \times 10^2 \frac{w}{t}\sqrt{\frac{T}{M}} \ .$$

To be certain that the 0.243 cm diameter orifices were not too large, a 0.180 cm diameter orifice was employed in the series E exposures, for which the vapor pressure equation is

$$P = 6.740 \times 10^2 \frac{w}{t}\sqrt{\frac{T}{M}} \ .$$

The logarithm of the calculated vapor pressure values of Table 4 are plotted against the reciprocal of the absolute temperature in Figure 15; the continuous straight line through the points is based on the following equation calculated by the method of least squares

$$\log P = \frac{-170025}{T} \pm \frac{478}{T} + 6.538 \pm 0.395$$

The heat of vaporization of lanthanum calculated from the slope of this line is -78.0 ± 2.2 Kcal. mole^{-1}; the extrapolated normal boiling point is 4650 ± 500°K.

The plot of the data from these exposures showed more scatter than was consistent with the accuracy of the measurements. A possible reason for some of the scatter was that,

TABLE 4

VAPOR PRESSURE OF LANTHANUM

SERIES A

Run	Temperature °K	Time Secs.	Wt. loss Mg.	$\frac{1}{T^{\circ}_K} \times 10^{-4}$	-log P
2A	1866	2220	6.45	5.360	2.476
4A	1839	7920	16.24	5.436	2.558
1B	1776	10320	12.11	5.630	2.808
2B	1745	27300	14.60	5.730	3.152
3B	1694	20100	3.92	5.901	3.598
4B	1654	61800	7.68	6.045	3.798
5B	1617	50400	3.83	6.185	4.016
6B	1623	22800	1.97	6.161	3.960
8B	1758	11700	4.72	5.689	3.273
9B	1891	7200	18.50	5.286	2.453
2C1	1799	14460	14.71	5.558	2.867
2C2	1852	28560	34.10	5.400	2.791
3C	1879	3240	6.14	5.320	2.587
4C	1838	10740	14.78	5.439	2.731
5C1	1815	3900	3.54	5.510	2.915
5C2	1820	10380	9.93	5.495	2.899
6C1	1756	4740	2.40	5.695	3.175
6C2	1767	12240	7.40	5.660	3.097
7C	1716	7200	2.19	5.828	3.401
2E	1831	10800	7.32	5.460	2.769
3E1	1796	4500	2.30	5.565	2.896
3E2	1796	6300	2.92	5.565	2.938
4E	1710	7500	1.91	5.848	3.209
1F	1790	8340	4.36	5.585	3.157
2F	1732	20460	8.48	5.773	3.265
3F	1648	32400	5.53	6.065	3.661
4F	1835	4800	10.93	5.450	2.513
5F	1704	12480	2.97	5.870	3.510
6F	1658	11440	1.76	6.030	3.704
7F	1680	12000	2.70	5.951	3.536

