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EXPLORATORY DEVELOPMENT TO STUDY GRAPHITE
VAPORIZATION KINETICS AND THERMODYNAMICS
USING THE MODULATED BEAM MASS SPECTROMETER

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ABSTRACT

Progress is reported in a program of mass spectrometric studies of graphite vaporization kinetics. A renewed search for polymers in the carbon vapor over very hot graphite has resulted in detection of the new species C_{12} , C_{13} , C_{14} , and C_{15} . A new carbon vapor source producing a beam 99% atomic carbon has been developed for vapor reflection experiments. Some initial experiments are described which reveal unexpected C_3 desorption during flash vaporization of material condensed from the atomic beam on the graphite target.

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I. INTRODUCTION

As a prime candidate material for advanced re-entry vehicle applications, graphite appears particularly attractive for use when severe re-entry trajectories require survival under extreme conditions. In order to make the required calculations of recession rate, designers of graphitic components of such systems require a knowledge of the vaporization kinetics and thermo-chemistry of graphite. Experimental data on this subject has been limited, being confined mainly to studies of equilibrium vaporization below the temperature of 2800°K. Although other aspects of graphite vaporization have received some attention, design data must still be obtained in part by extrapolation, estimation and theoretical calculation. The present program was designed to provide experimental answers in several of the outstanding problem areas. These include measurement of condensation and reflection coefficients for carbon vapor at graphite surfaces and determination of the polymeric composition of carbon vapor produced by free evaporation from a graphite surface.

In response to the need for better, more advanced methods for the study of gas-surface interactions, Avco developed for the Air Force Materials Laboratory, a modulated beam mass spectrometer apparatus.¹ This unique apparatus allows reactions between a heated solid material and discrete pulses of the gas. Vaporizing reaction products are analyzed individually by the mass spectrometer. By synchronizing the spectrometer detection system to the vapor beam modulator, the periodic time-intensity waveform of the gaseous reaction products can be constructed, providing important information on the kinetics of the reaction under observation. This apparatus is now being applied to studies of graphite-carbon vapor interactions, an induction heated graphite cylinder providing a carbon vapor beam which impinges on a resistively heated graphite target.

