⑤ 819 485

(1)

63-4-2

[illegible]

AD No. 408370

DDC FILE COPY

408 370

TECHNICAL INFORMATION SERIES

R63SD06

HIGH TEMPERATURE VAPORIZATION STUDIES USING A RECORDING MICROBALANCE AND ELECTRON BOMBARDMENT HEATING

I. VAPOR PRESSURE OF SILVER
II. VAPOR PRESSURE OF PALLADIUM

TISIA A

P. D. ZAVITSANOS

SPACE SCIENCES LABORATORY
GENERAL ELECTRIC
MISSILE AND SPACE DIVISION

$2.60

(4) NA (5) 819 485

(7-9) NA

SPACE SCIENCES LABORATORY

AEROPHYSICS SECTION

(6) HIGH TEMPERATURE VAPORIZATION STUDIES USING A RECORDING MICROBALANCE AND ELECTRON BOMBARDMENT HEATING. I. VAPOR PRESSURE OF SILVER. II. VAPOR PRESSURE OF PALLADIUM.

(10) by

Peter D. Zavitsanos

(11) Jan 63,
(12) 24p.
(13) NA
(16) NA
(17) NA
(18) NA

(15)
This work was performed under Contract ~~No.~~ AF 04(694)-222 for the U. S. Air Force Ballistic Systems Division.

(19) NA
(20) U
(21) NA

(14) [illegible]
R63SD06
January 1963

MISSILE AND SPACE VEHICLE DEPARTMENT

GENERAL ELECTRIC

CONTENTS

PAGE

ABSTRACT

A method was ~~has been~~ developed for studying the equilibrium vapor pressure of high temperature inorganic materials, ~~It~~ consists of measuring the rate of vapor deposition on a target intercepting a known fraction of the total vapor flux effusing from the orifice of a Knudsen cell. The material ~~to be studied~~ contained in an effusion cell is heated by electron bombardment (to temperatures as high as 2500°C). Accurate temperature control was achieved by adjusting the filament current so that the emission current remained constant.

Rates of effusion are obtained by continuously weighing the target; vapor pressures and the heats of vaporization are calculated. The experimental and theoretical techniques are described, and the results of the reinvestigation of the vapor pressure of silver metal at 1273 to 1563°K are given. It is shown that the observed vapor pressure and ΔH^{o}_{298} are in excellent agreement with the best literature values.

The vaporization of palladium was studied in the temperature range 1537 to 1841°K. The vapor pressure is represented by the equation

$$\log P_{\text{atm.}} = 5.99 - \frac{18,898}{T}.$$

A heat of vaporization at 298°K was calculated, $\Delta H^{o}_{298} = 89.8 \pm 0.9$ kcal/mole and a b. p. of 3150 ± 100°K was estimated.

I. INTRODUCTION

In order to advance the state of technology in the fields of practical interest, such as leading edges of glide vehicles, re-entry heat shielding, rocket nozzles, communication and detection, considerable advancements in the knowledge of the chemical and physical properties of many new materials are needed.

A considerable amount of analytical and experimental work has been done in this laboratory in the area of vaporization of high temperature inorganic materials. The objective of this work was to develop a fast and accurate method for determining vapor pressures of high temperature materials.

II. DESCRIPTION OF THE METHOD

One of the most widely used methods in determining the vapor pressure of high temperature materials has been the Knudsen effusion method[1]. Considering a cell with an orifice of small diameter and infinitely small thickness, as the container, and applying kinetic theory considerations to the effusing vapor, one can derive an equation that relates the equilibrium pressure, P, and the rate of effusion, m, in the following manner:

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

where m = mass loss in gm. cm^{-2} sec^{-1}; M = average molecular weight of the vapor; T = temperature in ^{o}K and R = gas constant.

The rate of effusion is usually determined by weighing the cell or by measuring the rate of condensation of the vapor on a collector plate. The collector plate technique was improved here by introducing a sensitive microbalance into the vacuum system, and thus follow the weight of the collector as the vaporization proceeds, Figure 1.

The sample is heated by electron bombardment in a Knudsen cell while a well-defined portion of the effusing beam is intercepted by the conical collector. The weight gain is observed, continuously during the experiment, with a Sartorius-Electrona microbalance connected to a recorder.

This technique tends to eliminate a number of errors introduced by the conventional techniques and has the following advantages:

1. Breaking the vacuum for each measurement is not necessary.
2. Errors associated with warm-up and cooling are eliminated.

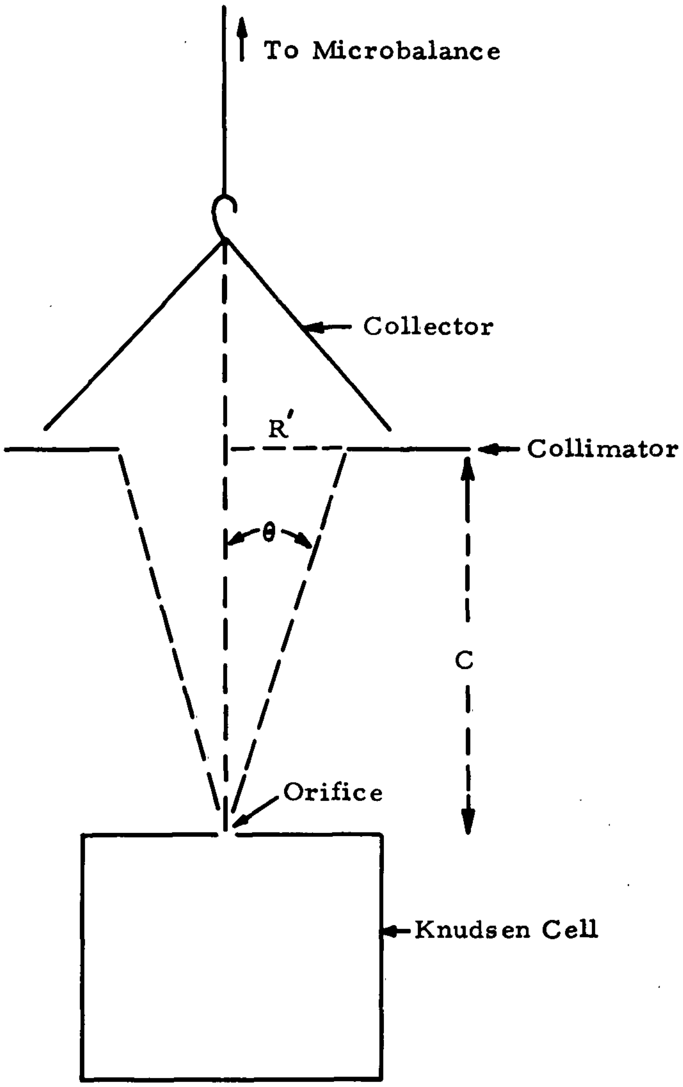


FIG. 1. GEOMETRY OF THE KNUDSEN CELL AND COLLECTOR

3. Errors associated with nucleation and difficulties in sticking of the vapor on foreign substrates are eliminated by depositing considerable amounts of material before we start taking measurements.
4. Measurements are taken only when the furnace is brought to the desired temperature and only during constant temperature intervals.
5. Very reliable rates are obtained in short time intervals by being able to measure extremely small weight changes ($0.5\,\mu g$).

