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Aerospace Nuclear Safety Program

REVIEW OF GRAPHITE ABLATION THEORY AND EXPERIMENTAL DATA

by L. L. PERINI

THE JOHNS HOPKINS UNIVERSITY ■ APPLIED PHYSICS LABORATORY

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FOREWORD

The work reported herein was conducted by the Applied Physics Laboratory Aeronautics Division for the Atomic Energy Commission Safety Branch, Space Nuclear Systems Office. Activities of the Aeronautics Division are under the general supervision of Dr. William H. Avery. The Project Engineer for the Aerospace Nuclear Safety Program is James C. Hagan.

ABSTRACT

This memorandum reviews theoretical graphite ablation models and supporting experimental data with the purpose of determining the degree of confidence to be placed in predictions of graphite ablation from the methods currently in use. From this review of theory and data available to date, it is recommended, for the present, that graphite mass loss predictions for the Pioneer F fuel capsule reentries be based on "moderate" oxidation rates (following Metzger, et al.), Scala's CO diffusion limit, and a thermochemical model for the high temperature sublimation regime based on JANAF(69) species data along with an empirical correlation for erosion losses.

SUMMARY

The assumptions employed in developing the graphite ablation loss model, currently being used in the Aerospace Nuclear Safety Thermal analysis program, are reviewed and the requisite empirical information (rate parameters, thermochemical species, and diffusion limit mass transfer parameter) is discussed.

The experimental data are grouped into two classes: laboratory tests and engineering tests. Laboratory test data (furnace) for the oxidation rate of pyrolytic graphite (PG) from six sources are compared, and the rate parameters are developed from the data. The resulting rates predict oxidation losses considerably less than ATJ graphite; however, test data from engineering tests (arc jets) do not substantiate the lower rates for PG. A number of reasons for this anomaly can be postulated (mechanical erosion, measurement techniques), but there is insufficient information to resolve the discrepancy. Engineering test data for ATJ graphite from five sources covering a wide temperature range (800 to 4000°K) are compared to the theoretical model. In the transition region between reaction-rate controlled and diffusion-limited oxidation rates, the "moderate" rates developed by Metzger, et al., represent the bulk of the data, and in the diffusion-limited region there is a scatter in the data amounting to a +10% to -50% variation about the theoretical predictions. Sublimation predictions based on the JANAF(69) thermodynamic data result in underestimates of experimental mass losses reaching a peak value of -70% at the data extreme of $p = 4$ atm and $T = 4000^{\circ}\text{K}$. A correlation, as suggested by Lundell and

Dickey, is developed for the difference which is attributed to mechanical erosion losses. However, there is insufficient information to decide what percentages of the differences are due to mechanical erosion and/or the neglect of higher-order carbon species.

In view of the scatter in the data a conservative model, for graphite ablation, is currently recommended consisting of the "moderate" rate, coupled with Scala's CO diffusion limited value for the oxidation regime and the JANAF(69) thermochemical data along with the correlation developed for mechanical erosion effects for the sublimation regime. Variations about this base case should be performed for the critical trajectories.

Experimental data for POCO graphite (currently favored heat shield material) is lacking and modifications to the theoretical model will be performed when the oxidation characteristics of POCO are determined.

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I. INTRODUCTION

The Applied Physics Laboratory is aiding the Atomic Energy Commission in the evaluation of safety aspects of spacecraft employing nuclear power sources, including predictions of the probability of maintaining an intact fuel source in the event of an abort. These predictions require the analysis of aerothermodynamic behavior for a variety of reentry configurations on a variety of possible trajectories. Since safety is the primary concern, reentry configurations and trajectories are selected, based on mission abort probabilities, that yield the severest conditions of possible failure modes leading to breaching of the fuel source container; i.e., thermal stress, ablation and impact. For the current Pioneer F mission, for example, the superorbital and orbital decay trajectories have been utilized for thermal studies.¹ To illustrate the variety of gas dynamic phenomena encountered, Fig. 1 shows altitude-velocity profiles of the trajectories for a reentry configuration with a ballistic coefficient (at 400 K ft) of 28 lb/ft². Superimposed on the figure are various curves indicating the stagnation pressure and temperature levels encountered, the chemistry of the flow and the gas dynamic regimes encountered which must be considered in a thorough reentry analysis. In the studies, knowledge of the heating rate distributions and ablation losses are fundamental.

This memorandum is restricted to reviewing theoretical models for graphite ablation and supporting experimental data. The results presented herein evolved from a review of the open literature in an attempt to determine the degree of confidence to be associated with the methods currently in use in estimating the ablation of a graphite material. Similar reviews of

other aspects of reentry aerothermodynamic analyses will be conducted in the future.

A comprehensive analysis, covering the oxidation and sublimation loss of a carbon material, was developed by Scala and coworkers at General Electric in 1958-1963² and has formed the basis and standard of comparison for subsequent models. The generally accepted physical description of the processes is as follows. As a body reenters the atmosphere, its surface temperature rises. When the temperature reaches a certain level, which depends on the surface material's reactivity, a heterogeneous chemical reaction (oxidation) between the hot boundary layer and the surface material ensues. In this first 'reaction-rate-controlled' regime, the surface oxidation rate increases exponentially with surface temperature (e.g., by an Arrhenius kinetic mechanism). Reaction-rate control persists with increasing surface temperature until the diffusional transport of oxidant to the surface becomes too slow to maintain the exponential increase in reaction rate. This 'transition regime' extends to the temperature level where the surface reaction becomes completely diffusion controlled. At this condition, the reaction is said to be in the diffusion-limited regime and is characterized by surface oxidation occurring in stoichiometric proportions (the stoichiometry depending on the products formed). As the surface temperature continues to increase, the oxidation rate remains diffusion-limited until a critical temperature/pressure condition is reached at which the graphitic material also begins to sublime. In this sublimation regime the mass loss rate again increases exponentially with surface temperature as dictated by the partial pressure of the vaporizing carbon species.

Section II presents a qualitative description of the above model, Section III discusses the available experimental data, and Section IV presents a comparison of the theoretical model and the experimental data.

II. REVIEW OF PERTINENT ABLATION THEORY

The numerical solutions upon which current graphite ablation models are based have been generated from the basic conservation equations of continuity, species, momentum and energy subject to laminar, steady-state boundary layer assumptions. These equations are:*

Global Continuity

$$\frac{\partial(\rho u \bar{k})}{\partial x} + \frac{\partial(\rho v \bar{k})}{\partial y} = 0 \quad (1)$$

Species Conservation

$$\rho u \frac{\partial C_i}{\partial x} + \rho v \frac{\partial C_i}{\partial y} = \frac{\partial}{\partial y} \left(D_i \rho \frac{\partial C_i}{\partial y} \right) + \omega_i \quad (2)$$

Energy

$$\rho u \frac{\partial h}{\partial x} + \rho v \frac{\partial h}{\partial y} = \frac{\partial}{\partial y} \left(k \frac{\partial T}{\partial y} \right) + u \frac{\partial p}{\partial x} + \mu \left(\frac{\partial u}{\partial y} \right)^2 + \frac{\partial}{\partial y} \left[\sum_i D_i \rho h_i \frac{\partial C_i}{\partial y} \right] \quad (3)$$

Momentum

$$\begin{array}{l} \text{x-direction} \\ \text{(tangential)} \end{array} \quad \rho u \frac{\partial u}{\partial x} + \rho v \frac{\partial u}{\partial y} = - \frac{\partial p}{\partial x} + \frac{\partial}{\partial y} \left(\mu \frac{\partial u}{\partial y} \right) \quad (4)$$

$$\begin{array}{l} \text{y-direction (normal)} \end{array} \quad \frac{\partial p}{\partial y} = 0 \quad (5)$$

