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FINAL REPORT

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EXPERIMENTAL STUDY OF THE SUBLIMATION OF GRAPHITE
AT HIGH TEMPERATURES

BY

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FOREWORD

This final technical report constitutes partial fulfillment of Contract AT(929-1)-789 of the Materials Sciences Division of the Sandia Laboratories. Drs. G. A. Carlson and C. H. Williams have been the SANDIA Technical Monitors and their constructive comments have indeed been helpful throughout the contract period. Mr. A. J. Phillips was the SANDIA Buyer.

The work was conducted within the Aeromechanics and Materials Laboratory of the Research and Engineering Component of Re-Entry and Environmental Systems Division. The principal investigator and project manager was Dr. Peter D. Zavitsanos of the Aeromechanics and Materials Laboratory.

ABSTRACT

The equilibrium vaporization of pyrolytic graphite was studied using RF induction heating and the time-of-flight mass spectrometer.

RF induction heating was demonstrated for the first time as a compatible and practical heating technique for High Temperature - Mass Spectrometry.

Relative ion intensities were measured for $C_1(g)$, $C_2(g)$, $C_3(g)$ and $C_4(g)$ in the temperature range $2423^{\circ}K$ - $3003^{\circ}K$ and partial vapor pressures were obtained. The vapor pressure of C_2 and C_3 can be represented by

$$\log P_{C_2} \text{ (atm)} = 10.106 - \frac{44830}{T(^{\circ}K)}$$

$$\log P_{C_3} \text{ (atm)} = 10.168 - \frac{41343}{T(^{\circ}K)}$$

Respective heats of vaporization were obtained by the second and third-law methods and are as follows:

$$\text{Second Law: } \Delta H_{298}^{\circ} 1 = 170.3 \pm 1.1 \text{ kcal/mole}$$

$$\Delta H_{298}^{\circ} 2 = \begin{array}{l} 206.7 \pm 1.3 \text{ kcal/mole} \\ 209.1 \pm 1.1 \text{ kcal/mole} \end{array}$$

$$\Delta H_{298}^{\circ} 3 = 194.5 \pm 1.2 \text{ kcal/mole}$$

Third Law: Using JANAF free energy functions

$$\Delta H_{298}^{\circ} \text{) }_2 = 203.5 \pm 1.2 \text{ kcal/mole}$$

$$\Delta H_{298}^{\circ} \text{) }_4 = 241.5 \text{ kcal/mole}$$

If increased JANAF free energy function by 12% $\Delta H_{298}^{\circ} \text{) }_4 = 257 \text{ kcal/mole}$. If free energy function by Strauss and Thiele are used

$$\Delta H_{298}^{\circ} \text{) }_3 = 201.9 \pm 1.5 \text{ kcal/mole}$$

Free energy function by Altman produces a

$$\Delta H_{298}^{\circ} \text{) }_3 = 192.8 \pm 1.5 \text{ kcal/mole}$$

As far as the entropy of C_3 is concerned this work produces a

$\Delta S_{2700}^{\circ} = 46.5 \text{ eu}$ to be compared to the calculated values of Strauss and Altman $\Delta S_{2700}^{\circ} = 48.5$ and 43 eu respectively.

I. INTRODUCTION AND BACKGROUND

Graphite, because of its resistance to sublimation and high strength to density ratio at high temperatures, has been receiving a great deal of attention as a structural material in aerospace applications. Some of these applications provide temperatures as high as 4000°K; yet, its vaporization properties had not been studied (prior to this investigation) at temperatures above 2700°K.

The complexity of the carbon vapor was demonstrated by mass spectrometric studies by Chupka and Inghram¹ and Honig². Subsequent studies by Drowart, et al³ using Knudsen-effusion and mass spectrometry, produced relative ion intensity measurements for C_n , with $n=1$ to 5 over a wider temperature range (2000-2700°K). C_1 was taken as a standard and its pressure was calculated using a heat of formation $\Delta H_o^0 = 169.58$ kcal/mole. Partial pressures relative to C_1 were calculated for C_2 , C_3 , C_4 , and C_5 ; then respective heats of vaporization were calculated by the Third Law Method using free energy functions from the JANAF Tables⁴ as calculated by Pitzer and Clementi⁵. Heats of vaporization were also calculated by the Second Law Method from plots of $\log P$ vs $1/T$.