The total rate of effusion is obtained by using the cosine law of evaporation: If the collimating slit has a radius R' and is placed at a distance C from the cell, then the fraction f of the effusing vapor arriving at the target is

$$f = \frac{R'^2}{C^2 + R'^2} \tag{2}$$

then total rate = measured rate x $\frac{C^2 + R'^2}{R'^2}$. The vapor pressure is then calculated using the Knudsen equation

$$\log P\ (\text{atm.}) = \log m + \tfrac{1}{2}\log M + \tfrac{1}{2}\log T - 1.647 \tag{3}$$

where m = total rate of effusion in moles$\cdot$cm$^{-2}\cdot$sec^{-1}.

III. EXPERIMENTAL APPARATUS

The apparatus is shown in Figure 2 (schematically) and in Photo 2-A. The vacuum system utilizes, besides the forepump, two three-stage diffusion pumps, and the conventional thermocouple and ion gauges. A vacuum as good as 10^{-7} mm Hg can be achieved when the furnace is cold, and most of the data reported here were taken at a pressure of 10^{-5} mm Hg or better.

The vaporization is carried out in a quartz envelope (Figure 3 and Photo 3-A) sealed at the bottom with a brass plate B. Three "Carborundum" glass-to-metal seals, C, enter through the plate and serve as electrodes. Three tantalum rods (.1 in. thick) supported on the seals, hold the Knudsen cell and the helical tungsten filament (15-20 mil). The cell electrode is connected to the positive of a 5 KV 1 A DC power supply, while the filament is heated by resistance with a 10 V, 20 A power supply. The thermal electrons produced on the filament are attracted by the positive cell and heat it up by bombardment. The temperature of the cell, therefore, depends mainly on the number of emitted electrons and the accelerating voltage. The temperature is kept constant by controlling the filament current so that the emission current remains constant while the work function of the metal changes with the stage of outgassing.

Accurate control was achieved through an emission regulator with a saturable reactor, Figure 4. When the furnace is heated to temperatures higher than 2000°K, the filament receives an appreciable amount of heat by radiation (from the cell) and only 7-8 amps of heating current were required

