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THE VAPORIZATION COEFFICIENT OF GRAPHITE

Michael Hoch, et al

Cincinnati University

Prepared for:

Air Force Materials Laboratory

December 1972

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THE VAPORIZATION COEFFICIENT OF GRAPHITE

M. HOCH AND M. YAMAWAKI

Department of Materials Science
and Metallurgical Engineering
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Cincinnati, Ohio 45221

Technical Report AFML-TR-72-273

DECEMBER 1972



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54

AD 759203

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author)		2a. REPORT SECURITY CLASSIFICATION	
University of Cincinnati Cincinnati, OH 45221		Unclassified	
2. REPORT TITLE		2b. GROUP	
The Vaporization Coefficient of Graphite		N.A.	
3. DESCRIPTIVE NOTES (Type of report and inclusive dates)			
Final, 15 April 1970 to 1 January 1972.			
4. AUTHOR(S) (First name, middle initial, last name)			
Michael Hoch and Michio Yamawaki			
5. REPORT DATE	7a. TOTAL NO. OF PAGES	7b. NO. OF REFS	
December 1972	44	23	
6a. CONTRACT OR GRANT NO.	9a. ORIGINATOR'S REPORT NUMBER(S)		
F33615-69-C-1531	AFML-TR-72-273		
b. PROJECT NO.	9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)		
7360			
c.			
736001			
d.			
10. DISTRIBUTION STATEMENT			
Approved for public release; distribution unlimited.			
11. SUPPLEMENTARY NOTES		12. SPONSORING MILITARY ACTIVITY	
		Air Force Materials Laboratory Electromagnetic Mat. Div. Wright Patterson AFB, OH 45433	
13. ABSTRACT			
<p>Relative values of the vaporization coefficients of C, C₂ and C₃, the predominant vapor species of graphite, were evaluated by comparing the ratios between the ion intensities of different carbon vapor species obtained in a free (Langmuir) vaporization experiment and in an equilibrium (Knudsen) vaporization experiment. The measurements of the ion intensities of carbon vapor species over the spectrographic electrode grade graphite were carried out using a RF induction heating furnace coupled with a Bendix Time-of-Flight mass spectrometer. The ion intensity ratio method used here is highly reliable in getting good data of relative values of the vaporization coefficients of carbon vapor species because the need of accurately knowing the temperature and also the mass spectrometer constants, ionization cross sections etc. does not arise. Both tantalum and tungsten Knudsen cells were used in the Knudsen experiments. The tantalum Knudsen cell was found to react with carbon vapor forming TaC and the TaC exchanged preferentially with C₁: the composition of the vapor was strongly affected showing a large C₃ to C₁ ratio. The tungsten Knudsen cell, on the other hand, showed no detectable evidence of reaction between the cell and the carbon vapor. By comparing the ion intensity ratios obtained in the free vaporization runs and in the Knudsen vaporization runs using tungsten cell, it was found that the vaporization coefficients of C, C₂ and C₃ over the spectrographic graphite are equal to each other within experimental scatter.</p> <p>(continued)</p>			

14 KEY WORDS	LINE A		LINE B		LINE C	
	ROLE	WT	ROLE	WT	ROLE	WT
<p>Graphite Vaporization</p> <p>(Abstract Continued)</p> <p>The ion intensity ratio method was also applied to all the experimental data in the literature; this also showed that the vaporization coefficients of C, C₂ and C₃ over conventional graphites are equal to each other within experimental error. The most reliable value for α₁, α₂ and α₃ is 3 x 10⁻² which was obtained for the condensation coefficients of C₂ and C₃ using the isotopic exchange method.</p> <p>The data in literature on pyrolytic graphite was also analyzed; an interpretation of the vaporization coefficients of pyrolytic graphite is difficult as the pyrolytic graphite vaporizes predominantly from cracks, etc.</p>						

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Unclassified

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FORWORD

This report was prepared by the University of Cincinnati, Cincinnati, Ohio, 45221, under USAF Contract F33615-69-C-1531. This contract was initiated under Project No. 7360, "Thermal and Chemical Behavior of Advanced Weapon System Materials," Task No. 736001, "Chemical, Physical and Thermodynamic Properties of Aircraft, Missile, and Spacecraft Materials." The work was administered under the direction of the Air Force Materials Laboratory, Air Force Systems Command, with Paul W. Dimiduk, AFML/LPH, acting as project engineer.

This report covers work conducted from 15 April 1970 to 1 January 1972.

The manuscript was released by the authors in October 1972 for publication as a technical report.

This technical report has been reviewed and is approved.


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EXPLANATION OF SYMBOLS USED IN FIGURES 6, 7, 8, 9, 10

<u>Symbols</u>	<u>Experiment</u>	<u>Researchers</u>	<u>Kind of Graphite</u>	<u>Type of Cell</u>	<u>Hole Diameter</u>
○	Free Vaporization.			Free	-
□	Equilibrium (K-cell) Vaporization.				
∅	Equilibrium (K-cell) Vaporization. Ta in cell or lid.				
◇	Ta K-cell Vaporization, this research.				
<u>Symbols</u>					
1		Wachi and Gilmartin ⁶	c-face of PG UT-6		
2		Drowart et al ⁵	Finely granulated graphite	Ta or W cell with graphite liner	$h/s < 10^{-5}$
3		Chupka and Inghram ¹²	Acheson Graphite	Ta cell with graphite liner	0.040"
4		Steele and Bourgeois ¹¹	RG-504	Graphite cell with Ta cap	0.025"
5		Present Work	Spectrographic graphite	W-cell Ta-cell (only for ◇)	0.04" 0.02"
6		Zavitsanos ⁸	Pyrolytic graphite	Free	
6P		Zavitsanos ⁷	Pyrolytic graphite	PG K-cell	0.03"
6T		Zavitsanos ⁷	Pyrolytic graphite	TaC K-cell	0.03"
7		Wachi and Gilmartin ²³	Spectrographic grade	Ta cell	0.04"

INTRODUCTION

The vaporization of graphite has been studied by a number of researchers¹⁻⁷ and shown to be a quite complicated process. Carbon vapor over graphite is composed of several polyatomic species, such as C_2 , C_3 , C_4 , and C_5 , as well as atomic C.^{5,6,8}

The vaporization coefficient of graphite has been determined by comparing the free evaporation rate and the effusion rate from a Knudsen cell. The experimental values reported varied between 0.001 and 0.4.

Recently, Ramakrishnan and Hoch⁹ determined the condensation coefficients of C_2 and C_3 using the isotopic exchange technique and a Bendix Time-of-Flight mass spectrometer. The isotopic exchange technique used by them involved heating two powder compacts of $C^{12}(s)$ and $C^{13}(s)$ to 2663°K in a tungsten Knudsen cell. [C(s) means C atoms in the solid state.] Initially, the vaporization of $C^{12}(s)$ and $C^{13}(s)$ will produce $C^{12}(g)$, $C^{13}(g)$, $C_2^{12}(g)$, $C_2^{13}(g)$, $C_3^{12}(g)$ and $C_3^{13}(g)$ as the predominant vapor species. [C(g), $C_2(g)$ and $C_3(g)$ mean monatomic, diatomic and triatomic carbon vapor species in the gas phase, respectively.] Exchange reactions between the gaseous species and the solid generated isotopically mixed molecules $C^{12}C^{13}(g)$, $C_2^{12}C^{13}(g)$ and $C^{12}C_2^{13}(g)$ in the vapor. The exchange reactions were

studied by analyzing the vapor effusing from the Knudsen cell using a Bendix Time-of-Flight mass spectrometer. The condensation coefficient β_2 of C_2 was evaluated from the steady state concentration of $C^{12}C^{13}(g)$. The condensation coefficient β_3 of C_3 was determined from the steady state concentration of $[C_2^{12}C^{13}(g) + C^{12}C^{13}(g)]$. The experimental values obtained at 2663°K by Ramakrishnan and Hoch were 4×10^{-2} for β_2 and 2.3×10^{-2} for β_3 .

The only other experimental values of the vaporization coefficients on non-pyrolytic graphite are those given by Thorn and Winslow.⁴ They estimated, from their overall vaporization data and the mass spectrometric data of Chupka and Inghram,¹² that the values of the vaporization coefficients at 2450°K were $\alpha_1 = 0.37$, $\alpha_2 = 0.34$, and $\alpha_3 = 0.08$. The values of the vaporization coefficients of pyrolytic graphite have been measured by Burns et al.¹⁰ and Zavitsanos.⁸ These values, and those of Thorn and Winslow, are given in Table I. Though pyrolytic graphite is highly anisotropic, the coefficients given in Table I for the two crystal faces are quite similar because as Wachi and Gilmartin⁶ noted "for the C-face, the C_2 and C_5 molecules appear to have evaporated predominantly from the edges of the ab-plane (basal plane) of the crystallites at grain boundaries, and from other discontinuities". This observation is confirmed recently by the fact that etch pits have been observed with a scanning electron microscope

to 3000°K.¹⁸ Other problems associated with the free vaporization of ordinary graphites have also been described by Wachi and Gilmartin who found that with the long duration heating of graphite samples, the intensity of C₃, C₂ and C₁ varies with time and that the rate of evaporation from the surfaces increased drastically above 2900°K. Thus it is problematical that a simple vaporization was observed. The time dependency of the vaporization rate was explained by Wachi and Gilmartin as follows: "in essence the continuous transformation of closed pores to open pores and vice-versa, the gradual attainment of steady state vapor pressure in the open pores, the continuous changes in surface areas and surface morphology and the continuous diminution of C₁ and C₂ by preferential condensation and by recombination reactions could account for the relatively large abundance of C₃ and for the time dependency of species distribution at constant surface temperature." The rapid increase of total vaporization at 2900°K was ascribed by Wachi and Gilmartin to the graphitization of the binder.

