

1963

# Vapor pressures of the rare earth metals

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HABERMANN, Clarence Edward, 1931-  
VAPOR PRESSURES OF THE RARE EARTH  
METALS.

Iowa State University of Science and Technology  
Ph.D., 1963  
Chemistry, physical

University Microfilms, Inc., Ann Arbor, Michigan

VAPOR PRESSURES OF THE RARE EARTH METALS

by

Clarence Edward Habermann

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

Major Subject: Physical Chemistry

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Ames, Iowa

1963

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## I. INTRODUCTION

Within the past 10 years, moderate success has been realized in preparing pure rare earth metals in appreciable quantities making possible the determination of their physical properties. A survey of the present literature indicates a steadily increasing amount of data on the physical properties of these elements, but in many cases only estimates of values are available, and often discrepancies exist among the reported values.

The interpretation of the spectra for the gaseous atoms of some rare earth elements has been very difficult because of the complexity of the spectra. For lanthanum, gadolinium, and lutetium, the electronic ground state configuration (1) is known to be  $4f^n 5d^1 6s^2$  where  $n$  is 0, 7 and 14 respectively, whereas the other rare earths whose configurations are definitely known, have no d-electrons. For terbium, the  $4f^8 5d^1 6s^2$  configuration was found to be a low lying excited state (2), which caused earlier workers some confusion in the assignment of its ground state configuration. When the reported heats of sublimation for lanthanum, gadolinium and lutetium are compared in light of their similar electronic structures, it appears that gadolinium is somewhat anomalous. For most rare earth compounds, especially in aqueous solutions, three electrons are involved in bonding and the filling of the 4f sublevel does not follow the irregularities shown by

the gaseous atoms, but instead increases uniformly across the series. The tendency of ions to reach the more stable configuration of an empty, half-filled or filled 4f orbital is reflected in the other valences observed for the rare earth elements, but of the uncommon valences, only  $Ce^{+4}$  is stable in aqueous solution. The increased nuclear charge as one crosses the series causes a decrease in the ionic radii and helps to explain the gradual change in the chemical properties of the series. Much of the early rare earth chemistry was concerned with aqueous solutions, where the change in chemical properties across the series is also tempered by the large sphere of hydration surrounding the +3 ions. It is therefore quite understandable why early workers considered these elements to be similar.

The metals do not reflect the degree of similarity exhibited by the ions, with quite large variations existing in some metallic properties. This is especially true of the vapor pressures, with the elements europium and ytterbium (and to a lesser extent, samarium) being 3 to 4 orders of magnitude more volatile than the other members of the series. For all the metals, except europium and ytterbium, three electrons are believed to be in the conduction band (3). However, the high atomic volumes and magnetic susceptibilities for these two elements indicate only two electrons are present in their conduction bands.

The rare earth family holds a unique position in the development of atomic and alloying theories because of the large number of elements with closely related crystal structures and outer electronic configurations, with only the ionic radii exhibiting a gradual change. As the list of physical properties of the individual atoms is completed, better theories and experiments concerning the alloying behavior of metals can be devised, instead of simply studying alloy systems at random.

Whereas many equilibrium phase diagrams have been determined by thermal analysis, metallographic and X-ray diffraction techniques, fewer studies have been completed on the activities of the components in an alloy system. The study of activities of metals in alloys would be particularly easy by the vapor pressure technique since the activity equals the ratio of the vapor pressure over the alloy to the vapor pressure of the pure component. With the completion of vapor pressure studies on the pure rare earth metals, activity studies and consequently free energy calculations for various alloying reactions of these metals can be made.

Of the vaporization studies made on the rare earth metals by different investigators, close agreement on the heats of sublimation at 298<sup>o</sup>K has been reached on only five elements. In some cases, two investigators have agreed, while a third disagrees completely. These inconsistencies are possibly due



to varying purities of material, variations in the methods of temperature measurement and calibration, or lack of thermal equilibrium within the Knudsen cells. Consequently, it was of interest to complete additional work with particular emphasis on correcting the above problems in an attempt to resolve some of the discrepancies. Also it is important to have data available for the complete series from the same investigating group so that any experimental errors will be reflected consistently throughout the series, thus allowing more meaningful correlations to be made with other physical properties.

During the past few years, techniques have been devised in this laboratory for preparing rare earth metals of high purity (4, 5), making possible more precise determination of their physical properties. Since the heat content measurements on some of the rare earth metals have been completed within the past year,\* it is also possible to apply the third law test to the vapor pressure measurements based on entropy data. This can serve as a check on the vapor pressure measurements, and provide a second method for calculating the heat of sublimation at room temperature.

From a theoretical standpoint, the studies of vaporization processes of the rare earth metals and alloys should

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\*Dennison, D. H., Ames Laboratory, Iowa State University of Science and Technology, Ames, Iowa. Heat content data of rare earth metals. Private communication. 1963.

reveal a clearer picture of the nature and energetics of binding in the gaseous and solid states and help to establish the character and kinetics of high temperature reactions.

## II. HISTORICAL

### A. Methods and Theory

Vapor pressure measurements on metals are usually divided into two main groups: 1) high pressure methods used in the range from 10 to  $10^3$  mm of Hg, which have been used for the Group 1A and 2A metals, 2) low pressure techniques ranging from  $10^{-8}$  to  $10^{-1}$  mm of Hg, which in general have been applied to the transition metals. In this second class, the two principal methods that have been used are the Langmuir and Knudsen methods. The Langmuir method (6) is based on the theory that when a solid and its vapor are in dynamic equilibrium, the rate at which vapor atoms strike the solid surface and condense is equal to the rate at which atoms leave the metal surface. At very low pressures, the rate of condensation depends solely on the vapor pressure, but the rate of escape is assumed to be independent of pressure; depending only upon the rate at which atoms acquire sufficient kinetic energy to overcome the force of attraction of their neighbors. Consequently, it follows that the equilibrium vapor pressure of the metal can be determined from a measurement of the number of atoms which leave a surface. The condensation coefficient of the vapor on the hot metal surface is required for this method but quite often is unknown. One other objection to this method is that liquid metals are more difficult to work with

since the surface area may vary greatly depending on the amount of liquid metal which creeps up the container walls.

The Knudsen effusion method (7) depends on the rate of effusion of vapor from a space where the vapor is at equilibrium with a condensed phase through an orifice into a high vacuum. If this method is properly utilized it is independent of the condensation coefficient and can be readily adapted to the study of liquids.

A modification of the Langmuir method was used by Wakefield (8), in which he surrounded the evaporating surface of holmium metal with a graphite condenser. The holmium vapor then formed a stable nonvolatile carbide on the condenser, and the vapor pressure was calculated from the weight gain of the condenser.

Several modifications of the Knudsen technique are being used today, differing primarily in the method of determining the weight loss of the cell.

#### 1. Beam sampling technique

A certain portion of the vapor beam is collimated and condensed on a target, and if the geometry of the collimating system is known, one can calculate the vapor pressure from the amount of material collected on the target. Here again, Wakefield (8) used a graphite condenser to capture the vapor coming from a Knudsen cell in the determination of the vapor

pressure of holmium. Nachman et al. (9) have used this method to measure the vapor pressure of neodymium and praseodymium by weighing the amount of vapor condensed on a silver target attached to an analytical balance. If the original sample is radioactive, one can use radiochemical methods to measure the quantity of vapor collected on a target, as in the work of Phipps et al. (10) on plutonium. The amount of material condensed on the target can also be determined by chemical analysis as in Rudberg's work on calcium (11).

One of the principal objections to the target method is that the condensation coefficient for the condensation of vapor on the target must be known. This method, however, has the distinct advantage over some older techniques in that cooling of the furnace after each exposure is unnecessary, since a magazine can be incorporated into the system, making possible a number of measurements prior to opening the furnace.

## 2. Weight loss method

The principal procedure is to suspend the effusion cell from a microbalance and measure the weight of vapor effused out of the cell directly, as in the work of Daane on lanthanum (12).

### 3. Torsional momentum method

This involves measuring the resulting torque on a quartz fiber when a beam is either impinged on a vane or when it leaves an effusion cell having two orifices arranged as a couple. Theoretically, this method is advantageous because the molecular weight of the vapor species can be calculated from the vapor pressure, but thus far, the molecular weights measured by this method have been disappointing (13).

In this laboratory, the direct weight loss modification of the Knudsen effusion technique has been used in conjunction with a quartz fiber microbalance of the type developed by Edwards and Baldwin (14). The method has proved reliable in the pressure range of  $10^{-1}$  to  $10^{-4}$  mm of Hg, and is also advantageous as one can read the temperature on the interior of the effusion cell with an optical pyrometer, which is not possible with some of the other methods.

The kinetic theory of matter provides the means of relating the evaporation rate to the pressure in a Knudsen experiment. This theory involves two basic assumptions: 1) matter is made up of extremely small non-interacting particles, and 2) the atoms are in constant motion, and this motion is intimately related to the temperature. For a monoatomic gas in equilibrium with a condensed phase, the effect of increasing the temperature is evidenced by increased pressure on the enclosing walls because of the impact of molecules on these

walls. The number of molecules  $N$  that strike one square centimeter of a vessel wall per second is

$$N = \frac{\bar{c} d}{4} \quad (1)$$

where  $\bar{c}$  is the mean velocity of a molecule in cm/sec and  $d$  is the number of molecules per cubic centimeter in the gaseous phase. If the mass of a molecule is  $m$  grams, then the total mass  $W'$  striking the wall per  $\text{cm}^2$  over a period of time will be

$$W' = \frac{\bar{c} m d t}{4} \quad (2)$$

where  $t$  is the time in seconds. Since the pressures encountered in these experiments are quite low, the gas can be assumed to behave ideally, then

$$d = \frac{PM}{RT} \quad (3)$$

from the ideal gas law. From the Maxwell-Boltzman distribution of velocities, we can write the mean velocity as

$$\bar{c} = \left( \frac{8RT}{\pi M} \right)^{1/2} = 14553 \left( \frac{T}{M} \right)^{1/2} \quad (4)$$

Now equation 2 can be rewritten

$$W' = .05833 Pt \left( \frac{M}{T} \right)^{1/2} \quad (5)$$

where  $T$  is the absolute temperature,  $R$  is the gas constant in  $\text{mm cm}^3 \text{ mole}^{-1} \text{ degree}^{-1}$ ,  $P$  is the vapor pressure in millimeters of mercury and  $M$  is the molecular weight. In terms of the orifice area, equation 5 can be written

$$P = \frac{17.145 W}{At} \left( \frac{T}{M} \right)^{1/2} \quad (6)$$

where A is the orifice area in square centimeters and W represents the weight of vapor effusing through the orifice. For a Langmuir evaporation, the rate of sublimation from a heated filament equals the vapor pressure, as was described earlier in this section. It can be shown from the kinetic gas theory that the equilibrium pressure is related to the rate of sublimation by equation 6 with the addition of the condensation coefficient in the denominator. The condensation coefficient for most metals has been found to be unity; materials which vaporize to molecular species usually have a condensation coefficient less than unity.

The above derivation is made assuming that the orifice is infinitely thin, and that none of the vapor atoms are deflected back into the cell by the walls of the orifice. However, since the orifice has a finite thickness, a correction (the Clausing factor) due to the ratio of the orifice height to its radius should be made to the calculations. In addition, the atoms must not suffer any collisions among themselves as they pass through the orifice; that is, they must experience free molecular flow. Knudsen (7) established the criterion for free molecular flow to be a ratio of the mean free path of the vapor atoms to the diameter of the orifice greater than 10.

Speiser and Johnston (15) have shown that when an opening



is made in an effusion cell, the pressure on the inside of the vessel is not exactly equal to the vapor pressure because of the escape of some of the atoms. They have shown that if the ratio of the orifice area to the effective evaporating surface area is small compared to the accommodation coefficient, the number of atoms effusing does not seriously upset the equilibrium. However, the equation

$$P_{\text{calc}} = P_{\text{eq}} \cdot \frac{\alpha}{h/s + \alpha} \quad (7)$$

can be used to make this small correction, where  $\alpha$  is the condensation coefficient,  $h$  is the orifice area and  $S$  is the effective sample area.

#### B. Previous Measurements on Rare Earth Metals

Experimental studies on the physical properties of the rare earth metals and alloys have been carried out in this laboratory for many years. Specifically, vapor pressure measurements on these metals were begun in the year 1950, and until this work was begun, ten elements had been investigated to some extent. Only estimates from metallurgical observations were available for the remaining members of the family.

The first work on the vapor pressures of the rare earth metals was that of Ahmann (16) on cerium. He vaporized a radioactive sample onto a target using a modification of the Knudsen method and obtained a heat of vaporization of 107 kcal/mole from the slope of the vapor pressure curve. Brewer

(17) reported in Quill that cerium had a heat of vaporization of 80 kcal/mole and pressures 10 times that found by Ahmann. Gilles and Jackson (18) have measured the vapor pressure of cerium by analyzing the vapor condensed on a target using a coulometric procedure, and they reported a heat of vaporization of 114 kcal/mole.

The vapor pressures of lanthanum and praseodymium were studied by Daane (12) in 1950 using a quartz fiber microbalance to measure the effusion rate; heats of vaporization of 81 and 79 kcal/mole respectively were obtained. In 1958, Daane (19) reported the heats of vaporization of lanthanum and cerium to be 94 and 93 kcal/mole respectively using the same method as before. He also reported the heats of vaporization of dysprosium, neodymium and yttrium to be 69, 71 and 80 kcal/mole respectively at the temperatures of investigation (20, 21).

Nachman and Lundin (9) have measured the vapor pressures of praseodymium and neodymium using a target condensation modification of the Knudsen technique and found heats of vaporization of 84.42 and 84.06 kcal/mole respectively. The vapor pressure of europium metal was reported by Hanak et al. (22), who obtained a heat of sublimation of 41.1 kcal/mole, and the vapor pressure of holmium was measured by Wakefield (8) over the pressure range 10 mm to  $10^{-8}$  mm resulting in a calculated heat of sublimation of 69.5 kcal/mole at the measured temperature. The vapor pressure of thulium was

measured over a range of  $10^6$  mm of Hg by the radioactive tracer technique by Barton et al. (23) who obtained a  $\Delta H$  of 59.1 kcal/mole.

The vapor pressures of lanthanum, scandium and yttrium were measured by Ackermann and Rauh (24) in 1962 using a vacuum balance, and the heats of vaporization were measured with a mass spectrometer. They obtained heats of vaporization of 100.4, 77.9 and 91.3 kcal/mole respectively. Wakefield et al. (25) in 1959 also reported the vapor pressure of scandium, measured by the Knudsen technique in conjunction with a quartz fiber microbalance, and he obtained a heat of sublimation of 78.61 kcal/mole. More recently (1963), Krikorian (26) measured the vapor pressure of scandium by a Knudsen effusion technique and obtained a heat of sublimation of 88.0 kcal/mole at 1600°K, in disagreement with the previous reports.

Several Russian scientists have reported vapor pressure studies on the rare earth metals in recent years. Savitskii et al. (27) measured the vapor pressure of erbium metal using the Knudsen technique in which the vapor was condensed on a mica plate supported on a quartz fiber microbalance. Five points were taken and the heat of sublimation reported was 64.75 kcal/mole. Nesmeyanov et al. (28) have measured the vapor pressure of yttrium by a Knudsen technique and reported a heat of sublimation of 84.71 kcal/mole. The same authors (29) have recently investigated scandium metal and reported

a  $\Delta H_{298}^{\circ}$  of 83.1 kcal/mole by the second law method.

The rare earth metals have been studied by many investigators using mass spectrometric methods. These measurements give the temperature dependence of the vapor pressure rather than an absolute value of the vapor pressure. Absolute values are much more difficult to obtain, since the geometry of the system must be calibrated and the ionization cross sections must be known for the species involved. However, this method has the distinct advantages of obtaining results quickly and being able to observe all the various possible species emitted from the effusion cell. The results of these studies along with the enthalpies obtained from vapor pressure measurements are summarized in Table 1.

In order to complete the study of the vapor pressures of the rare earth metals, the work reported in this thesis was begun. Vapor pressures for samarium, gadolinium, terbium, ytterbium and lutetium not previously reported are presented as well as nine others which have been remeasured.

Table 1. Vaporization data (kcal/mole)

Element	Temp. range °K	Vapor pressure data		Mass spectrometric		Ref.
		$\Delta H_T$	$\Delta H_{298}$	$\Delta H_T$	$\Delta H_{298}$	
La	1640-2017	93.85 $\pm$ .93	99.5			19
	1665-2167	100.4 $\pm$ .7	103.9			24
	1723-1873				99 $\pm$ 7	30
Ce	1460-1720	107	--			16
	1611-2038	92.91 $\pm$ .37	97.6			19
	--	114	--			18
Pr	1425-1692	78.6 $\pm$ 1.1	--			12
	1724-1874	84.42 $\pm$ 1.9	--			9
	1505-1797			71.8 $\pm$ .6	77.9	31
	1380			79.3 $\pm$ 2	85.1	32
Nd	1340-1610	70.6 $\pm$ 2.0	75.6			12
	1638-1791	84.06	--			9
	1381-1792			70.2 $\pm$ .9	76.3	31
	1348			70.6 $\pm$ 2	75.0	32
Sm	700-950			48.66 $\pm$ .4 <sup>a</sup>	49.9	33
Eu	696-900	41.1 <sup>a</sup>	42.1			22
	727			42.0 $\pm$ .25 <sup>a</sup>	43.1	34
Gd	1685-2044			76.9 $\pm$ 1.0	83.6	31
	1370			78.2 $\pm$ .32 <sup>a</sup>	81.2	34
Tb	1492-1644			85.0 $\pm$ 1.6 <sup>a</sup>	87.2	31
	1655-1967			81.1 $\pm$ .8		31
	1437			88.94 $\pm$ .59 <sup>a</sup>		91.9
Dy	1245	69.0 <sup>a</sup>	--			20
	1215			69.3 $\pm$ .6 <sup>a</sup>	71.4	33
	1278-1566			60.1 $\pm$ .3 <sup>a</sup>	61.6	31
Ho	923-2023	69.3 $\pm$ .5 <sup>a</sup>	70.6			8
		64.7 $\pm$ .5				
	1248			72.9 $\pm$ .44 <sup>a</sup>	75.0	34
1253-1566			68.0 $\pm$ 1.2	69.5	31	

<sup>a</sup>Heat of sublimation.

Table 1. (Continued)

Element	Temp. range °K	Vapor pressure data		Mass spectrometric		Ref.
		$\Delta H_T$	$\Delta H_{298}$	$\Delta H_T$	$\Delta H_{298}$	
Er	1373-1573	64.75 <sup>a</sup>	--			27
	1349-1743			64.5 $\pm$ .6 <sup>a</sup>	66.4	31
	1208			73.18 $\pm$ .34 <sup>a</sup>	75.4	34
Tm	809-1219	57.44 $\pm$ .2 <sup>a</sup>	59.1			23
	937			56.2 $\pm$ .4 <sup>a</sup>	57.6	33
Yb	667			39.5 $\pm$ .5 <sup>a</sup>	40.0	33
Lu	1691-1937			92.3 $\pm$ 1.6 <sup>a</sup>	94.7	31
	1758			98.96 $\pm$ .4 <sup>a</sup>	102.8	34
So	1505-1748	78.61 $\pm$ .7 <sup>a</sup>	80.79			25
	1423-1789	77.9 $\pm$ .4 <sup>a</sup>	80.1			24
	1200-1570	88.0 $\pm$ .2 <sup>a</sup>	91.1			26
	1301-1644		83.1			29
Y	1523-1805	80 <sup>a</sup>	--			21
	1774-2103	91.3 $\pm$ .4	97.8			24
	1405-1733	84.71 <sup>a</sup>	--			28

### III. EXPERIMENTAL

#### A. Materials

The rare earth metals used in this study, with the exception of samarium and ytterbium, were prepared from spectroscopically pure oxide by the calcium reduction of the fluoride as described by Spedding and Daane (5). The reduced metal was then vacuum melted to remove any volatile impurities and in all cases except lanthanum and cerium, this was followed by distillation at higher temperatures. The general procedures for the distillation of the rare earth metals have been described by several investigators (4, 22, 25), but minor variations were used in this work to produce the best possible material for this investigation.

The lanthanum and cerium, while not being purified by distillation, were of quite high purity, since additional precautions were taken to prevent their contamination during the preparation process. Praseodymium and neodymium have sufficiently high vapor pressures for distillation on a small scale at temperatures below 2000°C, but they must be collected as liquids which causes some contamination from the tantalum condensing surface. The procedure used for these metals was similar to the procedure described by Daane (4), except the distillation column was heated by an eddy current concentrator of a design similar to that used by Johnson (35). The use of

the eddy current concentrator allows one to maintain a high vacuum in the collector area; which corrects one of the big problems of the apparatus described previously. The resulting material from these experiments was found to possess a very clean microstructure; it also exhibited a much higher oxidation resistance than that of metals not distilled, which has been found to correlate directly with purity.

Gadolinium, terbium, scandium and lutetium were distilled following a procedure described by Habermann and Daane (36) for yttrium, with the addition of an equal quantity of tungsten powder to the distillation column to facilitate the removal of certain impurities. It has been shown in this laboratory (37) that porous tungsten filters can be used to remove several metallic impurities from yttrium metal when liquid yttrium is allowed to run through the filters. Using this as a guide, tungsten metal added to a distillation mixture was found to cause the removal of iron and fluorine from the metals being distilled; other elements such as titanium, zirconium, etc., may also be removed, but were not checked in the rare earth metals used.

Samarium and ytterbium were prepared by the lanthanum reduction of their respective oxides as described by Daane et al. (38), followed by distillation in a high vacuum furnace using an ion pump as the pumping system. These metals were distilled at a pressure lower than  $5 \times 10^{-8}$  mm of Hg in an attempt to lower the gaseous impurities to a very low level.



This procedure required a very long distillation time since the metals outgassed badly at these pressures. Samarium was particularly difficult to distill in this furnace since it emitted a gas for which the ion pump had a very low pumping speed. Of the common gases, only the hydrocarbons and the rare gases have low pumping speeds and the hydrocarbons would appear to be ruled out by the low carbon analysis of the original materials. This may indicate a strange behavior between the rare earth metals and the rare gases, but the results are certainly non-conclusive at the present time. Dysprosium and holmium metals were also prepared in very high purity by this technique.

The analyses for the metals used in this investigation are presented in Table 2.

#### B. Furnace

The furnace chamber was primarily made of steel except for the pyrex arm holding the quartz-fiber balance, which was sealed to the metal part of the furnace jacket with Apiezon "W" vacuum wax. The system was heated by a tantalum tube resistance furnace 2.5 cm in diameter by 25 cm high surrounded by molybdenum shielding. Shielding on the top and the bottom consisted of discs 2 cm in diameter, placed approximately 1.5 cm apart leaving a 15 cm zone in the middle of the heater which was nearly isothermal. A schematic drawing of the furnace appears in Figure 1.