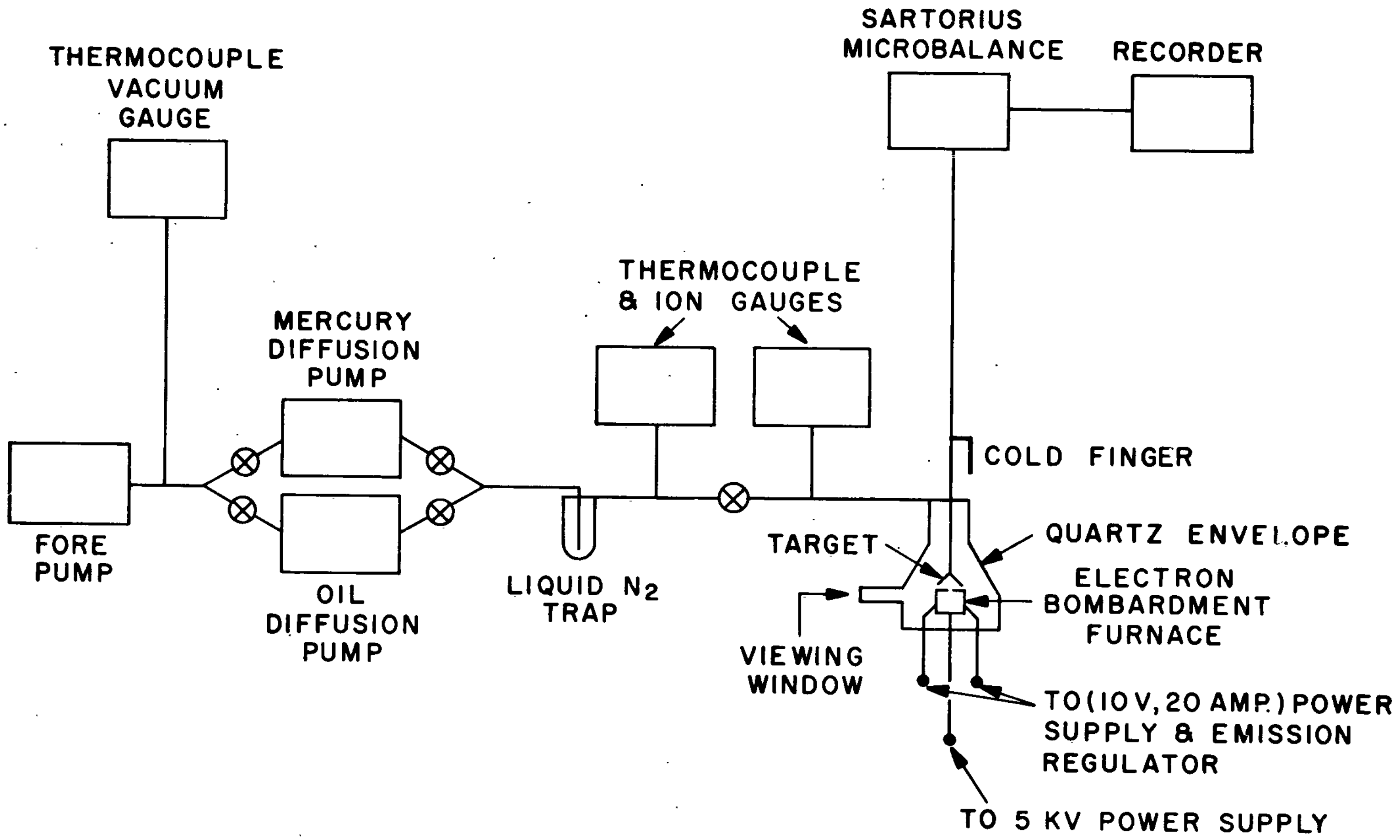


FIGURE 2

Vaporization Apparatus