To obtain the vaporization coefficients of the various carbon species, it was necessary to compare rates of effusion from a Knudsen cell, which are related to the equilibrium vaporization rates, and vaporization rates from free surfaces often referred to as Langmuir rates. These two different types of measurements are generally carried out in different laboratories and therefore direct comparison

is quite difficult. Table II contains the heats of vaporization under Knudsen "equilibrium" conditions as given by Zavitsanos.⁷ Table III, summarizing the activation energies for vaporization from free surfaces as reported by various authors, was taken from the paper by Steel and Bourgelas¹¹ with our addition of the uncertainties as given by Wachi and Gilmartin.⁶ Since Table III shows such large standard deviations in heats for free vaporization it is meaningless to compare the data given in Tables II and III to obtain α_1 . On the other hand in the work of Ramakrishnan and Hoch⁹ the condensation coefficient was determined in one experiment, the errors which result from the uncertainties in the temperature of two independent determinations and the errors in the mass spectrometer constants, ionization cross sections, etc. did not arise. The aim of the present work was to confirm the fact that $\alpha_2 \approx \alpha_3$, (as was found that $\beta_2 \approx \beta_3$) and also to obtain a value for α_1 which could not be obtained in the isotopic exchange measurements. It must be pointed out that under equilibrium conditions $\alpha_i = \beta_i$.

The aim of the method used here again is to be able to compare vaporization rate measurements on two different species in a single experiment and thus avoid the inaccuracies of temperature measurements at high temperatures. Finally, the method developed will be applied to the experimental data of other workers, and hopefully the result will be a

unified picture of the available data on the vaporization of graphite. This will be possible because the method developed here compares data on two different species obtained in a single experiment.

THEORY

The kinetic theory of gases gives for the rates of vaporization from a free surface:

$$m_i = \alpha_i P_i \left(\frac{M_i}{2\pi RT} \right)^{1/2} \quad (1)$$

where $i = 1, 2, 3, \dots$

m = rate of vaporization in $\text{g} \times \text{cm}^{-2} \times \text{sec}^{-1}$

α = vaporization coefficient

P = equilibrium vapor pressure in atm

M = molecular weight

T = temperature in $^{\circ}\text{K}$.

By measuring relative ion intensities in the mass spectrometer under equilibrium (Knudsen) and free vaporization (Langmuir) conditions, I^K and I^L , respectively, ratios of vaporization coefficients can be calculated independently of any knowledge or relative ionization cross sections, multiplier efficiencies, and accurate knowledge of the temperature.

For "equilibrium" (Knudsen) conditions,

$$\frac{P_j}{P_i} = \frac{I_i^K}{I_i^K} \times \frac{\sigma_i}{\sigma_j} \times \frac{E - A_i}{E - A_j} \times \frac{\left(1 + \frac{h}{\alpha_j S}\right)}{\left(1 + \frac{h}{\alpha_i S}\right)} \quad (2)$$

For a non-equilibrium (Langmuir) vaporization,

$$\frac{\alpha_j P_j}{\alpha_i P_i} = \frac{I_j^L}{I_i^L} \times \frac{\sigma_i}{\sigma_j} \times \frac{(E - A_i)}{(E - A_j)} \quad (3)$$

where σ = relative cross section for ionization

E = energy of ionizing electrons

A = appearance potential

h = effusion orifice area

S = vaporizing surface area.

Combining equations (2) and (3)

$$\frac{\alpha_j}{\alpha_i} = \frac{I_j^L}{I_i^L} \times \frac{I_i^K}{I_j^K} \times \frac{\left(1 + \frac{h}{\alpha_i S}\right)}{\left(1 + \frac{h}{\alpha_j S}\right)} \quad (4)$$

In most cases $\frac{h}{\alpha_i S} \ll 1$, and then

$$\frac{\alpha_j}{\alpha_i} = \frac{I_j^L}{I_i^L} \times \frac{I_i^K}{I_j^K} = \frac{R_{j,i}^L}{R_{j,i}^K} \quad (5)$$

for abbreviation $R_{j,i}^L$ stands for $\frac{I_j^L}{I_i^L}$. Equation (5) is the working equation of the present method. The ratio $R_{j,i}^L$ can be determined in one experiment, and $R_{j,i}^K$ in another. The ratios do not vary greatly with temperature; as long as the temperature difference between the two measurements is less than 100°, the temperature variation can be neglected, and this method again is temperature insensitive.

SAMPLES

The samples used were made of the ultra purity spectrographic electrode grade graphite, grade UF4F, supplied by Ultra Carbon Corporation, Bay City, Michigan.

The properties of the spectrographic graphite grade UF4F specimen are given in Table IV. Prior to measurements the sample was outgassed by heating in the mass spectrometer at 2050°K for 1 hour and then at 2400°K for 45 minutes.

APPARATUS

The conventional Knudsen cell electron bombardment heating system attached to the Bendix Time-of-Flight mass spectrometer was previously found to be inadequate for obtaining temperatures higher than 2663°K by Ramakrishnan and Hoch.⁹ In order to get an intense mass spectrum of carbon vapor species, temperatures higher than 2663°K are needed. The most practical method of attaining temperatures in the range 2200-3000°K was assumed to be radio frequency induction heating, even though the RF signal might interfere with the operation of the mass spectrometer.

The RF heating method in conjunction with the Bendix Time-of-Flight mass spectrometer was tested as in an arrangement shown in Fig. 1. The design of the induction heating assembly was patterned after the conventional Bendix electron bombardment Knudsen cell heating tower. A schematic sketch of the induction heating system is shown in Fig. 2. The assembly essentially consisted of three parts: (1) A stainless steel base flange, (2) a water-cooled copper work coil, and (3) a crucible

support assembly. RF power was fed into the heating coil through two high frequency feedthroughs.²² The base plate was cooled by a separate water line which consisted of a double turn of copper tubing brazed to the bottom surface of the plate and two 1/4" diameter brass tubes brazed to the top surface of the plate at right angles to the feedthroughs. The two brass tubes supported a copper plate which was positioned above the top of the work coil. The copper plate was fitted with a removable 1 1/4" diameter copper disc containing a 3/32" diameter hole which is aligned with the slit of the ion source of the mass spectrometer. After testing several coil designs, an acceptable copper coil was made which consisted of five turns of 1/8" I.D. (3/16" O.D.) copper tubing with a 13/16" internal coil diameter. The Knudsen cell was supported by three 1/16" diameter tungsten rods spaced at 120° apart. The three tungsten rods were fixed to a tantalum stand. The entire crucible support assembly was movable. After aligning the hole of the Knudsen cell with the hole in the copper disc, the crucible support assembly was held in position by two clamps. When the hole in the Knudsen cell was lined up with the hole in the copper disc, the effusion flow from the cell could enter the ion source of the mass spectrometer.

Power for the induction heating coil was supplied by a 20 kw Thermonic radio frequency generator model 1070 which operated at a frequency of 460 kc. The efficiency

of the heater was increased by using a variable ratio step-down transformer provided with taps for 3, 4 or 5 turns of the secondary of the transformer. The step-down transformer was a model TD-74 manufactured by Taylor-Winfield Corporation, Warren, Ohio.

Before using the induction heater in the mass spectrometer, its performance was tested in a specially constructed vacuum system. A tungsten Knudsen cell and a graphite block were heated in the vacuum system. The temperatures of the cell and the block were measured with a Leeds & Northrup disappearing filament type optical pyrometer. The pyrometer readings were corrected for the emissivity of the sample and for the glass window absorption. While the tungsten cell was heated to 2683°K without trouble, the graphite block, when continuously heated up to 2773°K, produced arcing and a glow discharge in the system. Examination of the heater after the conclusion of the run indicated a layer coating of thick carbon on the coil and the base of the feedthroughs. The high vaporization rate of graphite at 2770°K resulted in the rapid buildup of a conductive layer of carbon in the system. The carbon deposit shorted the induction coil feedthroughs to the base plate.

Since it was thought earlier that a slow pumping speed of the vacuum system can bring about arcing in the system,⁹ the original vacuum system attached to the Knudsen

cell heating tower which had been supplied by Bendix Corporation, Cincinnati Division, was replaced by a new vacuum system, consisting of a 4" diffusion oil pump, a 2" diameter copper tubing connecting the pump and the heating tower and a 2" diameter vacuum valve.

EXPERIMENTAL PROCEDURE

Using RF heating and the Bendix Time-of-Flight mass spectrometer, as previously described, the carbon vapor over spectrographic electrode grade graphite was analyzed both under free vaporization and equilibrium vaporization conditions. For the free vaporization experiments, cylindrical blocks of 1/2" diameter and 7/16" height were cut out from a spectrographic graphite cylindrical block of 13/16" diameter and 1 1/2" height which had been out-gassed in an outside furnace in such a manner as described in the section entitled SPECIMEN and used. In order to avoid rapid buildup of a conductive layer of carbon in the heating system, a tantalum sleeve was used in the free vaporization experiments. The tantalum sleeve is in a shape of cylindrical cup of 5/8" outer diameter and 5/8" height, covering all sides of the cylindrical graphite block specimen except the top. The top surface of the specimen was polished with 4/0 emery paper.

In the equilibrium vaporization experiments, two kinds of Knudsen cells were used; one made of tantalum and

the other made of tungsten. The tantalum Knudsen cell has an orifice of 0.040" diameter and in some runs was provided with a graphite liner made from the same block as the specimen itself was made from. A schematic sketch of the tantalum Knudsen cell and the graphite liner is shown in Fig. 3. The tungsten Knudsen cell has an orifice of 0.040" diameter and in some run was provided with a tantalum insert. Another tungsten Knudsen cell having a smaller orifice of 0.026" diameter was also used in some runs. A schematic sketch of the tungsten Knudsen cell and the tantalum insert is shown in Fig. 3 in the report by Ramakrishnan and Hoch.⁹ In general, the orifice area to total sample area ratio, h/S , was always less than 10^{-3} .

The temperature was measured by sighting into the orifice of the cell with a calibrated Leeds & Northrup disappearing filament type optical pyrometer. Corrections due to prism and glass window absorption were made as described previously.⁹

RESULTS

Ionization efficiency runs were made using a tantalum crucible containing small chunks of spectrographic graphite. The effective relative ion intensities at 2620°K for the three predominant species (C_1 , C_2 , C_3) were obtained by subtracting the heights of the ion peaks

at mass numbers 12, 24 and 36 recorded with the shutter in closed position, from the corresponding peak heights recorded with the shutter in open position, respectively. Each intensity datum is the average of at least four readings. The ionization efficiency curves as a function of bombarding electron energy, for C^+ , C_2^+ and C_3^+ are shown in Fig. 4. The ion efficiency curve for Ar^+ was also obtained from the ion intensity measurement as a function of bombarding electron energy at room temperature and is shown in Fig. 4. It is apparent that at electron energies up to 20 volts no significant amount of fragmentation takes place.