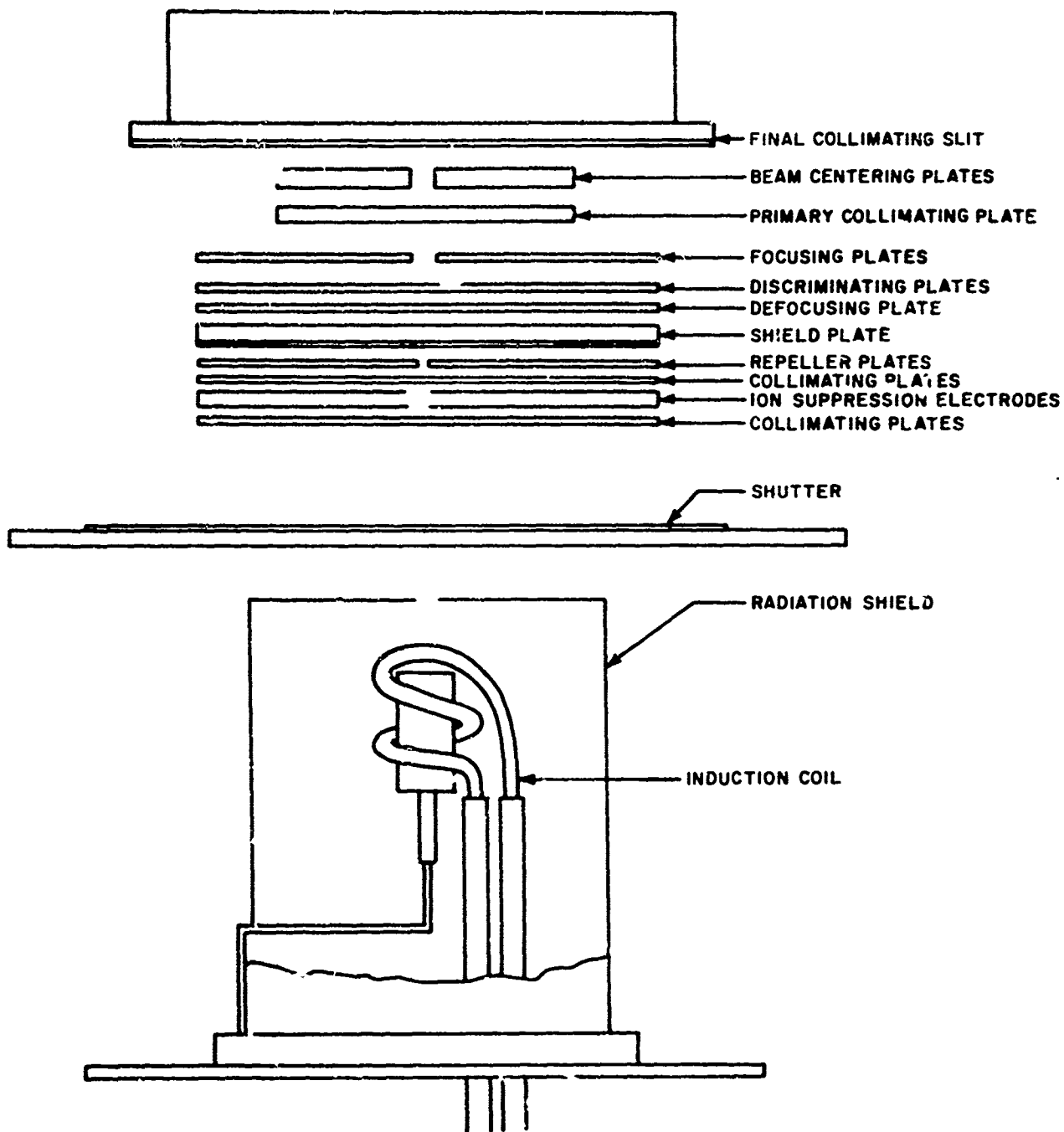
In the following sections, progress is reported in our studies of the kinetics of graphite vaporization. New results are described for the polymeric composition of carbon vapors. The species C_{11} , ... C_{14} , C_{15} have been discovered and are discussed. A new carbon vapor beam source for the condensation/reflection experiments is described. The beam from this new source is composed 99% of carbon atoms. Flash vaporization of layers condensed from this atomic beam show a large C_3 component. Possible surface modification by the beam is suggested.

II. HIGH TEMPERATURE VAPOR COMPOSITION

In the previous quarter², we initiated a search for high polymers of carbon in the vapor over very hot graphite. The purpose of this search was to reconfirm our previous detection of species as large as C₁₀, since others have not reported these polymers. This effort proved successful as both C₉ and C₁₀ were observed. In addition, we re-examined our procedures and, by avoiding unnecessary specimen deterioration, were able to observe the next higher polymer, C₁₁. This very encouraging result prompted us to continue the search. The new observations are described below.

These studies were performed with a Nucleide HT-12-60 mass spectrometer using an induction heating apparatus, as illustrated in Figure 1. A graphite cylinder 0.25 inch in diameter by 0.625 inch in length is supported in the induction coil by a tungsten rod. The temperature is measured by optical pyrometry, sighting on a blackbody hole (0.025 inch diameter by 0.15 inch deep) drilled 0.1 inch below the top surface of the cylinder. Atoms or molecules of carbon vaporizing from this top surface can traverse a line-of-sight path through a slit in the movable shutter, through the mass spectrometer ion source into the mass analyzer region of the spectrometer. The shutter can be moved to block the line-of-sight path as an aid in discrimination of desired signal due to vaporizing species from spurious background signals.

When searching for high molecular weight carbon polymers in the vapor over graphite, two experimental features dictate special care and procedures. These are the very high temperature involved and the low level of the mass spectrometric signals to be detected. Both require a clean, thoroughly baked-out apparatus, since at these high temperatures adsorbed gases may be driven from walls to obscure the small amount of vaporizing polymer.