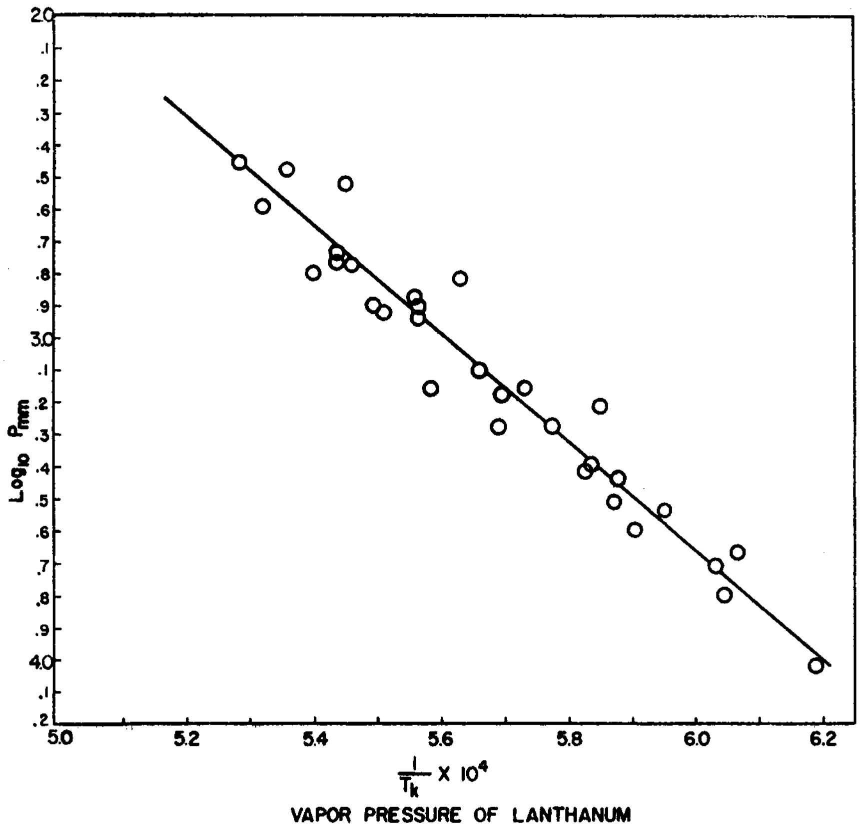


Figure 15. Vapor pressure of lanthanum

with the furnace coil and effusion vessel arranged to give the desired temperature distribution as described above, the effusion vessel experienced an upward force when the furnace was turned on. This phenomenon was probably due to the fact that in obtaining the desired temperature distribution, the effusion vessel was hanging in the lower portion of the induction coil where the field from the coil was axially inhomogeneous; as a result the effusion vessel, or the sample in the vessel, or both the sample and the vessel were being forced from a region or lower field strength at the end of the coil to a region of higher field strength in the center of the coil. It follows that there was a chance that some metal was removed by the vessel by this force so that it did not escape by true effusion. In an attempt to reduce the chances of this possibility, the positions of the furnace coil, inductor and effusion vessel were adjusted so that the temperature distribution in the furnace was the same as in the series A, B, C and F exposures; however, the position of the effusion vessel in the field of the induction coil was such that the forces acting on the vessel were at a minimum and only caused the balance to oscillate randomly across the null position. Two additional series of exposures were made under the above conditions, with 0.5 gram of lanthanum in the effusion vessels, and with 0.203 cm diameter orifices. The data from these runs are presented in Table 5. The vapor pressure equation for these exposures is

$$P = 5.297 \times 10^2 \frac{w}{t}\sqrt{\frac{T}{M}} .$$

The logarithm of the calculated vapor pressure values for the above experiments are plotted against the reciprocal of the absolute temperature in Figure 16; the continuous straight line through the points is based on the following equation calculated by the method of least squares

$$\log P = \frac{-17753}{T} \pm \frac{308}{T} + 6.816 \pm 0.166 .$$

The heat of vaporization calculated from the slope of this line is -81.0 ± 1.4 Kcal. mole^{-1}; the extrapolated normal boiling point is 4515 ± 150°K.

A vapor pressure-temperature equation representing the combined data of Tables 4 and 5 was calculated by the method of least squares. This equation is

$$\log P = \frac{-17185}{T} \pm 372 + 6.605 \pm 0.201.$$

This represents a heat of vaporization of -79.5 ± 1.7 Kcal. mole^{-1}, and an extrapolated normal boiling point of 4610 ± 260°K.

Praseodymium

The samples of praseodymium were prepared by the technique described in the first section of this thesis. The

TABLE 5

VAPOR PRESSURE OF LANTHANUM

SERIES B

Run	Temperature °K	Time Secs.	Wt. loss Mg.	$\frac{1}{T°_K} \times 10^{-4}$	-log P
1G	1784	4200	2.62	5.608	3.083
2G	1762	5400	2.40	5.675	3.233
3G	1842	3600	4.81	5.428	2.745
4G	1895	2400	5.61	5.275	2.496
6G	1711	8880	1.79	5.840	3.583
7G	1614	32820	2.09	6.195	4.095
8G	1660	13620	1.26	6.020	3.927
9G	1911	2760	6.19	5.230	2.512
1H	1796	6200	2.92	5.565	3.178
2H	1708	12900	2.34	5.855	3.629

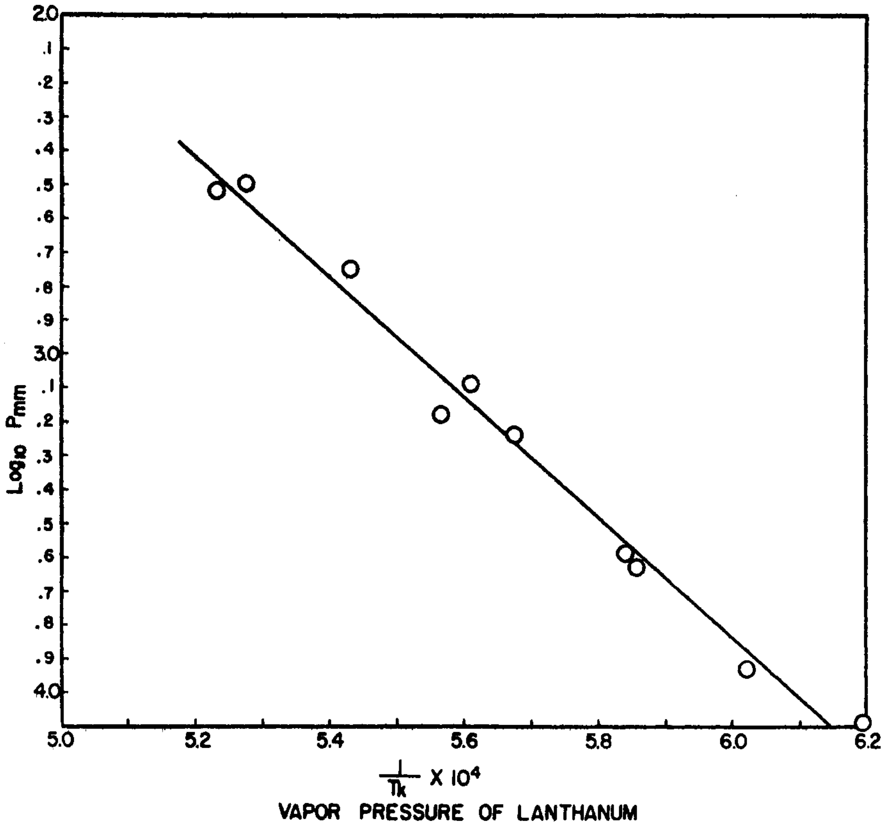


Figure 16. Vapor pressure of lanthanum

higher vapor pressure of this metal made it a much easier element to study than was lanthanum; the temperature control was much easier because the temperature was lower for the pressure range covered. A 0.214 cm diameter orifice was used for this series of exposures, resulting in a general vapor pressure equation