In both the free vaporization and the Knudsen cell vaporization runs, relative ion intensities were measured using an electron energy of 20 volts with the shutter in the open and the closed positions, and in the temperature range $2300^\circ-2800^\circ K$. When the shutter was closed during the measurement, at an electron energy of 20 eV, the peak heights diminished to zero except for the mass 36. The height of the mass 36 peak diminished by over 96% when the shutter was closed. The measured effective relative ion intensities, I_{12} , I_{24} , and I_{36} , and the calculated ion intensity ratios, I_{36}/I_{24} , I_{36}/I_{12} and I_{24}/I_{12} , are summarized in Table V. Each relative ion intensity value is the average of at least five readings. The standard deviation of each effective

relative ion intensity value and the maximum error range of each ion intensity ratio value are also given in Table V. It should be noted that among the peak heights, I_{12} , I_{24} and I_{36} of C , C_2 and C_3 , I_{36} is generally the largest and I_{24} is the smallest with the exception of the results of Runs 6 and 7 in which the tantalum Knudsen cells were used. In Runs 6 and 7, the I_{12} peak was the smallest, (not counting I_{48} and I_{60}) while the peak I_{36} was still the largest.

The peak heights of the carbon vapor species heavier than C_3 were not usually large enough to allow for their measurement except in Run 7. In Run 7, ion peaks of C_4 and C_5 were high enough to allow the measurements of their heights. In Table V the measured effective relative ion intensities, I_{48} and I_{60} , and the calculated ion intensity ratios, I_{48}/I_{12} and I_{60}/I_{12} , are given.

After each vaporization run, the crucible and the specimen were visually inspected. The tantalum Knudsen cell was found to have reacted with the carbon vapor resulting in color change of the inner wall and the orifice wall of the cell from metallic to golden yellow. This color change of the cell was attributed to the formation of a TaC layer on the tantalum. Aside from the coating of yellow color, the central circular part of the flat internal surface of the top and the corresponding

part of the bottom of the cell were found to be covered by a thick gray fragile layer. These layers were determined to consist of carbon by means of powder x-ray diffraction. In Fig. 5, a macrophotograph of the tantalum Knudsen cell heated with the graphite liner fitted inside is shown. The central part of the inside surface of the top of the cell is seen to be of dull gray color in Fig. 5. This part is covered by a deposited carbon layer. Such a carbon layer was easily peeled off by a strong blast of air. The fragments which are seen between the top and the bottom in Fig. 5 are part of the layer which was peeled off in such a way from the central part of the inside surface of the bottom. Under the deposited carbon layer, a yellow TaC layer was again found to be present. After the conclusion of the run in which the graphite liner was used, the outer surface of the side of the liner was found to have recessed markedly; and had become much rougher than the inner surface of the liner or the surfaces of the graphite chunks inside the liner. This is indicative of the fact that marked vaporization occurred from the outer surface of the side of the graphite liner. On the other hand, no evidence of recognizable amount of reaction between the tungsten cell and carbon vapors was observed.

Combining the free vaporization and the equilibrium vaporization data, ratios of the vaporization coefficients

of the carbon species on spectrographic graphite were calculated. In the calculation, the average of the results of Runs 1 and 2 and the average of the results of Runs 3 and 4 were used. The data obtained using the tantalum cells were omitted in the calculation because of the reaction of the cells with carbon vapors. Based on the data obtained from Runs 1 to 4, we get $\alpha_2/\alpha_1 = 0.98$ and $\alpha_3/\alpha_1 = 1.52$, in the temperature range from 2350° to 2800°K, for the vaporization coefficient ratios of the spectrographic graphite. This can be identically rewritten as follows: The vaporization coefficients of the three predominant carbon vapor species, C, C₂ and C₃ over the spectrographic graphite are equal to each other within a factor of two. In the DISCUSSION section, the ratios of vaporization coefficient will be evaluated in detail using all available data in the literature.

DISCUSSION

The important considerations of the results presented in Table V are that the free vaporization data seem to be consistent. The Knudsen vaporization data using the tungsten Knudsen cell and Ta insert are identical. However, the data using tantalum Knudsen cells, with and without graphite liners, show that the ratios increase which in turn seem to indicate that C₁ reacts with tantalum and also tantalum carbide preferentially. C₂ also reacts

whereas C_3 appears to be completely inert. The significance of this observation is the following: Most people either use tantalum or tantalum carbide Knudsen cells, and therefore the ratios calculated later will have to be evaluated with this in mind. Therefore note that not every experimentalist using a very similar arrangement would obtain equivalent reaction. If one uses a tantalum Knudsen cell in which there is a large amount of graphite surface, a large effusion hole, and the collimating system into the mass spectrometer is sufficiently good so that only gas from the Knudsen cell itself enters the ionization chamber (and not gas molecules which hit the orifice or channel walls), then the intensity ratio $\frac{I_n}{I_1}$ would not be influenced. If, however, one uses a tantalum cell with a small orifice, or an inefficient collimating system (as we have been using) to collect all the vapor (including that which strikes the orifice walls), then the ratio of the intensities, $\frac{I_n}{I_1}$, is going to be falsified in a fashion that would make it seem to be much larger than if tantalum would not be present. The use of a tantalum carbide Knudsen cell does not change the effect. C_1 reacts with the tantalum carbide while C_3 either does not or only does so to a much lesser extent. Therefore even on completely carburized TaC, C_1 condenses and some C vaporizes, probably forming equilibrium ratios of

C_1 and C_3 . Thus $\frac{I_3}{I_1}$ will be higher even if there is no net carbon gain by the TaC. This happened in Run #7 where the $\frac{I_3}{I_1}$ ratio did not change with time even though the tantalum had long been carburized to yellow TaC. The intensity of the C_2 peak can similarly be explained.

In order to use equation (5) to evaluate the ratios of the vaporization coefficients, all available data in the literature were scrutinized. Most people, when they show their data, plot the log IT (the mass spectrometry intensity multiplied by the temperature) versus $\frac{1}{T}$. From those graphs we have read off the intensities and calculated the ratios at $\frac{1}{T} = 3.6, 3.8, 4.0, 4.2 \times 10^{-4}$ and so on, and obtained the ratios shown in Table VI. In cases where the experimental data had to be linearly extrapolated, the ratios are in parentheses.

Since only Steele and Bourgelas have carried out both Knudsen and Langmuir measurements, a comparison of the ratios of $\frac{\alpha_n}{\alpha_1}$ from their data and our data is given in Table VII. Table VII also contains the values of $\frac{\beta_3}{\beta_2}$ determined earlier.⁹

As expected, the data of Steele and Bourgelas and ours agree well, especially if one takes into account that Steele and Bourgelas used a tantalum cap during their measurements. If the C_1 from the Knudsen cell reacts with the tantalum cap and thus lowers the C_1 equilibrium pressure, then one will obtain a higher

value of α_1 than should be expected under normal conditions. This would lower the values $\frac{\alpha_n}{\alpha_1}$ if, as we discussed before, C_n reacts less with the tantalum than does C_1 . Within experimental error, Steele and Bourgelas and our data agree indicating that $\alpha_2 = \alpha_1 = \alpha_3$. One has to remember here that we are using intensity ratios and that a factor of 3 in the ratio amounts to a difference in the heats of vaporization at 3000°K of :7 kilocalories. If the factor of 3 arises from errors in all four intensity measurements, each measurement may just be off 30% to account for it; deviation in the normal log IT versus $\frac{1}{T}$ presentation will not be observable.

Other investigators' data who have used either the Knudsen or Langmuir technique are plotted in Figs. 6 and 7 from Table VI, which contains the intensity ratios, $R_{j,i}$ versus $\frac{1}{T}$. On the top of the figures we have plotted the results obtained by us using tantalum Knudsen cells, to show that some of the Knudsen data (where Ta or TaC was present) changes with temperature similarly to ours. The reason for this is at high temperature C_1 reacts more giving a higher $R_{3,1}^K$ ratio. Even if one uses a tungsten Knudsen cell for equilibrium measurements, one is not sure that no reaction will occur between carbon and the tungsten. If again, one assumes that the reactivity of C_1 is highest with the tungsten Knudsen cell, then comparison of free vaporization and equilibrium

vaporization can only be made insofar as to say that if $R_{n,1}^L$ is equal to or smaller than $R_{n,1}^K$, then probably the measurements are correct. Looking first at Fig. 6, one sees that the data of Steele and Bourgelas,¹¹ both Knudsen and free vaporization ratios, vary with temperature and they move in parallel. However our data and Wachi's⁶ data seem to fall on a horizontal line and our Knudsen measurements and the Knudsen measurements of Chupka and Inghram also seem to be temperature independent. If one draws a line in this Figure for $R_{2,1}$ at .45 to .5, independent of temperature; this line would represent within the experimental scatter both the Knudsen and Langmuir data, taking into account the use of tantalum Knudsen cells and the correction to be applied to those.

The situation in the case of $R_{3,1}$ is not so simple, all data seem to vary with temperature. However, looking on at our data, taken with a tantalum crucible, one also sees a large temperature dependence. At low temperature the reactivity of C_1 with tantalum is small. With this fact in mind, if one uses the Knudsen data at low temperature of Drowart et al⁵ and Chupka and Inghram¹² ($\frac{1}{T} \geq 4.4$), the free vaporization data of Wachi, and the present Knudsen and Langmuir measurements, one can draw a horizontal line for $R_{3,1}$ at 4.5; which is again independent of whether it is a Knudsen or Langmuir measurement.

This evaluation indicates that the vaporization coefficients are equal, $\alpha_1 = \alpha_2 = \alpha_3$, as was indicated earlier in Table VII. This result of the evaluation is thought to be highly reliable, because the ion intensity ratio method used here does not require an accurate knowledge of the temperature or of the mass spectrometer constants, ionization cross sections, etc. Thus, it is concluded that the vaporization coefficients of C, C₂ and C₃ over conventional graphites are all equal to 3×10^{-2} , which was obtained for the condensation coefficients of C₂ and C₃ earlier⁹ using the isotopic exchange method.