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Figure 1 ION SOURCE AND HIGH TEMPERATURE CARBON SOURCE

Thorough degassing of the graphite specimen is required also. At 3000°K specimen deterioration is rapid and it is necessary to work quickly, even though the detection system time constant must be long to measure the weak ion signal. These limitations have led to adoption of the following procedures. After thorough bakeout and outgassing, the apparatus is allowed to cool. The graphite sample is heated to about 2400°K and the C₃ beam (mass 36) is used to adjust the mass spectrometer to focus species vaporizing from the graphite and discriminate against background gases. The ionizing electron energy is set for 17 eV and several points of I⁺ vs T are determined for C₃ for calibration purposes. The magnetic field is then adjusted to focus at the mass of the parent ion of the highest polymeric species being sought (without recourse to our previous policy of seeking and verifying each species above C₃ in sequence, advancing 12 mass units at a step. This produced increasing specimen deterioration as the polymer size increased). The graphite sample temperature is raised until a useful signal is recorded by the mass spectrometer. Three fairly rapid tests are then employed: the movable shutter is placed in the closed position and the signal change noted (but a complete shutter profile is not attempted); with the shutter open the ion source filament is turned off; and, with the shutter open and ion source on, the RF induction heater is abruptly shut off. Response to the first and third tests serve to distinguish true polymer vaporization from background, while the second test detects signals due to thermal ionization at the graphite surface. The temperature may then be raised and the sequence repeated. Tests are also performed on adjacent mass peaks to provide a behavioral comparison. Developing surface porosity, coatings on the RF induction coil and coatings on the optical viewing port all combine to limit the operating time available for a single graphite

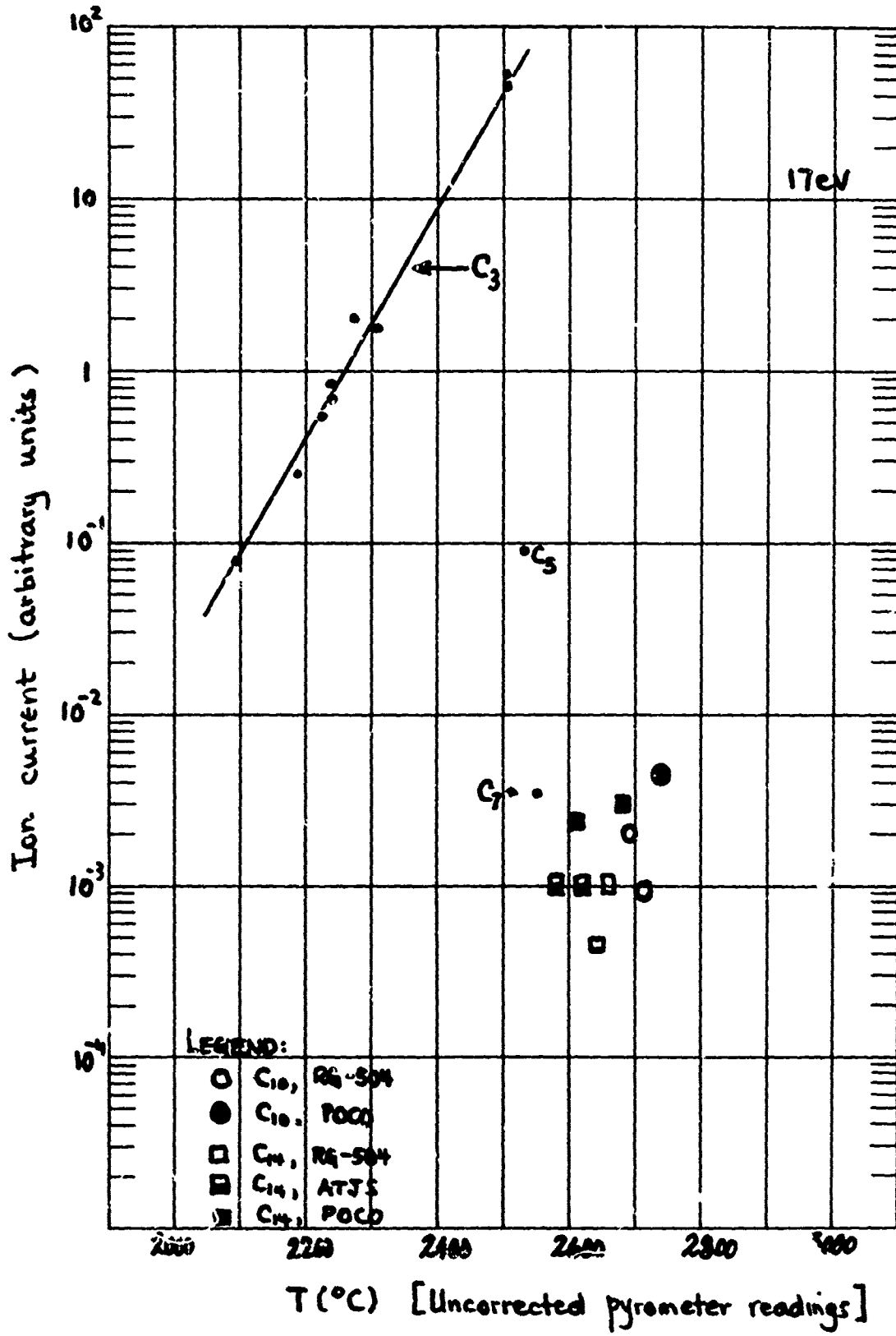
specimen.

