# 605199

TECHNICAL INFORMATION SERIES



R64SD55

# THE SUBLIMATION OF GRAPHITE AT

HYPERSONIC SPEEDS DDC

S.M. SCALA L.M. GILBERT

> SPACE SCIENCES LABORATORY

GENERAL 🐲 ELECTRIC

MISSILE AND SPACE DIVISION

# SPACE SCIENCES LABORATORY

**AEROPHYSICS SECTION** 

# THE SUBLIMATION OF GRAPHITE AT HYPERSONIC SPEEDS

By

T

1

S. M. Scala

L. M. Gilbert

Work sponsored by the USAF Ballistic Systems Division, under Contracts No. 04(647)-269 and AF 04(694)-222.

R64SD55

-----

August 1964

MISSILE AND SPACE DIVISION



TABLE OF CONTENTS		
	LIST OF FIGURES	ii
	LIST OF SYMBOLS	i <b>v</b> i
1.	SUMMARY	1
2.	INTRODUCTION	1
3.	CONSERVATION LAWS	8
4.	TRANSPORT AND THERMODYNAMIC PROPERTIES	11
5.	CHEMICAL CONSTRAINTS	13
6.	BOUNDARY CONDITIONS	19
7.	DISCUSSION OF RESULTS	23
8.	CONCLUSIONS	39
9.	ACKNOWLEDGEMENTS	40
10.	REFERENCES	41
	TABLES	
I.	Gas Constants	44
II.	Comparison of "Constant" Property and Variable Property Solutions for Graphite Sublimation	45
III.	Equilibrium Constants	46
	FIGURES	
	i	

•

### LIST OF FIGURES

- 1. Mass Transfer Regimes For Ablating Graphite
- 2. Partial Pressure of Vaporized Species for Graphite Sublimation
- 3. Coordinate System
- 4. Viscosity Coefficients
- 5. Self Diffusion Coefficients
- 6. Binary Diffusion Coefficients, Lennard-Jones Potential
- 7. Specific Heat vs. Temperature
- 8. Enthalpy of Pure Species for Graphite Ablation
- 9. Chemical Composition at a Graphite Surface
- 10. Variation of the Elemental Mass Fractions with Surface Temperature and Pressure
- 11. Concentration Profiles ( $T_{uv} = 6500^{\circ} R$ )
- 12. Chemical Source Terms ( $T_{u} = 6500^{\circ} R$ )
- 13. Concentration Profiles ( $T_{ur} = 7500^{\circ}$ R)
- 14. Chemical Source Terms ( $T_{uv} = 7500^{\circ}R$ )
- 15. Temperature and Velocity Profiles
- 16. Normalized Graphite Sublimation Rate
- 17. Normalized Hypersonic Ablation Rate of Graphite over the Entire Range of Surface Temperature
- 18. Typical Multicomponent Lewis Numbers at the Surface of Subliming Graphite
- 19. Heat Transfer Correlation for Graphite Sublimation
- 20. Slope of Reduction in Heat Transfer Rate in Sublimation Regime

# LIST OF FIGURES (Continued)

- 21. Prandtl Number of the Gas Mixture at the Surface of Subliming Graphite
- 22. Skin Friction Correlation for Graphite Sublimation
- 23. Comparison of Temperature and Velocity Profiles

•

# SYMBOLS

Α	Angstroms
B <sub>i</sub>	referred mole fraction of species i, $X_i / \overline{\mathcal{M}}_i$
c <sub>i</sub>	mass fraction of species i
C <sub>₹</sub>	effective mass fraction of the k <sup>th</sup> chemical element
°°°	specific heat of the i <sup>th</sup> species at constant pressure
ē,	frozen specific heat of mixture
e ij	binary diffusion coefficient
D <sub>ij</sub>	multicomponent diffusion coefficient
E	activation energy
f	dimensionless stream function
F	external force
н	stagnation enthalpy
h <sub>i</sub>	static enthalpy of the i <sup>th</sup> species, including chemical
h	static enthalpy of the mixture = $\sum_{i} C_{i}h_{i}$
$\Delta h_{f_i}^{o}$	enthalpy of formation of the i <sup>th</sup> species
j	diffusion flux vector, defined in eq. (35)
k	Boltzmann's constant
к	frozen thermal conductivity of the mixture
ĸ	effective collision frequency
ĸ	equilibrium constant
m	molecular weight of species i
M	mass of species i