Several authors determined the vaporization coefficient of pyrolytic graphite. Table I contains the data and graphite descriptions from Burns¹⁰ and Zavitsanos.⁸ The data of Burns¹⁰ cannot be analyzed further, as they only gave the vaporization coefficient parallel and perpendicular to the C face, from which we cannot calculate the ratio of the peak intensities. On Figures 8 and 9, $R_{2,1}$ and $R_{3,1}$ intensity ratios are plotted both for free vaporization and also for the Knudsen vaporization. The lines marked in each Figure are the equilibrium Knudsen ratios derived earlier using non-pyrolytic graphites. One can see that the data of Zavitsanos⁷ using pyrolytic graphite and TaC Knudsen cells, seem to scatter around this "equilibrium line". There is a temperature dependence of Zavitsanos⁷ equilibrium data. The ratio increases

when the temperature increases. A similar increase but of a larger magnitude can be seen in the free vaporization measurements of Zavitsanos⁸ and of Wachi and Gilmartin.⁶

The Knudsen measurements, using pyrolytic graphite and ordinary graphite must show the same intensity ratios, and temperature dependence. If they do not, then, probably the pyrolytic graphite, is not undergoing equilibrium vaporization in the Knudsen cell. We have to assume that the variation in the Knudsen data of Zavitsanos' pyrolytic graphite measurements⁶ is just scatter and the horizontal lines in both Figures 8 and 9 represent the equilibrium ratios. Comparing now the free vaporization ratios for pyrolytic graphite one notices that the $R_{2,1}^L$ ratio increases with temperature but its value is about that for ordinary graphites; the $R_{3,1}^L$ ratio also increases with temperature, but its value is much smaller than that for ordinary graphites. Thus, in the free vaporization of pyrolytic graphite we find that the $R_{2,1}$ ratio is higher than the one in Knudsen measurements and also higher than in the free vaporization measurements of ordinary graphite, whereas the $R_{3,1}$ ratio is lower than the one in the ordinary graphite and also lower than in the equilibrium measurements. If one plots the $R_{3,2}^L$ ratio for free vaporization, Fig. 10, one finds that this ratio is independent of temperature. Thus, the temperature dependence in the $R_{2,1}^L$ and $R_{3,1}^L$ ratios must be due to some reactivity of C_1 with the pyrolytic graphite surface, whose net effect seems to be the same as when we have reactivity with tantalum carbide.

From the ratios of free vaporization, one has to conclude that from a pyrolytic graphite surface, C_2 comes out easiest, i.e. its vaporization coefficient is closer to unity. C_1 comes out less readily and C_3 comes out with the lowest vaporization coefficient. However, this statement would only be valid if all the species would come off from the surface. As Wachi and Gilmartin⁶ already noted this is not the case. Thus, it is not really possible to talk about vaporization coefficients for pyrolytic graphite.

FUTURE WORK

The vaporization characteristics of different grades of graphite which are commercially available will be studied using the triple Knudsen cell and RF induction heating tower coupled with a Bendix Time-of-Flight mass spectrometer. The triple Knudsen cell technique was developed by Hackworth¹⁶ for the determination of thermodynamic activity of alloys. The alloy for which one component's activity is to be measured is placed in one of two effusion chambers of the triple cell and the pure isotopic standard in the other. The atomic or molecular beams from each chamber effuse into a third chamber and through a collimating hole into the ion source of the mass spectrometer. The recorded intensities are proportional to the vapor pressures within the chambers.

A simple calculation based upon the ratio of intensities gives a direct determination of the activity of the component of alloy. In this investigation the isotopic standard will be C^{13} . Samples of the various grades of graphite, in turn, will be placed in one of the chambers while the C^{13} standard sample is placed in the other. The vapor pressures of the carbon vapor species will be proportional to the ion signals corresponding to the C^{12} , C_2^{12} , and C_3^{12} from the normal graphite and C^{13} , C_2^{13} , and C_3^{13} from the enriched sample.

TABLE I
VAPORIZATION COEFFICIENTS OF CARBON VAPOR SPECIES
OVER GRAPHITE AND THEIR RATIOS

Researchers	Type of Graphite	Electron Energy, eV	Temperature °K	Vaporization Coefficients and Their Ratios				
				a_1	a_2	a_3	a_2/a_1	a_3/a_1
Thorn & Winslow ⁴	Reactor Grade	--	2450	0.37	0.34	0.08	0.92	0.22
Burns et al. ¹⁰	Pyrolytic, a-face	15,17, 20	2500	0.23	0.38	0.04	1.7	0.17
	Pyrolytic, c-face	15,17, 20	2500	0.14	0.26	0.03	1.8	0.21
Zavitsanos ⁸	Pyrolytic, c-face	20	2618 ~ 2760	0.24	0.50	0.023	2.1	0.096

TABLE II

"EQUILIBRIUM" HEATS OF VAPORIZATION (kcal/mole) AT 298°K FOR C_n

Species	Zavitsanos ⁸		Zavitsanos ⁷		Drowart et al ⁵		Modified* Drowart et al		"Approximately- Best" Values By Palmer and Shelef ¹⁹
	3rd Law	2nd Law	3rd Law	2nd Law	3rd Law	2nd Law	3rd Law	2nd Law	
C	173.5±1	170.3±1.1							170.89
C ₂	202.0±1.1	209.1±1.1	203.5±1.2	197.8±1.7	200.0±1.7	197±2			199.02
C ₃	188.8±1	194.5±1.2	187.2±1.5	188.2±1.5	189.6±2.3	185.6±2.5			193.5**
		(196.7±1)**	(201.9±1.5)**						
			(192.8±1.5)***						
C ₄			241.5	231.3±7.1	242.3±5.8	234.8±8			257.8 ^a
			257 ^a						

Free Energy functions from the JANAF Tables (unless stated)

*Using modified ionization cross sections¹⁹ (same as in Zavitsanos' work)**Using free energy functions by Strauss²⁰

***Using free energy functions by Altman (private communication to Zavitsanos)

^aUsed free energy function 128 higher than JANAF

TABLE III
 ACTIVATION ENERGIES OF VAPORIZATION FROM
 POLYCRYSTALLINE GRAPHITE SURFACES

Species	Honig ¹⁷	Chupka and Inghram ²¹	Wachi and Gilmartin ⁶	Steele and Bourgelas ¹¹
C ₁	178 ₋ 10	177 ₋ 6	179 ₋ 5	(170)
C ₂	199 ₋ 20	200 ₋ 10	195 ₋ 5	189
C ₃	178 ₋ 10	200 ₋ 10	197 ₋ 10	187
C ₄	-	-	241 ₋ 10	234
C ₅	-	-	242 ₋ 6	236

TABLE IV
 PROPERTIES OF ULTRA PURITY SPECTROGRAPHIC
 ELECTRODES, GRADE UF4F*

Ash Content	10 ppm
Grain Size	max. 0.008"
Bulk Density	1.76
Porosity	22.7 percent
Electrical Resistivity	0.00045 ohm-in
Coefficient of Thermal Expansion	
With Grain:	2.1×10^{-6} in/in/°C
Against Grain:	3.5×10^{-6} in/in/°C
Flexural Strength	
With Grain:	4,200 psi
Against Grain:	3,100 psi
Tensile Strength, with grain	2,200 psi
Compressive Strength, with grain	8,700 psi
Oxidation Threshold	426°C

* Extruded graphite.

TABLE V
RELATIVE ION INTENSITIES AND RATIOS OF CARBON VAPOR
SPECIES OVER SPECTROGRAPHIC GRAPHITE UF4F

No. of Run	Experimental Condition	Temp. °K	Relative Ion Intensity (Arbitrary Unit)				Ion Intensity Ratio				
			I ₁₂	I ₂₄	I ₃₆	I ₆₀	I ₂₄ /I ₁₂	I ₃₆ /I ₁₂	I ₄₈ /I ₁₂	I ₆₀ /I ₁₂	
1	Free vaporization	2355	45.2±1.6	28.8±1.7	330±12		0.63±0.06	7.3±0.5			
2	Free vaporization	2497	49.6±3.8	12.6±1.7	220±8		0.25±0.05	4.4±0.5			
3	Tungsten K-cell with a Small Orifice	2634	3.6±1.8	1.4±1.0	13.2±2.0		0.39±0.49	3.7±2.4			
		2675	6.4±1.3	2.7±2.7	--		0.42±0.50	--			
4	Tungsten K-cell with a Large Orifice	2792	9.3±2.2	5.2±0.7	35.4±2.3		0.56±0.22	3.8±1.2			
5	Tungsten K-cell with a Large Orifice with Tantalum Insert	2415	7.7±1.6	2.6±0.6	14.5±1.6		0.34±0.15	1.9±0.6			
6	Tantalum K-cell	2435	7.9±1.2	9.8±1.1	160±4		1.24±0.33	20.3±3.6			
		2487	13.4±1.2	32.8±2.4	513±5		2.45±0.40	38.3±3.8			
7	Tantalum K-cell with Graphite Liner	2553	1.5±1.1	6.8±0.9	288±22		4.5±3.9	192±155			
		2620	4.5±0.4	11.5±0.4	434±57		2.6±0.3	96±21			
		2692	5.6±2.6	17.0±2.3	710±30		3.0±1.8	127±64			
		2661	7.7±2.6	21±5.5	683±19	2.5±1.2	5.8±1.2	2.7±1.6	89±33	0.32±0.26	0.75±0.41
		2671	32±3.4	93±1.7	2470±59	7.0±2.7	23±3	2.9±0.4	77±10	0.22±0.11	0.72±0.17

TABLE VI
 RATIOS OF ION INTENSITIES OF CARBON VAPOR SPECIES OVER CONVENTIONAL
 GRAPHITES TAKEN FROM THE PREVIOUS DATA IN LITERATURE