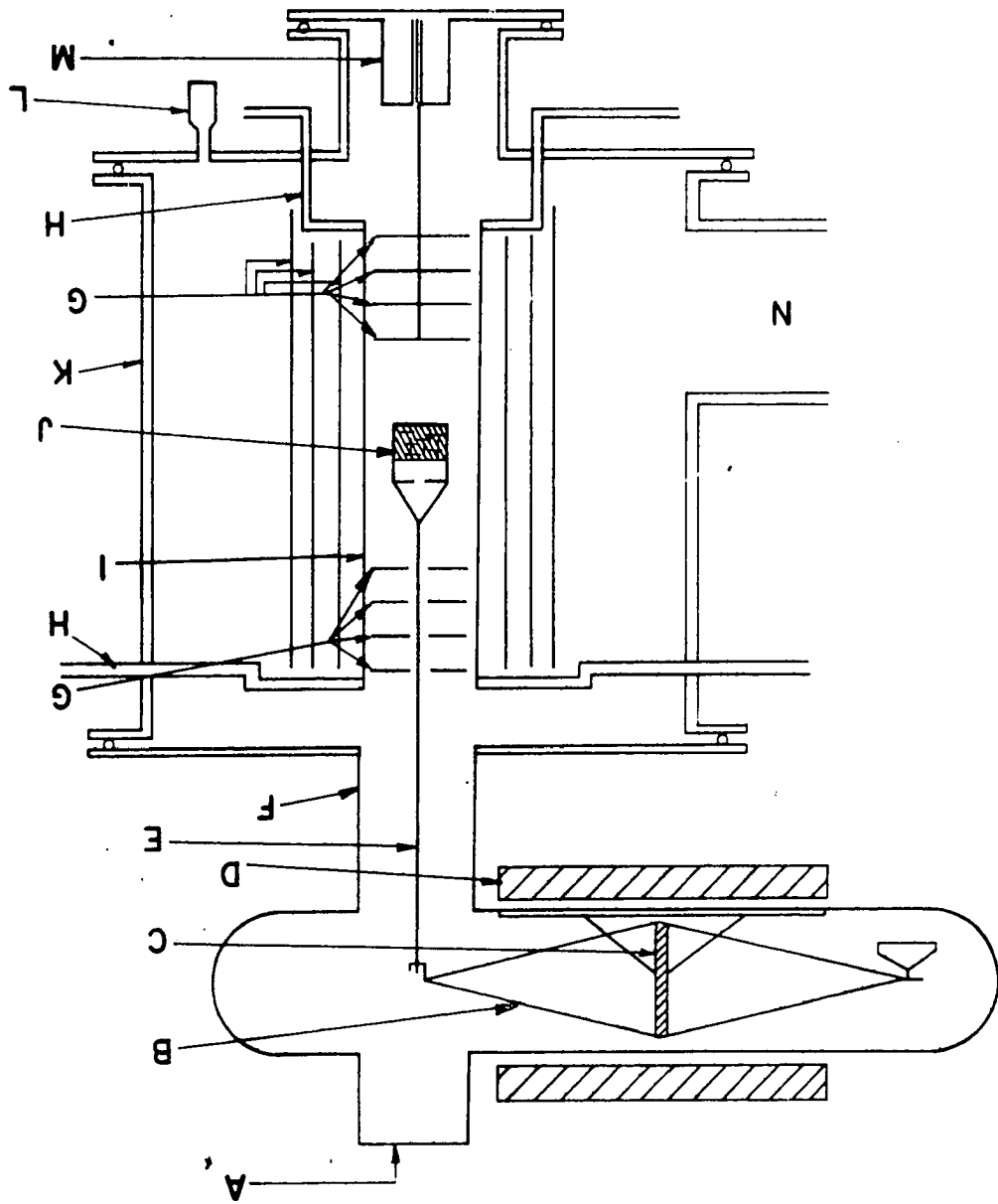
Table 2. Analyses of rare earth metals (ppm)

Element	Impurity											Other rare earths
	Ca	Ta	Si	Fe	Cu	Mg	O	C	N	F	H	
Sc	50	250	150	180	45	20	500	200	50	200	--	--
Y	10	400	30	150	--	5	300	150	10	100	10	--
La	10	≥500 <sup>a</sup>	60	75	--	5	57	125	10	150	5	--
Ce	10	100	25	250	--	--	345	200	150	50	10	--
Pr	20	≥500 <sup>a</sup>	25	30	--	≥100 <sup>a</sup>	700	75	30	20	20	--
Nd	20	≥500 <sup>a</sup>	<10	90	--	50	800	80	26	22	--	--
Sm	20	≥500 <sup>a</sup>	<50	5	--	--	--	95	20	35	--	--
Gd	<50	≥500 <sup>a</sup>	≥250 <sup>a</sup>	20	--	--	90	15	9	28	--	--
Tb	10	<200	20	T	--	5	380	25	15	35	12	--
Dy	100	<100	20	10	--	50	310	60	2	100	20	--
Er	20	≥500 <sup>a</sup>	<50	110	--	≥200 <sup>a</sup>	<50	60	45	15	--	--
Tm	20	≥500 <sup>a</sup>	25	5	--	≥200 <sup>a</sup>	--	70	50	300	--	--
Yb	--	≥500 <sup>a</sup>	25	5	--	--	--	35	50	100	--	--
Lu	20	40	25	50	--	--	210	20	12	64	--	--

<sup>a</sup>The actual amounts are probably much less than these values which represent the lower calibration limit.

Figure 1. Schematic drawing of vapor pressure furnace

A--Sight window, B--Quartz fiber micro balance,  
C--Alnico magnet, D--Solenoid, E--Suspension  
wire, F--Glass to metal seal, G--Thermal  
shielding, H--Current leads to heater,  
I--Tantalum heater, J--Effusion cell containing  
sample, K--Furnace chamber wall, L--Cold  
cathode vacuum gage, M--Shield holder,  
N--Vacuum port



Power was supplied to the heating element through a 208 volt, 5 KVA voltage regulator, a "double gang" variable powerstat and a 10 KVA step-down transformer. The maximum current which could be obtained from this arrangement was approximately 500 amperes at 8 volts, which would readily produce temperatures in the furnace of 2200°C. It was possible to maintain any desired temperature below 2000°C within an estimated limit of  $\pm 1^\circ\text{C}$  after an equilibrating time of about 5 minutes. Somewhat better temperature control could be achieved at lower temperatures by the use of a temperature controller developed by Svec *et al.* (39), which operates on a Wheatstone bridge principle with one leg of the bridge being a tantalum wire sensing element inserted into the middle of the furnace.

The vacuum pumping system consisted of a Welch Duoseal #1397B fore pump, a 10 cm MCF-300 oil diffusion pump using Octoil-S fluid, and a liquid nitrogen trap. After initially outgassing the furnace and the effusion cell to the highest temperature for a particular run, the pressure in the furnace was maintained at less than  $1 \times 10^{-6}$  mm of Hg during the remainder of the measurements. The pressure in the furnace was measured by a cold cathode gauge placed in the bottom of the furnace jacket.

The balance shown in Figure 2, which was used to measure the weight changes of the effusion cell, was a magnetically

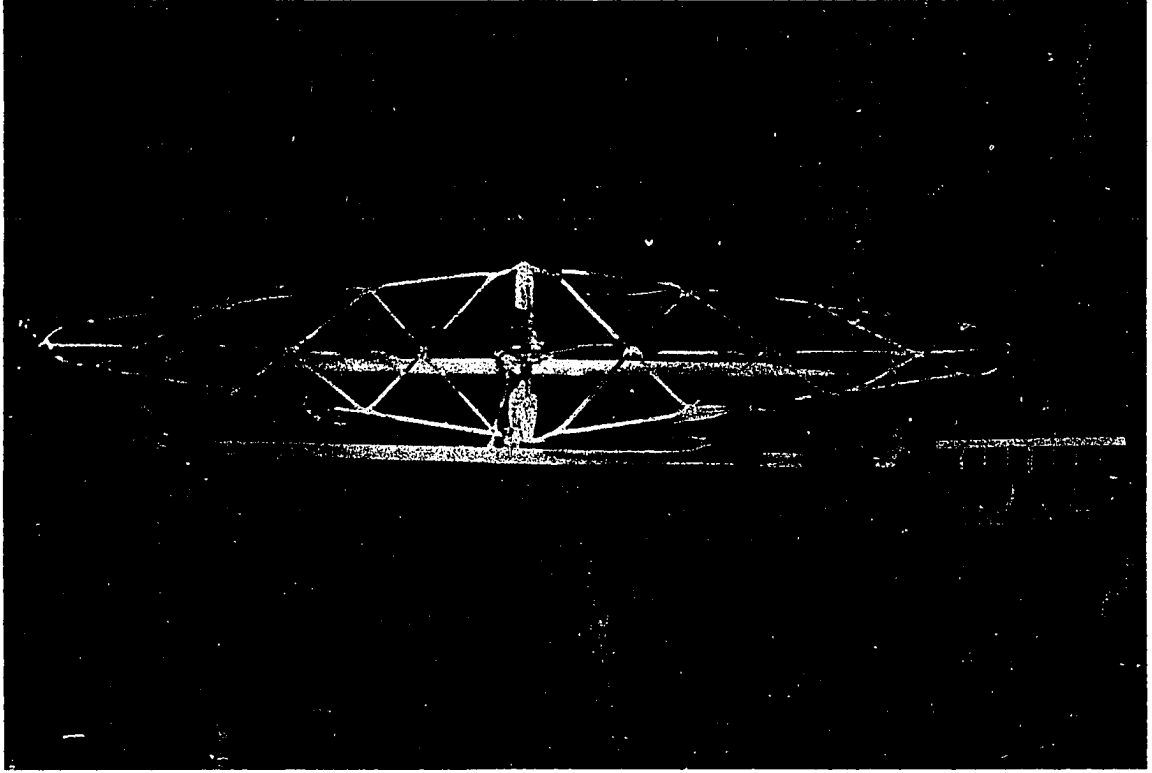


Figure 2. Quartz fiber microbalance

controlled quartz fiber balance described by Edwards and Baldwin (14) and later by Daane (12). A maximum load of 5 grams could be suspended from both ends of the balance, but usually an attempt was made to maintain the effusion cell weight at less than 2 grams, so a maximum balance sensitivity would be realized. The beam of the balance was constructed of 0.8 mm quartz rod with one small Alnico magnet mounted vertically in the center. The balance was placed in the center of a coil consisting of 2500 turns of #24 B & S gauge formvar insulated copper wire wound on a brass spool 8 cm long by 4.5 cm in diameter.

The current controlling circuit for this coil contained in series, a 0-100 milliamperere D.C. ammeter, a 5000 ohm helipot potentiometer, a switch for reversing the current, a decade resistance box for changing the current through the coil, a six volt storage battery and a standard resistor made of constantan wire. The current was measured by determining the voltage drop across the standard resistor using a precision potentiometer in conjunction with an electronic null detector. The relative position of the balance beam was determined by projection of an image of the balance pointer and the zero point indicator onto an etched glass screen through a microscope having a magnification of 20X.

The balance was calibrated in millivolts per milligram by observing the change in coil current required to return

the balance to the zero position after adding a five milligram standard weight to one side of the beam. The entire calibration, over a 100 milligram range, was made using two riders by replacing them at 10 milligram intervals with other weights of approximately 10 milligrams. This provided consistency in the calibration procedure, which resulted in a constant calibration curve over the entire range. The sensitivity of the balance was estimated at 5 micrograms, but varied slightly depending on the particular suspension fiber being used. The range of weight loss or weight gain possible for the balance was approximately 200 milligrams using the reversing switch in the line.

The temperature of the effusion cell was measured by a Leeds and Northrup disappearing filament type optical pyrometer above 1200°C; below 1000°C, a Pt-Pt/13% Rh thermocouple was used and between the two temperatures, either or both methods were utilized. The vacuum furnace had to undergo minor modifications to allow the use of a thermocouple; this consisted of passing the thermocouple through a 2-hole Stupakoff seal soldered into a Cenco vacuum coupling, so that the bead could be placed within 3 mm of the bottom of the effusion cell. A heavy tantalum container 2 cm in diameter and 6 cm long was placed around the effusion cells and the thermocouple bead to insure a constant temperature over this small distance. The voltage produced by the thermocouple



was measured by a Leeds and Northrup K-3 potentiometer and null detector with the reference junction in a water-ice mixture. Considerable effort was put forth to determine a correct calibration curve for the thermocouples and the optical pyrometer. The thermocouples were calibrated "in situ" against the melting point of pure lead, aluminum and copper metals, and a copper-silver eutectic. The optical pyrometer was also calibrated "in situ" against a calibrated Pt-Pt/13% Rh thermocouple as well as by observing the temperatures at which nickel, iron, distilled gadolinium, terbium, scandium and pure platinum metals melted. The melting points of the gadolinium and terbium metals, as determined by thermal analysis in a thermal analysis furnace, were found to be 1312 and 1351°C respectively, and the transition temperatures were 1234 and 1284°C respectively.

A shutter covered the optical pyrometer observation window when no temperature readings were being made to prevent coating of the window by the vapor beam from the effusion cell. Temperature readings were made by sighting through the orifice, thus giving the closest approach to black body conditions possible.

### C. Effusion Cell Preparation

Tantalum effusion cells 1 cm in diameter and 1 cm high were used in this study, because they could be easily formed

and since the amount of tantalum which would dissolve in the metal samples was known to be very small in most cases. Of the metals studied lanthanum, cerium, praseodymium, neodymium, gadolinium, terbium and yttrium were studied in the liquid state; of these only yttrium dissolves an appreciable amount of tantalum.

The effusion cells, shown in Figure 3, were drawn from 12 mil sheet by the Fansteel Metallurgical Corporation and therefore contained no welded seams along which creeping could occur. The flange on top of the cell was cupped with a special die to provide an edge which could be crimped down over the lid for welding. The cells weighed about 5 grams when purchased, and after adding a lid and a small quantity of rare earth metal were too heavy for the microbalance. Consequently, the cells had to be reduced in weight, which was accomplished by leaching the cells in a 50-50 mixture of nitric and hydrofluoric acids for 3-4 minutes, thus reducing the weight to about 1 gram. They were then outgassed at 1600°C under a vacuum of  $10^{-6}$  mm of Hg to remove any absorbed gases. The lids were prepared from 2 mil tantalum sheet by holding the tantalum firmly between brass plates and drilling through the brass and tantalum with high speed drills, which ranged in size from 0.06 to 0.3 cm; the orifice was then burnished with emery paper to remove any burrs. A traveling microscope with an accuracy of 0.0005 cm was used to measure

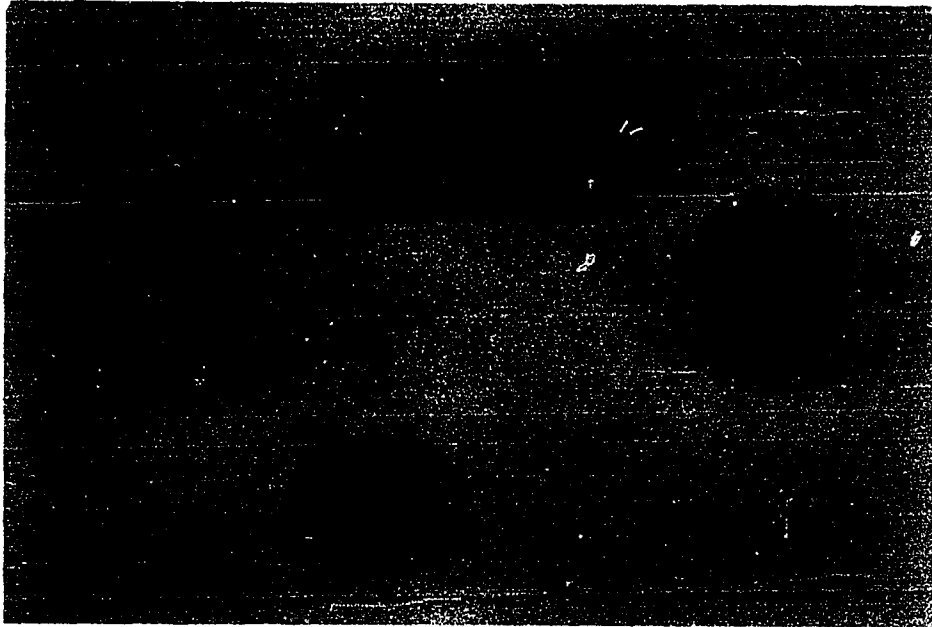


Figure 3. Tantalum effusion cell

the diameter of the orifice, and the final value used for the diameter was an average of several readings at different positions across the orifice. The length of the orifice or the thickness of the lid was measured with a metric micrometer, so that Clausing factors could be applied in calculating the pressure. After placing the metal to be studied in the cell, the lid was welded on by melting the crimped flange of the cell to the lid in an inert gas arc welder described by Miller et al. (40). For some of the more volatile rare earth elements, it was necessary to place the effusion cell in a closely fitted copper holder which had sufficient heat capacity to keep the rare earth metals from reaching a high enough temperature to vaporize.

The suspension wire between the cell and the balance was made of 5 mil tantalum wire which had been straightened by heating in an inert atmosphere to  $1000^{\circ}\text{C}$  while a weight was attached to one end. By weighing the suspension wire before and after a run, it was found that the weight gain due to condensed metal was negligible in comparison to the weight losses of the vapor pressure measurements.

#### D. Procedure

When the furnace was being prepared for a run, a counterweight was placed opposite the effusion cell on the balance so 60 milliamperes of current was required to hold the cell

up in the furnace. This amount of current through the standard resistor gave a full scale reading on the potentiometer. During a run, weight losses could be followed by decreasing the current through the coil to zero, and then by reversing the polarity, returning to full current. Before placing the effusion cell in position, the furnace was evacuated to a pressure of  $5 \times 10^{-6}$  mm of Hg, outgassed to  $2000^{\circ}\text{C}$  and backfilled with argon. At this time the sample was put in place and outgassed to a temperature slightly higher than the highest temperature at which measurements were to be made. After measurements were begun, the furnace and effusion cell were allowed to equilibrate for 5 to 10 minutes at each temperature setting before a weight loss measurement was started. The weight of vapor effusing out of the cell in a timed interval was obtained by bringing the balance to the zero position at the beginning and end of the interval; then taking the difference in the voltage reading across the standard resistor and multiplying by the balance constant previously determined.

A point on the vapor pressure plot then represents the time required to lose approximately 2-4 milligrams of weight at a particular temperature. Temperature checks were made several times during each measurement to make certain there were no fluctuations. Each run consisted of 15 to 30 such measurements. The quantity of metal effused in a particular

run was usually 10% of the original sample, so that all the measurements were made on a sample of constant composition. Of each element studied, several runs were made using different batches of metal; the number of runs depending on the reproducibility of the vapor pressure measurements between runs, usually varying from 2 to 10 with an average of 5 per element. The number of points taken per element varied from 34 to 200 with an average of 91 points per element.

#### E. Data Processing

Rough calculations were made on each run at the time the measurements were being made to provide an indication of whether the run was progressing satisfactorily. Final calculations, including refinements for orifice thickness, orifice area expansion with temperature and lack of saturation of the gaseous phase in the effusion cell as described by Speiser and Johnston (15), were made on an IBM 7074 computer programmed to make the calculations and to provide a straight line fit of the points by the least squares treatment to the equation

$$\log P_{mm} = - \frac{A}{T} + B . \quad (8)$$

The results from all of the runs were then combined and again fitted by the least squares treatment to a single straight line. Theoretically, a slight curvature would be expected in the plot of  $\log P$  versus the reciprocal of temperature,

and therefore the equation

$$\log P = - \frac{A}{T} + B \ln T + C \quad (9)$$

should fit the situation better. In practice the experimental error is the same order of magnitude as the expected curvature, so the straight line equation is almost universally used. The values of the Clausius factors used in these calculations were taken from the compilation by DeMarcus (41).

#### F. Errors

There are essentially two categories of errors which affect the vapor pressures as reported in this thesis:

- (1) Statistical errors which are due to random variations in measuring time, temperature and weight loss.
- (2) Systematic errors resulting from uncertainties in temperature, orifice area, balance constant and lack of equilibrium pressures in the effusion cell, which affect the vapor pressure at all points by a constant amount.

##### 1. Statistical errors

Errors included in this section are discussed individually below, and an order of magnitude value for individual runs and for the combined runs of each element is given by the standard deviations listed in the results section of this thesis.

a. Time Time was measured with a Labchron electric timer, which has an estimated accuracy of 0.2 of a second. However, an error of not more than 1 second per measurement was made in reading the time at the beginning and end of a measurement. An average time for a measurement was about  $10^3$  seconds, thus causing an average error of about 0.1%.

b. Temperature Below  $1000^{\circ}\text{C}$ , the error in the temperature measurements should fall well below  $1^{\circ}\text{C}$ , which would be less than 0.2% error in the pressure. Above  $1000^{\circ}\text{C}$  where the temperatures were most often read with an optical pyrometer, the variation due to the inability to reproduce a color match was about  $2^{\circ}\text{C}$ , and the temperature fluctuations of the furnace were around  $1^{\circ}\text{C}$  during a measurement giving a total of  $3^{\circ}\text{C}$ ; this would again result in an average error of about 0.2% in the pressure.

c. Weight loss Errors in the weight loss measurements resulted from reading the potentiometer and in determining the exact zero position of the balance. The potentiometer can be read easily to 0.005 mv., which would be a 0.1% error, and the error in determining the zero position is estimated to also be about 0.1% giving a total error of 0.2% in the pressure.

The total statistical error would therefore be 0.5%, which agrees closely with the standard deviations quoted in the data section. Of course, the effect of these errors is



less when a large number of measurements are made.

## 2. Systematic errors

The data presented in this thesis is subject to the following systematic errors.

a. Temperature An error in the temperature arises from the calibration of the thermocouples and the optical pyrometer. For the optical pyrometer, this is estimated to be 5°C, and the corresponding figure for the thermocouples would certainly be lower. This would result in a maximum error of 0.3% in the pressure and 2% in the slope.

b. Orifice area The diameter of the orifice was measured with an estimated error of 0.4%, which corresponds to an error of 0.7% in the pressure. The change in the orifice area with temperature was found to cause an error of about 2.0% in the vapor pressure and approximately 0.1% error in the slope. Consequently, this correction was made for each one of the points. The thermal expansion coefficient of tantalum (42) was reported to be

$$\alpha = 6.5 \times 10^{-6} + .34 \times 10^{-9}t + .12 \times 10^{-12}t^2 .$$

c. Balance constant The calibration of the balance was made using standard 5 mg weights accurate to 0.002 mg, which would result in an error of less than 0.1% in the pressure.

d. Lack of equilibrium pressure in the effusion cell

Speiser and Johnston (15) have shown that true equilibrium will not be maintained in the effusion cell, if the orifice area is large compared to the effective evaporating surface of the sample. The pressures calculated in this work were therefore corrected by applying equation 7 where  $\alpha$ , the accommodation coefficient was assumed to be unity.