* See p. 39 for a nomenclature list.

$$\bar{k}_0 = 0 \text{ for planar flow and } 1 \text{ for axisymmetric flow}$$

$$P_r = \bar{C}_p \mu / k = \text{Prandtl number}$$

$$L_e = \rho \bar{C}_p D_i / k = \text{Lewis number}$$

$$\bar{C}_p = \sum_i C_i C_{p_i}$$

$$h = \sum_i h_i = \sum_i \int_{298}^T C_{p_i} dt + \sum_i h_i^{298} \quad (6)$$

This set of equations has been employed in previous studies of heat transfer³ and ablation⁴ for axisymmetric bodies. The equations are reduced to a set of ordinary differential equations by assuming flow similarity (i.e., the profiles across the boundary layer are a function of a single variable). The applicability of similarity to the thermochemical equilibrium solution in general has been discussed by Lees.⁵ For the axisymmetric stagnation point the similarity assumption is valid.⁵ The formulation of the boundary condition as well as flow chemistry depends on the problem under study. Normally equilibrium and/or frozen thermochemistry assumptions are employed so as to bracket the effects of kinetics. Scala,⁴ in his studies of the diffusion-limited region, assumed both equilibrium and frozen chemistry and computed boundary layer transport properties (k , μ and D_i) based on statistical mechanics considerations by employing the rigid sphere model and the Leonard-Jones 6-12 potential function. Scala concluded that the mass loss rates were independent of the chemistry assumption employed, i.e., frozen or equilibrium. Fay and Riddell,³ in a study of the heat transfer at the stagnation point of a blunt axisymmetric body, also assumed both frozen and equilibrium flow and concluded that surface heat transfer is independent of

the chemistry as long as the surface is catalytic. This conclusion was also arrived at by Lees.⁵ In these numerical studies ionization effects were not considered, and diffusion effects due to pressure and temperature gradients were neglected. In terms of the elemental mass fraction, α_j , the species conservation equation transforms to

$$\rho u \frac{\partial \alpha_j}{\partial x} + \rho v \frac{\partial \alpha_j}{\partial y} = \frac{\partial}{\partial y} \left(D_{12} \rho \frac{\partial \alpha_j}{\partial y} \right) \quad (7)$$

It has been assumed in deriving Eq. (7) that the diffusion coefficients D_i can be replaced by a binary diffusion coefficient D_{12} . As shown by Lees,⁶ this assumption is consistent with Ficks law and considers the gas to be composed of two typical species; for air a typical atom and molecule, i.e., all atomic species have approximately the same molecular weight and the same collision cross section as do all the molecular species.* The energy equation, by employing the binary diffusion assumption, can now be written:

$$\begin{aligned} \rho u \frac{\partial h_t}{\partial x} + \rho v \frac{\partial h_t}{\partial y} = & \frac{\partial}{\partial y} \left(\frac{\mu}{P_r} \frac{\partial h_t}{\partial y} \right) + \frac{\partial}{\partial y} \left[\mu \left(1 - \frac{1}{P_r} \right) \frac{\partial (u^2/2)}{\partial y} \right] \\ & + \frac{\partial}{\partial y} \left[D_{12} \rho \left(1 - \frac{1}{L_e} \right) \sum h_i \frac{\partial C_i}{\partial y} \right] \end{aligned} \quad (8)$$

where $h_t = h + u^2/2$ is the total stream enthalpy. Equations (7)

and (8) are the basic equations from which the simplified solution is

*Knuth⁷ in a note takes issue on the conceptual model of Ficks Law and indicates the approximation is only good when describing the diffusion of each of these two groups of species, not the individual species.

derived. The assumption $L_e = P_r = 1$ reduces Eqs. (7) and (8) to the same form, i.e.,

$$\rho u \frac{\partial \alpha_j}{\partial x} + \rho v \frac{\partial \alpha_j}{\partial y} = \frac{\partial}{\partial y} \left(\mu \frac{\partial \alpha_j}{\partial y} \right)$$

$$\rho u \frac{\partial h_t}{\partial x} + \rho v \frac{\partial h_t}{\partial y} = \frac{\partial}{\partial y} \left(\mu \frac{\partial h_t}{\partial y} \right)$$

and indicates that the total enthalpy and elemental species concentration gradients across the boundary layer possess local similarity. By assuming a linear gradient across the boundary layer, then

$$\frac{\alpha_j - \alpha_{j_w}}{\alpha_{j_e} - \alpha_{j_w}} = \frac{h_t - h_{t_w}}{h_{t_e} - h_{t_w}} \quad (9)$$

The α_j are the elemental mass fractions. They are related to the species mass fractions via

$$\alpha_j = \sum_i a_{ji} C_i m_j / m_i \quad (10)$$

where a_{ji} is the number of j atoms in the i th species. In general, the net mass flux at the surface, (ρv) , is equal to the sum of the convective $(\rho v \alpha_j)$ and diffusion $(\rho V_j \alpha_j)$ fluxes, i.e.,

$$(\rho v)_w = (\rho v \alpha_j)_w + (\rho V_j \alpha_j)_w$$

For a binary mixture, Fick's law states that

$$\rho V_j \alpha_j = - \rho D_{12} (\partial \alpha_j / \partial y)$$

Therefore,

$$(\rho v)_w = (\rho v \alpha_j)_w - \left(\rho D_{12} \frac{\partial \alpha_j}{\partial y} \right)_w \quad (11)$$

The standard definition for the Stanton number C_h is

$$\rho_e U_e C_h = \frac{\dot{q}}{h_{t_e} - h_{t_w}} = \frac{k(\partial h_t / \partial y)_w}{\bar{C}_p (h_{t_e} - h_{t_w})} = \frac{\rho D_{12} (\partial h_t / \partial y)_w}{(h_{t_e} - h_{t_w})} \quad (12)$$

and the definition for the blowing rate B' (also called the dimensionless driving force, 'mass transfer parameter') is

$$B' \equiv (\rho v)_w / \rho_e U_e C_h \quad (13)$$

For a non-surface element, the net flux $(\rho v)_w = 0$, so that, from Eqs. (9) and (11-13),

$$\alpha_{j_w} = \alpha_{j_e} / (1 + B') \quad (14)$$

For a surface element, the concentration at the boundary layer edge $\alpha_{j_e} = 0$, and, at the surface,

$$\alpha_{j_w} = B' / (1 + B') \quad (15)$$

As an example, consider a C-N-O system applicable to the carbon-air reaction. For this case, carbon is the surface material and the elemental concentrations at the surface are

$$\alpha_{O_w} = \alpha_{O_e} / (1 + B'), \alpha_{N_w} = \alpha_{N_e} / (1 + B'), \text{ and } \alpha_{C_w} = B' / (1 + B') \quad (16)$$

From these concentration equations,

$$\alpha_{C_w} / (\alpha_{O_e} + \alpha_{N_e}) = B' \quad (17)$$

which states that B' can be interpreted as the surface's local 'fuel-air' weight ratio. For an air model composed of 21% O_2 and 79% N_2 by volume, then $\alpha_{O_e} = 0.23$ and $\alpha_{N_e} = 0.77$. Equations (12), (13), and (16), along with relations describing the surface reaction and chemistry assumptions, represent the basic equations utilized in forming a simple graphite ablation model for the unity Lewis number case. The remainder of this review is restricted to this unity Lewis number model. Free stream flow conditions and body geometry enter in the evaluation of C_h which combined with the governing surface chemistry, dictate the value of B' .

