THE PREPARATION AND THERMODYNAMICS OF EUROPIUM DICARBIDE

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Harry A. Eick
Major professor

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THE PREPARATION AND THERMODYNAMICS OF EUROPIUM DICARBIDE

By

Robert E. Gebelt

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ABSTRACT

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OF EUROPIUM DICARBIDE

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Europium dicarbide was prepared by the reaction of europium metal and graphite in a stainless steel bomb. Chemical analysis indicated an average composition of $EuC_{1.87 \pm 0.07}$. X-ray powder diffraction analysis showed the compound to be of body-centered tetragonal symmetry, space group D_{4h}^{17} - I4/mmm, with lattice parameters: a_o = 4.045 Å; c_o = 6.645 Å. Vapor phase chromatographic analysis indicated that ninety-eight per cent of the product of acid hydrolysis of europium dicarbide was the hydrocarbon, acetylene. The analytical data lead to the conclusion that europium dicarbide resembles the alkaline earth dicarbides more than the other lanthanon dicarbides.

The vaporization of europium dicarbide over the temperature range 1150° to 1600° K was investigated by the Knudsen effusion method. The effusate was either collected and analyzed chemically or observed with a time-of-flight mass spectrometer. The method involving chemical analysis of the effusate did not yield as precise data as did the method utilizing the mass spectrometer.

Gaseous europium and europium dicarbide were both found in equilibrium with solid europium dicarbide in concentrations of 99% and 1% respectively. Instrumental limitations prevented determination of the concentration of the gaseous dicarbide as a function of temperature. Calibration of the mass spectrometer with silver permitted the calculation

of the pressures corresponding to the observed ion intensities. An empirical equation, fitted to the data for europium by the method of least squares, gave:

$$\ln_e P_{(atm)} = (-23709 \pm 715)/T + 9.270 \pm 0.886.$$

By means of the second law of thermodynamics the following values were found:

For the reaction

$$EuC_{2(s)} \rightleftarrows Eu_{(g)} + 2C_{(graphite)}$$

$$\Delta H^{o}_{298} = 51.09 \pm 1.42 \text{ kcal./mole}$$

$$\Delta S^{o}_{298} = 18.43 \pm 1.75 \text{ e.u.}$$

Values of the free energy function for $EuC_{2(s)}$ were estimated and combined with published data to yield, for the same reaction, the following value calculated from the third law of thermodynamics:

$$\Delta H^{o}_{298} = 51.22 \pm 0.80 \text{ kcal./mole.}$$

The enthalpies obtained for the dissociation reaction were combined with published data on the enthalpy of vaporization of europium to yield the following value for the standard enthalpy of formation of EuC_2:

$$\Delta H^{o}_{298} = -9.17 \pm 1.15 \text{ kcal./mole.}$$

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I. INTRODUCTION

A. Incentives for this Research

In recent years, mass spectrometric and thermochemical studies have demonstrated the existence of unsuspected gaseous molecules containing heavy metal atoms in the vapor phase above refractory compounds. These findings require new theories of bonding which can be tested only by the examination of other compounds.

A study of vaporization processes not only provides for the measurement of vapor pressure and the preparation of new compounds, but also helps to establish the nature and kinetics of high temperature reactions. Good thermochemical measurements on a large number of refractory compounds are necessary to provide the information needed to elucidate the nature of these high temperature reactions. To date, much of the necessary information has not been obtained, and in addition, much of the available data are unreliable.

While no single study can hope to provide more than a small contribution, each investigation of a particular compound provides more useful information. The study of the preparation and vaporization of europium dicarbide was undertaken with these interests in mind.

B. Previous Investigations of Lanthanon-Carbon Systems

1. Preparations and Properties

Compounds of the type MC_2, in which M is a lanthanon, have been known for some time. Pattersson (1) reported the preparation of the dicarbides of lanthanum, yttrium and cerium in 1895. His method of preparation was to melt a powdered mixture of the oxide and carbon in

a high current electric arc. Chemical analysis gave the formulas $YC_{1.87}$ and $LaC_{1.85}$; no data were given for cerium. This low metal to carbon ratio was probably the result of oxide contamination of the sample. However, it is possible that an actual non-stoichiometric compound was present. About this same time, Moissan (2,3) and Moissan and Etard (4) also reported the preparation of, and hydrolytic studies on, lanthanum, neodymium and praseodymium dicarbides.

Sometime later, Damiens (5,6) prepared the dicarbides of lanthanum, cerium, praseodymium, neodymium and samarium by reacting the oxide with carbon. He then studied the hydrolysis of these compounds.

In 1930, von Stackelberg (7,8) reported studies on the crystal structure of a number of carbides, among them several of the lighter lanthanon dicarbides. His investigations showed the crystal structure of these compounds to be face-centered tetragonal (D_{4h}^{17} - $I\,^4/_{mmm}$). Later work, which will be discussed shortly, showed von Stackelberg's work to be correct; his was the first good structural investigation of these compounds.

In 1946, Frevel, Rinn and Anderson (9) tabulated the structural data of a large number of tetragonal compounds. These authors list the data for both the alkaline earth and the lanthanon dicarbides known at the time. In 1951, Villelume (10) prepared lanthanum dicarbide by reduction of the oxide with carbon at 2000^{o} and then studied the hydrolysis of the product.

Gaume-Mahn (11) summarizes the data of a number of lanthanon borides, nitrides, sulfides and carbides. The data presented are similar to those presented by previous authors. Gaume-Mahn, however, suggests the addition of hydrogen to the oxide-carbon reaction mixture to promote the reduction.

Atoji and co-workers (12) report structural data for lanthanum dicarbide and sesquicarbide. The use of both x-ray and neutron diffraction in their investigations allowed determination of both metal and carbon positions in the crystal lattice. These authors give complete structural data including atomic positions in the unit cell and the carbon-carbon bond distance.

In 1959, Spedding, Gschneidner and Daane (13) reported a phase study of the lanthanum-carbon system. They varied the carbon concentration from zero to twenty-four weight per cent, preparing their specimen by melting massive mixtures of the metal and carbon in an inert atmosphere. Along with the phase composition data, they show that the electrical conductivity of the dicarbide is near that of the metal, indicating a compound of the type $La^{+3}C_2^{-2}$ in which the third electron on the metal is in the conduction band of the crystal.

These same authors (14) report the preparation of a large number of lanthanon carbides of three different types: M_3C, M_2C_3 and MC_2. These compounds were prepared by reaction of the elements at high temperature.

The tri-lanthanon carbides are face-centered cubic and are reported to exist only for the heavier lanthanon metals (samarium to lutetium) and for yttrium. The lighter lanthanons are probably too large to permit the formation of this type of compound. In the tri-lanthanon carbide series, tri-yttrium carbide was investigated most thoroughly. The composition of this phase ranges from $YC_{0.25}$ to $YC_{0.40}$. Here, one is probably dealing with an interstitial compound in which the carbon atom occupies some of the octahedral holes in the metal lattice. No attempts were made to find the composition range for the similar

lanthanon compounds, but the authors feel that the range of composition would be similar to that of the yttrium compound.

The lanthanon sesquicarbides are body-centered cubic for the series lanthanum to dysprosium. Holmium shows both a body-centered cubic phase and a phase of lower symmetry. Erbium, thulium, lutetium and yttrium also form this lower symmetry phase, the structure of which was not determined.

All of the lanthanons form a dicarbide phase of tetragonal symmetry, the space group being D_{4h}^{17} - I $^4/_{mmm}$. No unexpected results or trends appear in this series except that no mention of any europium-carbon compound is made.

Hydrolytic studies on these lanthanon-carbon compounds led Spedding, Gschneidner and Daane to state that the M_3C compounds are methanides since only methane and hydrogen result from the hydrolysis. The M_2C_3 and MC_2 compounds are classed as acetylides since the principal hydrolysis product is acetylene. However, a number of hydrocarbons are produced in hydrolysis of these compounds since the free electron in the conduction band can participate in the reaction. Ytterbium produced somewhat more acetylene, according to these authors, and had larger than expected lattice parameters, indicating that it was more like an alkaline earth dicarbide. This behavior might be expected since ytterbium frequently forms a +2 ion.

Shortly after the work just discussed appeared, Vickery, Sedlacek and Ruben (15,16,17) published independently a series of papers dealing with the preparation and properties of most of the lanthanon dicarbides. Their work agrees well with that of Spedding and co-workers. They prepared the dicarbides by reduction of the oxide with carbon. In this

study some of the oxide-carbon samples were quenched and examined just after melting occurred. These quenched samples were found to contain the free lanthanon metals. This is probably one of a very few instances in which reduction occurs via the metal.

Vickery and co-workers (16) studied the magnetochemistry of the carbides and found that the correct formula for most of the dicarbides is $M^{+3}C_2^{-2}$, as expected. Samarium and ytterbium tended to be divalent. Europium was not studied.

Recently, Greenwood and Osborn (18) proposed a new method for obtaining very pure lanthanum dicarbide. They first formed lanthanum hydride which was then mixed with carbon and heated under high vacuum to give the dicarbide. It was felt that this method would give a very pure product with low oxygen contamination. This method could probably be utilized for the formation of most of the other lanthanon dicarbides.

Samsonov and co-workers (19) have reported preparative work involving scandium, yttrium and lanthanum carbides. The most interesting and original part of this research is the preparation of compounds of the formula Sc_2C_2O and Y_2C_2O. This type of compound should exist for the other lanthanons, but has not been reported.

Another lanthanon carbide phase was reported by Dancy, Everett and McCabe in 1962 (20). These workers studied the system M-H-CH_4 in which M was cerium or praseodymium. They present evidence, from x-ray and hydrolysis data, for a carbide of formula MC. These compounds exhibit a face-centered cubic structure. To date, no other lanthanon monocarbides have been reported.

There is some question about the existence of lanthanon monocarbides. Spedding, Gschneidner and Daane (13) were unable to prepare cerium or

praseodymium monocarbide by direct combination of the elements. In addition, Dancy, Everett and McCabe (20) found that their monocarbides decomposed in an argon-filled dry box containing minute amounts of oxygen. If these authors were actually dealing with an MCH compound, extreme sensitivity to oxygen might be more easily understood since a lanthanon monocarbide would not be expected to react with oxygen at the rapid rate reported.

2. Crystal Structure of the Lanthanon Dicarbides

The dicarbides, which were of interest in this study, will be discussed in more detail in this section.

Most of the authors cited previously give some structural data for the lanthanon carbides; however, Spedding, Gschneidner and Daane (14) give the most recent and most complete listing of lattice parameters. These data, which are in agreement with previous work are probably the most accurate reported since high purity lanthanon metals were used as reactants. Atoji (21) has studied the neutron diffraction patterns of some of the lanthanon dicarbides and has determined the carbon-carbon bond distance in each dicarbide, as well as the metal-carbon distance. A compilation of lattice constants for the lanthanon dicarbides and several of the alkaline earth dicarbides is given in Table I.

Examination of these data shows a regular decrease in lattice parameters for the lanthanon dicarbides following the lanthanide contraction. The increase in lattice parameters at ytterbium is probably due to a contribution from M^{+2}, a species which is not found in the other carbides. While not enough carbon-carbon bond distances are given to establish whether or not this distance is related to the metal

Table I. Lattice parameters for some tetragonal dicarbides

Metal	a_o	c_o	C-C Distance
La	3.934 Å	6.572 Å	1.303 Å
Ce	3.878	6.488	1.283
Pr	3.855	6.434	---
Nd	3.823	6.504	---
Sm	3.770	6.331	---
Gd	3.718	6.275	---
Tb	3.690	6.217	1.293
Dy	3.669	6.176	---
Ho	3.643	6.139	---
Er	3.620	6.094	---
Tm	3.600	6.047	---
Yb	3.637	6.109	1.287
Lu	3.563	5.964	1.276
Y	3.664	6.169	1.275
Ca	3.89	6.38	1.191
Sr[a]	4.11	6.68	---
Ba[a]	4.39	7.05	---

[a]Data from ref. (9)

radius, any change in this distance with changing metal radius is small.

The dicarbides listed in Table I belong to the space group D_{4h}^{17} - I $^4/mmm$. The metal atoms are at (000, ½½½) and the carbon atoms at (000, ½½½) ± (00Z). For lanthanum, Atoji (12) has found that Z = 0.043 ± 0.002.

3. Vapor Pressure Studies

Although reports of high temperature vaporization studies are quite common, very little work dealing with lanthanon carbides has appeared. Chupka and co-workers (22), using a mass spectrometer, have studied the vapor species above a number of carbides, among them lanthanum dicarbide. These authors found two gaseous species, La and LaC_2. The ratio of the pressures of the two species was a function of temperature and was 1:2 at 2300° K. From their data, the enthalpy of the reaction

$$La_{(g)} + 2C_{(s)} \longrightarrow LaC_{2(g)} \qquad (1\text{-}1)$$

was determined by a third law treatment to be 38 kcal/mole and by a second law treatment to be 46 kcal/mole. The agreement of the two numbers was considered satisfactory by the authors.

Wakefield (23) has studied the vapor pressure of holmium and the decomposition pressure of holmium dicarbide at high temperatures. This study utilized weight loss data; the sample was vaporized and the rate of weight loss determined, with a balance, as a function of temperature. The author covered a temperature range of 650° to 1750° with corresponding vapor pressures of 10^{-8} torr to 10 torr. To achieve high sensitivity at low temperatures, a Langmuir type experiment was performed. In order to increase the rate of weight loss, the vapor was allowed to

evaporate directly from the surface of a large sample of the material. At high temperatures, the conventional Knudsen cell was used, and at the highest temperatures, the Knudsen cell was fitted with a long channel orifice in order to retard the escape of the vapor. The dicarbide was found to vaporize according to the equation:

$$HoC_{2(s)} \longrightarrow Ho_{(g)} + 2C_{(graphite)}. \qquad (1\text{-}2)$$

No thermodynamic data were given in the reference consulted. In this same study, holmium sesquicarbide was found to vaporize according to the equation:

$$2Ho_2C_{3(s)} \longrightarrow Ho_{(g)} + 3HoC_{2(s)} \qquad (1\text{-}3)$$

In the third reported vaporization study of a lanthanon dicarbide, Jackson, Barton, Krikorian and Newbury (24) studied gadolinium and thorium dicarbides. The vaporization process was followed with a mass spectrometer which was calibrated for quantitative measurement of pressure with silver and molybdenum. The gadolinium dicarbide was prepared by reacting a powdered mixture of the elements in the mass spectrometer. The primary species above the dicarbide at high temperature was gadolinium. Gadolinium dicarbide was found as a minor constituent ranging from 1% of the effusate at 2000° K to 5.8% at 2422° K. No other gadolinium-containing molecules were found in the vapor. The following enthalpies were reported at 2150° K:

$$GdC_{2(s)} \longrightarrow GdC_{2(g)} \quad ; \Delta H = 143 \text{ kcal/mole} \qquad (1\text{-}4)$$

$$GdC_{2(s)} \longrightarrow Gd_{(g)} + 2C_{(s)} \quad ; \Delta H = 101 \text{ kcal/mole} \qquad (1\text{-}5)$$

$$Gd_{(g)} + 2C_{(s)} \longrightarrow GdC_{2(g)} \quad ; \Delta H = 38 \text{ kcal/mole}. \qquad (1\text{-}6)$$

Chupka and Inghram (25,26,27) have studied extensively the vaporization of graphite. The vapor pressures and enthalpies of sublimation were determined for C_1, C_2 and C_3, the latter being the principal species in the gas phase. Honig (28) has also studied the vaporization of graphite and his data are in agreement with the results of Chupka and Inghram. Thorn and Winslow (29) have combined Chupka and Inghram's mass spectrometric measurements with data they obtained on the rate of effusion of graphite. The combined data allowed Thorn and Winslow to calculate the partial pressure of the species C_1, C_2 and C_3 above graphite and the corresponding enthalpies and entropies of vaporization.

4. Vaporization Studies Utilizing the Mass Spectrometer

A number of reports have appeared in the literature dealing with the adaptation of the mass spectrometer to high temperature vaporization studies. Several of these are of general interest and will be discussed briefly.

White, Sommers, Walsh and Goldstein (30) discuss the application of a time-of-flight mass spectrometer, similar to the one used in this study, to the study of inorganic materials at high temperature. They present a general treatment of the apparatus, methods and treatment of data, and also discuss their instrument's reliability and its method of determination. Using this instrument, White and co-workers (31,32) showed that the lanthanon metals vaporize as monomeric species and that lanthanum and neodymium sesquioxides vaporize to give the monoxides, MO, and oxygen.

Inghram and Drowart (33) discuss the advantages and disadvantages of the mass spectrometer in its application to the study of high

temperature processes. They present general requirements concerning the sample source and the instrument itself. Finally, the authors discuss the treatment of data obtained from the mass spectrometer and tabulate the species observed in the gas phase over a large number of inorganic compounds along with the enthalpy for the corresponding reactions.

C. This Research

In reviewing all of the work presented above concerning the lanthanon dicarbides, only one reference (34) was found which gave any indication of a carbide compound of europium. This work, presented in the foreign patent literature, indicated that a compound of the formula EuC was formed in a carbide-type reactor fuel element. No information as to how the compound was identified or how it was formed is available. The only information given was that the presence of ZrC lowered the vapor pressure of EuC by a factor of 10^6.

Since the preparation of europium dicarbide and a subsequent study of its thermodynamic properties would be of general interest, this research was undertaken. The general plan of attack was to first investigate the preparation of the compound using the various methods previously reported, and second, to study the vaporization of europium dicarbide using the Knudsen effusion technique. Two methods of analysis of the vapor were to be used for the second portion of the investigation. First, the effusate from a Knudsen cell was to be analyzed chemically to determine the vapor pressure. Second, the effusate was to be observed in a time-of-flight mass spectrometer to determine the molecular composition of the vapor and to provide additional data on the vapor pressure.

II. THEORETICAL CONSIDERATIONS

A. General

The enthalpy and entropy changes which accompany a vaporization process may be calculated for both the condensed and the vapor phase from a determination of the partial pressure of the equilibrium vapor at various temperatures. Consider a two component system consisting of a solid and a vapor. According to the well known phase rule

$$F = 4 - P. \qquad (2\text{-}1)$$

F is the number of degrees of freedom and P is the number of phases present at equilibrium. For the state of the system to be a function of one variable only, the phase rule implies that either of two constraints must be present. The system must contain the vapor and two solid phases or the vapor and one solid and one liquid phase; or the vapor must have the same composition as the solid phase. This latter case, termed congruent vaporization, can be demonstrated by showing that the composition of the solid and the vapor are identical.

For each increase in the number of components, the number of constraints must be increased correspondingly in order that the state of the system remain a function of temperature only.

A determination of the vapor pressure as a function of temperature, combined with both chemical and x-ray powder diffraction analysis, both before and after vaporization occurs, allows one to deduce the behavior of the condensed phase and to correlate the thermodynamic data obtained with the actual reactions occurring in the system.

B. Thermodynamic Relationships in Vaporization

For the vaporization reaction

$$A_{(s \text{ or } l)} \rightleftarrows A_{(g)} \tag{2-2}$$

the free energy is defined as:

$$\Delta G_T^o = \Delta H_T^o - T\Delta S_T^o = -RT \ln K. \tag{2-3}$$

In the simple case in which only one species is present in the gas, at low pressures K equals P_A, where P_A indicates the pressure of A.

If the change in heat capacity, ΔCp, is considered constant for the above reaction, then

$$\Delta H_T^o = \Delta H^* + \int_{T^*}^{T} \Delta Cp dT = \Delta H^* + \Delta Cp(T - T^*) \tag{2-4}$$

and

$$\Delta S_T^o = \Delta S^* + \int_{T^*}^{T} \Delta Cp \, d \ln T \tag{2-5}$$

where ΔH^* and ΔS^* are the enthalpy and entropy at the reference temperature, T^*, which is usually taken as 298.15^o K. Combining equations 2-3, 2-4 and 2-5 yields:

$$\Delta G_T^o = -RT \ln P_A = \Delta H^* + \Delta Cp(T - T^*) - T\Delta S^* - T\Delta Cp \ln T/T^*. \tag{2-6}$$

If ΔCp is assumed to be zero, then

$$RT \ln P_A = -\Delta H^* + T\Delta S^* \tag{2-7}$$

or

$$\ln P_A = - \Delta H^*/RT + \Delta S^*/R. \tag{2-8}$$

Equation 2-8 is the familiar Clausius-Clapeyron equation in which R is the molar gas constant. A graph of ln P_A vs 1/T, for the temperature range over which P_A is measured as a function of T, yields ΔH^* from the slope and ΔS^* from the intercept.