ρ

σ

# SYMBOLS (Continued)

m	mean molecular weight of the gas mixture
• m i	mass flux of species i
Р	static gas pressure
Q	heat transfer, collision cross section
R	universal gas constant
R B	body radius
t	time
Т	temperature
u,v	velocity components
<u>v</u>	macroscopic gas velocity
v ⊣i	absolute velocity of species i
V <sub>∞</sub>	flight speed
• w <sub>i</sub>	chemical source term, net mass rate of production of species i per unit volume by chemical reaction
X <sub>i</sub>	mole fraction of species i
x, y, r	coordinate system
β	pressure gradient parameter
η, ξ	similarity variables
$\theta = \frac{T}{T_e}$	dimensionless temperature
$\mu_{i}$	viscosity of the i species
₹	pressure tensor
ρ	density
σ	collision diameter

.

# SYMBOLS (Continued)

**n**<sup>\*</sup> reduced collision integral

# Subscripts

The UN THE

D	diffusion controlled oxidation regime
e	edge of viscous layer
g	gas
i	i species
Min.	minimum
Mix.	mixture
8	stagnation region, condensed phase, sublimation regime
R	reaction rate controlled regime
w	wall, surface of vehicle
η	denotes differentiation with respect to $\eta$

ANALLIA DI CAMENDA

Dimensionless Groups

$$C_{H} = \frac{Q_{w}}{\rho_{e} u_{e} (H_{e} - h_{w})}$$
, Stanton number

$$C_{f} = \frac{\frac{w}{w}}{\frac{1}{2}\rho_{e}u_{e}^{2}} \text{ skin friction coefficient}$$

$$\ell = \frac{\rho\mu}{\rho_w \mu_w}$$

$$L_{ij} = \frac{p C D}{K}, \text{ multicomponent Lewis number}$$

vi

Nu = 
$$\frac{Q_w C_p x}{K_w (H_e - h_w)}$$
, Nusselt number

$$Pr = \frac{\mu \overline{C}}{K}, Prandtl number$$

$$Re_{s} = \frac{\rho_{\infty} V_{\infty} R_{B}}{\mu_{e}}, \text{ shock Reynolds number}$$

$$\operatorname{Re}_{W} = \frac{\rho_{W}^{u} e^{X}}{\mu_{W}}, \text{ wall Reynolds number}$$

•

- -

### 1. SUMMARY

In this paper, a new theoretical model is presented for the sublimation of graphite at hypersonic flight speeds. The aerothermochemical interactions between dissociated air and graphite are treated by means of a nine component model, including O,  $O_2$ , N,  $N_2$ , CO,  $CO_2$ , C,  $C_3$  and CN. The mass transfer rate, the heat transfer rate, and the skin friction coefficient are determined numerically and are then correlated by means of algebraic equations, as a function of stagnation pressure, stagnation enthalpy and wall temperature in the high Reynolds number laminar flow regime.

### 2. INTRODUCTION

An understanding of the thermophysical characteristics of refractory materials is necessary for the successful design of advanced aerospace vehicles. The outer skin of these vehicles must function under conditions of extreme thermal loading, which, in turn, results in extremely high local surface temperatures. This requirement leads directly to the consideration of a family of refractory structural materials known as graphite.