The evaluation of conditions for the four thermochemical regimes of graphite, i.e., reaction rate controlled, transition, diffusion control and sublimation, as based on this simplified model, is discussed below.

A. Reaction-Rate Controlled Regime

Experimental surface reaction rate data is normally presented in the Arrhenius plane, i.e., $\log \dot{m}$ vs $1/T$, in an attempt to correlate the data with the empirical Arrhenius rate equation,

$$\dot{m} = P_{O_w}^n k_0 e^{-E/RT_w} \quad (18)$$

where $\dot{m}$ is the carbon mass loss rate, k_0 is the 'frequency factor' or 'reaction rate constant', n is the order of the reaction, E is the activation energy, and P_{O_w} is the partial pressure of the oxidant at the surface.

It is acknowledged that Eq. (18) is a gross simplification of the graphite surface reaction rate, and other more complex forms have been advocated⁸ attempting to account for other influences such as adsorption of reactants and desorption of products. Values of k_0 , n , and E reported by various experimentalists show a great degree of disparity, attesting somewhat^{*} to the inapplicability of Eq. (18) for a heterogeneous carbon reaction. However, judging from published arc-jet experimental data on ATJ graphite (discussed in Section IIIB) and the state of knowledge existing in understanding the fundamental kinetic processes occurring in the carbon-air surface reaction, it appears that Eq. (18) is as valid as any of the other methods. (The conclusion in a comprehensive review of the subject,¹⁰ published in 1959, appears to be still valid: "At present, however, there is no clear understanding of why a given carbon reacts at a particular rate with a given gas under a fixed set of operating conditions".) Scala,⁴ in an attempt to bracket the available data, utilized a set of 'slow' and 'fast' values for E and k_0 with $n = 1/2$. Subsequently Metzger, et al.¹¹ based on experimental arc-jet data, formulated a third set that resulted in rates between the 'fast' and 'slow' values of Scala and labeled herein as the 'moderate' rates. (The resulting values of E and k_0 are reproduced in Fig. 2.)

B. Transition Regime

Defining

$$\dot{m}_R \equiv (PX_{O_e})^n k_0 e^{-E/RT_w} \quad (19)$$

*Some authorities⁹ believe that differing experimental techniques are also influencing the reported differences.

where the mole fraction $X_{O_e} = P_{O_e}/P$, Eq. (18) can be written as

$$\dot{m} = \dot{m}_R (\alpha_{O_w} / \alpha_{O_e})^n \quad (20)$$

It is assumed that $P_{O_w}/P_{O_e} \approx \alpha_{O_w}/\alpha_{O_e}$. The assumption is not seriously in error since the values of B' in the transition region are small ($0 < B' < 0.175$) for carbon. The mass flux of oxygen arriving at the wall is given by combining Eqs. (11), (9), and (12) to give

$$\dot{m}_O = \rho_e u_e C_h (\alpha_{O_e} - \alpha_{O_w}) \quad (21)$$

At this point, the conversion from $\dot{m}_O$ to $\dot{m}$ must be made requiring an assumption to be made on the stoichiometry. If one assumes that CO is the carbon product then

Assuming, however, that CO_2 is the carbon product, then

The question of what determines the primary product, CO or CO_2 , has as yet not been established. It appears that CO and CO_2 are both primary products with the ratio CO/CO_2 increasing sharply with temperature, so that above $\sim 1300^\circ K$, the primary product becomes CO^9 solely. This is essentially in agreement with equilibrium calculations of the $C + CO_2 \rightarrow 2CO$ reaction presented in Ref. 10, wherein for $P = 1$ atm and $T = 1300^\circ K$, $CO/CO_2 \approx 200$

whereas at $T = 1000^\circ\text{K}$, $\text{CO}/\text{CO}_2 \approx 2$. Based on these considerations, we have assumed that CO is the primary product, so that

$$\dot{m} = \rho_e u_e C_h \left(\frac{3}{4} \alpha_{O_e} \right) \left(1 - \frac{\alpha_{O_w}}{\alpha_{O_e}} \right).$$

If we define

$$\dot{m}_D = \rho_e u_e C_h \frac{3}{4} \alpha_{O_e} \quad (22)$$

then

$$\dot{m} = \dot{m}_D \cdot \left[1 - (\alpha_{O_w} / \alpha_{O_e}) \right] \quad (23)$$

when comparing Eqs. (22) and (13), it is found that, in the diffusion-limited regime with CO as the primary product, $B'_D = \frac{3}{4} \alpha_{O_e}$. For air, with $\alpha_{O_e} = 0.23$, $B'_D = 0.1725$. The two rates given by Eqs. (23) and (20) must be equal. Assuming a first-order reaction ($n = 1$), we obtain, for the transition regime,

$$\dot{m}/\dot{m}_D = [1 + (\dot{m}_D/\dot{m}_R)]^{-1} \quad (24)$$

whereas for a 1/2-order reaction ($n = 1/2$),

$$\dot{m}/\dot{m}_D \simeq \left\{ \frac{1}{2} + \left[\frac{1}{4} + (\dot{m}_D/\dot{m}_R)^2 \right]^{\frac{1}{2}} \right\}^{-1} \quad (25)$$

Equation (24) represents the so-called 'resistance in series' formula, as developed by Frank-Kamenetskii,¹² and utilized by Scala in an early paper⁴ for a 1/2-order reaction. In later papers,² the expression

$$\dot{m}/\dot{m}_D = \left[1 + (\dot{m}_D/\dot{m}_R)^2 \right]^{-\frac{1}{2}} \quad (26)$$

was used and is a close approximation to Eq. (25). Another method for the transition region was advocated by Welsh and Chung¹³ and consists basically of utilizing equilibrium considerations to determine the constant in Eq. (22) as a function of temperature and pressure. This results in the 'double plateau' theory where the first plateau corresponds to a CO₂ diffusion limit and the second plateau to the CO limit.

C. Diffusion Limit

The correlation equation arrived at by Scala² from numerical solutions of the basic boundary layer equations in the diffusion limited regime is

$$\dot{m}_D = 0.00635^* (P_s/R_N)^{\frac{1}{2}} \text{ lb/sec-ft}^2 \quad (27)$$

where the stagnation pressure P_s is in atm, and the nose radius R_N is in feet. Scala found that the differences between frozen and equilibrium assumptions was small and that the increase in heat transfer due to chemical reaction in the boundary layer was approximately offset by the reduction in heat transfer due to mass transfer addition to the boundary layer via surface ablation (i.e., blowing). Utilizing this latter finding and by assuming CO to be the primary product, then, from Eq. (22),

$$\dot{m}_D = 0.1725 \rho_e u_e C_{h_o} \quad (28)$$

*The original report⁴ listed the constant as 0.0062, however, a more recent report² lists the value as 0.00635.