The assumption that ΔCp is zero, while mathematically and experimentally the most simple case, is probably never true in practice since it implies the same heat capacity for the solid and gaseous phases. If this assumption is badly in error, the ln P_A vs 1/T plot will show curvature and the more complex treatment described below is necessary.

If ΔCp is constant, but not zero, we have from equation 2-6,

$$\ln P_A = -\Delta H^*/RT - (\Delta Cp/RT)(T-T^*) + \Delta S^*/R + (\Delta Cp/R)(\ln T/T^*) \quad (2\text{-}9)$$

or

$$\ln P_A = -A/T + B \ln T + C. \quad (2\text{-}10)$$

Data may be fitted to this equation by mathematical methods.

When the heat capacity is known as a function of temperature for each species, ΔCp can be calculated. This ΔCp can then be combined with equation 2-4, equation 2-5 and equation 2-3 to convert the measured thermodynamic quanities to their standard states. In practice, the heat capacity as a function of temperature is known for very few compounds and either must be estimated or a simpler treatment must be used.

Examination of equation 2-8 or equation 2-10 shows that the slope of these lines is sensitive to the temperature. That is, small errors in the temperature determination will produce large errors in the slope. Therefore, whenever possible, the enthalpy determined by the second

law method described above should be checked by a method based on the third law of thermodynamics since this method is less sensitive to temperature errors. The temperature errors contribute less to this method because an enthalpy is calculated for each pressure and these values are then averaged. Thus, random temperature errors will tend to cancel each other and non-random errors will result in a change in the enthalpy with temperature.

The third law method makes use of the free energy function, fef, which is defined as:

$$\text{fef} = [(G^{o}_{T} - H^{o}_{298})/T]. \tag{2-11}$$

For the reaction in equation 2-2,

$$\Delta\text{fef} = [(G^{o}_{T}-H^{o}_{298})/T]_{(g)} - [(G^{o}_{T}-H^{o}_{298})/T]_{(s \text{ or } l)} = \Delta G^{o}_{T}/T - \Delta H^{o}_{298}/T. \tag{2-12}$$

Equation 2-3 combined with equation 2-12 yields:

$$\Delta H^{o}_{298} = -T\Delta\text{fef} - RT \ln P_{A}. \tag{2-13}$$

Thus, if free energy functions are available or can be calculated from available data, ΔH^{o}_{298} can be evaluated for each temperature-pressure set.

The free energy function can be evaluated from heat capacity data using the relationship:

$$\text{fef} = 1/T \int_{o}^{T} \text{Cp}dT - \int_{298}^{T} \text{Cp}d \ln T - S^{o}_{298}. \tag{2-14}$$

The free energy function can also be calculated using the methods of statistical mechanics if spectroscopic data which give the energy states of the molecule or atom of interest are available.

Unfortunately, the data needed to evaluate the free energy function

are usually not available and one must make estimates using available data for similar compounds. In such a case, the data obtained from the slope and the intercept of the plot ln P_A vs 1/T may be more reliable and the values calculated from the third law are used only as a check on the other method.

C. The Knudsen Effusion Method

1. Mathematical Relationships

In 1909, Knudsen (35,36,37) published a series of papers on the effusion of gases through small orifices and tubes at low pressures. If one considers a container at uniform temperature, located in a vacuum and containing a gas at equilibrium, the number of particles striking a unit area of the container wall is given by $n\bar{c}/4$, in which n is the number density and $\bar{c}$ is the average speed of the molecules. If the container wall is thin and perforated with a small knife-edged orifice, the number of particles passing through the orifice in a given time will be the same as the number striking an equal area of the wall during that same time. Thus, a determination of the number of particles passing through the orifice permits calculation of the pressure in the container.

There are several methods by which one can determine the number of particles passing through the orifice in a given time. Bockris, White and Mackenzie (38) discuss these methods in detail. Of particular interest to the work reported herein are the target collection and mass spectrometric techniques.

The partial pressure in atmospheres, P, can be determined from the following equation:

$$P = w/S_o t \ (2\pi RT/M)^{\frac{1}{2}} \qquad (2\text{-}15)$$

where w equals weight loss in grams, M equals the molecular weight expressed in grams, S_o is the orifice area in $cm.^2$, t is time in seconds and T is temperature, ^oK. In the target collection technique, a circular target of radius r, is situated at a distance, d, from the orifice and placed coaxially to it. From the cosine law (38,39) the pressure, P, is related to the weight of material on the target by the equation:

$$P = 0.022557\ w/S_o t\ (T/M)^{\frac{1}{2}}\ (1 + d^2/r^2). \qquad (2\text{-}16)$$

The derivation of the equation for Knudsen flow assumes that the pressure in the cell is so low that molecular collisions in the gas are infrequent. Knudsen (35) observed that as the cell pressure rises, a transition occurs from molecular flow to hydrodynamic flow through the orifice, resulting in a greater mass of gas leaving the cell per unit time than would be expected. Carlson (39) discusses the conditions necessary for molecular flow and concludes that a value of unity for the ratio of mean free path, $\underline{\lambda}$, to orifice diameter is the upper limit of molecular effusion, and thus, the limit of the effusion method.

The mean free path is the average distance a gas molecule travels between collisions and is given by:

$$\lambda = 1/\sqrt{2}\ \pi n \sigma^2 \qquad (2\text{-}17)$$

where $\underline{n}$ is the number of molecules per cubic centimeter and $\underline{\sigma}$ is the molecular diameter. A unit ratio of mean free path to orifice diameter indicates that the effusing molecules will have a large collision frequency, and thus, that the flow is not molecular.

If the orifice of the Knudsen cell is not knife-edged, but has the shape of a cone of finite length, the distribution of molecules effusing

from the orifice will not follow the cosine law because relfections from the orifice wall will change the angular distribution.

Edwards (40) and Freeman and Edwards (41) have treated the conical orifice theoretically and have calculated the transmission probabilities, W_o, for a large number of orifices of varying shapes. Their treatment includes the common cylindrical orifice as a special case. When the transmission probabilities are applied, equation 2-15 becomes:

$$P = 0.022557\ w/W_o S_o t\ (T/M)^{\frac{1}{2}}. \qquad (2\text{-}18)$$

When only those molecules leaving the cell in the forward direction are collected for analysis, this correction may be neglected, since only those molecules emanating from the bottom of the cell are detected. These molecules pass directly from the bottom of the cell without collision.

2. Practical Requirements

There are a number of practical requirements in Knudsen effusion experiments. Some of these apply to the method in general and others to the particular system under study.

(a) The residual pressures in the vacuum system must be low enough to preclude reaction of the residual molecules with the gas or scattering of the molecular beam.

(b) The fraction of effusing molecules which strikes the target and sticks to it must be known and the walls of the vacuum chamber must condense all the effusing molecules which strike them.

(c) In effusion experiments in which the weight of the effusing substance is measured, the molecular weights and relative abundance of

the effusing molecules must be known.

(d) The physical dimensions of the apparatus at the experimental temperature must be known.

(e) The sample in the Knudsen cell must be large enough to maintain equilibrium vapor pressure in the cell. In addition, the orifice size and shape must be such that they do not alter the equilibrium pressure of the temperature uniformity of the cell. Carlson (39) discusses these problems.

(f) A reaction between the sample and crucible material may alter the vapor pressure. Galloway and Eick (42) have shown that when samarium hexaboride is heated in contact with molybdenum, molybdenum boride, MoB, results presumably accompanied by the evolution of gaseous samarium. Thus, in a study of the vaporization of SmB_6 in a molybdenum crucible, and anomalously high samarium pressure would be observed. Spinar and Margrave (43) have recently shown that when nonreactive crucibles of magnesium oxide are used to measure the vapor pressure of the alkali hydroxides, the vapor pressures are many times higher than those reported by early workers who had used nickel crucibles. The low vapor pressures presumably resulted from reaction of the sample with the crucible. Changes in the crucible material may reveal reactions between the crucible and sample. Thus, chemical and x-ray analyses should be performed on all materials involved in the experiment.

(g) The effusion crucible and sample must be at a known, uniform temperature. Winterbottom and Hirth (44) have shown that if the top of the effusion crucible is hotter than the bottom, a departure from cosine law distribution results from surface diffusion through the orifice and along the crucible top. In addition, if the crucible top is colder than

the bottom, mass transfer from the sample to the crucible top may occur, resulting in a change of orifice shape, and possibly, total closing of the orifice.

D. The Mass Spectrometric Method

Inghram, Chupka and Porter (45) give the relationship between the measured ion intensity of a molecule in the vapor and the pressure of that species as:

$$P_x = (1/r_i k)(\sigma_s/\sigma_x)\ (T_x/T_s)\ (S_w/S_x)\ I_i \qquad (2\text{-}19)$$

where P_x is the partial pressure of species x

r_i is the isotopic fraction of the ion measured

σ is the ionization cross section

T is the temperature in ^oK

S is the sensitivity of the ion detector

I_i is the intensity of the ion measured in arbitrary units

s indicates a standard substance

x indicates an unknown substance

k is the sensitivity of the mass spectrometer in units of ion intensity per atmosphere of the vapor of a standard.

The isotopic fraction, r_i, is included in the equation, since generally the intensity of one isotope is observed as a function of temperature. The species x may contain more than one isotope; for example, europium gas contains isotopes of mass 151 and 153.

The ionization cross section is a measure of the efficiency of ionization by the electron beam in the mass spectrometer ion source. Otvös and Stevenson (46) have calculated ionization cross sections for

a number of atoms for ionization by electron impact, but have not included the lanthanons in their calculations. To determine the ionization cross section, a method described by Chupka and Inghram (27) can be used. The ionization cross section is proportional to the gas kinetic cross section, which is, in turn, proportional to the square of the interatomic distances in the crystal. Thus, the cross section ratio for silver to carbon is $(2.88/1.54)^2$, which is approximately 3.5. This is corrected to 4.0, since the ionization potential of carbon, 11.2, is much higher than that of silver, 7.54. The higher the ionization potential, the more difficult is ionization, and therefore, the calculated ratio is increased to account for this. This procedure is said to produce an error in the cross section ratio of no more than a factor of two.

The ratio of the sensitivities of the ion detector is the ratio of the number of electrons released by each species upon impact with the detector. Since in practice, it is usually not possible to determine this ratio, it is considered to be unity.

The sensitivity, k, is experimentally determined: An inert standard material of known vapor pressure is added together with the sample, to the cell. The ion intensity of the standard is measured at constant temperature as a function of time. The sensitivity is then defined by:

$$k = [\Sigma_j \, I\Delta t_j/t](1/P_s). \qquad (2\text{-}20)$$

The first term in equation 2-20 is the average ion intensity over the time needed to vaporize all of the standard. P_s is the pressure of the standard at the temperature of measurement.

When dealing with any given species x, equation 2-19 may be rewritten as

$$P_x = K\ (I_x T_x) \tag{2-21}$$

since all the other terms are constant for a given experiment. Combining equations 2-8 and 2-21 yields:

$$\ln P_x = \ln K\ T_x I_i = (-\Delta H^*/RT) + \Delta S/R \tag{2-22}$$

or

$$\ln I_i T_x = (-\Delta H^*/RT) + C \tag{2-23}$$

where $C = \Delta S/R - \ln K$. Thus, the slope of a graph of ln IT vs 1/T is equal to the enthalpy of reaction divided by R. The entropy may be determined from the intercept, C, if the constant K is known. Substitution of the calculated pressures into equation 2-13 permits an independent determination of the enthalpy of the reaction.

Wiley (47) and Wiley and McLaren (48) have described the theory of the time-of-flight mass spectrometer.

III. EXPERIMENTAL

A. Introduction

An examination of previously reported preparations of the lanthanon dicarbides indicates that two basic methods were used: the reduction of the metal oxide with carbon at high temperature *in vacuo* and the reaction of the elements at high temperature. No data have been presented concerning the relative merits of these different methods and it appears that either works equally well for most of the lanthanons.

The oxalate method for the quantitative determination of the lanthanons has been used for a number of years and needs no additional discussion. However, methods for determining microgram quantities of the lanthanons are relatively recent and not too numerous. The method chosen for the analysis of europium appeared to be the best available for use in aqueous solution.

The Knudsen effusion technique used in this study has been applied successfully to a large number of systems. While some difficulties are present in this method, it is currently the most accurate available for the determination of vapor pressures at high temperature.

B. Summary

Two methods were used in the attempt to prepare europium dicarbide. The first, the reaction of europium sesquioxide with carbon heated *in vacuo*, proved unsuccessful. The second, the reaction of europium with carbon in a closed stainless steel container, proved successful. The reaction product was characterized by both chemical and x-ray analyses.

The dicarbide was studied by the Knudsen effusion method, using both mass spectrometric and material collection techniques to determine the pressure of the effusate.

C. Preparation of Compounds

1. Materials

Both the europium sesquioxide (99.8% pure) and the europium metal (99% pure) were obtained from Michigan Chemical Corporation, St. Louis, Michigan. The graphite, listed as graphite grade UF-4-S was obtained from Ultra Carbon Corporation, Bay City, Michigan, and was a high density material of spectroscopic purity.

2. Reaction of Europium Sesquioxide with Graphite

The sesquioxide was calcined at 900° to remove volatile impurities and to convert any carbonate present to the oxide. The crushed graphite was heated under vacuum in a graphite crucible to a temperature of 1800° to remove absorbed impurities. The oxide and carbon were then intimately mixed in proportions according to equation 3-1:

$$Eu_2O_3 + 7C \rightleftarrows 2EuC_2 + 3CO \qquad (3\text{-}1)$$

and placed in a previously outgassed graphite crucible. A slight excess of graphite was used to insure complete reduction. The crucible had a snug fitting lid containing an orifice to allow escape of the carbon monoxide evolved.

The graphite crucible was then heated by induction in a vacuum line. Heating was initiated after the residual pressure in the system had decreased to 1×10^{-5} torr or less. The onset of the reaction was evidenced by both a rapid rise in pressure due to the evolution of carbon

monoxide and a darkening of the walls of the Vycor condenser around the crucible. When the pressure had decreased again to the residual value, heating was terminated. The crucible was removed from the vacuum line and taken into a helium filled dry box. A sample of the product was loaded into a capillary tube for x-ray powder diffraction analysis.

The material on the walls of the Vycor condenser was dissolved in dilute hydrochloric or nitric acid. During solution, which was very rapid, a gas with the characteristic odor of acetylene was evolved. This gas, however, was not analyzed because of the difficulty involved in the collecting of a sample. The resulting solution was analyzed for europium using the oxalate method to be described.

3. Reaction of Europium with Carbon

In additional attempts to prepare europium dicarbide, the metal and carbon were placed in a metal bomb and heated for varying lengths of time. Initially, the bombs were fashioned from type 316 stainless steel. However, when both halves of the bomb were constructed of the same material, the bomb could not be opened after heating since the threads seized. The combination of type 310 stainless steel for the bottom with type 316 for the top eliminated this problem. During the course of the experiments, a bomb was made from molybdenum as one method of determining whether or not the sample was reacting with the bomb.

The bombs were all constructed in the following manner: A piece of 2.54 cm. stock was reduced in diameter slightly so that the resulting piece would fit into the tube furnace. A 0.953 cm. diameter hole was then drilled in the bomb. This hole was enlarged at the top and then tapped to provide a 5/8 - 18 thread 1.91 cm. deep. A 0.952 cm. x 1.714

cm. hole which contained the sample remained below the thread. The top of the bomb was machined to give a matching thread. Flats were milled on both the top and bottom of the bomb to provide a gripping surface for tightening. The bomb was sealed with a 0.13 mm. thick platinum washer.

Prior to use, the bombs were cleaned in hot nitric acid, dried at 110° and prepared for loading in the dry box. The metal was added as a solid piece; the carbon as a granular powder. The ratio of metal to carbon was varied to give a composition range from $EuC_{1.5}$ to EuC_3. The top of the bomb was partially tightened in the dry box after loading. The top was retightened to insure a good seal after the bomb was removed from the dry box. The bomb was then placed in a Vycor tube through which helium was passed. The Vycor tube was placed in a tube furnace wound with Kanthal type A-1 resistance wire on an alumina tube.

After the tube had been thoroughly flushed with helium, heating commenced. The heating time was varied from twenty to sixty hours while the temperature was varied from 1000° to 1100°. Temperature was measured with a chromel alumel thermocouple in contact with the bomb. Since extremely accurate temperature measurements were not necessary, room temperature was used as reference and temperatures were corrected appropriately.

The bomb was allowed to cool in the helium atmosphere. It was necessary to break the gasket seal in air since sufficient torque could not be applied in the dry box. Immediately after the top had been loosened the bomb was placed in the dry box where its contents were removed with the aid of a 0.952 cm. drill ground flat on the end. Although the material in the bomb was somewhat difficult to remove, it

could be ground easily with an agate mortar and pestle. Some of the resulting product was loaded into an x-ray capillary tube for analysis; the rest was stored in a closed vial in the dry box.

In some of the preparations, a small sample was dissolved in nitric acid. Thiocyanate ion was added to test the sample for iron contamination since iron was the bomb constituent of greatest concentration.

4. Preparation of Praseodymium Dicarbide

Praseodymium dicarbide was prepared according to equation 3-2:

$$Pr_6O_{11} + 21\ C \rightarrow 6PrC_2 + 9CO + O_2. \qquad (3\text{-}2)$$

Oxygen appears as a product since the Pr_6O_{11} loses oxygen at a temperature below which reduction occurs (800°). The reactants were placed in a graphite crucible and heated by induction to 1300°, at which temperature the pressure rise in the system, indicating the initiation of the reaction, began. The temperature was slowly increased to 1500°. At this temperature, the reaction was essentially over as indicated by a pressure drop. The temperature then elevated to 1725° for one half hour. At this temperature the pressure was 9×10^{-7} torr -- essentially background pressure, and heating was terminated. The crucible was removed to the dry box for x-ray powder diffraction analysis of the product.

D. Methods of Analysis

1. X-Ray Analysis

X-ray powder diffraction photographs of the samples were taken using either CuKα radiation ($\lambda_{\alpha\mu}$ = 1.5418 Å) or FeKα radiation ($\lambda_{\alpha\mu}$ = 1.9373 Å) and a Debye-Scherrer x-ray powder camera of 114.59 mm. diameter. Since copper radiation produces florescence with europium specimens, iron

radiation is more desirable. All samples were contained in 0.3 mm. diameter Pyrex capillary tubes which were filled in a helium atmosphere.

2. Chemical Analysis

The dicarbide samples were analyzed using standard gravimetric techniques. The sample was dissolved in dilute hydrochloric or nitric acid (1N) and was then digested on a hot plate to insure complete solution. Any insoluble residue was assumed to be unreacted graphite and was collected in a fritted glass crucible, dried at 110° and weighed. The remaining solution was adjusted to pH 4 to 5 with ammonium hydroxide and excess saturated oxalic acid solution was added.

The oxalate precipitate, after digestion for a minimum of four hours, was collected in a tared alundum filter crucible and fired at 900° in a muffle furnace, in most cases overnight, to convert it to the oxide. The crucible was reweighed after cooling and bound carbon was determined by difference.

Europium deposited on the targets during a collection effusion run was analyzed by the method of Rinehart (49) with minor modifications to simplify the procedure. A brief description of the method follows:

The platinum discs used as targets were placed in fifty milliliter beakers and ten milliliters of 1 N $HClO_4$ were added. The samples were digested on a hot plate for one hour. These solutions were then quantitatively transferred to twenty-five or fifty milliliter volumetric flasks (the volume of the flask depended on the quantity of europium thought to be in solution) and diluted to volume with the perchloric acid. These solutions served as the samples for the analysis. A standard solution was prepared by dissolving calcined europium oxide in 1 N $HClO_4$ to make

a solution of approximately 1 mg./ml. Portions of this solution were analyzed by the oxalate method to determine the actual concentration. The results of this analysis are given in Table II. This solution was successively diluted to give standards of 1, 2, 5, 10, 20, 50, 70 and 100 micrograms per milliliter.

The step by step procedure was as follows:

1) Add 1.0 ml. of sample to a 10 ml. volumetric flask.
2) Add 1 drop of 0.025% phenyl red indicator.
3) Add 1 N NaOH dropwise until near the color change. Follow with 0.2 N NaOH to the color change.
4) Add 0.03 N HCl until color just reappears.
5) Add 0.5 ml. of 2 N $NH_4C_2H_3O_2$-$HC_2H_3O_2$ buffer.
6) Add 2.0 ml. of 0.1% sodium alizarin sulfonate.
7) Dilute to volume.
8) Using the Beckman DU spectrophotometer read the absorbancy at 550 mμ against a reagent blank.
9) Determine the unknown from the standard curve.