$$P = 4.790 \times 10^2 \frac{w}{t}\sqrt{\frac{T}{M}} .$$

The data obtained in these exposures are given in Table 6. The logarithm of the calculated vapor pressure values are plotted against the reciprocal of the absolute temperature in Figure 17; the continuous straight line through the points is based on the following equation calculated by the method of least squares

$$\log P = \frac{-17188}{T} \pm \frac{243}{T} + 8.098 \pm 0.156 .$$

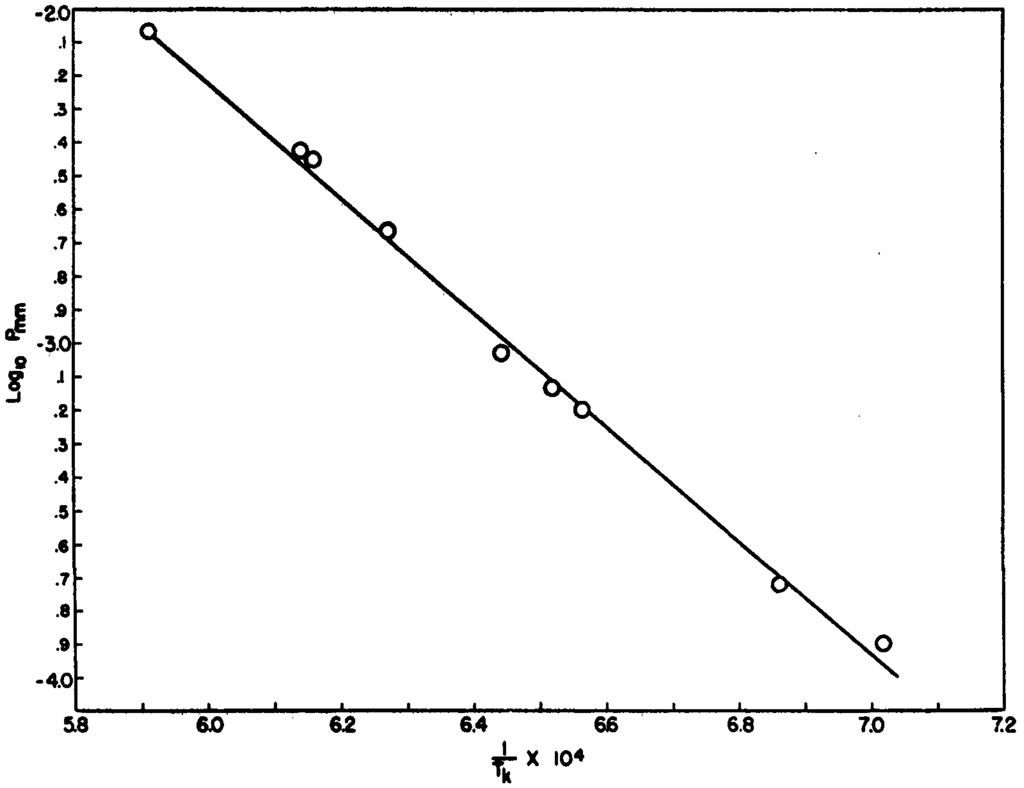
The heat of vaporization calculated from the slope of this line is -79.5 ± 1.1 Kcal. mole^{-1}; the extrapolated normal boiling point is 3290 ± 90°K.

It was noticed during these vapor pressure studies that the beam from the effusion vessel in the copper and silver studies cast a shadow on top of the Pyrex apparatus. However, in the case of lanthanum and praseodymium, no such shadow was observed. This phenomenon may be due in part to the fact that larger amounts of copper and silver

TABLE 6

VAPOR PRESSURE OF PRASEODYMIUM

Run	Temperature °K	Time Secs.	Wt. loss Mg.	$\frac{1}{T°_K} \times 10^{-4}$	-log P
1A	1624	3600	7.90	6.158	2.447
2A	1692	900	4.72	6.910	2.067
5A	1552	3300	1.95	6.440	3.027
6A	1458	36000	4.43	6.860	3.722
7A	1534	7200	3.36	6.518	3.132
8A	1500	10800	4.50	6.563	3.196
9A	1594	2400	3.26	6.272	2.660
10A	1629	1500	3.49	6.140	2.421
12A	1425	39600	3.43	7.016	3.897



VAPOR PRESSURE OF PRASEODYMIUM

Figure 17.

were vaporized during these runs, although the shadow appeared soon after the first exposures were made.

Discussion

The data on the vapor pressures of copper and silver obtained in this study are in general agreement with those published in the literature. While the values for the heats of vaporization and the extrapolated normal boiling points differ slightly from the other published data, they show reasonable agreement within the limits of experimental error.