Zavitsanos⁶ carried out experiments similar to those of Drowart et al, but extended by inclusion of a measurement of the total effusion rate, using a microbalance technique. A high purity pyrolytic graphite was used as the vapor source. The work is particularly valuable in representing a

completely independent effort, and hence in indicating the reproducibility of experimental data. Zavitsanos confirms the finding that C_1 , C_2 and C_3 are dominant species in the equilibrium vapor at 2400-2700°K with partial vapor pressures in essential agreement with the work of Drowart et al. The Third Law heats are $\Delta H_{298}^{\circ})_1 = 173.5 \pm 1$ kcal/mole, $\Delta H_{298}^{\circ})_2 = 203.5 \pm 1$ kcal/mole, and $\Delta H_{298}^{\circ})_3 = 192 \pm 1.1$ kcal/mole using JANAF free energy function. If the free energy functions of Strauss and Thiele⁷ for C_3 are used the $\Delta H_{298}^{\circ})_3$ is 206.7 ± 1.1 kcal/mole which is in disagreement with the Second Law value of 186.7 ± 1.7 as reported by Drowart et al³.

This briefly constitutes the background up to 1968. For more detailed discussion on this topic the excellent review by Palmer and Shelef⁸ is highly recommended.

Because of the uncertainties relative to the heat of C_3 and higher species and lack of detailed knowledge of vapor pressures at high temperatures, considerable amount of research is presently going on in several laboratories.

Wachi and Gilmartin⁹ have studied the free evaporation of several types of graphite ATJ, ZTA, UT-6 and PG. Over pyrolytic graphite they have measured activation energies of vaporization for C_1 , C_2 , ..., C_5 of 175, 193, 201, 208 and 199 kcal/mole respectively. The first three values agree rather well with those of Zavitsanos^{6a}, i.e. 180, 199 and 207 kcal/mole respectively; the latter two were measured for the first time. Steel¹⁰ has

measured the activation energies of vaporization and his reported value for C_3 is 189 kcal.

Additional free evaporation studies are being carried out by Hoch et al¹¹. Their objective is to measure condensation coefficients of carbon species by the isotopic exchange technique using triple Knudsen crucibles and RF induction heating in the time-of-flight mass spectrometer.

Williams¹², also using the time-of-flight mass spectrometer, has been making detailed appearance potential measurements of positive and negative ions. The importance of this work is that electron affinity data are being generated for the carbon vapor species. This is an area where relatively little is known.

Finally, the work of Milne et al¹³ is directed in mass-analyzing carbon vapor at high pressures by skimmer techniques.

II. EXPERIMENTAL

A. Specimens

The results which follow were obtained during the vaporization of pyrolytic graphite, obtained from High Temperature Materials Inc., Lowell, Mass., which was heated either in pyrolytic graphite crucibles supplied by Space Age Materials Corporation, (Pyrogenics) Woodside, N. Y., or in tantalum carbide crucibles made by Cerac Hot Pressing Inc., (Menomonee Falls, Wisc.) The P-G samples had a density of 2.2 g cm^{-3} and high purity. Although no chemical analysis was performed on these specific samples previous measurements⁶ on this type of

material showed total ash content of 0.005% by weight with Si being the most abundant impurity with traces of Al, Ca, Zr, V, Fe, Ti, Ta and W. However, from previous experience with P-G it became apparent that residual hydrogen and hydrocarbons do evolve during the heating process. Thus, prior to actual measurements the sample was heated long enough so that the removal of hydrocarbons was nearly complete. This was verified with actual mass spectrometric measurements.

B. Apparatus - Induction Heating and Temperature Measurements

The objectives of this study were to: (a) check certain aspects of old work on the vaporization of graphite at low temperatures; (b) extend the measurements to a new temperature regime, i. e., $T > 2700^{\circ}\text{K}$. In line with these objectives all heating methods were considered and induction-heating was selected as the most practical for applications at $T > 2700^{\circ}\text{K}$. The only reservation was possible RF interference with the operation of the mass spectrometer. Thus, the method in conjunction with the (Bendix) Time-of-Flight Mass spectrometer was tested in an arrangement shown in Figure 1. The water-cooled five-turn induction coil (A) enters the furnace chamber from the bottom flange while the crucible (C) and its holder are supported on three tantalum rods on the conventional Bendix Knudsen inlet assembly. Background

Figure 1. Inductively Heated Knudsen Furnace and Time-of-Flight Mass Spectrometer

mass spectra were recorded with the RF field off and on with no detectible differences in intensity or type. Some broadening of the baseline was observed on the scope output which was corrected by shielding the leads to the multipliers with aluminum foil.