Table II. Europium concentration in standard solutions

Sample Number	Sample Volume	Total Eu Concentration	Eu Concentration
1	20 ml.	20.210 mg.	1.0105 mg./ml.
2	20	19.216	0.9608
3	20	21.030	1.0515
4	20	21.202	1.0601
		Average	1.0207 mg./ml.

3. Hydrolysis Product Analysis

Several samples of europium dicarbide were hydrolyzed in 3 N HCl in a confined system through which helium was flowing. The helium carried the gaseous hydrolysis products through a "Drierite" filled drying column into a liquid nitrogen covered U-tube fitted with a rubber septum and loosely packed with Pyrex wool. The gas sample condensed at the entrance of the tube at the liquid nitrogen level, but was recondensed at the bottom of the tube by gentle warming and subsequent cooling. The tube was then evacuated for one to two seconds to remove most of the helium.

After the gas sample reached room temperature, it was analyzed using an F & M Model 590 flame ionization gas chromatograph using helium as the carrier gas on an alumina column. The column was programmed for a 4.6° per minute temperature rise. The instrument was calibrated for each run with welding grade acetylene and natural gas.

E. Temperature Measurement

Temperature was measured with a Leeds and Northrup Model No. 8622-C disappearing-filament type optical pyrometer, serial No. 1619073. The pyrometer was calibrated at the National Bureau of Standards. Scale readings, together with the true temperatures, as determined by the National Bureau of Standards, are listed in Appendix A. A graph of $T^{\circ}C_{NBS} - T^{\circ}C_{Scale}$ vs $T^{\circ}C_{Scale}$ was made for each temperature range and was used to correct the observed temperature.

Before and after each series of experiments, either effusion collection or mass spectrometric, the transmissivity of both the window and prism through which the temperature was determined was measured. If the before and after measurements differed, the average value of the

two was used. A deposit of silver formed rapidly on the window at high temperature in the mass spectrometric experiments involving this metal. The onset of deposition could be observed by a sudden lowering of temperature with time at constant power setting. In these cases, the "before" value of transmissivity was used with the temperature observed before the deposit formed and the "after" value was used with successive temperatures. Some error resulted from this procedure, but no other method was available.

To measure the transmissivity, the temperature of a tungsten band lamp, heated to a temperature near 1500^{o}, was read directly with the pyrometer and through the window and prism. The correction for transmissivity follows from Wien's radiation law and is defined by the equations:

$$\Delta\ 1/T_W = 1/T_W - 1/T \tag{3-3}$$

and

$$\Delta\ 1/T_p = 1/T_p - 1/T \tag{3-4}$$

where T_W and T_p are the observed temperature of the hot object viewed through the window or prism and T is the observed temperature with nothing in the light path. The pyrometer readings were corrected to the true temperatures using the National Bureau of Standards corrections. The total window and prism correction is:

$$\Delta\ 1/T_T = \Delta\ 1/T_W + \Delta\ 1/T_p. \tag{3-5}$$

The quantity $\Delta\ 1/T_T$ is nearly constant for all temperatures, and the relationship

$$1/T = 1/T_o - \Delta\ 1/T_T \qquad (3\text{-}6)$$

in which T_o is the observed temperature, was used to calculate true temperatures from the apparent measured temperatures. In some experiments, a magnifying lens was used on the optical pyrometer in lieu of the standard lens. A correction factor, as described above, was determined for this lens and applied where necessary.

The design of the Knudsen cell used in these experiments prevents the machining of a black body hole in the bottom of the cell. This creates no problem in the mass spectrometric experiments since the temperature can be measured by sighting directly through the orifice into the cell. In the effusion experiments, however, material was collected on targets and it was necessary to sight onto the bottom surface of the cell. Therefore, a series of temperature measurements was made in which the bottom surface, top surface and orifice temperatures were determined at selected temperatures over the range of interest. The results, which are shown in Table III, were corrected to the true temperature using the National Bureau of Standards corrections and the window and prism absorption correction. Inspection of these data shows the top surface temperature to be higher than bottom surface temperature. This difference, not shown in Table III, showed no temperature trend. The average temperature difference is nine degrees. It is fortunate that the top of the cell is hotter than the bottom since, under these conditions, no mass transport, which could result in plugging of the orifice, would be expected. The difference, $T^{o}\ K_{BB} - T^{o}\ K_{BS}$, when plotted against $T^{o}\ K_{BS}$, gives a line with slight upward curvature. This curve was used to correct the observed surface temperature to the true temperature of the Knudsen cell.

Table III. Temperature profile of the Knudsen cell

$T^{o}K_{BS}$	$T^{o}K_{TS}$	$T^{o}K_{BB}$	$T^{o}K_{BB} - T^{o}K_{BS}$
1180	1190	1243	63
1225	1238	1289	64
1265	1272	1331	66
1275	1283	1342	67
1295	1305	1364	69
1327	1336	1398	71
1360	1373	1436	76
1380	1389	1458	78
1398	1411	1478	80
1431	1438	1515	84
1450	1459	1535	85
1455	1462	1542	87
1497	1505	1591	94
1515	1524	1611	96
1564	1573	1669	105
1584	1592	1689	105
1607	1618	1713	106
1637	1643	1745	109
1645	1657	1754	109
1663	1671	1779	116
1695	1707	1841	146

[a] $T^{o}K_{BS}$ = bottom surface temperature

[b] $T^{o}K_{TS}$ = top surface temperature

[c] $T^{o}K_{BB}$ = orifice surface temperature (a black body)

All temperature measurements were made in groups of at least three to permit determination of temperature with a precision of $\pm 1^{o}$. Temperatures were read often enough to give a minimum of four determinations during a target exposure. The average of all readings was taken as the temperature of the exposure. In the experiments involving target collection of the effusate, the temperature tended to drift upward with time at the higher temperatures, probably as a result of deposits which formed on the walls of the condenser and reflected radiation back to the crucible. When the temperature of the Knudsen cell was decreased, this effect was eliminated.

In the mass spectrometric experiments, the temperature remained constant for periods of thirty minutes, within the limits of error of the pyrometer readings at all temperatures. Thirty minutes was the maximum period of time any sample was held at one temperature. Since less than thirty minutes was required to obtain the desired information with the mass spectrometer, only two temperature readings were made.

F. The Mass Spectrometer

1. The Instrument

The mass spectrometer used in these studies was constructed in this laboratory by Mr. Norman Fishel, Dr. Richard A. Kent and myself, from components supplied by the Bendix Corporation. While not physically similar to the corresponding commercial unit, the Model 12-101, electronically it is identical, with one modification. The unit is equipped with a 167 cm. drift-tube instead of the normal 100 cm. tube. This alteration required electronic circuitry modifications which were performed by the Bendix Corporation.

The mass spectrometer was equipped with a high temperature Knudsen inlet system described in Appendix B. The inlet system (separated from the main vacuum system by a small slit) was evacuated by a 15 liter per second Vac-Ion pump (Varian Associates, Palo Alto, California). Thus, a differential pumping system was effected. The vacuum in the inlet system was monitored by measuring the current flowing through the pump. Measured pressures varied during an experimental run and were of the order of 10^{-5} to 10^{-6} torr. The vacuum in the ionization and drift chamber was monitored by a Veeco (Vacuum Electronic Engineering Company) ionization gauge. When the mass spectrometer was initially put into operation, a pressure of 1×10^{-8} torr was achieved. Under experimental operating conditions, however, pressures of 1 to 6×10^{-7} torr were considered adequate.

The output of the ion multiplier of the mass spectrometer was observed on an oscilloscope. Two electrometers were also present. Any portion of the mass spectrum could be observed with these units by means of a self-containing scanning system which pulsed a gate in the ion multiplier to remove the electrons corresponding to the mass of interest. The output of these electrometers was recorded on a Baush and Lomb VOM 5 strip chart recorder.

The two electrometers did not give the same ion intensity when observing the same mass peak. For quantitative work, it would have been necessary to calibrate one against the other and to ascertain the stability of this calibration. Since it was not necessary in this investigation to perform quantitative observations on two species simultaneously, only electrometer one was used. The second electrometer was used only as an auxiliary device to observe other portions of the spectrum.

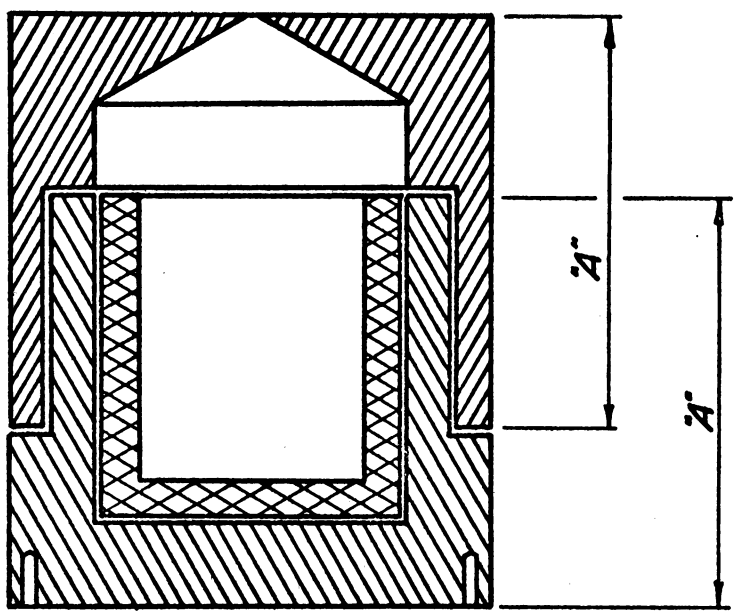
Ion intensities were measured with this electrometer recorder combination using the peak height on the chart combined with the scale factors from the electrometer. The intensities were recorded in units of nanoamperes.

2. Experimental Procedure

The Knudsen crucible used in these studies was fabricated from molybdenum rod and spectroscopic grade graphite. It is shown in cross section in Figure 1. The cell was machined in three parts: top, bottom and graphite liner. The top was pressed onto the bottom after the liner had been put in place and the bottom cooled in liquid nitrogen. The assembly was then heated to 2000° to bond the molybdenum together and to remove any volatile impurities.

The cell was heated to a similar temperature before each experiment as a cleaning procedure. A similar cell without the graphite liner was used for some of the experiments with silver. After outgassing, the cell was taken into a helium filled dry box and the sample loaded into the cell through the orifice; europium dicarbide as a finely ground powder, silver as thin wire. The cell was weighed before and after addition of the sample. The cell was then removed from the dry box and placed as rapidly as possible in the electron bombardment heating assembly of the mass spectrometer. The complete assembly was attached to the mass spectrometer which was evacuated immediately. The sample was exposed to the atmosphere for two to three minutes.

The cell was heated in the mass spectrometer by electron bombardment. A brief description of the power supply is given in Appendix C. Crucible temperatures below 800° were obtained by radiant heat from the



CELL TOP

CELL BOTTOM

CARBON LINER

FIGURE 1 THE CARBON-LINED MOLYBDENUM EFFUSION CELL.

tungsten filament. Although 800° is not an upper limit for radiant heating, no reliable method of controlling the filament current exists on the power supply and this method of heating was not used above that temperature. To achieve higher temperatures, a D. C. potential was applied between the hot tungsten filament and the crucible; the filament being negative and the crucible at ground potential. The electrons that "boil" off the hot filament are accelerated by the potential field and gain kinetic energy. When these electrons hit the crucible they release this energy to the crucible, thus heating it. The temperature is controlled by varying the power of the bombarding electrons. The method by which this control is achieved is described in Appendix C.

After the pressure in the mass spectrometer had decreased to 10^{-6} torr, the Knudsen cell was heated slowly to 800° to outgas both it and the sample. Outgassing was considered finished when the pressure in the sample region had decreased to 1×10^{-5} torr or less. In no case was the pressure allowed to exceed 5×10^{-4} torr during outgassing.

After outgassing, the D. C. potential was applied to the filament and the control unit set for automatic regulation. The desired temperature was then selected using the appropriate setting on the power supply. In general, the power control was changed by five units or multiples thereof for each temperature change in order to provide a convenient number should it be necessary to return to a given temperature. Once a given power level was set, the corresponding temperature was read with the optical pyrometer. Once a desired setting was made, the power supply would maintain the selected power level within the accuracy of the meters used for measurement. This stability was further confirmed by the temperature readings which showed no change, within the limits of

error of the measurement, over periods of thirty minutes.

Once temperature equilibrium was established, (ten minutes or less) the electrometer and recorder were set to scan the region 145 to 200 a.m.u. This mass region includes the ions Eu^+, EuO^+, EuC^+, EuN^+ and EuC_2^+ which might be expected above a europium carbide sample. The ion intensity data were then determined from the recorder charts. Other mass ranges were observed periodically to check for other species that might be significant. During several experiments the ion intensity was also measured as a function of the energy of the electrons used to form the ions. These measurements were made for mass 151, europium, mass 18, and mass 28 which was used as a reference since it was always present as background in the instrument. These data were plotted according to the method of White, et al. (30) and the straight line portion of the curve was extrapolated to give the appearance potential.

The crucible temperature was varied in two different ways. In some experiments, the temperature was increased step-wise to a maximum and then decreased in like manner. In other experiments, the temperature was first increased about twenty degrees, then decreased ten degrees, then increased twenty degrees, etc. -- the temperature trend being upward. After the maximum temperature was reached, the process was reversed and the temperature was decreased. When a sample was observed on succeeding days, after being at room temperature overnight, a similar temperature schedule was followed.

When silver was added to the europium dicarbide sample, the temperature was first raised to approximately 1100^o. The ion intensity of Ag^{107} was measured as a function of time until all of the silver had evaporated from the cell. The measurements on the dicarbide were then carried out

in the usual manner.

3. Treatment of Data

The temperature data from the mass spectrometer were corrected as outlined on page 31 and then combined with the corresponding intensity data to give the product IT for europium 151 and europium 153. These numbers along with the temperature, were treated by the method of least squares on a Control Data Corporation 3600 digital computer using the equation:

$$\ln IT = A/T + B. \qquad (3\text{-}7)$$

The program to accomplish this was written following the equations given by Youden (50). This program, which is given in Appendix D, calculated the slope and intercept of the best straight line through the data. The standard deviation of these quantities and the standard deviation of an individual IT value were then calculated. Calculated values of IT were generated for each T value and were compared with the input data. If the difference between the calculated and the input value was more than three times the standard deviation, the point was rejected and the parameters for the line were recalculated. Dr. George D. Sturgeon modified the program so that the datum with the maximum deviation from the expected value was tested for reliability first.

G. Effusion Experiments

1. Apparatus

Kent (51) has described the apparatus used in these experiments. The Knudsen cell used for these experiments was the same as that used in the mass spectrometric work.

2. Preparation of Targets

The effusate from the Knudsen cell was collected on platinum discs, 2.48 cm. in diameter and 0.13 mm. thick. The discs were cleaned in boiling nitric acid, washed in distilled water and heated bright red in a hydrogen flame. The targets were individually mounted in aluminum cassettes and held in place by a phosphor-bronze spring. Eighteen targets were loaded into the copper magazine of the effusion apparatus.

A knowledge of three dimensions is needed to calculate the vapor pressure. These are the crucible orifice diameter, the distance from orifice to target collimator and the diameter of the collimator.

The orifice diameter was measured using a set of number drills. A drill was found which fit the orifice most closely and its diameter was measured with a micrometer.

The orifice to collimator distance was measured with a Gaertner Scientific, Model No. M911, serial No. 1585a, cathetometer. The scale could be read with a vernier to 0.05 mm. and readings were estimated to 0.01 mm. The measurements were made after the apparatus had been assembled and evacuated for a minimum of one-half hour to seat the greased glass joints. The vacuum system was then opened to the air, the shutter assembly was removed and the height of the collimator was determined. The system was re-evacuated and the height of the crucible was measured through the Vycor condenser. Each measurement was made ten times and the average value was used.

The collimator diameter was measured using a telescoping gauge and a micrometer. Ten readings were taken on randomly spaced diameters and the results averaged.

3. Procedure for Effusion Measurements

The procedure used during an effusion experiment was as follows: The sample was loaded (in the dry box) through the orifice into the effusion crucible. The targets were put in the magazine, the sample crucible placed on its stand and the apparatus assembled and evacuated. This last step was carried out as rapidly as possible to minimize reaction of the sample with air. Helium was continuously passed through the system to minimize sample reaction while the distance measurements were made. The system was then re-evacuated. When the pressure had decreased to 1×10^{-6} torr, the magazine Dewar was filled with liquid nitrogen and heating was begun. After the temperature had stabilized, the shutter was opened and target one was exposed. The time interval during which the shutter was open was measured with a Precision Scientific Company "Time-It" electrical timer which was graduated to read to 0.01 minutes. The temperature was measured several times during the exposure. When the desired time had elapsed, the shutter was closed and the target was ejected from the magazine. A new temperature was then selected and the cycle repeated. The series of targets was exposed, first at successively increasing temperatures over the range of interest, then at successively decreasing temperatures. After the run was completed and the sample had cooled, the crucible was placed in the dry box and the sample removed for analysis. The crucible was then returned to the vacuum line for measurement of top versus bottom temperatures. The targets were analyzed as described previously (pp. 28-29).

The second effusion run, as well as two sets of targets in the first run, was designed to determine the efficiency of the collection of

effusate on the targets. The procedure was like that described above except that two target cassettes held two targets back to back with a 1.58 mm. diameter hole in the center of each. The second cassette held a solid target. The operation was as follows: The first target intercepted most of the effusate beam, the third target intercepted that which passed through the holes in the first two, and the second target collected that material which bounced off the third target. The analytical data for targets two and three yielded the fraction of material adhering to the upper target.

IV. RESULTS AND DISCUSSION

A. The Preparation and Some Physical Properties of Europium Dicarbide

The two methods for the preparation of lanthanon dicarbides discussed in Chapter III gave different results with europium and will be discussed separately in this chapter.

1. Experiments Involving Europium Sesquioxide and Carbon

Three similar experiments were carried out in an attempt to prepare europium dicarbide by the reduction of the sesquioxide with carbon. The data are summarized in Table IV.

In experiment 1, the sample was heated three times. In the first heating, a heavy black deposit, which was thought to be an impurity and was disgarded, was found on the walls of the vacuum chamber. In subsequent heatings, when this deposit was analyzed chemically, europium was found. But since some of the effusing material had been disgarded, quantitative calculations could not be made.

In experiments 2 and 3, all of the material deposited on the condenser walls was retained so that accurate mass balance data could be obtained. The quantity of carbon monoxide given in Table IV was calculated assuming that reduction was complete and occurred according to the equations:

$$Eu_2O_{3(s)} + 3C_{(s)} \rightarrow Eu_{(g)} + 3CO_{(g)} \qquad (4\text{-}1)$$

and

$$Eu_2O_{3(s)} + 7C_{(s)} \rightarrow EuC_{2(s)} + 3CO_{(g)}. \qquad (4\text{-}2)$$

The values for free carbon and europium were determined as described in Chapter III.

Table IV. Data for Eu_2O_3 - carbon experiments

Experiment Number	T^oC	$\frac{C}{Eu}$[a]	CO	C	Eu	R[b]	S[c]	I[d]	P[e]
1b	1350	0.51	---	7.94mg	196.38mg	---	---	---	---
1c	1310	0.26	---	9.66	228.17	---	---	---	---
2	1500	1.11	48.05mg	14.72	160.06	40.67mg	263.50mg	276.22mg	91.5
3	1450	0.59	47.89	6.33	130.9	67.04	251.16	270.57	93.5

[a]The ratio of free carbon to europium found on the wall of the vacuum system

[b]R = residue remaining in the crucible

[c]S = summation of the values for CO, C, Eu and R

[d]I = initial sample weight

[e]P = per cent of material accounted for

Table IV shows that 91.5% and 93.5% of the material put into the crucible was accounted for in experiments 2 and 3 respectively. The remaining material probably escaped as gaseous hydrocarbons when the material on the condenser walls was hydrolyzed (the odor characteristic of acetylene was evident during hydrolysis).