Summing the above systematic errors not taken into account in the calculations, the probable error in the pressure would be 1.1% and in the slope 2.1%. Adding this to the statistical errors, the total estimated error in pressure would be 1.6% and in the slope 2.6%.

In addition to the sources of error mentioned above, there are other possible errors:

- (1) Avogadro's number
- (2) Molecular weights of elements
- (3) Gas constant
- (4) Vapor ideality
- (5) Lack of black body conditions
- (6) Other vapor species besides monoatomic

The errors encountered due to these factors are assumed to be negligible compared to the others mentioned. The molecular weights used conform to the 1961 values approved by the International Union of Pure and Applied Chemistry.

## IV. RESULTS AND CALCULATIONS

## A. General

The data observed in the vapor pressure measurements on the rare earth metals are tabulated in Tables 3 through 24, and the results of the calculations made by the IBM computer are plotted in Figures 4 through 16 where the reciprocal of the absolute temperature is plotted against minus  $\log P_{\text{mm}}$ . Since there were several runs made on each element, it would be difficult to include all the data observed; consequently, the data presented is one run typical of the series of runs for a particular element, and represented a close fit to the equation obtained when all the data for one element were combined. The points plotted in the figures are also typical of all the data, and give an indication of the amount of scatter obtained between runs.

The limits of error following the heats of sublimation and vaporization values represent the standard deviations from the reported values. This measure provides a somewhat more pessimistic error figure than the "probable error" sometimes used, but actually has similar significance. The errors stated for the constants in the straight line equation are also standard deviations as defined in Worthing and Geffner (43). The root mean square deviation in the values of  $\log P$  are given in the heading for each run tabulated, along with

the constants A and B of equation 8.

### B. Thermodynamics

Let us consider the equilibrium between the condensed state of a metal and its vapor,



for which the Clausius-Clapeyron equation applies

$$\frac{d \ln P}{dT} = \frac{\Delta H_T}{RT^2} \quad , \quad (11)$$

assuming the vapor is a perfect gas and the molar volume of the gas is much greater than the molar volume of the condensed phase. The symbol P represents the pressure in atmospheres,  $\Delta H_T$  is the heat of transition at temperature T°K and R is the universal gas constant. If equation 11 is integrated to give

$$\log P = - \frac{\Delta H_T}{2.303 RT} + C \quad , \quad (12)$$

the result is the equation of a straight line, where the slope is equal to  $\frac{\Delta H_T}{2.303 R}$ . If  $\Delta H$  is required at some other temperature, for instance 298°K, it must be corrected for the difference in the enthalpies of the condensed and vapor phases between T and 298°K.

$$\Delta H_{298} = \Delta H_T + \int_T^{298} (C_{p(\text{vapor})} - C_{p(\text{cond.})}) dT \quad . \quad (13)$$

In order to make a third law calculation, we use the relation

$$\Delta F_T^{\circ} = \Delta H_T^{\circ} - T \Delta S_T^{\circ} \quad (14)$$

where the superscripts refer to the standard states. The standard free energy can be related to the vapor pressure for the equilibrium process in equation 10 by

$$\Delta F_T^{\circ} = -RT \ln K_{(eq)} \quad (15)$$

$$\Delta F_T^{\circ} = -RT \ln P \quad (16)$$

where  $P$  is in atmospheres.  $\Delta S_T^{\circ}$  in equation 14 is the difference between the entropy of the vapor in its standard state and the entropy of the condensed phase in its standard state at temperature  $T$ . The entropy can be expressed by

$$S_T^{\circ} = - \left( \frac{F_T^{\circ} - H_T^{\circ}}{T} \right) = - \left( \frac{F_T^{\circ} - H_{298}^{\circ}}{T} \right) + \left( \frac{H_T^{\circ} - H_{298}^{\circ}}{T} \right) \quad (17)$$

which on rearranging is

$$- \left( \frac{F_T^{\circ} - H_{298}^{\circ}}{T} \right) = S_T^{\circ} - \left( \frac{H_T^{\circ} - H_{298}^{\circ}}{T} \right). \quad (18)$$

For the condensed state, this can be computed from the heat capacity by the relation

$$- \left( \frac{F_T^{\circ} - H_{298}^{\circ}}{T} \right)_c = \int_0^T C_p \, d \ln T - \frac{1}{T} \int_{298}^T C_p \, dT. \quad (19)$$

The corresponding free energy function for a perfect monatomic vapor can be calculated from statistical mechanics by the use of the Sackur-Tetrode equation and spectroscopic data.

When the entropy of the gas is subtracted from the entropy of the condensed phase making use of equation 17, one obtains

$$\Delta S_T^0 = - \left( \frac{F_T^0 - H_{298}^0}{T} \right)_g + \left( \frac{H_T^0 - H_{298}^0}{T} \right)_g + \left( \frac{F_T^0 - H_{298}^0}{T} \right)_c - \left( \frac{H_T^0 - H_{298}^0}{T} \right)_c \quad (20)$$

$$\Delta S_T^0 = - \left( \frac{F_T^0 - H_{298}^0}{T} \right)_g + \left( \frac{F_T^0 - H_{298}^0}{T} \right)_c + \frac{\Delta H_T^0}{T} - \frac{\Delta H_{298}^0}{T} \quad (21)$$

Combining equations 14, 16 and 20 results in the equation

$$R \ln P = - \left( \frac{F_T^0 - H_{298}^0}{T} \right)_g + \left( \frac{F_T^0 - H_{298}^0}{T} \right)_c - \frac{\Delta H_{298}^0}{T} \quad (22)$$

from which  $\Delta H_{298}^0$  can be calculated from the vapor pressure and the free energy functions. When  $P$  is equal to 1 atmosphere,  $T$  will be by definition the normal boiling point of the metal.

### C. Data

#### 1. Scandium

Measurements on scandium were made on the solid in order to avoid the high solubility of tantalum in liquid scandium observed by Spedding *et al.* (25). The extensive attack below the melting point reported by these authors was not confirmed.

Samples from three different batches of metal were used and the results of run #2 are tabulated in Table 3. A plot of the data is shown in Figure 4; the equation of the best straight line through all the points (71 points, 4 runs) made on scandium is

$$\log P_{\text{mm}} = 9.452 \pm .052 - \frac{19140 \pm 88}{T}, \quad (23)$$

and the average mid-range temperature was 1670°K, where the heat of sublimation obtained from the slope of the line is  $87.585 \pm 0.4$  kcal/mole.

Third law calculations based on the vapor pressure data of run #2 are tabulated in Table 4. The average value of the heat of sublimation at 298°K was  $90.981 \pm .173$  kcal/mole compared to the value of  $92.201 \pm 0.5$  kcal/mole obtained from the second law method. The normal boiling point calculated from equation 22, using the third law  $\Delta H_{298}^{\circ}$  is  $3105 \pm 15^{\circ}\text{K}$ . The third law calculations were made using thermodynamic quantities for condensed scandium based on the high temperature heat content data of Dennison,\* and the low temperature data of Weller (44). Thermodynamic quantities for the ideal monatomic vapor are from Stull and Sinke (45). In order to make the boiling point calculation, it was necessary to

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\*Dennison, D. H., Ames Laboratory, Iowa State University of Science and Technology, Ames, Iowa. Heat content of scandium metal. Private communication. 1963.

Table 3. Vapor pressure data for scandium

Run #2  $\Delta H$  89.132  $\pm$  .92 kcal/mole  
 Orifice area - 34.407 x 10<sup>-3</sup> cm<sup>2</sup> A 19478  $\pm$  200  
 Clausing factor - .9763 B 9.659  $\pm$  .121  
 RMSD in log P - .0267

Point	Mass, mg	Time, sec	Temperature °K	10 <sup>4</sup> /T	-log P <sub>mm</sub>
1	12.499	30818	1543	6.481	2.9111
2	2.696	4466	1568	6.378	2.7350
3	2.882	2953	1598	6.258	2.5225
4	2.741	2064	1614	6.196	2.3867
5	2.682	1359	1636	6.112	2.2118
6	2.553	970	1657	6.035	2.0841
7	2.160	665	1669	5.992	1.9914
8	2.175	457	1693	5.907	1.8224
9	2.275	360	1708	5.855	1.6976
10	3.253	13347	1529	6.540	3.1341
11	2.855	4386	1579	6.333	2.7008
12	2.549	2061	1615	6.192	2.4174
13	2.907	1957	1624	6.158	2.3368
14	3.336	1705	1643	6.086	2.2146
15	2.370	755	1674	5.974	2.0055
16	2.683	534	1702	5.875	1.7978
17	2.825	422	1719	5.817	1.6712
18	2.785	315	1739	5.750	1.5480
19	2.562	222	1760	5.682	1.4299
20	2.730	190	1773	5.640	1.3332
21	2.830	156	1790	5.587	1.2300
22	3.004	155	1797	5.565	1.2004
23	4.117	16618	1528	6.545	3.1272



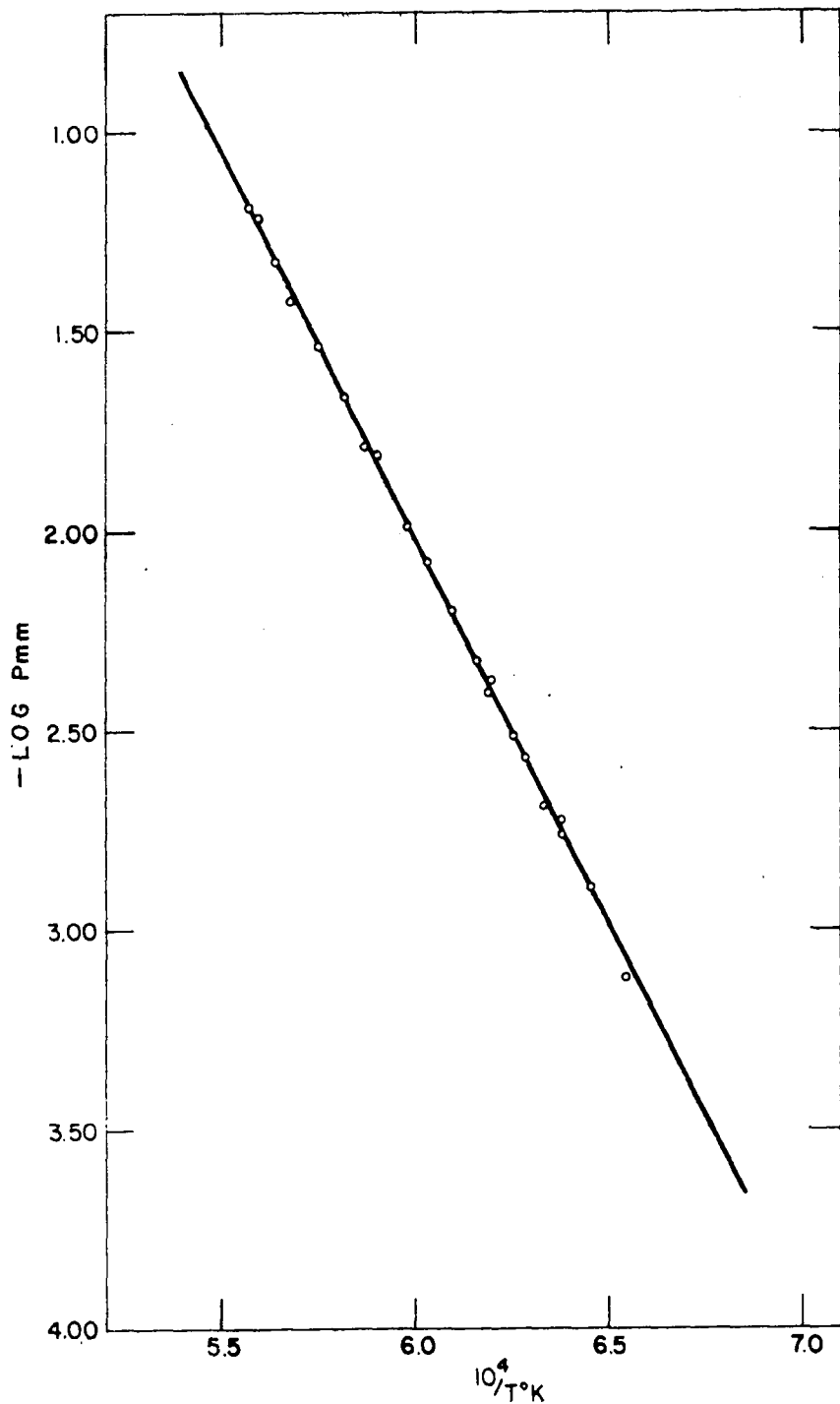


Figure 4. Vapor pressure of scandium (1521-1813°K)

Table 4. Thermodynamic calculations for scandium metal

Temp. °K	$-\left(\frac{F_T^O - H_{298}^O}{T}\right)_c$	$-\left(\frac{F_T^O - H_{298}^O}{T}\right)_g$	$-\log$ P <sub>atm.</sub>	$\Delta H_{298}^O$ kcal/mole
1543	13.71	46.01	5.7919	90.735
1568	13.81	46.08	5.6158	90.894
1598	13.92	46.15	5.4033	91.016
1614	13.99	46.20	5.2675	90.891
1636	14.08	46.25	5.0926	90.755
1657	14.17	46.31	4.9649	90.901
1669	14.21	46.34	4.8722	90.835
1693	14.31	46.40	4.7032	90.765
1708	14.37	46.44	4.5784	90.560
1529	13.66	45.98	6.0149	91.501
1579	13.86	46.11	5.5816	91.268
1615	13.99	46.20	5.3082	91.248
1624	14.03	46.22	5.2176	91.051
1643	14.11	46.27	5.0954	91.149
1674	14.23	46.35	4.8863	91.200
1702	14.35	46.42	4.6786	91.021
1719	14.42	46.47	4.5520	90.901
1739	14.50	46.51	4.4288	90.856
1760	14.58	46.56	4.3107	91.003
1773	14.63	46.60	4.2140	90.872
1790	14.70	46.64	4.1108	90.844
1797	14.73	46.65	4.0812	90.921
1528	13.66	45.97	6.0080	<u>91.379</u>
Average				90.981 ± .173

estimate the heat capacity of the liquid (10.0 cal/deg) and assume that it is constant over the whole temperature range. A change of 0.5 cal/deg in the heat capacity from the estimated value of 10.0 cal/deg would change the calculated boiling point by about 5°, and since the heat capacity figure is believed to be quite good ( $\pm 1$  cal/deg) the value reported for the normal boiling point is believed to be fairly accurate.

## 2. Yttrium

The vapor pressure measurements on yttrium metal were made in the liquid region on two different batches of metal; the vapor pressure was too low in the solid state to obtain an appreciable weight loss. The data for run #4 are tabulated in Table 5, and are typical of the measurements on yttrium; a plot of the data is given in Figure 5, for which the equation representing the straight line through all the data points (62 points, 3 runs) is

$$\log P_{\text{mm}} = 8.836 \pm .056 - \frac{20685 \pm 112}{T} . \quad (24)$$

The heat of vaporization at the average mid-range temperature of 2000°K was  $94.654 \pm 0.51$  kcal/mole obtained from the slope of the line.

Third law calculations made on the data of run #4 are tabulated in Table 6. The average value of the heat of

Table 5. Vapor pressure data for yttrium

Run #4	$\Delta H$ 95.278 $\pm$ .81 kcal/mole
Orifice area - 15.284 $\times 10^{-3}$ cm <sup>2</sup>	A 20821 $\pm$ 178
Clousing factor - .9666	B 8.882 $\pm$ .0877
	RMSD in log P - .0168

Point	Mass, mg	Time, sec	Temperature °K	10 <sup>4</sup> /T	-log P <sub>mm</sub>
1	3.620	100.7	2178	4.591	.6915
2	3.564	104.5	2171	4.606	.7151
3	3.164	123	2150	4.651	.8395
4	3.635	151	2131	4.693	.8701
5	3.257	167	2109	4.742	.9636
6	1.560	80.8	2109	4.742	.9679
7	2.859	204	2084	4.798	1.1096
8	2.926	260	2062	4.850	1.2070
9	2.852	314	2048	4.883	1.3015
10	2.731	370	2027	4.933	1.3936
11	2.827	457	2012	4.970	1.4718
12	2.806	574	1991	5.023	1.5762
13	2.438	598	1973	5.068	1.6568
14	2.444	767	1953	5.120	1.7660
15	2.334	948	1934	5.171	1.8799
16	2.884	1470	1913	5.227	1.9808
17	1.237	1005	1884	5.308	2.1864
18	2.628	3045	1858	5.382	2.3434

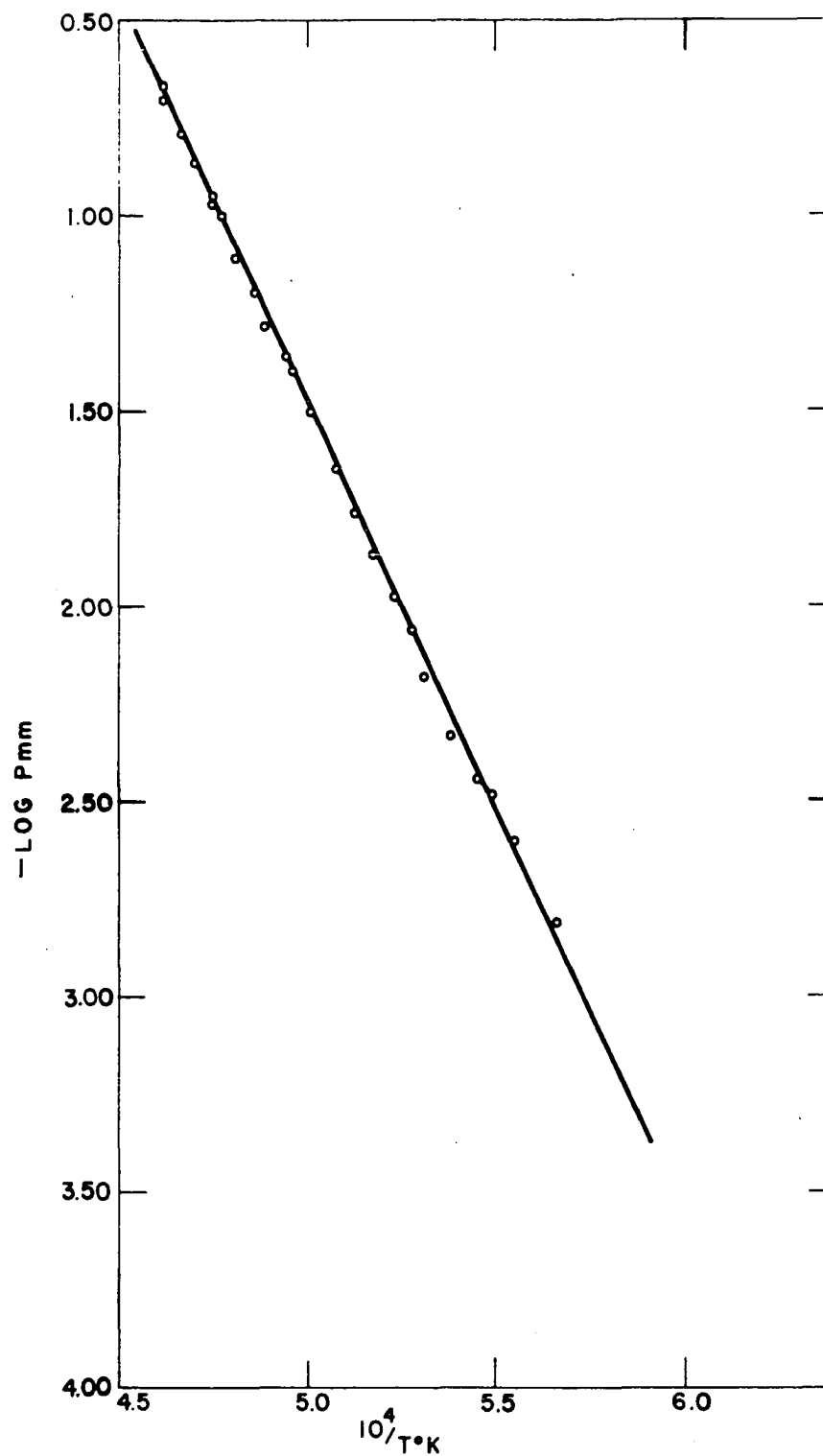


Figure 5. Vapor pressure of yttrium (1780-2185°K)

Table 6. Thermodynamic calculations for yttrium metal

Temp. °K	$-\left(\frac{F_T^0 - H_{298}^0}{T}\right)_c$	$-\left(\frac{F_T^0 - H_{298}^0}{T}\right)_g$	$-\log P_{atm.}$	$\Delta H_{298}^0$ kcal/mole
2178	18.98	49.23	3.5723	101.488
2171	18.95	49.22	3.5959	101.440
2150	18.87	49.18	3.7203	101.768
2131	18.79	49.14	3.7509	101.252
2109	18.70	49.09	3.8444	101.194
2109	18.70	49.09	3.8487	101.236
2084	18.59	49.03	3.9904	101.491
2062	18.50	48.98	4.0878	101.422
2048	18.44	48.95	4.1823	101.679
2027	18.35	48.90	4.2744	101.573
2012	18.28	48.87	4.3526	101.620
1991	18.19	48.82	4.4570	101.591
1973	18.11	48.78	4.5376	101.479
1953	18.02	48.73	4.6468	101.505
1934	17.94	48.68	4.7607	101.583
1913	17.85	48.63	4.8616	101.441
1884	17.71	48.56	5.0672	101.808
1858	17.59	48.50	5.2242	<u>101.848</u>
Average				101.523 ± .146

sublimation at 298°K is  $101.523 \pm .146$  kcal/mole compared to  $102.963 \pm 0.6$  kcal/mole obtained from the second law treatment. The normal boiling point calculated using the third law  $\Delta H_{298}^{\circ}$  is  $3610 \pm 5^{\circ}$ K. These calculations are based on the thermodynamic properties of condensed yttrium reported by Berg (46) and an extension of his data assuming a constant heat capacity for the liquid. The thermodynamic properties of yttrium vapor were taken from Stull and Sinke (45).

### 3. Lanthanum

The data for run #3 is given in Table 7, and a plot of the vapor pressure data is shown in Figure 6. The equation for the most accurate straight line through all the data points (40 points, 2 runs) for lanthanum is

$$\log P_{\text{mm}} = 8.876 \pm .078 - \frac{22019 \pm 157}{T} \quad (25)$$

and the heat of vaporization at the average mid-range temperature of 2040°K obtained from the slope of the line is  $100.758 \pm 0.72$  kcal/mole.