where C_{h_o} is the non-blowing Stanton number. By employing the basic form of Fay and Riddell's³ correlation equations for a cold wall at conditions of $L_e = 1$, $P_r = 0.70$ and $\rho_s \mu_s = \rho_e \mu_e$, then

$$\rho_e u_e C_{h_o} = \dot{q}_{c_w} / h_{t_e} = 0.94 \left[\rho_s \mu_s \left(\frac{du}{dx} \right)_s \right]^{\frac{1}{2}}$$

when considering standard hypersonic flow assumptions [i.e., $(du/dx)_s = \sqrt{(\gamma-1)/\gamma} u_o / R_N$ and $C_p T_s = u_o^2 / 2$], the equation of state, $\rho_s = P_s / (R_g T_s)$, the Sutherland viscosity relation for $T_s \gg 200^\circ R$, $\mu_s = C_1 T_s^{\frac{1}{2}}$ where T_s is in $^\circ R$, and $C_1 = 0.725 \times 10^{-6}$ lb/ft-sec- $R^{\frac{1}{2}}$, and finally the perfect gas relation, $C_p = \frac{\gamma}{\gamma-1} R_g$ the following expression is obtained:

$$\rho_e u_e C_{h_o} = 0.94 \left[C_1 \frac{P_s}{R_N} \sqrt{\frac{2g}{R_g}} \right]^{\frac{1}{2}}$$

Using this latter relation in Eq. (28), with $R_g = 53.3$ ft-lb/lb- $^\circ R$ and $g = 32.2$ ft/sec², gives

$$\dot{m}_D = 0.00666 (P_s / R_N)^{\frac{1}{2}} \text{ lb/sec-ft}^2 \quad (29)$$

The close agreement of Eq. (29) with Eq. (27) (within 5%) is fortuitous; however, it does show the general form of Eq. (27) to be theoretically valid.

Oxidation-rate profiles based on Eq. (19) for $\dot{m}_R$, Eq. (27) for $\dot{m}_D$, and Eq. (25) for $\dot{m}/\dot{m}_D$ are illustrated in Fig. 2. The reaction rate constants k_o and E for the 'fast', 'slow' and 'moderate' Arrhenius models utilized in these calculations are shown in Fig. 2. Since $\dot{m}_R$ and $\dot{m}_D$ are both proportional to $\sqrt{P_s}$, the resulting $\dot{m}/\dot{m}_D$ ratio is independent of pressure.

Also shown for comparison is the 'moderate' rate profile using Eq. (26). As noted, the mass loss ratio computed with Eq. (25), yields slightly lower mass ratios. A nose radius R_N of 1/2" was used in the calculations. Increases in R_N would lead to increases in $\dot{m}/\dot{m}_D$. The rate profile curve labeled 'very slow' will be discussed in Section III.

D. Sublimation Regime

In the sublimation region, graphite mass loss becomes primarily dependent upon the partial pressure of the carbon vapor species at the surface. Scala also developed the following mass loss correlation* for graphite sublimation based on numerical solutions of the boundary layer equations for a nine species (O , O_2 , N , N_2 , CO , CO_2 , C , C_3 and CN) equilibrium model:

$$\dot{m}/\dot{m}_D = 1 + 16 \times 10^6 P_s^{-2/3} e^{-1.11 \times 10^5/T_w} \quad (30)$$

where P_s is in atm, and T_w is in °R. In Fig. 3, Eq. (30), for $P_s \approx 1$ atm, is shown as the 'SCALA' curve. Scala also concluded that the mass flux rate could be "approximated closely in a very simple manner, i.e., by the solution of a set of algebraic thermochemical equations which yields the elemental carbon composition at the wall."¹⁴ This procedure is followed in the computer programs developed by the Aerotherm Corporation,¹⁵ which are used at APL in evaluating one-dimensional ablation characteristics..

*Equation (30) is obtained by combining Eqs. (33) and (37) from Ref. 14.

In terms of the mass transfer parameter, B' , the elemental carbon mass fraction is given by the last of Eqs. (17), i.e.,

$$\alpha_{c_w} = B' / (1 + B') \quad (31)$$

It remains to relate B' to surface temperature and pressure. The mass loss ratio is given by

$$\dot{m} / \dot{m}_D = \frac{B'}{B'_D} \frac{(C_h / C_{h_o})}{(C_h / C_{h_o})_D} \quad (32)$$

where C_{h_o} is the non-blowing Stanton number. Various correlations are currently in use relating C_h / C_{h_o} to B' . The classic Mickley-Spalding¹⁶ blowing relation is assumed to apply, i.e.,

$$C_h / C_{h_o} = [\ln(1 + B')] / B' \quad (33)$$

Combining Eqs. (31) and (32) gives

$$\dot{m} / \dot{m}_D = \ln(1 + B') / \ln(1 + B'_D) \quad (34)$$

In an equilibrium, homogeneous thermochemical solution, the independent parameters are basically pressure and temperature. The sublimation process involves a heterogeneous surface reaction involving the equilibrium state, dictated by the vapor pressure of the sublimating species, between the solid and gaseous phases. This additional constraint, in accordance

*The selection of a more appropriate correlation should be a subject for further study. Other correlations have been proposed¹⁷ that attempt to account for a non-air gas.

with Gibbs' phase rule, reduces the number of degrees of freedom by one, so that, for example one need specify only the pressure.

To illustrate the procedure, let us consider the carbon-air system. At the high temperatures under consideration, and for the sake of simplicity, we assume that all of the oxygen has combined to form CO, that C_3 is the dominant carbon species, and that N_2 has not dissociated. For this '3-component' (CO, C_3, N_2) model the gaseous reactions are:

and N_2 is treated as an inert component. The surface condition is represented by

Elemental conservation, in conjunction with Eqs. (16) give

$$\begin{aligned} \alpha_{O_w} &= \frac{m_O}{Pm} P_{CO} = \frac{\alpha_O}{1+B}, \\ \alpha_{N_w} &= 2 \frac{m_N}{Pm} P_{N_2} = \frac{\alpha_N}{1+B}, \text{ and} \\ \alpha_{C_w} &= \frac{m_C}{Pm} (P_{CO} + 3P_{C_3}) = \frac{B'}{1+B}. \end{aligned} \quad (35)$$

The mixture molecular weight is given by

$$m = (P_{CO} m_{CO} + P_{N_2} m_{N_2} + P_{C_3} m_{C_3}) / P. \quad (36)$$

Dalton's law of partial pressure is

$$P = P_{CO} + P_{N_2} + P_{C_3} \quad (37)$$

and the surface reaction equilibrium is represented as

$$K_{P_{C_3}} = P_{C_3} \quad (38)$$

where $K_{P_{C_3}}$ is the equilibrium constant (i.e., the partial pressure) between C_3 and $C(s)$. Solving for P_{C_3}/P from Eqs. (35-37) gives

$$\frac{P_{C_3}}{P} = \frac{B' - \alpha_{O_e} m_C/m_O}{B' + 2 \alpha_{O_e} m_C/m_O + \frac{3}{2} \alpha_{N_e} m_C/m_N}$$

Using $B'_D = \alpha_{O_e} m_C/m_O$ and noting that $\frac{3}{2} \alpha_{N_e} m_C/m_N \approx 1$, we have

$$\frac{P_{C_3}}{P} = \frac{B' - B'_D}{B' + 2B'_D + 1} \quad (39)$$

From thermochemical tabulations¹⁸ of $K_{P_{C_3}}$ we have

$$\log_{10} P_{C_3} = 9.64 - 39800T^{-1} \quad (40)$$

where T is in °K. The procedure is to select a B' (elemental composition) and stagnation pressure $P = P_s$, solve for the surface temperature ($T = T_w$) from Eqs. (39) and (40) and $\dot{m}/\dot{m}_D$ from Eq. (34). The results (labeled 'simple C_3 model') are shown in Fig. 3 for $P_s = 1$ atm. Also shown for

comparison, are the results of a 14-species model (labeled 'JANAF (69)') with carbon species including C_1 through C_5 as derived from a thermochemical equilibrium computer program¹⁹ using current ('1969') JANAF thermochemical data. As noted, the simple C_3 model tends to underestimate the mass loss ratios for a given temperature; however, the trends are similar. The differences between the 'JANAF (69)' and 'SCALA' results are due to differences in the thermochemical data and in the methods of solution. It should be remarked that the comparisons between the 'JANAF (69)' and 'SCALA' curves could be altered by selection of a different blowing relationship. At a given surface temperature, increasing the pressure results in lower mass loss ratios.