An extrapolation of the data of Thorn and Winslow (29) for the trimeric and monomeric species, $C_{3(g)}$ and $C_{1(g)}$, which are the principal vapor species in equilibrium with graphite at high temperatures, indicates that at 1600°, the partial pressure of each is about 2×10^{-13} atm. This low pressure, substantiated by the constant weight obtained when empty graphite crucibles were heated at 1450° to 1500° for a few hours, indicates that any carbon found in the condensate when europirum sesquioxide and graphite were heated either left the crucible as a volatile carbon species or was produced by reaction between carbon monoxide gas (present in the system at pressures of about 10^{-3} torr) and the vaporizing species, europium. However, the presence of a volatile carbide would not be surprising since Chupka and co-workers (22) report that lanthanum dicarbide is a major component in the vapor in equilibrium with solid lanthanum dicarbide.

The disturbing variation in the europium to graphite ratio in the condensate may result from either differences in the heats of sublimation of europium and europium dicarbide, from the use of different acids in the hydrolysis technique, from different reaction rates of europium with carbon monoxide gas or from combinations of the three. Since precise data could not be obtained readily by this method, additional sesquioxide-graphite experiments were not performed. In summary, two important

observations can be deduced from these data: First, since carbon is found in the condensate, some volatile europium-carbon species may be present in the vapor. Second, if such a species exists, its vapor pressure is much higher than that of other lanthanon dicarbides.

2. The Preparation of Praseodymium Dicarbide

In order to determine whether or not the procedure just discussed, involving europium sesquioxide and carbon, would yield a lanthanon dicarbide with some other lanthanon oxide, a sample of Pr_6O_{11} was reduced with carbon.

X-ray powder diffraction analysis of the praseodymium-carbon preparation showed only lines attributable to the tetragonal praseodymium dicarbide. The calculated lattice constants were: $a_o = 3.835\text{Å}$; $c_o = 6.391\text{Å}$. These values compare favorably with the data of Spedding and co-workers (14): $a_o = 3.855\text{Å}$; $c_o = 6.434\text{Å}$.

3. Experiments Involving Europium and Carbon

(a) General

Since the sesquioxide-carbon experiments indicated the probable existence of a highly volatile europium-carbon compound, the reaction of europium and graphite in a closed container seemed a logical method to attempt for the isolation of that compound. Stainless steel was chosen for the container material since it was readily obtained and easily machined. In addition, the low melting point of europium (875^o) did not require the use of a refractory metal. The construction of the bomb is discussed in Chapter III.

The results of the tests used to check for the absence of contamination of the sample by the bomb are as follows:

The thiocyanate ion test used to check for the presence of iron, the major component of the bomb, was negative. From this test, it was concluded that no iron dissolved in the europium sample. The x-ray powder diffraction pattern of the sample prepared in a molybdenum bomb and those of the samples prepared in the stainless steel bomb gave identical d-spacings. From this observation, it was concluded that neither bomb was reacting with the europium sample. Thus, it is evident that the stainless steel bomb used was a suitable container for europium dicarbide preparations. Table V lists the europium carbide samples that were prepared, the starting composition and the results of the chemical analyses that were performed on those samples which were used for futher studies.

The reaction between europium and carbon in the stainless steel bomb produced a soft crystalline material that was easily removed with the aid of a tool made by grinding flat the end of a 3/8" drill. This black material was ground easily to a fine powder in an agate mortar. When it was exposed to the air, the sample reacted rapidly with moisture. For this reason, sample manipulation was carried out in an inert atmosphere whenever possible. The analytical data gave an average sample composition of Eu $C_{1.87\pm0.08}$ where the error is the standard deviation.

(b) Vapor phase chromatographic analysis

Samples 1-16P, 1-17P and 1-30bP were hydrolyzed with dilute (1:10v/v) hydrochloric acid and the resulting gas was collected for vapor phase chromatographic analysis as described in Chapter III, section D-3. The results for sample 1-16P were inconclusive due to technical difficulties. A chromatogram from the successful analysis of one of the other two samples is shown in Figure 2. The first small peak and the large peak correspond

Table V. Europium dicarbide preparations

Sample Number	Starting Composition	Analysis
1-15P	2.04	
1-16P	2.02	
1-17P	2.05	$EuC_{1.93}$
1-23P	2.02	
1-24P	1.78	$EuC_{1.89}$
1-26P	1.95	$EuC_{2.26}$[b]
1-28P	2.00	$EuC_{1.92}$
1-30bP	1.50	
1-31P	2.20	$EuC_{1.91}$
1-34P	3.09	
1-35P	1.79	$EuC_{1.79}$
1-36P	1.83	
1-43P	1.91	
1-44P	a	$EuC_{1.89}$
1-62P	2.07	$EuC_{1.70}$
2-19P	2.56	$EuC_{1.94}$

[a]Composition unknown - prepared by the addition of carbon to unanlyzed sample 1-43P

[b]Analysis data believed to be invalid

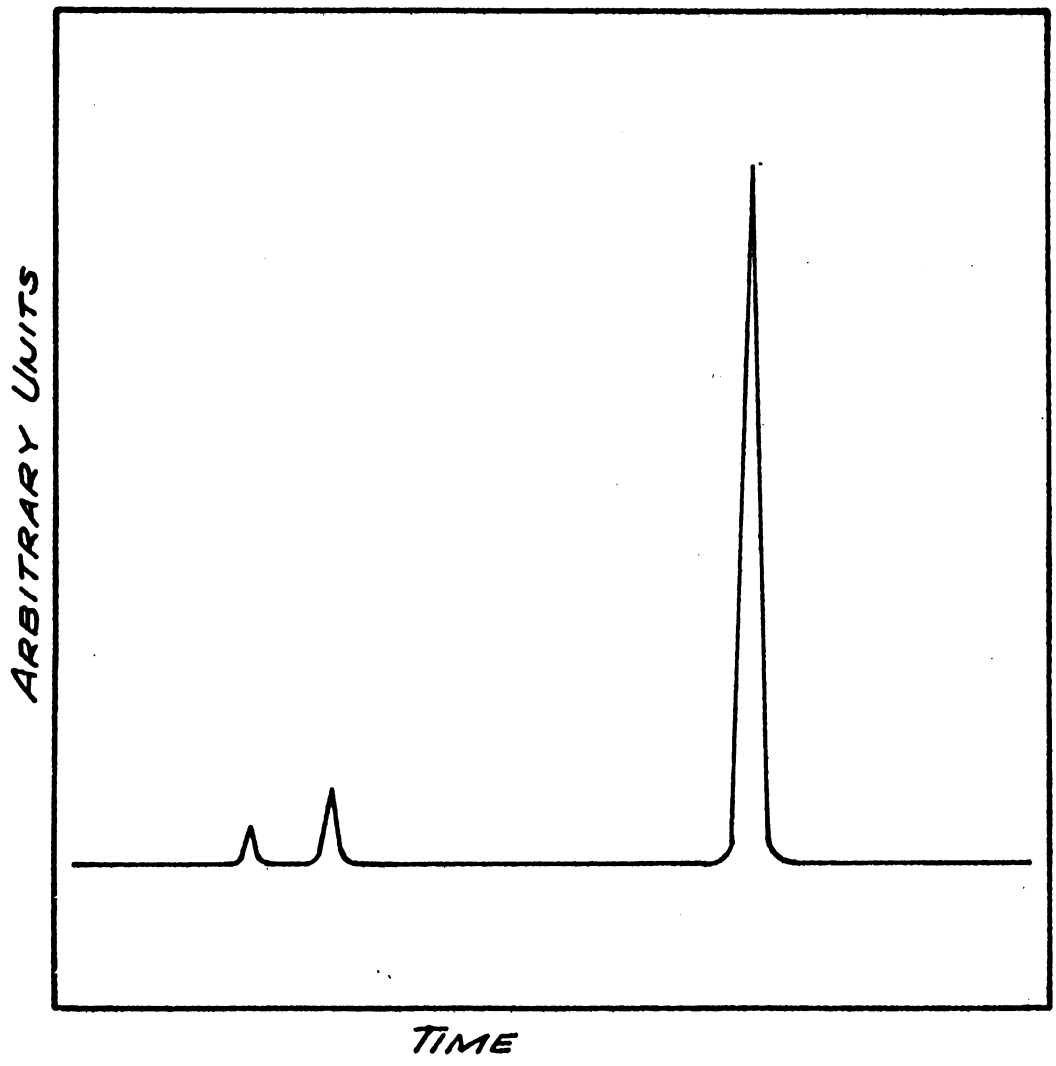


FIGURE 2 VAPOR PHASE CHROMATOGRAM OF THE HYDROLYSIS PRODUCT OF EUROPIUM DICARBIDE.

to methane and acetylene respectively, as determined by comparison of the retention times with those of standard samples. The second small peak was assigned to ethane, but may be assignable to some other C_2 or C_3 hydrocarbon since no ethane or propane standards were used. It was not possible to condense any hydrogen resulting from the hydrolysis with the apparatus used. Therefore, accurate values for sample composition can not be given since hydrogen was probably present. However, if the results are based only on the hydrocarbons detected, it is possible to state that acetylene was present in at least 98% concentration.

Palenik and Warf (52), Svec, Capallen and Saalfeld (53) and Greenwood and Osborn (18) have studied the hydrolysis of the lanthanon dicarbides. While these authors differ slightly in the relative quantities of the hydrolysis products, they all report hydrogen, ethane, ethene, ethyne and C_4 hydrocarbons as the major products formed upon hydrolysis of the dicarbides with dilute acid. A typical analysis would be: hydrogen 18%; ethane 6%; ethene 8%; ethyne 60%; C_4 4%; others 4%. As is evident from Figure 2, the data from the hydrolysis of europium dicarbide bear no resemblance to these data. Greenwood and Osborn (18) also studied the hydrolysis of calcium dicarbide and found the resulting gas to contain 98% acetylene, some carbon dioxide and no other hydrocarbons. Therefore, I conclude that europium dicarbide resembles the alkaline earth dicarbides more than the other lanthanon dicarbides.

B. X-ray Analysis

All of the solid europium dicarbide preparations were analyzed by x-ray powder diffraction and all gave similar powder patterns. Patterns were similar but not identical-- the d-values were the same on every

film, but the relative intensities of the lines varied with sample composition. The x-ray powder photographs were characteristic of the body-centered tetragonal structure common to the other lanthanon dicarbides and the alkaline earth dicarbides. The calculated lattice parameters were: $a_o = 4.045$ Å; $c_o = 6.645$ Å. Interplanar d-values together with their observed intensities are listed in Table VI.

In all preparations, a second phase was apparent, as indicated by the three unindexed lines in Table VI. This phase could be reduced to minor proportions by extended heating at 1060°, but could not be removed. This phase could be obtained in higher concentration by using a lower carbon to europium ratio and by heating at lower temperatures.

The extra lines observed in the x-ray powder diffraction pattern did not correspond either to the M_2C_3 or M_3C phase reported by Spedding and co-workers (14) for other lanthanons. This lack of comparison is to be expected, however, since europium dicarbide is more alkaline earth in character. The d-values for these extra lines were also compared to the d-values for europium metal, europium (II) oxide, europium (III) oxide, europium nitride and graphite with negative results in all cases. Consequently, this second phase is assumed to be a europium carbide with a different crystal structure.

The volume of the unit cell for europium dicarbide (107 Å) is substantially larger than that of the neighboring samarium and gadolinium dicarbides (90 Å and 86.9 Å respectively). In this respect it is analogous to ytterbium dicarbide, which, according to Spedding (14), is also larger than its neighbors. This behavior is indicative of a divalent metal ion, which is to be expected for europium, and it indicates that the dicarbide should be similar to an alkaline earth dicarbide.

Table VI. Interplanar d-spacings for EuC_2 sample 1-24P

Miller Indices (h k l)	d calc Å	d obs Å	I rel[a]
101	3.450	3.450	m
102	3.322	3.322	m
---	---	3.070	w
110	2.853	2.853	s
---	---	2.561	w
112	2.165	2.169	w
200	2.006	2.020	w
103	1.936	1.941	w
---	---	1.805	w
211	1.747	1.748	m

[a] s = strong; m = medium; w = weak

The lattice parameters and volume reported (9) for strontium dicarbide (a_o = 4.11 Å; c_o = 6.68 Å; V = 112.7 Å^3) are reasonably close to those observed for the europium dicarbide phase. In addition, the chemical reactivities are similar.

From the data of Atoji (21), it is possible to calculate the radii of the lanthanon ions in the dicarbide phase. Some of these radii are given in Table VII with the metallic radii calculated from the data reported by Spedding (14). The radii calculated from the dicarbide lattice parameters compare favorably with the metallic radii of the lanthanons, with the exception of ytterbium. This discrepancy may be explained on the basis of the crystal structure of the metal. As Hall, Barnett and Merrill (55) have shown, the metallic radius of ytterbium, in its body-centered cubic modification which is stable at high pressures, is 1.75 Å. Since the dicarbide is a body-centered type structure, its metallic radius would be expected to agree more closely with this form of the metal, rather than with the closest-packed form of ytterbium which exists normally.

C. Knudsen Effusion Experiments Involving Target Collection

1. General

Mass spectrometric results, which will be discussed later, show that europium constituted at least 99% of the vapor in equilibrium with europium dicarbide. Thus equation 2-15

$$P = w/S_o t \quad (2\pi RT/M)^{\frac{1}{2}} \qquad (2\text{-}15)$$

defines the vapor pressure when M is taken as 152.00. This equation, or its modified form, equation 2-16, was used to calculate the vapor pressures reported in this section.

Table VII. Radii of the lanthanons in the dicarbide phase (Å)

	$r_{metallic}$[a]	C - C	r_{calc}[c]
Sm	1.802	1.285[b]	1.880
Eu	1.984[d]	1.285	2.038
Gd	1.802	1.285	1.852
Tb	1.782	1.293	1.820
Yb	1.940 (fcc)	1.287	1.768
	1.75 (bcc)[e]		

[a]Metallic radius calculated from the lattice constants for the metal

[b]Average C-C distance given by Atoji(21)

[c]Metallic radius calculated from the lattice constants of the dicarbides

[d]Calculated from data of Spedding, Hanak and Daane (54)

[e]Data from ref. (55)

2. Preliminary Experiment

A preliminary effusion experiment was undertaken to determine if the rate of vaporization of europium dicarbide could be measured. A portion of sample 1-35P was heated four times successively. All of the material effusing from the cell was collected and analyzed chemically. The results of the four preliminary effusion runs are shown in Table VIII.

The crucible and contents were not weighed between heatings since this would have involved exposure to the air, resulting in sample decomposition. The average time the crucible was exposed to the air while the collection tubes were being changed was estimated to be twenty seconds. Since the vacuum was broken by the admission of helium to the system, the crucible contained helium and the brief exposure to the air should have resulted in negligible sample decomposition.

The data in Table VIII show considerable scatter. However, since these were only preliminary data, the scatter may be attributed to random error and we may conclude that the vaporization process is occurring at a constant rate even when about one half of the sample is removed from the cell by vaporization. A non-constant effusion rate would indicate that equilibrium was not being maintained in the effusion cell. Since the use of the Knudsen method requires maintenance of equilibrium, a non-equilibrium process cannot be treated by this method.

Another important observation, not shown in the table, was that the effusing material covered the inverted test tube from a level below the bottom of the crucible to the top of the tube. This indicated that some europium species was passing directly through the walls of the crucible in addition to effusing through the orifice. Such cell leakage would produce high values for the calculated pressure together with

Table VIII. Effusion data for sample 1-35P

Heating Number	Temperature ^{o}K	Time min.	Free Graphite mg.	Eu Collected mg.	Effusion Rate mg./min.	Pressure atm.x10^{4}
1	1565	8	0.00	37.07	4.63	3.52
2	1637	6	7.00	59.89	9.98	7.75
3	1637	7	0.00	57.59	8.23	6.39
4	1642	10	0.00	95.90	9.59	7.53

Orifice diameter: 0.711 mm. at room temperature

scatter in the data. Therefore, graphite is not a suitable crucible material for the study of europium dicarbide.

3. Individual Experiments

(a) Experiment E-1

In order to eliminate the problem of material passing through the walls of the effusion crucible, the carbon lined molybdenum cell described in Chapter III, section F-2, was used in this and all subsequent effusion experiments. The exposure temperatures were arbitrarily varied. After the initial degassing of the crucible at temperatures between 400° to 900°, the pressure in the system, continuously monitored with a Veeco vacuum gauge, remained below 5×10^{-6} torr throughout the remainder of the experiment.

Chemical analysis of sample 1-44P before the experiment was begun showed the stoichiometry to be $EuC_{1.89}$. It was not possible to analyze the residue since an insufficient quantity remained in the cell. An x-ray powder diffraction photograph of the residue indicated graphite was the principal product.

Duplicate analyses of the material on the target gave widely differing absorbancy values. The difficulty was investigated in detail using standard solutions. A faulty cleaning procedure used on the glassware caused the erratic results. The original procedure was to clean the glassware thoroughly in detergent and then rinse well with water. When the detergent cleaning was followed by treatment with "aqua regia" and then a thorough water rinse, consistent results were obtained for the standard solutions. Apparently all of the europium on the glass from previous analyses was not removed by the detergent solution or perhaps

some of the detergent remained on the glass and hindered the formation of the colored europium complex.

When the analytical method was functioning properly, the solutions from the targets were reanalyzed with reasonably good results which are shown in Table IX. During the course of the analysis, new solutions had to be made and therefore, the absorbancy values for two different samples of the same concentration may not be the same.

The concentration data from the analysis were used to calculate the pressures in the Knudsen cell corresponding to each target exposure. The results are shown in Table X. A plot of ln P vs $10^4/T$ is shown in Figure 3. The line in Figure 3 was calculated by a least squares treatment of the data.

A large amount of scatter is present in the pressures. There are two probable causes of this scatter. The first, which would be expected to give a random error, is error in the analysis. The second is bouncing from the target.

A least squares treatment of the absorbancy values for the standard europium solutions gave the equation:

$$A_s = (5.538 \pm 0.008 \times 10^{-3})C - (6.253 \pm 2.8 \times 10^{-3}) \quad (4\text{-}3)$$

where A_s is the absorbancy and C is the concentration, in micrograms, of europium in the sample taken for analysis. Solving this equation for C gives:

$$C = \frac{A_s + 6.253 \times 10^{-3}}{5.538 \times 10^{-3}} . \quad (4\text{-}4)$$

It is evident from equation 4-4 that a change in A_s of 6×10^{-3} will

Table IX. Analytical data for targets from experiment E-1

Target No.	Absorbancy[a]		Eu μg./ml.	Eu total μg./target
1	.003	.001	1.49	74.5
2	.026	.027	5.91	148
3	.009	.015	3.30	165
4	.034	.026	6.55	327
5	.081	.073	15.03	752
6a*	.034	.037	7.54	377
6b	.026	.028	6.00	150
7	.041	.055	9.80	245
10	.056	.059	5.75	144
11	.065	.061	6.00	300
12	.044	.048	2.85	142
13a*	.051	.044	3.20	160
13b	.062	.055	5.00	125
14	.057	.062	5.25	131
15	.043	.037	2.00	100
16	.019	.017	4.38	133
17	.011	.006	2.66	219
18	.011	.007	2.75	138

[a]Values are for duplicate analyses of samples

*Targets 6 and 7 and 13 and 14 were used to check for bouncing.

Table X. Data for experiment E-1

Target No.	Temperature ^{o}K	Exposure Time min.	$Eu_{collected}$ x 10^{-6} (gm.)	P_{Eu} atm.
16	1404	120	219	7.53×10^{-5}
1	1450	120	74.5	2.60×10^{-5}
2	1321	180	148	3.29×10^{-5}
3	1609	90	165	8.09×10^{-5}
4	1672	30	327	4.91×10^{-4}
5	1578	60	752	5.48×10^{-4}
10	1335	180	144	3.21×10^{-5}
11	1246	220	300	5.30×10^{-5}
12	1486	90	142	6.72×10^{-5}
15	1661	30	100	1.50×10^{-4}
17	1503	90	133	6.31×10^{-5}
18	1542	90	138	6.61×10^{-5}
6a	1625	30	377	
6b	1625	30	150	1.14×10^{-3}*
7	1625	30	245	
13a	1358	245	160	
13b	1358	245	125	7.64×10^{-5}*
14	1358	245	131	

$\Delta\ 1/T = 7.51 \times 10^{-6}$

Orifice diameter: 0.80264 mm. at room temperature
0.80664 mm. at exposure temperature

Collimator diameter: 1.9076 ± 0.0051 cm.

Orifice to collimator distance: 12.858 ± 0.004 cm.

*Pressure calculated from the sum of europium collected on targets 6a, 6b and 7 and 13a, 13b and 14.