In a sequence of earlier theoretical studies, the combustion of graphite was treated in the diffusion controlled regime (Refs. 1-3) and in the rate controlled and transition regimes (Ref. 3). These results were utilized in considering the ablation response of a graphite heat shield for a ballistic re-entry satellite (Refs. 2, 4) and the transient thermochemical response of a pyrolytic graphite leading edge for the control surface of a hypersonic lifting re-entry vehicle, (Refs. 5, 6).

As discussed in Refs. 2 and 3, chemical reactions between a number of chemically reacting gases (i.e. air, oxygen, carbon dioxide, nitrogen) and either carbon, coal or graphite have been studied extensively for over one hundred years. Much attention has been given to three mass loss regimes, including the reaction rate controlled, transition, and diffusion controlled oxidation regimes (see Figure 1). The oxidation rate of carbonaceous materials in each of these regimes is dependent to a different extent " on the surface temperature, the pressure, enthalpy and chemical reactivity of the gaseous boundary layer, the flow geometry and the chemical reactivity of the particular type of material considered.

At the lowest surface temperatures,  $(T_w \sim 1500^{\circ} R)$ , the reaction of carbon with oxygen results in the formation of both carbon monoxide and carbon dioxide at active sites in the surface lattice. The number of such active sites is a strong function of surface temperature, while the coverage of these sites by free stream oxygen depends on the local ambient pressure and the gas particle temperature. At first, the chemical reactions will occur directly between the lattice and the adsorbed oxygen monolayer, and hence the ambient pressure may have little influence on the monolayerlattice chemistry, at least, until the monolayer itself is affected by the wall temperature. It should be noted that there is also a possibility of interaction between the microstructure of the carbonaceous material (such as pores), and the adsorbed monolayer which could alter the apparent order of the chemical reaction. However, in the absence of pores, the mass loss should be zeroth order initially, since the monolayer is not depleted rapidly by the active sites. 2

At a somewhat higher surface temperature, the number of active sites begins to increase exponentially, and in addition, new intermediate chemical complexes may be formed, e.g.,  $CO_2^*$ ,  $CO^*$ . If the mass loss in the reaction rate controlled regime were dependent only on the arrival of oxygenor oxygen-bearing species and the coverage of the active sites in the lattice, one would expect the overall order of the reaction to be first order in the pressure. However, experimental data have been reported for this regime covering a range of reaction orders from zero to one, (Refs. 7,8) and, in some cases, one-half has been recommended, (Refs. 9, 10).

It has also been observed (Ref. 11) that as the surface temperature rises, the ratio of the mass fraction of carbon monoxide to that of carbon dioxide at the surface, increases exponentially, which may be explained in terms of a heterogeneous chemical reaction between  $CO_2$  and C(s) to form CO. Here, it is noted that the formation of CO at the surface could follow a complex sequence of steps including adsorption, dissociation, formation of one or more chemical complexes, and desorption of two CO molecules.

As the surface temperature rises still further ( $T_w \sim 2000^\circ R$ ), there is a transition from the reaction rate to the diffusion controlled oxidation regime. In this transition regime, the rate of mass loss is controlled by both fluid dynamic and chemical kinetic rate processes, (Refs. 3, 12, 13). For a range of surface temperatures, approximately between 2500°R and  $5000^\circ R$ , the rate of the overall mass loss is dominated by the slowest step, which is the counterdiffusion process in the multicomponent boundary layer.

In Ref. 3, a detailed analysis was presented for the oxidation of graphite in a high velocity stream of dissociated air, in which a six component model of chemically reacting species was utilized, including dissociated  $air(O, O_2, N and N_2)$  and the volatile combustion products CO and CO<sub>2</sub>. The effects of different free stream conditions and surface temperatures, and geometry, were included, and the resulting heat transfer rate, (including conduction, convection, diffusion, and combustion), the mass transfer rate and the skin friction at the surface were all determined, and empirical correlation formulas were given.