Sublimation loss rates for graphite have been computed, utilizing the procedure outline above and assuming the existence of higher order carbon species. Dolton, et al.,²⁰ in an attempt to investigate sublimation kinetics, considered C_1 to C_{16} and generated the requisite thermodynamic data for the postulated higher-order species based on the method of Pitzer and Clementi (a method which utilizes measured data for C_3). At approximately the same time, Kratsch et al.²¹ published sublimated mass loss rates assuming C_1 to C_{30} carbon species. The thermodynamic data for the carbon species were generated by "theoretical methods substantially different from those used by Pitzer and Clementi." The Dolton and Kratsch studies both state that the resulting thermodynamic data yielded good agreement with measurements of the triple-point temperature measurements of graphite. Rindall and Powars,²² in a review of the sublimation region, concluded on the basis of Dolton's

results that "the calculations for the kinetic case may be approximated by assuming thermochemical equilibrium and simply ignoring high molecular weight carbon vapor species from consideration in the calculations." Data for the Dolton species C_3 to C_{16} have been obtained from the Aerochem Corporation.²³ The data, as received (curve fits), are referenced to a 0°K base and limited in general to $T > 900^\circ\text{K}$. In view of the uncertainty in the data (Ref. 21 indicates a $\pm 20\%$ uncertainty in the free energy function) the curve fits were converted to the JANAF 298°K base by subtracting 5% of the enthalpy at 3000°K. The remaining species C, C_2 , NO, N, N_2 , CO, O, O_2 , CO_2 , CN, C_2N_2 , C_4N_2 and C(S) were obtained from the JANAF data. Based on these species, a thermochemical equilibrium computer program¹⁹ was utilized to generate the $B'-T_w$ relationship, and the mass loss ratio was determined via Eq. (34). The results for $P_s = 1 \text{ atm}$ are labeled 'DOLTON' in Fig. 3 and indicate a much higher mass loss rate for a given temperature than either the 'JANAF (69)' or 'SCALA' curves. In light of the conclusion by Rindall and Powars, as discussed above, the 'DOLTON' curve can be viewed as the equilibrium limit and the 'JANAF (69)' curve as the kinetic limit. Recent experimental measurements by Lundell and Dicky,²⁴ to be discussed in Section III, lend support to the 'JANAF (69)' model, i.e., the sublimation process is kinetically controlled and the higher order carbon species do not have time to form.

E. Summary

The model for graphite ablation predictions that has been reviewed in this section is relatively simple to apply and can be adapted to other

materials. The basic inputs are the rate parameters E and k_o for the rate-controlled regime, the Stanton number C_h and stoichiometry for the diffusion-limited regime, and vapor pressure data and a blowing relationship for the sublimation regime. The model distinguishes between different types of carbon only in the rate-controlled regime, through the parameters E and k_o . The reentry body's geometry enters in the specification of C_h . From Lee's relationship,⁵ C_h depends on the dimensionality of the flow by the factor $2^{\bar{k}/2}$, where $\bar{k} = 1$ for axisymmetric flow (e.g., hemispherical and flat-faced cylinders) and $\bar{k} = 0$ for planar flow (e.g., infinite length cylinders). The body shape also enters into the determination of the stagnation point velocity gradient. The method is somewhat restricted in that mechanical erosion, turbulence, rarified flow, and radiation are not included; however, these effects are normally accounted for by assuming that the phenomena are uncoupled and therefore additive.

III. EXPERIMENTAL DATA ON GRAPHITE ABLATION

The experimental data fall into two categories: 1) laboratory tests of small rods or plates that are heated either electrically or in a furnace to gain fundamental knowledge concerning the surface reaction mechanisms, and 2) engineering tests of somewhat larger specimen (~ 1 " in diameter) configured to represent aerodynamic shapes of interest. The latter tests usually are performed in high-enthalpy, arc-heated tunnels to obtain usable data applicable to the design of thermal protective systems.

A. Laboratory Tests

The majority of tests over the past four decades are of this nature. This morass of information has been reviewed by others.^{9,10} About the only general conclusion that can be formulated from it is that the oxidation rate of carbon depends on factors that have not as yet been universally accounted for by experimentalists (e.g., porosity, atomic structure, surface structure, impurity content, etc.). For the artificial graphites, these factors have been shown to strongly influence physical properties (e.g., density, thermal expansion, Young's modulus, etc.)²⁵ and also appear to have a bearing on oxidation characteristics.

Figure 4 shows oxidation rate data for pyrolytic graphite (PG) from six papers,²⁶⁻³¹ plotted on Arrhenius coordinates ($\log \dot{m}$ vs $1/T_w$). The conditions for all the data (see Table I) are applicable to the oxidation of PG at atmospheric pressure in air; PG is of interest to the reentry safety analysis program as it is utilized as a backup insulation material for the Pioneer F heat source. PG is characterized by its low porosity, high density, (i.e., ~99% theoretical density), and high degree of anisotropy. It is manufactured by chemical vapor deposition (usually methane) on a suitable substrate. The deposition temperature appears to have a pronounced influence on the physical properties.²⁵ The data scatter in Fig. 4 spans one to two orders of magnitude. Horton,²⁶ Nagle and Strickland-Constable²⁷ and Walls and Strickland-Constable²⁸ claim the data are true surface reaction rate data free from diffusional effects. Schiff²⁹ acknowledges that the results are relatively crude and presents the indicated shaded region

rather than data points. Levy³⁰ concluded that above 1144°K (represented by the breaks in the four curves in Fig. 4), diffusional effects were influencing the results. The data from Nagle and Walls show a relatively good degree of reproducibility (a factor of 2) and represent two different pyrolytic graphites. In addition, their data tend to agree with the Levy^{30,31} data. The Horton results show relative agreement with the results of Schiff.

Ignoring the apparent peak in the data at 2000°K, a straight line (dotted in Fig. 4) has been drawn through the preponderance of data. This line gives $k_o = 13.97 \text{ lb}(\text{ft}^{3/2} \text{-sec-atm}^{1/2})$ and $E = 27670 \text{ cal/mole}$. Using Eq. (19) and assuming a half order ($n = 1/2$) reaction, the resulting 'rate equation' for T_w in °K is given as

$$\dot{m}_R = 13.97 (PX_{O_e})^{1/2} e^{-27670/RT_w} \text{ lb}/(\text{ft}^2\text{-sec}) \quad (41)$$

The rate constant, k_o , and activation energy, E , were evaluated by assuming $X_{O_e} = 0.21$, $P = 1 \text{ atm}$ and $R = 1.986 \text{ cal/mole-}^\circ\text{K}$.

In comparison, the Metzger correlation for ATJ graphite data obtained in arc jet tests (discussed later) is

$$\dot{m}_R = 9.65 \times 10^5 (PX_{O_e})^{1/2} e^{-44000/RT_w} \text{ lb}/(\text{ft}^2\text{-sec}) \quad (42)$$

which indicates oxidation rates for ATJ ~ 20 times greater at $T = 1000^\circ\text{K}$, and ~ 300 times greater at $T_w = 1500^\circ\text{K}$, than the corresponding PG rates. The trends are as expected, since ATJ with its higher porosity would be

expected to oxidize more rapidly. In addition, the divergence between the two as surface temperature increases can be rationalized as due to the increase in surface area for the ATJ graphite as the pores enlarge due to oxidation.