In order to maximize the efficiency of the induction heater (G.E. 25 KW, 450 KC) several coil designs and step-down transformers were tested. Finally an acceptable copper coil was made consisting of five turns with a 7/8 in. diameter; the copper is 1/8 in I.D. and 3/16 in O.D. Proper coupling and maximum efficiency were achieved with a voltage step-down transformer (12:1 ratio, LTC-4, Lepel). With this particular arrangement graphite specimens (1" x 1" cylinders) were heated to 3700⁰ K in 1 Atm. air or helium without approaching full output of the heater. In vacuum, however, reaching temperatures higher than 3000⁰ K for long periods of time presented problems associated with glowing and arcing. This was probably due to increases in the local pressure.

The Knudsen furnace as shown in Figure 2 consisted of: (1) cylindrical radiation shields (slotted at three points) 11/16" O.D. x 11/16" long, made of pyrolytic graphite, (2) support block 11/16" dia. x 0.15" thick with three holes for the Ta support rods and a 0.01" depression for the crucible (also made of P-G), (3) Knudsen crucible, 0.25" I.D. x 0.45" deep with a 0.05" wall and a cover

- A. INDUCTION COIL
 - B. PG HEAT SHIELD-SLOTTED
 - C. CRUCIBLE AND LID (PG or TaC)
 - D. Ta SHIELD- SLOTTED
 - E. (PG) SUPPORT BLOCK
 - F. Ta SUPPORT LEGS
 - G. POWDER PG SAMPLE
- SCALE: 1 IN. = 0.5 IN.
 $\equiv$ a-b PLANE

Figure 2. Inductively Heated Knudsen Furnace

0.125" thick x 0.35" dia. with 60° conical orifice whose diameter is 0.03" (both made of PG or TaC), (4) tantalum shield. The function of the last item is to prevent carbon vapor resulting from surface evaporation from entering the ion source of the mass spectrometer.* A diagram of the furnace assembly is shown in Figure 3.

The temperature of the crucible was measured with an L&N optical pyrometer by sighting into the orifice in another agreement. Corrections due to prism and windows were always made in reported temperature values. Since temperature uniformity in the Knudsen crucible is an important consideration a separate vacuum system was built whereby the specimen can be heated in the same manner as in the chamber of the mass spectrometer with the advantage that the crucible can now be viewed for temperature measurements along the side and the top. Clear quartz windows for temperature measurements were installed on the side and the top of a quartz bell-jar (9 in. height, 6 in. diameter). The complete system is shown in Figures 4 and 5.

*The diameter of the shield orifice was 0.06". The temperature, although not measured, had to be much lower than that of the cell because it was slotted. The composition of the carbon vapor was measured on several occasions without the shield and found unchanged.

- A. INDUCTION COIL (H_2O COOLED)
- B. SPECIMEN OR KNUDSEN CRUCIBLE
- C. SUPPORTS
- D. ENTRANCE SLIT
- E. WATER JACKET
- F. ALIGNMENT MECHANISM (BELLOWS)
- G. INSULATION (TEFLON)

Figure 3. Furnace Assembly

Figure 4. Apparatus for Crucible Temperature Uniformity Measurements

Fig. 5 - Apparatus for Temperature Distribution Measurements

Temperature uniformity of continuously deposited PG crucibles (Figure 2) was tested by sighting through a "side-hole" about half way down from the top of the cell and also through the top orifice. Typical measurements are shown below.

<u>Side Hole</u>	<u>Top Orifice</u>
1593°K	1583°K
2163	2153
2513	2500

One of the problems in working at temperatures approaching 3000°K is the temperature measurement itself due to carbon deposition on the viewing window. This problem was solved during the course of this contract by designing and building a multi-window assembly which provides six windows on a rotating flange. The assembly is shown in Figures 6, 6A, 6B, and is attached to the top of the cross of the Bendix Time-of-Flight mass spectrometer. This attachment was used successfully in connection with the results obtained from the tantalum carbide crucible.