In this present study, we are concerned with even higher surface temperatures ( $T_w \ge 5000^{\circ}$ R), i.e., the sublimation regime. We will define the sublimation regime as the range of conditions where the mass loss due to vaporization exceeds the diffusion controlled oxidation mass loss rate. It is noted that at the high surface temperatures to be treated here, i.e.,  $5000^{\circ}$ R <  $T_w < 10,000^{\circ}$ R, not only do chemical reactions occur between carbon and oxygen, but also, nitrogen reacts with carbon to form cyanogen(CN)<sub>2</sub> and the cyano radical CN. We must therefore be concerned with both the homogeneous and heterogeneous chemical reactions involving the nitrogen which is present in the boundary layer. As the surface temperature rises, the vaporization rate of atomic and molecular carbon species, such as C,  $C_2$ ,  $C_3$ ,  $C_4$  and  $C_5$ , all increase exponentially. Upon examination of the thermodynamic properties and the vaporization rate data (Figure 2), of Vidale (Ref. 14), the authors have selected a nine component gas model to represent the aerothermochemical interactions, i.e., O,  $O_2$ , N,  $N_2$ , CO,  $CO_2$ , C, C<sub>3</sub> and CN.

It is always a difficult matter to decide on the total number of species to be included in a theoretical model for a multicomponent chemically reacting gas, since one is faced with the following dilemma, If one simply includes all possible species, the problem becomes unwieldy since the bookkeeping can easily exceed the storage capacity of even the largest present-day digital computer. On the other hand, if too few species are included, the model is poorly chosen and the final numerical results may not be representative of physical reality. Our approach therefore has been to include all of the dominant species and a few of the trace species. By dominant, it is meant, all those species which contribute five percent or more to the total gas enthalpy at a point in the stream; the trace species each contribute between one and five percent. It is doubtful that, in the absence of radiative transport, one need include species whose individual contribution to the total enthalpy is less than one percent, unless the total contribution of such species exceeds one percent. The presence of the species NO,  $(CN)_2$  and  $C_2$  has therefore been neglected, since it was found that their contribution was usually something less than that of a trace species, as defined above.

The fluid dynamic treatment was within the hypersonic boundary layer approximation for a multicomponent gas, and hence, it is noted that for each value of the stagnation pressure, there is a critical value of the surface temperature beyond which the present model would become invalid. That is, as the surface temperature rises, the sum of the partial pressures of the vaporizing species will exceed the stagnation pressure, and there will

then be a significant pressure gradient normal to the surface. However, since the boundary layer approximation requires that  $\frac{\partial P}{\partial y} = 0$ , boundary layer theory would then become less representative of reality in treating sublimation effects above this critical temperature (see Figure 1).

It is noted that an earlier solution to the problem of the sublimation of graphite at hypersonic speeds was obtained by Denison and Dooley (Ref. 15), who utilized the constant property boundary layer equations for a flat plate, and the Emmons and Leigh (Ref. 16) correlation between skin friction and mass transfer on a flat plate, to obtain numerical results. However, since they restricted their chemical model to include only six species (i.e. the presence of  $CO_2$ ,  $C_3$  and CN was neglected), and since a large number of assumptions was introduced in Ref. 15 in order to reduce the general equations to the constant property, flat plate form, thereby avoiding new digital computations, their final numerical results differ appreciably from ours.

In a treatment of sublimation into a boundary layer, it is important to note that the overall mass loss may be either an "equilibrium" process or a non-equilibrium process (Ref. 17). In general, one may always observe that a net mass loss occurs because the individual products of vaporization are condensing and vaporizing at unequal rates. If these forward and backward rates were equal, clearly, no mass loss due to sublimation could occur.

Associated with each vaporizing species is a vaporization coefficient which is a measure of the rate of forward vaporization of that species (Ref. 17). However, the vaporization coefficient alone does not determine whether the overall process will be diffusion controlled equilibrium vaporization, or

a non-equilibrium process which depends on the coupling between the forward rate of vaporization and the aerodynamic processes in the boundary layer.