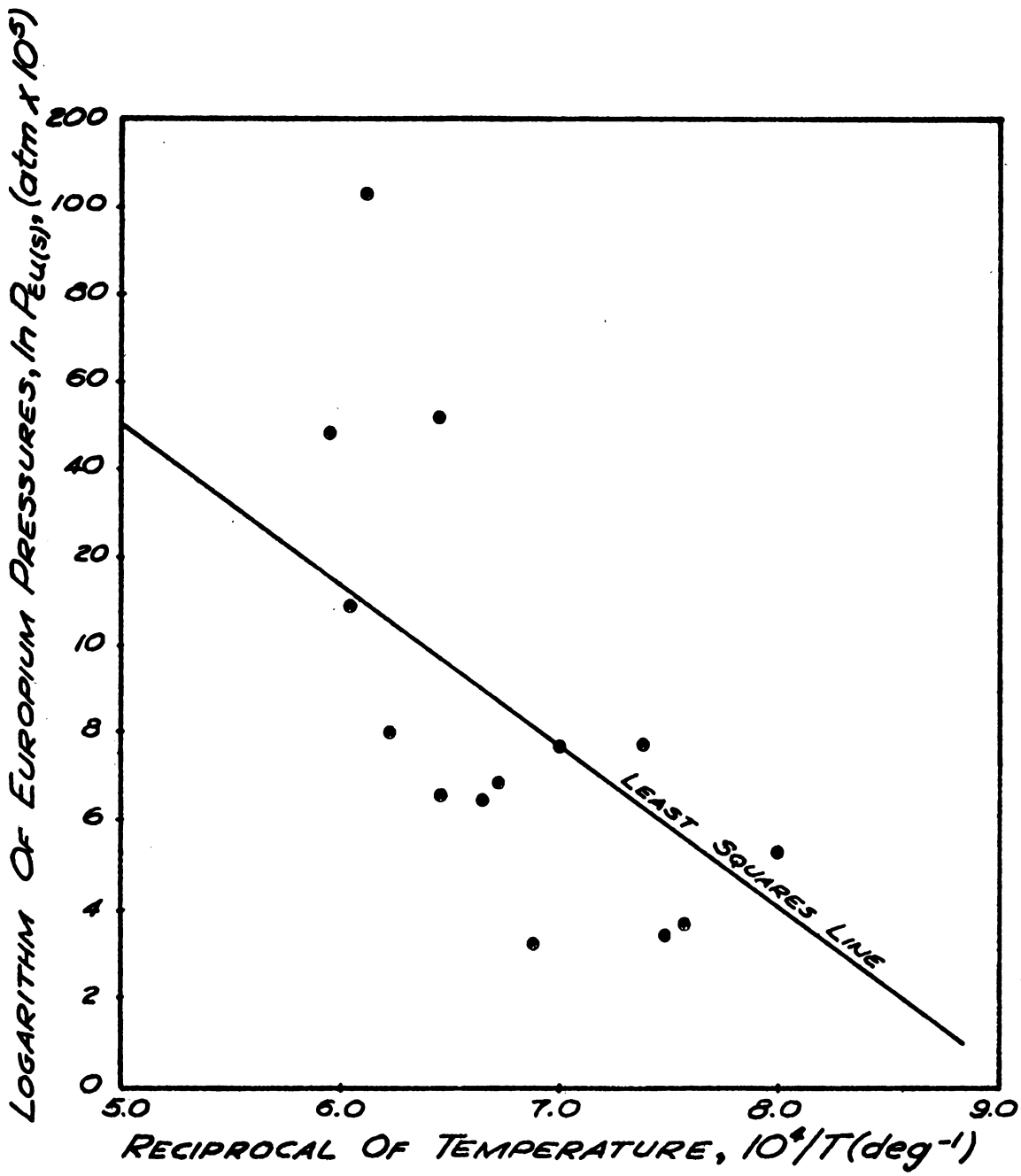


Figure 3 The Vapor Pressure Of Europium Dicarbide As A Function Of Reciprocal Temperature.

result in an error of roughly one microgram in the calculated concentration. Table IX shows that, on the average, this is the difference in the absorbancy values for duplicate samples. Thus, the average error in the measured concentration is approximately ±1μg. For most of the measured concentrations, this amounts to a twenty to seventy per cent error. These data, therefore, are not sufficiently precise to yield accurate calculated pressures.

Target pairs 6 and 7 and 13 and 14 were exposed simultaneously to check for bouncing of the effusate from the target, as described in Chapter III, section G-3. For the pair 6-7, 38% bouncing is indicated; for pair 13-14, 49% bouncing is indicated. Since these targets were exposed at different temperatures (see Table X) an error that may be a function of temperature is introduced. These two sets of data are not sufficient to determine whether bouncing actually varies with temperature or whether analysis errors are present, but they do indicate that an error due to less than total adherence to the target is present.

(b) Experiment E-2

This experiment was designed specifically to determine the extent of bouncing present and its temperature dependence. The same crucible used in experiment E-1 was charged with a portion of sample 2-19P (stoichiometry $EuC_{1.94}$). The first two targets were "exposed" with the shutter closed in order to determine the shutter efficiency. The remaining targets were exposed in groups of two, as described in Chapter III, section G-3. The results of this experiment are shown in Table XI. Targets 13 and 18 were used to check shutter efficiency. While some europium may have been present on the target, the quantity was below the limits of detection of the method (25 micrograms) and the results are

Table XI. Data for experiment E-2

Target No.	Observed Temperature °C	Exposure time min.	Europium on Target μg.	Bouncing %
13[a]	850	400	<25	---
18[a]	1198	30	<25	---
1a	1200	60	213	---
1b	1200	60	72	46
2	1200	60	85	
3a	1117	90	118	
3b	1117	90	82	43
4	1117	90	110	
5a	1180	60	150	
5b	1180	60	42	31
6	1180	60	92	
7a	1085	90	100	
7b	1085	90	64	54

Orifice diameter: 0.8026 mm. at room temperature

0.8066 mm. at exposure temperature

Collimator diameter: 1.90756 ± 0.0051 cm.

Orifice to collimator distance: 13.125 ± 0.004 cm.

[a]Targets "exposed" with shutter closed

therefore listed as less than twenty-five micrograms. Thus, the shutter was operating properly and shielding the target from the molecular beam.

The analytical data for the remaining targets indicate that a very large bouncing effect is present; on the average, 43%. Although great care was taken in order to make the chemical analysis as accurate as possible, a difference of one microgram was still evident for duplicate samples. When a dilution factor of twenty-five is applied, a possible error of twenty-five micrograms results. If this error is assumed to be non-random and in such a direction as to reduce the calculated bouncing, an average bouncing effect of twenty-six per cent is calculated. Since there is no valid reason for assuming a non-random error, only fifty-seven per cent of the effusing molecules which strike the collector are adhering to it.

In order to eliminate or reduce bouncing to an acceptable level of one to ten per cent, it would have been necessary to redesign the apparatus to bring the liquid nitrogen into closer proximity to the targets. Also, in all probability, a number of other variables would have needed examination. These difficulties, combined with the absence of a precise method for the analysis of europium at low concentrations, led to the conclusion that further work in this area would not yield results in proportion to the time spent. Therefore, the experiments involving chemical analysis of the collected effusate were terminated in favor of the use of the mass spectrometer to determine the decomposition pressure of europium dicarbide.

D. Mass Spectrometric Studies of Europium Dicarbide

1. Introduction

Since the collection technique and the chemical analysis of the effusate from the Knudsen cell did not yield reproducible data, the use of the mass spectrometer for an extensive study of europium dicarbide seemed mandatory. The mass spectrometer eliminates the difficulties encountered in chemical analysis. The physical arrangement of the Knudsen source in the spectrometer is such that very few of the effusing molecules which bounce from the radiation shielding can enter the ionizing region of the mass spectrometer. Use of the mass spectrometer, does, however, introduce a different source of error since it must be calibrated with a substance of known vapor pressure in order to obtain partial pressures of europium. This calibration, which involves assumptions that introduce some error, will be discussed more fully subsequently.

When the mass spectrometer is used for the quantitative determination of gaseous species, temperature and ion intensity are measured. As a result of the phase rule, the temperature determines the ion intensity.

2. Conventions for Treatment of Data

The experimental data indicated that europium gas was the major vapor component (99%) above europium dicarbide, thus indicating the reaction:

$$EuC_{2(s)} \rightarrow Eu_{(g)} + 2C_{(s)}. \qquad (4\text{-}5)$$

The intensities of Eu^{151} and Eu^{153} were determined as a function of temperature. Equation 2-22,

$$\ln k\ IT = -\Delta H^{o}/RT + \Delta S^{o}/R \qquad (2\text{-}22)$$

shows that a graph of ln IT vs 1/T yields the value of ΔH^{o} from the

slope. The intensity data for the two europium isotopes were treated separately by the method of least squares to yield two enthalpy values for each experiment. For the experiment in which silver was used as a calibrating substance, the value of k in equation 2-22 was determined and then used to calculate the entropy change for equation 4-5. The value of k was also used to calculate the pressures corresponding to the measured ion intensities. These pressures were then used in the third law method discussed in Chapter II, section B, to determine the enthalpy of vaporization. In most of the experiments discussed in this section, large numbers of intensity-temperature measurements were taken. The data for europium dicarbide are tabulated in Appendix E.

3. Individual Experiments

(a) Experiment MS-1

The carbon-lined molybdenum effusion crucible was filled with a portion of sample 1-44P and situated in the Knudsen source region of the mass spectrometer. After the Knudsen source region had been degassed at 900° for several hours, the cell temperature was increased and intensity data were collected as a function of temperature. When the instrument was left overnight, the sample was maintained at 800° by the hot filament. This procedure resulted in probable contamination of the sample since the liquid nitrogen source failed, resulting in the release of a large quantity of water vapor from the cold trap. Since the sample was exposed to air and to water vapor in the vacuum system the data obtained from this sample are probably not quantitatively accurate; however, they are presented as an indication of what might be expected in further experiments.

The data were plotted separately according to the day obtained. The results are summarized in Table XII. The two europium mass peaks, 151 and 153, were the major species observed in the spectrum, along with two much smaller peaks identified as europium dicarbide, masses 175 and 177. The intensity of these small peaks was less than one per cent of that of the europium peaks -- so low that a temperature dependence could not be measured. No other mass peaks (above background) were observed. The energy of the ionizing electrons was low enough (15 electron volts) so that no doubly charged ions would have been expected. None was observed.

(b) Experiment MS-2

The effusion crucible used previously was charged with a portion of sample 1-62P. Data were collected over a period of several days. On the second day, a capacitor in the power supply of the mass spectrometer failed. After the instrument was repaired, the operating parameters of the instrument were readjusted. For this reason, the data are broken down into two portions, those taken before and those taken after readjustment, and are listed under the headings MS-2a and MS-2b respectively in Table XIII. The data for MS-2a, when plotted as ln IT vs 1/T, fell on a straight line. All the data for MS-2b, when plotted similarly, lie on another straight line, even though they were taken on different days. Therefore, these data were treated as one set.

The enthalpy values for MS-2a are considered unreliable. The probable causes of unreliability were changes in the instrument prior to, and caused by, the failure of the capacitor.

A large peak corresponding to nitrogen, carbon monoxide, or both was observed at mass 28. Nitrogen is the major species present in the

Table XII. Summary of experiment MS-1

Day	Isotope Observed	Temperature Range °K	Enthalpy kcal./mole
1	Eu^{151}	1214 - 1369	37.6 ± 2.89[a]
1	Eu^{153}	1214 - 1369	38.4 ± 2.76
2	Eu^{151}	1204 - 1434	40.1 ± 1.87
2	Eu^{153}	1204 - 1434	43.7 ± 1.23
	$\Delta\ 1/T = 8.77 \times 10^{-6}$		

[a]Standard deviation

Table XIII. Summary of experiment MS-2

Number	Isotope Observed	Temperature Range ^{o}K	Enthalpy kcal./mole
MS-2a	Eu^{151}	1326 - 1451	61.43 ± 3.57[a]
MS-2a	Eu^{153}	1326 - 1451	57.02 ± 2.48
MS-2b	Eu^{151}	1326 - 1697	50.31 ± 1.35
MS-2b	Eu^{153}	1326 - 1697	51.68 ± 1.71
	Δ 1/T = 10.58 x 10^{-6}		

[a]Standard deviation

residual gas in the vacuum system. Its intensity should increase as the Knudsen source region is heated as a result of degassing of the radiation shields and vacuum chamber walls. Alcock, et al. (56) have shown that carbon monoxide is present when uranium dicarbide is heated; therefore, it would be expected here also. Since the instrument cannot distinguish between these two molecules, quantitative estimates of their relative proportions cannot be made.

Several times during the course of this experiment, the ion intensity of Eu^{151} was observed at constant temperature as a function of time. The results are shown in Table XIV. Several important observations can be made from these data. For periods of up to twenty-seven minutes, the temperature remained constant within the reading limits of the optical pyrometer. With the exception of the fifteen minute observation, the ion current remained constant with time, indicating a constant rate of effusion from the Knudsen cell. The fifteen minute observation showed an upward drift during the first half of the observation period and then remained constant. This drift may have resulted from a temperature drift, but the magnitude of the intensity change was greater than would be expected for the measured temperature change. Finally, when the temperature was returned to 1495° K, after sixteen hours at operating temperature, the ion intensity also returned to the initial value of 0.023 as indicated by the first and last entries in Table XIV. The constancy of the effusion rate indicates that equilibrium was maintained in the cell and that the dicarbide composition was not changing. Eick, Rauh and Thorn (57) have shown that in the uranium-carbon system, the sample composition changes during the vaporization process and that, as a result, the measured vapor pressure decreases with time, since equilibrium is

Table XIV. Data on the ion intensity of mass 151 as a function of time

Duration of Observation min.	Initial		Final	
	Ion Intensity nanoamps	Temperature °K	Ion Intensity nanoamps	Temperature °K
8	0.0236	1469	0.0234	1469
15	0.045	1581	0.053	1585
6	0.083	1589	0.082	1599
6	0.162	1677	0.162	1677
27	0.024	1465	0.023	1463

not established rapidly.

(c) Experiment MS-3

In this experiment, a portion of sample 2-19P was used. The method and operating conditions were the same as those described previously. I believe the results obtained in this experiment are all reliable. When these data were treated by the method of least squares, the enthalpy values for the disproportionation reaction (4-5) were found to be:

$$\Delta H^{o} = 52.10 \pm 0.61 \text{ kcal./mole} \quad ; \quad \text{mass } 151$$

and

$$\Delta H^{o} = 53.92 \pm 0.61 \text{ kcal./mole} \quad ; \quad \text{mass } 153.$$

There was insufficient residue to permit chemical analysis. X-ray powder diffraction analysis indicated graphite to be the only phase present in the residue which was not present in the starting material.

In this experiment, small peaks attributable to europium dicarbide were present, but the intensities could not be determined as a function of temperature since they were too low to measure accurately. No other europium containing species was observed. The ion intensity of Eu^{151} was observed at constant temperature as a function of time and was found to be constant, as before.

(d) Experiment MS-4

In this experiment, a silver wire was cleaned by abrasion and heat. It was then placed in a molybdenum crucible, similar to the one used previously, but without the carbon liner and with a larger orifice (1.181 mm. as compared to 0.803 mm.) The crucible was placed in the mass spectrometer and the intensities of Ag^{107} and Ag^{109} were observed

as a function of temperature. The ion intensity-temperature data are listed in Appendix E.

As is indicated in Appendix E, a visible coating appeared on the window at a cell temperature of 1372° K. The temperature was immediately reduced to prevent the formation of an extensive deposit. The window and prism correction measured before the experiment was applied to the data taken before extensive deposit formation; and the correction measured after the experiment was applied to the data taken after the visible deposit formed. Admittedly, this procedure introduces some error, but since deposit formation occurs more rapidly at high temperatures than at low temperatures, less error would be introduced than if average values were used.

Prior to this experiment, a shutter was installed between the Knudsen source and the ionization chamber of the mass spectrometer. When this shutter was closed during operation, the intensity of the silver peaks fell to zero indicating that the total intensity of the peaks at masses 107 and 109 resulted from atoms leaving the Knudsen cell.

The enthalpies of vaporization calculated from these data are:

$$\Delta H^{\circ} = 74.23 \pm 1.13 \text{ kcal./mole} \quad ; \text{ mass } 107$$

$$\Delta H^{\circ} = 74.03 \pm 0.86 \text{ kcal./mole} \quad ; \text{ mass } 109.$$

These values are much higher than the accepted value of 64.4 kcal./mole calculated from the data in Stull and Sinke (58). Mrs. Rebecca Jacobs, using the same instrument and the same crucible, also experienced difficulty obtaining reliable data for the vaporization of silver. She also investigated the vaporization of copper and obtained data in agreement with reported values.

There are some possible explanations for the discrepancy in the data. A temperature error could have resulted from the formation of a silver deposit on the window. Every effort was made to measure the transmittance of the deposit through the same area as was used in the temperature measurement. However, since this area is small, exact duplication of the area is difficult. The thickness of the deposit decreases rapidly outward from the center, and thus, a small shift in the measuring point would result in a large error in the measured transmittance. A low correction factor based on this transmittance would result in calculated temperatures lower than the true temperatures. The high temperature measurements are more affected by transmittancy error since deposit formation is extensive only at high temperatures. If temperatures lower than the true temperatures are used for the high temperature points, the slope of the curve ln IT vs 1/T is increased, resulting in a high value for the calculated enthalpy. Another possible source of error may have resulted from the use of too small a silver sample. If the volume of silver present were insufficient to cover the bottom of the crucible, the orifice would "see" both silver and molybdenum. The result would be that the distribution of particles leaving the effusion cell would no longer follow the cosine law. Since ninety per cent of the silver in the crucible was vaporized, a changing sample area would change the distribution of particles effusing from the cell.

Since Mrs. Jacobs and the author both experienced, under similar conditions, trouble in the vaporization of silver, and since she obtained reliable data for the vaporization of copper, it is assumed that it was something in the design of the experiments, and not the mass spectrometer itself, which was at fault.

(e) Experiment MS-5

In this experiment, a portion of sample 2-19P was placed in the Knudsen cell along with 6.04 mg. of silver wire. After the crucible had been outgassed, the temperature of the cell was rapidly increased to 1367^{o} K and the intensity of Ag^{107} was observed as a function of time. The Ag^{107} pressure in the Knudsen cell, calculated from the time required to vaporize all of the silver, was 4.06×10^{-5} atm., as compared to the accepted value of 3.77×10^{-5} atm. at this temperature. The sensitivity of the mass spectrometer was calculated according to equation 2-20:

$$k = \frac{\sum_j I_{Ag} \Delta t_j / T}{P_{Ag}} \qquad (4\text{-}6)$$

and was found to be 2.488×10^{2} nanoamps/atm. of Ag^{107}.

After the silver had vaporized, the intensities of the europium peaks were observed in the usual manner.

The pressures corresponding to the observed intensities were calculated according to equation 4-7:

$$P = 1/r_i k \ (\sigma_{Ag}/\sigma_{Eu}) \ (I_{Eu}/I_{Ag}) \ (S_{Ag}/S_{Eu}) I^{*}_{Eu}. \qquad (4\text{-}7)$$

The ratio of multiplier sensitivities (S_{Ag}/S_{Eu}) was taken as unity. The ratio of the cross section (σ_{Ag}/σ_{Eu}) was estimated from the metal-metal distances in the crystal as given by Pauling (59). The resulting ratio was:

$$\sigma_{Ag}/\sigma_{Eu} = (2.878/4.168)^2 = 0.4768. \qquad (4\text{-}8)$$

The ln fT was plotted against 1/T, and the enthalpy of vaporization calculated from the slope was:

$$\Delta H = 49.17 \pm 0.77 \text{ kcal./mole.}$$

Figure 4 shows this plot for Eu^{151}. The scatter about the line in this graph is typical of the scatter found in the mass spectrometric data from the other experiments. The entropy was calculated from the intercept using the constant K from the equations:

$$P = KI_{Eu}T_{Eu} \tag{4-9}$$

and

$$\ln P = \ln IT + \ln K = - \Delta H/RT + \Delta S/R \tag{4-10}$$

so that

$$\text{Intercept} = \Delta S/R - \ln K. \tag{4-11}$$

K was calculated to be 2.9317×10^{-6} for mass 151 and 2.6852×10^{-6} for mass 153. The resulting value for the entropy for reaction 4-5 is:

$$\Delta S = 18.43 \pm 0.57 \text{ e.u.}$$

The error in both the enthalpy and entropy is the standard deviation obtained from the least squares treatment.