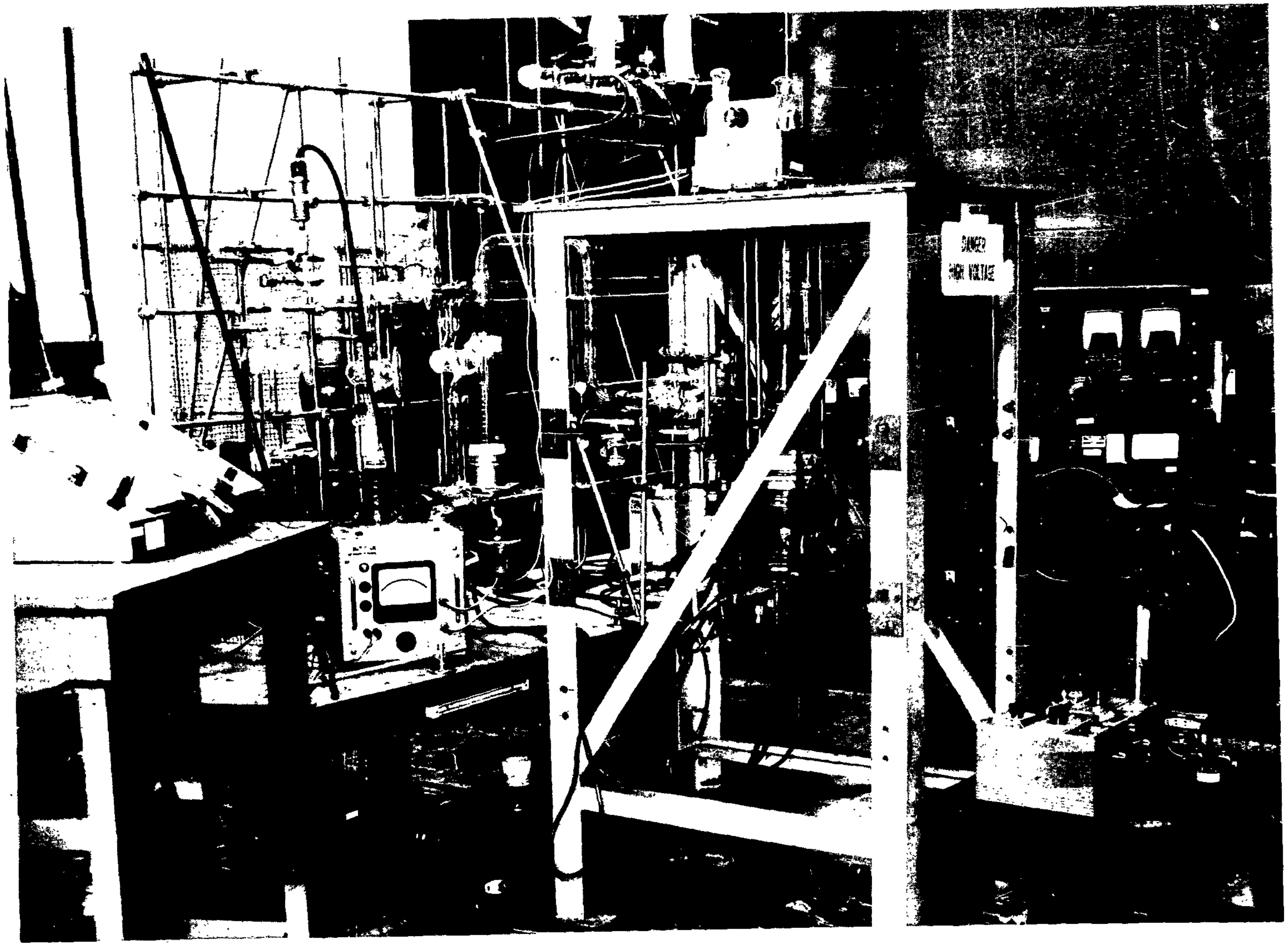
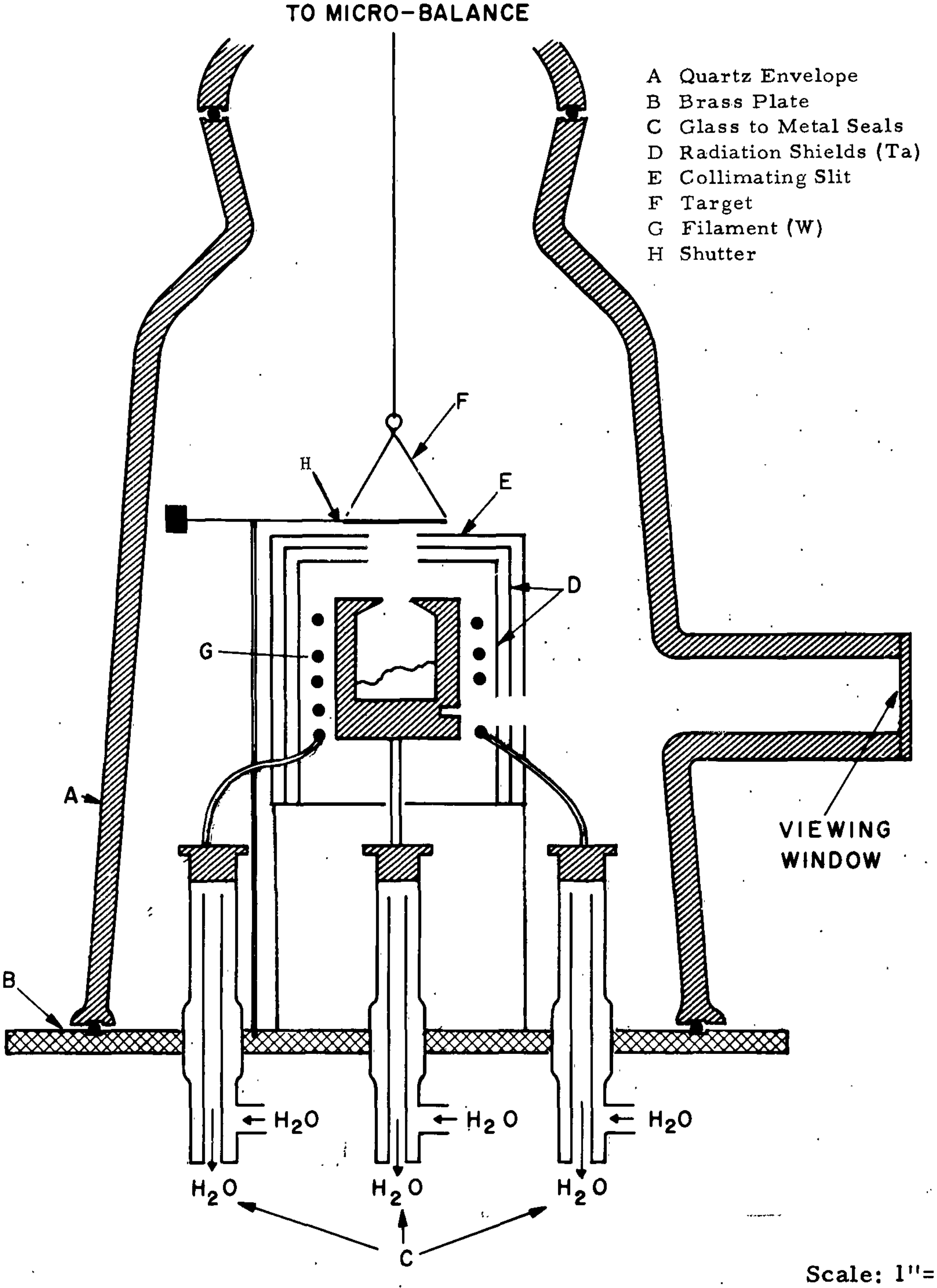