Results obtained by this procedure are partially depicted in Figure 2. This shows raw experimental data of typical experiments. A more complete tabulation will show a scatter approaching $\pm 50\%$ for these high molecular weight polymers. However, these results present a very interesting picture. In addition to the species C_1, C_2, \dots, C_{10} and the more recently detected C_{11} , we now have evidence for the newly observed molecules C_{13}, C_{14} , and C_{15} . Of these, C_{14} is especially interesting because of its unexpectedly high concentration. In order to insure that the polymer vaporization is not characteristics of a single kind of graphite, we have performed these experiments on three different brands of commercially available material. These are: Aremco's RG-504, POCO HPD-1, and ATJS. In each case we were able to detect C_{10} and C_{14} in comparable concentrations.

Although this is the first time $C_{11}, \dots, C_{14}, C_{15}$ have been detected in the carbon vapor over graphited heated by conventional means, the species C_1, C_2, \dots, C_{11} and C_{14} have been detected in the blowoff vapors from graphite impulse heated by the light output of a pulsed ruby laser. Berkowitz and Chupka³ used mass spectrometric analysis of the laser ejected vapor to show that the neutral polymer to C_3 ratio was 0.32/100 for C_{10} and 0.042/100 for C_{14} . The relative concentration ratio C_{10}/C_{14} was 7.6. They estimated a temperature of 4000°K had been reached. Our results show a polymer to C_3 ratio of about 10^{-6} for both C_{10} and C_{14} at 3000°K. A second interesting comparison is the polymeric distribution of C_n^+ ions formed by a discharge between graphite electrodes. The mass spectrographic data of Dornenburg and Hintenberger⁴ shows a concentration enhancement at C_{10}^+ and C_{14}^+ , and species to C_{31}^+ were detected.

Theoretical calculations generally predict small contributions to the

Figure 2. Carbon Vapor Composition



carbon vapor pressure by species larger than C_5 in the temperature regions accessible for our experiments. However, it is very interesting to note that both Strickler and Pitzer⁵ and Hoffman⁶ predict stable ring structures for C_{10} and C_{14} , with rings favored over chains. These structures may account for our observations.

III. CARBON VAPOR SOURCE DEVELOPMENT

A. Tantalum Tube Furnace

We have previously described² a small tantalum tube furnace developed especially for use with isotopically labelled graphite powder. This molecular beam source is fashioned from a tantalum tube of 0.1 inch inner diameter. One end of the tube is crimped to produce a very narrow slit 0.15 inch high. It is filled with graphite powder and set on a base of graphite rod. This source is heated by RF induction with the graphite rod base slightly below the RF coil. An intense carbon vapor beam is produced by heating to the 2700°K region, with the intensity and useful lifetime perhaps even surpassing that of the original source made of rod only.