During the experiment, the intensities of the peaks at masses 151, 28 and 18 were measured as a function of the energy of the ionizing electrons. The data, plotted as ion intensity versus electron energy, are shown in Figure 5.

When the straight line portions of the curves were extrapolated to zero ion intensity, electron volt values of 8.0, 16.0 and 18.6 were found for masses 151, 18 and 28 respectively. If the peak at mass 28

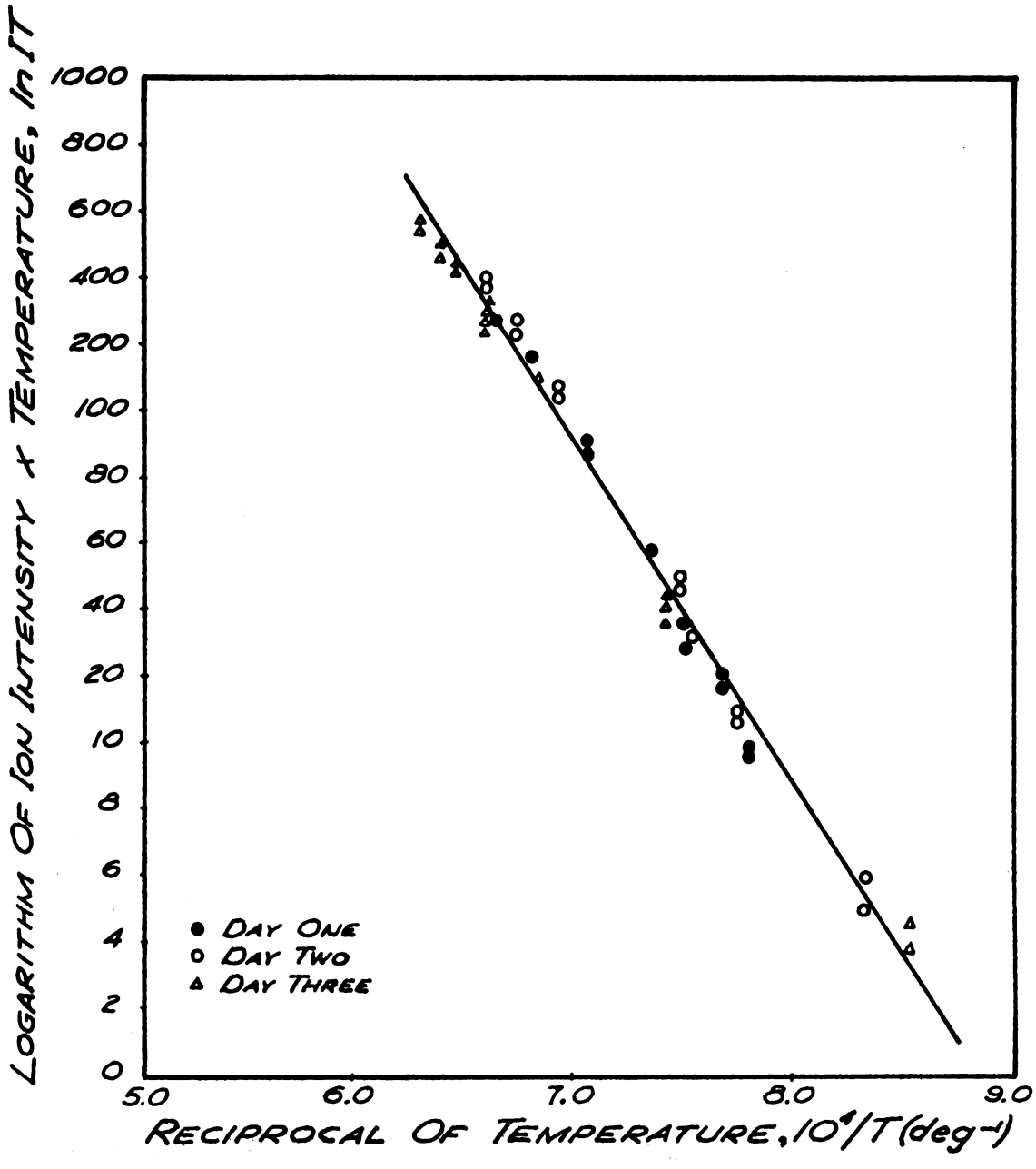


FIGURE 4 THE TEMPERATURE DEPENDENCE OF THE EUROPIUM ION INTENSITY.

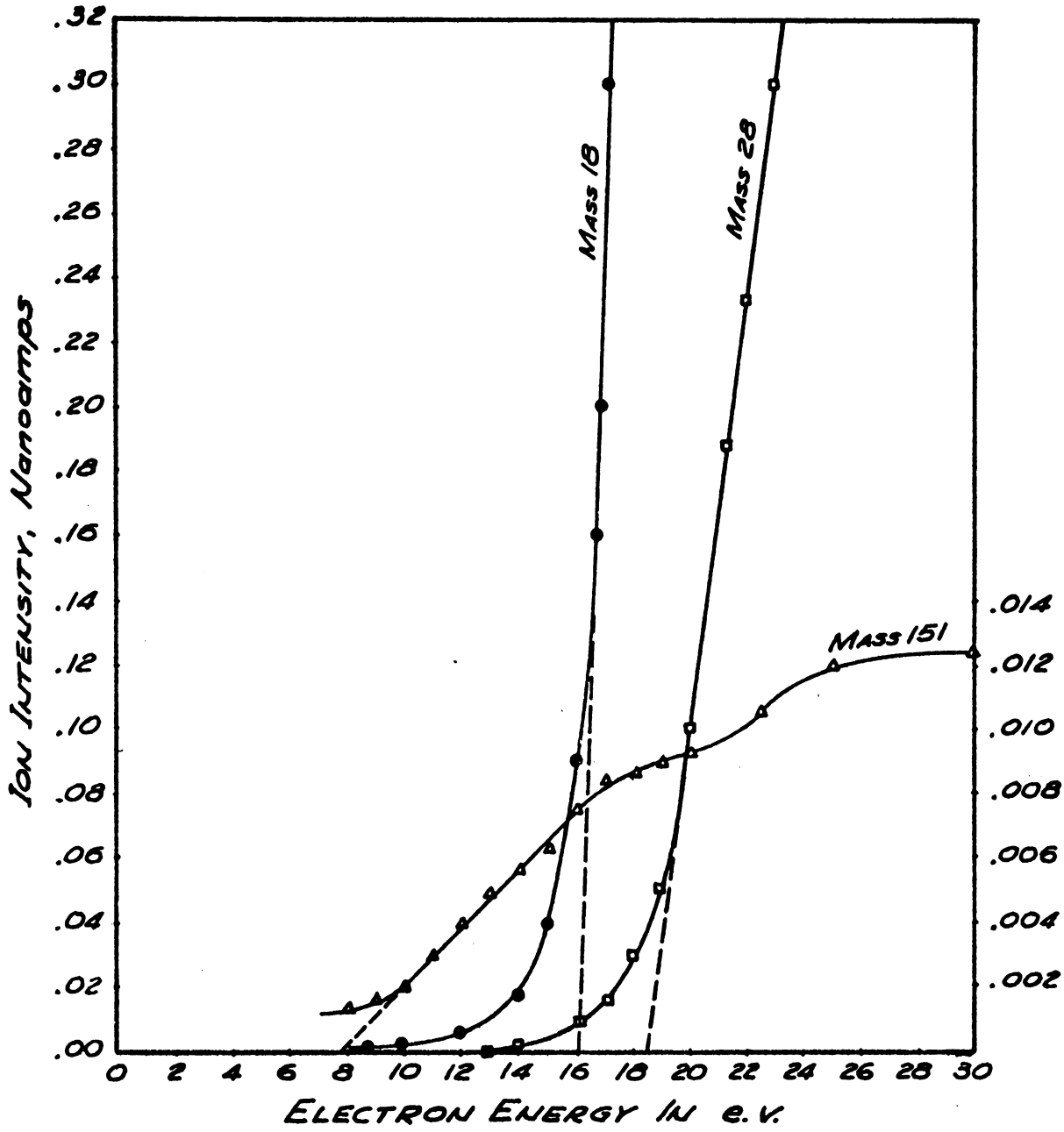


FIGURE 5 APPEARANCE POTENTIAL CURVES

is assumed to be nitrogen, the intercept for this curve should be 15.6 e.v. By applying the difference between the measured appearance potential and the ionization potential for nitrogen as a correction factor to the other two values, ionization potentials of 5.0 e.v. and 13.0 e.v. were obtained for europium and water, respectively. The accepted values are 5.6 e.v. and 12.8 e.v. The close agreement between accepted and calculated ionization potentials indicates that europium atoms are present as a component of the vapor from the Knudsen cell and that the europium atoms do not result from fragmentation of some higher molecular weight species.

In this experiment, an attempt was made to measure the concentration of gaseous europium dicarbide as a function of temperature. The spectrum was scanned with low energy ionizing electrons (10 e.v.) in order to prevent fragmentation of any unstable dicarbide molecule.

A typical mass spectrum of the europium-europium dicarbide peaks obtained at 1479° K is shown in Figure 6. The intensities of the dicarbide peaks obtained at this and other temperatures are on the order of one per cent of the intensity of the europium peaks. The dicarbide peaks were not present when the ionization energy was raised to the normal operating value of 18.0 e.v. Thus, gaseous europium dicarbide is present in the vapor phase above solid europium dicarbide, but the molecule is quite unstable.

After completion of the experiment, there was insufficient residue to permit chemical analysis. X-ray powder diffraction analysis showed that graphite was the only material present in the residue which was not present in the starting material, as was typical of previous experiments.

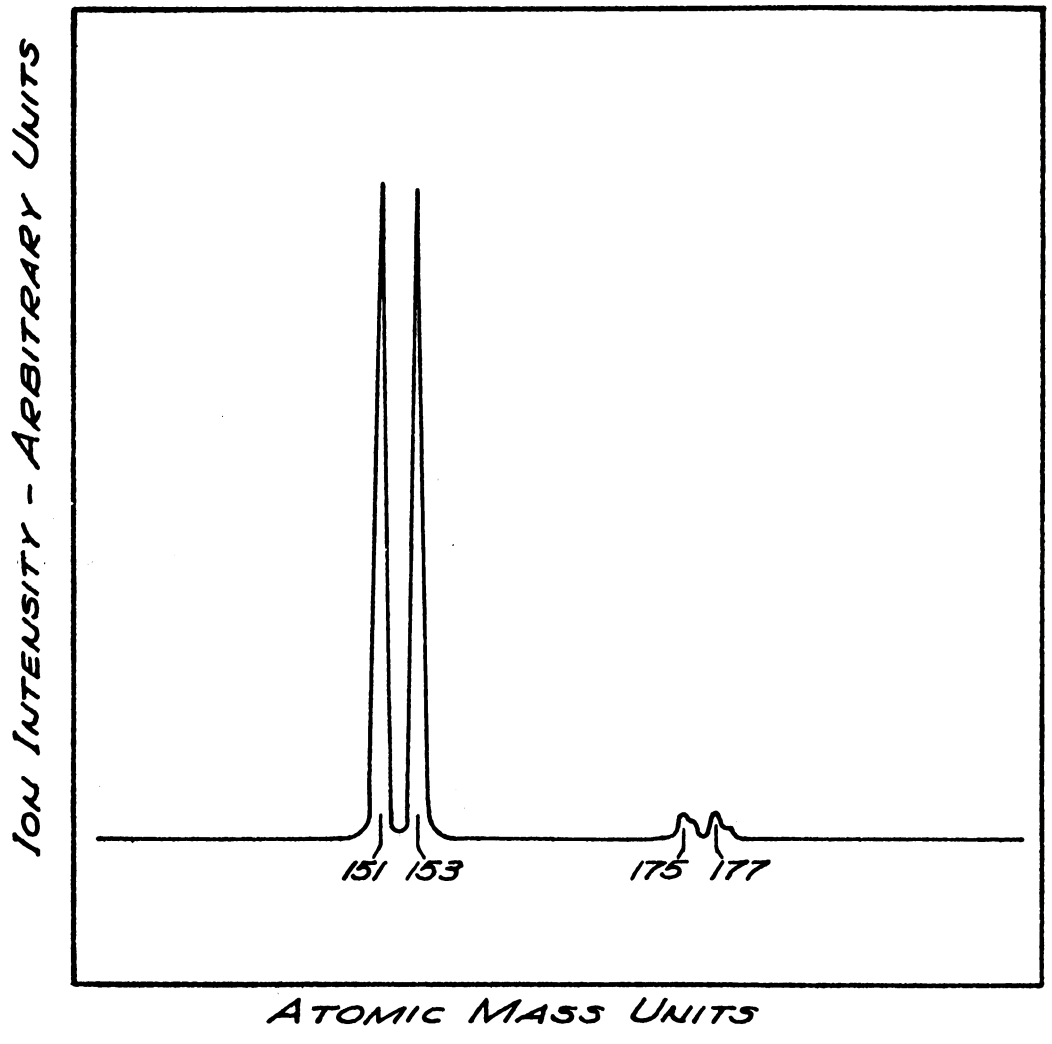


Figure 6 The Mass Spectrum Of Europium - Europium Dicarbide.

4. Treatment of data

(a) Calculation of ΔH_F

The data for the enthalpy of vaporization of europium dicarbide from experiments MS-2, MS-3 and MS-5 were combined with the enthalpy of vaporization of europium (42.066 kcal./mole) reported by Spedding, Hanak and Daane (54). The resulting enthalpies of formation, assuming ΔCp is zero, are for equation 4-12:

$$Eu_{(s)} + 1.87\ C_{(s)} \rightleftarrows EuC_{1.87(s)} \qquad (4\text{-}12)$$

$$\Delta H^{\circ}_{298} = -8.93 \pm 2.18 \text{ kcal./mole} \quad ; \text{MS-2}$$

$$\Delta H^{\circ}_{298} = -11.04 \pm 0.86 \text{ kcal./mole} \quad ; \text{MS-3}$$

$$\Delta H^{\circ}_{298} = -7.10 \pm 0.77 \text{ kcal./mole} \quad ; \text{MS-5.}$$

(b) Calculation of the Free Energy Functions

It was shown that the vaporization of europium dicarbide proceeds according to the reaction:

$$EuC_{1.87} \rightleftarrows Eu_{(g)} + 1.87\ C_{(s)}. \qquad (4\text{-}5)$$

The second law value of the enthalpy of vaporization obtained from a plot of ln IT vs 1/T can be checked by means of a third law calculation based on the equation:

$$\Delta H^{\circ}_{298} = -T\ [\Delta(G^{\circ}_{T} - H^{\circ}_{298}/T)] - RT \ln P. \qquad (4\text{-}13)$$

The necessary free energy functions were taken from published reports or estimated as follows:

1) $Eu_{(s\ \&\ g)}$

Taken from Stull and Sinke (58).

2) $\underline{Ca_{(s)}}$

Taken from Stull and Sinke (58).

3) Graphite

Taken from Stull and Sinke (58).

4) $\underline{EuC_{2(s)}}$

No data were available for this compound; therefore, the free energy functions were estimated as a function of temperature from the data on calcium carbide given by Kelly (60) and Kelly and King (61). The calculations were based on the hypothetical reaction:

$$CaC_{2(s)} + Eu_{(s)} \rightarrow EuC_{2(s)} + Ca_{(s)}. \qquad (4\text{-}14)$$

The free energy function for europium dicarbide then becomes:

$$fef_{EuC_2} = fef_{CaC_2} - fef_{Ca} + fef_{Eu}. \qquad (4\text{-}15)$$

The estimated values of the free energy function for europium dicarbide were combined with the free energy functions for europium gas and graphite to give the change in the free energy function for reaction 4-5. The results are shown in Table XV and Figure 7. The enthalpy of the vaporization reaction was then calculated using these data and the pressure data from experiment MS-5. The results shown in Table XVI lead to the average value:

$$\Delta H^{o}_{298} = 51.22 \pm 0.80 \text{ kcal./mole.}$$

This value, combined with the enthalpy of vaporization for europium,

Table XV. Free energy functions for EuC_2

T °K	-fef $EuC_{2(s)}$ cal./deg.-mole	-fef $Eu_{(g)}$ cal./deg.-mole	-fef Graphite(s) cal./deg.-mole	-Δfef cal./deg.-mole
1100	27.01	47.96	3.31	20.70
1200	28.21	48.29	3.60	20.47
1300	29.34	48.59	3.86	20.18
1400	30.18	48.87	4.11	20.15
1500	31.42	49.15	4.37	19.71
1600	32.37	49.41	4.61	19.51

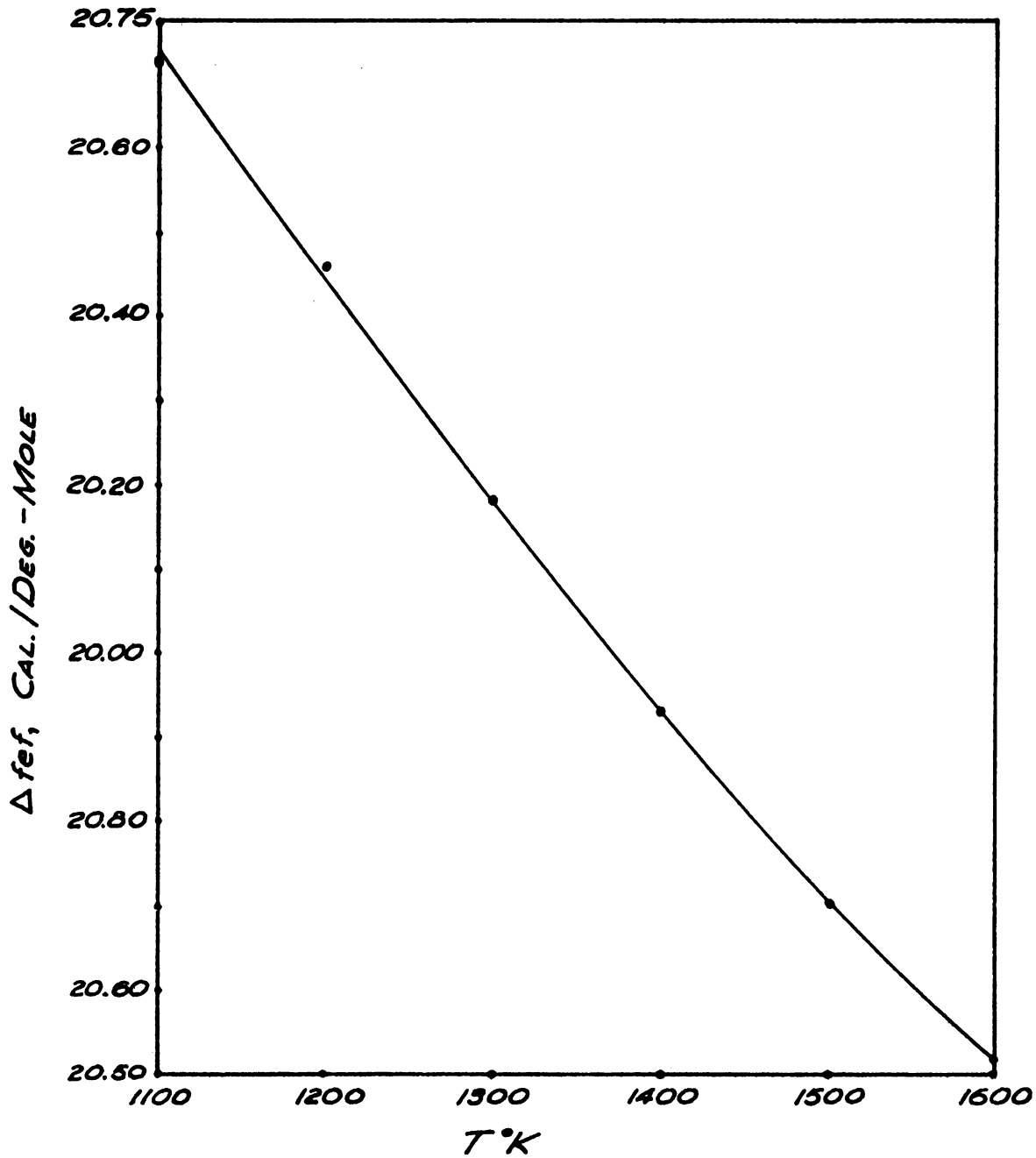


FIGURE 7 Δfef FOR EUROPIUM DICARBIDE AS A FUNCTION OF TEMPERATURE

Table XVI. Third law values of the enthalpy of vaporization for EuC_2

Temperature °K	From mass 151 ΔH^o_{298} kcal./mole	From mass 153 ΔH^o_{298} kcal./mole
1263	51.875	52.336
1263	51.975	51.705
1298	51.677	51.627
1298	51.299	50.128
1339	51.253	51.568
1339	51.731	50.043
1372	51.061	51.177
1372	51.061	51.177
1401	51.004	51.071
1401	50.834	50.946
1464	50.764	50.933
1464	50.764	50.805
1335	51.242	51.772
1335	51.242	51.227
1139	51.668	51.861
1214	51.697	51.648
1214	51.727	51.648
1280	51.965	51.573
1280	51.920	51.598
1350	51.000	51.051
1350	51.000	51.081
1412	50.822	50.638
1412	50.673	50.638
1479	50.992	50.858
1479	50.868	50.932
1537	50.978	50.755
1537	50.846	50.886
1190	50.905	51.063
1190	51.239	51.397
1356	51.510	51.408
1356	51.403	51.408
1457	51.215	51.308
1457	51.053	51.308
1518	51.062	50.932
1518	51.002	50.932
1554	51.052	51.194
1554	51.281	51.237
1568	50.989	51.187
1568	51.029	51.187
1587	51.257	51.275
1587	51.082	51.193
1520	51.248	51.272
1520	51.443	51.272
1356	51.894	51.915
1356	51.852	52.049

Mean of all values: 51.22 kcal./mole; Standard deviation: 0.80 kcal./mole

yields a value of -9.16 ± 0.80 kcal./mole for the enthalpy of formation of europium dicarbide.