C. Mass Spectrometric Analysis

Using RF heating, as previously described, and the Bendix Model - 12 time-of-flight mass spectrometer the vapor over

FIGURE 6 - MULTI-WINDOW ADJUSTING ASS'Y

Fig. 6 A - Multiwindow Assembly

Fig. 6B - Multiwindow Assembly

pyrolytic graphite and effusing from PG and TaC Knudsen crucibles was analyzed as a function of temperature under equilibrium conditions. In general the orifice area to sample-surface area ratio was always less than 10^{-3} . A photograph of the apparatus is shown in Figure 7. The temperature of the sample was measured by sighting into the orifice of the crucible with an optical pyrometer. The recorded readings were corrected for prism and window.

After proper collimation, a small fraction of the vapor effusing from the crucible enters the ionization region of the ion source where a pulsed electron beam (directed perpendicular to the neutral beam) ionizes a fraction of the gas and mass analysis is carried out by the time-of-flight method. Relative ion intensities were recorded using the scanning mode (mass range 12-200 mass units) and an oscillograph.

III. RESULTS

A. Knudsen Effusion

Positive ions were formed with an electron beam set at 20 volts and relative intensities were measured.

Partial vapor pressures were then calculated from the equation:

$$PC_n = PC_1 \times \frac{I_n}{I_1} \times \frac{G_1}{G_n} \times \frac{(E-A_1)}{(E-A_n)} \quad (1)$$

Fig. 7 - Inductively Heated Furnace - Time-of-Flight Mass Spectrometer

where PC_n = partial vapor pressure of a carbon molecule consisting of n atoms, I = ion intensity σ = relative cross section for ionization, E = energy of ionizing electrons, A = appearance potential ($A_1 = 11.3$, $A_2 = 12.0$, $A_3 = 12.6$ and $A_4 = 12.6$ volts, reference 3). All the results were obtained at a low electron energy (i. e., $E = 20$ volts) in order to avoid fragmentation of the molecular species. The ratios of cross sections were assumed to follow the relationship as stated by Palmer and Shelef⁸:

$$\sigma_n / \sigma_1 = (1.5)^{n/2}$$

Using the vapor pressure data as calculated by equation (1), respective heats of vaporization can be obtained by:

- a) The Second-Law method which involves plotting $\log P$ vs. $1/T$ for each species and using the Clausius-Clapeyron equation

$$d \ln P / d(1/T) = - \Delta H_{Tav.}^0 / R \quad (2)$$

where $\Delta H_{Tav.}^0$ = heat of vaporization of species n at the average temperature of the experiment $T_{av.}$ and R = gas constant (1.9865).

If one knows the heat capacities of products and reactants, the heat of vaporization at $298^\circ K$ can be calculated:

$$\Delta H_{298}^0 = \Delta H_{Tav.}^0 - \int_{298}^{T_{av.}} \Delta C_p dT \quad (3)$$

where

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

b) The Third-Law method which utilizes the free energy functions, f_{ef} , given as

$$f_{ef} = \left(\frac{F_T^0 - H_{298}^0}{T} \right) = \left(\frac{H_T^0 - H_{298}^0}{T} \right) - S_T^0 \quad (4)$$

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

$$f_{ef} = \frac{1}{T} \int_0^T C_p dT - \int_0^T C_p d \ln T. \quad (5)$$

Values of f_{ef} have been tabulated for the elements and a great number of compounds⁴. Then, for reaction: solid $\rightarrow$ gas

$$\begin{aligned} f_{ef} &= \left(\frac{F_T^0 - H_{298}^0}{T} \right)_{(gas)} - \left(\frac{F_T^0 - H_{298}^0}{T} \right)_{(solid)} \\ &= \frac{\Delta F_T^0}{T} - \frac{\Delta H_{298}^0}{T} \end{aligned} \quad (6)$$

$$\Delta F_T^0 = -RT \ln K_{eq} = -RT \ln P \quad (7)$$

or

$$\Delta H_{298}^0 = -T \left\{ R \ln P + \Delta f_{ef} \right\} \quad (8)$$

By substituting $\ln P$ with the measured values of the vapor pressure, one can determine ΔH_{298}^0

1. Pyrolytic Graphite Crucibles

Ionization efficiency runs were made using a pyrolytic graphite cell containing small chunks of pyrolytic graphite. The crucible and the lid were made from plate material 1 in. thick, so that the $a \times b$ plane was approximately parallel to the turns of the induction coil. In order to avoid interference by vapor emanating directly from the top surface of the lid a slotted piece of tantalum (item D of Figure 2) was placed on the top of the lid with a hole twice that of the cell. The ion intensities at 2713°K for the three observed species (C_1 , C_2 , C_3) were recorded by placing the gates on the peaks and reading the respective intensities on the output meters (this is the only case where the scanning mode was not used). The temperature was measured by sighting into the orifice of the cell with a calibrated optical pyrometer. The data shown in Figure 8 constitute typical ionization efficiency curves (as obtained by electron bombardment heating) showing the induction heating is indeed a compatible heating method. In addition, it is apparent that at electron energies up to 20 volts no significant amount of fragmentation takes place.