Values of the heat of vaporization of lanthanum, calculated from the vapor pressure data, are in good agreement with Brewer's (35) figure of -80 Kcal mole^{-1}, and are reasonably close to the value of -85 Kcal mole^{-1} obtained by combining the heat of sublimation value for lanthanum given by Bichowsky and Rossini (93) with Cavallero's (94) figure for the heat of fusion of lanthanum. There is no literature value of the heat of vaporization of praseodymium with which to compare the figure of -79.6 Kcal mole^{-1} obtained in the present work, although it appears to be reasonable and consistent with the lanthanum data.

The extrapolated normal boiling points of lanthanum have no comparable data in literature. Calculated values for lanthanum of 1800 ± 1000°K (95) and 3000 ± 200-300°K (35) are all much lower than that of 4515 ± 150°K reported in this thesis.

The possible errors occurring in vapor pressure studies of the type represented by this thesis have been placed in the following categories by Phipps, Seifert, Simpson and co-workers (14):

1. Inherent errors arising from the incomplete knowledge of some quantity not measured in the experiment;
2. Systematic errors due to an uncertainty in a measured quantity which affects in a non-random manner all values of the computed quantity;
3. Statistical errors which are due to an uncertainty in a measured quantity which affects in a random manner each value of the computed quantity;
4. Basic errors which arise from failure of the experiment to fulfill an ideal condition necessary for the validity of the vapor pressure equation.

The errors in the present work will be grouped and discussed according to the above categories.

Inherent errors. Several constants were employed in deriving the final vapor pressure equation; any errors in the magnitude of these constants would become inherent errors. The constants to be considered are $\underline{A}$, Avagadro's number; $\underline{M}$, the molecular weight of the element; and $\underline{R}$, the gas constant.

(a) Avagadro's number. Straumanis (96), in a report of some x-ray studies, has shown that since calcite is not pure calcium carbonate but is a mixed crystal with a molecular weight of 100.095, the value of Avagadro's number has been calculated to be $6.02403 \pm 0.0003 \times 10^{23}$, which introduces an error of 0.02% in the calculated value of P.

(b) Atomic weights. The latest report of the committee on atomic weights includes a value of the atomic weight of lanthanum as determined by isotope ratio studies carried out by Inghram, Hayden and Hess (97) with a mass spectrometer. They report the concentrations of La^{139} and La^{138} as 99.911 ± 0.001% and 0.089 ± 0.001%, respectively, to give a value of 138.92 for the atomic weight of normal lanthanum with an uncertainty of 0.001% in the value of P. The corresponding error in the case of silver, copper and praseodymium has been assumed to be no larger than ± 0.001%.

It has been assumed in these calculations that the rare earth metals are monatomic in the vapor state. This assumption appears to be reasonable in the light of the studies by King and Carter (98) on the spectra of the rare earths in which they observed the thermal excitation of neutral rare earth atoms, but did not report the existence of any band spectra which would indicate the presence of polyatomic molecules. Ditchburn and Gilmore (72) have also observed that, with exceptions in the IA and VB groups of the periodic table, all of the metals are monatomic in the vapor state.

It has also been assumed that at the temperatures of the experiments, the neutral atom is liberated from the sample. If ionized atoms and electrons were emitted, the inhomogeniety of the field from the induction coil might influence the free escape of these particles from the effusion vessel. While it is not believed that this factor is important, it is recognized as a possible source of error.

(c) The gas constant. Wentsel (99) and de Groot (100) have given the best value of the gas constant as $8.3145 \pm 0.0010 \times 10^7$ erg; this uncertainty corresponds to an error in _p_ of 0.001%.

Thus, the error in _p_, due to recognized inherent errors of the experiment, is the sum of these errors, or 0.032%; in the light of larger errors elsewhere, this error is not significant.

Systematic errors. The data presented in this thesis may be subject to the four systematic errors discussed below.

(a) Orifice area. The radius of the orifice was measured with an estimated error of ± 0.5%, which corresponded to an error of ± 1% in both the orifice area and the calculated vapor pressure.

(b) Balance conversion factor. The uncertainties in the values of the calibration weights were such that the errors in the balance conversion factor was ± 1%, giving rise to a like error in the value of *p*.

(c) Temperature. A systematic error in the temperature arises from the uncertainty in the calibration of the standard lamp used to calibrate the optical pyrometer, and also in the actual calibration operation itself. Although the data from the supplier did not indicate the exact error in the values for the calibrated lamp, this has been estimated to be about 2°C; this leads to an error of ± 0.12% in the temperature range employed in the work of this thesis. In calibrating the optical pyrometer, a series of readings at each of 4 points showed an uncertainty of ± 5°C, or ± 0.3%. Thus, the total systematic error in the temperature was ± 0.42%, giving a ± 0.3% error in P.

(d) Liquid-gaseous equilibrium. Speiser and Johnson (73) have shown that if the effusion orifice is large compared with the effective evaporating surface of the sample within the vessel, true equilibrium will not be maintained in the effusion vessel; as a result the calculated vapor pressure will be smaller than the true vapor pressure by the estimated factor

$$P_{calc} = P_{true} \frac{\alpha}{\alpha + \frac{h}{s}}$$

in which α is the accommodation coefficient, h is the area of the orifice and s is the area of the evaporating surface of the sample. In the present work, the ratio of h to s was never greater than 1:49, which would mean that the calculated vapor pressures might be too small by 2%.