FIGURE 2-A. Vaporization Apparatus



A Quartz Envelope
B Brass Plate
C Glass to Metal Seals
D Radiation Shields (Ta)
E Collimating Slit
F Target
G Filament (W)
H Shutter

Scale: 1"=1.5"

Figure 3. Electron Bombardment Furnace

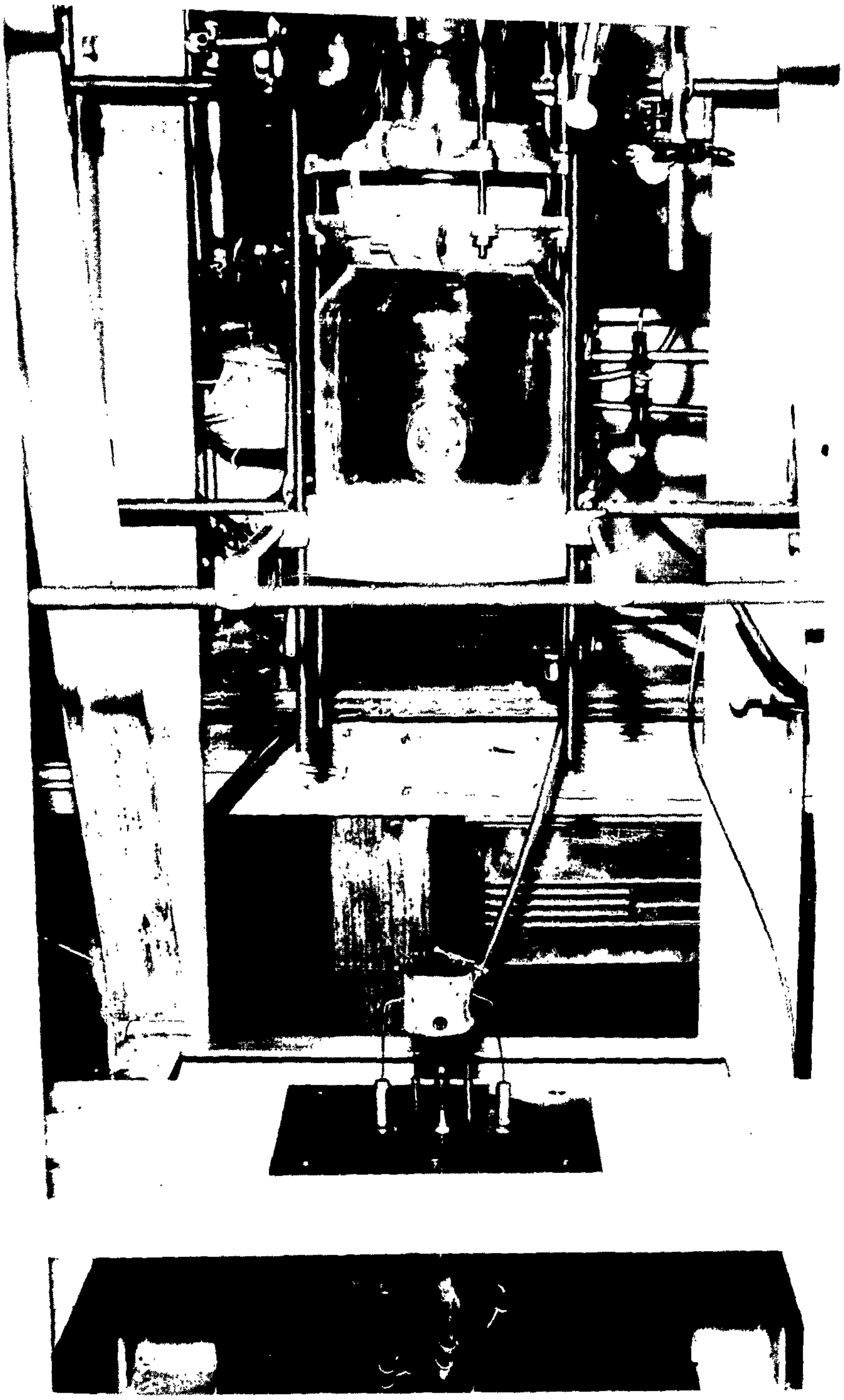


FIGURE 3-A. Electron Bombardment Furnace

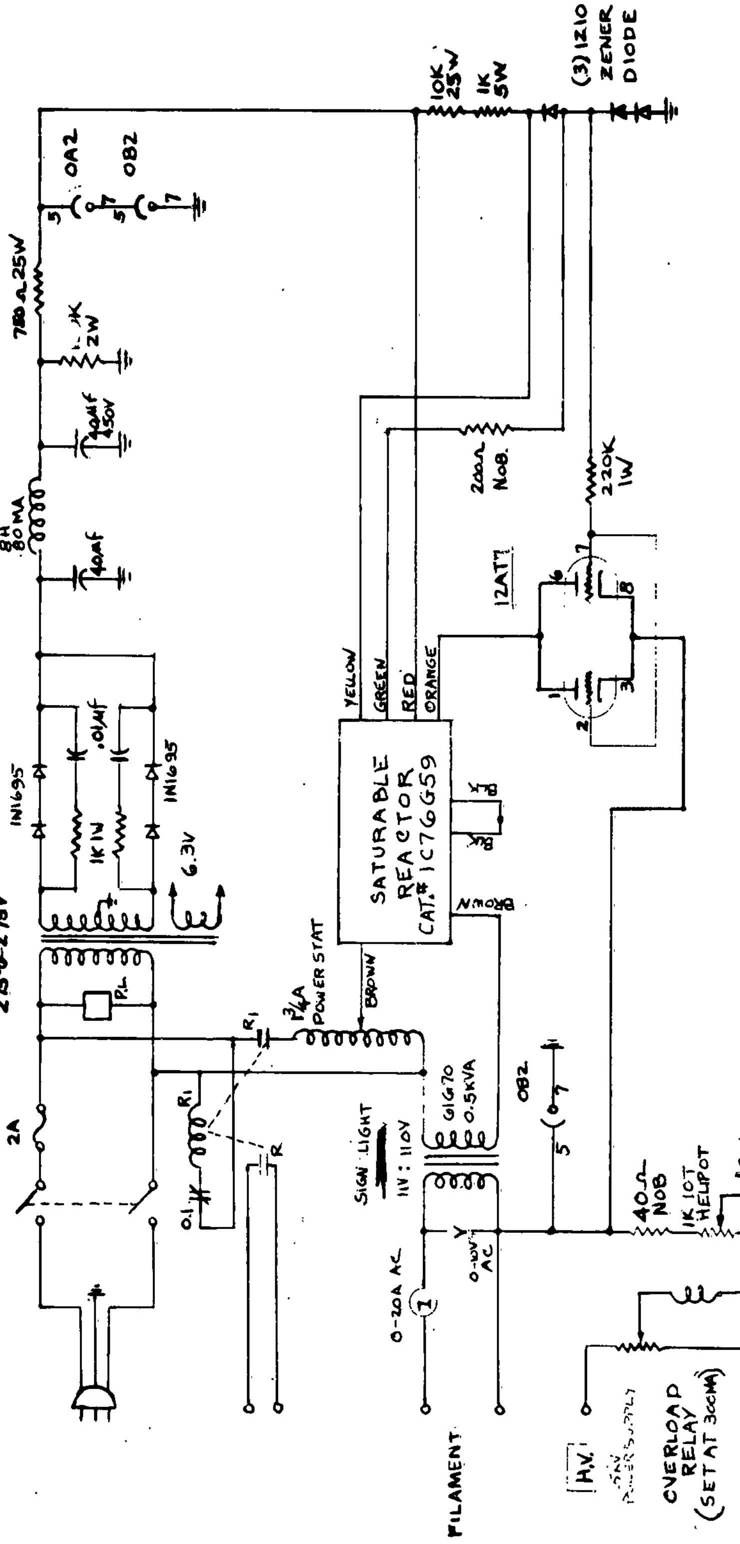


Figure 4. Emission Regulator

for an emission current of 0.2-0.3 amps. Temperature control of ± 2°C was achieved. The critical condition for operation is the maintenance of pressures $\leq 2 \times 10^{-4}$ mm Hg so that gaseous discharge does not occur.

The temperature of the cell was read to within ± 2° by focussing an optical pyrometer on a black body hole. The pyrometer was calibrated against an NBS lamp and all readings were adjusted for window corrections. The window was kept clean from furnace vapors by covering the inside surface with a steel slug. The slug was removed only for temperature readings.

The furnace is provided with grounded tantalum radiation shields, to minimize radiation losses and achieve better temperature uniformity. A glass or metal target, conical in shape, is suspended from the microbalance and intercepts all the vapor effusing through the collimating slit. Then from the rate of the weight gain, shown by a recorder, the cosine law of evaporation and the Knudsen equation, total rates of effusion and vapor pressures are calculated.

A shutter (operated magnetically from outside the system) can turn the beam on and off. The purpose for this was to study the thermal effects caused by the hot furnace and possible electrostatic effects caused by the high positive charge of the cell, in order to investigate the possible application of momentum transfer in the direct measurement of the vapor pressure.

IV. TREATMENT OF DATA AND THERMODYNAMIC RELATIONS

Vapor pressure measurements can be used in order to calculate heats of vaporization.

For the reaction A(s or l) $\longrightarrow$ A(g) (4)

$$\Delta F^o_T = \Delta H^o_T - T\Delta S^o_T = - R\ln K = - RT\ln P \qquad (5)$$

where P is the vapor pressure.

Using the second law method,

$$\frac{\partial}{\partial T}\left(\frac{\Delta F^o}{T}\right)_P = - \frac{\Delta H^o}{T^2} \qquad (6)$$

or

$$\left(\frac{\partial \ln K}{\partial T}\right)_P = \frac{\Delta H^o}{RT^2} \qquad (6\text{-A})$$

or

$$\frac{d\ln P}{\partial (1/T)} = - \frac{\Delta H^o}{R} \qquad (6\text{-B})$$

and the plot of log K (or log P) vs. 1/T has a slope at each temperature equal to $\Delta H^o_{T_{av.}}/R$. If one knows the heat capacities of products and reactants, the heat of vaporization at 298°K can be calculated:

$$\Delta H^o_{298} = \Delta H^o_{T_{av.}} - \int_{298}^{T_{av.}} \Delta CpdT \qquad (7)$$

where

$$\Delta Cp = \sum_{\text{Products}} Cp - \sum_{\text{Reactants}} Cp$$

Another way to use vapor pressures in thermodynamics is known as the third law method and utilizes the free energy functions, fef, given as

$$\mathrm{fef} = \left(\frac{F_T^o - H_{298}^o}{T}\right) = \left(\frac{H_T^o - H_{298}^o}{T}\right) - S_T^o \tag{8}$$