In the case of "equilibrium vaporization", the net mass loss, due to diffusion and convection is very small compared to the forward rate of vaporization. Thus, the condensation rate and the vaporization rate are nearly equal. Hence, the sum of the partial pressures, within a mean free path from the surface, is nearly equal to the equilibrium vapor pressure and the overall process can be considered to be equilibrium diffusion controlled sublimation.

On the other hand, if the vaporization coefficient is very small, (Ref. 17) then any finite net mass loss by diffusion and convection in the boundary layer, results in a reduction in the individual partial pressures of the vaporizing species below their equilibrium vapor pressure values. In this case, the net mass loss cannot be determined from a knowledge of the equilibrium vapor pressures alone, since the driving force for diffusion and convection is now the non-equilibrium partial pressure of the vaporizing species. In this case, one must determine the partial pressures of the vaporizing species by utilizing compatibility constraints due to gas kinetic microscopic and fluid mechanic macroscopic considerations, (Ref. 18).

# 3. CONSERVATION LAWS

The non-linear partial differential equations of change for a multicomponent chemically reacting gas are derived, for example, in Reference 19 and include the conservation of mass, chemical species, momentum and energy as shown below:

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \underline{v}) = 0 \tag{1}$$

$$\frac{\partial \rho_i}{\partial t} + \nabla \cdot (\rho_i \underline{v}_i) = \dot{w}_i$$
(2)

$$\rho \frac{dv}{dt} = \nabla \cdot \pi + \sum_{i} \rho_{i} F_{i}$$
(3)

$$\rho \frac{\mathrm{d}\mathbf{e}}{\mathrm{d}\mathbf{t}} = -\nabla \cdot \mathbf{Q} + \pi : \nabla \mathbf{y} + \sum_{\mathbf{i}} \rho_{\mathbf{i}} \mathbf{y}_{\mathbf{i}} \cdot \mathbf{F}_{\mathbf{i}}$$
(4)

Upon introducing the boundary layer approximations for a bodyoriented coordinate system (see Fig. 3), the conservation of mass becomes (Ref. 20)

$$\frac{\partial}{\partial \mathbf{x}} (\rho \mathbf{r} \mathbf{u}) + \frac{\partial}{\partial \mathbf{y}} (\rho \mathbf{r} \mathbf{v}) = 0$$
 (5)

The conservation equation for species i becomes (neglecting thermal diffusion and other higher order effects):

$$\rho \mathcal{M}_{i} \left( u \frac{\partial B_{i}}{\partial x} + v \frac{\partial B_{i}}{\partial y} \right) + \frac{\partial}{\partial y} \left[ \sum_{j \neq i}^{\Sigma} \frac{\mathcal{M}_{i} \mathcal{M}_{j}}{\overline{\mathcal{M}}_{i}^{2}} \rho D_{ij} \frac{\partial X_{j}}{\partial y} \right] = \dot{w}_{i}$$
(6)

where

$$B_i = X_i / \overline{M}$$

The stream wise component of momentum yields:

$$\rho u \quad \frac{\partial u}{\partial x} + \rho v \frac{\partial u}{\partial x} = - \frac{\partial P}{\partial x} + \frac{\partial}{\partial y} \left( \mu \frac{\partial u}{\partial y} \right)$$
(7)

In the high Reynolds number regime, for moderately high mass transfer rates we may write that the normal component of momentum yields:

$$\frac{\partial \mathbf{P}}{\partial \mathbf{y}} = \mathbf{0} \tag{8}$$

In this study, criteria are developed for determining the conditions when eq. (8) no longer applies, (see fig. 1)

