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VAPOR PRESSURE OF HOLMIUM METAL AND DECOMPOSITION PRESSURES OF HOLMIUM CARBIDES

by

Gene Felix Wakefield

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

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Approved:

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In Charge of Major Work

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Signature was redacted for privacy.

Dean of Graduate College

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Ames, Iowa

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I. INTRODUCTION

The work of Joseph Black greatly advanced the science of thermodynamics by his explanation that quantity and intensity (temperature) of heat are not identical and that all substances do not have identical specific heats. Foreshadowing the more highly publicized developments in this field by Laplace and Lavoisier in 1783, Black found in 1760 that the amount of heat liberated by ice in freezing is equivalent to the amount required for melting and that the temperature remains constant through the phase change. In 1884 Van't Hoff expounded the Principle of Mobile Equilibrium: "Every equilibrium between two systems is displaced by fall of temperature in the direction of that system in the production of which heat is evolved." At this same period, Helmholtz established that the true criteria which governs the direction of reactions is not the heat evolved, but rather the alteration of the available, or free, energy. Though many have followed in this field, this is the place from which thermodynamics grew, for here are the concepts which later are so tightly interwoven: temperature, heat, reaction direction, equilibrium, free energy.

The importance of thermodynamics stems from its universal application in technology since it is one of the main tools of the engineer and scientist. To aid in their endeavors, these workers are constantly in need of new materials or improvement of those of the present. While many applications of a material can be made without even knowing its composition, much better utilization of its properties is often dependent upon the understanding of its constituents and how they interact with each other.

Perhaps the most desirable place to begin to build an understanding of the total nature of the surroundings is by a thorough investigation into the properties of the elements, and then starting to generalize to the more complex systems. While a goodly number of the properties of the commonly available elements have been measured to satisfactory accuracy, continued research has been to add to the number of elements with which work is to be done. One example of this has been in the production of the elements whose nuclei are unstable. Even though they do not occur naturally, it is still important to understand their chemical behavior. Another example was that of the element scandium which had been studied very little in the pure state, but has now become available in sufficient quantities for its complete study. More striking is the example of the group of rare earths which includes nearly one-fifth of the metals of the periodic chart. The properties of these elements had not been thoroughly studied due to the difficulty in obtaining them. However, the development of ion exchange method of separation during the 1940's (1) made the pure compounds available in quantity and shortly afterward techniques for the preparation of the pure elements (2) were devised.

The rare earths have the additional advantage that aside from their potential importance as individual elements, as a group they offer a quite unique testing ground for many atomic theories which are concerned with relation of properties to electronic structure. The placement of this series in the periodic chart is due to the filling of the 4f shell which lies beneath the surface of the electron cloud, while retaining a similar exterior configuration generally involving three electrons. The consideration of this fact which results in the similarities observed among many of the rare earths leads to the potential offered to observe the effects on physical properties in alloys by controlled variation of one of the parameters. As mentioned, however, a more complete knowledge of the individual elements is needed to lay a more stable foundation before expanding to more complex systems.

This present study was undertaken to provide some information about a little studied member of the rare earth series, holmium. This element, whose name indicates its Swedish origin, was discovered by D. T. Cleve in 1879, with the pure oxide, Ho_2O_3, being isolated by Homberg in 1911. The element ranks 56th in order of abundance in the earth's crust, twice as abundant as mercury, 12 times that of silver, and 250 times that of platinum. If an important commercial use were found for holmium it could be made available, as it is in the same order of abundance as germanium and selenium.

Some of the important properties of holmium which have been measured are summarized in Table 1. Two of the most striking deficiencies in the information are the high temperature heat capacity and the vapor pressure, for these values are necessary for evaluation of many high temperature processes.

Table 1. Properties of holmium metal[a]

melting point	1461 °C
boiling point	2720 °C (this study)
structure, 25 °C, hcp	a = 3.5761 Å
	c = 5.6174 Å
density	8.803 gm cm^{-3}
resistivity, 25 °C	94 μ ohm cm
$S^{o}_{298.16}$	17.97 e. u.
ΔH_{s298}	69.5 (3)
	71.4 (4)
	69.6 (this study)

[a] Values taken from Reference 2 except where noted.

To supply one of the needed experimental values, a study of the vapor pressure of holmium metal was undertaken. Consideration of the problem indicated that it could be best solved by use of the techniques developed by Knudsen (5) and

Langmuir (6). These allow an extensive range to be measured since they are applicable to different magnitudes of pressure, the Langmuir method valid for the range of 10^{-8} to 10^{-4} mm and the Knudsen method of 10^{-5} to 10^{-2} mm, with no reliable method available immediately above the Knudsen range. Since the methods differ somewhat in theoretical development, measurement of the vapor pressure by both would allow a correlation and comparison of the data and the methods.

The measurement of the change of vapor pressure as a function of temperature yields the enthalpy associated with the process occurring as given by the Clapeyron-Clausius equation:

$$\frac{dp}{dt} = \frac{\Delta H}{T\,\Delta V}$$

Thus, measurement of the vapor pressure of the solid yields the heat of sublimation;

$$(\text{solid}) \rightarrow (\text{gas})$$

and measurement of the vapor pressure of the liquid yields the heat of vaporization;

$$(\text{liquid}) \rightarrow (\text{gas}) \quad .$$

The difference in the enthalpies for these reactions yields the heat of fusion, since it is the ΔH of the reaction

$$(\text{solid}) \rightarrow (\text{liquid}) \quad .$$

A method for the measurement of pressures immediately above the Knudsen range was needed in this study since the vapor pressure of liquid holmium is higher than can be measured by that method. Measurement of the vapor pressure of both the liquid and solid phases was desired to obtain the heat of fusion.

One factor which must be considered in the flow of vapors through tubes or pipes is the restriction imposed on the flow due to the length of the pipe. (An orifice in a thin sheet, such as used in the Knudsen method, could be considered a very short tube.) This restrictive nature of a long tube has been measured and treated mathematically (7,8) and the information obtained offered the possibility of capitalizing upon a usually annoying feature since this factor could be used to extend vapor pressure measurements to higher pressures.

The knowledge of the vapor pressure of holmium obtained is of more value when it can be used in the study of other problems. To demonstrate this it was used in a problem which arose in the course of the vapor pressure study by evaluating the decomposition pressures of some of the holmium carbides.

II. VAPOR PRESSURE STUDIES

A. Historical

There are many experimental methods for the determination of the vapor pressures of materials in the region of 10^{-2} to 10^{-8} mm Hg in use at the present time; however most of them owe their original derivation to M. Knudsen (5) or I. Langmuir (6). The theory of the Langmuir method is developed by considering the equilibrium existing between a condensed surface and the vapor over the surface. When the equilibrium vapor pressure is established, the number of vapor atoms which strike the surface and condense will be equal to the number of atoms which escape from this surface. While the number of atoms which strike the surface is directly dependent on the pressure of the vapor above the surface, at very low pressures the assumption is made that the number of atoms which escape is independent of the pressure above the surface. Under these conditions, the number of atoms which escape depends only upon the rate at which the atoms acquire sufficient thermal energy to separate from their neighbors. Thus it is seen that the condensation rate is pressure-dependent and the evaporation rate is pressure-independent; however, these rates are equal at equilibrium. It is therefore possible to determine the number of atoms which would leave a metal surface, at any specified temperature, from the calculation of the number of atoms which would strike the surface from the vapor phase at the equilibrium pressure; conversely, by measurement of the number of atoms which leave the evaporation surface, it is possible to calculate the equilibrium vapor pressure.

From the kinetic theory of gases it can be shown that the mass, m, of vapor atoms which strike a unit area of a solid surface in a unit time is given by

$$m = \frac{1}{4} d \overline{V}$$

where d is the density of the vapor and $\overline{V}$ is the mean velocity of the atoms. The mean velocity of the atoms is given by

$$\overline{V} = \left(\frac{8RT}{\pi M}\right)^{\frac{1}{2}}$$

where R is the gas constant, T is the absolute temperature and M is the molecular weight of the vapor. From the ideal gas law $PV = \frac{g}{m} RT$, the pressure, P, can be calculated as follows:

$$P = d\frac{RT}{M} = \left(\frac{RT}{M}\right) \cdot \frac{4m}{\overline{V}} = \frac{RT}{M} \cdot 4m \cdot \left(\frac{\pi M}{8RT}\right)^{\frac{1}{2}}$$

$$= m \cdot \left(\frac{2\pi RT}{M}\right)^{\frac{1}{2}} \quad .$$

This relation describes the pressure when every atom which strikes the surface condenses. However if a certain fraction of the atoms, denoted by r, is elastically reflected from the surface, the true pressure, P_t, is related to the calculated pressure, P_c, by the equation:

$$P_t = \frac{1}{1 - r} P_c \quad .$$

The fraction of the vapor atoms which condense, $\alpha = 1 - r$, was named the accomodation coefficient by Knudsen and has been found to be unity within the limits of experimental error for many metals. There has been considerable concern expressed as to the validity of assuming α to be unity in all cases.

Hirth and Pound (9) have derived an expression whereby α, which they chose to rename the evaporation coefficient, is described in a limiting expression as a function of pressure and temperature by

$$\alpha = 2/3 \frac{P}{P_e} + 1/3$$

where P is the pressure of metal vapor above the metal surface and P_e is the equilibrium vapor pressure. From this expression it can be seen that an experiment devised to reduce the vapor pressure above the surface to zero, such as by trapping the metal vapors, would result in an accomodation coefficient of 1/3. The originators have indicated that this equation is applicable to large metal crystals that are relatively free of surface imperfections.

In the Knudsen type experiment, the pressure is calculated from the determination of the mass of vapor which escapes into a vacuum through a small orifice from a vessel containing the condensed phase in equilibrium with its vapor. By controlling the experimental conditions so that the orifice area is quite small compared to the evaporation area of the sample, it is assumed that the amount of vapor which escapes is too small to disturb the metal-vapor equilibrium significantly. The vapor pressure can thus be calculated from kinetic theory as in the Langmuir derivation by:

$$P = \frac{m}{a}\left(\frac{2\pi RT}{M}\right)^{\frac{1}{2}}$$

where a is the area of the orifice. This derivation has assumed that every vapor atom which strikes the orifice area escapes and none of the atoms are reflected back into the vessel by the walls of the orifice. If instead of being a small hole in a thin sheet, the orifice is replaced by a tube or pipe, the orifice walls will then have an appreciable length which results in reflection of some of the vapor and a correction associated with the Clausing factor must be added to the calculations. The mathematical derivation requires that the vapor obey a free molecular type flow and to assure this, from mathematical considerations, Knudsen has set the qualification that the mean free path must be at least 10 times the radius of the orifice.

The many existing modifications used for measuring vapor pressures of metals in the range of 10^{-2} to 10^{-8} mm Hg differ primarily only in the manner in which the mass of escaping vapor is measured. These can conveniently be divided into two classes: those which determine the mass after condensation on a target and those which measure the loss of mass directly. In the more common methods of the first type, the mass is measured on the target by direct weighing, by chemical analysis upon removal of the condensate from the target, or by utilizing a radioactive isotope of the metal in question. The more common methods of direct determination of mass have been by measurement of the current produced by ionization of the stream of vapor atoms, by suspension of the effusion vessel from a sensitive microbalance, or by measuring the torsional force exerted by the escaping vapor stream on a quartz fiber. Theoretically, the last method has the advantage that the molecular weight of the vapor species can be calculated from the observed pressures, but in practice it has not yielded accurate results.

In this laboratory, Knudsen vapor pressure determinations (10) have been carried out through direct measurement of the mass of escaping vapor by suspending the effusion vessel into an induction- or resistance-heated furnace from a sensitive quartz microbalance of the type developed by Edwards and Baldwin (11). This method has proven to be reliable for pressures in the range of 10^{-1} to 10^{-4} mm Hg, the limits being imposed by the convenience of measuring the mass loss per unit time.

B. Modifications

A study was undertaken to determine the feasibility of extending the range and improving the precision of the vapor pressure measurements in anticipation of the possibility of obtaining more thermodynamic information from vapor pressure studies of the rare earth metals.

As greater sensitivity of the microbalance could be obtained by decreasing the total weight of the load supported by the balance beam, the effusion vessel was placed on a support inside the furnace and a light weight cylindrical graphite condenser suspended from the balance beam in such a manner as to surround the upper portion of the effusion vessel as in Figure 1. The stationary mounting of the vessel removed the restriction placed on the weight of the effusion vessel by the relatively small capacity of the balance, and thus allowed the possibility of using more massive samples, or using a heavier tungsten crucible for those rare earth metals which tend to dissolve tantalum metal. The effusing metal vapors strike the condenser and are kept from redistilling by formation of a non-volatile rare earth carbide. This carbide was shown by x-ray diffraction to be the dicarbide in the case of holmium metal.

The upper pressure that can be determined is imposed by

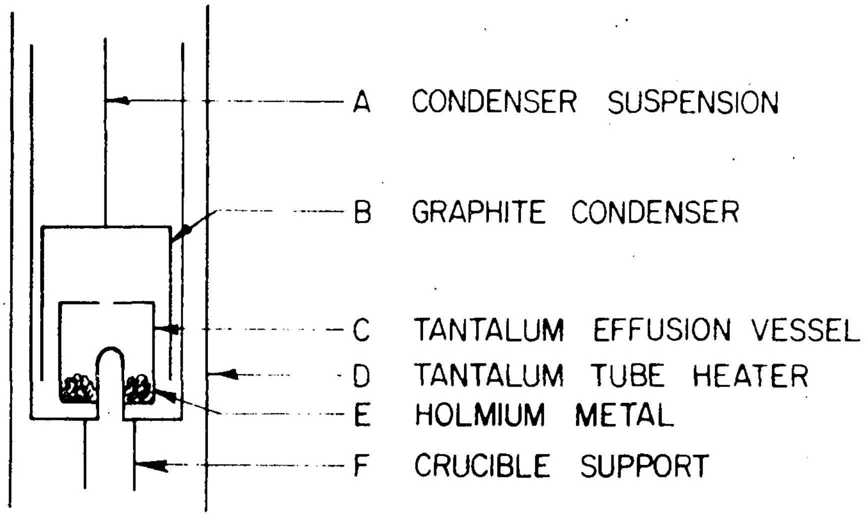
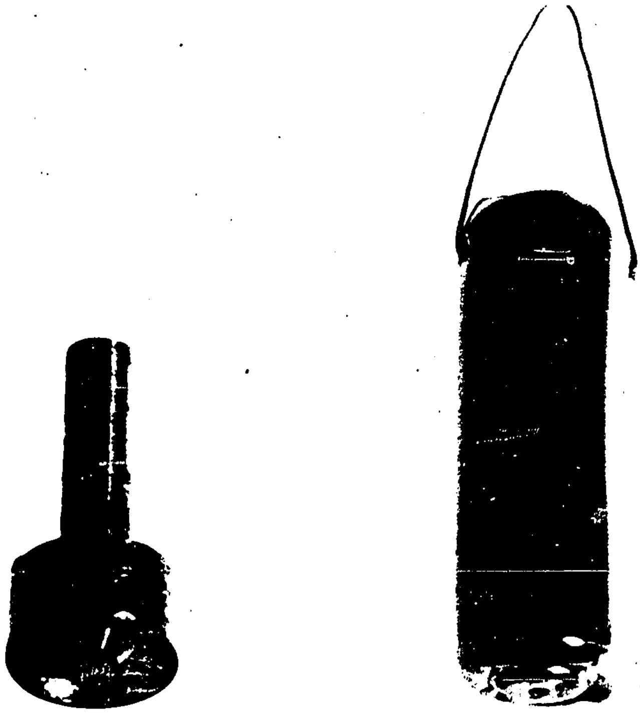


Figure 1. Knudsen effusion cell with graphite condenser

the maximum conveniently measurable weight loss per unit time. In order to lower this rate, the orifice was replaced by a pipe or a "tube" orifice, which caused a considerable percentage of the vapor atoms to be reflected from the orifice walls back into the vessel. Several tube orifices were made by drilling a small hole through a ½" length of ¼" diameter tantalum rod and then welding the rod to the top of the effusion vessel as shown in Figure 2. For a tube of 0.014" radius and ½" length the Clausing factor, K, was 0.070, i.e. 93% of the vapor atoms would be reflected back into the vessel by the orifice walls. The value of K must be known to the accuracy of the other experimental variables to calculate absolute values of pressure.

A tube orifice was used to measure the vapor pressure of holmium from 10^{-2} to 9 mm Hg and it was found to agree well with the measurements taken from the overlapping high pressure regions of a true Knudsen experiment, using a value for K taken from Dushman (12). Above the range of the Knudsen experiments the pressures corresponded to a straight line extrapolation of the lower values. Although it was realized that at pressures near and above 1 mm, the mean free path of the vapor atoms is less than ten times the orifice diameter as required in Knudsen's original derivation, the equations he derived should be applicable up to the pressure where the escaping vapor fails to obey a "free molecular" flow and is partially transformed into a hydrodynamic type of

Figure 2. Photograph of "tube" orifice and tube effusion cell (magnification 4x)



flow. According to Dushman, a significant contribution from hydrodynamic flow should occur near the pressure where the ratio of mean free path to orifice diameter approaches 1. This would occur in the neighborhood of 2 mm (1625 °C) for holmium metal.