In order to illustrate the differences, between ATJ and PG, values of $\dot{m}/\dot{m}_D$ were computed using Eq. (25) with $\dot{m}_D$ given by Eq. (27) and $\dot{m}_R$ from Eqs. (41) and (42). The resulting curves are shown in Fig. 5. As noted, the PG oxidation rates are below the diffusion limited value up to the sublimation region ($T_w \sim 3000-3500^\circ\text{K}$). Also shown in Fig. 5 are arc-tunnel ablation-rate measurements for PG graphite obtained by Maahs³⁷ in four facilities as discussed later (Section III-B-5). One should be cautious in drawing conclusions on the basis of the data, as other tests by Maahs encompassed three other grades of graphite (including ATJ) and showed no discernable trends as to oxidation rate differences between ATJ and PG (see Fig. 9).

B. Engineering Tests

The tests in this category are specifically directed toward obtaining ablation loss rates for the purpose of generating design information for aerospace configurations. As with the laboratory type of tests, reproducibility is difficult to attain. In addition, the measurement of surface temperature, heating rates, ablation rates and gas dynamic properties represents a formidable task in the usually severe test environments. Furthermore, the quality and gas dynamic nature (i.e., steadiness and

uniformity) of the flow emanating from the arcs can be difficult to control. In spite of these obstacles, a fair amount of data has been accumulated throughout the thermochemical temperature range of interest, (i.e., 900-4000°K) for ATJ grade graphite over the past decade. These data are briefly summarized below. The data of Golovina and Khaustovich³² are an exception since they represent electrically heated electrode carbon specimens tested in a laboratory environment. However, they are included since it has recently been recommended that these data be considered representative for "other less graphitic carbons" than pyrolytic graphite.⁸

1) Golovina and Khaustovich, Russia, 1962, Ref. 32

The tests were conducted for electrode carbon ($\rho = 1.71$ g/cc) spheres, 15 mm in diameter. The specimens were electrically heated and the air flow rate was maintained at ~ 2 ft/sec. A spring balance was used to measure weight changes and a photoelectric pyrometer for temperature measurements. No pressure data were reported. The results encompass a temperature range from 1070 to 2772°K (37 data points) and the theoretical calculations of diffusional rates (assuming CO as the primary product) given by the authors were used to form the $\dot{m}/\dot{m}_D$ ratio. The results are shown plotted in Fig. 6. In a discussion of these results R.H. Essenhigh³³ expressed the opinion, based on considerations of the diffusional boundary layer thickness, that the tests were free of diffusional effects, in contrast to Golovina and Khaustovich's conclusion.

2) Welsh and Chung, Aerospace Corp., 1963, Ref. 13

Welsh and Chung, in support of their postulated 'double-plateau' theory, reported ATJ graphite ablation data (17 data points) encompassing

the temperature range of 890 to 2250°K. A subsonic air jet heated by an electric plasma was impinged "normally on one end of an ATJ-grade graphite cylindrical specimen." Further details (e.g., pressure, measurement techniques, etc.) were not reported. The data were presented as the $\dot{m}/\dot{m}_D$ ratio and used as given. The results are shown plotted in Fig. 6.

3) Metzger, Engel and Dioconis, General Electric Co., 1965, Ref. 11

The authors presented a summary of an experimental program on the "graphite degradation in reentry environments." Preliminary data, included in this summary paper, were reported in 1962.³⁴ The tests were performed in an arc-heated hypersonic tunnel at the Space Sciences Laboratory of the General Electric Co. Electrode contamination is claimed to be low (~100 parts per million). The bulk of the data was obtained for ATJ graphite utilizing flat-faced cylindrical specimens of 1/16, 1/4 and 1 inch diameter. Surface temperatures ranged from 1100 to 2900°K, and stagnation (body) pressures ranged from 0.007 to 0.056 atm. Pressures were measured with a pitot probe, heat transfer with calorimeter models, and surface temperatures with a two-color pyrometer. Mass loss data were obtained by measuring specimen length changes at the stagnation point after exposure to the test stream.

The data, used herein, were modified on two accounts by Metzger, et al. Due to test facility limitations, the test specimen's local flow conditions ranged from continuum to near-free molecular flow. The data obtained at rarefied flow conditions were adjusted to permit comparison to continuum flow theory. The adjustment consisted of "applying a Stanton number ratio correction factor to the data in the diffusion controlled regime or an effective pressure ratio correction factor to data in the reaction rate controlled regime." A second correction was applied to convert the results to an equivalent spherical geometry.

The resulting data (over 200) are shown in Fig. 7. The values tabulated in Ref. 11^{*} were divided by the diffusion limit given by Eq. (27) to form the $\dot{m}/\dot{m}_D$ ratio. The low-temperature oxidation data were used by Metzger, et al., to arrive at the reaction rate constants, k_0 and E , listed in Fig. 2 as the 'moderate' values.

4) Miller and Sutton, NASA Langley, 1966, Ref. 36

The investigation encompassed three grades of graphite, ATJ ($\rho = 1.73$ g/cc), AHDG ($\rho = 1.90$ g/cc) and AGSX ($\rho = 1.67$ g/cc); three hemispherical shaped models, $d = 0.375, 0.50$ and 1.0 inches; and three Langley test facilities, the 11" ceramic-storage-heated tunnel ($P_s = 5.2$ to 7.5 atm), the arc-heated materials jet (6.4 to 8.3 atm) and the 20" hypersonic arc-heated tunnel (0.60 to 0.20 atm). The purpose was to investigate the diffusion-limited oxidation regime. The mass fraction of O_2 within the test stream was varied from 0.059 to 0.232 (i.e., air).

Low contamination for all facilities was claimed by the authors. Mass loss rates were obtained by photographic and post-test measurements of surface recession. Surface temperatures were determined with a photographic pyrometer and ranged from 1600 to $2330^\circ K$. Stagnation heat transfer rates were evidently computed from the Fay and Riddell³ theory although details are not given (e.g., Le number). It is also not clear how the stagnation pressure values were obtained.

The resulting data (~ 80 points), normalized to the CO diffusion limit theoretical values,^{**} are reproduced in Fig. 8. The mass loss ratios

* A subsequent version of this reference appeared in the AIAA Journal (Ref. 35), but did not include a tabulation of the data.

** Maahs³⁷ pointed out that the theoretical values employed by Miller and Sutton are $\sim 14\%$ lower than the diffusion limit of Scala.

were taken directly from Fig. 13 of Ref. 36. The authors concluded that a diffusion controlled reaction for all three grades of graphite was evident only above 2000°K. Below 2000°K, ablation rates were temperature-dependent, indicating a transition region between the chemical control and diffusion control oxidation regions. The AHDG and AGSX graphite specimens became highly eroded in the high pressure environments.

5) Maahs, NASA Langley, 1970, Ref. 37

This test series encompassed the following four grades of graphite: two glass-like carbons, LMSC ($\rho = 1.41$ g/cc) and Vitreous carbon ($\rho = 1.49$ g/cc); a pyrolytic graphite ($\rho = 2.15$ g/cc); and an ATJ graphite ($\rho = 1.72$ g/cc). Four Langley facilities were utilized, the same three used by Miller and Sutton plus the high-enthalpy arc tunnel. Model stagnation pressures varied from 0.035 to 15 atm and surface temperatures from 1600 to 3450°K. The test specimens were hemispherical cylinders of 1/2" diameter. Mass loss rates were determined from motion pictures, surface temperatures were measured with a photographic pyrometer, pitot probes were used to record test stream stagnation pressures, and heating rates were measured with a Gardon asymptotic calorimeter. The resulting data are plotted in Fig. 9. The values of $\dot{m}_D$ used to normalize the rates were taken from Maah's Fig. 5.³⁷ He stated that in the high pressure condition ($P_s = 15$ atm), considerable mechanical erosion was witnessed for the ATJ graphite. He concluded that the measured rates did not confirm the diffusion-limited theoretical predictions of Scala.