The pressure data from experiment E-1 were used to calculate enthalpies of vaporization. The results are given in Table XVII. These data show considerable scatter as would be expected from the scatter in the pressure data used in the calculations. Comparison of these enthalpies with those calculated from experiment MS-5 shows these data to be, in general, higher than the latter. This is expected, since the "bouncing", found in experiments E-1 and E-2, would cause the calculated pressure to be low.

Even though these data show considerable scatter, the average value (56.29 kcal./mole) is close to the average value calculated from the data from experiment MS-5 (51.22 kcal./mole). This closeness indicates that the pressures calculated from the mass spectrometric data are true pressures and thus, that the enthalpy of vaporization obtained from these data is correct.

In summary, the second law method yields the following heats of vaporization for europium dicarbide:

51.00 ± 2.18 kcal./mole ; MS-2

53.11 ± 0.86 kcal./mole ; MS-3

49.17 ± 0.77 kcal./mole ; MS-5.

The average value is 51.09 ± 1.42./mole. The third law calculation of the enthalpy of vaporization yields a value of 51.22 ± 0.80 kcal./mole, in excellent agreement with the second law value. The enthalpy of formation calculated for europium dicarbide from the second law is

Table XVII. Third law values of the enthalpy of vaporization for EuC_2 calculated from experiment E-1

Temperature °K		ΔH°_{298} kcal./mole
1404		54.61
1450		59.15
1321		53.69
1609		61.49
1672		57.71
1578		54.39
1335		54.26
1246		49.67
1486		57.34
1661		61.28
1503		58.51
1542		59.75
1625		53.10
1358		52.79
	mean	56.29

-9.02 ± 1.42 kcal./mole and is in excellent agreement with the third law value of -9.16 ± 0.80 kcal./mole.

Chupka and co-workers (22) found the heat of formation of lanthanum dicarbide to be -44 kcal./mole; Jackson and co-workers (24) found the heat of formation of gadolinium to be -26 kcal./mole. The heat of formation of calcium carbide is listed (62) as -15 kcal./mole. Comparison of these numbers with the heat of formation of europium dicarbide, -9.09 kcal./mole, supports the conclusion that europium dicarbide is more like the alkaline earth dicarbides than the other lanthanon dicarbides.

The pressure of europium gas in equilibrium with europium dicarbide may be described by the equation:

$$\ln_e P(atm) = - 23709 \pm 715/T + 9.270 \pm 0.886.$$

Thw slope of this line is the average value of the slope for experiments MS-2b, MS-3 and MS-5. The intercept is from the data from experiment MS-5.

5. Analysis of Errors

An examination of the errors involved in the determination of the experimental quantities should allow one to ascertain whether or not the scatter in the data plotted in Figure 4 can be ascribed to random errors in the measurements or whether other factors were involved. This evaluation can be made best by examining the error in one of the representative datum. The point selected is the one occurring at T = 1070° with intensity 0.031 nanoamps.

The observed scatter results from two sources. One is the error in measurement of the ion intensity; the other is the error in measurement of the temperature. The measured intensity was 0.031 ± 0.003; the

temperature $1070^{o} \pm 5.0^{o}$. The standard deviation of the term ln IT, as calculated from the computer program for the least squares treatment of the data, is ln IT = 3.7657 ± 0.112 or IT = 40.68 ± 1.12. The contribution from the error in temperature measurement is as follows: For an error, ΔT, in the temperature, the corresponding displacement is Δ 1/T which equals Δ T/T^2. From the estimated error in the temperature, the uncertainty in the reciprocal of the temperature is $7.37 \pm 0.03 \times 10^{-4}$.

Examination of Figure 4 shows that most of the points fall within the expected deviation. We can thus conclude that there are no random errors unaccounted for in these experimental data.

The determination of the pressure from the mass spectrometer with silver causes no additional error in the determination of the slope of the resulting line since a constant factor is applied to all of the data. However, an error in this constant will affect the intercept of the ln P vs 1/T graph and thus, the entropy calculated from this intercept.

According to Chupka and Inghram (25), the ratio of the ionization cross section in equation 4-7:

$$P = [(1/r_i k)(\sigma_{Ag}/\sigma_{Eu})\ (1/T_{Ag})]\ I_{Eu} T_{Eu} \qquad (4\text{-}7)$$

may be in error by as much as a factor of two. If this is the case, this error will be, by far, the largest error in any of the above terms. The excellent agreement between the second and third law values for the enthalpy of vaporization indicates that pressures calculated from the above equation are very close to the true pressures, and that this ratio is substantially correct. However, if we assume that this error is large, we can calculate the maximum expected error in the entropy,

neglecting the error in the other quantities since they are small. The bracketed term in equation 4-7 was calculated to be $2.932^{+2.932}_{-1.466} \times 10^{-6}$ for the data for mass 151. The intercept and the error in it from the ln IT vs 1/T graph of data of experiment MS-5 are 21.90 ± 0.19. Combination of this intercept and its error, with K and its estimated error, results in an entropy and error of $\Delta S^{o}_{298} = 18.20 \pm 1.75$ e.u. When this value is combined with the data for mass 153, the resulting average entropy and its error are: $\Delta S^{o}_{298} = 18.43 \pm 1.75$ e.u.

E. Suggestions for Further Research

As has already been indicated, the europium dicarbide samples used in this study always contained small quantities of another europium-carbon phase. Additional studies are necessary to prepare pure europium dicarbide and to determine the composition of this minor phase. A complete phase study of this system should be instructive. One method for accomplishing this goal would be to prepare samples of various europium to carbon ratios, in a system that could be quenched rapidly to freeze in any metastable phase that might be present at high temperatures.

If a pure sample of europium dicarbide could be prepared, its heat capacity should be determined as a function of temperature in order to obtain accurate values for the free energy function. Most of the thermodynamic functions reported for europium are estimates. A determination of these quantities should be made.

Europium dicarbide should be examined by Knudsen techniques involving collection and subsequent analysis of the effusate in order to determine more accurately the decomposition pressure. One method for

accomplishing this would be to redesign the apparatus used in this study in order to cool more effectively the targets used to collect the effusate.

Finally, the europium-oxygen-carbon system should be studied to determine the effect of small quantities of oxygen on the stability of the solid phase.

LITERATURE CITED

1. O. Pattersson, Bericht., 28, 2419 (1895).

2. H. Moissan, Comp. Rend., 123, 148 (1896).

3. Ibid., 131, 595 (1900).

4. H. Moissan and A. Etard, Comp. Rend., 122, 573 (1896).

5. M. A. Damiens, Comp. Rend., 157, 214 (1913).

6. M. A. Damiens, Ann. Chim., 10, 137 (1918).

7. M. von Stackelberg, Z. Electrochem., 37, 542 (1931).

8. M. von Stackelberg, Z. Phys. Chem., Abt. B9, 437 (1930).

9. L. K. Frevel, H. W. Rinn and H. C. Anderson, Anal. Chem., 18, 83 (1946).

10. M. J. Villelume, Comp. Rend., 232, 235 (1951).

11. F. Gaume-Mahn, Bull. Soc. Chim. France, 1956, 1862.

12. M. Atoji, K. Gschneidner, Jr., A. H. Daane, R. E. Rundel and F. H. Spedding, J. Am. Chem. Soc., 80, 1804 (1958).

13. F. H. Spedding, K. Gschneidner, Jr., and A. H. Daane, AMIE Trans., 215, 192 (1959).

14. F. H. Spedding, K. Gschneidner, Jr., and A. H. Daane, J. Am. Chem. Soc., 80, 4499 (1958).

15. R. C. Vickery, R. Sedlacek and A. Ruben, J. Chem. Soc., 1959, 498.

16. Ibid., 503.

17. Ibid., 505.

18. N. N. Greenwood and A. J. Osborn, J. Chem. Soc., 1961, 1775.

19. G. V. Samsonov, T. Ya. Kosolapova, M. D. Lyutoga and G. N. Makarenko, Analit. Khim., 1963, 8.

20. E. A. Dancy, L. H. Everett and C. L. McCabe, AMIE Trans., 224, 1095 (1962).

21. M. Atoji, J. Chem. Phys., 35, 1950 (1961).

22. W. A. Chupka, J. Berkowitz and M. G. Inghram, J. Phys. Chem., 62 611 (1958).

23. G. F. Wakefield, Dissertation Abstr., 22, 3433 (1962).

24. D. D. Jackson, G. W. Barton, O. H. Krikorian and R. S. Newbury, University of California Radiation Laboratory, UCRL - 6701 (1962).

25. W. A. Chupka and M. G. Inghram, J. Chem. Phys., 21, 371 (1953).

26. Ibid., 1313 (1953).

27. W. A. Chupka and M. G. Inghram, J. Phys. Chem., 59, 100 (1955).

28. R. E. Honig, J. Chem. Phys., 22, 126 (1954).

29. R. J. Thorn and G. H. Winslow, J. Chem. Phys., 26, 186 (1957).

30. D. White, A. Sommer, P. N. Walsh and H. W. Goldstein, in Advances in Mass Spectrometry, vol. 2, Pergamon Press, New York, 1962.

31. H. W. Goldstein, P. N. Walsh and D. White, J. Phys. Chem., 65, 1400 (1961).

32. D. White, P. N. Walsh, H. W. Goldstein and D. F. Dever, ibid., 1404 (1961).

33. M. G. Inghram and J. Drowart, Mass Spectrometry Applied to High Temperature Chemistry, Proceedings of an International Symposium on High Temperature Technology, McGraw-Hill, 1960, pp. 219 - 240.

34. Chem. Abstr., 55, 2304 (1961).

35. M. Knudsen, Ann. Physik., 28, 75 (1909).

36. Ibid., 999 (1909).

37. Ibid., 29, 179 (1909).

38. J. Bockris, J. L. White and J. D. Mackenzie, Physiocochemical Measurements at High Temperatures, Butterworth Scientific Publications, London, 1959.

39. K. D. Carlson, Argonne National Laboratory Report, ANL - 6156 (1960).

40. J. G. Edwards, Ph.D. Thesis, Oklahoma State University, Stillwater, Oklahoma (1964).

41. R. D. Freeman and J. G. Edwards, Technical Documentary Report, ASD - TDR - 63 - 754 (1963).

42. G. L. Galloway and H. A. Eick, J. Inorg. Nucl. Chem., in press.

43. L. H. Spinar and J. L. Margrave, Spectrochem. Acta, 12, 244 (1958).

44. W. L. Winterbottom and J. P. Hirth, J. Chem. Phys., 37, 784 (1962).

45. M. G. Inghram, W. A. Chupka and R. F. Porter, J. Chem. Phys., 23, 2159 (1955).

46. J. W. Otvös and D. P. Stevenson, J. Am. Chem. Soc., 78, 546 (1956).

47. W. C. Wiley, Science, 124, 817 (1956).

48. W. C. Wiley and I. H. McLaren, Rev. Sci. Instr., 26, 1150 (1955).

49. R. W. Rinehart, Anal. Chem., 26, 1820 (1954).

50. W. J. Youden, Statistical Methods for Chemists, John Wiley & Sons, New York, 1951.

51. R. A. Kent, Ph.D. Thesis, Michigan State University, East Lansing, Michigan (1963).

52. G. P. Palenik and J. C. Warf, Inorg. Chem., 1, 345 (1962).

53. H. V. Svec, J. Capellen and F. E. Saalfeld, J. Inorg. Nucl. Chem., 26, 721 (1964).

54. F. H. Spedding, J. J. Hanak and A. H. Daane, AMIE Trans., 212, 379 (1958).

55. H. T. Hall, J. D. Barnett and L. Merrill, Science, 139, 111 (1963).

56. C. B. Alcock, H. A. Eick, E. G. Rauh and R. J. Thorn, A Comparison of the Calculated and Observed Vaporization Behavior of the Uranium Dicarbide Phase, Nuclear Metallurgy, vol. X, 1964.

57. H. A. Eick, E. G. Rauh and R. J. Thorn, Vaporization Studies of the Uranium Dicarbide Phase, Thermodynamics of Nuclear Materials, IAEA, Vienna, 1962.

58. G. R. Stull and G. C. Sinke, Thermodynamic Properties of the Elements, American Chemical Society, Washington, D. C., 1956.

59. L. Pauling, The Nature of the Chemical Bond, Cornell University Press, Ithica, New York, 1960.

60. K. K. Kelley, Contributions to the Data on Theoretical Metallurgy, XII, U. S. Bureau of Mines Bulletin 584, (1960).

61 K. K. Kelley and E. G. King, Contributions to the Data on Theoretical Metallurgy, XIV, U. S. Bureau of Mines Bulletin 592 (1961).

62. E. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine and I. Jaffe, Circular of the National Bureau of Standards, 500, 1952.

63. E. G. Rauh, R. C. Sadler and R. J. Thorn, Argonne National Laboratory Report, ANL - 6536 (1962).

APPENDICES

APPENDIX A

Table AI. Correction for Leeds and Northrup Pyrometer Serial No. 1619073

Low Range		High Range	
$T^{o}C_{Scale}$	$T^{o}C_{NBS}$	$T^{o}C_{Scale}$	$T^{o}C_{NBS}$
800	796	1100	1092
850	845	1200	1189
900	893	1300	1289
950	943	1400	1391
1000	994	1500	1494
1050	1045	1600	1598
1100	1097	1700	1702
1150	1149		
1200	1201		
1225	1226		

APPENDIX B

THE MASS SPECTROMETER KNUDSEN SOURCE

The high temperature Knudsen source constructed by the author for these studies was patterned after a model lent to Dr. H. A. Eick by Mr. E. G. Rauh of the Argonne National Laboratory. The details of this source have been reported by Rauh, Sadler and Thorn (63). The physical arrangement of this source is shown in Figure B-1.

The source used in this study was modified by replacing the helical filament with one of a hair pin design, as recommended by Mr. Rauh.

The source is shown standing on a lucite base which serves to support it when it is out of the mass spectrometer. The assembly is supported in the mass spectrometer by a stainless steel plate (A) through which pass six electrical connections and one movable rod (B) which is used to tilt the assembly for alignment with the mass spectrometer slit. Above this plate, a stainless steel ring (C) is supported on three 2.54 mm. (0.100") diameter tungsten legs, one of which is attached to the movable rod (B). This ring serves both as support for the assembly and for electrical isolation in conjunction with the three boron nitride plated (D). Immediately above the boron nitride plates are four tantalum radiation shields (E) spun from 0.5 mm. (0.020") sheet. The crucible is supported on three 2.54 mm. (0.100") tungsten legs which are pointed to reduce the contact area, and consequently, the heat transfer down these legs.

The filament (F) around the crucible (G) is made by bending 0.037 mm. (0.015") diameter tungsten wire in the form of a continued hair pin. It is supported on nine 2.54 mm. (0.100") diameter tungsten rods, two of which serve as electrical conductors. The filament and crucible are

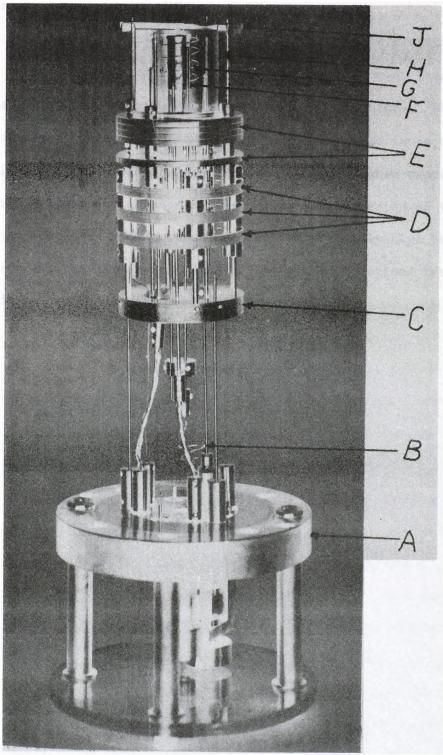


Figure B-1. The Mass Spectrometer Knudsen Source Assembly.

surrounded by a molybdenum radiation shield (H) which in turn supports two tantalum radiation shields (J).

In the initial construction, the three plates (D) were machined from Lava - Grade A. (American Lava Corporation, Chattanooga, Tennessee). This material, a hydrous aluminum silicate, is easily machined. When fired, it expands slightly and becomes very hard. Lava was found unsuitable since it apparently absorbs large quantities of gas when exposed to air. This absorbed gas is then released over a long period of time as the Lava is heated in vacuum, producing an objectionably high background pressure in the mass spectrometer. New plates, machined from boron nitride, eliminated this problem.

APPENDIX C

THE ELECTRON BOMBARDMENT POWER SUPPLY

The plans for the power supply were furnished by Mr. E. G. Rauh of Argonne National Laboratory. The schematic diagrams for the power supply are shown in Figures C-1 and C-2. These diagrams were followed exactly with the exception of the shield bias supply which was omitted entirely since it was not needed for the intended applications.

The basic operation of the power supply is as follows: The filament supply (Figure C-2), a low voltage high current transformer, supplies current to heat the filament in the Knudsen source to temperatures at which thermionic emission of electrons occurs. In manual control operation, the "set power" circuit supplies a selected potential to the input of the operational amplifier, which in turn supplies current to the Vectrol thyratron grid controls in the D. C. power circuit (Figure C-1). The grid controls in turn apply a potential to the grids of the thyratron tubes. The phase of this signal is varied with respect to the phase of the plate voltage, thereby causing the tubes to conduct for a certain fraction of a cycle. This fraction depends on the relative phase angles of the grid and plate voltages. The direct current output from the thyratrons is filtered and applied between the filament and crucible of the Knudsen source; the crucible being positive with respect to the filament. The electrons resulting from the thermionic emission of the filament are accelerated by this potential and gain kinetic energy which they release to the crucible upon impact, thereby heating the crucible.