The extension of the vapor pressure measurements to pressures lower than 10^{-4} mm is not convenient by the Knudsen method involving the direct weight loss due to the slow evaporation rate through the orifice. The Langmuir method may be used to determine pressures to 10^{-8} or lower by using rather large areas and/or long evaporation times. This method has the disadvantage that it is necessary to assume that the accomodation coefficient is equal to unity. By the use of a graphite condenser to capture all of the metal vapor in this present study, there was no significant condensation from the vapor phase back onto the evaporation surface and thus the accomodation coefficient would not be a factor in this type experiment. To achieve complete condensation on the condenser it is necessary that the evaporation surface-to-condenser distance be much shorter than the mean free path of the vapor atoms, so that there is only very slight chance for a collision of vapor atoms which might result in the return of some of the vapor to the sample. The mean free path (mfp) is given by:

$$\mathrm{mfp} = \frac{1}{\sqrt{2}\,\pi\, n\, \sigma^2}$$

n = number of atoms/cc

σ = diameter of atom

For the case of holmium metal at 1000 °C, the pressure is 4×10^{-4} mm, and $n = 6 \times 10^{11}$ atoms/cc, $\sigma = 2 \times 10^{-8}$ cm thus:

$$\mathrm{mfp} = \frac{1}{\sqrt{2}\,\pi \times 6 \times 10^{11} \times 4 \times 10^{-16}} \cong 1 \times 10^{3} \text{ cm}$$

The surface-to-condenser distance was 0.15 cm, so that the necessity of considering the accomodation coefficient is removed since there should be no condensation of vapor on the sample.

This type of experiment, as illustrated in Figures 3 and 4, was run using evaporation areas from 1 to 30 cm^2 and was found to yield values of vapor pressures in agreement with those taken by a true Knudsen effusion method in the overlapping pressure region ($10^{-3.5}$ to 10^{-5} mm), and the values below the Knudsen range corresponded to a straight line extrapolation from the higher temperatures.

C. Discussion and Evaluation

The preceding parts A and B described a method for the determination of vapor pressures from 10 to 10^{-8} mm by direct measurement of the mass of transferred vapor. The success of

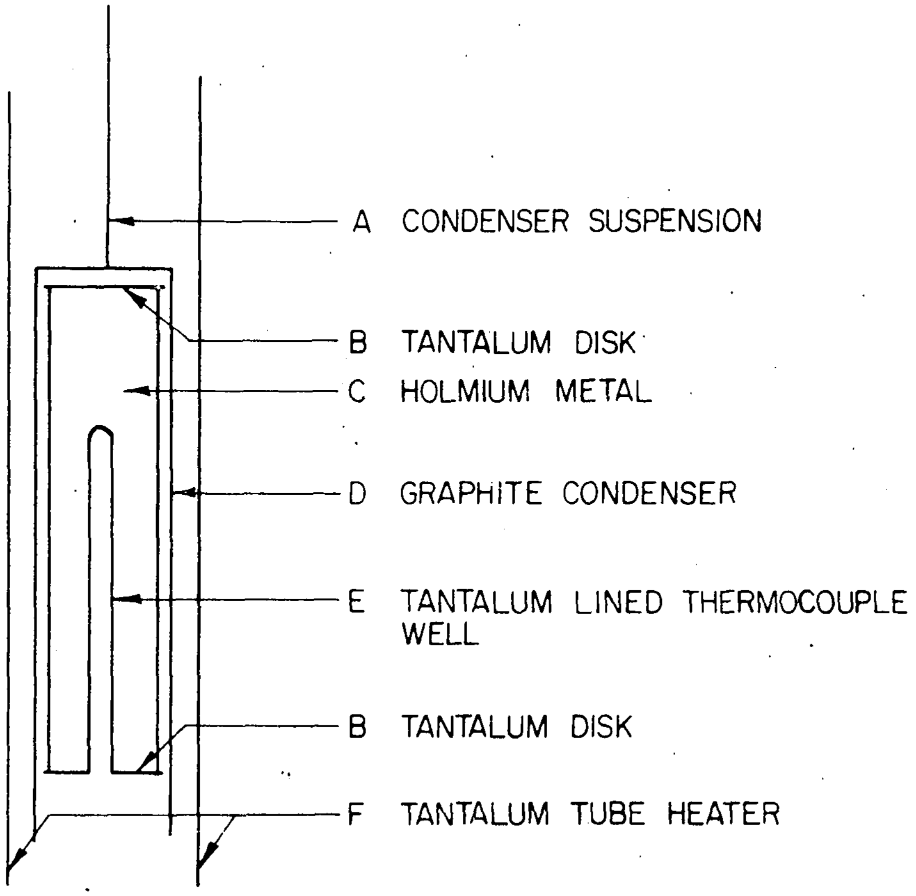
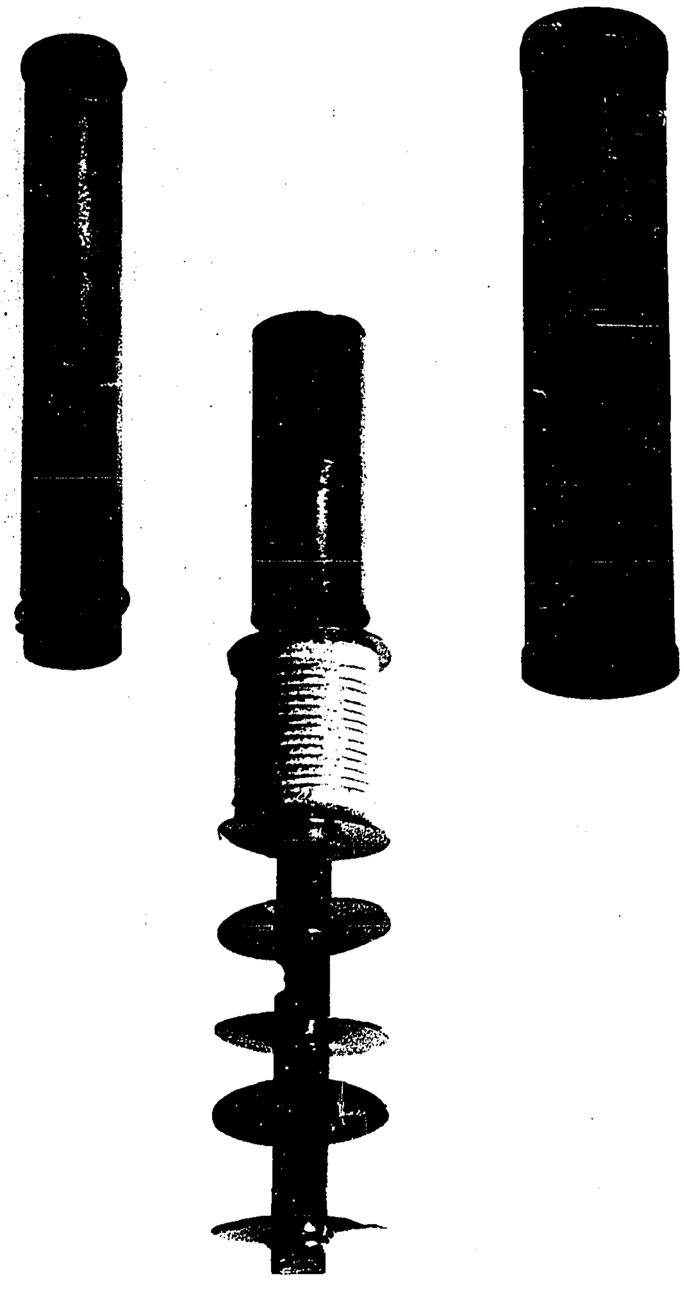


Figure 3. Langmuir vapor pressure sample with graphite condenser

Figure 4. Photograph of Langmuir method samples and condenser. Left to right: thin sheet of metal formed into a cylinder; solid cylinder sample on support rod with temperature sensing element below sample; graphite condenser



this technique in the lower pressure regions depends upon the formation of a nonvolatile carbide on the graphite condenser to prevent redistillation of any of the metal. This condition is satisfied by some of the rare earth metals as indicated by the agreement of vapor pressures determined by this method and those determined by a true Knudsen method, by the total weight gain on the condenser being equal (within ± 0.2%) to the total weight loss of the vessel and by the fact that all the condensed metal is observed as a sharply defined deposit on the condenser in the region corresponding to the sample position and dimensions. Redistillation or reflection would cause the condensate to be more randomly distributed over the condenser.

The use of a condenser allows the use of a more sensitive microbalance since it is reasonably well established that the sensitivity of a balance follows roughly as an inverse relation to the total weight to be supported by the balance. More precise measurements could therefore be made by suspending the condenser, which weighed only 1.2 grams, rather than the Knudsen effusion cell weighing 4-5 grams. In the Langmuir method studies, it was not readily apparent how to obtain an evaporation area of 30-40 cm^2 which could be supported on a balance having a capacity of 4 grams. However the graphite condenser for this method weighed only 3.5 grams.

The extended range of measurement should permit a more accurate determination of the slope of the log P vs. 1/T curve which is related to the thermodynamic quantities, and also enhance the possibility of the determination of the enthalpy associated with any phase transformation by measurement of the vapor pressures of the constituent phases. It would be desirable to achieve sufficient precision to enable the determination of the ΔC_p term, which occurs in the integrated form of the vapor pressure equation and gives a slight curvature to the vapor pressure curve. From this term and the heat capacity of the metal vapor from spectroscopic data, the heat capacity of the metal could be calculated. This would appear to be beyond the present limits of the method as the ΔC_p term contributes approximately 0.2 Kcal per mole per 100^{o}, which is the same order of magnitude as the probable error.

III. VAPOR PRESSURE OF HOLMIUM METAL

A. Historical

Until the 1940's, the difficulties encountered in separation of the rare earths from each other and foreign materials were so great that only by diligent and persistant efforts (13) could even small amounts of pure rare earth compounds be obtained. Now the application of ion exchange methods of separation has eased that problem and has brought up the less tedious but still perplexing task of preparation of the pure elements and the determination of their properties. This work is presently well under way, for it is observed that in general each new redetermination of some property of the metals differs less from the previous values, indicating that perhaps the truth is being approached.

Attempts to apply the process of vacuum melting to the rare earths showed that with some of the metals this was very successful, while with others it was discovered that considerable portions of the metal would be transferred from the crucible to cooler parts of the furnace (14). This seemed to indicate that the vapor pressure was one of the physical properties which would show marked variation among members of the rare earth series, and encouraged the quantitative study of their vapor pressures.

Although no vapor pressure measurements had been carried out prior to 1948, Trombe (15) had shown that lanthanum was difficult to distill while europium and samarium are more volatile. Using metal prepared in refactory oxide containers, Ahmann (16) determined the vapor pressure of cerium by the radioisotope method developed by T. E. Phipps _et al_. (17). From the slope of the vapor pressure curve he obtained a ΔH of 108 with a root mean square error of the pressure of 11%. Brewer (18) mentions in Quill that the evaporation of cerium in the range of 1200-1600 °C was carried out at the Berkeley laboratories. From their data they report a value of 80 kcal/mole for the ΔH, and pressures about 10 times those of Ahmann. Daane (10) measured the vapor pressure of lanthanum and praseodymium metals, which had been produced in a tantalum container, by the Knudsen method modified to utilize a quartz fiber microbalance. He obtained a $\Delta H = 81.0 \pm 1.4$ for lanthanum and 79.5 ± 1.1 for praseodymium. The vapor pressure of liquid cerium was determined by D. D. Jackson and P. W. Gilles (19) in an apparatus designed to minimize the effect of contamination of the metal due to a poor atmosphere. Utilizing the inductively heated Knudsen cell and assaying the vapor which condensed on a target by a coulometric procedure yielded data somewhat higher than that of Ahmann. The vapor pressure of thulium was measured over a range of 10^6 by a similar procedure by Spedding _et al_. (20) who obtained a ΔH of 59.1 ± 0.2. The effusion cell was resistance heated and the quantity of effused vapor determined by a radioisotope method. The vapor pressure of europium was measured by Spedding et al. (21) using a quartz fiber microbalance and resistance heating, and they obtained a value of 42.066 ± 0.075 for the heat of sublimation. The elements scandium (22) and yttrium (23), which are closely related to the rare earth metals, were measured in a similar manner and the ΔH values of 80.8 ± 0.7, and 93, respectively, were obtained. Savitskii (24) measured the vapor pressure of erbium metal by a Knudsen effusion technique in which the vapor was condensed on a mica plate supported on the end of a quartz fiber microbalance. Five points were taken on metal reported to be 99.35% purity and the slope indicated a heat of sublimation of 64.75 ± 0.215 Kcal/mole.

Since the successful introduction of the mass spectrometric methods to the determination of thermodynamic properties by many investigators (3,4,25,26) the rare earth metals have been studied by this method. The data from these studies are summarized, along with the Knudsen values for comparison, in Table 2. As is seen, this method has been quite productive even in its comparative youth due to its convenience of producing an immediate intensity reading of all of the species observed in the vapor, thereby serving to identify the major members as well as the impurities. The result obtained by this method is only the temperature coefficient rather than the absolute value of the pressure.

Table 2. Heats of sublimation of the rare earth metals

Element	Knudsen, Langmuir		Mass Spectrometer Methods	
Scandium	80.8[a]			
Yttrium	93[b]			
Lanthanum	97.3[c],	81[d]		
Cerium	113.8[e],	107.7[f],		
	80[g],	95[c]		
Praseodymium	79.5[d]		85.1[h]	77.5[i]
Neodymium	69[c]		75.0[h]	77.2[i]
Samarium			49.9[j]	
Europium	42.1[k]		43.13[l]	
Gadolinium			81.27[l]	83.6[i]
Terbium				87.5, 87.4[i]
Dysprosium	69[c]		71.4[j]	61.6[i]
Holmium			74.95[l]	69.5[i]
Erbium	64.75[m]		75.26[l]	66.4[i]
Thulium	59.1[n]		57.6[j]	
Ytterbium			40.0[j]	
Lutetium				94.7[i]

[a] Reference 22
[b] Reference 23
[c] Reference 2
[d] Reference 10
[e] Reference 19
[f] Reference 16
[g] Reference 21
[h] Reference 26
[i] Reference 3
[j] Reference 27
[k] Reference 21
[l] Reference 4
[m] Reference 24
[n] Reference 20

To resolve the data to absolute pressures requires calibration of the geometry of the system, the orifice, and ionization cross sections of the species involved, however due to the difficulties encountered in carrying out these calibrations it has seldom been done. Values of the enthalpy relationships obtained by the mass spectrometer methods are in reasonable agreement with those of Knudsen and Langmuir methods, and in general they have associated with them probable errors of approximately the same magnitude.

In continuing the determination of the properties of the rare earth metals, the vapor pressure of holmium metal was determined by the methods discussed in Part I from 10^{-8} mm (650 °C) to 9 mm (1650 °C). This range covered both the solid and liquid phases, allowing the determination of the heats of sublimation and vaporization, and from the difference between these two, the heat of fusion was calculated.

B. Material

The holmium metal used in this study was prepared from spectrographically pure Ho_2O_3 by a calcium reduction of the fluoride as described by Spedding and Daane (2). The metal was melted under a high vacuum to remove any volatile impurities and then heated to a higher temperature to distill the holmium onto a tantalum condenser. The condenser was turned off in a lathe yielding holmium metal having the following analysis:

Table 3. Analysis of holmium metal (HAB-6)

Element		Element	
Carbon	66 ppm	Silicon	0.02%
Nitrogen	19 ppm	Yttrium	0.01%[a]
Calcium	0.05%[a]	Dysprosium	0.01%[a,b]
Iron	0.01%	Erbium	0.01%[a]
Tantalum	0.1%[a]	Thulium	0.01%[a,b]

No other rare earths detected.

[a] The actual percentage could be much less than these values which represent the lower calibration limit.