This quantity is particularly easy to evaluate for gases with known partition functions (from spectroscopic data) and, for substances which have measured heat capacities,

$$\mathrm{fef} = \frac{1}{T}\int_0^T C_p dT - \int_0^T C_p d\ln T. \tag{9}$$

Values of fef have been tabulated for the elements[2] and a great number of compounds[3]. Then, for reaction (4)

$$\begin{aligned}\Delta \mathrm{fef} &= \left(\frac{F_T^o - H_{298}^o}{T}\right)_{(g)} - \left(\frac{F_T^o - H_{298}^o}{T}\right)_{(s\ \mathrm{or}\ 1)} \\ &= \frac{\Delta F_T^o}{T} - \frac{\Delta H_{298}^o}{T}\end{aligned} \tag{10}$$

$$\Delta F_T^o = -RT\ln K_{eq} = -RT\ln P \tag{11}$$

or

$$-\ln P = \Delta \mathrm{fef} + \frac{\Delta H_{298}^o}{T} \tag{11-A}$$

By substituting - lnP with the measured values of the vapor pressure, one can determine ΔH_{298}^o and obtain an expression for Log P as a function of T.

The advantage of the third law method is that, by using measured values of the vapor pressure at different temperatures, one calculates a value for ΔH^{o}_{298} for each value of P. The average deviation in the heat is an indication of the errors in the temperature.

V. RESULTS AND DISCUSSION

A. Vaporization of Silver

The method was tested using silver metal, Fisher Certified Reagent 99.95% pure. A molybdenum cell (1.5" x 2"), with an effusion orifice equal to .0056 cm^2, was used as a container. A collimating slit with R = 0.317 cm was placed 1.22 cm from the orifice. Measured rates and vapor pressures are shown in Table 1. The data were obtained by continuously weighing the target; checks were made on the validity of the technique by taking some measurements where the target was weighed before and after the run in vacuum and with the furnace cold. Such measurements were taken at 1383°K and are the last three in Table 1. The agreement with the rest of the data is obvious.

The least squares line through the data is given by:

$$\log P_{atm.} = 5.606 - \frac{13,616}{T}$$

and shown in Figure 5.

A second law treatment gives a $\Delta H^o = 62.28$ kcal/mole at $T_{av.} = 1406^oK$, which corrected to 298°K, using Stull and Sinke[2], gives $\Delta H^o_{298} = 67.4$ kcal/mole.

The third law method produces a value of $\Delta H^o_{298} = 67.97 \pm 0.52$ kcal/mole. Thes values are in excellent agreement with the average literature value[4] of 68.1.

TABLE 1

VAPORIZATION OF SILVER

$T^{o}K$	$1000/T^{o}K$	Rate (μg/min.)	- log P (atm.)	$-\Delta H^{o}_{298}$ kcal/mole
1315	.761	3.60	4.919	69.02
1315	.761	4.25	4.845	68.58
1315	.761	5	4.776	68.16
1330	.752	7.38	4.666	68.16
1379	.725	6.18	4.273	68.01
1381	.724	24	4.145	67.30
1381	.724	18.5	4.258	68.02
1381	.724	14	4.379	68.78
1424	.702	48.8	3.837	67.23
1425	.702	48.7	3.836	67.23
1425	.702	38.8	3.930	67.89
1442	.694	50	3.817	67.90
1486	.673	120	3.430	67.20
1503	.665	118	3.437	67.97
1504	.665	147	3.341	67.35
1504	.665	115	3.446	68.08
1524	.656	165	3.286	67.78
1538	.650	179	3.249	68.10

TABLE 1 (Continued)

T^oK	$1000/T^oK$	Rate (μg/min.)	- log P (atm.)	$-\Delta H^o_{298}$ kcal/mole
1563	.640	319	2.995	67.40
1473	.679	110.3	3.474	66.95
1467	.682	117.1	3.444	66.49
1273	.7855	1.67	5.260	68.89
1372	.729	11.50	4.405	68.52
1376	.727	10.92	4.427	68.84
1383	.723	4.13*	4.314	68.45
1383	.723	13.75*	4.326	68.53
1383	.723	14.9*	4.291	68.31

ΔH^o_{298} (ave.) = 67.97 ± 0.52 kcal/mole

* Rates were obtained by weighing the target before and after the run.