Figure 8 - Ionization Efficiency Curves for Carbon Vapor Species

Although some additional data (with a high degree of scatter) were obtained with this crucible the most successful runs were made with PG crucibles furnished by Space Age Materials Corp. according to Figure 2. Ion intensities (I) were measured at 20 volts for C_1 , C_2 , and C_3 in the temperature range 2493°K - 2929°K . These data are shown in Figure 9 where $\log IT$ is plotted vs. $1/T$. Since IT is proportional to the vapor pressure the slopes of these least square fitted lines produce second-law heats according to equation (2). Such values are shown in Table I.

2. Tantalum Carbide Crucibles

Because the pyrolytic graphite crucibles developed problems at the higher temperatures due to evaporation and splitting, additional data were taken with tantalum carbide crucibles made by Cerac Hot Pressing Inc. in the same dimensions as the PG crucibles and run in the same arrangement as in Figure 2.

Ion intensities at 20 Volts were obtained in the temperature range 2423 - 3003°K for C_1 , C_2 , and C_3 . C_4 was observed only at the highest temperature. A background peak at mass 60 (about twice the intensity of C_4) prevented identification of the C_5 molecule.

The data obtained with the tantalum carbide crucibles are shown in Table II and Figure 10. Taking the vapor pressure of C_1 as a standard from the JANAF Tables, (See Figure 11) partial vapor pressures were calculated from equation (1) for C_2 , C_3 and

Figure 9. Relative Ion Intensities as a Function of Temperature (PG-Crucible)

TABLE I
THE HEATS OF VAPORIZATION OF CARBON SPECIES
BY SECOND-LAW METHOD
(P-G CRUCIBLES)

<u>Cn</u>	<u>SLOPE</u>	<u>ΔH° (T_{ave} = 2713° K)</u>	<u>ΔH°_{298} *</u>
1	3.71	169.7 $\pm$ 1.1 kcal/mole	170.3 $\pm$ 1.1 kcal/mole
2	4.50	205.8 $\pm$ 1.1 kcal/mole	209.1 $\pm$ 1.1 kcal/mole
3	4.13	188.9 $\pm$ 1.2 kcal/mole	194.5 $\pm$ 1.2 kcal/mole

*Used JANAF Tables for $H_T - H_{298}$ to correct for 298°K.

TABLE II

MASS SPECTROMETRIC ANALYSIS OF THE CARBON VAPOR
(KNUDSEN EFFUSION FROM TANTALUM CARBIDE CRUCIBLE)

$T^{\circ}\text{K}$	$10^4 T$	Vapor Species Cn n	I T (Arbitrary Units)	-Log P_{atm}
2423	4.12	1	4.3	7.21
		2	-	
		3	19.4	6.78
2503	3.99	1	10	6.73
		2	-	
		3	33	6.40
2573	3.88	1	30	6.33
		2	5	7.25
		3	180	5.75
2673	3.74	1	100	5.80
		2	21	6.62
		3	380	5.42
2733	3.65	1	165	5.45
		2	31	6.32
		3	990	4.96
2773	3.60	1	246	5.28
		2	78	5.93
		3	1334	4.64
2853	3.5	1	720	4.90
		2	235	5.53
		3	4490	4.30
2893	3.46	1	980	4.72
		2	400	5.26
		3	7000	4.07
2933	3.40	1	1620	4.55
		2	640	5.10
		3	12400	3.86
3003	3.33	1	2900	4.26
		2	1230	4.78
		3	20000	3.62
		4	60	6.12

TABLE II (CON'T)