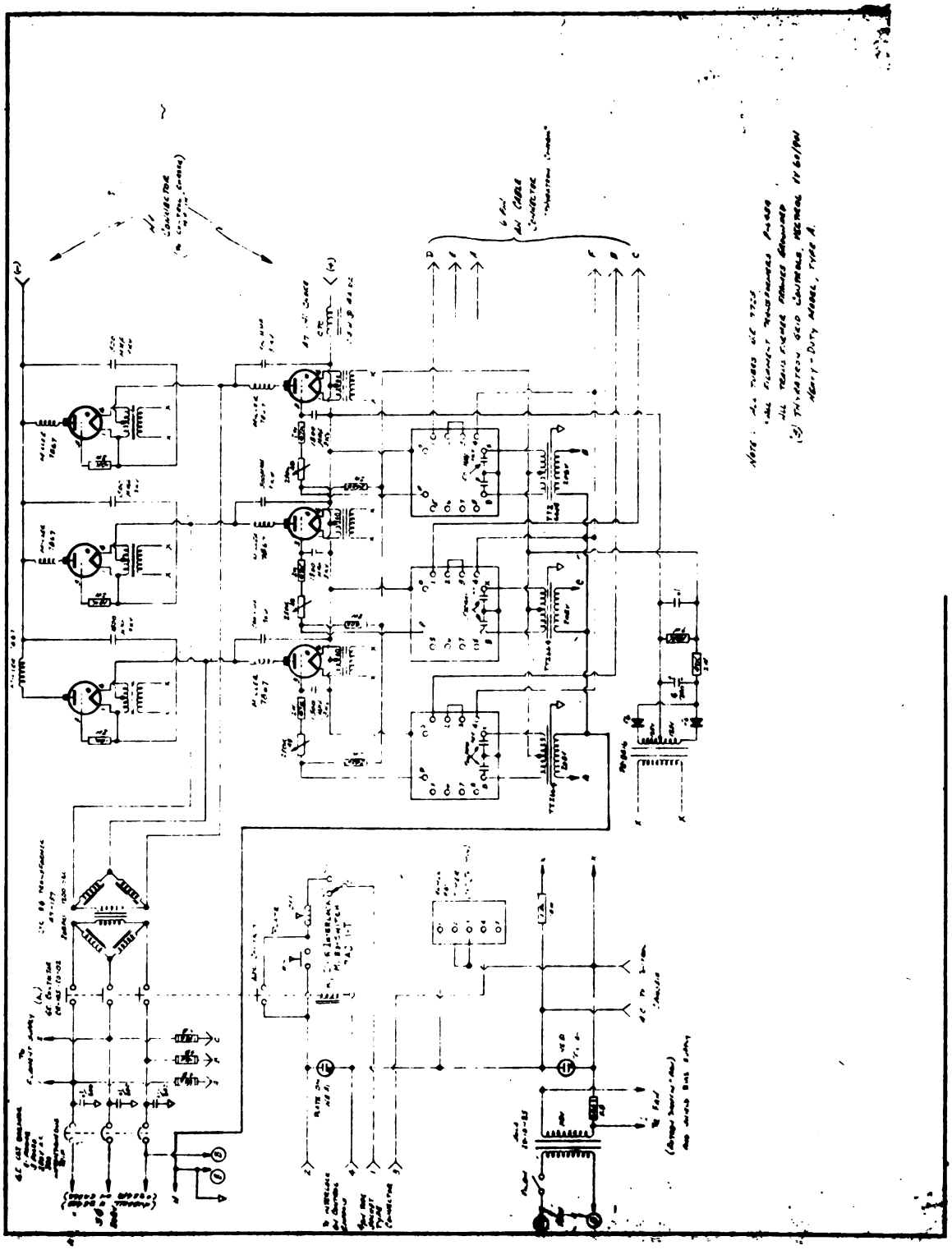


Figure C-1. Electron Bombardment Power Supply - Power Circuit

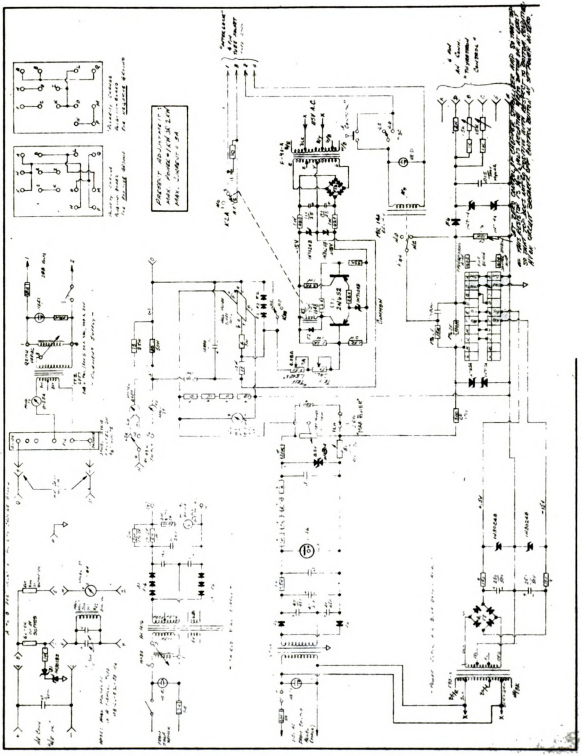


Figure C-2. Electron Bombardment Power Supply - Control Circuit

When operated manually, the potential between the filament and crucible is held constant. As the crucible heats, radiation from the crucible supplies additional heat to the filament, resulting in greater thermionic emission of electrons. These electrons are accelerated and heat the crucible to a higher temperature. Thus a cycle sets in; the crucible temperature increases rapidly and excessive current flows in the power supply. This condition is termed "run-away".

To prevent "run-away", a Hall Multiplier (Siemens Type MB26-EI-38/MU), shown in Figure C-2, is placed in the direct current circuit in such a manner that a voltage which is proportional to the D. C. potential between the filament and crucible is impressed across the coil of the multiplier. A current which is proportional to the bombarding electron current is also passed through the Hall probe. The Hall Multiplier operates in such a manner that the output of the Hall probe is proportional to the product of the voltage across the multiplier coil and the current through the probe.

The output of the Hall probe is added algebraically to the output of the "set power" circuit. This difference-signal is then amplified by the operational amplifier, now operating at a higher gain since the difference signal is small. The operation from this point is the same as in manual control.

Additional circuits are shown in Figures C-1 and C-2, these are power supplies which supply the necessary operating voltage and currents to the electronic components and safety circuits which prevent damage to the power supply and personnel. The design of these circuits is standard and need not be discussed here.

APPENDIX D

COMPUTER PROGRAM FOR LEAST SQUARES DATA FITTING

This program was written to perform least squares fitting of data to a straight line of the form $y = ax + b$. The program also calculates the standard deviation of the calculated slope and intercept, as well as the expected standard deviation for an individual y value. The equations were taken from Youden (50).

Two input parameters, N and J, are used in the program. N is the number of x-y pairs in the data set and is necessary in the calculations. J is an arbitrary parameter. A value of zero for J causes the program, using statements 29 and 30, to compute the reciprocal of x. This is used, for example, when treating ln P vs 1/T data. A value of J greater than zero causes the program to skip statements 29 and 30.

Statements 45, 46 and 47 are optional and may be deleted from the program if desired. Their function is to convert the input value of y to ln y.

After the slope, intercept, and standard deviations are calculated, a set of values for y are calculated from the slope and intercept and the input values of x. These "y calc" values are compared to the input y values and if the difference is more than three times the standard deviation, the y value is rejected and the computations repeated. Dr. George Sturgeon modified the program so that the maximum difference of $|y \text{ calc} - y|$ is tested first. This procedure is necessary since a point rejected when it is just outside the limit of acceptance, might fall within this limit when a point with a larger difference is subsequently rejected.

The complete program follows:

```
    PROGRAM LSTSQRS
    DIMENSION X(50),Y(50),YCALC(50),DEV(50),T(50),Z(50)
10 READ11,N,J
11 FORMAT(212)
    IF(N)12,16,12
12 READ13,(X(I),Y(I),I=1,N)
13 FORMAT (2F10.5)
45 DO471=1,N
46 Z(I)=Y(I)
47 Y(I)=LOFG(Y(I))
29 IF(J)30,30,14
30 DO31I=1,N
31  X(I)=1.0/X(I)
14 SUMX=0
    SUMY=0
    SUMXY=0
    SUMX2=0
    SUMY2=0
40 DO50I=1,N
    SUMX=SUMX+X(I)
    SUMY=SUMY+Y(I)
    SUMXY=SUMXY+X(I)*Y(I)
    SUMX2=SUMX2+X(I)**2
50 SUMY2=SUMY2+Y(I)**2
    FN=N
   A=(FN*SUMXY-SUMX*SUMY)/(FN*SUMX2-SUMX**2)
   B=(SUMY*SUMX2-SUMXY*SUMX)/(FN*SUMX2-SUMX**2)
   PRINT60,A,B
60 FORMAT(1HO,2X,6HSLOPE=,E12.6,5X,10HINTERCEPT=,E12.6)
   FRACT=((SUMXY-SUMX*SUMY/FN)**2)/(SUMX2-SUMX**2/FN)
   E=SUMY2-(SUMY**2/FN)-FRACT
   S2=E/(FN-2.0)
   S=SQRTF(S2)
   SA2=S2/(SUMX2-(SUMX**2/FN))
   SA=SQRTF(SA2)
   SB2=S2*SUMX2/(FN*SUMX2-SUMX**2)
   SB=SQRTF(SB2)
   PRINT70,S,SA,SB
70 FORMAT(1HO,2X,22HSTD DEV OF A SINGLE Y=,E14.8,/,
  117HSTD DEV OF SLOPE=,E14.8,/,
  221HSTD DEV OF INTERCEPT=,E14.8)
    DO80I=1,N
80 YCALC(I)=A*X(I)+B
   DO90I=1,N
   T(I)=ABSF(Y(I)-YCALC(I))
90 CONTINUE
   VMAX = T(1)
   DO 89 I= 1,N
   TEST = VMAX - T(I)
   IF (TEST) 82,89,89
82 VMAX = T(I)
   JAM = I
89 CONTINUE
```

```
    PROGRAM LSTSQRS
    DIMENSION X(50),Y(50),YCALC(50),DEV(50),T(50),Z(50)
10 READ11,N,J
11 FORMAT(212)
    IF(N)12,16,12
12 READ13,(X(I),Y(I),I=1,N)
13 FORMAT (2F10.5)
45 DO471=1,N
46 Z(I)=Y(I)
47 Y(I)=LOFG(Y(I))
29 IF(J)30,30,14
30 DO31I=1,N
31  X(I)=1.0/X(I)
14 SUMX=0
    SUMY=0
    SUMXY=0
    SUMX2=0
    SUMY2=0
40 DO50I=1,N
    SUMX=SUMX+X(I)
    SUMY=SUMY+Y(I)
    SUMXY=SUMXY+X(I)*Y(I)
    SUMX2=SUMX2+X(I)**2
50 SUMY2=SUMY2+Y(I)**2
    FN=N
   A=(FN*SUMXY-SUMX*SUMY)/(FN*SUMX2-SUMX**2)
   B=(SUMY*SUMX2-SUMXY*SUMX)/(FN*SUMX2-SUMX**2)
   PRINT60,A,B
60 FORMAT(1HO,2X,6HSLOPE=,E12.6,5X,10HINTERCEPT=,E12.6)
   FRACT=((SUMXY-SUMX*SUMY/FN)**2)/(SUMX2-SUMX**2/FN)
   E=SUMY2-(SUMY**2/FN)-FRACT
   S2=E/(FN-2.0)
   S=SQRTF(S2)
   SA2=S2/(SUMX2-(SUMX**2/FN))
   SA=SQRTF(SA2)
   SB2=S2*SUMX2/(FN*SUMX2-SUMX**2)
   SB=SQRTF(SB2)
   PRINT70,S,SA,SB
70 FORMAT(1HO,2X,22HSTD DEV OF A SINGLE Y=,E14.8,/,
  117HSTD DEV OF SLOPE=,E14.8,/,
  221HSTD DEV OF INTERCEPT=,E14.8)
    DO80I=1,N
80 YCALC(I)=A*X(I)+B
   DO90I=1,N
   T(I)=ABSF(Y(I)-YCALC(I))
90 CONTINUE
   VMAX = T(1)
   DO 89 I= 1,N
   TEST = VMAX - T(I)
   IF (TEST) 82,89,89
82 VMAX = T(I)
   JAM = I
89 CONTINUE
```

```
      DEV=T(JAM)-3.0*S
      IF(DEV)  115,100,100
  100 PRINT 200, Y(JAM)
  200 FORMAT(1HO,2X,14HREJECTED POINT,5S,E14.8)
      DO 110 I = JAM,N
      X(I) = X(I+1)
      Z(I)=Z(I+1)
  110 Y(I) = Y(I + 1)
      N = N - 1
      GO TO 14
  115 PRINT 120(Z(I),Y(I),YCALC(I),T(I),I=1,N)
  120 FORMAT(1HO,2X,4HYIN=,16X,2HY=,16X,6HYCALC=,16X,2HT=,///,
     1(2X,4(E14.8,2X)))
      GO TO 10
   16 STOP
      END
      END
```

APPENDIX E

COMPILATION OF MASS SPECTROMETRIC DATA

Table E-1. Data for experiments MS-2 and MS-3

$T^{o}C$ (Observed)	$10^4/T^a$ (True)	Intensity mass 151 nanoamps	Intensity mass 153 nanoamps
	MS-2a		
975	7.948	0.0047	0.0047
1040	7.539	0.0064	0.0086
1040	7.539	0.0080	0.0086
1060	7.471	0.0086	0.0104
1060	7.471	0.0092	0.0102
1060	7.421	0.0112	0.0128
1075	7.334	0.0152	0.0140
1130	7.030	0.0316	0.0316
1130	7.030	0.0304	0.0352
1157	6.981	0.0480	0.0480
	MS-2b		
1040	7.539	0.0034	0.0026
1040	7.539	0.0036	0.0029
1065	7.392	0.0038	0.0062
1153	6.910	0.0128	0.0148
1153	6.910	0.0138	0.0148
1145	6.951	0.0132	0.0140
1170	6.824	0.0236	0.0232
1170	6.824	0.0220	0.0220
1184	6.808	0.0236	---[b]
1220	6.644	0.0340	0.0390
1220	6.642	0.0335	---
1176	6.846	0.0210	0.0250
1176	6.846	0.0230	0.0200
1214	6.737	0.0340	0.0340
1214	6.737	0.0350	---
1249	6.512	0.0465	0.0465
1249	6.512	0.0465	0.0485
1296	6.312	0.0640	0.0640
1297	6.308	0.0530	---
1259	6.469	0.0400	0.0500
1310	6.254	0.0800	0.0800
1310	6.254	0.0820	---
1339	6.137	0.1180	0.1000
1384	5.963	0.1600	0.1600
1384	5.863	0.1620	---
1403	5.892	0.1600	0.1800

Table E-1. (continued)

1117	7.099	0.0150	0.0190
1043	7.522	0.0039	0.0034
1138	6.987	0.0130	0.0156
1170	6.824	0.0250	0.0250
1170	6.824	0.0240	---
1168	6.834	0.0230	---
1217	6.655	0.0350	0.0400
1237	6.565	0.0450	0.0500
1255	6.486	0.0500	0.0550
		MS-3	
883	8.606	0.0016	0.0020
881	8.621	0.0011	0.0014
917	8.358	0.0034	0.0026
917	8.358	0.0037	0.0045
964	8.033	0.0048	0.0073
970	7.993	0.0055	---
970	7.993	0.0050	---
970	7.993	0.0055	---
887	8.576	0.0019	0.0017
887	8.576	0.0021	0.0021
926	8.295	0.0046	0.0036
928	8.281	0.0041	0.0046
927	8.287	0.0045	0.0030
970	7.993	0.0075	0.0085
972	7.980	0.0116	---
1018	7.685	0.0208	0.0208
1018	7.685	0.0200	0.0220
1103	7.187	0.0790	0.0790
1102	7.193	0.0750	0.0800
1069	7.380	0.0450	0.0420
1067	7.392	0.0450	0.0450
927	8.289	0.0046	0.0046
929	8.274	0.0038	0.0060
1026	7.636	0.0220	0.0240
1026	7.636	0.0232	---
977	7.946	0.0041	0.0060
977	7.946	0.0050	0.0050
1026	7.636	0.0212	0.0260
1108	7.161	0.0860	0.0860
1064	7.409	0.0490	0.0490
1064	7.409	0.0530	---
1170	6.836	0.1800	0.1800
1170	6.836	0.0800	0.1800
1210	6.699	0.2400	0.2800
1212	6.690	0.2400	---
1257	6.489	0.3750	0.4000
1297	6.320	0.5000	0.5200
1298	6.316	0.5000	---
1275	6.412	0.4000	0.4000

[a] $\Delta\ 1/T = 10.58 \times 10^{-6}$ for MS-2; $\Delta\ 1/T = 9.39 \times 10^{-6}$ for MS-3

[b] A blank in this column indicates that the intensity of mass 151 was measured as a function of time at the corresponding temperature.

Table E-2. Data for experiment MS-4-Ag.

$T^{o}C$ (Observed)	$10^4/T^a$ (True)	Intensity mass 107 nanoamps	Intensity mass 109 nanoamps
983	7.889	0.0240	0.0244
983	7.889	0.0248	0.0248
960	8.041	0.0144	0.0122
960	8.041	0.0112	0.0104
953	8.086	0.0122	0.0102
1021	7.648	0.0440	0.0360
1021	7.648	0.0430	---[b]
965	8.008	0.0192	0.0168
965	8.008	0.0192	0.0172
983	7.889	0.0268	0.0228
983	7.889	0.0252	0.0252
1023	7.638	0.0600	0.0640
1023	7.638	0.0600	0.0560
1001	7.773	0.0430	0.0400
1001	7.773	0.0420	0.0410
1050	7.473	0.1300	0.1160
1050	7.473	0.1260	0.1200
1030	7.592	0.0800	0.0800
1030	7.592	0.0900	0.0780
1074	7.332	0.1700	0.1640
1074	7.332	0.1700	0.1640
1050	7.473	0.1200	0.1160
1050	7.473	0.1200	0.1100
1075[c]	7.290	0.2480	0.2200
1075	7.290	0.2600	0.2280
973	7.917	0.0260	0.0240
973	7.917	0.0272	0.0240
944	8.114	0.0112	0.0104
944	8.114	0.0090	0.0106
903	8.404	0.0048	0.0036
903	8.404	0.0038	0.0043

[a] Δ 1/T = 3.957 x 10^{-6} before the experiment
Δ 1/T = 6.627 x 10^{-6} after the experiment

[b] Intensity not measured

[c] Visible coating appeared on the window

Table E-3. Data for experiment MS-5

T^oC (Observed)	$10^4/T^a$ (True)	Intensity mass 151 nanoamps	Pressure mass 151_5 atm. x 10^5	Intensity mass 153 nanoamps	Pressure mass 153_5 atm. x 10^5
982	7.915	0.0077	2.852	0.0070	2.375
982	7.915	0.0074	2.741	0.0090	3.053
1015	7.705	0.0140	5.327	0.0150	5.228
1015	7.705	0.0156	5.937	0.0150	5.228
1054	7.468	0.0268	10.52	0.0260	9.347
1054	7.468	0.0224	8.792	0.0260	9.347
1085	7.289	0.0430	17.29	0.0450	16.58
1085	7.289	0.0430	17.29	0.0450	16.58
1112	7.139	0.0610	25.05	0.0650	24.45
1112	7.139	0.0630	25.87	0.0680	25.58
1171	6.832	0.1300	55.79	0.1340	52.66
1171	6.832	0.1300	55.79	0.1400	55.02
1050	7.492	0.0240	9.393	0.0228	8.174
1050	7.492	0.0240	9.393	0.0280	10.57
860	8.781	0.0012	0.4008	0.0012	0.3671
934	8.239	0.0048	1.708	0.0044	1.434
934	8.239	0.0039	1.388	0.0044	1.434
998	7.812	0.0110	4.128	0.0120	4.124
998	7.812	0.0108	4.055	0.0104	4.111
1064	7.410	0.0336	13.29	0.0360	13.04
1064	7.410	0.0332	13.13	0.0356	12.90
1123	7.080	0.0740	30.64	0.0860	32.63
1123	7.080	0.0780	32.31	0.0860	32.63
1185	6.763	0.1400	60.69	0.1600	63.53
1185	6.763	0.1460	63.30	0.1560	61.95
1252	6.512	0.2600	117.1	0.2880	118.8
1252	6.512	0.2560	115.2	0.2760	113.8
911	8.402	0.0038	1.326	0.0038	1.214
911	8.402	0.0033	1.151	0.0033	1.055
1070	7.375	0.0300	11.93	0.0340	12.38
1070	7.375	0.0312	12.40	0.0340	12.38
1165	6.862	0.1040	44.44	0.1100	43.04
1165	6.862	0.1100	47.00	0.1100	43.04
1235	6.587	0.2000	89.01	0.2280	92.93
1235	6.587	0.2040	90.79	0.2280	92.93
1270	6.434	0.2800	127.6	0.2920	121.9
1270	6.434	0.2600	118.5	0.2880	120.2
1283	6.379	0.3200	147.1	0.3280	138.1
1283	6.379	0.3160	145.2	0.3280	138.1
1302	6.300	0.3500	162.9	0.3800	162.0
1302	6.300	0.3700	172.2	0.3900	166.2
1237	6.578	0.1920	85.58	0.2080	84.91
1237	6.578	0.1800	80.21	0.2080	84.91
1070	7.375	0.0260	10.33	0.0278	10.12
1070	7.375	0.0264	10.44	0.0268	9.758

[a] $\Delta\ 1/T = 9.33 \times 10^{-6}$