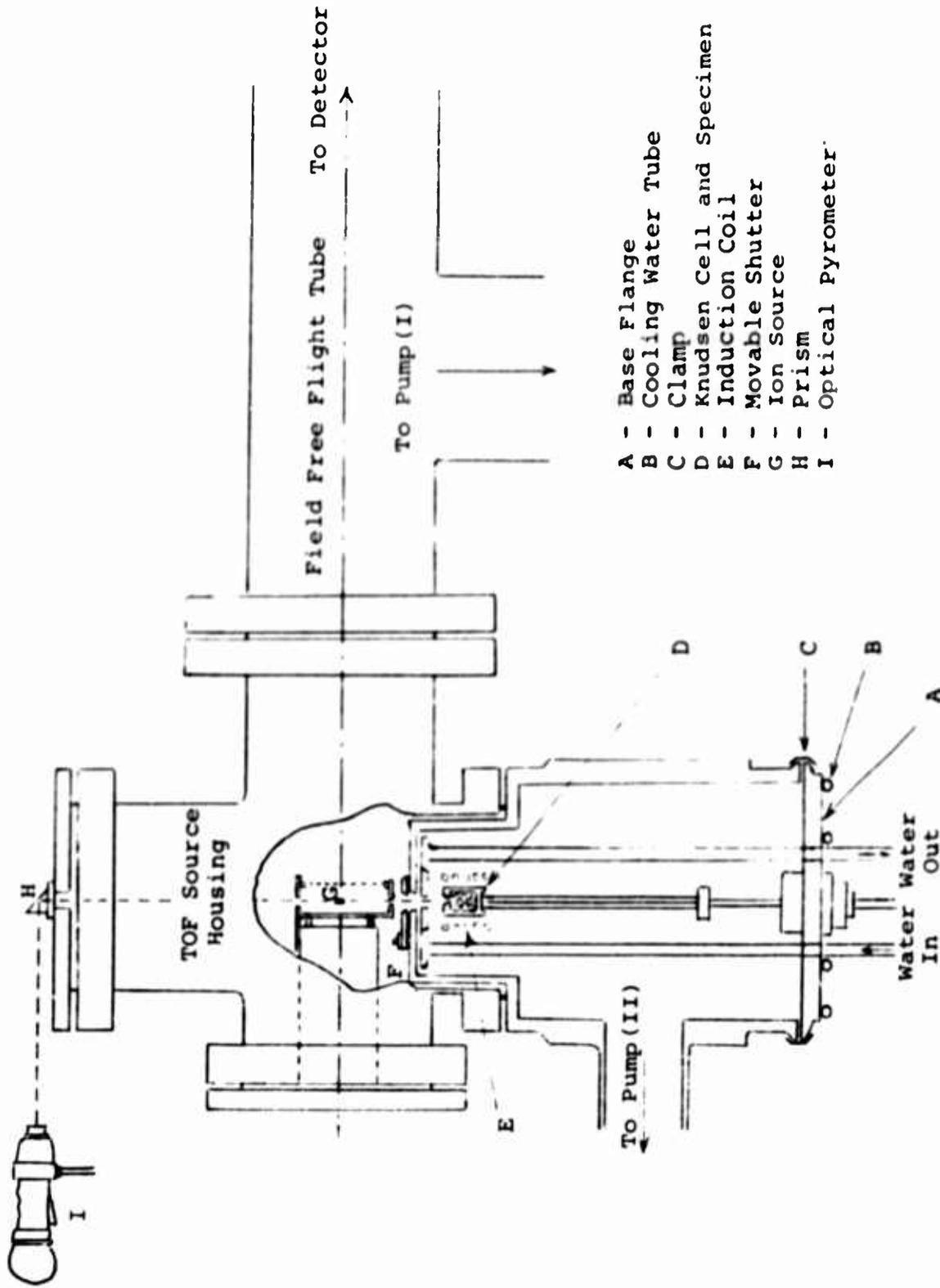
Researcher	Type of Graphite	Experimental Condition	Ion In- tensity Ratio										
			3.5	3.6	3.8	$10^4/T(^{\circ}K)$							
						4.0	4.1	4.2	4.4	4.6	4.8		
Wachi and Gilmartin ⁶	UT-G	Free	R ₂ , ^L	0.48	0.46	0.44							
			R ₃ , ^L	4.52	4.42	4.5							
			R ₄ , ^L	0.063	0.0442	0.023							
			R ₅ , ^L	0.0863	0.0596	0.028							
Drowart et al ⁵	Finely Granu- lated Graphite	Ta or W K-cell (h/s < 10 ⁻⁵)	R ₂ , ^K				0.53		0.326		0.218		
			R ₃ , ^K				6.71		4.88		3.91		
			R ₄ , ^K				9.16x10 ⁻³		3.28x10 ⁻³		(1.15x10 ⁻³)		
			R ₅ , ^K				1.88x10 ⁻²		6.01x10 ⁻³		(1.97x10 ⁻³)		
			R ₅ , ^L						0.500		0.505		
Chupka and Inghram ¹²	Acheson With Graphite Liner	Ta K-cell (0.040" d orifice)	R ₂ , ^K				0.513						
			R ₃ , ^K				6.85		5.41		4.63		
Steele and Bourgeois ¹¹	Aremco RG-504	Free	R ₂ , ^L	0.629	0.490				0.334				
			R ₃ , ^L	(2.87)	2.22				1.373				
			R ₄ , ^L	3.59x10 ⁻³	(2.40x10 ⁻³)				(1.090x10 ⁻³)				
			R ₅ , ^L	1.132x10 ⁻²	(5.58x10 ⁻³)				(1.349x10 ⁻³)				
			R ₅ , ^K	0.492	0.363				0.220				
Wachi and Gilmartin ²³	27A inside Ta cell	Graphite K- cell (0.025" d Orifice) With Ta Cap	R ₂ , ^K	9.64	7.72				5.27				
			R ₃ , ^K	1.24x10 ⁻²	6.15x10 ⁻³				(1.58x10 ⁻³)				
			R ₂ , ^L				0.51						
			R ₃ , ^L				12.0						

TABLE VII
RATIOS OF RELATIVE ION INTENSITIES AND VAPORIZATION OR
CONDENSATION COEFFICIENTS OF CARBON VAPOR SPECIES OVER GRAPHITE

Type Of Graphite	Temp. °K	Ion Intensity Ratio						Ratios of Vaporization or Condensation Coefficient			
		$R_{2,l}^K$	$R_{3,l}^K$	$R_{4,l}^K$	$R_{2,l}^L$	$R_{3,l}^L$	$R_{4,l}^L$	α_{2/a_1}	α_{3/a_1}	α_{4/a_1}	β_{3/β_2}
Researcher											
Steele	2378	0.220	5.27	(1.58×10^{-3})	0.334	1.373	(1.090×10^{-3})	1.52	0.26	0.69	
and Aremco	2630	0.363	7.72	6.15×10^{-3}	0.490	2.22	(2.40×10^{-3})	1.35	0.29	0.39	
Bourgelas ¹¹	2780	0.492	9.64	1.24×10^{-2}	0.629	(2.87)	3.59×10^{-3}	1.28	0.30	0.29	
Present	2350										
Work	~2800	0.45	3.8		0.44	5.8		0.98	1.52		
Ramakrishnan											
and Hoch ⁹	2663										0.58
Powder											

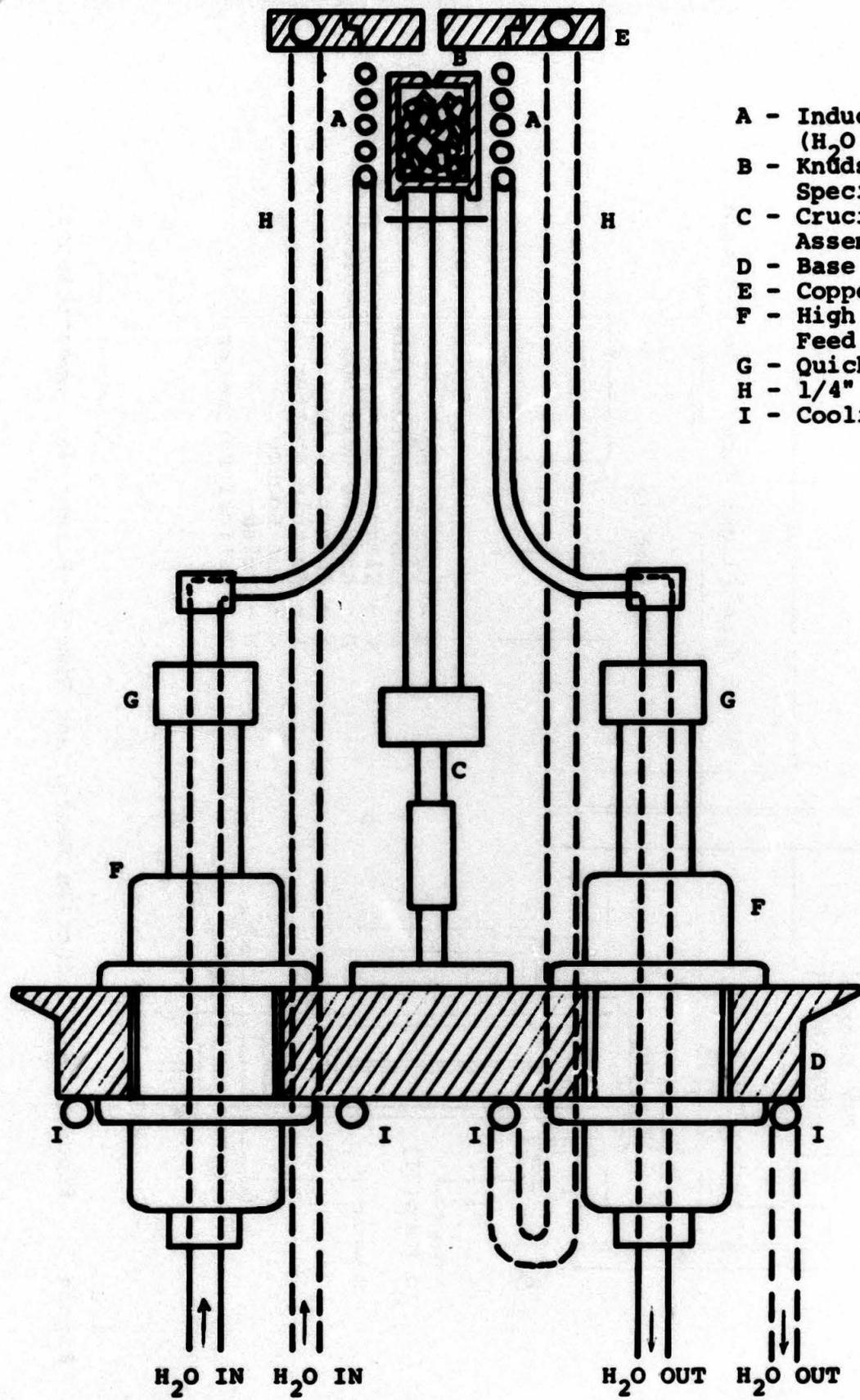
TABLE VIII
 RATIOS OF ION INTENSITIES OF CARBON VAPOR SPECIES OVER PYROLYTIC
 GRAPHITE TAKEN FROM THE PREVIOUS DATA IN LITERATURE