<u>T °K</u>	<u>10⁴ T</u>	<u>Vapor Species Cn n</u>	<u>I T (Arbitrary Units)</u>	<u>-Log P_{atm}</u>
2523	3.97	1	14.5	6.75
		2	-	
		3	62	6.32
2593	3.86	1	35	6.25
		2	7.2	7.23
		3	144	5.83
2693	3.71	1	125	5.70
		2	32	6.58
		3	640	5.19
2773	3.61	1	285	5.32
		2	81	6.16
		3	1660	4.75
2833	3.53	1	540	5.03
		2	175	5.78
		3	3220	4.25
2893	3.46	1	910	4.76
		2	340	5.46
		3	6300	4.12
2953	3.39	1	1900	4.50
		2	640	5.26
		3	11400	3.92

at 2700°K, $C_1^+ : C_2^+ : C_3^+ = 1.0 : 0.23 : 5.1$

Figure 10. Relative Ion Intensities as a Function of Temperature (TaC-Crucible)

Figure 11. The Vapor Pressure of C_1 (JANAF - Tables)

C_4 as shown in Table II and Figure 12. The use of C_1 as a standard eliminates the effect of errors in temperature measurements on the second law heats.

Using the data of Figure 12 second law heats were evaluated for C_2 and C_3 where (ΔH_{298}^0)₁ = 170.89 kcal/mole was taken as standard). Table III also shows the second law heats and (least square) expression of the vapor pressure.

$$\text{Log } PC_n = A - M \frac{10^4}{T} \quad n = 1, 2, 3$$

Following the procedure as outlined by equation (4), third-law heats were calculated for C_2 , C_3 and C_4 . These values are shown in Table IV and are ΔH_{298}^0)₂ = 201.9 $\pm$ 1.2,

ΔH_{298}^0)₄ = 241.5 and ΔH_{298}^0)₃ = 187.2, 192.8 or 201.9 (all $\pm$ 1.5 kcal/mole) depending on whose free energy functions one uses. The new set of free energy functions for C_3 as calculated by Altman¹⁴ are shown in Table V.

Figure 12. Equilibrium Vaporization of Pyrolytic Graphite

TABLE III

THE VAPOR PRESSURE OF CARBON AND HEATS OF VAPORIZATION
(SECOND-LAW METHOD, TaC CRUCIBLE)

$$\text{Log } P_{C_n} = A - M (10^4 / T)$$

<u>n</u>	<u>A</u>	<u>M</u>	<u>$\Delta H^{\circ}(T_{\text{ave}} = 2700^{\circ}\text{K})$</u>	<u>ΔH°_{298*}</u>
1	8.072	3.7180	170.3 kcal/mole	(170.89) kcal/mole
2	10.106	4.4830	203.4 $\pm$ 1.3 kcal/mole	206.7 $\pm$ 1.3 kcal/mole
3	10.168	4.1343	189.1 $\pm$ 1.0 kcal/mole	194.7 $\pm$ 1.0 kcal/mole

*Used JANAF Tables for $H_T - H_{298}$ to correct for 298°K.

TABLE IV

HEATS OF VAPORIZATION FOR $C(g)$, $C_2(g)$ AND $C_3(g)$ AS CALCULATED
BY THE THIRD-LAW METHOD

$T^\circ K$	$n = 1$	$n^* = 2$	$n^* = 3$	$n^* = 4$	$n^{***} = 3$	$n^{**} = 3$
2423	(170.89)	----	185.8		192.8	
2503		----	190.7		196.7	
2577		203.5	185.9		190.9	
2673		203.5	188.0		194.8	
2733		203.4	186.0		191.7	
2773		201.6	186.1		190.9	
2853		202.4	185.8		191.8	
2893		201.6	186.0		191.6	
2933		202.5	185.8		192.0	
3003		202.6	186.6	241.5	191.8	
2523		----	188.9		193.7	
2593		204.3	190.6		196.9	
2693		204.7	185.5		190.8	
2773		205.5	186.8		191.7	
2833		204.5	187.0		192.9	
2893		204.6	186.7		191.8	
2953		206.4	189.7		194.7	
	AVG.	203.5	187.2	241.5	192.8	201.9
		+ 1.2	+ 1.5		+ 1.5	+ 1.5

*Using JANAF⁴ free energy functions

**Free energy functions by Strauss⁷

***Using Altman's¹⁴ free energy functions

TABLE V
THERMODYNAMIC PROPERTIES OF GASEOUS C₃
(CALCULATED BY ALTMAN¹⁴)