6) Lundell and Dickey, NASA Ames, 1971, Ref. 24

These tests were conducted to investigate the sublimation region for ATJ graphite ($\rho = 1.73 \text{ g/cc}$). The models were blunted and hemispherically-capped cylindrical specimens in two sizes, 0.60" and 1.20" diameter. The tests were conducted in the Ames Heat Transfer Tunnel and encompassed model stagnation pressures from 0.30 to 4.40 atm and surface temperatures from 2600 to 4033°K. Stagnation heating rate profiles across the test stream were measured with a water-cooled calorimeter; pressure profiles, with pitot probes; recession rates, with motion pictures; and surface temperatures, with automatic optical pyrometers. The resulting data are plotted in Fig. 10, along with two sublimation predictions based on the JANAF thermochemical tabulations. The curve labeled 'JANAF (69)' was discussed in Section II. The 'JANAF (61)' curve is based on JANAF thermochemical data published in 1960-61 for the C_3 to C_5 carbon species. The $\dot{m}_D$ values used to normalize the measured rates were computed from Eq. (27) using the values of pressure and effective nose radius tabulated by Lundell and Dickey,²⁴ who assumed that the JANAF (61) species were applicable to the sublimation region and regarded the differences between the measured rates and the JANAF (61) predictions as due to mechanical erosion. Mechanical erosion was observed during the test; however, the procedure utilized in quantitatively evaluating erosion appears tenuous as it assumes that a) the JANAF (61) species are correct and b) the blowing relationship utilized by Lundell and Dickey,

$$\frac{C_h}{C_{h_o}} = \frac{\ln(1.28 B' + 1)}{1.28 B'} \quad , \quad (43)$$

is applicable. Variations in either the assumed species, thermodynamic data, or blowing relationship could materially alter the 'erosion' estimates. Figure 11 shows $\dot{m}_i/\dot{m}_s$ versus temperature, where $\dot{m}_i$ is the increment between the data point and the $\dot{m}_s$ given by the JANAF (69) sublimation curve, as defined in Section II, at the same surface temperature and pressure. The resulting values of $\dot{m}_i$ based on the JANAF (69) thermochemical data are lower than the values reported by Lundell and Dickey, with reductions of 50% occurring at the higher surface temperatures. A curve fit through the bulk of the points, as represented by the solid line, gives

$$\frac{\dot{m}_i}{\dot{m}_s} = \frac{314}{4178 - T_w} - 0.155 \quad (44)$$

which is applicable over the temperature range, $2500^\circ \leq T_w \leq 4050^\circ\text{K}$, and stagnation pressure range, $0.3 \leq P_s \leq 4.40$. As pointed out by Lundell and Dickey, no noticeable effect of pressure on mechanical erosion was evident. However, it should be noted that the values of $\dot{m}_i/\dot{m}_s$ from the reduced data at the higher surface temperatures are based entirely on data measured at the high pressure test condition. It should be emphasized that Eq. (44) is only applicable to the theoretical sublimation curve as defined above and should be viewed as a correction to be applied to the JANAF (69) $\dot{m}_s$ curve in order to provide reasonable agreement with the Lundell and Dickey data.

C. Summary

This section has presented available experimental data (unclassified) on oxidation and sublimation rates for various graphitic materials

(notably, ATJ). Major questions, beyond the validity of the data itself, remain as to the utilization of the information. For instance, the relationship of the laboratory data to arc jet results. The PG predictions based on the laboratory tests and illustrated in Fig. 5 indicate good performance in terms of oxidation resistance characteristics, but there are insufficient data to either support or disprove the results.

It appears there is no reliable method of establishing the effect of mechanical erosion for graphites either experimentally or theoretically, as the thermochemical mass loss rates and particulate mass loss rates are strongly coupled. The experimental data of Lundell and Dickey show higher mass losses than the JANAF (69) thermochemical predictions in the sublimation region. The differences are substantial, amounting to $\sim 70\%$ at 4000°K . For the current safety analysis of the Pionner F at APL, it is assumed that the differences are due to mechanical erosion; this is a more conservative approach, especially for the extreme superorbital trajectories, than to assume that there is simply a deficiency in the sublimation thermochemical model.

An attempt was made to gain some insight on the effect of test facility and experimentalist based on the results of Maahs³⁷ and Miller and Sutton.³⁶ Figure 12 shows experimental rates for ATJ graphite as measured by both studies in three corresponding facilities. The number of data points are sparse and the scatter is large. Agreement among the studies is limited to two points in the AHMJ facility, and disagreement for some points is as great as a factor of 2 (e.g, at $T_s = 2050\text{-}2075^\circ\text{K}$ in the HAHT facility).

For the current Pioneer F heat source (SNAP-19), the heat shield material is a fine-grain POCO graphite with $\rho \approx 1.80$ g/cc. Mass loss rates for a POCO AXF-5Q grade graphite are reported in Ref. 38; however, the test conditions are more representative of ballistic reentries (i.e., stagnation pressures of 75-100 atm). Consequently, the mass loss data reflect inordinately high percentages of mechanical erosion and are too severe to be applicable to the current reentry configuration with a ballistic coefficient (at 400 Kft) of 28 lb/ft^2 , where maximum stagnation pressures are on the order of 10 atm. POCO AXF-5Q ablation results were also reported in Ref. 39; however, the usefulness of the data is limited since surface temperatures were not measured. Here again, stagnation pressures were high (6 to 165 atm) with resulting large percentages of mechanical erosion. This test series encompassed seven materials and six test facilities. It was concluded that "material and testing variables do not permit differentiation in ablation performance among the bulk graphites" and "that five of the six test facilities provided similar results."

IV. Comparison of Theory and Experiment

Section II reviewed a theoretical graphite ablation model, based essentially on the work of Lees and of Scala and coworkers at G.E., and Section III presented experimental data on graphite mass loss from the open literature. Figure 13 is a composite graph covering the complete temperature range from the rate-controlled oxidation regime to the sublimation regime.

This figures includes a) predicted oxidation mass loss profiles based on four sets of reaction rate constants (k_o and E ; see Fig. 2) representing 'fast', 'moderate', 'slow', and 'very slow' reaction rates; b) sublimation predictions based on the Dolton and JANAF (69) thermochemical models with the blowing relationship given by Eq. (33); and c) the experimental data presented in Section III for ATJ graphite. The $\dot{m}/\dot{m}_D$ ratios are as presented in Section III recognizing the fact that there are variations in the definition of $\dot{m}_D$ among the various sets of data. The Lundell and Dickey sublimation data include only that data for the pressure range, $0.9 \leq P_s \leq 1.1$ atm. The majority of the data lend support to the 'moderate' oxidation rate, the Scala diffusion limit, and the JANAF sublimation model. However, the data of Maahs³⁷ and Miller and Sutton³⁶ show much lower oxidation rates in the diffusion-limited regime. Theoretical models based on the latter data would lead to substantial reductions in heat shield ablation losses below those indicated by the bulk of the data for most Pioneer F heat source re-entries. The oxidation profile labeled 'very slow' represents the optimistic extreme, encompassing all of the data, and was arrived at by arbitrarily reducing k_o to $965 \text{ lb}/(\text{ft}^2\text{-sec}) \sqrt{\text{atm}/\text{ft}}$ with $E = 44000 \text{ cal/mole}$.