Summing the above errors, the maximum probable error in P is 4.3%, although it should be noted again that these errors affect each value of P in a non-random manner. For example, in case the orifice diameter used in the calculation of the vapor pressure is smaller than the true diameter, all calculated values of P will be larger than the true values by the same error. It follows that the plot of the logarithm of the pressure against the reciprocal of the temperature will be displaced in the reference frame, giving rise to an error in the extrapolated normal boiling point; however, the slope of the curve and the distribution of the points about the curve will not be affected, so that the calculated heat of vaporization will not be changed.

Statistical errors. Errors included in this section are those incurred in measuring time, weight loss and temperature.

(a) Time. Since in timing the runs, the starting time is taken when the furnace is turned on after the balance was set the second time, there is a period of about 30 seconds in which the temperature is increasing to the running temperature; there results a smaller rate of weight loss for this period than after the running temperature has been reached. However, at the end of a run, the terminal time is taken when the furnace is turned off, and the balance is then set; as a consequence, some weight loss is experienced after the run is completed, but before the balance is set. It has been estimated that the error incurred in each of these "end" periods is equal in magnitude, but opposite in sign so that they effectively cancel each other. However, the error in observing the time of the run is estimated to be ± 20 seconds. The percent error in the time of the run is not constant since the length of the runs vary; over 95% of the readings were for 2000 seconds or longer; using the above as the standard exposure time, the resultant error in P is ± 1%.

(b) Weight loss. The uncertainty in setting the balance to determine weight losses was estimated to be ± 0.04 milligrams at each setting; for two settings per exposure this amounted to ± 0.08 milligrams. Since the magnitude of the weight loss w in each exposure was not the same, the error in P introduced in w is not uniform. Since more than 80% of the exposures resulted in weight losses of over 2 milligrams, this value is used as the standard weight loss, which gives a ± 4% error in P.

(c) Temperature. Statistical errors in the reported temperatures were due to the inability of the observer to distinguish the color match in the optical pyrometer to better than ± 5°C at the temperatures encountered in this work; a ± 0.25% error in the value of P resulted. This same error was estimated in the temperature measurements by chromel-alumel thermocouples in the studies on copper and silver.

The total maximum probable error in P from statistical errors was then ± 5.25%.

Basic errors. The existence of some basic errors in this work would be difficult to detect as well as to evaluate. However, the following are possible sources of basic errors:

(a) Knudsen's empirical restrictions. Knudsen (13) found that true molecular effusion did not prevail in this type of work if the mean free path of the gas molecules was not at least ten times the orifice diameter. Calculations made under the extremes of the conditions employed in the present studies indicated that all work was carried out well within the limits of the above restriction. Another of the requirements given by Knudsen was that the orifice diameter should be at least ten times the orifice height (or lid thickness). Since all of the lids were made from 2-mil tantalum sheet, this condition was safely met in this work.

(b) Deviations of the metal vapor from conformity with the laws of perfect gases. The validity of the perfect gas law for the metal vapor was assumed in the derivation of the vapor pressure equation. Since the vapor was at very low pressures and very high temperatures, the deviations from perfect behavior were probably vanishingly small. Moreover, in integrating the Clausius-Clapeyron equation, the volume of the condensed phase of the sample has been considered to be vanishingly small with respect to the volume of the vapor phase. This error may be seen to be inconsequential by comparing the molar volume of the metal, 23 cm^3, to the molar volume of the vapor at 1400°C and 10^{-3} mm Hg pressure, 1×10^{11} cm^3.

(c) Lack of black body conditions for optical pyrometer readings. This error is not conveniently evaluated; it may be assumed that any error of this nature has been included in the systematic errors in temperature measurement.

Thus, if all of the above errors were additive, the calculated total maximum probable error is 7.6%.

Several applications and extensions of the present work are outlined below. The separation of samarium from gadolinium in the preparation of gadolinium metal might be used to effect separations of the normal trivalent rare earths from those possessing a stable divalency, such as samarium, europium and ytterbium. This procedure would be particularly valuable with mixtures containing amounts of these elements too small to be efficiently separated by chemical methods.

An interesting application of the vapor pressure technique of this thesis would be in studies on activities of metals in liquid solutions. Research of this type has been reported by Hildebrand and Eastman (101, 102) and practical application of activity data of metals has been made by Schneider and Schmidt (103). Chipman (104) has pointed out that vapor pressure measurements provide the easiest and most direct method of determining activities of metals in liquid alloys, but that in studies of this type, adequate consideration has not been given to parameters such as atomic radii in the thermodynamics of alloys. Dushman (105) has also discussed this subject of activities of metals, and has emphasized the fact that, because of experimental difficulties, these studies have been confined to the more volatile metals such as mercury, zinc, cadmium and the alkali metals. It should be possible to carry out studies of activities of the rare earth metals in alloys with one another by slightly modifying the technique developed in this thesis for measuring vapor pressures of metals.