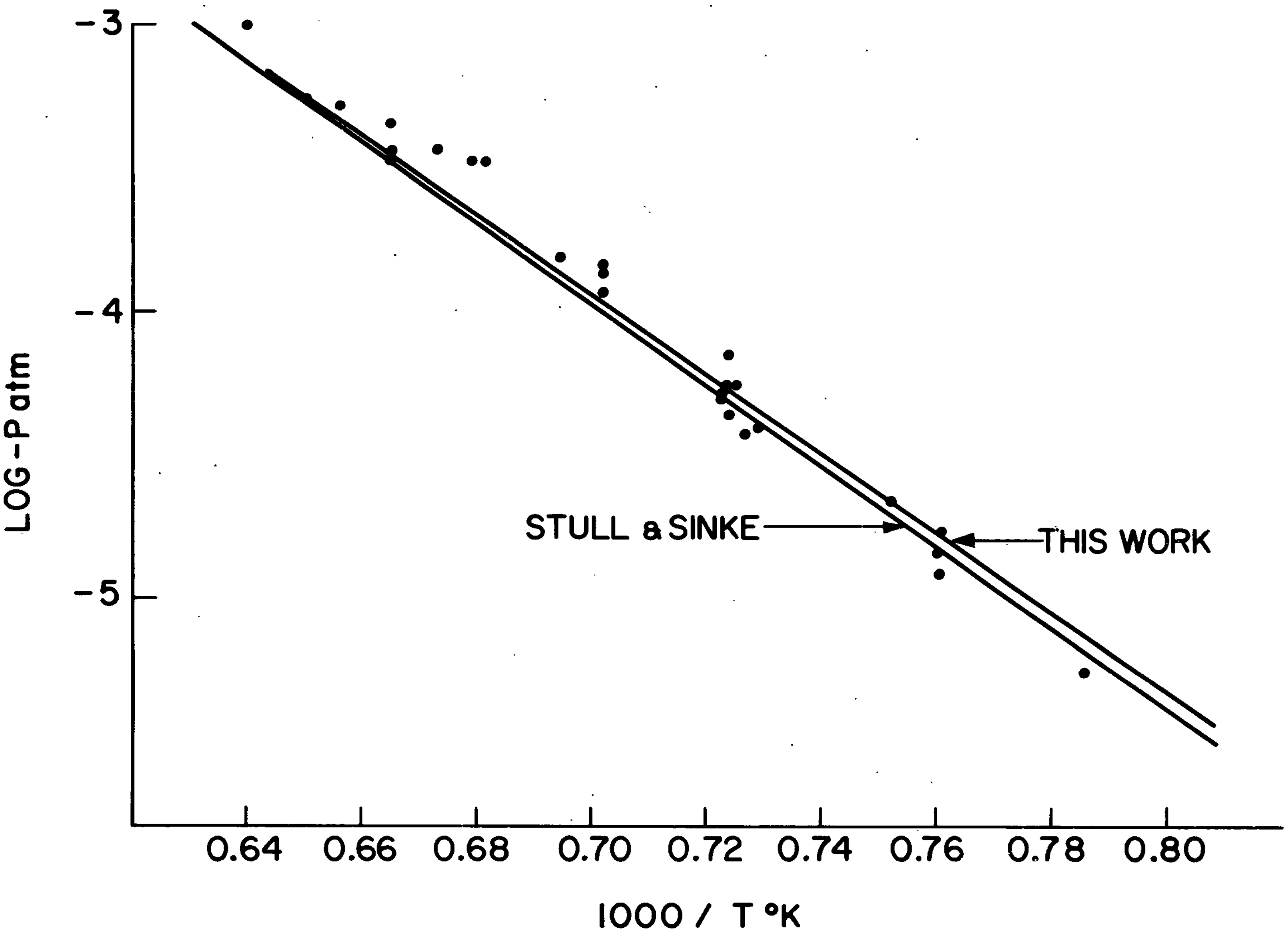


Figure 5. The Vapor Pressure of Silver

B. Vaporization of Palladium

In order to further test the method at higher temperatures, a metal with less known vaporization properties was studied. Surprisingly enough, the quantitative studies of the vapor pressure of palladium was rather unsatisfactory until recently, when Dreger and Margrave[5] measured the rate of sublimation in the temperature range 1220-1640°K using the Langmuir method.

Using our technique, we carried the investigation out at higher temperatures (1537-1841°K). The sample was obtained from Fisher Scientific and was the "Purified Pd Black Type". A (1.8 x 2 cm) tungsten cell was used as the container, with an orifice of 0.0126 cm^2. The collimating slit was placed 1.7 cm from the orifice and had a hole radius of .325 cm. Tungsten was chosen as the container material because palladium will not attack it.

The rate of effusion was measured by continuously weighing the target and also by weighing the target before and after the run. The measured rates and the calculated vapor pressures are shown in Tables 2 and 3. It is obvious that the results are the same regardless of whether one observes the weight change continuously (with the furnace hot) or weighs the target before and after the run (with the furnace cold). A least squares plot of the data, described by the equation

$$\log P_{atm.} = 5.698 - \frac{18,425}{T}$$

is shown in Figure 6.

TABLE 2

VAPORIZATION OF PALLADIUM

Continuous Weighing

$T^{o}K$	$10^{3}/T$	Rate (μg/min.)	- log P (atm.)	$\Delta H^{o}_{298^{o}K}$
1832	.546	17.5	4.22	88.93
1841	.543	16.5	4.25	89.60
1587	.630	0.23	6.124	91.38
1623	.616	0.63	5.69	90.02
1624	.616	0.50	5.792	90.83
1674	.594	2.50	5.086	88.13
1721	.581	3.60	4.92	89.24
1720	.581	3.34	4.96	89.45
1703	.587	2.25	5.13	89.95
1701	.588	2.55	5.07	89.42
1649	.606	1.60	5.28	88.33
1592	.628	0.233	6.227	92.22

ΔH^{o}_{298} (ave.) = 89.79 ± 0.90 kcal/mole

TABLE 3

VAPORIZATION OF PALLADIUM

"Before and After" Weighing

$T^{o}K$	$10^3/T$	Rate (µg/min.)	- log P (atm.)	$\Delta H^{o}_{298^{o}K}$
1792	.558	5.35	4.74	91.35
1698	.589	2.08	5.16	89.91
1649	.606	0.861	5.55	90.36
1806	.554	5.83	4.61	90.96
1537	.651	0.242	6.12	88.38
1543	.648	0.183	6.24	89.74
1570	.637	0.456	5.84	88.21

ΔH^{o}_{298} (ave.) = $89.84 \pm 0.91 \ \frac{\text{kcal}}{\text{mole}}$

The third law method gives a ΔH^{o}_{298} = 89.8 ± 0.9 kcal/mole. If one uses this value of ΔH^{o}_{298} and the fef functions, the vapor pressure is represented by

$$\log P_{atm.} = 5.99 - \frac{18,898}{T}$$

and a boiling point of 3150 ± 100 is calculated. The second law value of ΔH^{o}_{298} was 86.7 kcal/mole.

These results are in disagreement with the work of Haefling and Daene[6] and Gross and Walker[7] but in good agreement with Dreger and Margrave[5], where