In view of Fig. 13 and considering the conservative approach required in the safety analysis, it is concluded that the Scala diffusion limit, the 'moderate' rates and the JANAF (69) species along with Eq. (44) should be utilized as the nominal case for purposes of estimating ablation losses. Variations about the above model to encompass the majority of the data are; a) in the transition regime a variation of $10^{\pm 1} k_o$, plus and minus an order of magnitude of the moderate reaction rate constant, k_o , b) in the

diffusion regime, + 10% to - 50% of $\dot{m}_D$ and c) in the sublimation regime $\pm 20\%$ of $\dot{m}$.

The POCO graphite (currently favored heat shield material) has a higher density ($\sim 6\%$) than ATJ, and it is generally accepted that the oxidation resistance is proportional to density since the porosity is $\propto 1/\rho$. This trend has been verified when comparing PG and a low density graphite,²⁸ however, in an experimental study directed toward determining the relationship between oxidation behavior and density⁴⁰ it was concluded that for the four graphites tested ($\rho = 1.55$ to 2.08 g/cc, temperatures from 1500 to 2300°K) there was no relationship between the rate of reaction and the density. Consideration of the above results, the absence of experimental data for POCO and the scatter in the ATJ data about the 'moderate' curve it appears that there is no justification for a reduction in the 'moderate' ablation rates for the POCO grade graphite.

Thermal studies of the Pioneer-F heat source, on various trajectories, utilizing the models documented herein will be reported in a forthcoming memorandum.

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NOMENCLATURE

a_{ij}	=	Number of j atoms in the i molecule
B'	=	Mass transfer coefficient
C	=	Species mass fraction
C_1	=	Constant in viscosity relationship = $0.725 \times 10^{-6} \text{ lb}/(\text{ft}\cdot\text{sec}\cdot^\circ\text{R}^{\frac{1}{2}})$
C_p	=	Specific heat at constant pressure
C_h	=	Staton number with blowing
C_{ho}	=	Staton number in the absence of blowing
D	=	Diffusion coefficient
D_{12}	=	Binary diffusion coefficient
d	=	Diameter
E	=	Activation energy
g	=	$32.174 \text{ ft}/\text{sec}^2$
h	=	Enthalpy
h^{298}	=	Heat of formation at $T = 298^\circ\text{K}$
k	=	Thermal conductivity
k_o	=	Reaction rate constant
Le	=	Lewis number
M	=	Mach number
$\dot{m}$	=	Material mass loss rate
$\dot{m}_R$	=	Mass loss rate in reaction region
$\dot{m}_s$	=	Mass loss rate in sublimation region
$\dot{m}_i$	=	Mass loss rate increment, see Eq. 44

n	=	Reaction order
P	=	Pressure
P_i	=	Partial pressure of i^{th} species, $i = O, N, CO, \text{etc.}$
P_r	=	Prandtl number
$\dot{q}_{cw}$	=	Cold wall heat flux
r	=	Cross sectional radius
R	=	Universal gas constant
R_N	=	Nose radius
R_g	=	Gas constant, air
R_e	=	Reynolds number
T	=	Temperature
u	=	Velocity parallel to surface
u_o	=	Free stream velocity
v	=	Velocity normal to surface
V	=	Diffusion velocity
X	=	Mole fraction
x	=	Distance along body surface
y	=	Distance normal to surface
Z	=	Altitude
α	=	Elemental mass fraction
β	=	Ballistic coefficient ($W/C_D A$)
γ	=	Ratio of specific heats
μ	=	Viscosity, absolute

ρ = Density
 ω = Species production rate
 m = Molecular weight
 $\sim$ = Approximately

Subscripts

D = Diffusion region
e = Edge of boundary layer
g = Gaseous phase
i = Chemical species
j = Chemical elements
s = Stagnation point, solid phase
t = Total conditions
W = Wall

Table I Pyrolytic Graphite Test Conditions for Data in Fig. 4

<u>Symbol</u>	<u>Ref.</u>	<u>Gas</u>	<u>P (ATM)</u>	<u>$\Delta T, ^\circ K$</u>	<u>u, FPS</u>	<u>ρ g/cc</u>	<u>Heating^a</u>	<u>Specimen</u>
+	31	Air	1	950-1030	0	2.20	F	0.37 x 0.37 x 0.13"
□	30	Air	1	1035-1255	0.8	2.20	F	0.37 x 0.37 x 0.13"
□	30	Air	1	1035-1255	1.6	2.20	F	0.37 x 0.37 x 0.13"
□	30	Air	1	1035-1255	2.5	2.20	F	0.37 x 0.37 x 0.13"
□	30	Air	1	1035-1255	3.3	2.20	F	0.37 x 0.37 x 0.13"
△	26	Air, O ₂	1	890-1840	0.5-1.0	2.15	F	Discs, d = 2 cm, t = 0.5 → 2mm
○	27	O ₂	.23	1275-2275	230	2.19	E	Rod, 4mm x 2mm
○	27	O ₂	.20	1275-2275	36	2.19	E	Rod, 4mm x 2mm
D	28	O ₂	.21	1275-2675	230	2.19	E	Rod, 4mm x 2mm
◇	28	O ₂	.21	1275-2675	> 82	2.20	E	Rod, 4mm x 2mm
Shaded region	29	Air	1	1475-2555	?	?	?	?

^aE = electrically heated specimen; used a jet of unheated O₂ impinging normal to the rod axis.
F = furnace.

FIG. 1. AEROTHERMODYNAMIC ENVIRONMENT FOR A SUPERSONIC AND AN ORBITAL DECAY TRAJECTORY. $R = 28 \text{ LB/FT}^2$ AT $Z = 400 \text{ KFT.}$, $R_N = 0.5 \text{ FT.}$

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FIG. 2. COMPARISON OF TRANSITION REGION MASS LOSS SOLUTIONS, $R_N = 0.5$ INCHES.

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FIG. 3 - COMPARISON OF SUBLIMATION MASS LOSS SOLUTIONS. $P = 1 \text{ ATM.}$

FIG. 4. EXPERIMENTAL OXIDATION RATES FOR PYROLYTIC GRAPHITE

FIG. 5. PYROLYTIC GRAPHITE TRANSITION REGION MASS LOSS RATES.

FIG. 6. EXPERIMENTAL ABLATION RATES. GOLOVINA AND KHAUSTOVICH³² AND WELSH AND CHUNG¹³.

FIG.7. EXPERIMENTAL ABLATION RATES - METZGER, ENGEL AND DICICCI¹¹

FIG.8. EXPERIMENTAL ABLATION RATES. MILLER AND SUTTON³⁶

FIG. 9 . EXPERIMENTAL ABLATION RATES. MAP 37

FIG. 10 EXPERIMENTAL SUBLIMATION RATES, LUNDELL AND DICKEY²⁴ JANAF CURVES FOR $P = 1$ ATM

FIG. 11. INCREMENTAL MASS LOSS RATE ($\dot{m}_i$) ABOVE JANAF (69) RATES.

FIG. 12. COMPARISON OF MAARS³⁷ AND MILLER AND SUTTON³⁶ TEST DATA.

Fig. 13 Comparison of theoretical models and experimental data for axisymmetric bodies.