Researcher	Type of Pyrolytic Graphite and Its Manufacturer	Experimental Condition	Ion Intensity Ratio	$10^4/T(^{\circ}K)$							
				3.2	3.4	3.6	3.7	3.8	4.0		
Wachi and Gilmartin ⁶	Continuously Nucleated Pyrolytic, High Temperature Material Co.	Free Vaporization from c-face	$R_{2,1}^L$	1.68	1.54	1.07					
			$R_{3,1}^L$	3.16	2.68	1.82					
			$R_{4,1}^L$	2.06×10^{-2}	1.60×10^{-2}	(9.8×10^{-3})					
			$R_{5,1}^L$	1.93×10^{-2}	1.74×10^{-2}	(1.21×10^{-2})					
			$R_{2,1}^K$		0.648	0.422				0.298	
Zavitsanos ⁷	Density of the PG sample 2.2 g.cm ⁻³ , High Temperature Materials, Inc. Lowell, Mass.	PG K-cell (0.03" d Orifice)	$R_{3,1}^K$		5.49	4.43			3.44		
			$R_{2,1}^K$		0.377				0.203 (0.156)		
			$R_{3,1}^K$		7.26				4.97	4.19	
Zavitsanos ⁸	Surface Nucleated Piece, Density 2.21 g.cm ⁻³ , GE, Detroit	Free Vaporization from c-face	$R_{2,1}^L$			0.952	0.857	0.788			
			$R_{3,1}^L$			0.606	0.526	0.463			



- A - Base Flange
- B - Cooling Water Tube
- C - Clamp
- D - Knudsen Cell and Specimen
- E - Induction Coil
- F - Movable Shutter
- G - Ion Source
- H - Prism
- I - Optical Pyrometer

Figure 1. Knudsen Cell Induction Heater and Time-of-Flight Mass Spectrometer.



- A - Induction Coil (H₂O Cooled)
- B - Knudsen Cell and Specimen
- C - Crucible Support Assembly
- D - Base Flange
- E - Copper Plate
- F - High Frequency Feed Throughs
- G - Quick Coupling Nuts
- H - 1/4" Brass Tubing
- I - Cooling Water Tubing

Figure 2. Knudsen Cell Induction Heating Assembly.

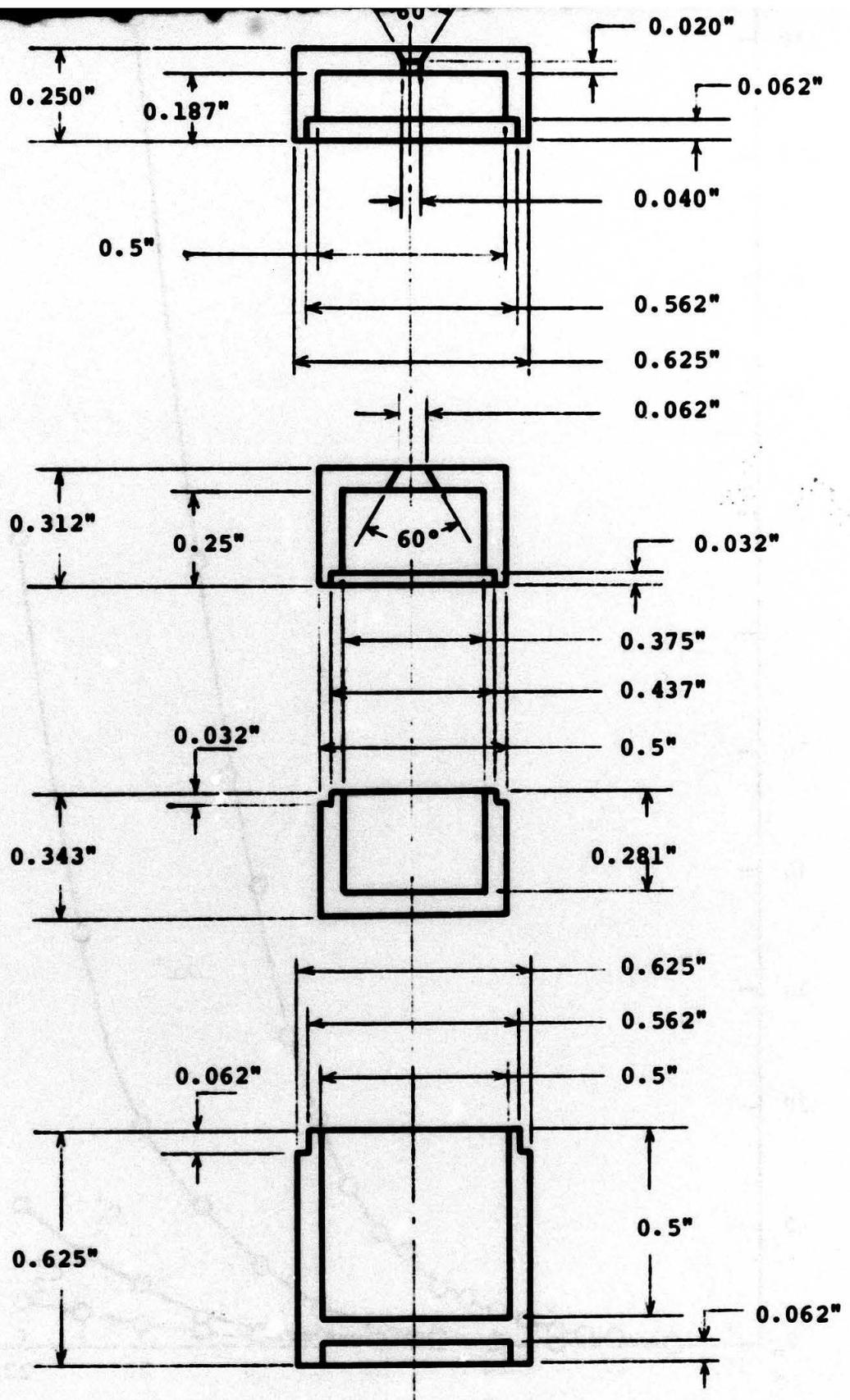


Figure 3. Tantalum Knudsen Cell and Graphite Liner.

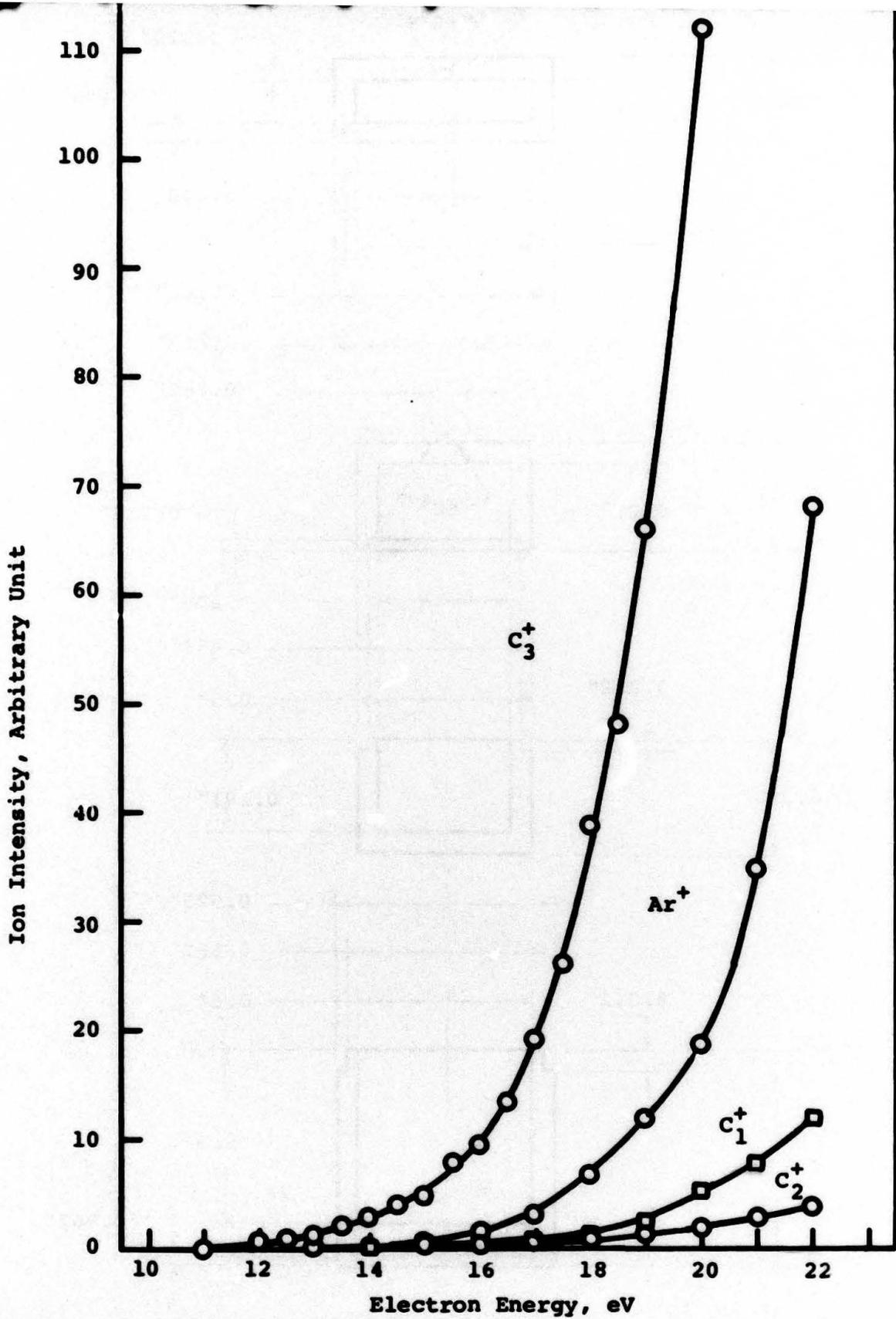


Figure 4. Ionization Efficiency Curves for Carbon Vapor Species and Argon Atom.