The first two runs on lanthanum metal were made starting at the highest temperature of the run with subsequent decreasing temperature as usual, when at a temperature of about 1780°K, the vapor pressure appeared to remain constant as the temperature was lowered still further. This phenomena was followed for about 50° before the runs were discontinued. The effusion cells were examined for possible leakage, and

Table 7. Vapor pressure data for lanthanum

Run #3  $\Delta H$  99.901  $\pm$  .92 kcal/mole  
 Orifice area - 15.592  $\times 10^{-3}$  cm<sup>2</sup> A 21831  $\pm$  200  
 Clausing factor - .9686 B 8.771  $\pm$  .0980  
 RMSD in log P - .0106

Point	Mass, mg	Time, sec	Temperature °K	10 <sup>4</sup> /T	-log P <sub>mm</sub>
1	1.507	1893	1939	5.157	2.4762
2	2.907	3067	1953	5.120	2.3989
3	3.028	2314	1979	5.053	2.2561
4	2.866	1925	1991	5.023	2.1989
5	2.979	1686	2007	4.983	2.1229
6	3.524	1699	2019	4.953	2.0520
7	3.594	1469	2035	4.914	1.9787
8	2.845	970	2047	4.885	1.8988
9	2.931	892	2052	4.873	1.8490
10	2.859	720	2071	4.829	1.7648
11	3.553	694	2093	4.778	1.6523
12	2.923	432	2119	4.719	1.5288
13	2.859	355	2135	4.684	1.4516
14	2.893	292	2155	4.640	1.3598



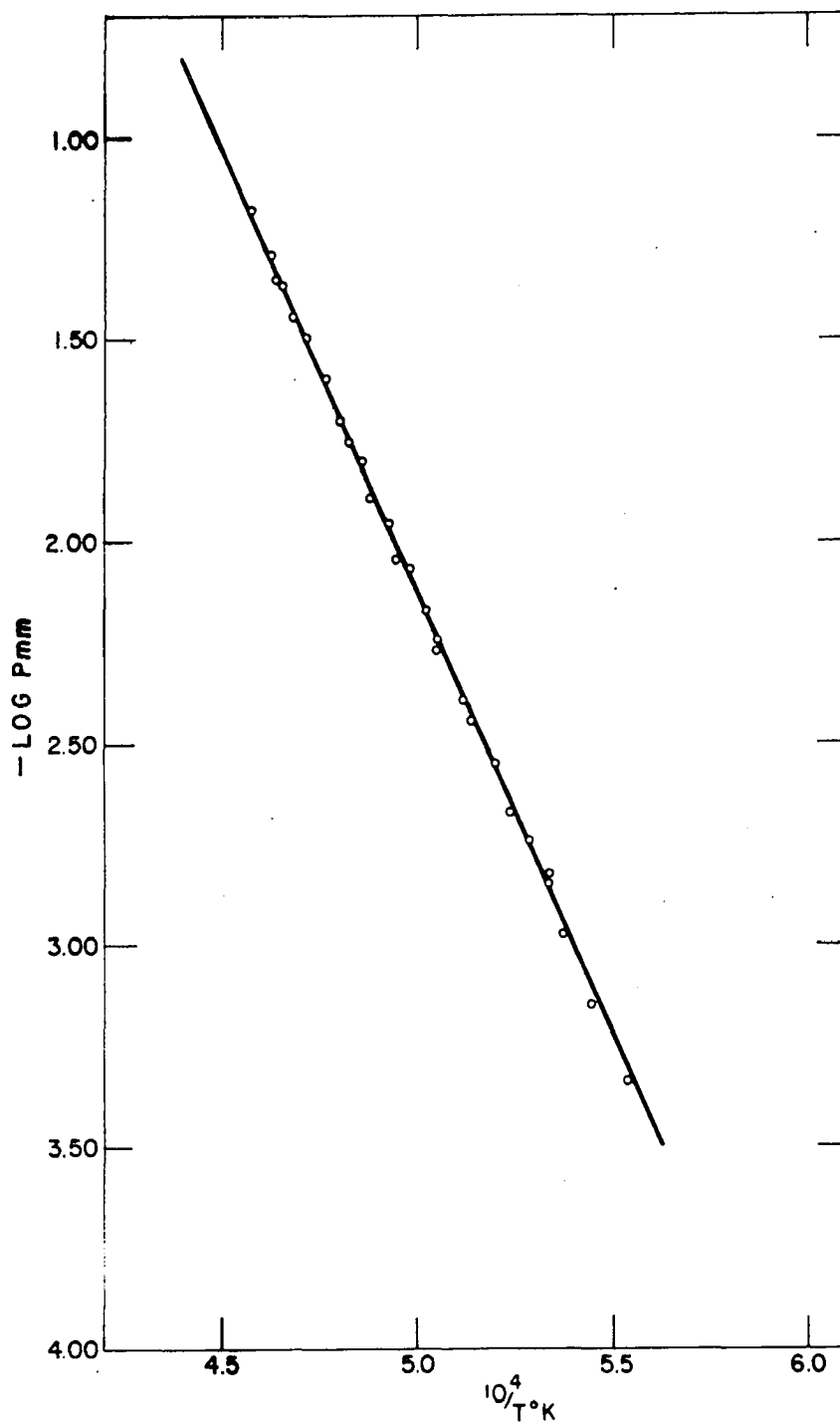


Figure 6. Vapor pressure of lanthanum (1874-2182°K)

a defective area in the tantalum around the orifices was discovered. The grain boundaries on the outer side of the lid had become greatly enlarged, and contained a deposit of lanthanum metal, which appeared to have diffused through the lid by way of the grain boundaries. Since this same phenomena occurred in two runs at almost the same temperature, it would appear to be more than coincidence, and suggests that some sort of reaction is taking place at the grain boundaries, induced by a transition in the tantalum or the lanthanum. When vapor pressure measurements were taken beginning at the lowest temperature with increasing temperature, the above phenomena was not encountered. Therefore, only those runs made using the latter procedure were used in the results presented in this thesis.

Third law calculations based on run #3 are tabulated in Table 8. The average value of  $\Delta H_{298}^{\circ}$  is  $102.964 \pm .074$  kcal/mole compared to  $104.062 \pm 0.8$  kcal/mole obtained from the second law method. The normal boiling point calculated from equation 22 using the third law heat of sublimation is  $3727 \pm 5^{\circ}\text{K}$ . The thermodynamic properties for the condensed phases of lanthanum were taken from Berg (46), and for the gaseous phase from Stull and Sinke (45). Berg's data was extended using a constant heat capacity for the liquid in order to make the boiling point calculation.

Table 8. Thermodynamic calculations for lanthanum metal

Temp. °K	$-\left(\frac{F_T^{\circ} - H_{298}^{\circ}}{T}\right)_c$	$-\left(\frac{F_T^{\circ} - H_{298}^{\circ}}{T}\right)_g$	$-\log P_{\text{atm.}}$	$\Delta H_{298}^{\circ}$ kcal/mole
1939	21.66	50.21	5.3570	102.891
1953	21.72	50.25	5.2797	102.904
1979	21.83	50.33	5.1369	102.920
1991	21.88	50.37	5.0797	103.004
2007	21.95	50.42	5.0037	103.094
2019	21.99	50.46	4.9328	103.054
2035	22.05	50.51	4.8595	103.168
2047	22.09	50.54	4.7796	103.007
2052	22.11	50.56	4.7298	102.793
2071	22.18	50.61	4.6457	102.906
2093	22.26	50.68	4.5331	102.898
2119	22.36	50.76	4.4096	102.937
2135	22.41	50.80	4.3324	102.939
2155	22.48	50.86	4.2406	<u>102.977</u>
				Average 102.964 ± .074

4. Cerium

The data in Table 9 are from run #2 for cerium metal, and a plot of minus the log of the vapor pressure versus the reciprocal of the absolute temperature is shown in Figure 7 for all the points (34 points, 2 runs). The vapor pressure data, when fitted to a straight line by a least squares treatment taking the temperature as the independent variable, give the equation

$$\log P_{mm} = 9.396 \pm .079 - \frac{22991 \pm 165}{T} . \quad (26)$$

This corresponds to a heat of vaporization of  $105.208 \pm 0.76$  kcal/mole at the average mid-range temperature of  $2100^{\circ}\text{K}$  from the slope of the line.

Third law calculations for cerium and several other rare earth elements are not possible at the present time since the thermodynamic properties of these metal vapors have not been evaluated, due to lack of data on the low lying electronic states. The difference in the enthalpies of the condensed and vapor phases therefore becomes a problem of estimating the heat capacities of the gases, since the heat capacities of all the condensed phases of the rare earth elements have been measured. For cerium, the difference in the enthalpies between the mid-range temperature and  $298^{\circ}\text{K}$  is about 6.3 kcal/mole, therefore the  $\Delta H_{298}^{\circ}$  would be 111.6 kcal/mole. The boiling point, based on the assumption that  $\Delta C_p$  between

Table 9. Vapor pressure data for cerium

Run #2  $\Delta H$  104.408  $\pm$  .87 kcal/mole  
 Orifice area - 46.951  $\times 10^{-3}$  cm<sup>2</sup> A 22816  $\pm$  171  
 Clausing factor - .9806 B 9.300  $\pm$  .0832  
 RMSD in log P - .0198

Point	Mass, mg	Time, sec	Temperature °K	10 <sup>4</sup> /T	-log P <sub>mm</sub>
1	7.544	71.6	2252	4.440	.7987
2	3.510	42.8	2232	4.480	.9093
3	5.128	77.9	2215	4.515	1.0063
4	3.979	75.0	2199	4.548	1.1014
5	3.466	82.1	2175	4.598	1.2028
6	3.750	112	2155	4.640	1.3054
7	2.411	88.2	2130	4.695	1.3958
8	2.848	138	2113	4.733	1.5195
9	2.827	178	2084	4.798	1.6360
10	3.286	261	2064	4.845	1.7388
11	2.910	302	2046	4.888	1.8568
12	2.856	378	2027	4.933	1.9643
13	2.840	504	1999	5.003	2.0945
14	2.157	506	1983	5.043	2.2173
15	1.885	566	1962	5.097	2.3267
16	2.100	901	1938	5.160	2.4841
17	1.659	950	1916	5.219	2.6119
18	1.440	1343	1887	5.299	2.8269
19	3.459	3943	1861	5.373	2.9168

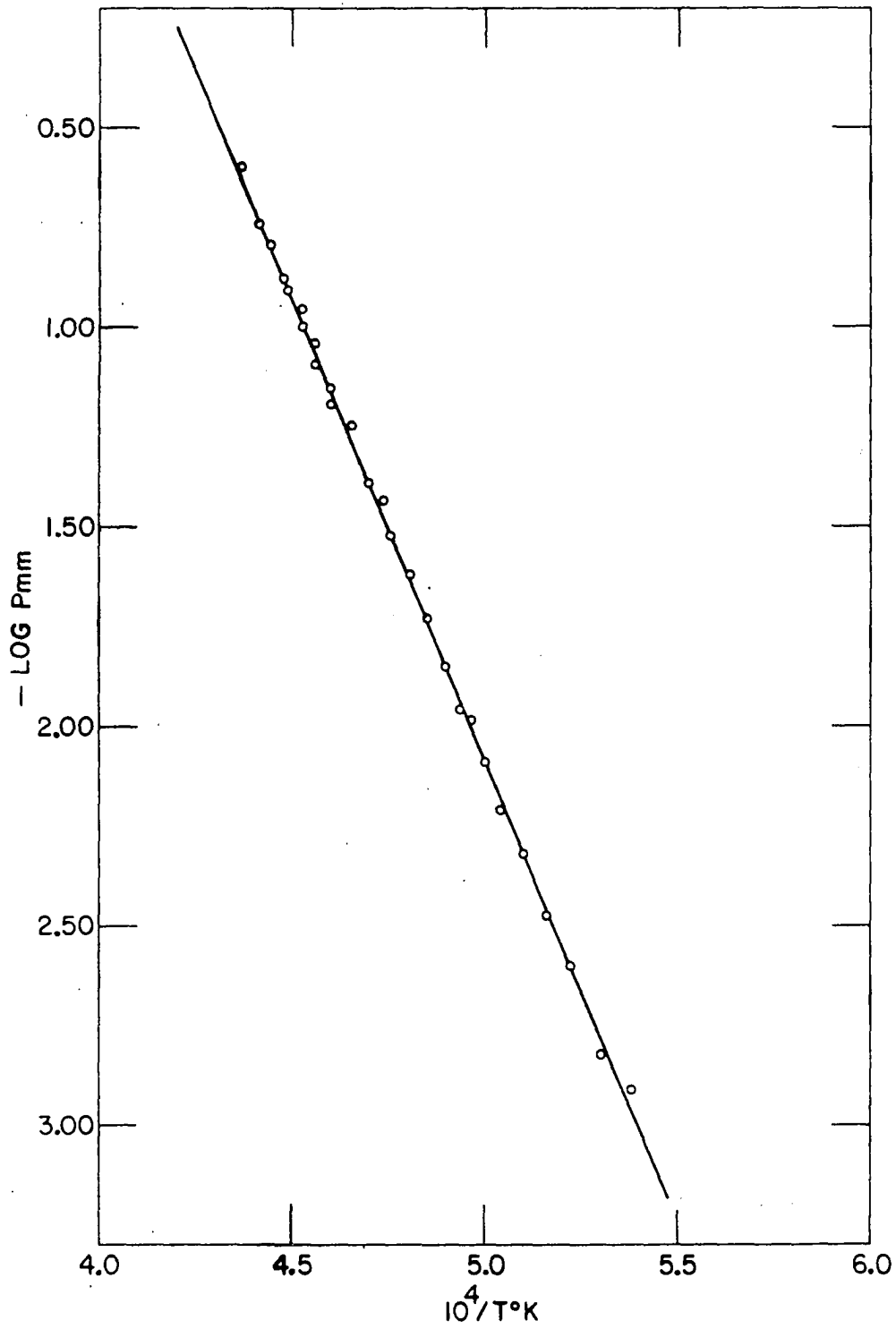


Figure 7. Vapor pressure of cerium (1861-2292°K)

the condensed and vapor phases is zero, would be  $3530 \pm 30^\circ\text{K}$ .

### 5. Praseodymium

The measurements on praseodymium are represented by run #2 tabulated in Table 10, and a plot of the data for this metal is shown in Figure 8. The data (70 points, 3 runs) when fitted to a straight line, give the equation

$$\log P_{\text{mm}} = 8.069 \pm .038 - \frac{18083 \pm 73}{T} . \quad (27)$$

The heat of vaporization is  $82.748 \pm 0.33$  kcal/mole at the average mid-range temperature of  $1900^\circ\text{K}$ .

As is the case with cerium, the thermodynamic properties of praseodymium vapor are unknown, so the difference in the enthalpies between the condensed and vapor phases was estimated to be 6.34 kcal/mole. This would make  $\Delta H_{298}^\circ = 89.09 \pm 0.4$  kcal/mole. The boiling point based on the assumption that  $\Delta C_p$  is zero would be  $3485 \pm 30^\circ\text{K}$ .

### 6. Neodymium

The vapor pressure measurements on neodymium are represented by run #4 tabulated in Table 11, and a plot of the data for this metal is shown in Figure 9. The data (76 points, 4 runs) when fitted to a straight line, give the equation

$$\log P_{\text{mm}} = 8.102 \pm .034 - \frac{16320 \pm 59}{T} . \quad (28)$$

Table 10. Vapor pressure data for praseodymium

Run #2  $\Delta H$  82.546  $\pm$  .85 kcal/mole  
 Orifice area -  $8.593 \times 10^{-3} \text{ cm}^2$  A 18039  $\pm$  186  
 Clausing factor - .9537 B 8.034  $\pm$  .0956  
 RMSD in log P - .0228

Point	Mass, mg	Time, sec	Temperature °K	$10^4/T$	$-\log P_{\text{mm}}$
1	4.824	107	2120	4.717	.4452
2	3.269	87.3	2105	4.751	.5272
3	3.907	112	2087	4.792	.5598
4	3.367	133	2076	4.817	.7000
5	3.085	131	2063	4.847	.7328
6	3.212	160	2049	4.880	.8035
7	3.775	223	2029	4.929	.8795
8	2.922	192	2007	4.983	.9280
9	2.850	225	1992	5.020	1.0091
10	2.830	255	1987	5.033	1.0670
11	2.843	324	1955	5.115	1.1724
12	2.854	394	1939	5.157	1.2573
13	2.947	510	1922	5.203	1.3573
14	2.862	611	1901	5.260	1.4506
15	3.847	1050	1882	5.313	1.5594
16	3.119	1130	1858	5.382	1.6850
17	2.613	1213	1837	5.444	1.7949
18	2.075	1298	1813	5.516	1.9272
19	2.614	2090	1788	5.593	2.0366
20	8.401	10549	1755	5.698	2.2365



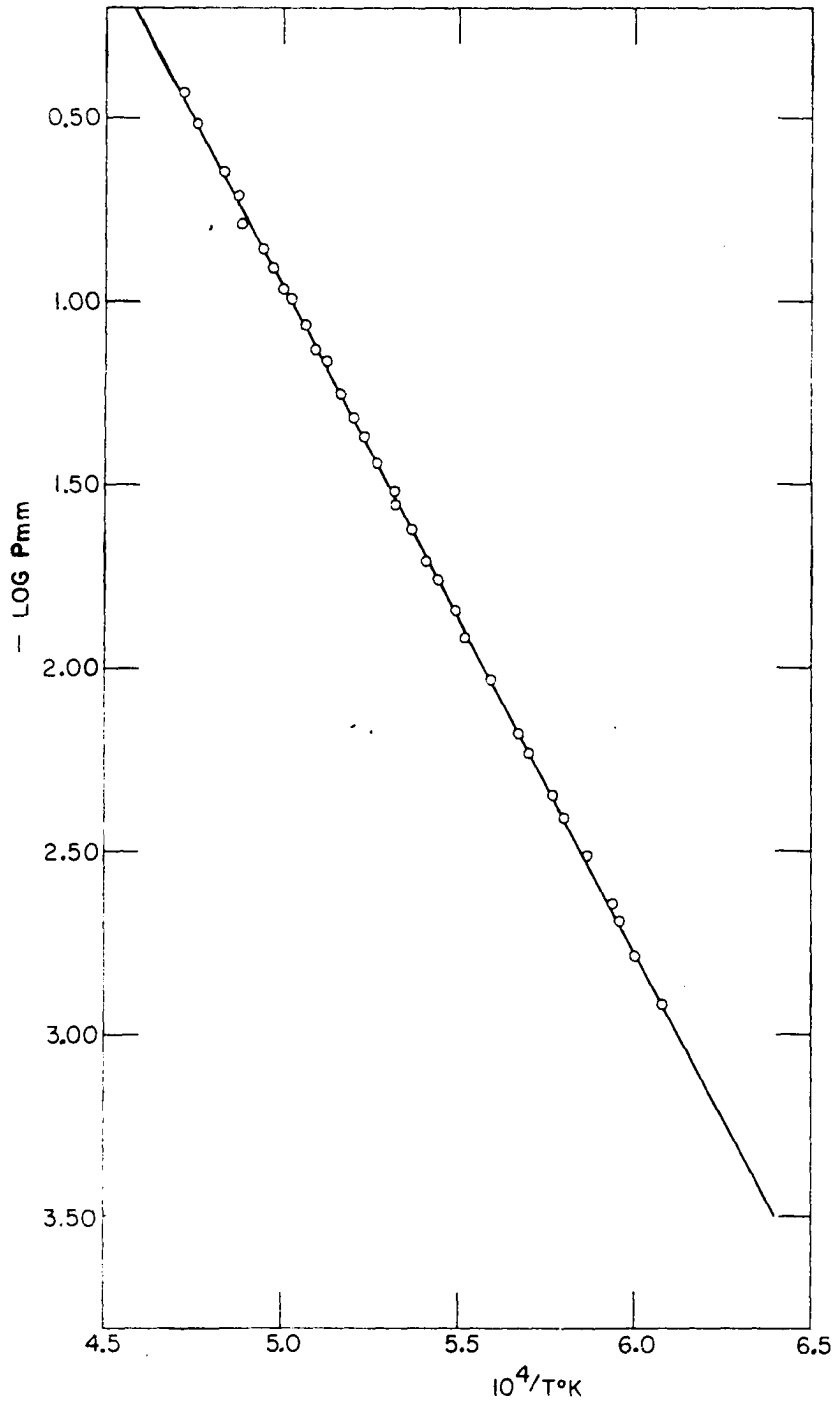


Figure 8. Vapor pressure of praseodymium (1644-2120°K)

Table 11. Vapor pressure data for neodymium

Run #4  $\Delta H$  74.670  $\pm$  .50 kcal/mole  
 Orifice area -  $8.626 \times 10^{-3}$  cm<sup>2</sup> A 16317  $\pm$  110  
 Clausing factor - .9582 B 8.097  $\pm$  .0624  
 RMSD in log P - .0171

Point	Mass, mg	Time, sec	Temperature °K	$10^4/T$	$-\log P_{\text{mm}}$
1	4.066	99	1894	5.280	.5173
2	4.882	104.4	1910	5.236	.4592
3	3.099	57	1923	5.200	.3924
4	3.488	77.6	1898	5.269	.4777
5	3.567	112.1	1870	5.348	.6308
6	2.921	105	1858	5.382	.6904
7	2.388	105	1838	5.441	.7801
8	4.324	230	1822	5.488	.8645
9	2.827	193	1793	5.577	.9763
10	3.138	245	1784	5.605	1.0356
11	2.871	283	1767	5.659	1.1387
12	3.736	462	1747	5.724	1.2396
13	3.382	521	1734	5.767	1.3365
14	3.081	591	1717	5.824	1.4338
15	2.853	732	1687	5.928	1.5637
16	3.193	988	1674	5.974	1.6467
17	2.143	963	1653	6.050	1.8112
18	2.278	1410	1618	6.180	1.9547
19	1.691	1788	1584	6.313	2.1917
20	5.466	12160	1538	6.502	2.5208

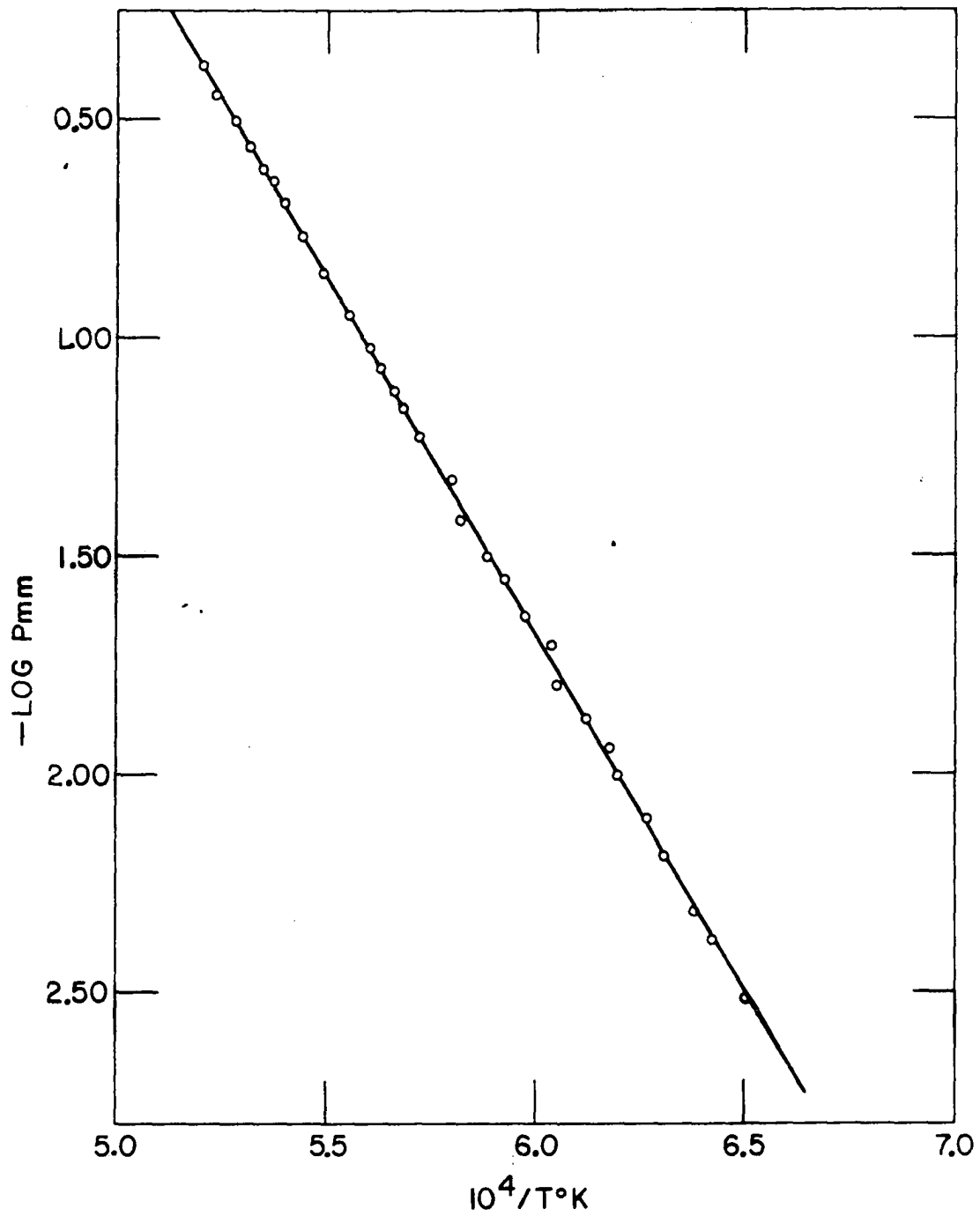


Figure 9. Vapor pressure of neodymium (1528-1923°K)

The heat of vaporization is  $74.682 \pm 0.27$  kcal/mole at an average mid-range temperature of  $1725^{\circ}\text{K}$ .