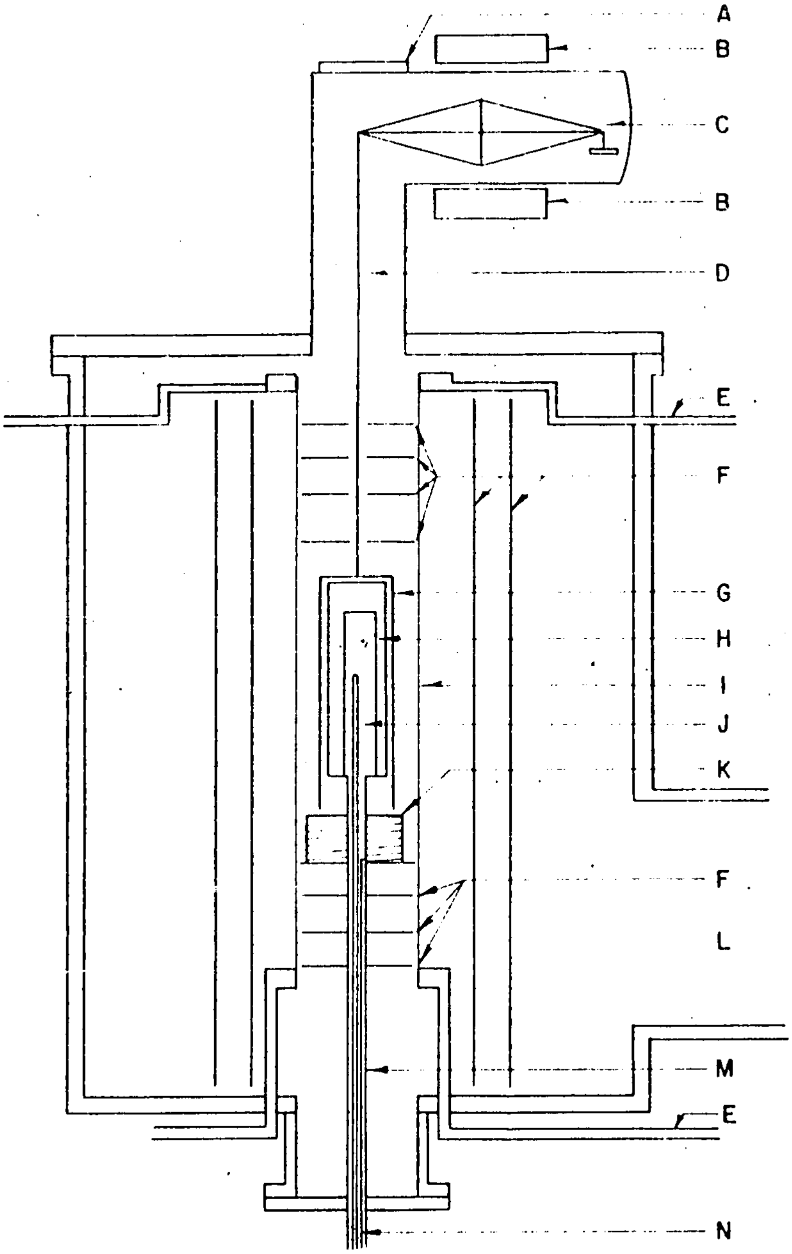
[b] Not detected.

C. Equipment

1. Vapor pressure furnace

The furnace was a tantalum resistance furnace constructed in this laboratory and is illustrated in Figure 5. Power was supplied to the heating element through a 208 volt, 5KVA Stabiline voltage regulator, a "double-gang" variable Powerstat manufactured by Superior Electric Co. and a 10KVA Banner step-down transformer. This supplied a maximum of 500 amperes at 8 volts to the heater which was sufficient to

Figure 5. Vapor pressure furnace. A--pyrometer window, B--balance coil, C--balance beam with tare weight pan, D--tantalum wire suspension for condenser, E--water cooled power leads, F--molybdenum radiation shielding, G--graphite condenser, H--metal sample, I--tantalum heating element, J--thermocouple well in sample, K--temperature sensing element, L--vacuum pump lead, M--sample support of $\frac{1}{4}$" diameter tantalum tubing, N--thermocouple and sensing element leads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produce temperatures in excess of 2200 °C in the furnace. It was possible to maintain any desired temperature below 1700 °C within 2 °C after a short thermal equilibrating time.

The vacuum pumping system consisted of a liquid nitrogen trap, a 4" diameter MCF-300 oil diffusion pump using Octoil-S fluid, and a Welch Duoseal Series 1397 B fore-pump. After initial outgassing of the furnace and condenser, the vacuum was maintained at less than 5×10^{-7} mm Hg during all vapor pressure determinations.

A 6 volt battery supplied the current for control of the balance and was regulated by a decade resistor box. The current was measured by determining the voltage drop across a standard resistor using a Leeds and Northrup K3 potentiometer with a Brown Electronik null indicator. Calibration of the balance in terms of millivolts per milligram was carried out by determining the change in current necessary to return the balance beam to a null position after addition of 5 mg rider weights obtained from Wm. Ainsworth and Sons. The calibration was found to be constant within experimental error over a 100 mg range with a sensitivity of 5 micrograms. The null position of the balance beam was determined by projection of an image of a pointer on the balance beam onto an etched glass screen through a 20x telescope with the converging lens removed from the eyepiece.

For the determinations below 1500 °C the furnace temperature was maintained constant to $\pm$ 0.2° by adaption of the resistance element controller developed at the Ames Laboratory by Svec, Reade and Hilker (28). A sensing element coil of .005" tantalum wire was wound around a threaded beryllia core and the element mounted inside the furnace heater immediately below the effusion vessel. Temperatures below 1450 °C were measured with a Pt-Pt13% Rh thermocouple, and above 1450 °C a Leeds and Northrup disappearing filament optical pyrometer was used. The optical pyrometer was calibrated "in situ" against a calibrated Pt-Pt13% Rh thermocouple and also by observing the temperature at which pure platinum melted.

2. Preparation of sample and effusion vessel

For determining the vapor pressure in the low pressure region of 10^{-5} to 10^{-8} mm Hg two types of samples having an area of 30-40 cm^2 were used. The first type was machined to the desired dimensions, 5/8" diameter by 2-3" long, from a rod of vacuum cast holmium metal. A thermocouple well was drilled to a depth that would place the junction 1/3 of the distance from the top of the sample. A 1/4" diameter tantalum tube with one end welded shut was inserted into the well to protect the thermocouple from attack by the holmium vapor. To the upper and lower faces of the sample were welded disks of .010" tantalum which protruded 0.005" over the side of the sample to remove any chance of contact of the condenser and sample which might lead to a transfer of mass to the condenser.

The second type sample was made by distilling a thin layer of holmium, ~10 mils thick, onto a 5 mil tantalum sheet. The tantalum sheet was then formed into a cylinder with the holmium exposed on the exterior to provide an evaporation surface for the vapor pressure determination.

The samples used in the pressure range from 10^{-6} to 10^{-3} mm Hg were made by machining a rod of holmium to fit tightly inside an open tantalum effusion vessel so that the exposed surface formed a 1 cm^2 evaporation area, or by filling a ½" diameter vessel with a freshly distilled holmium crystals. The thermocouple well was welded in the effusion vessel in such a manner as to place the thermocouple junction within 1/8" of the evaporation surface.

To determine vapor pressures in the range of 10^{-4} to 10^{-1} mm Hg, a conventional Knudsen cell was constructed by welding a 0.0005" tungsten lid containing an orifice 0.028 to 0.060" diameter to a ½" diameter effusion vessel. In the bottom of the vessel was welded a thermocouple well which projected into the cell to ½ its height so that the thermocouple junction would be in a region which was in thermal equilibrium with the metal vapor. The orifice area was determined by simultaneously photographing the orifice and a stage micrometer, as seen through the orifice, on a Bausch and Lomb metallographic microscope. The area of the orifice could be calculated from a knowledge of the image area and the true magnification determined from the image of the stage micrometer. The usual process of reaming and burnishing the edge of the orifice to reduce the wall thickness was not carried out as it was felt that greater accuracy could be obtained by applying a Clausing factor correction to orifice walls of known length.

The vapor pressures in the region from 10^{-2} to 9 mm were determined by utilizing a tube orifice made from a $\frac{1}{2}$" length of $\frac{1}{4}$" diameter tantalum rod with an orifice radius of 0.014". Attempts to capture the vapor effusing from the tube orifice by the use of a graphite condenser produced rather inconsistent results, with the measured pressures being lower than the expected values. When it was also noted that holmium vapor had condensed on places other than the condenser, this was attributed to the possible decomposition of the holmium carbide formed on the condenser. However, consistent results were obtained by suspending the effusion vessel from the balance beam and measuring the amount of holmium vapor lost through the orifice.

3. Condensers

The graphite condensers used for the samples of largest area were made by alternately sanding by hand and heating in air by means of a high frequency converter. Beginning with a 3/4" inside diameter by $3\frac{1}{2}$" long cylinder which had been machined to a wall thickness of 0.015", the sanding and burning process was used to reduce the wall thickness to approximately .005" and the weight to 2.5 grams. A graphite lid, containing a small hole for the suspension wire, was fastened to one end of the cylinder with tantalum wire pins. The condenser was hung from the balance beam and aligned in such a manner as to allow only 0.050" clearance between it and the sample.

The condenser used for all of the other samples was a machined graphite cup 5/8" inside diameter and 3/4" high with a wall thickness of 1/32". The total weight was 1.2 grams. To insure that the condensers would hang vertically, they were suspended by a 0.005" tantalum wire with a welded bead threaded through a hole in their top.

D. Procedure

In the preparation for a run, the vacuum furnace, complete except for the sample and thermocouple, was outgassed until a vacuum of less than 1 x 10^{-5} mm could be obtained at 2000 ^{o}C. The furnace was then backfilled with argon and the sample and thermocouple installed. The heating was begun slowly enough to prevent the pressure in the furnace from rising above 5 x 10^{-6} mm Hg. When a noticeable deflection of the balance beam indicated a measurable weight loss, a period of five to ten minutes was allowed for thermal equilibrium to be established. The mass of vapor transferred to the condenser in a timed interval was obtained from the difference in the current required to bring the balance beam to the null position. At least three readings were taken at each temperature setting and all readings at each temperature were combined to yield the points represented on the vapor pressure plots. A run would consist of going from the lowest to the highest pressures obtainable in the specific experiment several times in both directions, resulting in 20 to 30 points.

E. Calculations

The data were processed by calculation of the pressures on an IBM 650 computer which was programmed to provide a straight line fit of the points in each run by a least squares treatment to the equation

$$\log P = \frac{-A}{T} + C \quad .$$

The vapor pressures from all runs were then combined and fitted again by a least squares treatment on the computer to a single line. The vapor pressure of holmium metal is described by the equation

$$\log P\ \text{mm} = \frac{-1.5137 \times 10^4}{T\ {}^{\circ}K} + 8.426$$

and the vapor pressure of the liquid follows:

$$\log P\ \text{mm} = \frac{-1.4122 \times 10^4}{T\ {}^{\circ}K} + 7.849 \quad .$$

Estimating the difference in the enthalpies of the solid and the vapor between the mid-range temperature of the run (1061 °C) and 298 °C to be 1.1 kcal, the ΔH_s^o at 298 °C would be 70.6 kcal/mole.

The values of the Clausing factors used for calculation of vapor pressures from the tube orifice were obtained by interpolation of the values given in Dushman even though more recent calculations by Demarcus (8) have indicated that these values may be somewhat in error. Demarcus had not listed the values of the Clausing factor for a value of l/a, orifice length divided by orifice radius, corresponding to the orifice used in this study. Since the heat of sublimation values are related to the slope of the vapor pressure curve rather than the absolute value of the vapor pressure, agreement of values obtained by the tube orifice and those obtained by the Knudsen method is not absolutely mandatory to obtain a heat of sublimation. However, the overlapping region of the two methods was sufficient to compare the values listed for the Clausing factor correction and the agreement was found to be within experimental error.

F. Data

Tables 4 through 11 consist of the data which were observed and the calculated vapor pressures of holmium metal that are plotted in Figures 6 through 10. Each table represents the data from one run. The headings include the measured constants common to all points of the run and the computed values of the constants, A and B, in the log p equation, ΔH, and the probable error in the pressure (PEP) observed from the statistical variation observed in the points.

G. Errors

The formula used for the calculation of the vapor pressures is:

$$P = m \cdot \frac{1}{a} \cdot \left(\frac{2\pi R}{M}\right)^{\frac{1}{2}} \cdot (T)^{\frac{1}{2}}$$

The value of R was taken to be 8.314×10^7 erg $(^{\circ}C)^{-1}$ $(\text{mole})^{-1}$ (29) and the mass of holmium, 164.94, (30) was used. The error in these is so small in comparison to other errors as to be insignificant.

1. Area

The value of the area of the orifice was measured by the procedure described previously. While the absolute error is difficult to estimate, the deviation from the mean of the value obtained on several measurements was taken to be of the order of magnitude of the error and was found to be 0.2%.

Table 4. Vapor pressure data

Run Ho C-6 Results: H 66.47 ± .34

Area 4.14×10^{-3} cm^2 A 14527

Temperature measurement pyrometer B 6.479

Clausing factor 0.061 PEP 1.8%

Point	Time, sec	Mass, mv	Temperature, °K	$10^4/T$ °K	-Log P, mm
1	287	17.918	2055	4.866	-0.9845
2	701	1.125	1659	6.028	0.6520
3	969	4.248	1756	5.695	0.2032
4	441	2.471	1781	5.615	0.0935
5	490	3.546	1807	5.534	-0.0207
6	502	3.032	1790	5.587	0.0598
7	518	2.428	1764	5.669	0.1731
8	519	1.979	1745	5.731	0.2651
9	948	2.484	1712	5.841	0.4322
10	696	2.242	1731	5.777	0.3401
11	1327	1.876	1659	6.028	0.7070
12	7670	1.916	1524	6.562	1.478
13	46142	2.545	1435	6.969	2.147
14	1652	1.671	1632	6.127	0.8560
15	3803	1.860	1575	6.349	1.179
16	1008	2.381	1701	5.879	0.4786
17	568	2.676	1764	5.669	0.1709
18	224	1.624	1804	5.543	-0.0212
19	233	1.200	1773	5.640	0.1311
20	270	1.899	1807	5.534	-0.0083
21	222	1.990	1836	5.447	-0.1171
22	182	3.178	1907	5.244	-0.4150
23	219	5.171	1942	5.149	-0.5500
24	375	5.036	1879	5.322	-0.2977
25	726	7.530	1859	5.379	-0.1832
26	580	5.888	1836	5.447	-0.1712
27	431	10.309	1948	5.133	-0.5562
28	320	10.675	1991	5.023	-0.7055
29	241	11.829	2023	4.943	-0.8766

Table 5. Vapor pressure data

Run Ho C-11 Results: H 68.45 ± .23

Area 4.215 x 10^{-4} cm^2 A 1.4960

Temperature measurement thermocouple B 6.658

Balance constant 1.569 mv/mg PEP 1.1%

Point	Time, sec	Mass, mv	Temperature, ^{o}K	$10^4/T$ ^{o}K	-Log P, mm
1	567	2.268	1707	5.858	0.4764
2	739	2.663	1699	5.886	0.5227
3	741	2.394	1690	5.917	0.5713
4	935	2.253	1666	6.002	0.7018
5	750	5.0115	1752	5.708	0.2479
6	549	4.3452	1767	5.659	0.1725
7	25984	3.8243	1461	6.845	1.944
8	935	1.722	1643	6.0845	0.821
9	3589	.8080	1489	6.712	1.756
10	2254	.9810	1533	6.523	1.463
11	754	3.690	1725	5.797	0.3865
12	383	4.618	1808	5.531	-0.0153
13	1222	1.852	1627	6.146	0.9083
14	942	1.925	1650	6.061	0.7754
15	754	2.044	1674	5.974	0.6496
16	419	3.358	1767	5.658	0.1670
17	738	2.795	1699	5.886	0.5011
18	694	3.102	1713	5.838	0.4274
19	522	2.125	1705	5.865	0.4690
20	403	1.983	1723	5.804	0.3844
21	384	2.234	1736	5.760	0.3100
22	570	3.984	1751	5.711	0.2285
23	587	5.981	1785	5.602	0.0606
24	394	6.017	1825	5.479	-0.1199
25	383	7.863	1858	5.382	0.2523
26	24977	3.029	1443	6.930	2.031
27	2189	1.9451	1582	6.321	1.146
28	1066	1.234	1601	6.246	1.029
29	601	2.0029	1688	5.924	0.5581
30	1027	4.2261	1705	5.865	0.4643

Table 5 (Continued)

Point	Time, sec	Mass, mv	Temperature, ^{o}K	$10^4/T$ ^{o}K	-Log P, mm
31	406	2.726	1747	5.724	0.5581
32	465	3.976	1770	5.650	0.1386
33	474	5.238	1794	5.574	0.0243
34	409	5.616	1813	5.516	-0.0723
35	350	6.247	1838	5.441	-0.1892
36	293	6.507	1874	5.336	-0.2883
37	965	1.534	1620	6.170	0.8884

The values obtained with this method were compared to those obtained by measurement of the radius of the orifice with a Filar eyepiece and it was found that the areas agreed within the experimental error. The value of the radius of the tube orifices was not determined in the photographic method, but rather by measuring the diameter of the hole of each end of the orifice and using the average value in the calculations. Here the value of the error was taken to be equal to the deviation from the average and resulted in an error of 0.5%. The value of the evaporation area of the samples used for the Langmuir method were measured with a micrometer and were accurate to ± 0.01 cm, so that the 0.3% was added to the error in p.