T deg K	C _p ^o cal/mole deg K	H _T ^o - H ₂₉₈ ^o kcal/mole	-(F _T ^o - H ₂₉₈ ^o)/T cal/mole deg K	S _T ^o cal/mole deg K
0		-2.783		
298.15	8.865	0.000	56.348	56.348
300	8.857	0.016	56.348	56.403
400	8.618	0.887	56.691	58.908
500	8.679	1.750	57.334	60.834
600	8.872	2.627	58.054	62.433
700	9.104	3.526	58.781	63.817
800	9.331	4.448	59.489	65.048
900	9.535	5.391	60.169	66.159
1000	9.713	6.354	60.820	67.173
1100	9.865	7.333	61.440	68.106
1200	9.994	8.326	62.032	68.970
1300	10.103	9.331	62.597	69.775
1400	10.196	10.346	63.137	70.527
1500	10.275	11.369	63.653	71.233
1600	10.343	12.400	64.148	71.898
1700	10.401	13.438	64.623	72.527
1800	10.452	14.480	65.078	73.123
1900	10.496	15.528	65.517	73.689
2000	10.534	16.579	65.939	74.229
2100	10.567	17.634	66.346	74.744
2200	10.597	18.693	66.739	75.236
2300	10.623	19.754	67.119	75.708
2400	10.647	20.817	67.486	76.160
2500	10.667	21.883	67.842	76.595
2600	10.686	22.951	68.187	77.014
2700	10.703	24.020	68.521	77.418
2800	10.718	25.091	68.846	77.807
2900	10.732	26.164	69.161	78.183
3000	10.744	27.237	69.468	78.547
3500	10.792	32.622	70.887	80.208
4000	10.823	38.027	72.144	81.651
4500	10.845	43.444	73.273	82.927
5000	10.861	48.871	74.296	84.070
5500	10.873	54.304	75.233	85.106
6000	10.882	59.743	76.095	86.053

B. Negative Ions

In preparation for negative ion measurements on carbon vapor the instrument was tested with SF_6 and O_2 with the following results: Resonance capture to SF_6^- and dissociative attachment to $\text{SF}_5^- + \text{F}$ were observed at electron energies between 0 - 1 eV.

The dissociative attachment of O_2 to $\text{O}^- + \text{O}$ was observed in the energy range 4-8 eV, (Figure 13). Both results are in excellent agreement with the literature^{15, 16}.

Preliminary runs indicated that measurable quantities of C_2^- emanated from the graphite surface at surface $T \simeq 3,000^\circ\text{K}$.

Figure 13. Negative Ion Formation by Dissociative Attachment to O_2

IV. DISCUSSION AND CONCLUSIONS

This study clearly demonstrates the applicability of RF induction heating to high temperature mass spectrometric investigations. In an attempt to resolve the discrepancy concerning the heat of vaporization of C_3 as obtained by the second and third-law methods a successful attempt was made to minimize temperature gradients in the Knudsen crucible and thus check the previous work of Drowart³. Results obtained with crucibles made out of pyrolytic graphite and tantalum carbide with relatively small temperature variation (along the crucible) produced second-law heats

$\Delta H_{298}^0(C_3) = 194.5, 194.7 \pm 1.2$ kcal/mole respectively. This result is to be compared with Drowart's³ second-law value of 188.2 ± 1.5 on Table VI.

The values obtained by the third-law treatment using vapor pressure values from this work are as follows:

Using free energy functions by JANAF a value of 187.2 ± 1.5 kcal/mole was calculated for $\Delta H_{298}^0(C_3)$. In view of the fact that the low bending frequency of $63\text{-}70\text{ cm}^{-1}$ (reported by Gausset, et al¹⁷) was not used in the JANAF tabulations, the corresponding heat of vaporization is in error. It is interesting though, to note the agreement with modified* values of Drowart's³ and Zavitsanos⁶ 185.6 ± 2.5 and 188.8 ± 1 kcal/mole respectively, all

*Modifications as proposed by Palmer and Shelef⁸ where ionization cross section ratios $\sigma_n/\sigma_1 = (1.5)^{n/2}$.

adding up to a conclusion that the vapor pressure of C_3 is now known rather well and a reliable third-law value of the heat can be obtained from realistic free energy functions.