Third law calculations based on the data of run #4 are shown in Table 12. The average value for the heat of sublimation at  $298^{\circ}\text{K}$  was  $78.443 \pm 0.206$  kcal/mole compared to  $81.507 \pm 0.4$  kcal/mole from the second law treatment. The normal boiling point calculated from equation 22 using the third law value of  $\Delta H_{298}^{\circ}$  is  $3400^{\circ} \pm 5^{\circ}\text{K}$ . The heat capacities and thermodynamic functions for the condensed phases of neodymium were taken from Hultgren (47), who based his table on McKeown's (48) work, and the corresponding functions for the gas phase were taken from Stull and Sinke (45).

## 7. Samarium

The vapor pressure measurements on samarium metal are represented by run #4 tabulated in Table 13, and a plot of the data for this metal is given in Figure 10. The data (109 points, 5 runs) when fitted to a straight line give the equation

$$\log P_{\text{mm}} = 8.781 \pm .029 - \frac{10784 \pm 30}{T} . \quad (29)$$

The heat of sublimation, obtained from the slope of the line, is  $49.349 \pm 0.14$  kcal/mole, at an average mid-range temperature of  $1045^{\circ}\text{K}$ . Temperature measurements for the samarium runs were made with a Pt-Pt/13% Rh thermocouple.

Third law calculations based on the data of run #4 are

Table 12. Thermodynamic calculations for neodymium metal

Temp. °K	$-\left(\frac{F_T^0 - H_{298}^0}{T}\right)_c$	$-\left(\frac{F_T^0 - H_{298}^0}{T}\right)_g$	$-\log P_{\text{atm.}}$	$\Delta H_{298}^0$ kcal/mole
1894	25.74	51.46	3.3981	78.165
1910	25.82	51.51	3.3400	78.260
1923	25.89	51.55	3.2732	78.147
1898	25.76	51.47	3.3585	77.966
1870	25.61	51.39	3.5116	78.258
1858	25.54	51.35	3.5712	78.318
1838	25.44	51.29	3.6609	78.302
1822	25.35	51.25	3.7453	78.415
1793	25.19	51.16	3.8571	78.211
1784	25.14	51.13	3.9164	78.337
1767	25.05	51.08	4.0195	78.495
1747	24.94	51.02	4.1204	78.501
1734	24.87	50.98	4.2173	78.737
1717	24.78	50.93	4.3146	78.800
1687	24.62	50.84	4.4445	78.543
1674	24.55	50.79	4.5275	78.608
1653	24.44	50.72	4.6920	78.932
1618	24.25	50.60	4.8355	78.436
1584	24.06	50.49	5.0725	78.633
1538	23.82	50.34	5.4016	78.804
Average				78.443 ± .206

Table 13. Vapor pressure data for samarium

Run #4  $\Delta H$  49.919  $\pm$  .27 kcal/mole  
 Orifice area -  $3.349 \times 10^{-3}$  cm<sup>2</sup> A 10909  $\pm$  48  
 Clausing factor - .9351 B 8.901  $\pm$  .0441  
 RMSD in log P - .0155

Point	Mass, mg	Time, sec	Temperature °K	$10^4/T$	$-\log P_{\text{mm}}$
1	3.451	69.2	1208	8.278	.1155
2	4.051	105.9	1191	8.396	.2336
3	3.558	124.1	1176	8.503	.3616
4	4.371	69.1	1222	8.183	.0098
5	2.962	143	1159	8.628	.5058
6	2.998	169	1151	8.688	.5745
7	2.880	197	1141	8.764	.6604
8	4.202	320	1134	8.818	.7113
9	2.927	297	1121	8.921	.8354
10	4.311	524	1112	8.993	.9155
11	3.059	433	1104	9.058	.9831
12	4.854	808	1098	9.107	1.0547
13	2.827	550	1089	9.183	1.1241
14	3.125	685	1083	9.234	1.1771
15	6.010	1715	1072	9.328	1.2938
16	3.067	1165	1057	9.461	1.4210
17	3.049	1472	1048	9.542	1.5268
18	2.233	1324	1039	9.625	1.6181
19	4.044	3030	1027	9.737	1.7221
20	3.106	3890	1007	9.930	1.9493
21	4.442	44717	923	10.834	2.8729
22	2.167	10521	951	10.515	2.5498
23	1.706	4826	973	10.277	2.3104
24	1.415	3078	984	10.163	2.1940

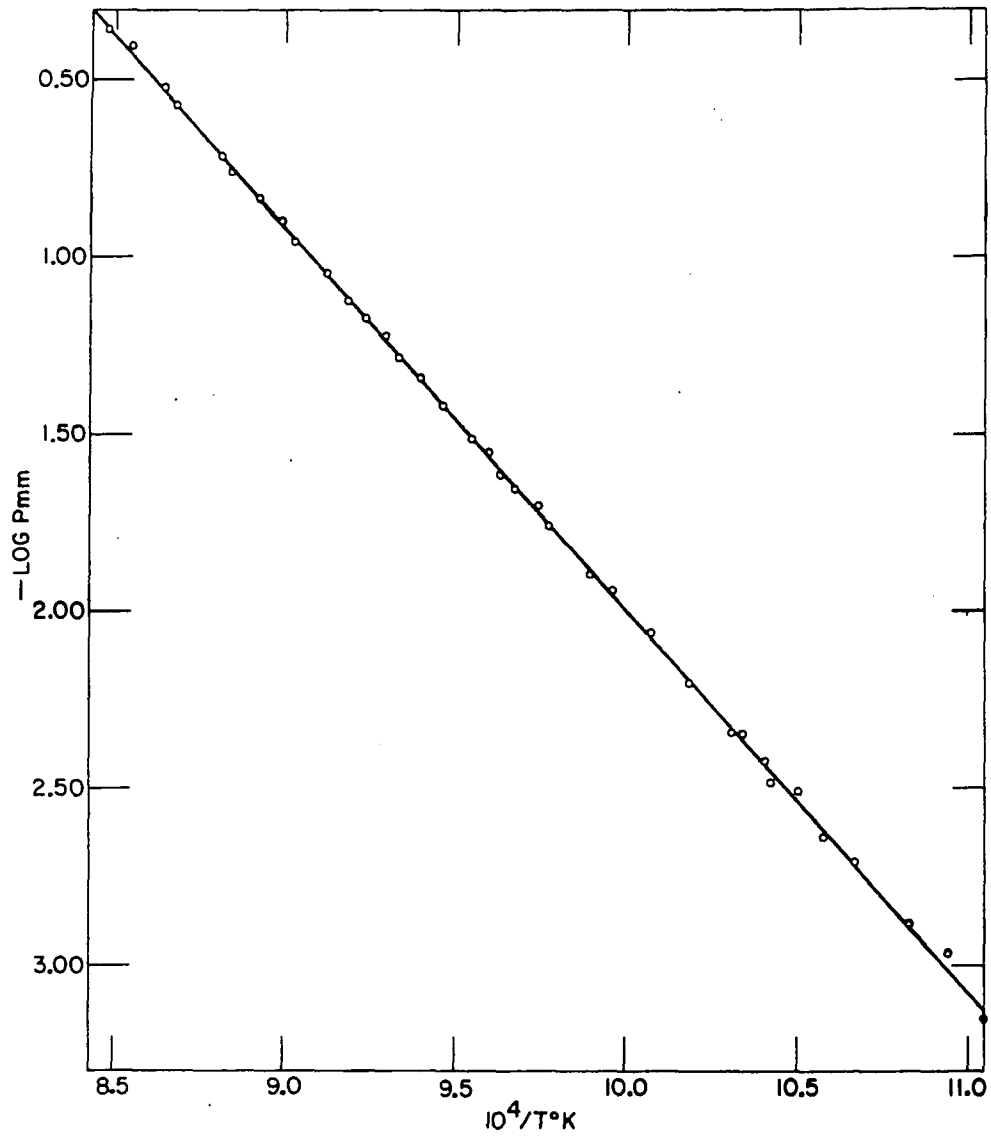


Figure 10. Vapor pressure of samarium (885-1222°K)

tabulated in Table 14. The average value for the heat of sublimation at 298°K was  $48.587 \pm .215$  kcal/mole compared to  $51.030 \pm 0.3$  kcal/mole from the second law treatment. The normal boiling point calculated from equation 22 using the third law value of  $\Delta H_{298}^{\circ}$  is  $2025^{\circ} \pm 15^{\circ}$ K. The heat capacities and thermodynamic functions for the condensed phases were taken from Hultgren (47), which was based on McKeown's (48) work, and the same quantities for the gas phase were again taken from Stull and Sinke (45).

## 8. Europium

The vapor pressure of europium metal was measured by Hanak (22), and was not re-measured in this investigation. Third law calculations based on Hanak's vapor pressure data are presented in Table 15. The average value for the heat of sublimation at 298°K was  $41.923 \pm 0.027$  kcal/mole compared to  $42.177 \pm .025$  by the second law method. The normal boiling point was found to be 1885°K compared to 1762°K obtained by Hanak from estimated thermodynamic data. The thermodynamic data for the condensed phases of europium were taken from Berg's (46) data along with the value of  $S_{298}^{\circ} = 19.307$  e.u. obtained from Gerstein.\*

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\*Gerstein, B. C., Ames Laboratory, Iowa State University of Science and Technology, Ames, Iowa. Entropy of europium metal at 298°K. Private communication. 1963.



Table 14. Thermodynamic calculations for samarium metal

Temp. °K	$-\left(\frac{F_T^{\circ} - H_{298}^{\circ}}{T}\right)_c$	$-\left(\frac{F_T^{\circ} - H_{298}^{\circ}}{T}\right)_g$	$-\log P_{\text{atm.}}$	$\Delta H_{298}^{\circ}$ kcal/mole
1208	22.29	48.46	2.9963	48.176
1191	22.21	48.38	3.1144	48.141
1176	22.11	48.30	3.2424	48.248
1222	22.39	48.52	2.8906	48.094
1159	22.00	48.22	3.3866	48.350
1151	21.95	48.18	3.4553	48.389
1141	21.89	48.14	3.5412	48.441
1134	21.85	48.10	3.5921	48.407
1121	21.76	48.04	3.7162	48.522
1112	21.71	48.00	3.7963	48.552
1104	21.66	47.96	3.8639	48.555
1098	21.62	47.93	3.9355	48.662
1089	21.56	47.89	4.0049	48.630
1083	21.52	47.86	4.0579	48.636
1072	21.45	47.78	4.1746	48.704
1057	21.35	47.73	4.3018	48.691
1048	21.29	47.69	4.4076	48.804
1039	21.23	47.64	4.4989	48.830
1027	21.25	47.58	4.6029	48.775
1007	21.02	47.48	4.8301	48.903
923	20.44	47.03	5.7537	48.844
951	20.63	47.19	5.4306	48.890
973	20.78	47.30	5.1912	48.918
984	20.86	47.36	5.0748	<u>48.926</u>
Average				48.587 ± .215

Table 15. Thermodynamic calculations for europium metal

Temp. °K	$-\left(\frac{F_T^O - H_{298}^O}{T}\right)_c$	$-\left(\frac{F_T^O - H_{298}^O}{T}\right)_g$	$-\log P_{atm.}$	$\Delta H_{298}^O$ kcal/mole
753	21.51	46.70	6.6754	41.970
801	21.78	46.89	5.9383	41.879
696	21.18	46.47	7.6566	41.988
773	21.62	46.78	6.3482	41.904
817	21.87	46.95	5.7243	41.891
862	22.11	47.13	5.1560	41.913
843	22.01	47.05	5.3989	41.935
830	21.94	47.00	5.5532	41.891
852	22.06	47.09	5.2820	41.918
791	21.72	46.85	6.0866	41.909
734	21.40	46.63	6.9548	41.878
881	22.22	47.20	4.9365	41.908
885	22.24	47.21	4.9020	41.951
899	22.31	47.27	4.7314	41.903
869	22.15	47.15	5.0810	41.930
764	21.57	46.75	6.4919	41.934
744	21.46	46.67	6.8262	41.997
783	21.67	46.82	6.2036	<u>41.920</u>
Average				41.923 ± .027

9. Gadolinium

The vapor pressure data obtained for gadolinium liquid is represented by run #9 tabulated in Table 16, and a plot of the data (161 points, 10 runs) when fitted to a straight line, shown in Figure 11, gives the equation

$$\log P_{\text{mm}} = 8.517 \pm .049 - \frac{19600 \pm 90}{T}, \quad (30)$$

the slope of which gives a heat of vaporization of  $89.689 \pm 0.41$  kcal/mole at the average mid-range temperature of  $1860^{\circ}\text{K}$ .

Third law calculations based on run #9 are tabulated in Table 17; the average value for the heat of sublimation at  $298^{\circ}\text{K}$  is  $95.752 \pm .067$  kcal/mole compared with  $95.987 \pm 0.5$  kcal/mole obtained by the second law treatment. The normal boiling point calculated from equation 22 using the third law  $\Delta H_{298}^{\circ}$  is  $3506^{\circ} \pm 5^{\circ}\text{K}$ . These calculations were based on the heat capacities and thermodynamic functions calculated from the heat content data of Dennison\* for the condensed phases, and the value of  $S_{298}^{\circ} = 15.774$  e.u. obtained by Griffel (49). The data for the thermodynamic properties of gadolinium vapor were again taken from Stull and Sinke (45).

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\*Dennison, D. H., Ames Laboratory, Iowa State University of Science and Technology, Ames, Iowa. Heat content of gadolinium. Private communication. 1963.

Table 16. Vapor pressure data for gadolinium

Run #9  $\Delta H$  89.797  $\pm$  .44 kcal/mole  
 Orifice area - 8.479 x 10<sup>-3</sup> cm<sup>2</sup> A 19623  $\pm$  97  
 Clausing factor - .9359 B 8.568  $\pm$  .0507  
 RMSD in log P - .00911

Point	Mass, mg	Time, sec	Temperature °K	10 <sup>4</sup> /T	-log P <sub>mm</sub>
1	2.655	163	2070	4.831	.9020
2	3.089	220	2058	4.859	.9677
3	3.182	296	2032	4.921	1.0863
4	3.070	360	2013	4.968	1.1887
5	2.974	465	1987	5.033	1.3163
6	3.604	696	1969	5.079	1.4098
7	2.688	692	1942	5.149	1.5376
8	6.749	4582	1862	5.371	1.9672
9	4.657	1786	1906	5.247	1.7144
10	5.906	2861	1888	5.297	1.8178
11	2.136	2110	1833	5.456	2.1332
12	2.175	2734	1813	5.516	2.2401
13	1.333	2557	1785	5.602	2.4268
14	4.032	11396	1760	5.682	2.5981

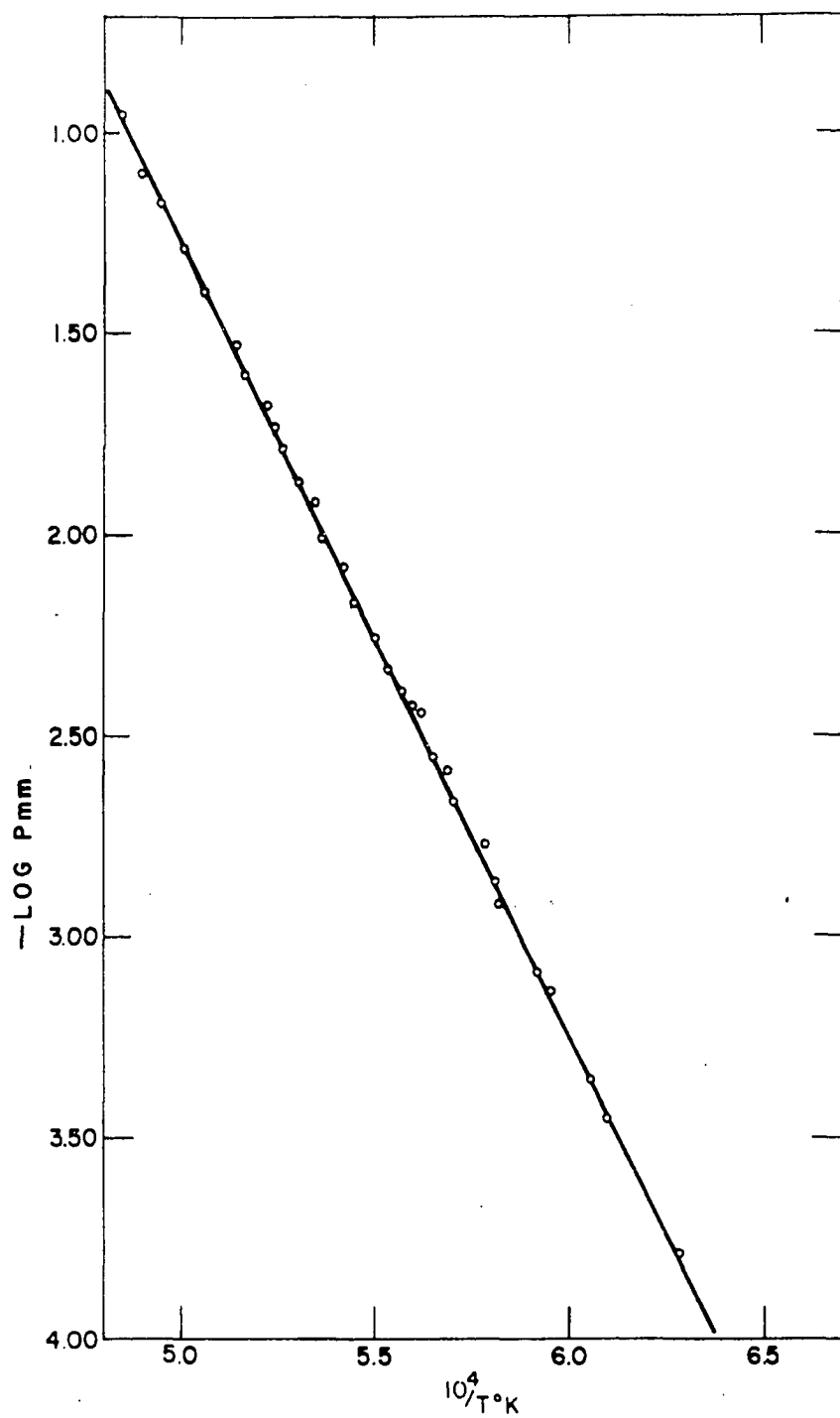


Figure 11. Vapor pressure of gadolinium (1620-2097°K)

Table 17. Thermodynamic calculations for gadolinium metal

Temp. °K	$-\left(\frac{F_T^O - H_{298}^O}{T}\right)_c$	$-\left(\frac{F_T^O - H_{298}^O}{T}\right)_g$	$-\log P_{atm.}$	$\Delta H_{298}^O$ kcal/mole
2070	24.31	53.19	3.7828	95.613
2058	24.26	53.16	3.8485	95.720
2032	24.15	53.09	3.9671	95.693
2013	24.07	53.04	4.0695	95.803
1987	23.96	52.98	4.1971	95.825
1969	23.88	52.93	4.2906	95.859
1942	23.76	52.86	4.4184	95.777
1862	23.41	52.65	4.8480	95.751
1906	23.61	52.77	4.5952	95.658
1888	23.53	52.72	4.6986	95.705
1833	23.28	52.57	5.0140	95.745
1813	23.19	52.52	5.1209	95.659
1785	23.06	52.44	5.3076	95.797
1760	22.93	52.36	5.4789	<u>95.922</u>
Average				95.752 ± .067

10. Terbium

The vapor pressure measurements on terbium liquid are represented by run #5 tabulated in Table 18, and a plot of the data for this metal is shown in Figure 12. The equation for the best straight line through all the data points (179 points, 10 runs) is

$$\log P_{\text{mm}} = 8.657 \pm .078 - \frac{19147 \pm 141}{T}, \quad (31)$$

the slope of which gives a heat of vaporization of  $87.619 \pm 0.65$  kcal/mole at the average mid-range temperature of  $1815^{\circ}\text{K}$ .