2. Mass

The balance calibration was carried out using the calibrated 5 mg riders which were accurate to ± 0.002 mg, but

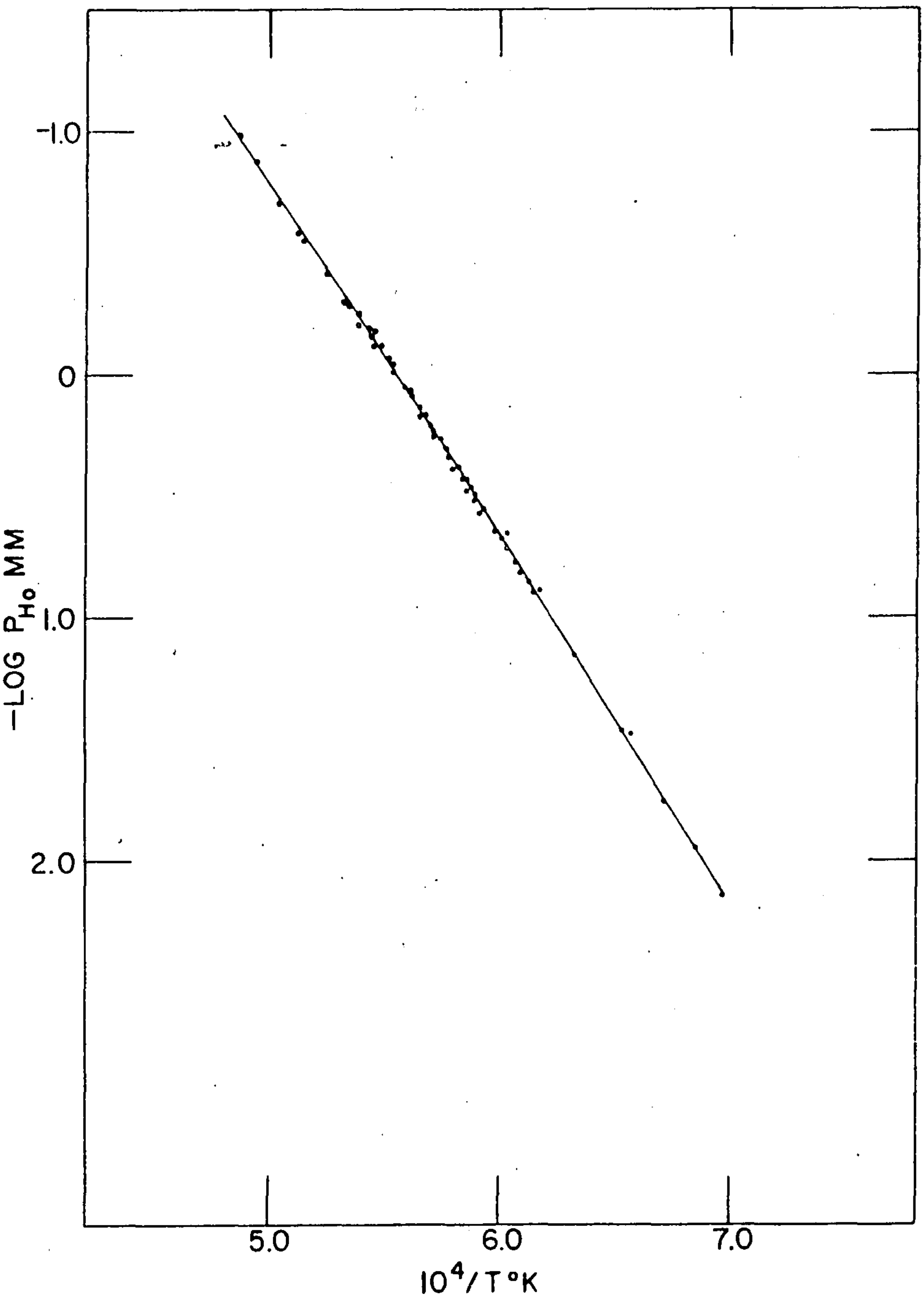

Figure 6. Vapor pressure of holmium metal determined with "tube" orifice

Table 6. Vapor pressure data

Run Ho C-3

Area 1.582 x 10^{-2} cm^2

Temperature measurement thermocouple

Clausing factor 0.992

Balance constant 1.569 mv/mg

Results:

H 71.01 ± .38

A 1.5518

B 11.495

PEP 1.2%

Point	Time, sec	Mass, mv	Temperature, °K	$10^4/T$ °K	-Log P, mm
1	657	1.890	1418	7.052	2.231
2	2147	3.729	1392.6	7.181	2.454
3	2958	3.226	1366.8	7.316	2.660
4	507	1.782	1432	6.983	2.142
5	757	3.150	1446	6.916	2.066
6	508	2.759	1459	6.854	1.949
7	382	2.543	1473.6	6.786	1.858
8	341	2.756	1486.9	6.725	1.772
9	343	3.375	1494.2	6.693	1.685
10	319	3.757	1513.3	6.608	1.605
11	874	2.165	1416	7.062	2.296
12	3054	2.031	1343.6	7.443	2.879
13	22181	3.162	1267.5	7.890	3.560
14	7067	1.942	1300	7.692	3.270
15	5275	2.195	1321	7.570	3.086

a more significant contribution to the accuracy of the balance is in the determination of the null point. It was determined that the null point could be reproduced on a reading to ± 0.003 mv which is ± 2 μgram, so that with the average weight loss used 0.2% would be the maximum error introduced into p from this cause.

Table 7. Vapor pressure data

Run Ho C-5	Results:	H	69.27 ± .39
Area 3.995×10^{-3} cm^2		A	1.5137
Temperature measurement thermocouple		B	9.155
Clausing factor 0.983		PEP	1.5%
Balance constant 1.616 mv/mg			

Point	Time, sec	Mass, mv	Temperature, °K	10^4/T °K	-Log p, mm
1	357	2.187	1556	6.427	1.294
2	1093	2.074	1477.5	6.768	1.814
3	4238	2.197	1400.8	7.139	2.389
4	5355	1.366	1361	7.348	2.703
5	1743	5.471	1515	6.601	1.590
6	417	4.609	1600	6.250	1.031
7	284	5.553	1648	6.068	0.7771
8	260	9.477	1702	5.875	0.4996
9	461	2.6622	1561	6.406	1.319
10	1294	1.2389	1443	6.930	2.116
11	22659	3.151	1331	7.513	2.971
12	4590	2.257	1402	7.133	2.412
13	365	1.945	1555	6.431	1.354

3. Temperature

Thermocouples were calibrated at the copper and aluminum melting points. The thermocouples were used to measure temperatures up to the range of 1450 °C, so that the accuracy in the range should fall well within ± 0.5°. Temperatures above 1450 °C were measured with an optical pyrometer which had been calibrated in situ as mentioned. The variation of the reading was within ± 2° and the accuracy estimated to be

Table 8. Vapor pressure data

Run Ho C-25	Results:	H	68.88 ± .29
Area 5.580×10^{-3} cm^2		A	1.5055
Temperature measurement thermocouple		B	8.481
Clausing factor 0.964		PEP	.9%
Balance constant 1.601 mv/mg			

Point	Time, sec	Mass, mv	Temperature, °K	$10^3/T$ °K	-Log P, mm
1	1445	1.415	1417	7.057	2.243
2	1227	3.954	1494.6	6.691	1.7144
3	923	2.560	1483.5	6.741	1.7811
4	1679	3.884	1471.7	6.795	1.8617
5	11330	.968	1281.5	7.803	3.324
6	23286	1.306	1263.7	7.913	3.510
7	5390	.628	1297.2	7.709	3.187
8	3732	.5730	1313.2	7.615	3.064
9	2980	.6720	1332.4	7.505	2.894
10	871	1.010	1427.9	7.003	2.168
11	1025	1.734	1451.3	6.890	1.993
12	1100	2.162	1461.4	6.843	1.927
13	903	2.776	1483.9	6.739	1.729
14	660	4.653	1544.8	6.473	1.360
15	581	4.755	1556.9	6.423	1.294
16	668	7.538	1580.8	6.326	1.151
17	712	9.803	1595.8	6.266	1.062
18	273	1.387	1522.8	6.567	1.505
19	5400	1.762	1354.5	7.383	2.723
20	2104	.9300	1371.5	7.291	2.589
21	2150	1.108	1379.5	7.249	2.521
22	1503	.9720	1392.3	7.182	2.420
23	944	.9580	1418.8	7.048	2.220
24	602	9.745	1610.6	6.209	0.9900
25	600	12.65	1630.2	6.134	0.8726

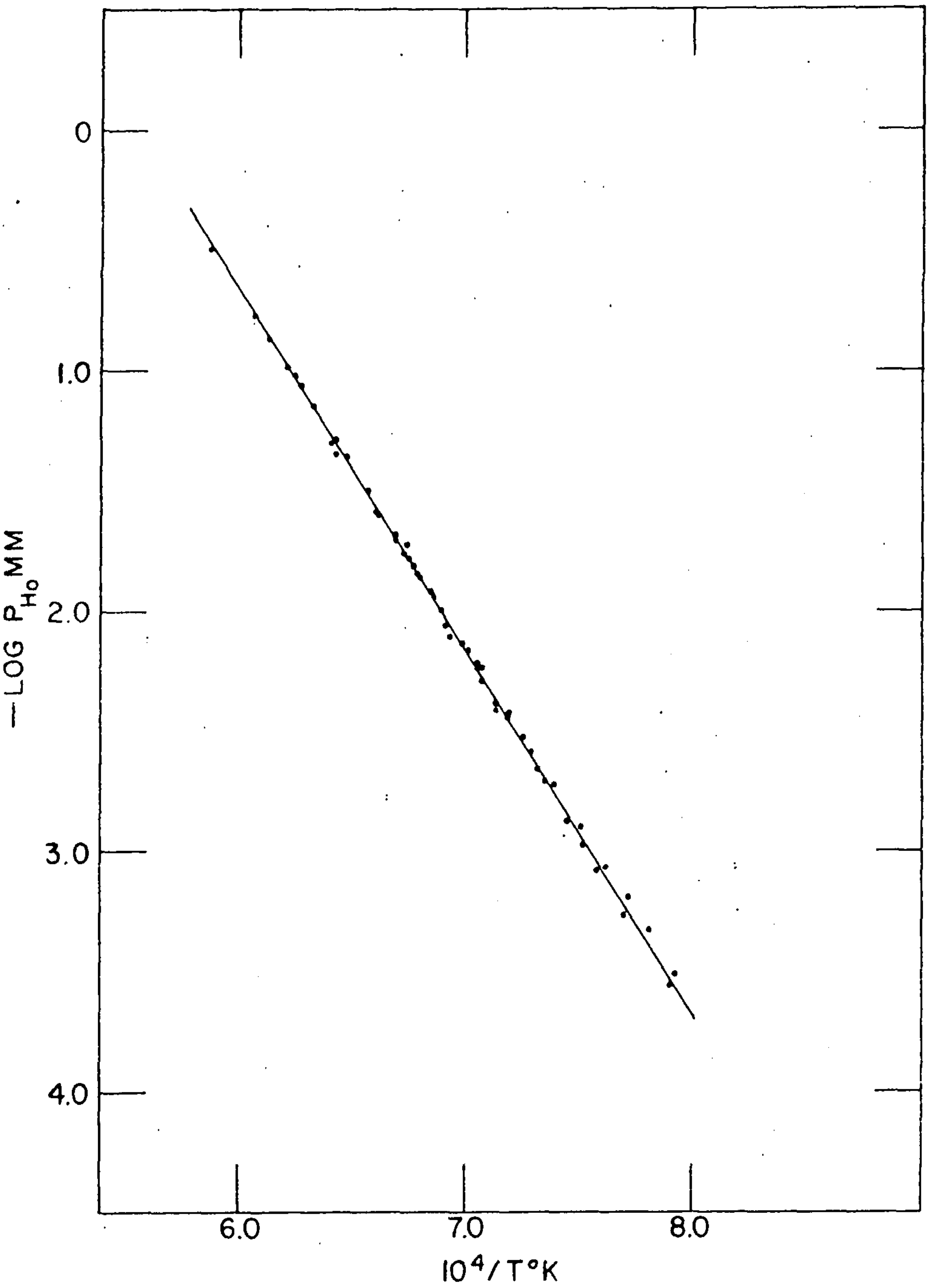

Figure 7. Vapor pressure of holmium metal determined by Knudsen method

Table 9. Vapor pressure data

Run Ho C-33 Results: H 69.79 ± .33

Area 1.160 cm^2 A 1.5228

Temperature measurement thermocouple B 8.472

Clausing factor 1.000 PEP 1.4%

Balance constant 1.575 mv/mg

Point	Time, sec	Mass, mv	Temperature, °K	$10^4/T$ °K	-Log P, mm
1	791	3.003	1217.9	8.211	4.017
2	1298	2.134	1183.1	8.452	4.386
3	849	2.495	1205.2	8.297	4.130
4	755	2.865	1216.6	8.220	4.017
5	589	4.040	1243.4	8.042	3.755
6	619	5.903	1259.7	7.938	3.609
7	1025	4.784	1225.4	8.161	3.926
8	879	1.950	1191.5	8.393	4.255
9	920	.9780	1163	8.598	4.580
10	631	1.538	1194.2	8.374	4.213
11	1193	1.091	1155.6	8.654	4.646
12	2152	1.183	1135.5	8.807	4.871
13	3218	1.3336	1124.9	8.890	4.996
14	2478	.6889	1111.7	8.995	5.172
15	3768	.7443	1099.2	9.098	5.323
16	5646	.6474	1081.4	9.247	5.562
17	5398	.4850	1073.2	9.318	5.670
18	18342	1.0076	1057.2	9.459	5.887
19	22571	.7713	1037.2	9.641	6.097
20	1094	.8236	1147.2	8.717	4.732
21	993	1.549	1176.5	8.500	4.411
22	659	4.648	1244.8	8.033	3.743
23	597	4.717	1250.1	7.999	3.693
24	437	4.240	1259.6	7.939	3.602
25	547	8.625	1284.2	7.787	3.387

Table 10. Vapor pressure data

Run Ho C-8

Area 29.280 cm^2

Temperature measurement thermocouple

Clausing factor 1.000

Balance constant 1.585 mv/mg

Results: H 70.82. ± .28

A 1.5476

B 9.896

PEP 1.8%

Point	Time, sec	Mass, mv	Temperature, °K	$10^4/T$ °K	-Log P, mm
1	307	3.460	1124.3	8.894	4.963
2	500	3.058	1102.3	9.072	5.233
3	765	2.384	1079.6	9.263	5.530
4	1471	2.277	1054.9	9.480	5.839
5	404	6.154	1134.9	8.811	4.830
6	279	8.230	1167.4	8.566	4.537
7	169	9.552	1186.7	8.427	4.251
8	1272	2.8502	1068.5	9.359	5.676
9	634	6.392	1119.7	8.931	5.013
10	4544	2.2865	1022.9	9.776	6.334
11	697	2.585	1085.7	9.211	5.454
12	278	5.925	1147.9	8.712	4.682
13	707	1.797	1072.2	9.327	5.620
14	5200	1.377	1002.4	9.976	6.617
15	15990	.959	960.2	10.41	7.272
16	1879	.464	1002.9	9.971	6.648
17	4530	1.196	1075.6	9.297	5.603
18	1785	1.622	1041.3	9.603	6.074
19	2260	.752	1012.6	9.876	6.516
20	10041	.937	976.6	10.24	7.076
21	8770	1.173	987	10.13	6.917
22	43011	1.266	947	10.56	7.584
23	2330	1.800	1036.9	9.644	6.145
24	706	2.394	1083.9	9.226	5.493
25	159	1.791	1124.3	8.894	4.964

Table 11. Vapor pressure data

Run Ho C-27	Results:	H	70.1 ± .8
Area 17.92 cm^2		A	1.532
Temperature measurement thermocouple		B	8.53
Balance constant 1.575 mv/mg		PEP	2.5%

Point	Time, sec	Mass, mv	Temperature, °K	10^4/T °K	-Log P, mm
1	907	1.563	1081.5	9.246	5.571
2	7730	2.696	1105.7	9.044	5.260
3	1206	2.521	1087.4	9.196	5.486
4	1306	1.810	1073.7	9.314	5.667
5	1964	1.671	1057.9	9.453	5.882
6	8540	1.971	1012	9.881	6.459

within ± 5°, so that the error introduced in p from this source in the region 1770 °K to 2055 °K would be estimated as 0.3%.

4. Time

Time was measured with a Labchron Electric timer so that the only significant error would be in reading and recording of the time. This error was estimated to be ± 1 second. On the shorter times this may amount to as much as 0.5%, but a more average value would be 0.2%.