Figure 5. Photograph of a Tantalum Knudsen Cell After Heated, With a Graphite Liner Fit Inside.
LEFT: Top of the Cell, RIGHT: Bottom of the Cell

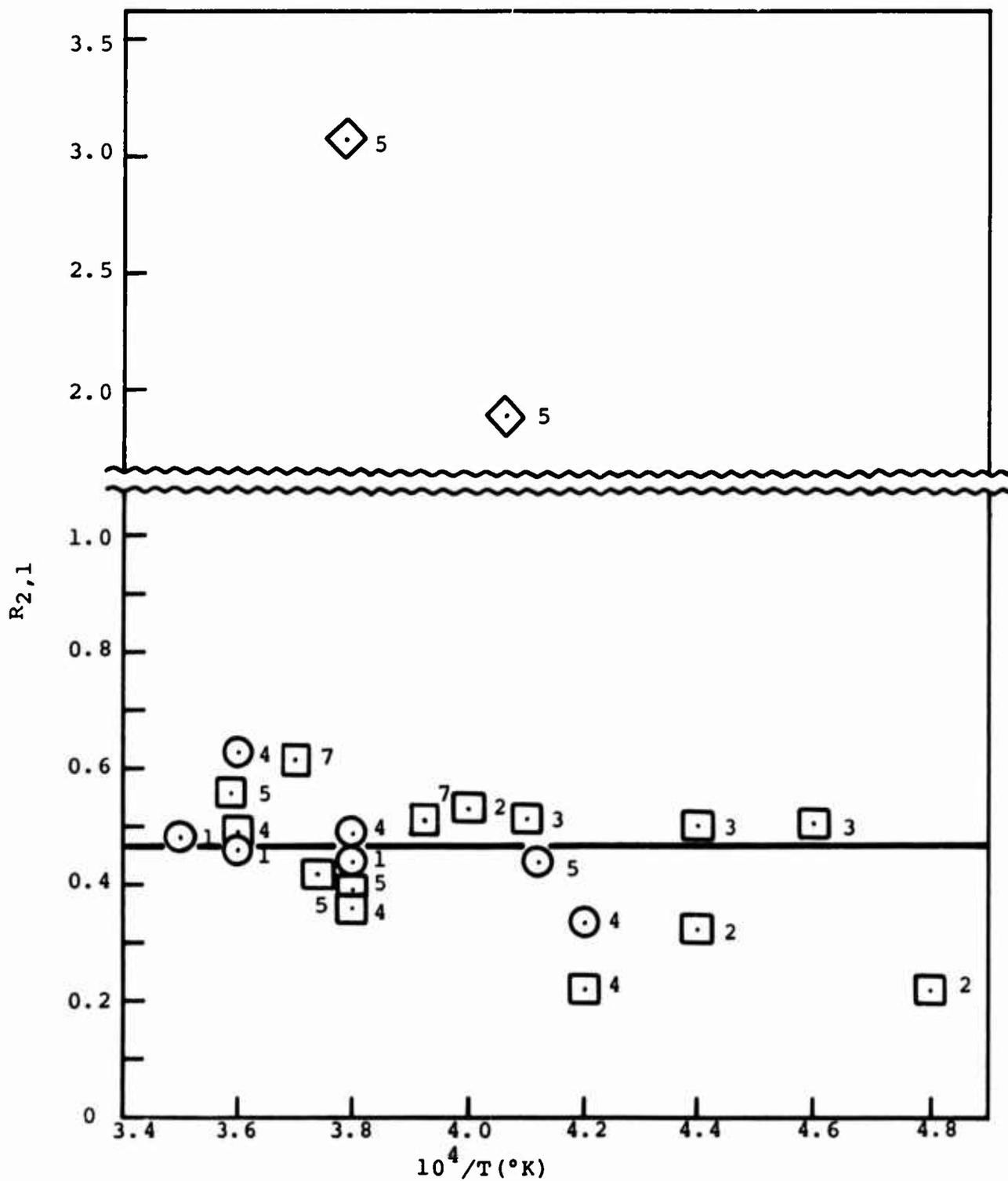


Figure 6. Plot of $R_{2,1}^K$ and $R_{2,1}^L$ vs. $\frac{1}{T}$ for Conventional Graphites.

(See page viii for symbols)

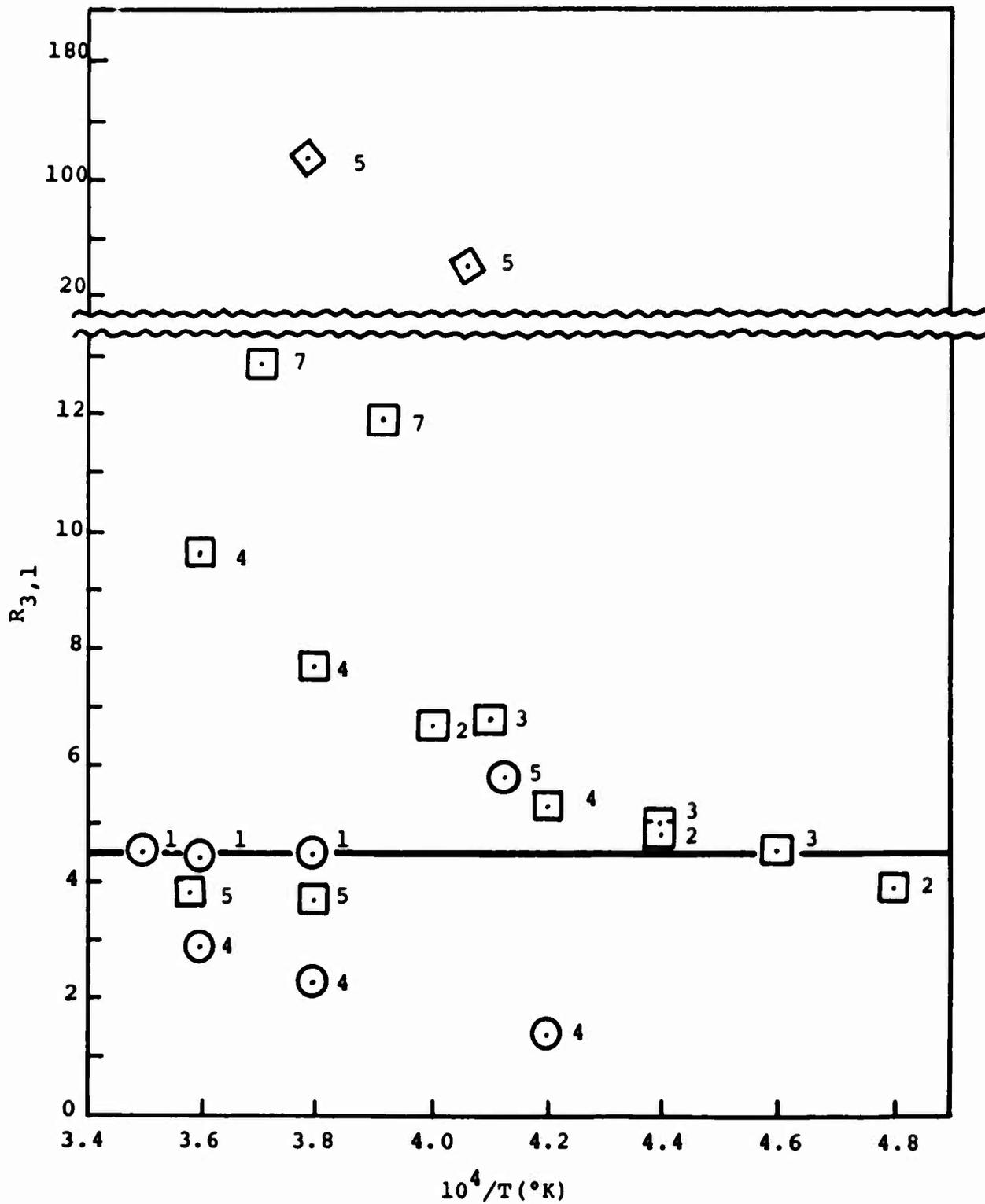


Figure 7. Plot of $R_{3,1}^K$ and $R_{3,1}^L$ vs. $\frac{1}{T}$ for Conventional Graphites.
(See page viii for symbols)