The energy equation becomes

$$\rho \overline{C}_{p} \left( u \frac{\partial T}{\partial x} + v \frac{\partial T}{\partial y} \right) = u \frac{\partial P}{\partial x} + \mu \left( \frac{\partial u}{\partial y} \right)^{2},$$

$$+ \frac{\partial}{\partial y} \left( K \frac{\partial T}{\partial y} \right) - \sum_{i} C_{p_{i}} \frac{\partial T}{\partial y} \sum_{j \neq i} \frac{\mathcal{M}_{i} \mathcal{M}_{j}}{\mathcal{T}_{i} 2} \rho D_{ij} \frac{\partial X_{j}}{\partial y} - \sum_{i} \dot{w}_{i} \dot{h}_{i} \qquad (9)$$

It is convenient to introduce the Mangler-Dorodnitsyn transformation (Ref. 21) in solving these laminar boundary layer equations:

$$\eta = \frac{\rho_e^{\ u}_e}{\sqrt{2\xi}} \int_0^y r \frac{\rho}{\rho_e} dy$$
(10)

$$\xi = \int_{0}^{x} \rho_{w} \mu_{w} u_{e} r^{2} dx \qquad (11)$$

and assuming that local similarity holds, then equations 5 through 9 may be reduced to a set of ordinary non-linear differential equations. The diffusion equation for the i<sup>th</sup> chemical species becomes:

$$\left[\frac{\ell}{\Pr}\sum_{j\neq i}\frac{\mathcal{M}_{i}\mathcal{M}_{j}}{\mathcal{T}_{i}^{\prime}}L_{ij}X_{j\eta}\right]_{\eta} - f\mathcal{M}_{i}B_{i\eta} = \frac{\beta}{\left(\frac{du}{dx}\right)}\frac{\dot{J}_{i}}{\rho}$$
(12)

where  $\beta = 2 d \ln u_e / d \ln \xi$ .

The conservation of momentum becomes:

$$(\ell f_{\eta\eta})_{\eta} + f f_{\eta\eta} + \beta \left[ \frac{\rho_e}{\rho} - f_{\eta}^2 \right] = 0$$
(13)

----

4

The energy equation becomes:

ľ

$$\left(\frac{\overline{C}}{Pr} \, \theta_{\eta}\right)_{\eta} + \overline{C}_{p} f \theta_{\eta} - \sum_{i} \frac{C_{p_{i}} \ell}{Pr} \, \theta_{\eta} \sum_{j \neq i} \frac{\mathcal{M}_{i} \mathcal{M}_{j}}{\mathcal{M}^{2}} L_{ij} X_{j\eta} + \frac{u^{2}}{r_{e}} \left[\ell \left(f_{\eta\eta}\right)^{2} + \beta f_{\eta} \left(\theta - \frac{\rho_{e}}{\rho}\right)\right] = \frac{\beta}{\frac{du}{dx}} \frac{\sum_{i} w_{i}h_{i}}{\rho T_{e}}$$
(14)

## 4. TRANSPORT AND THERMODYNAMIC PROPERTIES

Appearing in equations 12, 13, and 14 are the variable coefficients which represent the thermodynamic properties and transport coefficients of the gas mixture required for the definition of the physical problem. These include the normalized density and viscosity product  $(\ell)$ , the Prandtl number (Pr), the multicomponent Lewis numbers  $(L_{ij})$ , the frozen specific heat of the gas mixture  $(\overline{C}_p)$ , and the enthalpies  $(h_i)$  of the chemical species. In order to determine the bulk properties of the gas (i.e.  $\ell$ , Pr,  $L_{ij}$ ,  $\overline{C}_p$ ,  $K_{mix.}$ ,  $\mu_{mix.}$ , ...), one must first have a knowledge of the specific heat, the enthalpy, the viscosity coefficient, and the self diffusion coefficient for each of the n pure species present in the boundary layer. In addition,  $\frac{n^2-n}{2}$ symmetric binary diffusion coefficients are required to represent the transport interactions between unlike pairs of particles. The details concerning the calculation of the transport and thermodynamic properties of the pure species and also the bulk properties of a multicomponent, chemically reacting gas mixture are given in reference 19.