5. Clausing factor

The value of the Clausing coefficient was as an interpolated value from those listed in Dushman for the case

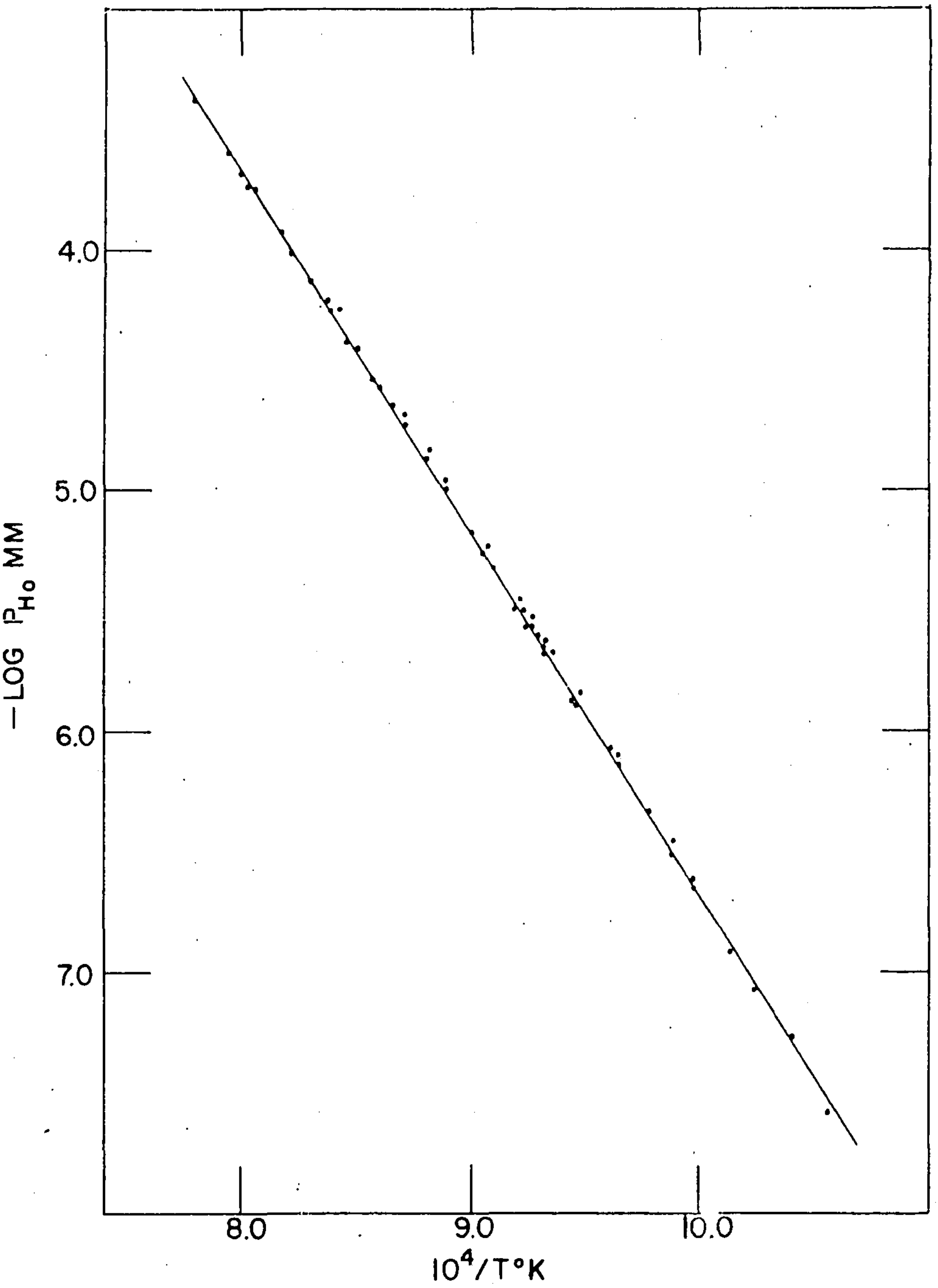

Figure 8. Vapor pressure of holmium metal determined by Langmuir method

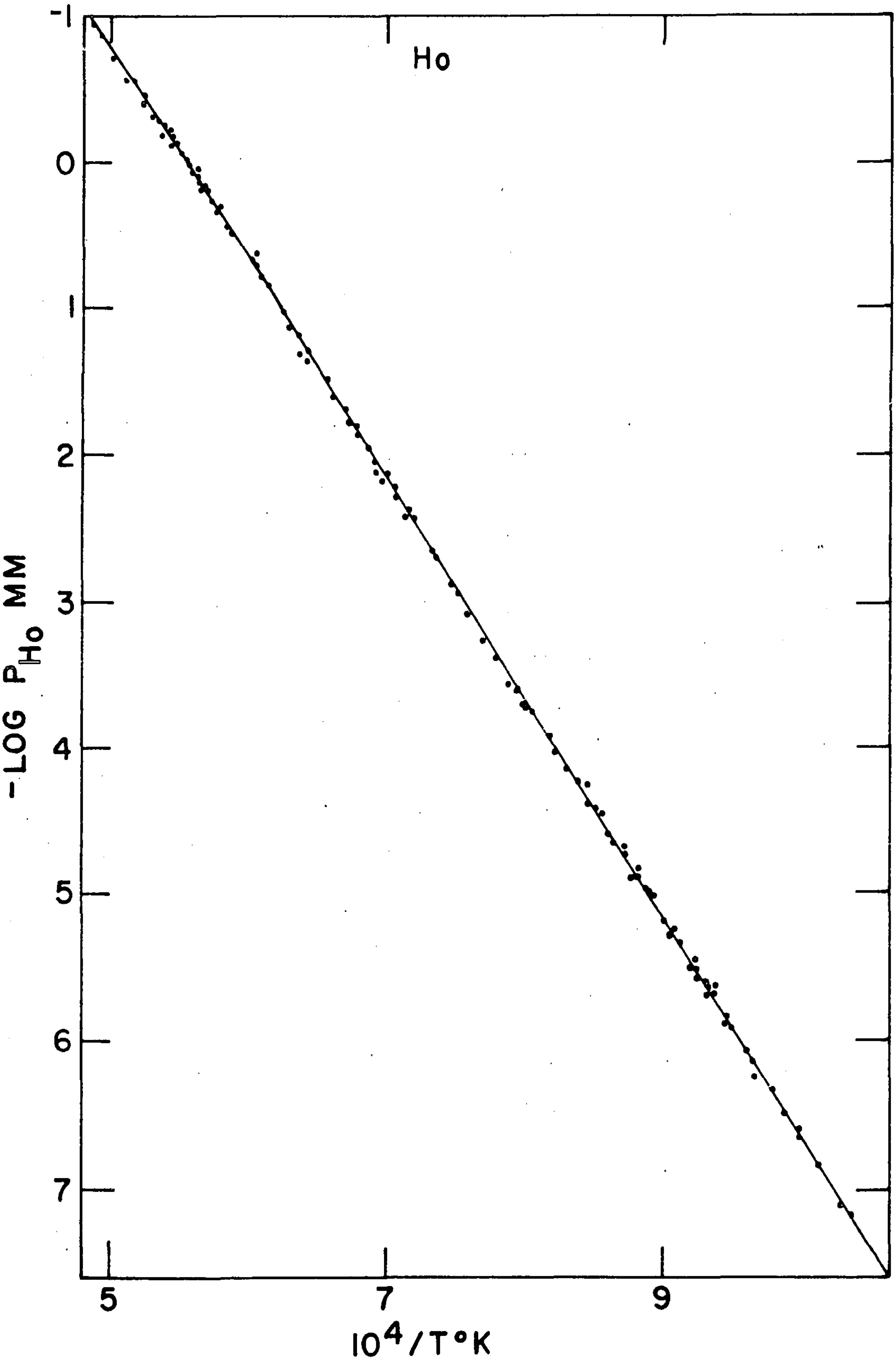

Figure 9. Vapor pressure of holmium metal from all three methods

of the tube orifice and as such would be subject to an estimated error of up to ± 1%. This large an error was estimated in consideration of the studies of Demarcus which indicate that there is some variation between the values he calculates and the less refined values of Clausing. For the correction to the thin walled orifices of the true Knudsen method, the values as interpolated from those in Demarcus were used. These were probably accurate to .2% and would add in correspondingly in p.

The total of the estimated maximum errors would be obtained by the summation:

area	0.5%
mass	0.2%
temperature	0.2%
time	0.5%
Clausing factor	1.0%
	2.4%

From the statistical variation of the points listed of probable error in p on the data sheets, the errors are seen to be less than the total error as estimated above. This is as would be expected, since the errors may add in such a manner as to cancel. Overall the agreement among the points in a run and among the various runs appears to be quite consistent.

H. Discussion

Utilizing the modifications of the Knudsen and Langmuir methods of vapor pressure measurement discussed in Part I, the vapor pressure of holmium metal has been measured from 9 to 10^{-8} mm. While the changes made are in part exceeding the restrictions placed on these methods by their originators, the apparent compatibility and consistency observed is offered as justification that the results are valid. It is expected that the methods can be applied in the general case to other metals. The essential requirements for using the graphite condenser would be that the metal form a carbide of sufficient stability in the temperature range to be studied. (Sufficient stability for the carbide was qualitatively defined as having a decomposition pressure of less than 10^{-4} times the vapor pressure of the metal. A factor of 10^{-2} was felt to be within an allowable error of 1% and the consideration that the condenser presents an evaporation area of 10^{2} that of the orifice introduces another factor of 10^{-2}.) In the case of the tube orifice, the maximum pressure measurable is where the Knudsen vapor pressure equations no longer relate the effusing weight and the pressure. If the weight loss can be related to the actual pressure by using both Knudsen flow and hydrodynamic flow equations, higher pressures can be measured. The higher pressures might be expected to enhance the possibility that atoms in the metal vapor form dimers, although this fact is at least in part negated by the higher temperature involved. Noting the work of Carlson (31) on the vapor pressure of mercury in an apparatus similar to the one used in this study, the deviation from Knudsen flow was observed to take place at a pressure of *ca*. 10 mm. As was inferred by Dushman and indicated by Carlson, this occurs wherein the mean free path and the orifice diameter become of equal magnitude. The data recorded for holmium at this pressure do not indicate a noticeable deviation, but the mfp of holmium at 10 mm (1750 °C) is considerably greater than the mfp of mercury at 10 mm which occurs at the lower temperature of 180 °C.

The extended range of the present work enhances the possibility that a first order transformation will lie in the range of convenient measurement, so that determination of the pressure over the higher and lower phases may be accomplished and from the difference of their enthalpies, the enthalpy of transformation obtained. For the case of holmium metal, the vapor pressure over both the solid and the liquid state was measured and the difference in enthalpies was assumed to be the heat of fusion. The enthalpies observed (in kcal/mole) were: vaporization 64.7 ± .5, sublimation 69.3 ± .4, fusion 4.6 ± .6. More properly the differences in the enthalpies were taken to be the ΔH for the reaction:

$$\text{holmium (hcp)} \rightarrow \text{holmium (liquid)} \quad .$$

It was observed that the points obtained immediately below the melting point show a greater scatter than those of other portions of the curve. One postulate offered to explain this is the possibility of some sort of "premelting phenomena". In their study of the heats of sublimation and vaporization of neodymium, Johnson _et al._ (26) observed a rather similar anomalous behavior wherein the sublimation and vaporization curves did not intersect at the melting point. Berg (32) noted in a calorimetric study of some of the rare earth metals that the enthalpy increased somewhat abnormally just below the melting point. The earlier melting points taken by the pointer indentation methods (33) were quite low due to the extreme softness of the metals below the melting point. A number of other examples have been cited by Schnieder (34) which indicate that this is not an extremely uncommon phenomenon. There is the possibility that a crystallographic transformation of holmium occurs in this region, since in a study by Hanak (35) an anomaly was observed in the thermal resistivity curve at 1442 °C. If such a high temperature reaction takes place, it would not be expected to be observed in this study due in part to the rather short temperature range of stability and also to an expected small heat of transformation, since the enthalpy of crystallographic transformations in other rare earth metals are in the order of 500 cal. Subsequent thermal resistivity studies of holmium metal carried out in this laboratory have not yet definitely confirmed such a transformation.[1]

In evaluating the results of vapor pressure studies, the

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[1] Habermann, C. E., Ames, Iowa. Data on the thermal resistivity of rare earth metals. Private communication. 1961.

calculation of the ΔH^{o}_{298} from the third law method (29,36) gives an extra check on the consistency of the data. For monatomic vapors, this method requires knowledge of experimental values only of the electronic energy levels of the gaseous atoms and the heat capacity of the solid to calculate the free energy functions.

One of the most challenging problems which has faced rare earth investigations has been the solution and correct assignment of energy levels of the gaseous atoms. This is usually done from the spectrographic data; however, the utter complexity of the spectra observed for some of the rare earths, due to the numerous low lying energy levels, has made an acceptable explanation of these levels impossibly difficult. Only in the recent literature (38) has even the simple assignment of the ground state of the vapors of dysprosium, erbium, holmium and praseodymium been reported from experimental data; the ground states of cerium and terbium have not yet been established.

The relationship of vapor pressure studies and electronic energy levels is used to evaluate the heat capacity of the vapor and obtain free energy functions to calculate the third law value of the heat of sublimation. Thus it is observed that if the free energy functions of the vapors are based on something other than experimental numbers, as would be the case in the absence of the electronic energy level measurements, the value of the third law calculation is lessened. In the case of an atom where the number of energy levels is restricted at the temperatures in question, the error associated with the neglect of the electronic contribution will be nil. However, holmium with its partially filled f shell and the possibility of interaction with the 5d levels would be expected to have a rather large electronic contribution to the free energy function. Therefore rather than estimate the free energy function associated with the vapor, it was considered more profitable to attempt the calculation of the electronic contribution to the free energy function from the measured values of vapor pressure. Stull and Sinke (38) have estimated the heat capacity and calculated the free energy values of solid holmium. It was assumed that the values in their table were reasonably accurate since comparison of their estimates with the measured values of Gerstein _et_ _al_. (39) shows agreement within the experimental error. The value of the heat of sublimation of holmium at 0 $^{\circ}$K was taken to be 71.0 Kcal/mole obtained from the slope of the measured vapor pressure curve by estimating the $\Delta (H^{o}_{298}-H^{o}_{o})$ to be 0.4 Kcal. The vapor pressure data were then used with these values to obtain the free energy function of the vapor. All of the contributing factors to the free energy function of the vapor except the electronic portion can then be subtracted to give the electronic contribution. The values of ln Q and Q are listed in Table 12.

Table 12. Calculation of log Q from vapor pressure data

^{o}K	fef (s)[a] 298	fef (s)[b] 0	fef (g) -R ln Q	-ln P atm	R ln P	$\frac{\Delta H^o_o}{T}$	R ln Q	Q
900	20.44	18.81	41.748	11.053	50.575	78.888	5.37	15.0
1000	21.44	19.53	42.272	9.363	42.842	71.000	5.42	15.4
1100	21.93	20.19	42.746	7.985	36.539	64.543	5.43	15.4
1200	20.44	20.63	43.178	6.851	31.350	59.166	5.44	15.6
1300	22.85	21.39	43.576	5.878	26.898	54.615	5.43	15.4
1400	23.27	21.90	43.944	5.043	23.077	50.714	5.58	16.7
1500	23.68	22.40	44.287	4.333	19.828	47.333	5.61	16.9
1600	24.07	22.87	44.608	3.695	16.908	44.375	5.71	17.7
1700	24.46	23.33	44.910	3.163	14.474	41.765	5.74	18.1
1800	24.86	23.80	45.193	2.663	12.186	39.444	5.86	19.2

[a] $\left(\frac{F^o - H^o_{298}}{T}\right)_s$

[b] $\left(\frac{F^o - H^o_o}{T}\right)_s$

In observing the values of Q obtained for holmium and compared to some of the more common elements in Table 13, more reason is seen for handling the calculations in this rather unorthodox method, since the effect of the numerous energy levels available is to increase the entropy of the vapor.

Table 13. Electronic contribution to $\left(\frac{F^o - H^o_o}{T^o}\right)_g$, cal/deg

	0^oK^a	1000^oK	1500^oK		0^oK^a	1000^oK	1500^oK
K	2	2.0	2.0	Sc	4	8.71	4.10
Rb	2	2.0	2.0	Y	4	6.80	7.61
Cs	2	2.0	2.0	La	4	5.56	7.32
Ca	1	1.0	1.0	Nd	9	11.6	14.4
Sr	1	1.0	1.0	Sm	1	8.88	10.1
Ba	1	1.0	1.002	Eu	8	7.95	7.91
Ra	1	1.0	1.0	Gd	5	14.3	22.8
Ti	5	1.56	17.2	Yb	1	1.0	1.01
Zr	5	9.63	12.18	Lu	6	4.28	4.86
Hf	5	5.03	5.57	Ho	16	15.4[b]	16.9[b]

Data from References 29, 38.

[a] For the vapor in the ground state.

[b] This study.

Some question exists as to the most informative manner to plot the values of Q as a function of the temperature, since the mathematical form of the function is the complicated summation:

$$Q = \sum (2J_i + 1) \exp \frac{-hc}{K} \cdot \frac{vi}{T} \quad .$$

It is noted from the table that the values of Q increase with temperature in the manner expected. The value of Q at 1000 °K (15.4) is less, though perhaps not by a significant amount, than the minimum predicted value (16) from the J value of the ground state of the vapor, and would indicate that some error exists in the data or in the estimated values of heat capacity.

In correlation with the spectroscopic energy levels being discussed, another interesting phenomenon occurring in the phase change process should be noted. The recently determined energy levels indicate that the vapor ground state is the $4f^{11}6s^2$ configuration. Noting the determinations of the electronic states of rare earth metals (40), there is reasonably well established agreement that holmium metal is tripositive, i.e. that of the thirteen electrons above the closed shells, there are only ten in the 4f shell while the other three electrons are involved in the metallic bonding. Thus it is observed that the effect of the interaction of the much nearer neighbors in the condensed phase is to "promote" one of the electrons from the 4f shell, the reverse being effected in the sublimation process. While this at first may seem unusual, it is not unreasonable, since the energies involved in this transfer are in the reverse order and no doubt of much smaller magnitude than the other process occurring: in the exothermic process of condensation, a small amount of energy is absorbed in the removing of the electron from the 4f shell, while in the endothermic process of sublimation, the electron would appear to give up energy by the process of dropping to the 4f shell. One might further speculate that this is actually the result of the added energy that is to be achieved by having three electrons take part in the metallic bonding rather than just the two 6s electrons, especially when it is noted that the rare earth metals which show an apparent divalency in the metallic state have much lower cohesive energies. This is exemplified by europium and ytterbium in which the tendency to form the half filled or filled 4f shell leads to additional stability by Hunds' Rules. The metal samarium would lie somewhere intermediate in both apparent valency and cohesive energy.