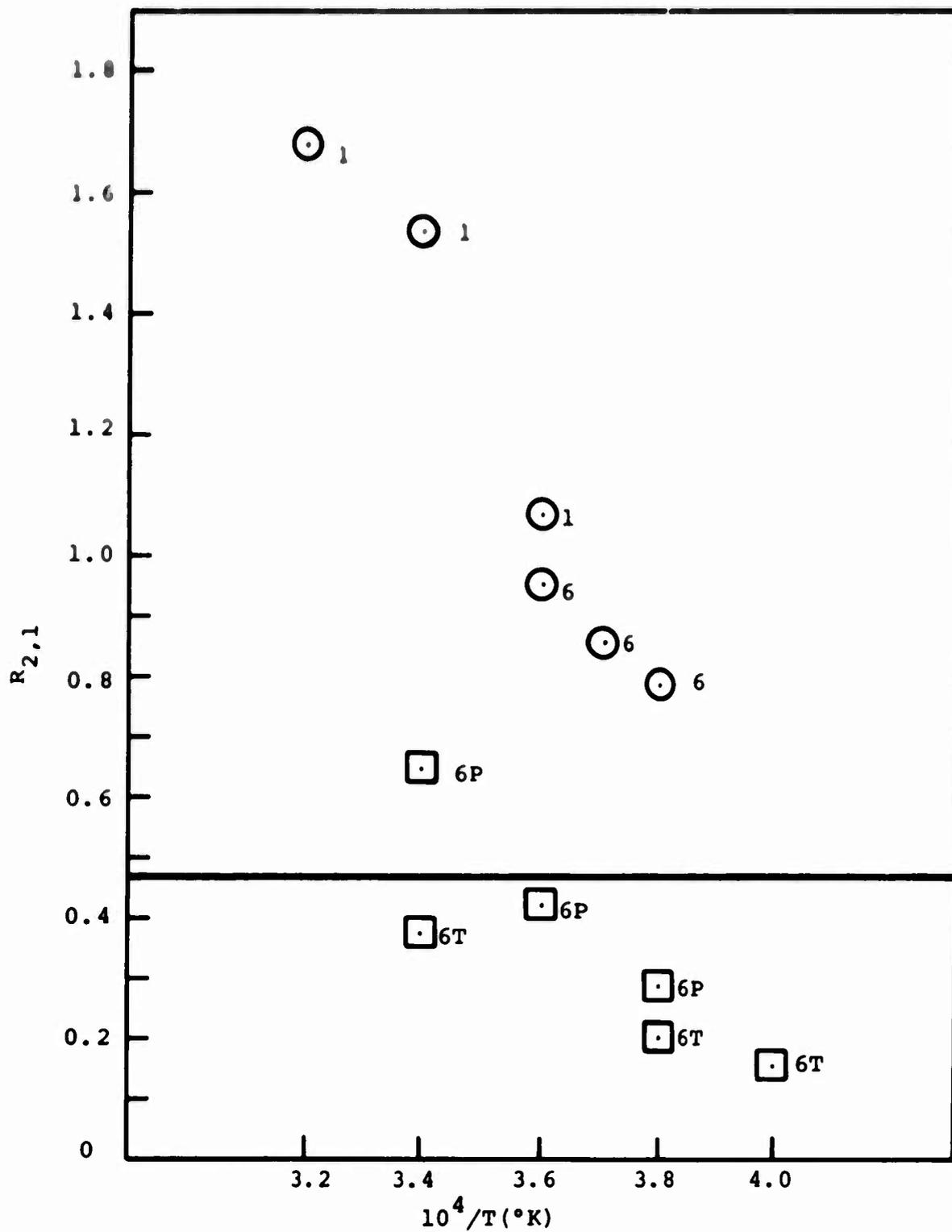


Figure 8. Plot of $R_{2,1}^K$ and $R_{2,1}^L$ vs. $\frac{1}{T}$ for Pyrolytic Graphite. $R_{2,1}^L$ (Free $R_{2,1}^L$ vaporization from c-face)
 (See page viii for symbols)

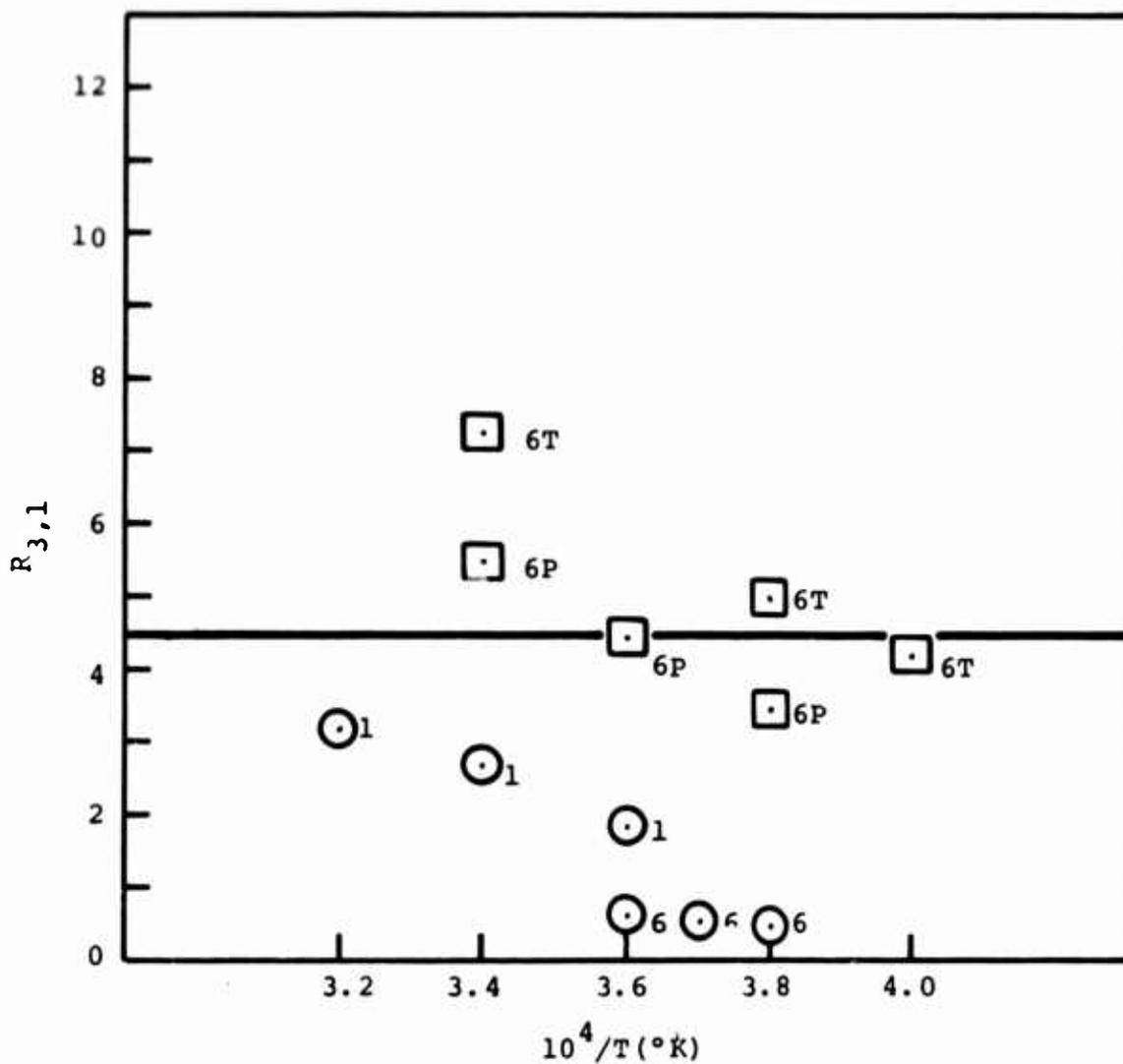


Figure 9. Plot of $R_{3,1}^K$ and $R_{3,1}^L$ vs. $\frac{1}{T}$ for Pyrolytic Graphite. $R_{3,1}^L$ (Free vaporization from c-face)

(See page viii for symbols)

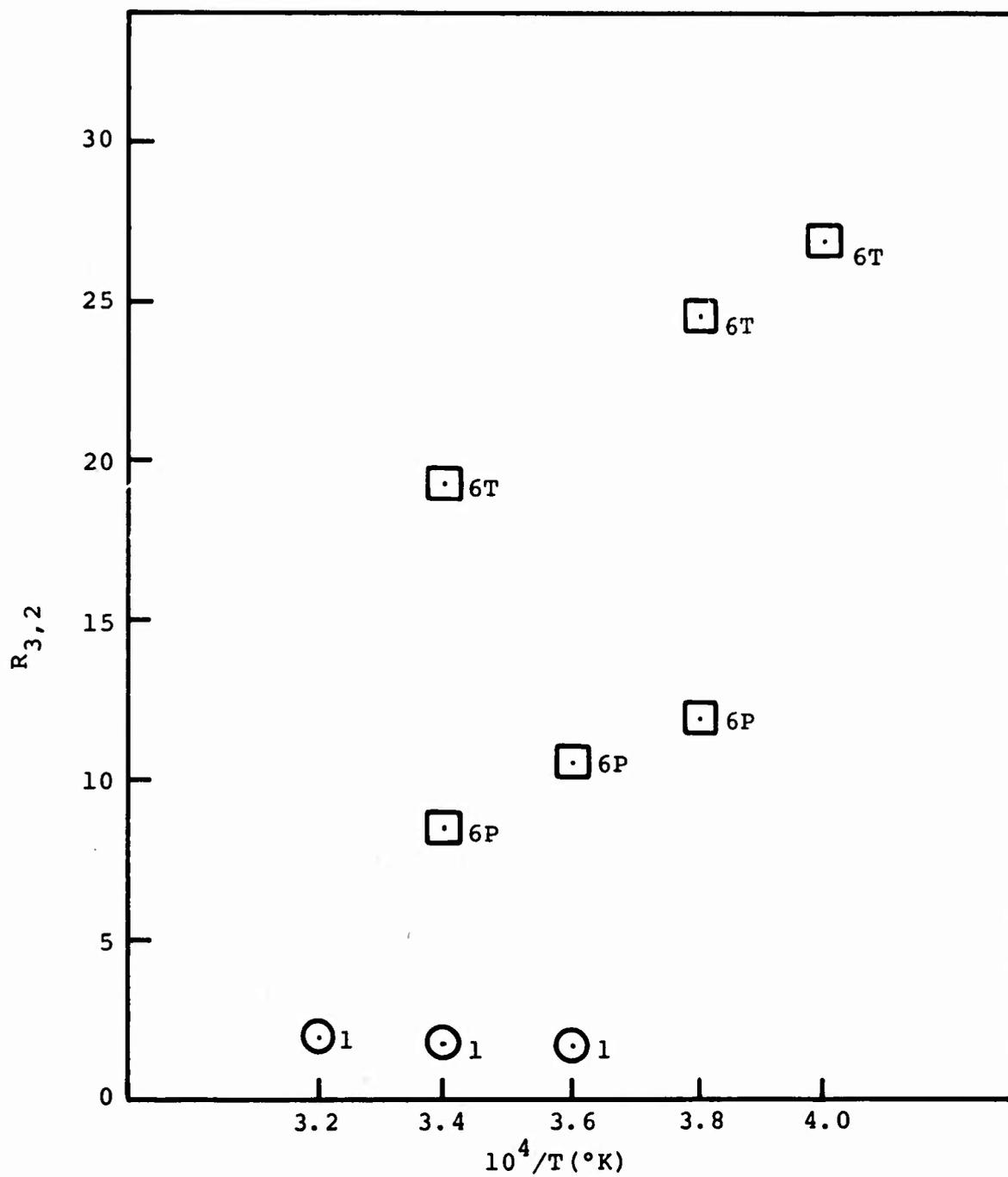


Figure 10. Plot of $R_{3,2}^K$ and $R_{3,2}^L$ vs. $\frac{1}{T}$ for Pyrolytic Graphite. (Free vaporization from c-face)

(See page viii for symbols)

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