Use of this source in our reflection experiments requires that we obtain a direct measure of the composition of the vapor emanating from it under actual experimental conditions. To accomplish this, the apparatus of Figure 1 was used and the vapors were sampled directly by the mass spectrometer. The results are summarized in Table I. In addition to the main molecular beam of carbon vapor emerging from the source slit, a profile obtained with the movable shutter revealed a sizeable component of the carbon atom beam to originate on the tantalum (carbide) surface along side the slit. No appreciable side component was observed for C₂ or C₃. The possibility that the carbon atoms of the side beam had diffused through the tantalum tube wall suggested the development described below.

Table I. VAPOR COMPOSITION FROM TUBE FURNACE
(T=2650°K)

<u>Species</u>	<u>I(C_n⁺)</u>
C ₁	{ 100 slit 320 side
C ₂	{ 30 slit 3 side
C ₃	400 slit only

B. Carbon Atom Source

In an attempt to obtain a carbon vapor beam composed solely of carbon atoms, the slit of a tantalum tube furnace was welded shut using an electron beam welder. The tube was packed with graphite powder and otherwise treated in the same manner as the previous source. Composition of the vapor beam detected by the mass spectrometer upon heating this source to 2650°K is tabulated in Table II. A beam containing over 99% carbon atoms was obtained. This source offers some important new advantages for study of carbon vapor-graphite surface interactions. In particular, this affords the opportunity to study atom combination reactions at the surface as well as to study atom reflection unperturbed by co-existing molecular species.

Table II. VAPOR COMPOSITION FROM ATOM SOURCE

<u>Species</u>	<u>I (C_n⁺)</u>
C ₁	100.
C ₂	1.0
C ₃	0.2

IV. REFLECTION/CONDENSATION OF CARBON ATOMS

Experiments have been initiated using the new carbon atomic beam source to study the reflection of carbon atoms by graphite surfaces. Results of a very preliminary nature show carbon atom reflection behavior very similar to that observed from molecular beam sources. Atom reflection increases gradually from a very small percentage of the beam at low reflecting surface temperatures to a large fraction of the beam as the surface temperature is raised to 2200°K. Above that temperature surface vaporization obscures the reflected beam. Molecular species (C_2 or C_3), which might be formed by atom combination and desorption at the surface, are not observed below the 2200°K surface temperature. At higher surface temperatures these molecular species would also be obscured by normal surface vaporization. Combination problems are more readily attacked by use of isotopic labelling of the carbon atom beam (^{13}C), and we are preparing for that experiment.

Another interesting effect of the beam-surface interaction has been observed. After exposure of the surface to the carbon atom beam, the surface can be cleaned of any condensed material by flash heating the graphite target to 2450°K. We have demonstrated before² that this procedure produces a quick flash desorption of adsorbed carbon (as C_1 , C_2 , and C_3) followed by steady surface vaporization when the material is condensed from a standard carbon vapor molecular beam source. We have now found that C_3 is also flash desorbed when the adsorbed layer is condensed from an atomic carbon beam. The amount of C_3 desorbed is much too large to be accounted for by the very small amount of C_3 (Table II) in the incident beam. Combination of adsorbed carbon atoms might be one explanation, but it seems more likely that the C_3 is created as a result of the gas-surface interaction and that one or more of the carbon atoms in the flash desorbed C_3 molecule originated in the

graphite target surface. The correctness of this hypothesis can be determined by isotopic labelling of the incident carbon atom beam. Carbon vapor enriched in ^{13}C (91.8%) should yield a flash desorption peak at mass 39 ($^{13}\text{C}_3$) if only vapor deposited atoms are involved in C_3 formation. If flash desorption involves only target atoms, the principal peak will be at mass 36 ($^{12}\text{C}_3$). Intermediate cases will occur at intermediate masses. Interestingly, our earlier work⁷ on flash desorbed layers condensed from standard molecular beam sources showed the desorption curve for C_3 to decay in a double exponential pattern, suggesting the existence of two sources of desorbing C_3 .