Since the thermodynamic properties of terbium, dysprosium, holmium, erbium and thulium vapors are unknown, third law calculations were not made for these metals. Estimating the difference in the enthalpies of terbium solid and vapor between the mid-range temperature and  $298^{\circ}\text{K}$  to be 6.3 kcal/mole, the  $\Delta H_{298}^{\circ}$  would be 93.96 kcal/mole. The boiling point, making the assumption that  $\Delta C_p$  between the condensed and gas phases is zero, is  $3314 \pm 30^{\circ}\text{K}$ .

11. Dysprosium

The vapor pressure measurements of dysprosium metal are represented by run #3 tabulated in Table 19, and a plot of the data is given in Figure 13. The equation for the best straight line through all the data points (79 points, 5 runs) is

Table 18. Vapor pressure data for terbium

Run #5  $\Delta H$  87.974  $\pm$  .92 kcal/mole  
 Orifice area -  $8.875 \times 10^{-3}$  cm<sup>2</sup> A 19225  $\pm$  200  
 Clausing factor - .9437 B 8.681  $\pm$  .114  
 RMSD in log P - .0233

Point	Mass, mg	Time, sec	Temperature °K	10 <sup>4</sup> /T	-log P <sub>mm</sub>
1	1.963	30850	1598	6.258	3.3887
2	1.660	10385	1648	6.068	2.9824
3	1.835	6748	1688	5.924	2.7467
4	4.128	10428	1708	5.855	2.5811
5	2.850	5631	1720	5.814	2.4730
6	2.780	3145	1762	5.675	2.2258
7	3.031	2744	1779	5.621	2.1272
8	2.179	1361	1802	5.549	1.9632
9	2.117	963	1828	5.470	1.8226
10	1.782	653	1850	5.405	1.7262
11	2.032	739	1850	5.405	1.7231
12	2.575	683	1874	5.336	1.5833
13	1.759	346	1900	5.263	1.4508
14	1.873	279	1918	5.214	1.3281
15	2.712	23767	1620	6.173	3.1322



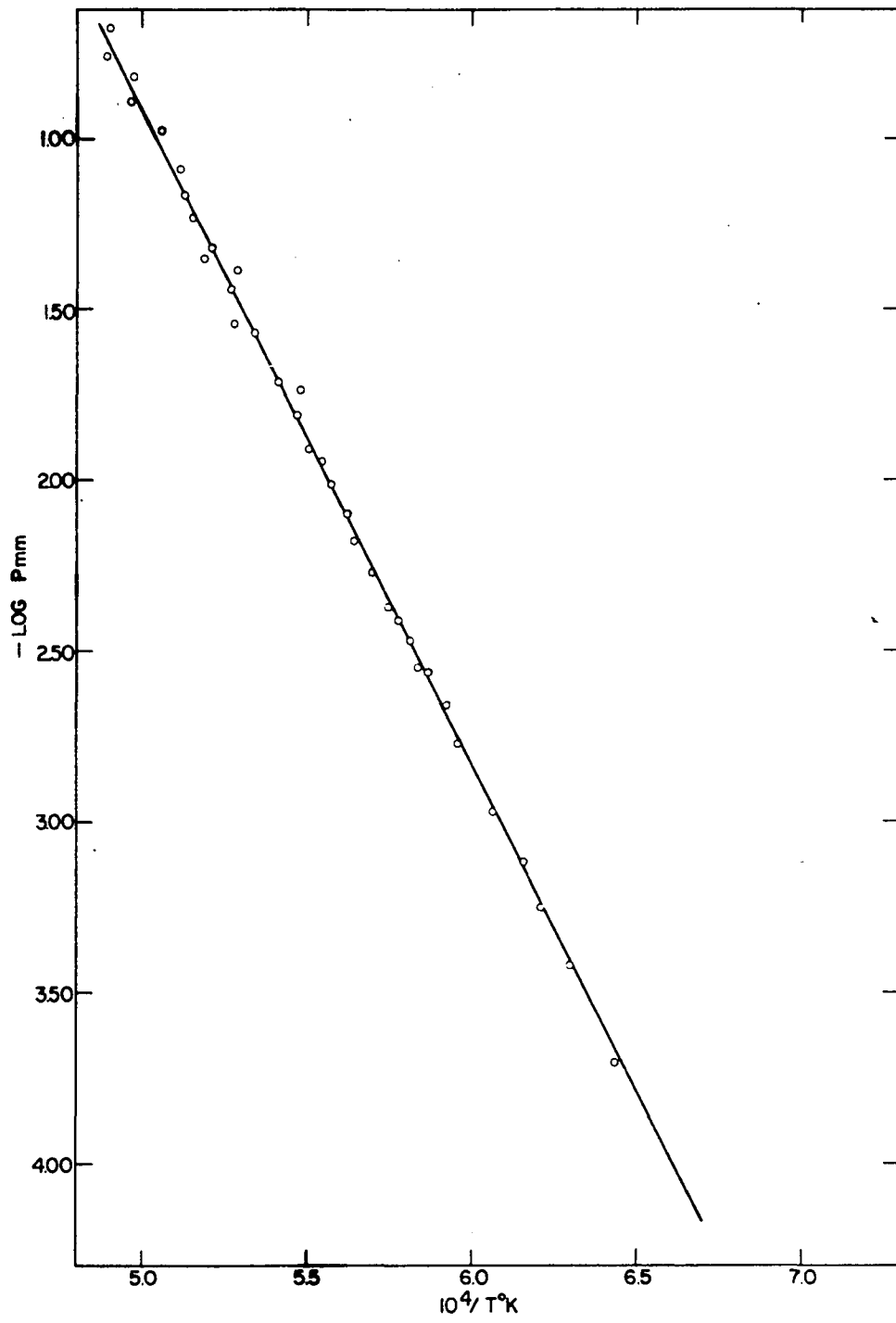


Figure 12. Vapor pressure of terbium (1625-2043°K)

Table 19. Vapor pressure data for dysprosium

Run #3  $\Delta H$  68.844  $\pm$  .67 kcal/mole  
 Orifice area - 8.709  $\times 10^{-3}$  cm<sup>2</sup> A 15044  $\pm$  147  
 Clausing factor - .9541 B 8.761  $\pm$  .0973  
 RLSD in log P - .0211

Point	Mass, mg	Time, sec	Temperature °K	10 <sup>4</sup> /T	-log P <sub>mm</sub>
1	8.267	102	1666	6.002	.2767
2	9.266	137	1650	6.061	.3573
3	5.272	106	1623	6.161	.4942
4	4.145	120	1595	6.270	.6561
5	3.221	138	1569	6.373	.8297
6	3.215	185	1548	6.460	.9606
7	2.739	226	1522	6.570	1.1207
8	2.786	333	1496	6.684	1.2851
9	2.707	494	1471	6.798	1.4724
10	2.877	723	1451	6.892	1.6143
11	2.810	1190	1421	7.037	1.8453
12	2.704	2043	1391	7.189	2.1011
13	2.162	3375	1339	7.468	2.4241

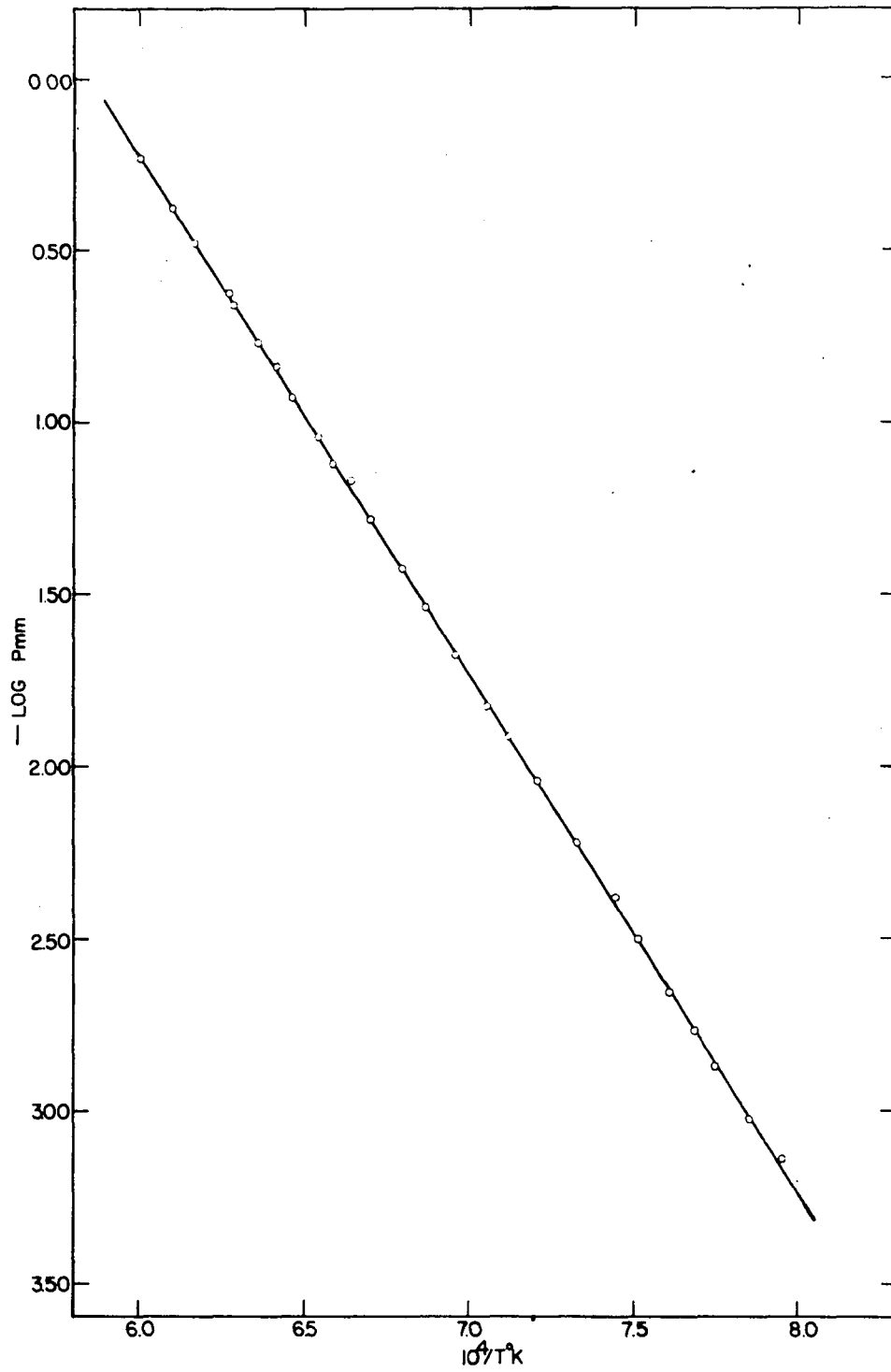


Figure 13. Vapor pressure of dysprosium (1257-1690°K)

$$\log P_{\text{mm}} = 8.822 \pm .035 - \frac{15090 \pm 52}{T}, \quad (32)$$

from which the heat of sublimation is calculated to be  $69.052 \pm 0.24$  kcal/mole at the average mid-range temperature of  $1485^{\circ}\text{K}$ . The difference in the enthalpies between the condensed and gaseous phases is approximately 1.9 kcal/mole, resulting in a value for  $\Delta H_{298}^{\circ}$  of 70.91 kcal/mole. The boiling point, again based on the assumption that  $\Delta C_p$  is zero, is  $2608^{\circ} \pm 20^{\circ}\text{K}$ .

## 12. Holmium

The vapor pressure of holmium has recently been measured in this laboratory by Wakefield (8), and was not repeated in this investigation.

## 13. Erbium

The vapor pressure measurements made on erbium metal are represented by run #5 tabulated in Table 20, and a plot of the data is given in Figure 14. The points (82 points, 5 runs) when fitted to a straight line, give the equation

$$\log P_{\text{mm}} = 9.222 \pm .037 - \frac{17324 \pm 60}{T}, \quad (33)$$

the slope of which gives a heat of sublimation of  $79.276 \pm 0.27$  kcal/mole at the average mid-range temperature of  $1615^{\circ}\text{K}$ .

The difference in the enthalpies of vapor and condensed

Table 20. Vapor pressure data for erbium

Run #5	$\Delta H$ 79.193 $\pm$ .38 kcal/mole
Orifice area - $8.692 \times 10^{-3} \text{ cm}^2$	A 17306 $\pm$ 84
Clausing factor - .9584	B 9.204 $\pm$ .0504
	RMSD in log P - .0156

Point	Mass, mg	Time, sec	Temperature °K	$10^4/T$	$-\log P_{\text{mm}}$
1	13.540	125	1859	5.379	.1354
2	10.732	114	1844	5.423	.1980
3	7.755	101	1824	5.482	.2888
4	7.487	128	1798	5.562	.4098
5	5.298	117	1779	5.621	.5232
6	5.831	144	1767	5.659	.5731
7	4.264	146	1744	5.734	.7177
8	3.754	166	1727	5.790	.8308
9	2.906	162	1701	5.879	.9346
10	2.784	203	1686	5.931	1.0530
11	2.764	272	1666	6.002	1.1856
12	5.002	624	1650	6.061	1.2906
13	3.564	644	1622	6.165	1.4550
14	2.732	633	1604	6.234	1.5653
15	2.814	1013	1578	6.337	1.7601
16	2.812	1838	1542	6.485	2.0239
17	2.904	3194	1512	6.614	2.2539
18	3.578	7767	1471	6.798	2.5506
19	2.302	9000	1443	6.930	2.8144

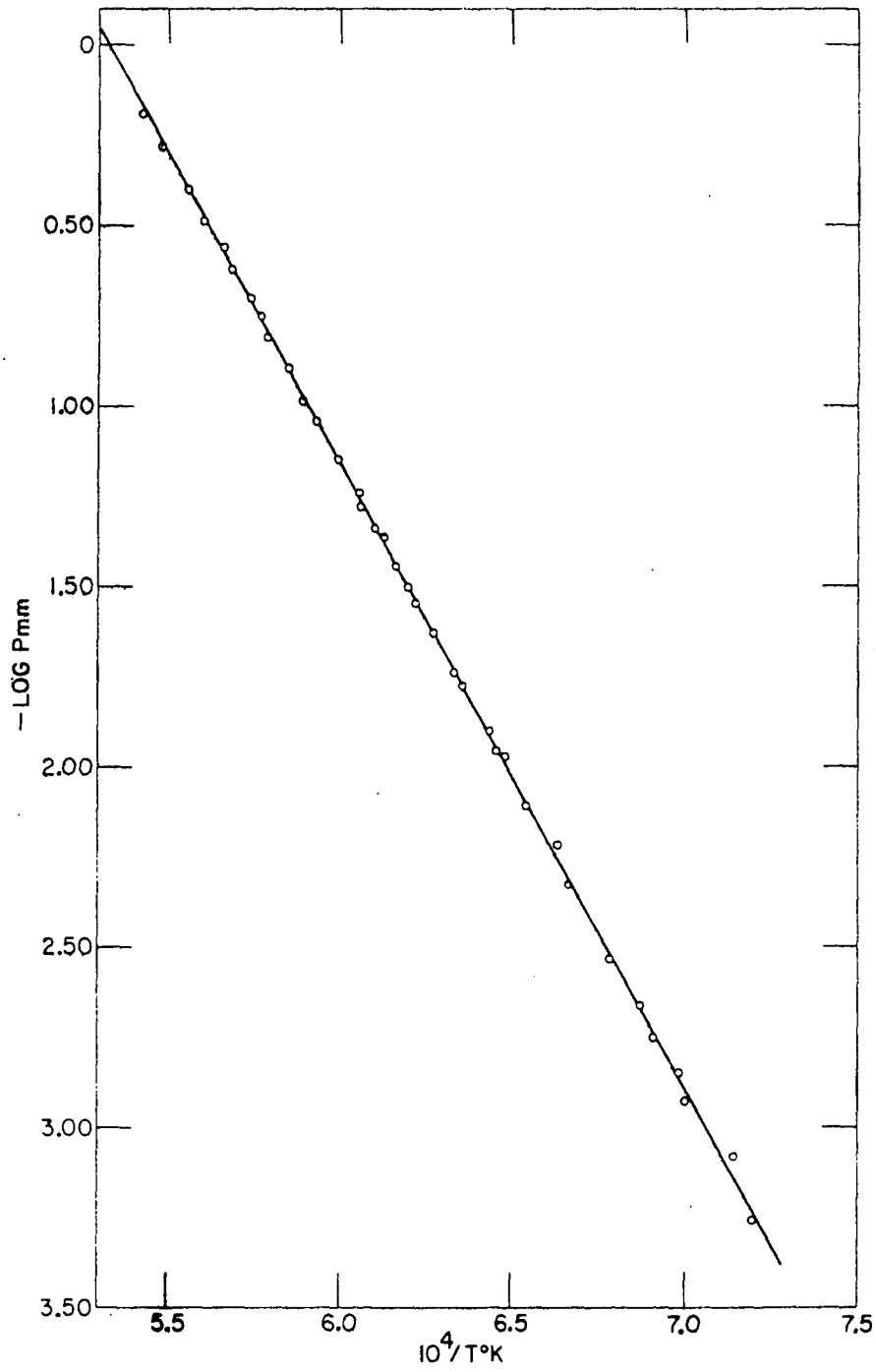


Figure 14. Vapor pressure of erbium (1392-1780°K)

phases would be about 2.5 kcal/mole resulting in  $\Delta H_{298}^{\circ} = 81.79$  kcal/mole. The boiling point, based on  $\Delta C_p = 0$  for erbium would be  $2783^{\circ} \pm 20^{\circ}\text{K}$ .

#### 14. Thulium

The vapor pressure of thulium has been measured in this laboratory by Barton (23), and the results of this investigation indicate no disagreement with his work.

#### 15. Ytterbium

The vapor pressure measurements obtained for ytterbium are represented by run #13 given in Table 21, and are plotted in Figure 15. The data (157 points, 8 runs) when fitted to a straight line, give the equation

$$\log P_{\text{mm}} = 8.295 \pm .043 - \frac{7696 \pm 33}{T}, \quad (34)$$

indicating a heat of sublimation of  $35.216 \pm 0.15$  kcal/mole at the mid-range temperature of  $777^{\circ}\text{K}$ . Temperature measurements for these runs were made with a Pt-Pt/13% Rh thermocouple.

Third law calculations based on run #13 are tabulated in Table 22; the average value for the heat of sublimation at  $298^{\circ}\text{K}$  is  $36.332 \pm .057$  kcal/mole compared to  $36.217 \pm 0.2$  kcal/mole obtained by the second law method. The normal boiling point calculated from equation 22 using the third law  $\Delta H_{298}^{\circ}$

Table 21. Vapor pressure data for ytterbium

Run #13 H 35.174  $\pm$  .16 kcal/mole  
 Orifice area - 3.526 x 10<sup>-3</sup> cm<sup>2</sup> A 7687  $\pm$  34  
 Clausing factor - .9362 B 8.325  $\pm$  .0430  
 RMSD in log P - .0145

Point	Mass, mg	Time, sec	Temperature °K	10 <sup>4</sup> /T	-log P <sub>mm</sub>
1	5.063	68.1	914	10.941	.0541
2	3.824	78.1	896	11.161	.2397
3	2.912	80.3	883	11.325	.3731
4	3.005	123	865	11.561	.5491
5	3.015	163	853	11.723	.6729
6	2.922	223	840	11.905	.8259
7	4.194	411	831	12.034	.9368
8	3.077	475	813	12.300	1.1387
9	2.963	572	805	12.422	1.2379
10	3.844	1076	791	12.642	1.4030
11	3.245	1223	781	12.804	1.5350
12	2.397	1360	766	13.055	1.7168
13	4.059	3405	753	13.280	1.8901
14	3.483	4586	737	13.569	2.0905
15	3.459	6618	725	13.793	2.2563
16	3.510	11420	710	14.085	2.4913
17	4.555	44979	679	14.728	2.9830
18	3.225	186	853	11.723	.7009
19	3.316	342	829	12.063	.9595
20	5.252	1004	806	12.407	1.2334



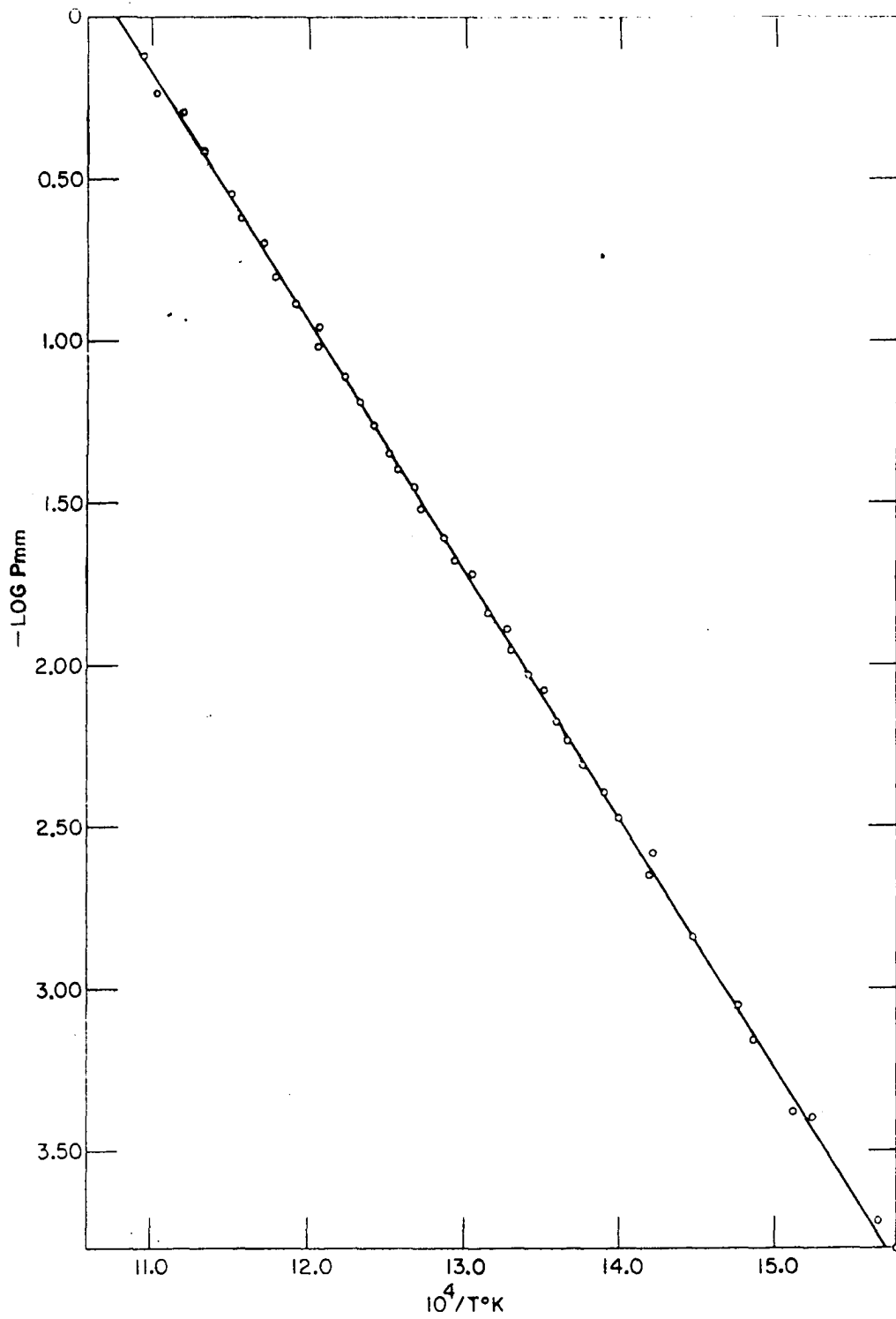


Figure 15. Vapor pressure of ytterbium (623-931°K)

Table 22. Thermodynamic calculations for ytterbium metal

Temp. °K	$-\left(\frac{F_T^O - H_{298}^O}{T}\right)_c$	$-\left(\frac{F_T^O - H_{298}^O}{T}\right)_g$	$-\log P_{atm.}$	$\Delta H_{298}^O$ kcal/mole
914	17.39	43.57	2.9349	36.204
896	17.30	43.51	3.1205	36.278
883	17.24	43.46	3.2539	36.300
865	17.13	43.39	3.4299	36.291
853	17.06	43.35	3.5537	36.297
840	16.99	43.30	3.7067	36.348
831	16.94	43.26	3.8176	36.389
813	16.84	43.20	4.0195	36.384
805	16.80	43.17	4.1187	36.400
791	16.72	43.09	4.2838	36.365
781	16.66	43.06	4.4158	36.400
766	16.58	43.00	4.5976	36.354
753	16.51	42.95	4.7709	36.349
737	16.42	42.88	4.9713	36.267
725	16.35	42.84	5.1371	36.248
710	16.27	42.78	5.3721	36.276
679	16.09	42.65	5.8638	36.254
853	17.06	43.35	3.5817	36.406
829	16.93	43.26	3.8403	36.396
806	16.80	43.17	4.1142	36.429
Average				36.332 ± .057

is  $1466^{\circ} \pm 5^{\circ}\text{K}$ . The thermodynamic functions used in these calculations were taken from Berg (46) along with the value of  $S_{298}^{\circ} = 14.311$  obtained from Gerstein\* for the condensed phases, and from Stull and Sinke (45) for the vapor phase.