Considering the correct value for the bending frequency and taking account of the considerable quartic anharmonicity of the bending vibration Strauss and Thiele⁷ calculated a set of free energy functions which, if used with the vapor pressure data of this work, a $\Delta H_{298}^{\circ})_3 = 201.9 \pm 1.5$ kcal/mole is calculated. This is 7.3 kcal higher than the second-law value (194.6 ± 1.2 kcal/mole). A more accurate calculation could be carried out if spectroscopic data were available with respect to other energy levels. However, the lowest theoretically possible heat according to the Strauss - Thiele approach would be computed at the cut-off in the potential¹⁸ and would be about 3 kcal lower. This would place the third-law heat ($\Delta H_{298}^{\circ})_3$ in the vicinity of 198.9 which is not in any serious disagreement with the second-law since the actual experimental error could be higher than the stated deviation from the least square fit.

The most recent calculations on C_3 - free energy functions were made by Altman¹⁴. He ended the summation procedure with the ninth vibrational level in order to yield apparent agreement with Drowart's experimental results. Using Altman's table and our vapor pressure data produced a third-law value $\Delta H_{298}^{\circ})_3 = 192.8 \pm 1.5$ which constitutes excellent agreement with the two second-law values, $194.5 + 194.7$ (Tables I and III). The only

problem is that this value was obtained by correcting to 298° (from Tave = 2700°K) using JANAF tables for $\Delta (H^{\circ}_{2700} - H^{\circ}_{298})$. If for the sake of consistency one used Altman's $\Delta (H^{\circ}_{2700} - H^{\circ}_{298})$ to convert to 298° a second-law $\Delta H^{\circ}_{298})_3 = 201$ kcal/mole is obtained; the comparison therefore, is between a 2nd-law value of 201 vs. a 3rd-law value of 192.8 kcal/mole, which shows more discrepancy than the Strauss method.

$$\text{As far as the entropy } (\Delta S^{\circ}_T = \frac{\Delta H^{\circ}_T}{T} - \frac{\Delta F^{\circ}_T}{T} - \frac{\Delta H^{\circ}_T}{T} + R \ln P)$$

is concerned, this work produces a $\Delta S^{\circ}_{2700} = 46.5$ eu to be compared with the theoretical values of 48.5 and 43.0 by Strauss⁷ and Altman¹⁴ respectively.

Based on the above discussion, a $\Delta H^{\circ}_{298})_3 = 194.6$ kcal/mole and a $\Delta S_{270} = 46.5$ eu are presented as the best values. The obtained heat is in excellent agreement with Palmer's "best" value of 193.5. Also, the free energy function of Strauss and Thiele is being favored.

The heat of vaporization of C₂ according to this work is $\Delta H^{\circ}_{298})_2 = 206.7 - 209.1$ kcal/mole from the second-law treatment and 203.5 ± 1.2 from the third-law treatment. These values are to be compared with Drowart's 2nd and 3rd law values of 197.8 ± 1.7 and 200.0 ± 1.7 respectively and with Palmer's "best" value of 199.02 (same as JANAF).

C₄ was observed only at the highest temperature and the third-law heat obtained $\Delta H^{\circ}_{298})_4$ is 241.5 kcal/mole to be compared to Drowart's

2nd and 3rd law values of 231.3 ± 7.1 and 242.3 ± 5.8 and Palmer's "best" value of 257.8. If free energy functions 12% higher than JANAF are used (as in Palmer's "best" value) a $\Delta H_{298}^{\circ} = 257$ is obtained.

TABLE VI

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

SPECIES	ZAVITSANOS ⁶ 3rd LAW	THIS WORK 2nd LAW	3rd LAW	DROWART et al ³ 2nd LAW	3rd LAW	MODIFIED* DROWART et al 3rd LAW	"APPROXIMATELY-BEST" VALUES BY PALMER AND SHELEF ⁸
C	173.5 ± 1	170.3 ± 1.1					170.89
C ₂	202.0 ± 1.1	209.1 ± 1.1 206.7 ± 1.3	203.5 ± 1.2	197.8 ± 1.7	200.0 ± 1.7	197 ± 2	199.02
C ₃	188.8 ± 1	194.5 ± 1.2 194.7 ± 1	187.2 ± 1.5 (201.9 ± 1.5)** (192.8 ± 1.5)***	188.2 ± 1.5	189.6 ± 2.3	185.6 ± 2.5	193.5**
C ₄			241.5 257 ^a	231.3 ± 7.1	242.3 ± 5.8	234.8 ± 8	257.8 ^a

Free Energy functions from the JANAF Tables (unless stated)

*Using modified ionization cross sections⁸ (same as in this work)**Using free energy functions by Strauss⁷***Using free energy functions by Altman¹⁴^aUsed free energy function 12% higher than JANAF

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