IV. DECOMPOSITION PRESSURES OF HOLMIUM CARBIDES

A. Historical

Although basic information about the elements is of value, further justification for making of measurements of properties is provided through the use of this knowledge. The opportunity to provide an example of how the knowledge gained about holmium could be used arose very naturally in this study. This was in the consideration of the nature of the reaction of the holmium metal vapor and the graphite condenser which was used to weigh it. While it was not within the intended scope of this study, the complete lack of thermodynamic data about the rare earth carbides prompted additional studies on the holmium carbides as well as the dicarbide. In a study of this type, however, a complete interpretation of the pressures measured requires that both the reactant and product phases be known.

The success of the method of using a graphite condenser to capture the rare earth metal vapors in the vapor pressure studies of part II depended on the stability of the carbide formed. This was because any loss of material, either metal or carbide, by vaporization from the condenser would invalidate the weight readings observed. By x-ray diffraction the material on the graphite condenser was identified to be holmium dicarbide first reported by Gschniedner (41). As he noted, the material is hard, brittle, gold colored and reacts very rapidly with any moisture to release a mixture of hydrocarbons.

The thermal stability of a rare earth dicarbide has been reported in the work of Chupka et al. (25), in which the decomposition pressure of lanthanum dicarbide was studied. It was discovered that LaC_2 vaporized congruently by measuring the relative mass intensities of the vapor species on a mass spectrometer. A peak of less intensity than the LaC_2 (g) peak was observed for La(g), and from these was calculated the quantity

$$K_{eq} = \frac{P\ La}{P\ LaC_2}$$

which is the equilibrium constant for the reaction

$$LaC_2\ (g) \rightarrow La\ (g) + 2C\ (s) \quad .$$

K_{eq} varied from 0.7 at 2530 ^{o}K to 0.21 at 2240 ^{o}K.

A study of a somewhat different nature of the rare earth carbides was carried out by C. L. McCabe (42) in which he describes some of the thermodynamic properties of compounds of praseodymium and cerium with carbon in the metal-H_2-CH_4 system. The ΔF^o_{298}, ΔH^o_{298}, and ΔS^o_{298} for the formation of PrC and CeC were calculated, though other investigators have not reported the existence of these phases in mixtures of the rare earth metal and carbon.

It has also been noted that the stability of the rare earth carbides is related to the volatility of the metals, in that the more volatile rare earths have relatively less stable carbides. Spedding et al. (41) stated that the dicarbide of ytterbium decomposed to the metal and graphite at the temperature of only 800 °C in vacuum and this fact has served as an aid in the preparation and separation of this metal from a mixture of other rare earth oxides (42). Quill (43) indicates that the dicarbides of Y, La, and Ce are unstable in the presence of water. Vickery (44) has studied the structures of the dicarbides of all the rare earth metals prepared by the reaction of rare earth oxide with powdered carbon. He also notes the reactivity of these materials with water, but does not comment on the relative thermal stabilities. Other investigators have prepared rare earth carbides in programs where they have studied the hydrolysis products of these compounds.

Spedding etal. (41) examined some holmium carbon alloys and found evidence for the dicarbide and sesquicarbide, which are isostructural with the corresponding lanthanum compounds, and the existence of a fcc phase which appeared to be "tri-rare earth carbide", plus some other structure or structures. They suggested a dimorphism of the sesquicarbide might be the cause of the extra lines observed in diffraction patterns of the low carbon content alloys. Evidently no attempt has been made to measure the thermal stability of the rare earth sesquicarbide compounds. No reports of the phase diagram studies of the heavy rare earth metals with carbon were found.

The Knudsen method of the determination of the decomposition pressure of the holmium carbides was chosen because of the availability of the equipment, convenience, and accuracy. Since this method measures the equilibrium pressure, this should represent the maximum rate at which material would leave the condenser. If the evaporation coefficient is less than unity, this would lead to a lowering of the weight loss rate. This procedure necessitated the characterization of the vapor phase to determine whether it had the same composition as the solid phase or was arising through some decomposition mechanism. This question becomes especially pertinent in the light of Chupkas' study on the dicarbide of lanthanum in which he observed both the metal and dicarbide vapors. To determine the composition of the vapor, a graphite condenser which had been used to determine the vapor pressure of holmium metal, and thus containing a known quantity of holmium, was heated in the absence of the effusion vessel to a temperature sufficient to cause a noticeable weight loss rate. It was observed that this rate could be measured at various temperatures and used to calculate a straight line relationship of weight loss rate versus 1/T, if a constant value was assumed for the molecular weight of the vapor and the orifice area was taken to be the opening in the condenser, i.e. .75" diameter. This rate was dependent only upon the temperature until a mass of ca. 95% of the mass of holmium metal originally added had been lost. Following this was a somewhat lowered weight loss rate until the condenser had returned to its original weight. Two other runs were made by vaporizing a known amount of holmium metal onto the graphite condenser to form the carbide and then measuring the rate of decomposition. (See Table 14.)

Table 14. Decomposition of carbides

Metal distilled onto condenser	Total distilled off condenser	Metal	Carbon	
161.0 mg Ho	161.6 mg	161.0 mg	.6 mg	$HoC_2 \rightarrow Ho(g) + 2C(s)$
164.5 mg Ho	170.5	169.5	1.0	$HoC_2 \rightarrow Ho(g) + 2C(s)$
147.5 mg La	110.0	67.6	42.4	$LaC_{7.2}$
168 mg La	92.9	64.4	28.5	$LaC_{4.9}$

The condensers were removed and ignited in a muffle furnace in air to verify that the holmium had been entirely vaporized, and resulted in less than 0.2 mg ash. From this it was concluded that the dicarbide of holmium dissociates into the metal vapor and graphite.

A similar series of experiments was run by vaporizing a known amount of lanthanum metal onto a graphite condenser.

Subsequent heating at 1850-2000 °C showed that the log of the weight loss rate was linear with respect to 1/T, but the apparent atomic ratio of carbon to lanthanum vaporized from the condenser varied from 7.2 to 4.9, so that unequivocal interpretation of the data was not possible.

The high loss of carbon observed for the LaC_2 determination indicated evaporation of free carbon. In an attempt to check this, the weight loss rate was observed at elevated temperatures using only a blank graphite condenser suspended from the balance. The vapor pressure of carbon was calculated from the weight loss observed assuming the following: i) the evaporation area was equal to the total exterior of the condenser, ii) the accomodation coefficient was unity, iii) the vapor was monomeric carbon atoms. The pressures thus measured are of the same magnitude as the vapor pressure data in Stull and Sinke (38) as compared in Table 15, indicating that the vapor pressure of carbon was

Table 15. Vapor pressure of graphite

Run Graphite -1 Balance constant 1.568 mv/mg

Area 14.2 cm^2 ΔH = 150 kcal

Time, sec	Mass, mv	Temperature, °K	$\frac{10^{-4}}{T\ °K}$	-Log Pc, mm Obs.	-Log Pc, mm S&S(38)
10,000	.656	2193	4.56	6.16	6.12
3,620	.575	2251	4.44	5.83	5.95
1,646	.524	2303	4.34	5.47	5.78

indeed such that it would invalidate the LaC_2 measurements.

B. Materials and Experimental Methods

1. Sample preparation

The holmium metal used was the same as that for the vapor pressure study. The graphite was "National Special Graphite Spectroscopic Electrodes". The carbides used in the decomposition pressure studies were prepared by arc melting the weighed amounts of holmium metal and spectrographic graphite under an atmosphere of argon. The arc melt button was then removed to the helium filled dry box and crushed to pass through a 200 mesh screen; then remelted and reground twice more. The sample was left in a finely divided state, as the grinding was considered to be an added precaution that the value of the carbon analysis would be more representative of the bulk of the sample. The carbides were stored in a vacuum dessicator until ready for use.

2. Crucibles and related equipment

The determination of the decomposition pressure of the carbides by the Knudsen method was carried out in direct weight loss method of suspending the crucible from the balance beam. To determine the pressures associated with the dicarbide, a tantalum effusion vessel was used which contained a graphite cup as a liner. The use of the graphite cup is not likely to produce adverse effects on the vapor pressure observed, since the equilibrium in question is that over the two phases of the reaction:

$$HoC_2 \rightarrow Ho(g) + 2\ C\ (s)$$

The reaction was followed by x-ray analysis of the original material and the powder patterns of the residue.

The tantalum vessels used for the determination of the decomposition pressure of the sesquicarbide and lower carbides were equipped with a tantalum carbide liner since a graphite liner would change the composition of the sample. To make the TaC liner, a cup 7/16" diameter and 1/4" high was cold drawn of .005" tantalum sheet. The cup was packed in granular graphite and heated in vacuum to a temperature estimated as 2500 °C for ten minutes. X-ray analysis of the crucible indicated only the lines of TaC, and the tantalum to carbon atomic ratio was determined 1:0.99 by igniting random samples of the crucibles to Ta_2O_5.

In preparation for a run, the vessel of tantalum containing the liner of graphite or TaC was fitted with a lid of .002" tantalum having an orifice which had been carefully measured. The lid was then welded to the vessel and the vessel was outgassed at a high temperature in a vacuum. The vessel was then weighed and placed in the dry box where the carbide was added to the vessel through the orifice. The vessel was taken from the dry box, weighed to determine the amount of carbide added, and quickly suspended from the balance. This operation required exposure to the air for approximately 30 seconds, and since the vessel was originally filled with helium it was considered that the amount of reaction of the carbide with the air was not such that would prevent the use of the material.

3. Temperature measurement

Where the carbon content of the material was below 5 w/o, the pressure developed in the vessel was in the measurable range of 10^{-4} mm to 10^{-1} mm at temperatures which could be determined with a Pt-Pt 13% Rh thermocouple. With higher carbon content samples it was necessary that an optical pyrometer be used to determine the temperature. Calibration of the pyrometer was carried out "in situ" by comparison with the thermocouple up to 1500 °C and the melting point of pure platinum. The reproducibility of the temperature readings was 2°, and the accuracy was estimated to be $\pm 5^{\circ}$. The thermocouples were calibrated at the aluminum and copper melting points and the accuracy was considered to be $\pm 1^{\circ}$. Where the temperatures were in the range of 1400 to 1500 °C, measurement of the temperature with both the pyrometer and the thermocouple were used to determine whether the long exposures at the elevated temperatures had caused a shift in the calibration of the thermocouple.

C. Holmium Dicarbide

The measurement of the decomposition pressure of the dicarbide of holmium was undertaken, as mentioned in the introduction, because of concern that the holmium captured on the condenser actually did remain there without a significant decomposition of the carbide resulting in weight loss from the condenser. The discovery that vaporization occurred by the loss of holmium vapor led to the measurement of the "dissociation pressure" by assuming the opening in the condenser to be acting as an orifice and the results appeared to yield a very good pressure versus temperature plot. (See Table 16 and Figure 10.) Since this was a rather new concept in the method of measurement of decomposition pressures, it was desired to run the dissociation pressure by some more conventional method to collaborate the values obtained. To this end, arc melted samples of holmium dicarbide were prepared and their decomposition pressures determined using a tantalum carbide crucible of 3/8" diameter and 1/4" high which was approximately 1/3 filled with holmium dicarbide (Run 4, Figure 10). After completing the runs, the residue was a sintered mass which appeared to have a dark layer on the top surface and the more normal gold color in the interior. X-ray diffraction analysis of the dark layer showed the lines of the dicarbide and those of graphite, while the interior of the mass showed only the lines of the dicarbide. Rather poor decomposition pressure curves were obtained and a gradually decreasing pressure at constant temperature was noted. It was assumed that the presence of the covering of graphite prevented the development of the equilibrium pressure. A run (Run 5, Figure 10) was then made in which the dicarbide was contained in a tantalum carbide crucible set in a tantalum vessel having an orifice of .110" diameter. The pressures measured with this vessel were considerably higher (approximately .7 $\log_{10}$ units) than those observed with the condenser evaporation runs, and of a somewhat higher slope. The scatter was greater than would be desired for a good determination. Since the equilibrium under consideration was the one between the dicarbide, graphite and holmium vapor, the most logical choice for a crucible liner was a graphite cup. From the preceding experiments it became apparent that the pressures obtained with the condensers were not valid representations of the true decomposition pressures due to non-equilibrium conditions. This would appear to have most probably arisen from the rather small evaporation area, in which slow diffusion could have allowed surface depletion of the more volatile species.

At this stage it was decided to proceed further using the following changes in the method: the liner for the tantalum effusion vessel would be a graphite cup, the holmium carbide would be ground to pass through a 200 mesh sieve and the orifice would be made as small as convenient with the pressure and temperature requirements. The results of this series (Series C-) are contained in the runs C-1, 2, and 4, and exhibit very good agreement with each other. (See Figure 11.) However, the apparent consistency of the data taken with the condensers casts some doubt as to which set of these values was correct. Two experiments were undertaken to elucidate this matter. The first (Run 8a) was one in which material prepared by vaporizing holmium metal onto a condenser was ground and placed in a vessel of the type used in the latter series. The agreement of the values obtained was sufficient to lend support to the accepted values of Series C-. The second experiment (Run 8b) was to take the material of Run 4, grind it to pass through the 200 mesh sieve and run in the normal manner. The values obtained were in agreement with the final curve of Series C- as represented in Figure 11, and so it is felt that this curve is reasonably accurate.

D. Holmium Sesquicarbide

The first determination on the decomposition pressure of holmium sesquicarbide was attempted in a graphite vessel having a 1/4" diameter orifice and yielded a continually decreasing pressure at constant temperature, apparently due to change in composition of the material through interaction with the crucible, or to the depletion of the volatile species on the evaporation surface. X-ray analysis of the residue indicated that it consisted of dicarbide, with no sesquicarbide remaining at the termination of the run.

Subsequent determinations were carried out using tantalum effusion vessels with a tantalum carbide liner to contain the finely ground sesquicarbide. The measured pressures were quite consistent (see Figure 12) and indicated little or no dependence on the area of the orifice, providing the orifice diameter was below .050". Little sintering of the residue was noted; in fact the residue could be shaken as a powder from the vessel through the orifice after a run. Visual examination of the tantalum carbide liner after a run indicated little reaction had occurred with the holmium carbide, and the weight change of the liner was always less than .5 mg.

E. Lower Carbides

The existence of a third carbide of holmium, Ho_3C, has been indicated by Spedding et al. (41), and an attempt was made to determine the equilibrium decomposition pressure of low (1-6 w/o) carbon content. Rather than the easily interpreted determinations as observed with the di- and sesqui-carbides, it was observed that the activity of the holmium decreased in a regular fashion as the carbon content was increased. This would be expected with an extensive range of solubility in the phase diagram. However, the x-ray diffraction patterns which were taken of the original vapor pressure sample material and of the residue did not indicate a single phase across this range of composition but rather that there were other unidentified phases present. Further decomposition pressure determinations were not made on this region of composition due to the apparent discrepency of the observed pressures and the unresolved structures.

F. Data

The data observed are listed in Tables 16 through 25 in a manner similar to the holmium metal vapor pressure data. The values of A and B correspond to the equation describing the pressure of holmium over the condensed phases in question, ΔH is the enthalpy observed and PEP is the statistical probable error in the values of pressure.