#### 16. Lutetium

The data from run #3 tabulated in Table 23 are typical of the vapor pressure measurements made on lutetium metal. A plot of the data (60 points, 5 runs) is shown in Figure 16, and the equation of the straight line best representing all the data points is

$$\log P_{\text{mm}} = 9.247 \pm .095 - \frac{21719 \pm 173}{T} \quad (35)$$

The heat of sublimation calculated from the slope of this line is  $99.386 \pm 0.80$  kcal/mole at the mid-range temperature of  $1820^{\circ}\text{K}$ .

Third law calculations based on run #3 are tabulated in Table 24; the average value for the heat of sublimation at  $298^{\circ}\text{K}$  is  $102.158 \pm .095$  kcal/mole compared to  $102.198 \pm 0.9$  kcal/mole obtained by the second law method. The normal boiling point calculated from equation 22 using the third law  $\Delta H_{298}^{\circ}$  is  $3588^{\circ} \pm 5^{\circ}\text{K}$ . These calculations are based on the heat capacities and thermodynamic functions calculated from

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\*Gerstein, B. C., Ames Laboratory, Iowa State University of Science and Technology, Ames, Iowa. Entropy of ytterbium metal at  $298^{\circ}\text{K}$ . Private communication. 1963.

Table 25. Vapor pressure data for lutetium

Run #3  $\Delta H$  100.751  $\pm$  .55 kcal/mole  
 Orifice area - 34.046  $\times 10^{-3}$  cm<sup>2</sup> A 22017  $\pm$  120  
 Clausing factor - .9762 B 9.425  $\pm$  .0663  
 RMSD in log P - .0103

Point	Mass, mg	Time, sec	Temperature °K	10 <sup>4</sup> /T	-log P <sub>mm</sub>
1	4.649	934	1918	5.214	2.0681
2	2.968	797	1896	5.274	2.1965
3	2.797	962	1876	5.330	2.3062
4	3.243	1338	1863	5.368	2.3866
5	2.786	1707	1834	5.453	2.5615
6	1.749	1367	1822	5.488	2.6687
7	4.662	4639	1803	5.546	2.7756
8	2.680	4045	1778	5.624	2.9594
9	2.398	5450	1750	5.714	3.1404
10	4.160	14404	1728	5.787	3.3258
11	7.318	40193	1701	5.879	3.5294
12	3.337	43746	1651	6.057	3.9134
13	3.257	543	1930	5.181	1.9859

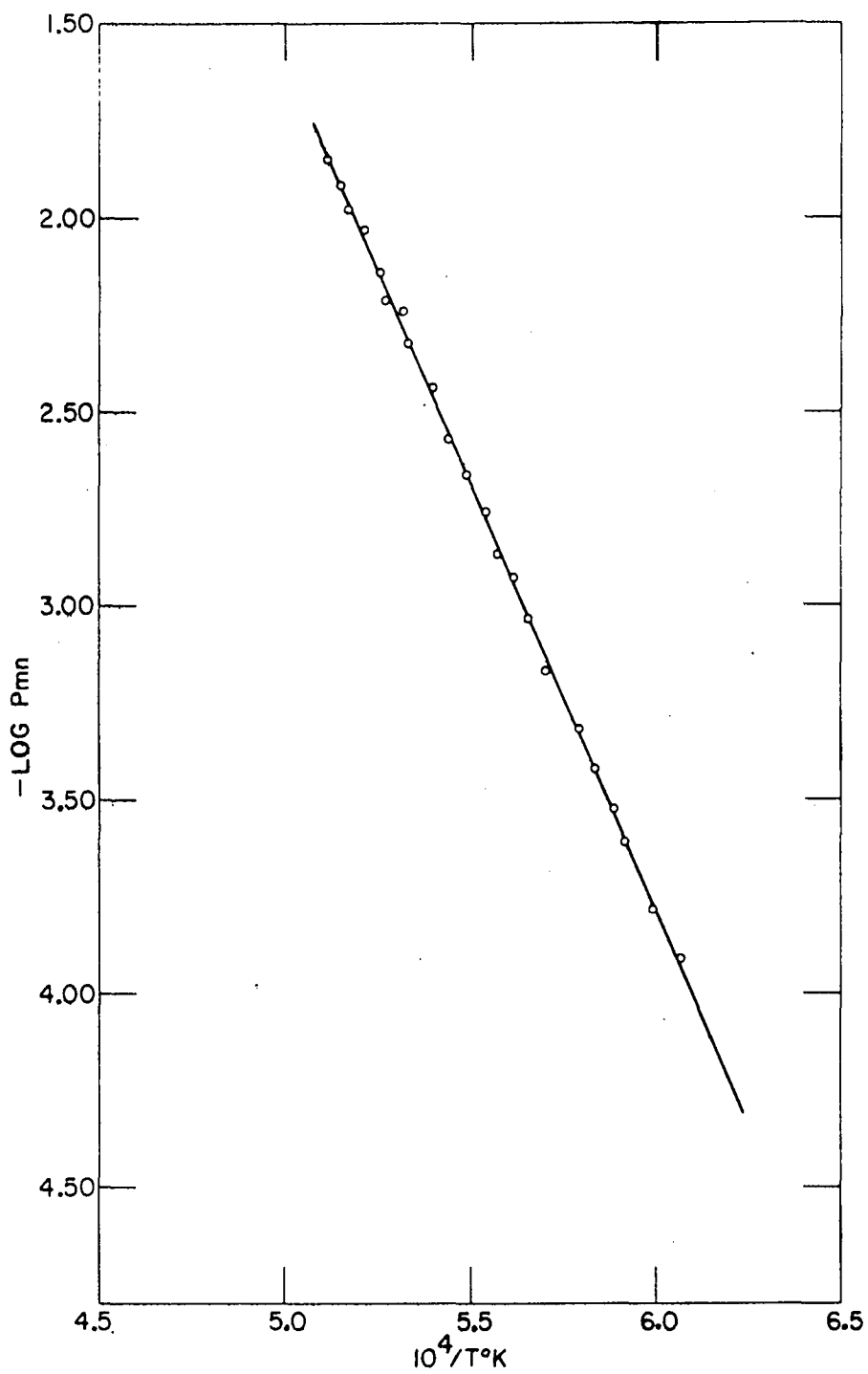


Figure 16. Vapor pressure of lutetium (1651-1932°K)

Table 24. Thermodynamic calculations for lutetium metal

Temp. °K	$-\left(\frac{F_T^{\circ} - H_{298}^{\circ}}{T}\right)_c$	$-\left(\frac{F_T^{\circ} - H_{298}^{\circ}}{T}\right)_g$	$-\log F_{\text{atm.}}$	$\Delta H_{298}^{\circ}$ kcal/mole
1930	19.23	49.84	4.8667	102.058
1918	19.18	49.81	4.9489	102.183
1896	19.11	49.75	5.0773	102.145
1876	19.03	49.70	5.1870	102.066
1863	18.98	49.66	5.2674	102.063
1834	18.88	49.58	5.4423	101.978
1822	18.83	49.55	5.5495	102.242
1803	18.76	49.50	5.6564	102.093
1778	18.67	49.43	5.8402	102.208
1750	18.57	49.35	6.0212	102.083
1728	18.48	49.29	6.2066	102.317
1701	18.38	49.21	6.4102	102.337
1651	18.20	49.06	6.7942	<u>102.279</u>
Average				102.158 ± .095

the heat content data of Dennison\* for the condensed phases, and the value of  $S_{298}^{\circ} = 12.18$  e.u. obtained by Jennings (50). The thermodynamic properties of lutetium vapor were taken from Stull and Sinke (45).

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\*Dennison, D. H., Ames Laboratory, Iowa State University of Science and Technology, Ames, Iowa. Heat content for lutetium. Private communication. 1963.

## V. DISCUSSION

### A. Knudsen Conditions

Using the methods described in Section III of this thesis, vapor pressure measurements were made on all but three of the rare earth metals. This represents data not previously reported in the case of samarium, gadolinium, terbium, ytterbium and lutetium and repetition of the work for the remainder of the elements. It was considered worthwhile to re-examine these elements so a consistent set of data based on one temperature calibration would be obtained in addition to resolving some of the discrepancies previously reported in the literature.

Vapor pressure measurements were made from approximately  $10^{-1}$  to  $10^{-4}$  mm of Hg on each element, corresponding to a 250-450 degree temperature range. Examining the data, one finds that the condition prescribed by Knudsen for free molecular flow, namely that the mean free path be 10 times greater than the orifice diameter, was not met in this work for about one-third of the pressure range covered. Table 25 shows the minimum value of this ratio for each element studied. However, the largest portion of the pressure range investigated was within the Knudsen condition, and the consistency of all the data seems to justify the assumption of free molecular flow for the entire range. Johnson (51)



Table 25. Minimum values for mean free path-to-orifice diameter ratio

Element	Orifice diameters (cm)	Ratio	Element	Orifice diameters (cm)	Ratio
Sc	0.14-0.24	2.5	Gd	0.08-0.26	3
Y	0.14	1.2	Tb	0.07-0.26	2
La	0.14-0.21	6.3	Dy	0.10	0.5
Ce	0.11-0.24	1.3	Er	0.10	0.5
Pr	0.10-0.14	1	Yb	0.07-0.15	0.5
Nd	0.10	1	Lu	0.10-0.30	2
Sm	0.07-0.14	0.5			

reported evidence that molecular flow occurs for a mean free path to orifice diameter ratio as low as 0.1, which is well into the region where Knudsen found isothermal diffusion. Carlson (52) observed in his detailed study of the phenomena of free molecular flow that deviation from the Knudsen flow condition took place at pressures of 0.1 mm of Hg with a mean free path to orifice diameter ratio of unity for mercury vapor, and Wakefield (8) reported no deviation in the vapor pressure of holmium for pressures as high as 10 mm of Hg. If all of these observations are considered to agree within an order of magnitude, one can conclude that molecular effusion occurs at least up to pressures corresponding to a mean free

path equal to the orifice diameter.

### B. Heats of Sublimation

Vapor pressure data are usually reported in the form of equation 8, and the heat of vaporization or sublimation at the temperature of the measurements equals  $2.303 RA$ , where  $R$  is the gas constant. When enthalpy data is unavailable for the liquid and vapor phases, equation 8 can be used to estimate the normal boiling point, but since this extrapolation usually covers a long temperature range, the accuracy is probably no better than  $100\text{--}200^\circ\text{C}$ . If the heat of sublimation is measured, the boiling point can be calculated from the Clausius-Clapyron equation, knowing the vapor pressure at the melting point and the heat of vaporization, obtained by subtracting the heat of fusion from the measured heat of sublimation. When free energy functions are available for both the gaseous and condensed phases, equation 22 is used to calculate the boiling point.

In order to compare the experimental heats of vaporization or sublimation, the measured quantities are usually converted to the heats of sublimation at  $298^\circ\text{K}$  using the heat capacities of the condensed and gas phases. If the heat capacities of the two phases are unknown, the conversion to  $298^\circ\text{K}$  requires an estimate of the enthalpy difference between the two phases. The heats of sublimation at  $298^\circ\text{K}$ , the normal

boiling points, and the constants A and B of the vapor pressure equation are summarized for the rare earth metals in Table 26.

For those elements whose heat contents and entropies are known and for which free energy functions can be obtained for both the condensed and gaseous phases, the third law test has been applied to the vapor pressure data. The calculated values of  $\Delta H_{298}^{\circ}$  for the individual measurements are then examined for consistency and for the existence of temperature dependent trends. The third law treatment is usually preferred since the attendant errors are smaller than those associated with finding the reaction heats from the slope of a line. However, one should compare the enthalpies derived by both methods as a check on the vapor pressure measurements and the entropy data.

The boiling point temperatures for the rare earth metals are plotted against atomic number in Figure 17. As previously stated, the heat capacities of several rare earth metal vapors are unknown, so the heat capacity corrections necessary for the boiling point calculations were ignored for those metals. The boiling points of these elements appear as open circles in the figure. When it becomes possible to make these corrections, the open circle points might be expected to be 100-200° higher. This would tend to straighten the curve between lanthanum and neodymium and bring terbium closer to gadolinium

Table 26. Vaporization and boiling point data

Element	Heat of vaporization				Vapor pressure data			Ref.
	Mid-range temp. °K	$\Delta H_T$ (kcal/mole)	$\Delta H_{298}^0$ (kcal/mole)		$\text{Log } P_{\text{mm}} = \frac{A}{T} + B$		Boiling temp. °K	
			2nd Law	3rd Law	-A	B		
Sc	1670	87.59 $\pm$ .4 <sup>a</sup>	92.20	90.98 $\pm$ .17	19140 $\pm$ 88	9.452 $\pm$ .052	3105 <sup>b</sup>	Author
Y	2000	94.65 $\pm$ .5	102.96	101.52 $\pm$ .15	20685 $\pm$ 112	8.836 $\pm$ .056	3610 <sup>b</sup>	"
La	2040	100.76 $\pm$ .7	104.06	102.96 $\pm$ .07	22019 $\pm$ 157	8.876 $\pm$ .078	3727 <sup>b</sup>	"
Ce	2100	105.21 $\pm$ .8	111.60		22991 $\pm$ 165	9.396 $\pm$ .079	3530 <sup>c</sup>	"
Pr	1900	82.75 $\pm$ .3	89.09		18083 $\pm$ 73	8.069 $\pm$ .038	3485 <sup>c</sup>	"
Nd	1725	74.68 $\pm$ .3	81.51	78.44 $\pm$ .21	16320 $\pm$ 59	8.102 $\pm$ .034	3400 <sup>b</sup>	"
Sm	1045	49.35 $\pm$ .1 <sup>a</sup>	51.03	48.59 $\pm$ .22	10784 $\pm$ 30	8.781 $\pm$ .029	2025 <sup>b</sup>	"
Eu	798	41.10 <sup>a</sup>	42.1	41.92 $\pm$ .03	8982 $\pm$ 16	8.160 $\pm$ .027	1885 <sup>b</sup>	22
Gd	1860	89.69 $\pm$ .4	95.99	95.75 $\pm$ .07	19600 $\pm$ 90	8.517 $\pm$ .049	3506 <sup>b</sup>	Author
Tb	1815	87.62 $\pm$ .7	93.96		19147 $\pm$ 141	8.659 $\pm$ .078	3314 <sup>c</sup>	"
Dy	1485	69.05 $\pm$ .2 <sup>a</sup>	70.91		15090 $\pm$ 52	8.822 $\pm$ .035	2608 <sup>d</sup>	"
Ho	1334	69.3 $\pm$ .6 <sup>a</sup>	70.6		15137	8.426	2845 <sup>d</sup>	8
Er	1615	79.28 $\pm$ .3 <sup>a</sup>	81.79		17324 $\pm$ 60	9.222 $\pm$ .037	2783 <sup>d</sup>	Author
Tm	1015	57.44 $\pm$ .2 <sup>a</sup>	59.1		12552 $\pm$ 45	9.176 $\pm$ .046	2005 <sup>d</sup>	23
Yb	777	35.22 $\pm$ .2 <sup>a</sup>	36.22	36.33 $\pm$ .06	7696 $\pm$ 33	8.295 $\pm$ .043	1466 <sup>b</sup>	Author
Lu	1820	99.39 $\pm$ .8 <sup>a</sup>	102.20	102.16 $\pm$ .10	21719 $\pm$ 173	9.247 $\pm$ .095	3588 <sup>b</sup>	"

<sup>a</sup>Heat of sublimation.<sup>b</sup>Using equation 22.<sup>c</sup>Using equation 8.<sup>d</sup>Using Clausius-Clayron equation.

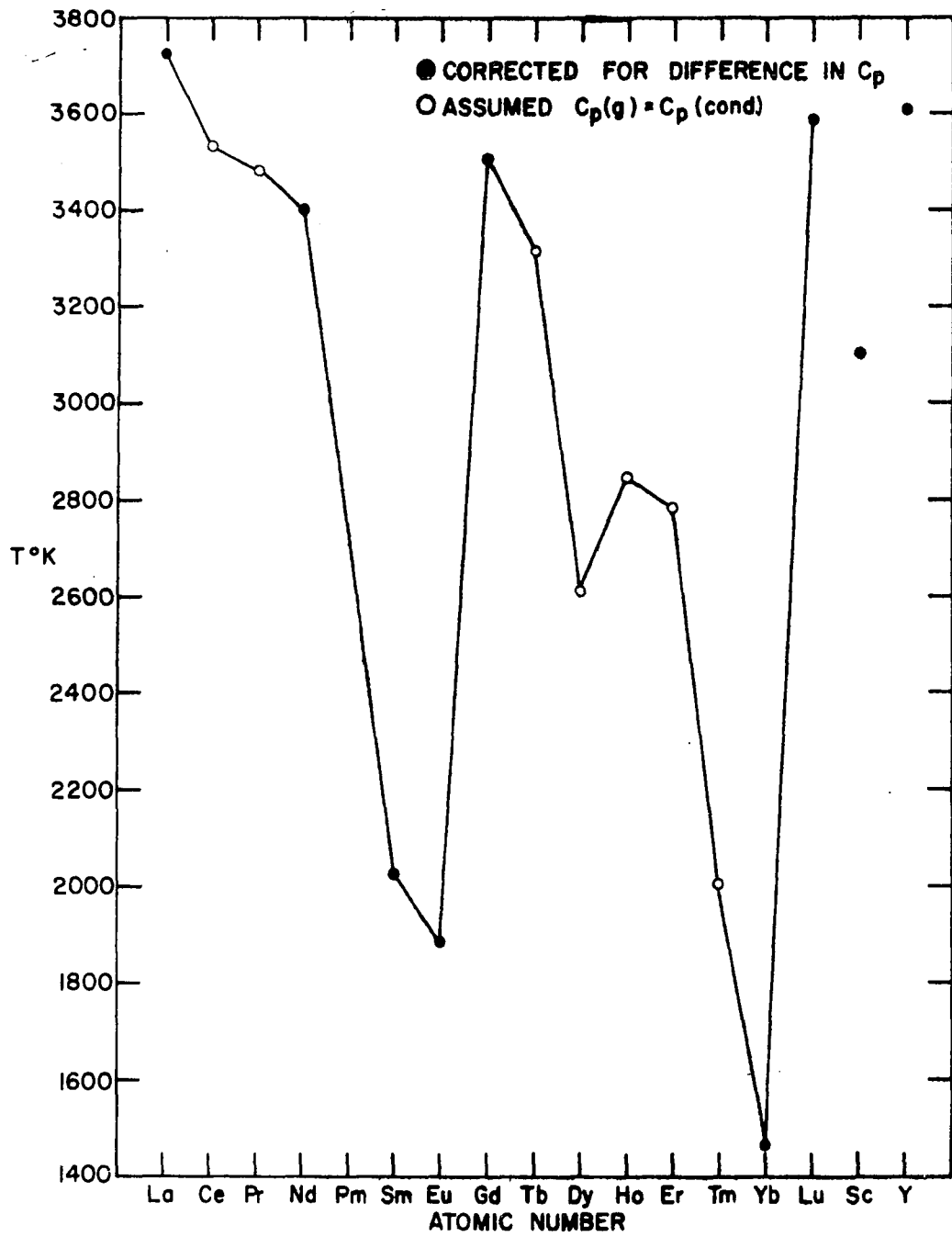


Figure 17. Boiling points of rare earth metals

but probably would not straighten out the hump near dysprosium, holmium and erbium. A similar plot of the melting points of the rare earth metals indicates that the lanthanide contraction affects the melting points more than the boiling points.

The heats of sublimation at  $298^{\circ}\text{K}$  for the rare earth metals are shown in Figure 18. When a third law calculation was possible, that value was selected; otherwise the second law heat was used. This curve follows the same general pattern indicated by the boiling points, as would be expected from their close relationship. Cerium and holmium might appear to be anomalous at first glance, but the reason for these inconsistencies is easily seen in Figure 19, where  $\text{minus log } P$  is plotted against the reciprocal of the absolute temperature for all the rare earth metals. One observes that cerium and lanthanum have nearly the same vapor pressure at  $2000^{\circ}\text{K}$ , but since the slope of the cerium curve is greater, a pressure of 760 mm of Hg is reached at a lower temperature than for lanthanum. The anomaly for holmium is explained similarly. Ytterbium is observed to be the most volatile rare earth by far, with most of the metals being grouped on the left side of the diagram.