$$\log P_{atm.} = 6.075 - \frac{19,425}{T},$$

$$\Delta H^{o}_{298} = 91 \pm 0.8 \text{ kcal/mole}$$

and Hampson and Walker[8], where

$$\log P_{atm.} = 5.749 - \frac{18,655}{T},$$

$$\Delta H^{o}_{298} = 89.2 \pm 0.8 \text{ kcal/mole.}$$

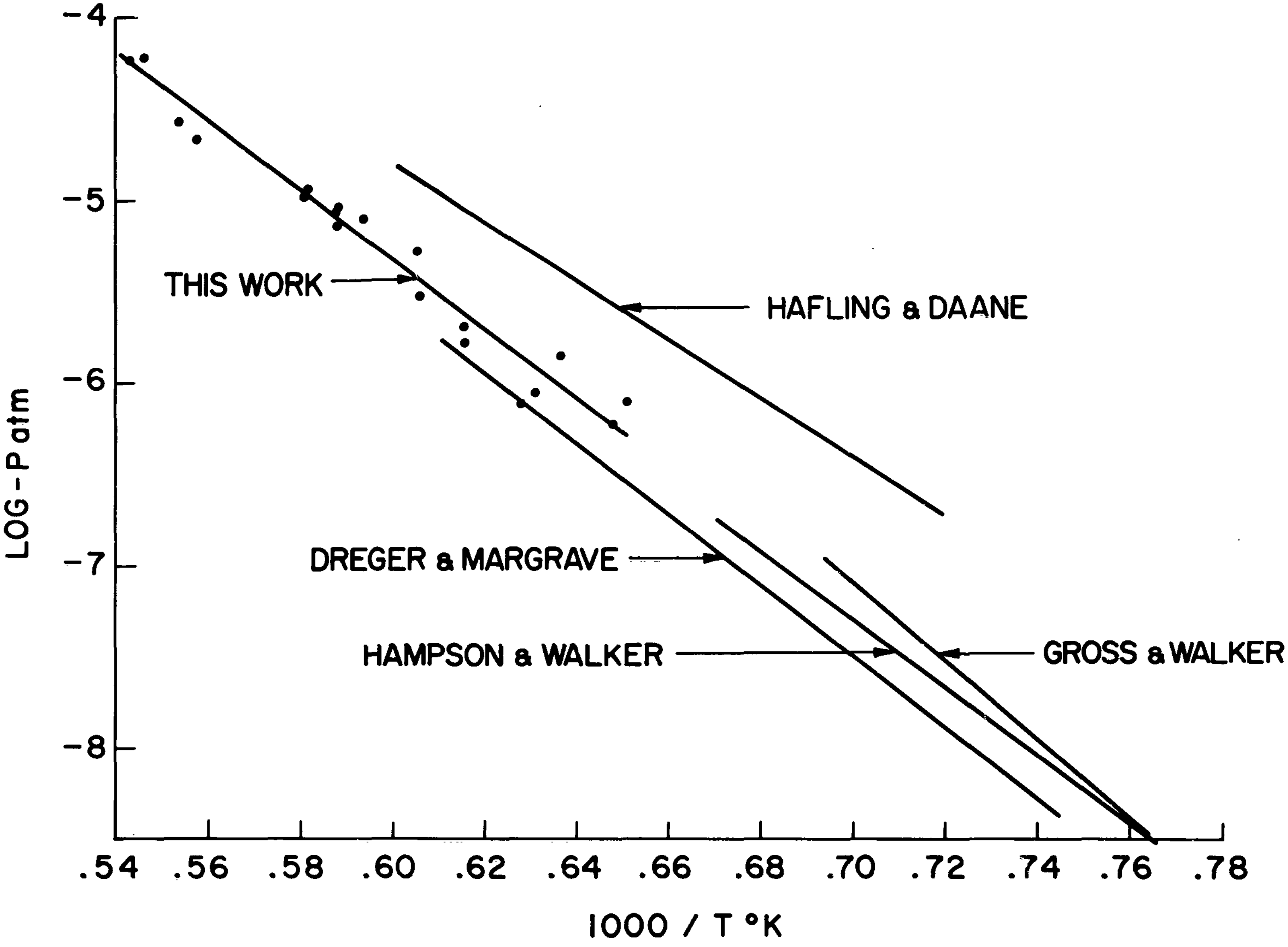


Figure 6. The Vapor Pressure of Palladium

References

1. Knudsen, Ann. Phys., 28, 75, 299; 29, 179 (1909).

2. Stull and Sinke, Thermodynamic Properties of the Elements, Adv. in Chem., Series 18, A. C. S. (1956).

3. JANAF "Thermochemical Data".

4. R. R. Hultgren, "Selected Values for the Thermodynamic Properties of Metals and Alloys", Report of the Minerals Res. Lab., University of California, Berkeley, 1956.

5. L. H. Dreger and J. L. Margrave, J. Phys. Chem. 64, 1323 (1960).

6. J. F. Heafling and A. H. Daane, Trans. Metal Soc., AIME, 212, 115 (1958).

7. R. F. Walker, et al., Phys. Chem. in Aerodynamics and Space Flight, J. Wiley and Sons, Inc., New York, N. Y. (1961).

8. R. F. Hampson and R. F. Walker, J. of Research of the National Bureau of Standards - A. Physics and Chemistry, Vol. 66A, No. 2, March-April (1962).

GENERAL ELECTRIC

SPACE SCIENCES LABORATORY
MISSILE AND SPACE DIVISION

TECHNICAL INFORMATION SERIES

AUTHOR Peter D. Zavitsanos	**SUBJECT CLASSIFICATION** Vaporization of High Temperature Materials	**NO.** R63SD06 **DATE** 1/11/63

TITLE HIGH TEMPERATURE VAPORIZATION STUDIES USING A RECORDING MICROBALANCE AND ELECTRON BOMBARDMENT HEATING. I. VAPOR PRESSURE OF SILVER. II. VAPOR PRESSURE OF PALLADIUM.

ABSTRACT A method has been developed for studying the equilibrium vapor pressure of high temperature inorganic materials. It consists of measuring the rate of vapor deposition on a target intercepting a known fraction of the total vapor flux effusing from the orifice of a Knudsen cell. The material to be studied contained in an effusion cell is heated by electron bombardment (to temperatures as high as 2500°C). Accurate temperature control was achieved by adjusting the filament current so that the emission current remained constant.

G. E. CLASS I	**REPRODUCIBLE COPY FILED AT MSD LIBRARY, DOCUMENTS LIBRARY UNIT, VALLEY FORGE SPACE TECHNOLOGY CENTER, KING OF PRUSSIA, PA.**	**NO. PAGES** 27
GOV. CLASS Unclassified		

ABSTRACT (Continued)

Rates of effusion are obtained by continuously weighing the target; vapor pressures and the heats of vaporization are calculated. The experimental and theoretical techniques are described, and the results of the reinvestigation of the vapor pressure of silver metal at 1273-1563°K are given. It is shown that the observed vapor pressure and ΔH^{o}_{298} are in excellent agreement with the best literature values.

The vaporization of palladium was studied in the temperature range 1537-1841°K. A heat of vaporization at 298°K was calculated, $\Delta H^{o}_{298} = 89.8 \pm 0.9$ kcal/mole and a b. p. of 3150 ± 100°K was estimated.

By cutting out this rectangle and folding on the center line, the above information can be fitted into a standard card file.

AUTHOR Peter D. Zavitsanos

COUNTERSIGNED Walter S. [illegible] Joseph [illegible]