It has been pointed out in this thesis that the vapor pres\sure measurements did not show the degree of precision that would be expected from the technique. The possible influence of the field of the induction coil on the effusion process has suggested some changes which could be made in the method of heating which might alleviate this possibility. Stansel (106) has shown that the depth of penetration of the field from a high frequency induction coil into a metal may be approximated as

$$D = \frac{23}{\sqrt{F}}$$

in which D is the depth of penetration in inches and F is the frequency of the field in cycles per second. The frequency spectrum of the furnace used in this work has a spread with a peak at 30,000 cycles per second; this would produce a depth of penetration of about 0.13 inch. If an inductor were employed which had walls slightly thicker than the above dimension, and in addition were long enough to extend several inches beyond the ends of the induction coil, the field should be kept away from the effusion vessel. Another possible solution to this problem would be to employ a tungsten resistance furnace in place of the induction furnace.

SUMMARY

The improved technique for preparing rare earth metals described in the present study has been successfully employed to prepare lanthanum, praseodymium and gadolinium metals in high yields on a scale of 250 milligrams and larger. This technique has several advantages over those previously reported in literature. For example,

(a) It can be applied to smaller charges.

(b) The resulting yields are higher.

(c) No "booster" or other side reaction is necessary.

(d) The recovery of scarce materials from unsuccessful runs is simplified and more complete.

(e) Separations of samarium and europium from other rare earths have been shown to be feasible.

(f) The presence of argon in the reaction vessel reduces the chances of contamination of the product metal by oxygen and nitrogen.

(g) The reaction vessels may be reused for many runs.

(h) By employing tantalum equipment, oxide contamination of the product metal is much lower than metal prepared in oxide refractories.

A technique for measuring the vapor pressures of metals has been devised which is an improvement over many of the methods currently in use. For example,

(a) The accommodation coefficient is not involved.

(b) The use of radioactive samples is not required.

(c) The amount of material effusing from the sample vessel is measured directly; it is therefore not necessary to analyze a target chemically or necessary to introduce possible errors inherent in chemical or radiochemical methods of analysis.

(d) Weighings can be made with the sample in place in a hot furnace, thus eliminating the necessity of calculating time-temperature integrals.

(e) Measurement of temperature by an optical pyrometer is not only convenient but may also be made under approximate black-body conditions.

A temperature controller for an induction furnace has been devised which may be employed over a wide range of temperatures.

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LITERATURE CITED

1. Yost, D. M., H. Russell, Jr., and C. S. Garner, "The Rare-Earth Elements and Their Compounds," John Wiley and Sons, Inc., New York, 1947.

2. Meggers, W. F., Rev. Modern Phys., 14, 96-103 (1942).

3. Meyer, S., Physik. Z., 26, 51-4 (1925).

4. Parkinson, D. H., F. Simon and F. H. Spedding. Paper submitted for publication in Proc. Roy. Soc. (London).

5. Seaborg, G. T., Electronic Structure of the Heaviest Elements. In Seaborg, G. T., J. J. Katz and W. M. Manning, "The Trans Uranium Elements," p. 1492-1524. McGraw-Hill Book Co., Inc., New York, 1950.

6. Klemm, W. and H. Bommer, Z. anorg. allgem. Chem., 231, 138-71 (1937).

7. Slater, J. C., "Introduction to Chemical Physics," McGraw-Hill Book Co., New York, 1939.

8. Spedding, F. H., E. I. Fulmer, T. A. Butler and J. E. Powell, J. Am. Chem. Soc., 72, 2349-54 (1950).

9. Spedding, F. H., E. I. Fulmer, J. E. Powell and T. A. Butler, J. Am. Chem. Soc., 72, 2354-61 (1950).

10. Jaeger, F. M., J. A. Bottema and E. Rosenbohm, Rec. trav. chim., 57, 1137-82 (1938).

11. Spedding, F. H., H. A. Wilhelm, W. H. Keller, D. H. Ahmann, A. H. Daane, C. C. Hach and R. P. Ericson, Publication of the U. S. Atomic Energy Commission, Journal of Metallurgy and Ceramics, #5, 7-12 (1950).

12. Ahmann, D. H., Report of the U. S. Atomic Energy Commission, ISC-68, 1950.

13. Knudsen, M., Ann. Physik, 28, 999-1016 (1909).

14. Phipps, T. E., N. D. Erdway, L. O. Gilpatrick, Z. V. Jasaitis, F. D. Johnson, G. W. Sears, R. L. Seifert, and O. C. Simpson, Report of the U. S. Atomic Energy Commission, CN-3223, 1945.

15. Isotopes Division, U. S. Atomic Energy Commission, "Isotopes," Catalog and Price List No. 3, 1949.

16. Langmuir, I., Phys. Rev., 2, 329-42 (1913).

17. Spedding, F. H., H. A. Wilhelm and W. H. Keller, Report of the U. S. Atomic Energy Commission, CT-2712, 1945.

18. Wilhelm, H. A., Report of the U. S. Atomic Energy Commission, TID-275, 1949.

19. Keller, W. H., R. P. Ericson and C. Hach, Report of the U. S. Atomic Energy Commission, CC-G-2396, 1945.

20. Mosander, C. G., Pogg. Ann., 11, 406-16 (1827).

21. Beringer, A., Ann., 42, 134-45 (1842).

22. de Marignac, J. C. G., Ann. chim. phys., [3] 38, 148-77 (1853).