G. Calculations

The calculation of the values of pressure and fitting of the values to a straight line relationship was done on the IBM 650 Computer. From the values of decomposition pressure and the standard free energy of formation of the dicarbide can be calculated according to the reaction:

Table 16. Decomposition of holmium dicarbide from graphite condensers

Run	Time, sec	Mass, mv	Temperature, ^{o}K	$10^4/T$ ^{o}K	-Log P, mm
1	1542	1.450	1745	5.70	4.54
1	1090	4.141	1865	5.36	4.159
1	496	3.544	1928	5.14	3.867
1	8610	1.735	1634	6.12	5.449
1	1353	0.906	1720	5.81	4.916
1	1046	1.068	1750	5.72	4.731
1	1593	2.631	1815	5.51	4.514
1	12820	0.833	1554	6.44	5.943
2	596	1.233	1805	5.55	4.419
2	938	2.779	1848	5.41	4.257
2	44280	2.261	1542	6.48	6.059
2	8070	1.743	1625	6.16	5.421
2	1160	.556	1706	5.87	5.064
2	6877	6.378	1750	5.72	4.773
2	778	1.252	1793	5.575	4.528
2	743	1.942	1833	5.45	4.313
2	940	2.232	1820	5.49	4.356
2	358	4.994	1998	5.00	3.566
2	294	6.128	2053	4.875	3.386
3	441	1.820	1867	5.26	4.111
3	457	3.635	1934	5.17	3.820
3	450	6.414	1983	5.04	3.559

$$\mathrm{Ho\ (g) + 2\ C\ (s) \rightarrow HoC_2(s)} \qquad \text{(I)}$$

$$\log P_{Ho}\ \mathrm{mm} = \frac{-1.9481}{T\ ^{o}K} \times 10^4 + 6.723$$

$$\Delta F_t = -RT\ln\left(\frac{1}{P_e}\right) = RT\ln P_e$$

$$= -89{,}103 + 18.60\ T\ \mathrm{cal/mole}$$

Table 17. Decomposition of holmium dicarbide

Run	Time, sec	Mass, mv	Temperature, °k	$10^4/T$ °K	-Log P, mm
4[a]	1790	2.341	1744	5.735	4.18
4	2956	7.474	1836	5.455	3.87
4	165	5.575	2189	4.575	2.72
4	3649	1.401	1779	5.65	4.80
4	1142	1.615	1866	5.36	4.19
4	753	1.638	1910	5.24	3.94
4	432	1.428	1944	5.145	3.76
4	406	1.936	1992	5.015	3.59
4	1301	3.173	2022	4.965	3.54
4	1494	2.672	1903	5.255	4.03
4	1080	2.8876	1937	5.17	3.85
4	281	2.8855	2080	4.805	3.25
4	514	0.3061	1815	5.515	4.51
5[b]	4950	1.083	1841	5.43	3.902
5	5160	2.589	1894	5.28	3.525
5	2488	2.518	1962	5.10	3.216
5	1797	2.555	2005	4.99	3.059
5	1796	1.411	1936	5.17	3.280
5	2435	1.406	1912	5.23	3.465
5	5742	1.675	1855	5.39	3.771
5	1960	1.352	1928	5.19	3.387
5	2195	2.131	1969	5.08	3.235
5	943	1.505	2025	4.94	3.012

[a] 3/8" diameter tantalum carbide crucible

[b] .110" diameter orifice

where P_e is the measured value of holmium pressure over the HoC_2-C mixtures. In the region above the melting point of holmium, ΔF^o_t for the reaction

$$\text{Ho (l)} + 2\ \text{C (s)} \rightarrow \text{HoC}_2\ \text{(s)} \qquad \text{(II)}$$

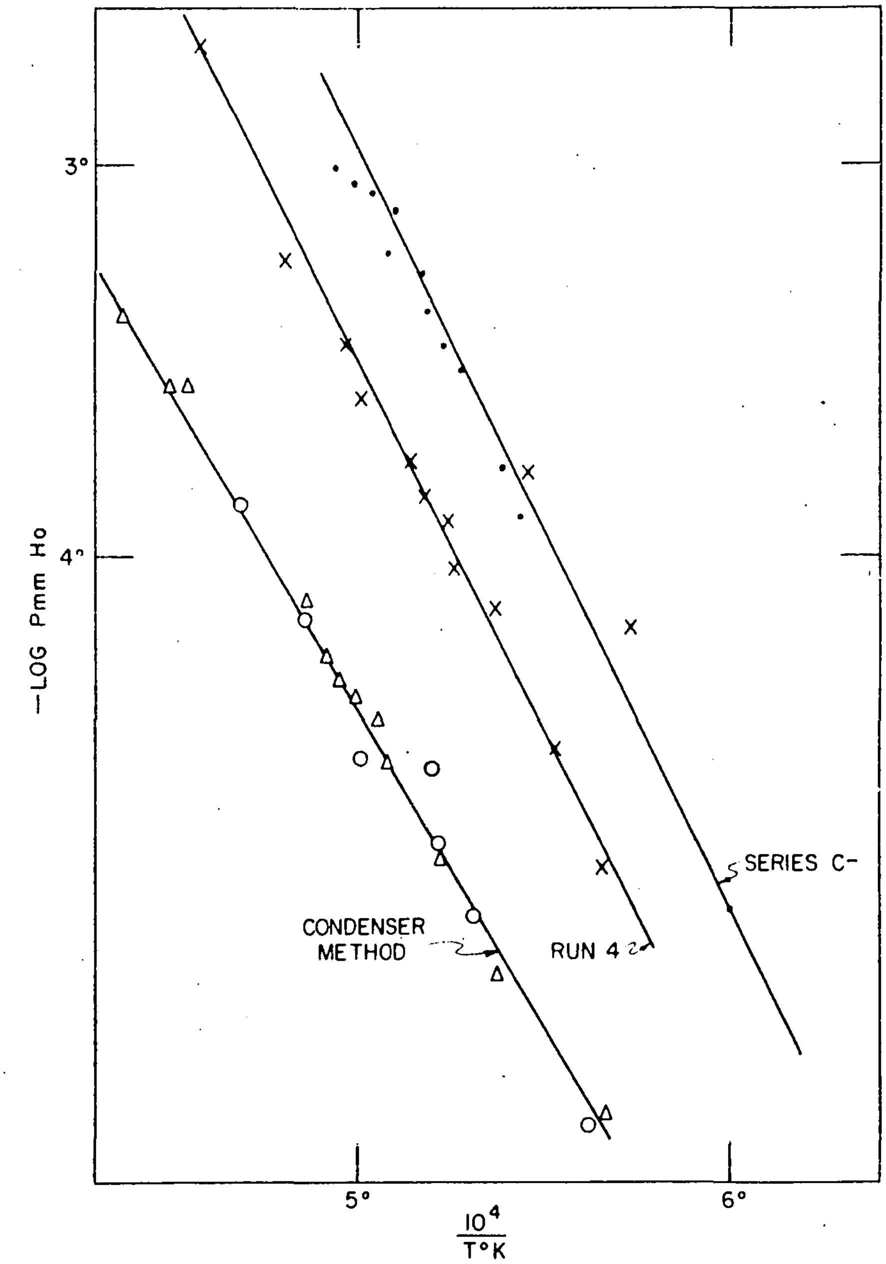

Figure 10. Preliminary determinations of the pressure of holmium over holmium dicarbide
x Run 4
• Run 5

Table 18. Decomposition pressure data

Run HoC_2-C-1

Area 1.528×10^{-2} cm^2

Temperature measurement pyrometer

Clausing factor 0.964

Balance constant 1.585 mv/mg

Results:
H 89.9 ± .3
A 1.9653×10^4
B 6.806
PEP 1.2%

Point	Time, sec	Mass, mv	Temperature, ^oK	$10^4/T$ ^oK	-Log P, mm
1	1212	2.204	2117	4.724	2.320
2	2292	3.206	2086	4.794	2.437
3	632	1.380	2128	4.699	2.240
4	695	1.933	2152	4.647	2.132
5	358	1.151	2177	4.593	2.067
6	1055	1.516	2088	4.789	2.426
7	4378	3.697	2035	4.914	2.661
8	1642	1.048	2008	4.980	2.786
9	7468	3.319	1976	5.061	2.947
10	1600	1.781	2062	4.850	2.539
11	2904	0.964	1953	5.120	3.076
12	7300	1.388	1911	5.233	3.323
13	1795	0.825	1981	5.048	2.932
14	1544	1.437	2047	4.885	2.618
15	840	1.529	2115	4.728	2.320
16	323	1.080	2174	4.600	2.050
17	331	1.388	2198	4.550	1.949
18	226	1.127	2217	4.511	1.872
19	169	0.990	2236	4.472	1.800
20	254	1.187	2213	4.519	1.901
21	805	2.305	2156	4.638	2.119
22	1132	1.854	2099	4.764	2.368
23	1904	1.450	2025	4.938	2.708
24	6235	0.936	1886	5.302	3.429
25	21649	1.2729	1821	5.491	3.843

Table 18 (Continued)

Point	Time, sec	Mass, mv	Temperature, °K	$10^4/T$ °K	-Log P, mm
26	7525	1.1013	1886	5.302	3.440
27	4818	.9528	1907	5.244	3.311
28	4545	1.110	1922	5.203	3.213
29	4300	1.3283	1936	5.165	3.110
30	9378	.9945	1856	5.388	3.583
31	53783	4.0284	1831	5.461	3.737
32	22605	.9912	1796	5.568	3.974

may be expressed as

$$\Delta F^o{}_t = -RT\ln(1/a_{Ho}) = RT\ln P^o/P_e$$

where P^o is the vapor pressure of pure holmium liquid. Thus,

$$\Delta F^o{}_t = -24{,}424 - 5.13T$$

obtained by combining the equations for P^o and P_e. From this equation it is seen that at 2000 °K

$$\Delta F^o{}_f = -34.78 \text{ Kcal}, \qquad \Delta S^o{}_f = -5.13 \text{ eu},$$

$$\Delta H^o{}_f = -24.52 \text{ Kcal}.$$

Combining equation I with the equation for the vapor pressure of solid holmium yields:

$$\text{Ho (s)} + 2\text{ C (s)} \rightarrow \text{HoC}_2\text{ (s)} \qquad \text{(III)}$$

$$\Delta F^o{}_t = -19{,}830 - 7.77T \quad .$$

Table 19. Decomposition pressure data

Run HoC$_2$-C-2

Area 3.290 x 10^{-3} cm

Temperature measurement pyrometer

Clausing factor 0.920

Balance constant 1.585 mv/mg

Results: H 87.1 ± .7
A 1.9042
B 6.538
PEP 1.3%

Point	Time, sec	Mass, mv	Temperature, °K	10^4/T °K	-Log P, mm
1	2062	1.445	2165	4.619	2.045
2	1010	0.864	2195	4.556	1.955
3	3850	1.195	2085	4.796	2.406
4	1528	1.223	2182	4.583	1.985
5	1360	1.428	2216	4.513	1.864
6	873	0.986	2239	4.466	1.830
7	1356	1.039	2184	4.579	2.004
8	10657	1.365	1998	5.005	2.800
9	3468	1.260	2098	4.766	2.337
10	1056	0.781	2177	4.593	2.020
11	771	0.824	2225	4.494	1.855
12	891	1.148	2245	4.454	1.772
13	798	1.155	2261	4.423	1.720
14	1209	0.757	2160	4.630	2.094
15	1981	0.866	2120	4.717	2.254
16	3620	0.759	2047	4.885	2.581
17	31634	2.075	1946	5.139	3.097
18	3792	0.534	2014	4.965	2.757
19	2403	1.228	2137	4.679	2.185

From this equation, the room temperature values would be calculated as:

$$\Delta F^{o}_{298} = -19.59 \text{ Kcal/Mole},$$

$$\Delta H^{o}_{298} = -19.83 \text{ Kcal/Mole},$$

Table 20. Decomposition pressure data

Run HoC_2- C-4	Results: H 90.6 ± .7
Area 1.528×10^{-2} cm	A 1.9800
Temperature measurement pyrometer	B 6.884
Clausing factor 0.964	PEP 1.8%
Balance constant 1.585 mv/mg	

Point	Time, sec	Mass, mv	Temperature, °K	$10^4/T$ °K	-Log P, mm
1	5780	0.630	1858	4.890	2.636
2	3488	3.122	2045	5.382	3.571
3	3982	1.063	1935	5.168	3.173
4	3557	2.663	1829	5.467	3.737
5	1178	1.329	2067	4.838	2.533
6	816	1.500	2114	4.730	2.316
7	523	1.558	2166	4.617	2.101
8	237	1.077	2215	4.515	1.912
9	453	1.114	2144	4.664	2.186
10	953	1.130	2074	4.822	2.510
11	3933	2.600	2017	4.958	2.770
12	3250	1.0806	1959	5.105	3.075
13	4216	0.816	1915	5.222	3.315
14	15740	1.2838	1852	5.400	3.697
15	33712	1.538	1806	5.537	3.955
16	3607	1.2933	1971	5.074	3.041

$$\Delta S^{o}_{298} = 7.77 \text{ e.u.}$$

The ΔF_f of holmium sesquicarbide was calculated by combining the equation for the free energy of formation of the dicarbide and the information obtained by measuring the decomposition pressures of the reaction:

Table 21. Decomposition pressure data

Run HoC$_2$-8a, b

Area 3.956×10^3 cm

Temperature measurement pyrometer

Clausing factor 0.925

Balance constant 1.572 mv/mg

Results: H 87.4 ± .9
A 19.071
B 6.471
PEP 2.1%

Point	Time, sec	Mass, mv	Temperature, ^oK	$10^4/T$ ^oK	-Log P, mm
1a	16438	1.605	1968	5.081	2.999
2a	3803	1.222	2091	4.782	2.469
3a	1185	0.721	2156	4.638	2.185
4a	1271	1.056	2189	4.568	2.047
5a	5360	1.9146	2084	4.798	2.424
6a	1240	0.714	2129	4.697	2.212
7a	1208	0.9849	2164	4.621	2.057
8a	1511	1.5643	2199	4.548	1.950
9a	1228	1.6113	2235	4.474	1.844
10a	1808	0.9406	2119	4.719	2.257
11a	3375	1.019	2070	4.831	2.499
12b	2407	1.140	2128	4.699	2.297
13b	1359	0.971	2168	4.613	2.114
14b	1159	1.125	2207	4.531	1.977
15b	831	1.005	2236	4.472	1.879
16b	603	0.898	2257	4.431	1.787
17b	2447	1.257	2130	4.695	2.262
18b	2520	0.977	2096	4.771	2.387
19b	6627	1.584	2053	4.871	2.602
20b	1425	1.325	2208	4.529	1.996
21b	671	0.799	2237	4.470	1.886
22b	1595	1.682	2219	4.507	1.940
23b	1192	1.252	2222	4.500	1.942
24b	824	1.174	2249	4.446	1.807
25b	1316	0.640	2118	4.721	2.287
26b	1375	1.076	2178	4.591	2.073
27b	7303	1.369	2028	4.931	2.710
28b	1540	2.277	2008	4.980	2.815
29b	1362	1.017	1946	5.139	3.119

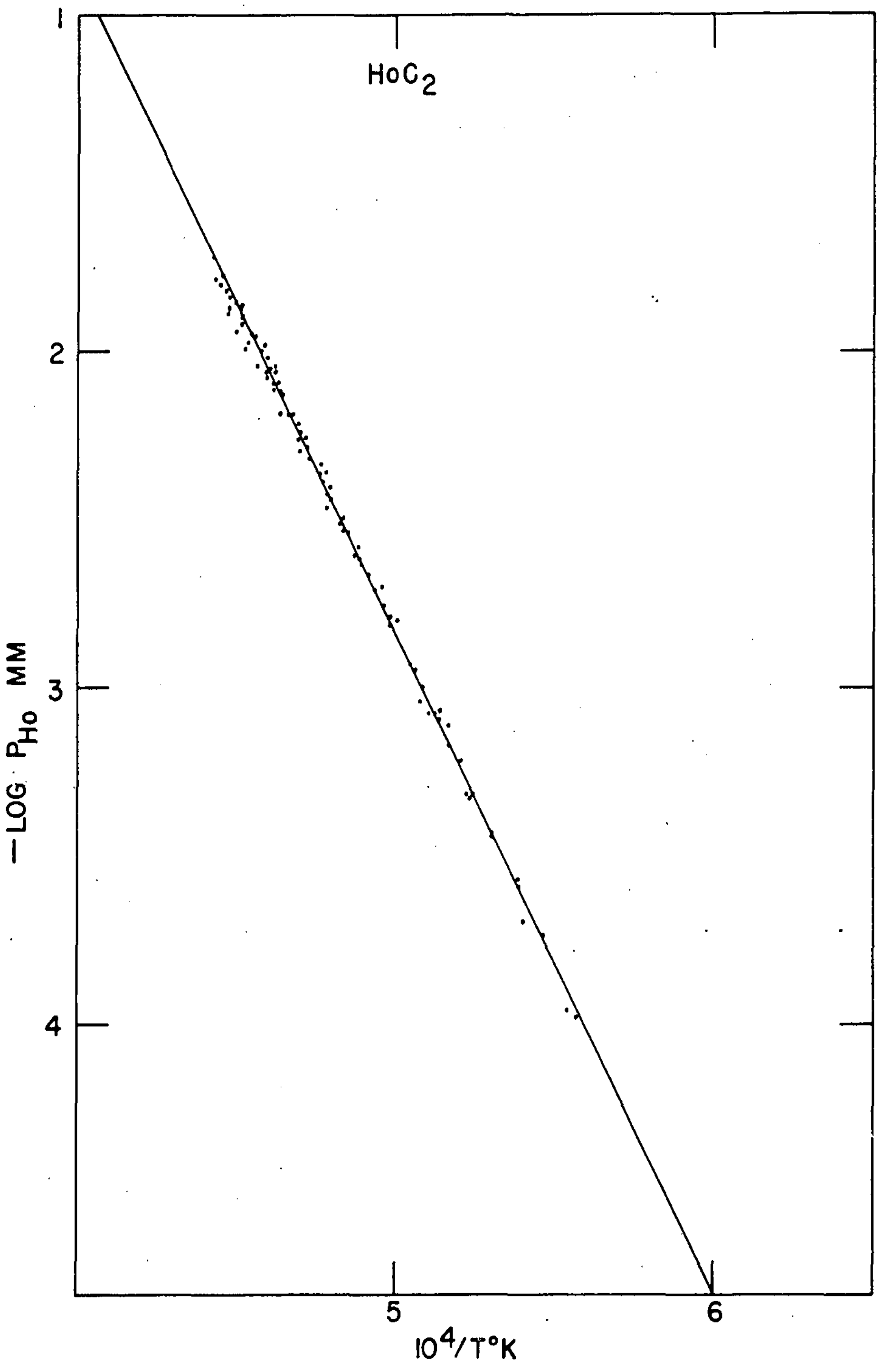

Figure 11. Decomposition pressure of holmium dicarbide

Table 22. Decomposition pressure data

Run Ho_2C_3-315 Results: H 102.5 ± .7

Area 3.955×10^{-3} cm^2 A 22397

Temperature measurement pyrometer B 10.614

Clausing factor 0.925 PEP 2.5%

Balance constant 1.585 mv/mg

Point	Time, sec	Mass, mv	Temperature, °K	$10^4/T$ °K	-Log P, mm
1	1475	1.571	1813	5.516	1.983
2	4260	1.552	1756	5.695	2.456
3	1910	1.539	1804	5.543	2.106
4	9475	0.636	1654	6.046	3.204
5	7400	0.855	1698	5.889	2.962
6	2330	1.158	1777	5.627	2.319
7	5200	1.205	1730	5.780	2.656
8	30300	1.380	1645	6.079	3.373
9	3817	0.759	1724	5.800	2.723
10	2143	0.754	1753	5.705	2.472
11	1081	0.724	1797	5.565	2.187
12	3554	1.312	1757	5.692	2.450
13	4105	1.882	1775	5.634	2.354
14	45650	1.357	1623	6.161	3.562
15	6890	0.819	1692	5.910	2.951
16	3588	0.975	1742	5.741	2.585
17	17811	1.220	1666	6.002	3.193
18	1075	1.024	1812	5.519	2.032
19	1040	1.163	1813	5.516	1.962
20	1825	1.576	1814	5.513	2.074
21	574	0.668	1833	5.456	1.942
22	828	1.070	1838	5.441	1.896
23	256	0.890	1909	5.238	1.458
24	220	1.250	1946	5.139	1.241
25	1725	1.431	1810	5.525	2.092
26	517	1.226	1883	5.310	1.627
27	302	1.074	1913	5.227	1.448
28	212	1.066	1938	5.160	1.295
29	179	1.526	1984	5.040	1.060
30	739	1.262	1861	5.373	1.773