There are discrepancies between some of the heats of sublimation of this study (Table 17) and those from previous studies (Table 1), with explanations being possible in some

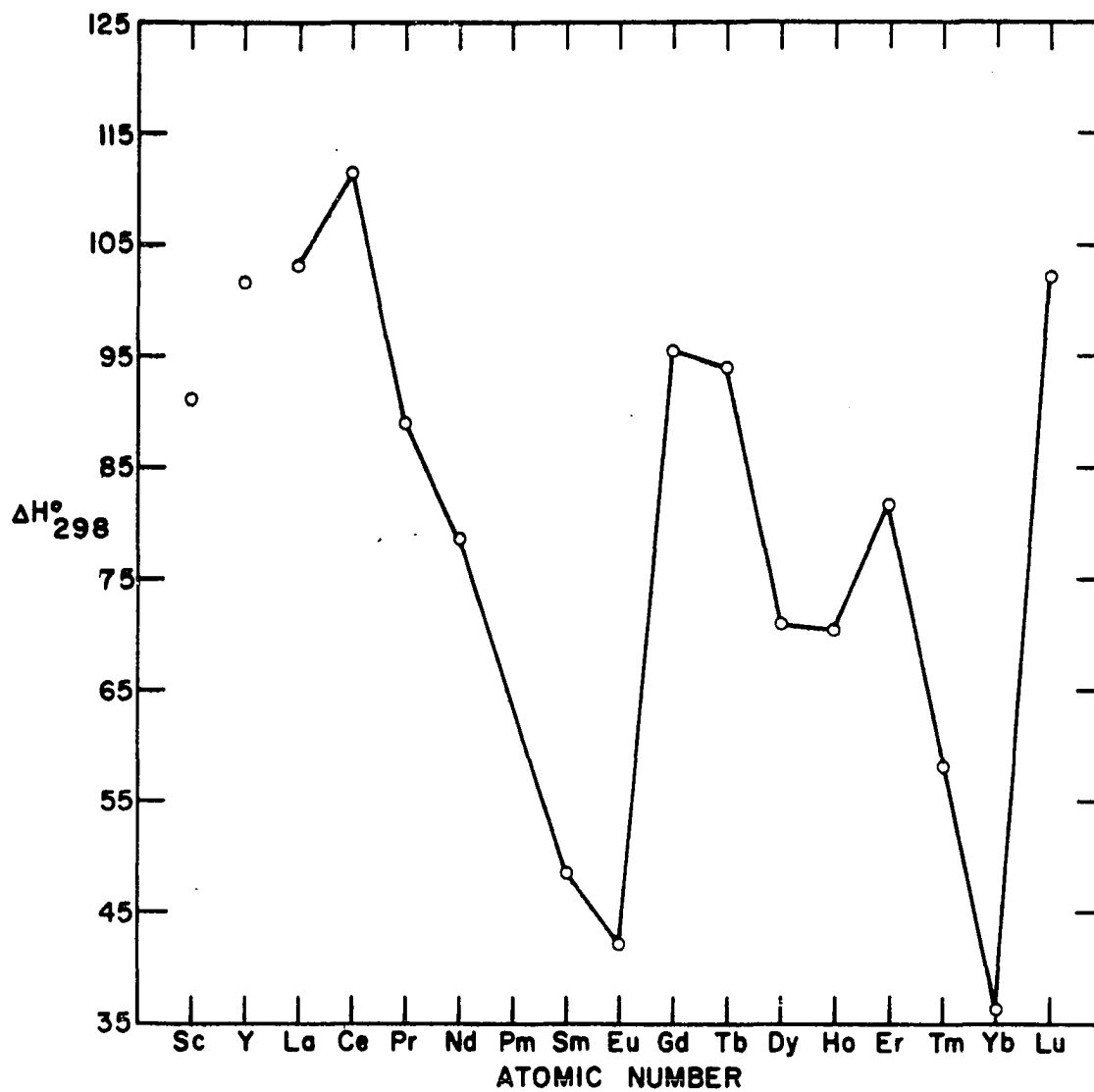


Figure 18. Heats of sublimation of rare earth metals

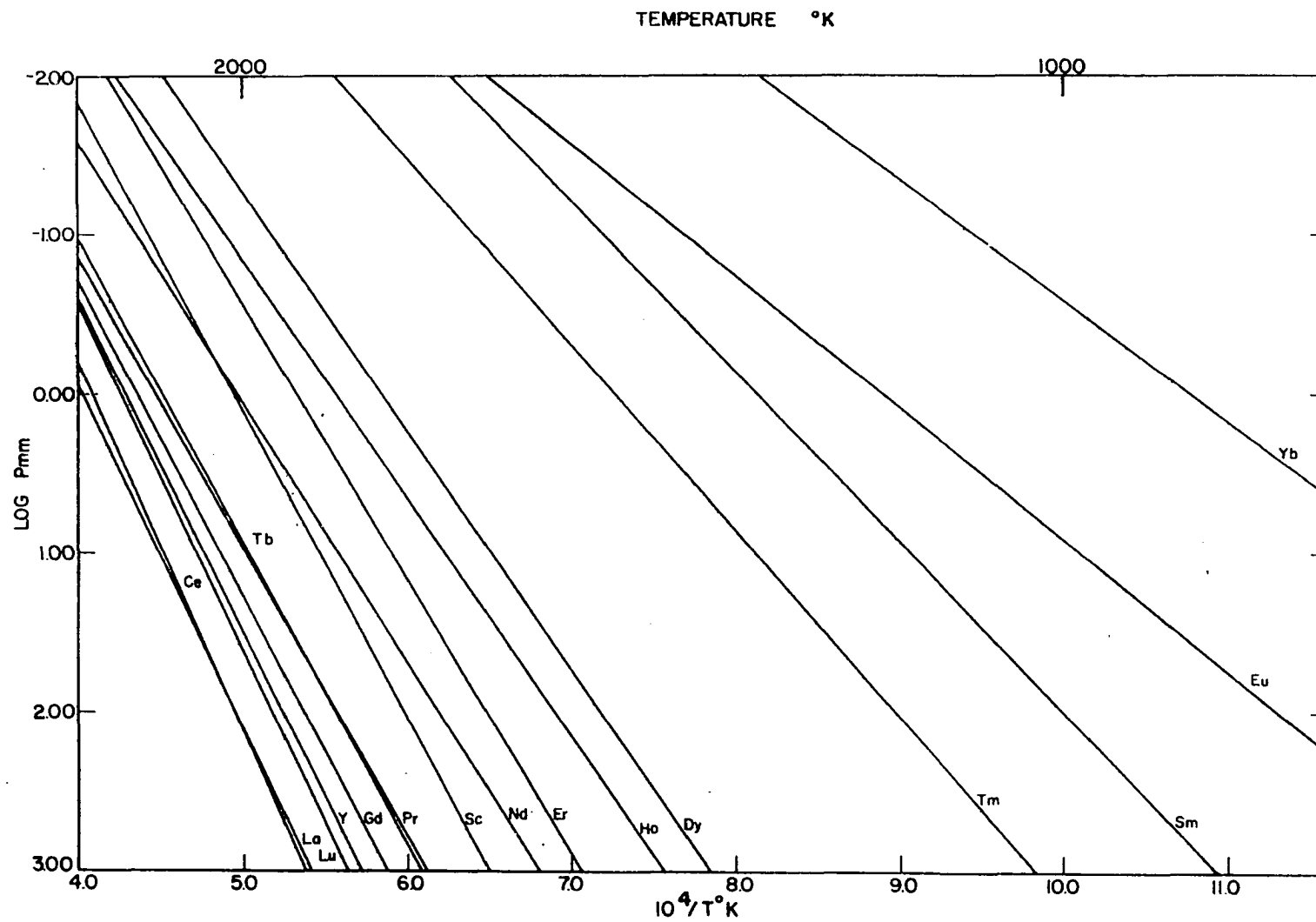


Figure 19. Vapor pressures of rare earth metals



cases. For scandium, the second law values of 80.1, 80.79, and 83.1 kcal/mole by Ackermann and Rauh (24), Spedding et al. (25) and Karelin et al. (29) agree quite well, and the value of 91.0 obtained by Krikorian agrees closely with the value presented here (92.2 kcal/mole). Third law calculations of the heat of sublimation based on the five sets of data resulted in values of 89.95, 90.12, 88.91, 91.46 and 90.98 kcal/mole respectively, which indicates systematic errors in the first three sets of data. The third law calculations given by Krikorian were based on estimated free energy functions, whereas the present calculations were based on measured heat content data. The second and third law values reported in this investigation differ by 1.2 kcal/mole which is well within the percent error estimated in the experimental section, so the true value for scandium is believed to be very close to the third law value of this investigation.

For yttrium, the second law value of Ackermann and Rauh (24) is close to the present value, whereas those reported by Daane (21) and Nesmeyanov et al. (28) are somewhat lower. A third law treatment of Ackermann's data results in  $\Delta H_{298}^{\circ}$  equal to 101.28 kcal/mole in good agreement with the third law treatment of the present data. The best value therefore would be the third law value which was within the estimated error of the second law value.

Three sets of data have appeared in the literature on

lanthanum, all of which are within 5% of each other. The present work agrees very well with that of Ackermann and Rauh (24), and the third law tests of all the reported vapor pressure data show close agreement with the present work. For cerium, the heats of vaporization at the measured temperature range from 93 to 114 kcal/mole, with the value reported here near the middle.

Two mass spectrometric and two vapor pressure measurements have been made on praseodymium resulting in a range of values from 72 to 84 kcal/mole at the measured temperatures with the present value near the upper limit. It may or may not be significant that the material used by Nachman et al. (9) was also prepared recently in the Ames Laboratory; both investigations resulting in nearly the same value for the heat of vaporization. The same investigators who worked on praseodymium also examined neodymium, so one should be able to make an additional comparison here. Whereas in the case of praseodymium, little agreement had been reached, the neodymium values agreed closely with one exception. The present value is between the highest and lowest reported results. The third law test of the present data resulted in a  $\Delta H_{298}^{\circ}$  of 78.44 kcal/mole, which is barely outside the estimated limit of errors between the second and third law methods. A slight temperature dependent trend of 0.5 kcal was also observed along the 400°C temperature range of these measurements, which

is difficult to understand since other elements measured over this same temperature range exhibited no temperature dependence in the third law calculations. A third law treatment of Nachman's data resulted in 76.4 kcal/mole, which is more than 10 kcal/mole different from his second law calculation.

Two measurements have been made on the heats of sublimation of both samarium and europium. The second law heats agree closely in both cases, and the third law calculation based on the europium vapor pressure data (22) agrees very well with the second law calculation. However, the third law treatment of the samarium vapor pressure data is 2.4 kcal/mole or 5% different from the second law value. This is outside the estimated limit of error by approximately 1.0 kcal/mole, and again a slight temperature dependence was noted in the third law calculations. It is coincidental that the only two elements (neodymium and samarium) showing any appreciable temperature dependence were based on the free energy functions reported by Spedding et al. (48). They also measured the heat content of cerium metal, for which only estimated free energy functions are available for the gas (53). Third law calculations based on these functions also show a temperature dependence.

Two mass spectrometric determinations have been reported for the heat of sublimation of gadolinium metal with very good agreement. However, both are about 13 kcal/mole lower

than the result of the present vapor pressure measurements. The third law calculations agree excellently with the second law value obtained in this investigation, and the higher heat is in closer agreement with the electronic structure for the gaseous gadolinium atom.

For terbium, only mass spectrometric measurements had been made previously with only limited agreement between the two sources. The present vapor pressure measurements agree closely with those measured by Jackson and reported by Trulson et al. (34). In the case of dysprosium, the same situation repeats itself, with agreement between the present work and Savage et al. (33) of this laboratory and considerable disagreement with White and coworkers (31). In this case, a previous unpublished report on the vapor pressure of dysprosium by Spedding and Daane (20) is also in agreement with the present work. For erbium, two investigators (27, 31) reported heats of sublimation 15 kcal/mole lower than the present work, while Trulson et al. (34) indicated a value 6 kcal/mole lower.

Savage et al. (33) have measured the heat of sublimation for ytterbium by a mass spectrometric method and reported 40.0 kcal/mole compared to 36.22 kcal/mole from the present work. However, the third law test is quite consistent with the measurement of the slope in this investigation, and is believed to be correct. For lutetium, good agreement resulted from the second and third law treatment of the vapor pressure

data and the mass spectrometric data obtained by Jackson and reported by Trulson et al. (34) while the data of White and co-workers (31) are about 7 kcal/mole lower.

On the whole, the agreement between this investigation and some of the earlier data is considered fairly good, except in the case of neodymium, gadolinium, erbium and ytterbium, but due to the improved purity of the metals used in this investigation, the present values are believed closer to the true values than the previous investigations, and this belief appears to be borne out by the consistency of the third law calculations made. The reasons for the discrepancies are difficult to evaluate for so many elements, but certainly some of the causes can be attributed to errors in the temperature measurements, temperature gradients in the effusion cells, oxygen impurity effects as described by Ackermann and Rauh (24), as well as impurities in general. In the mass spectrometric method, there are in addition to the previously mentioned difficulties, such things as ionization efficiencies which may be responsible for some of the lack of agreement.

### C. Metallic Binding

In principle, one should be able to predict all of the properties of metals from quantum mechanical considerations. However, this very complex problem will probably require years for an exact solution. Because of this, one must resort

to various empirical approaches to achieve some correlation of the properties of metals. Some investigators including Brooks (54) have used the free electron theory, band models and sphere approximations in an attempt to explain the properties of metals on a semi-quantitative basis. This has proved to be helpful in explaining some of the electrical properties of metals, but the agreement between theoretical cohesive energies and experimental values has been disappointing.

It is quite understandable why the theory of cohesive energies has progressed slowly, since it is clear from quantum mechanics that electronic interactions, and therefore the many particle aspects of electronic structure, are responsible for metallic bonding. Nevertheless, in retrospect, chemists have accumulated a large amount of information regarding the mechanisms which electrons use to bind atoms together, and considerable progress has been made.

Binding in solids is customarily classed into four categories: Van der Waals, covalent, ionic and metallic, although there is a continuous gradation between the distinct types. The Van der Waals forces are due to interactions of the electrons of an atom at comparatively large distances due to correlation through electrostatic interactions of the motions of electrons in closed shells. Covalent bonding results from the sharing of electrons between atoms and therefore consist

of directional bonds, whereas ionic bonding takes place when electrons move from one kind of atom to another. Ions are thus formed, and the forces within the structure are of an electrostatic nature. One finds many intermediate situations between these two extremes, and most metallic compounds are considered to fall in an intermediate class where both types contribute to the overall binding.

In metallic binding, the forces are produced by the electrostatic interactions between the ion cores and the nearly uniform sea of valence electrons. Thus there is very little directionality to the binding and metals tend to have close-packed structures. The exact types of interactions which hold the structure together are unknown, but it is obvious that the energy of the metal aggregate is lower than the sum of the energies of the separated atoms. Pauling (55, 56) regards the metallic bond as analogous to a covalent bond; a covalent bond between two atoms is formed by each atom contributing one electron to the bond, whereas the bonding in a metal is due to the resonance of the electrons among a large number of bond positions.

Brooks (54) describes an ideal metallic bond as one in which a rigid distinction can be made between the valence electrons and the core electrons. Ideally the core electrons form closed shells in a rare gas configuration of a size about one-half that of the atomic cell in the crystal, and also have

ionization energies at least five times that of the valence electrons. The transition metals and the rare earth metals do not fall into this class, and consequently the picture becomes extremely hazy.

Engel (57) has formulated some rules of binding which might assist in the problem at hand. 1) Bonding energy depends primarily on the average number of unpaired electrons per atom available for bonding; 2) the contribution to bonding of d-electrons increases with atomic number while the sp contribution decreases with atomic number. The contribution of the d-electron to bonding is evident by observing the change in cohesive energies from rubidium to cadmium across the periodic table, with most of the transition metals having large binding energies. The d-electrons also become increasingly more important in binding as one goes down in the periodic table, shown by the cohesive energies of vanadium, niobium and tantalum, or chromium, molybdenum and tungsten. This trend is also followed in group IIIA where the cohesive energy of scandium, yttrium and lanthanum increase in that order. The significantly larger increase from scandium to yttrium as compared to yttrium to lanthanum also follows the same general pattern as the transition metals. The enhanced bonding due to the d-electrons is particularly apparent when one considers the much weaker bonding in the alkaline earth elements where only s-electrons are available for bonding.



For the remainder of the rare earth metals, it is evident from Table 27 that the above reasoning is no longer satisfactory. Whereas in the transition metals, d-electrons are being added to the conduction band, it is seen that in this case all the elements have the same outer electronic configuration in the solid state (3) with the exceptions of europium and ytterbium, and these configurations are well established from magnetic measurements. From a first glance, one might conclude that all the cohesive energies should be approximately the same with the two exceptions noted above, with only minor variations due to changes in structure and the lanthanide contraction. This is quite obviously not the case as shown by the last column of Table 27 where the heats of sublimation at 298°K are listed.

When one considers the total process of vaporization, both the electronic structure of the condensed and vapor states are seen to affect the cohesive energies. By looking at Table 27 again, it is noticed that the outer electronic structure for a particular element changes from the solid to the vapor state in all but six cases. Of these six, europium and ytterbium do not have a d-electron present in their conduction bands, and it is expected they would be similar to the other divalent metals of group IIA. For lanthanum, cerium, gadolinium and lutetium the conduction band contains a d-electron, so a larger binding energy would be expected, as

Table 27. Electronic configurations of the rare earths

Metal	Atomic no.	Solid state <sup>a</sup>			Gaseous atoms <sup>b</sup>			H <sub>298</sub> <sup>0</sup> kcal/mole
		4f	5d	6s	4f	5d	6s	
La	57	0	1	2	0	1	2	102.96
Ce	58	1	1	2	1	1	2	111.6
Pr	59	2	1	2	3		2	89.1
Nd	60	3	1	2	4		2	78.44
Sm	62	5	1	2	6		2	48.59
Eu	63	7		2	7		2	41.92
Gd	64	7	1	2	7	1	2	95.75
Tb	65	8	1	2	9		2	94.0
Dy	66	9	1	2	10		2	70.9
Ho	67	10	1	2	11		2	70.6
Er	68	11	1	2	12		2	81.8
Tm	69	12	1	2	13		2	59.1
Yb	70	14		2	14		2	36.22
Lu	71	14	1	2	14	1	2	102.20
Sc	21	0	3d <sup>1</sup>	4s <sup>2</sup>	0	3d <sup>1</sup>	4s <sup>2</sup>	90.98
Y	39	0	4d <sup>1</sup>	5s <sup>2</sup>	0	4d <sup>1</sup>	5s <sup>2</sup>	101.52

<sup>a</sup>Reference number 3.<sup>b</sup>Reference number 1.

is observed. The electronic structures of the gaseous atoms are the same as the condensed structure for these four elements, which is similar to the situation observed for the transition metals.

For the remaining eight elements, the outer electronic structure of the gaseous atom is different from that of the conduction electron configurations. When the atoms of the metal are separated during vaporization or sublimation the one d-electron drops into a lower energy state, namely the 4f level. Therefore, energy would be given off and less heat would be necessary to vaporize the metal.

For terbium, the separation between the energy levels with configurations  $4f^9 6s^2$  and  $4f^8 5d^1 6s^2$  of the gaseous atoms has been determined to be  $20\overset{\circ}{\text{A}}$  (2), corresponding to about 0.5 kcal/mole of energy released during the vaporization process. Therefore the heat of sublimation of terbium should be this amount smaller than gadolinium for which the configuration of the solid and gas are the same. The difference observed between the heats of sublimation of gadolinium and terbium was 1.75 kcal/mole, which is of the right order of magnitude. The energy level separations between the  $4f^{n+1} 5d^0 6s^2$  and  $4f^n 5d^1 6s^2$  configurations for the remaining seven rare earth elements are not available, but one can assume the separations for these elements is probably greater, since there was no confusion in the assign-

ment of the ground state configurations for these elements as there was in the case of terbium vapor. In essence, what this means is that the rare earth gaseous atom has a greater tendency to be divalent on passing from lanthanum to europium and gadolinium to ytterbium.

There would appear to be at least two exceptions to this line of reasoning, that of erbium and cerium both of which have higher heats of sublimation than the preceding elements. For cerium, the cohesive energy picture is confused by the complexity of the electronic configuration of the gaseous atoms, for which the ground state is still in doubt, and by the band structure of the condensed phase. According to Gschneidner,\*  $\delta$ -cerium has a 4f state just below the Fermi surface from which electrons can be thermally excited into the conduction band. His calculations show that at room temperature 0.052 electrons will be promoted to the d-band, and this number will increase as the temperature increases providing the band structure remains the same. This additional fraction of a d-electron over and above the one already present in the conduction band would increase the binding energy of cerium as compared to lanthanum or some of the other rare earth metals. No explanation for the unusually

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\*Gschneidner, K., Ames Laboratory, Iowa State University of Science and Technology, Ames, Iowa. Band structure of cerium. Private communication. 1963.

high heat of sublimation of erbium is known at the present time.

From metallurgical observations, it appeared that europium metal was the most volatile of the rare earth metals. For instance, Daane et al. (4) reported that 750 grams of europium and 600 grams of ytterbium could be distilled from identical crucibles in one hour, and in the lanthanum reduction of europium and ytterbium oxides, it was found that temperatures of 900 and 1000°C respectively were necessary for best results. However, from the present measurements ytterbium was found to be approximately an order of magnitude more volatile than europium, and likewise has a lower heat of sublimation. This seems to follow Engel's rule which states that the sp contribution to metallic bonding decreases with atomic number.

In studying the vapor pressure of ytterbium, the modification of the Knudsen method used by Wakefield (8) was tried; he suspended a graphite condenser over the effusion cell and measured the weight gain of the condenser, as the holmium vapor was converted to the stable non-volatile carbide. The method was unsuccessful in the case of ytterbium, because the carbide formed was insufficiently stable to permit an accurate weight gain measurement. It was quite certain that a carbide had been formed, since the condenser had the odor of acetylene when exposed to the humid atmosphere. However, the carbide

formed at one temperature setting would decompose as the temperature was raised, which was observed as an apparent weight loss of the condenser. Then as the furnace came to equilibrium again at the higher temperature setting, additional carbide was formed. After several of these temperature jumps, it was found that the condenser had gained very little weight over its initial weight indicating almost complete decomposition each time the temperature was raised. The instability of ytterbium dicarbide has been reported previously by Spedding et al. (58) in their study on the structures of the rare earth carbides.

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## VII. ACKNOWLEDGMENTS

The author wishes to express appreciation to Dr. A. H. Daane, who gave helpful advice and criticism during the course of this study and to A. R. Kooser for his assistance in the preparation of the samples. The author is also grateful to his wife, Marlene, who helped in preparing the rough draft of this thesis and whose patience and understanding during the long hours of research should certainly not be overlooked. Acknowledgment is also made for the advice, discussions and cooperation given by the author's co-workers, and for the support of the Union Carbide Corporation's Grant in Aid.