23. Wohler, F., Ann., 144, 251-5 (1867).

24. Kremers, H. C., Trans. Am. Electrochem. Soc., 47, 365-71 (1925).

25. Zintl, E. and S. Neumayr, Z. Elektrochem., 39, 84-6 (1933).

26. Asprey, L. B., L. Eyring and W. Heppler, Report of the U. S. Atomic Energy Commission, UCRL-71, 1948.

27. Beck, G. and W. Nowacki, Naturwiss., 26, 495-6 (1938).

28. Moldenhauer, M., Chem. Ztg., 38, 147 (1914).

29. Karl, A., Bull. soc. chim., [5] 1, 871-7 (1934).

30. Trombe, F. and F. Mahn, Ann. chim., 19, 345-61 (1944).

31. Eyring, L. and B. B. Cunningham, Report of the U. S. Atomic Energy Commission, UCRL-264, 1948.

32. Derge, G. and A. E. Martin, Report of the U. S. Atomic Energy Commission, CT-2276, 1944.

33. Jantsch, G., N. Skalla and H. Grubitsch, Z. anorg. allgem. Chem., 216, 75-9 (1933).

34. Jantsch, G. and N. Skalla, Z. anorg. allgem. Chem., 193, 391-405 (1930).

35. Brewer, L., "The Thermodynamic and Physical Properties of the Elements," and "The Thermodynamic Properties of the Halides." In Quill, L. L., "The Chemistry and Metallurgy of Miscellaneous Materials." McGraw-Hill Book Co., Inc., New York, 1950.

36. Siebert, G. and E. Korten, German Patent, 355,485 (1920). [Original not available for examination; abstracted in Chem. Zentr., (1922) IV 425.]

37. Winkler, C., Ber., 23, 772-92 (1890).

38. Holm, H., "Beitrage zur Kenntnis der Cer," Munchen, 1902. [Original not available for examination; cited by Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. 5, p. 591. Longmans, Green and Co., London, 1922.]

39. Matignon, C. A., Compt. rend., 131, 837-9; 131, 891-2 (1900).

40. Schiffer, E. C., "Versuche zur reduktion d. Cerit-oxygen mit Aluminum," Dissertation Tech. Hochschule, Munchen, 1900. [Original not available for examination; cited by Hirsch, A., J. Ind. Eng. Chem., 3, 896 (1911).]

41. Muthmann, W. and L. Weiss, Ann., 331, 1-46 (1904).

42. Hirsch, A., J. Ind. Eng. Chem., 3, 880-97 (1911).

43. Kuhne, K. A., German Patent 179,403 (1904). [Original not available for examination; abstracted in Chem. Zentr., (1907) II, 1474.]

44. Kuzel, H., British Patent, 23,215 (1909). [Original not available for examination; cited by Trombe, F., Ann. chim., 6, 455 (1936).]

45. N. V. Philips' Gloeilampenfabriek, French Patent, 676,248 (1930). /Original not available for examination; abstracted in Chem. Zentr., (1930) I, 2942./

46. von Siemens, E. W. and J. G. Halske, British Patent, 10,867 (1900).

47. Muthmann, W., Ann., 331, 60-3 (1904).

48. Hillebrand, W. F. and T. H. Norton, Pogg. Ann., 156, 466-75 (1875).

49. Muthmann, W., H. Hofer and L. Weiss, Ann., 320, 231-70 (1902).

50. Muthmann, W. and K. Kraft, Ann., 325, 261-78 (1902).

51. Muthmann, W. and L. Weiss, Ann., 331, 1-46 (1904).

52. Kremers, H. C. and R. G. Stevens, J. Am. Chem. Soc., 45, 614-7 (1923).

53. Trombe, F., Ann. chim., 6, 349-458 (1936).

54. Trombe, F., Tech. moderne, 30, 855-61 (1938).

55. Hopkins, B. S., Trans Electrochem. Soc., 89, 295-300 (1946).

56. Jukkola, E. E., L. F. Audrieth and B. S. Hopkins, J. Am. Chem. Soc., 56, 303-4 (1934).

57. Meints, R. W., B. S. Hopkins and L. F. Audrieth, Z. anorg. allgem. Chem., 211, 237-40 (1933).

58. Kleinheksel, J. H. and H. C. Kremers, J. Am. Chem. Soc., 50, 959-67 (1928).

59. Daane, A. H., Chemist-Analyst, 37, 72 (1948).

60. Matheson Company, "Data Sheets on Compressed Gases and Gas Regulators," Mack Printing Company, Easton Pa., 1948.

61. Wilhelm, H. A., O. N. Carlson and R. M. Walrath, Report of the U. S. Atomic Energy Commission, ISC-25, 1948.

62. Ziegler, G. W., R. Speiser and H. L. Johnston, Rev. Sci. Instruments, 20, 367 (1949).

63. Newton, A. S., Declassified report of the U. S. Atomic Energy Commission, AECD-2135, 1948.

64. Svec, H. J., Iowa State College, private communication, Oct. 1950.

65. Eastman, E. D., D. D. Cubicciotti and C. D. Thurmond, Temperature-Composition Diagrams of Metal-Metal Halide Systems. In Quill, L. L., "The Chemistry and Metallurgy of Miscellaneous Materials." McGraw-Hill Book Co., Inc., New York, 1950.