Table 23. Decomposition pressure data

Run Ho_2C_3-415

Area 3.886×10^{-3} cm^2

Temperature measurement pyrometer

Clausing factor 0.925

Balance constant 1.585 mv/mg

Results: H 102.2 ± .4

A 22334

B 10.539

PEP 1.2%

Point	Time, sec	Mass, mv	Temperature, °K	$10^4/T$ °K	-Log P, mm
1	662	1.586	1872	5.342	1.617
2	240	0.876	1903	5.255	1.430
3	192	1.063	1935	5.168	1.246
4	717	1.275	1854	5.394	1.748
5	200	0.893	1917	5.216	1.341
6	136	1.001	1952	5.123	1.120
7	164	1.642	1979	5.053	0.984
8	337	1.058	1890	5.291	1.497
9	1777	1.8254	1819	5.498	1.991
10	982	1.5522	1844	5.423	1.801
11	4930	4.1954	1808	5.531	2.074
12	572	1.003	1856	5.388	1.754
13	325	1.019	1898	5.269	1.497
14	178	0.970	1934	5.171	1.253
15	160	1.219	1965	5.089	1.104
16	151	1.533	1985	5.038	0.977
17	1056	2.357	1874	5.336	1.647
18	1290	1.021	1799	5.559	2.106
19	5225	1.288	1726	5.794	2.622
20	1652	0.8921	1774	5.637	2.275
21	8816	2.2975	1732	5.774	2.597
22	37233	2.0143	1646	6.075	3.291
23	5777	0.8621	1701	5.879	2.843
24	1482	0.5570	1754	5.701	2.435
25	1770	1.172	1793	5.577	2.185

Table 24. Decomposition pressure data

Run Ho_2C_3-715	Results:	H	99.5 ± .5
Area 3.759 x 10^{-3} cm^2		A	21738
Temperature measurement pyrometer		B	10.283
Clausing factor 0.925		PEP	1.9%
Balance constant 1.585 mv/mg			

Point	Time, sec	Mass, mv	Temperature, °K	10^4/T °K	-Log P, mm
1	814	1.048	1833	5.456	1.877
2	508	1.048	1865	5.362	1.668
3	205	1.314	1948	5.133	1.166
4	104	1.045	1984	5.040	0.967
5	845	0.9680	1827	5.473	1.928
6	339	1.023	1896	5.274	1.499
7	233	1.068	1928	5.187	1.314
8	183	1.5715	1979	5.053	1.036
9	678	1.1227	1854	5.394	1.765
10	797	1.0281	1839	5.438	1.875
11	1082	0.9419	1808	5.531	2.049
12	1227	1.201	1810	5.525	1.998
13	313	1.5495	1935	5.168	1.280
14	182	1.456	1973	5.068	1.067
15	149	2.055	2024	4.941	0.825
16	139	1.979	2024	4.941	0.811
17	592	1.536	1883	5.311	1.566
18	1764	0.9650	1783	5.609	2.254
19	5700	0.8050	1698	5.889	2.853
20	45910	3.380	1665	6.006	3.140
21	3020	0.8920	1744	5.734	2.527
22	3520	1.5594	1770	5.650	2.347
23	6980	1.7902	1735	5.764	2.589
24	4490	0.7977	1714	5.834	2.751
25	6805	0.7426	1687	5.928	2.966
26	15020	0.6991	1630	6.135	3.344
27	181	2.035	1999	5.003	0.917
28	1014	11.503	2014	4.965	0.911

Table 25. Decomposition pressure data

Run Ho_2C_3-815 Results: H 100.9 ± 1.0

Area 3.969×10^{-3} A 22040

Temperature measurement pyrometer B 10.461

Clausing factor 0.925 PEP 3%

Balance constant 1.585 mv/mg

Point	Time, sec	Mass, mv	Temperature, °K	$10^4/T$ °K	-Log P, mm
1	1685	1.893	1838	5.441	1.959
2	520	1.464	1892	5.285	1.553
3	149	0.979	1959	5.105	1.178
4	129	1.392	1999	5.003	.958
5	4770	0.855	1717	5.824	2.771
6	1295	1.021	1795	5.571	2.118
7	4912	0.6120	1697	5.893	2.931

$$2\ Ho_2C_3 \rightarrow 3\ Ho\ C_2 + Ho\ (g,\ P'e) \qquad (IV)$$

$$\log P_{Ho}\ mm = \frac{-22.355}{T} \times 10^4 + 10.22$$

$$\Delta F^o{}_t = -RT\ln\ (a_{Ho}) = -RT\ln\ P'e/{}^oP$$

$$= -37{,}583 - 10.90\ T$$

and thus, for the reaction above the melting point of holmium,

$$2Ho\ (l) + 3C\ (s) \rightarrow Ho_2C_3\ (s) \qquad (V)$$

may be expressed as

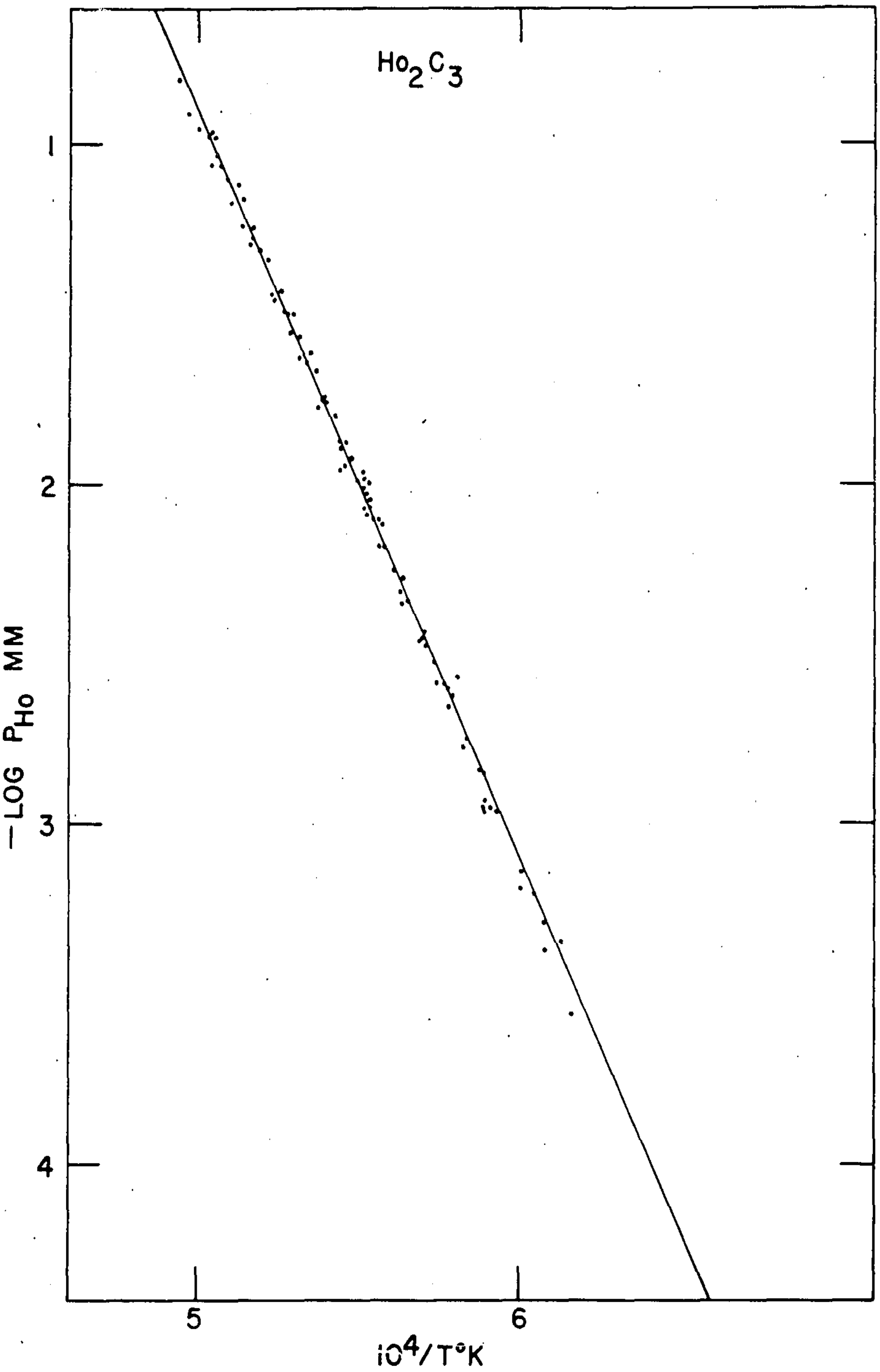

Figure 12. Decomposition pressure of holmium sesquicarbide

$$\Delta F^{o}_{f} = -17{,}994 - 2.24T \quad .$$

The free energy for the reaction of

$$2\ Ho\ (s) + 3C = Ho_2C_3\ (s) \qquad (VI)$$

may be expressed as

$$\Delta F^{o}_{f} = -11{,}053 - 5.21T$$

obtained by combining equations III and IV with the equation for the sublimation pressure of holmium metal.

H. Discussion

Few of the metallic carbides have been studied thermodynamically, so that there is not a great deal of material with which to compare the values of this study. Some of those carbides which have been measured and some of the more pertinent estimates are listed in Table 26. The values are listed on the basis of kcal per gram atom carbon to permit a more informative comparison. It is seen that the elements of Groups VB and VIB of the periodic chart form the most stable carbides, apparently due to the favorable bonding available as described by Rundle (48). In general the dicarbides of the heavier elements are next in order of stability and many of these have melting points over 2000 °C. The carbides of the Groups I, II and III are in general

Table 26. Thermodynamic values of formation metallic carbides

	ΔF^{o}_{298}	ΔH^{o}_{298}	ΔS^{o}_{298}	
TiC	-42.9	-43.8	-1.90	
ZrC	-38.9	-44.4	-2.7[a]	
TaC	-38.1	-38.5	-1.14	
Mn_3C	- 3.4	- 3.6	-0.53	
Fe_3C	4.8	5.8	3.4	
Co_3C	4.6	5.1	1.6	
$\frac{1}{2}Cr_3C_2$	-10.6	-10.5	-3.0[b]	
$\frac{1}{2}ThC_2$	-16.4	-16.5	-0.2	
$\frac{1}{2}CaC_2$	- 8.7	- 8.1	2.1	
$\frac{1}{2}UC_2$	-13.9	-13.5	1.4	
$1/3\ U_2C_3$	-23.6	-23.3	-0.3	
$\frac{1}{2}CeC_2$	(-15.7)	(-16)	(-1.0)	(estimated)
$1/3\ Ce_2C_3$	(-24.3)	(-25)	(-2.5)	(estimated)
$\frac{1}{2}LaC_2$		-21[c]		
$\frac{1}{2}HoC_2$	- 9.8	- 9.9	3.8[d]	
$1/3\ Ho_2C_3$	- 3.7	- 3.7	1.7[d]	

Taken from 43, 45 except as noted:

[a] Reference 46

[b] Reference 47

[c] Reference 25

[d] This study

somewhat less stable and usually are classified as ionic rather than metallic carbides. With the exception of Mg_2C_3 the only sesquicarbides are those of the actinide and lanthanide elements.

It was noted that the stability of the rare earth carbides varies somewhat on the same order as the volatility of the metals themselves. This is based on the observations of Chupka that LaC_2 vaporized congruently, and that HoC_2 was found to decompose into the metal and graphite in this study, and that the carbides of ytterbium and europium are difficult to prepare in the pure state. This same trend has been noted in the vaporization of the sesquioxides of the rare earths by Panish (49), in which the less volatile elements (lanthanum, neodynium, praseodynium, gadolinium, terbium and lutetium) have sesquioxides which vaporize according to the equation:

$$M_2O_3(s) \rightarrow 2\ MO\ (g) + O\ (g)$$

while the oxides of the more volatile elements of samarium, europium, and ytterbium vaporize according to the reaction:

$$M_2O_3(s) \rightarrow 2\ M\ (g) + 3\ O\ (g) \quad .$$

This might be taken to lend support to postulate of Chupka (25) who has suggested in the light of his work on the carbides and oxides that the C_2 group might be considered similar to the oxygen atom in stability and nature of compounds which they form. From this trend the carbides of samarium, europium, holmium, erbium, thulium, and ytterbium would be expected to decompose to the metal and graphite. The rather qualitative evidence obtained in the preparation of these compounds is in agreement with this postulate. It is interesting to note that the metals which have the tendency to form something less than the tripositive metallic state (Eu, Yb) do not have the tendency to form the compounds of divalent nature, such as MO and MC_2, in the vapor form.

From a qualitative viewpoint, the stability of the sesquicarbide compounds can be inferred in the cases of magnesium, lanthanum and uranium sesquicarbides from the fact that these compounds decompose peritectally. La_2C_3 was found by Spedding et al. (50) to decompose at 1415 °C according to the equation

$$2\ La_2C_3(s) \rightarrow 3\ LaC_2(s) + La(l)$$

and found that U_2C_3 decomposes at 2050° by the equation

$$U_2C_3 \rightarrow UC + UC_2 \quad .$$

With the exception of the magnesium compound, all of the sesquicarbides with established structure are isomorphous with Pu_2C_3. From the equations for the free energies of formation of holmium sesquicarbide and dicarbide, it can be calculated that the sesquicarbide is unstable with respect to disproportion to the dicarbide and pure holmium metal at 2400 °K. For this calculation it is assumed that the enthalpies of decomposition are constant in the temperature range in question. It is expected that this temperature is above the melting point of the compound, so that if the assumptions made are valid, the sesquicarbide should melt congruently.

The region of the holmium-carbon phase diagram listed here as Lower carbides is from 0-7 w/o carbon. The decomposition pressure curves of the alloys of less than 1 w/o carbon were very close to the vapor pressure of holmium metal in absolute value and slope. However there appeared to be some dependence of the pressure on the amount of holmium vaporized from the cell and the points were not reproducible. X-ray analysis of the material was identical at the beginning and end of the run and indicated the presence of holmium metal (hcp) and a fcc structure. The data taken from the alloys in this region are then interpreted qualitatively as indicating a rather low solubility of carbon in holmium at temperatures up to 1300 °C and the existence of a two phase (hcp) - (fcc) region.

In the region of the diagram from 1 to 7 w/o carbon, the activity of holmium was observed to decrease with increasing carbon concentrations. As previously noted, however, the x-ray diffraction patterns of the material could not be attributed to the presently known structures.

The structure of the tri-rare earth carbide was determined (41) to be a fcc structure with only a fraction of the octahedral interstices filled with the carbon atoms. In the case of yttrium, this fraction was noted to vary with a change of the carbon concentration. Thus it is not surprising to find that a rather extensive range of solubility was indicated by the decomposition pressures, since additional carbon atoms might be accomodated by filling more of the octahedral holes. It was observed that the pressure of holmium over the tri-rare earth phase was not greatly different than the pressure of holmium metal indicating that the phase is not very stable. This is as would be expected in view of the fact that this phase is observed with the heavy rare earth elements but not for the light rare earth elements.

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