66. Marsh, J. K., J. Chem. Soc., 1942, 398-401.

67. Brewer, L., The Fusion and Vaporization Data of the Halides. In Quill, L. L., "The Chemistry and Metallurgy of Miscellaneous Materials." McGraw-Hill Book Co., Inc., New York, 1950.

68. Hirsch, A., J. Ind. Eng. Chem., 3, 885-6 (1911).

69. Walsh, K. A., Report of the U. S. Atomic Energy Commission, ISC-94, 1950.

70. Mazza, L., Atti X° congr. intern. chim., 3, 604-9 (1939).

71. Billy, M. and F. Trombe, Compt. rend., 193, 421-3 (1931).

72. Ditchburn, R. W. and J. C. Gilmour, Rev. Modern Phys., 13, 310-27 (1941).

73. Speiser, R. and H. L. Johnston, Trans. Am. Soc. Metals, 42, 283-307 (1950).

74. Harteck, P., Z. physik. Chem., 134, 1-20 (1928).

75. Kelly, K. K., "Contributions to the Data on Theoretical Metallurgy. III. The Free Energies of Vaporization and Vapor Pressures of Inorganic Substances." U. S. Government Printing Office, Washington, D. C., 1935.

76. Weber, A. H. and S. C. Kirsch, Phys. Rev., 57, 1042-4 (1940).

77. Schadel, H. M., Jr., and C. E. Birchenall, J. Metals, 188, Trans., 1134-8 (1950).

78. Rudberg, E., Phys. Rev., 46, 763-7 (1934).

79. Marshall, A. L. and F. J. Norton, J. Am. Chem. Soc., 55, 431-2 (1933).

80. Speiser, R., H. L. Johnston and P. Blackburn, J. Am. Chem. Soc., 72, 4142-3 (1950).

81. Marshall, A. L., R. W. Dornte and F. J. Norton, J. Am. Chem. Soc., 59, 1161-6 (1937).

82. Brewer, L., The Thermodynamic and Physical Properties of the Elements. In Quill, L. L., "The Chemistry and Metallurgy of Miscellaneous Materials," p. 35. McGraw-Hill Book Co., Inc., New York, 1950.

83. Mack, E., G. G. Osterhof and H. M. Kraner, J. Am. Chem. Soc., 45, 617-23 (1923).

84. Jones, H. A., I. Langmuir and G. M. F. MacKay, Phys. Rev., 30, 201 (1927).

85. Knudsen, M., "The Kinetic Theory of Gases." Methuen and Co. Ltd., London, 1934.

86. Loeb, L. B., "The Kinetic Theory of Gases." McGraw-Hill Book Co., Inc., 1934.

87. Brewer, L. and D. F. Mastick, Report of the U. S. Atomic Energy Commission, UCRL-534, 1949.

88. Edwards, F. C. and R. R. Baldwin. Paper accepted for publication in Anal. Chem.

89. Dushman, S., "Scientific Foundations of Vacuum Technique," John Wiley and Sons, Inc., New York, 1949.

90. Sanford, R. L., Circular of the National Bureau of Standards, C448, "Permanent Magnets." U. S. Government Printing Office, Washington, D. C., 1944.

91. Strong. J., "Procedures in Experimental Physics." Prentice-Hall, Inc., New York, 1943.

92. Robinson, P. L. and H. V. A. Briscoe, J. Chem. Soc., 127, 140 (1925).

93. Bichowsky, F. R. and F. D. Rossini, "The Thermochemistry of the Chemical Substances," Reinhold Publishing Corp., New York, 1936.

94. Cavallero, L., Atti accad. Italia rend., [7] 4, 520 (1943).

95. National Research Council, "International Critical Tables of Numerical Data, Physics, Chemistry and Technology," McGraw-Hill Book Co., Inc., New York, 1926.

96. Straumanis, M. E., Z. Physik, 126, 65-9 (1949).

97. Inghram, M. G., R. J. Hayden and D. C. Hess, Jr., Phys. Rev., 72, 967-70 (1947).

98. King, A. S. and E. Carter, Astrophys. J., 65, 86-107 (1927).

99. Wensel, H. T., J. Research Natl. Bur. Standards, 22, 375-95 (1939).

100. de Groot, W., Nederland. Tijdschr. Natuurkunde, 9, 497-505 (1942).

101. Hildebrand, J. H., Trans. Am. Electrochem. Soc., 22, 319 (1912).

102. Hildebrand, J. H. and E. D. Eastman, J. Am. Chem. Soc., 37, 2452-9 (1915).

103. Schneider, A. and H. Schmidt, Z. Elektrochem., 48, 627-39 (1942).

104. Chipman, J., Discussions Faraday Soc., 1948, #4, 23-49.

105. Dushman, S., "Scientific Foundations of Vacuum Technique," p. 777. John Wiley and Sons, Inc., New York, 1949.

106. Stansel, N. R., "Induction Heating." McGraw-Hill Book Co., Inc., New York, 1949.