Some of the properties utilized in this sublimation study, particularly for low surface temperatures, have been given in reference 3. The species treated heretofore were O,  $O_2$ , N,  $N_2$ , CO and  $CO_2$ . The properties of the additional species included in this new study (i.e. C,  $C_3$  and CN), and also the new resulting binary interactions are shown in figures 4 through 8. The gas constants used for these calculations are assembled in Table I.

In general, an exact and rigorous numerical solution of the set of differential equations given above necessitates the evaluation of the transport

and thermodynamic properties of the gas mixture as a function of the local gas temperature and gas composition. Of course, great numerical simplifications result if one assumes values for the Prandtl and Lewis numbers which remain constant throughout the viscous layer. The usefulness of the results obtained by such approximations depend in part upon the specific application and in part on the rationale invoked for the evaluation of these constants.

We have made a comparison of a "constant" property solution with a variable property solution as applied to the graphite sublimation problem and the results are shown in Table II. In the numerical integration of the boundary layer equations for the "constant" property solution, the Prandtl number of the mixture and the multicomponent Lewis numbers were evaluated . at the surface conditions. However, the viscosity of the mixture and all thermodynamic coefficients were evaluated locally throughout the viscous layer for both cases.

The agreement between "constant" (as defined herein) property solutions and variable property solutions in the past (refs. 3, 22) has always been well-within the uncertanties existing in the high temperature transport properties themselves. The remarkable agreement shown in table II is probably due to the fact that the reduced temperature difference across the boundary layer peculiar to the high surface temperature graphite sublimation problem tends to smooth out the substantial gradients in the properties that otherwise would exist for lower surface temperature applications.

### 5. CHEMICAL CONSTRAINTS

It has been assumed that the total number of dominant chemical species present in the gas phase is nine, including atomic and molecular oxygen and atomic and molecular nitrogen and the ablation products, carbon dioxide, carbon monoxide, the cyano radical, and atomic and triatomic gaseous carbon. Thus, there are nine unknown chemical source terms  $\dot{w}_i$  and nine unknown concentrations  $X_i$  at each point within the boundary layer. At the surface, there are nine unknown concentrations which must satisfy the chemical constraints imposed by the heterogeneous kinetics of the gas-solid interactions and also must be a patible with the gas phase diffusion processes. At the outer edge of the boundary layer, the temperature, pressure, enthalpy, etc. are given by a solution of the normal shock equations followed by an isentropic compression calculation along the stagnation streamline (see Ref. 23). The chemical composition at the outer edge of the viscous layer is, of course, available as a result of these computations.

Let us first consider the chemical constraints in the gas phase. The conservation of chemical species in the gas phase requires that the overall mass rate of formation of the chemical species must be zero. This means that the masses of the individual chemical elements must be conserved. Since we are dealing with a gas system composed of three chemical elements (i.e., oxygen - nitrogen - carbon) we may write

$$\dot{\mathbf{w}} = 0 ; \dot{\mathbf{w}} = 0 ; \dot{\mathbf{w}} = 0$$

$$O \quad \widetilde{N} \quad \widetilde{C}$$
(15)

where

$$\dot{w}_{\tilde{O}} = \dot{w}_{O} + \dot{w}_{O_{2}} + \frac{\dot{m}_{O}}{\dot{m}_{CO}} \dot{w}_{CO} + \frac{\dot{m}_{O_{2}}}{\dot{m}_{CO_{2}}} \dot{w}_{CO_{2}}$$
 (16)

$$\dot{\mathbf{w}}_{\widetilde{\mathbf{N}}} = \dot{\mathbf{w}}_{\mathbf{N}} + \dot{\mathbf{w}}_{\mathbf{N}_{2}} + \frac{\dot{\mathbf{N}}_{\mathbf{N}_{1}}}{\dot{\mathbf{M}}_{\mathbf{CN}}} \dot{\mathbf{w}}_{\mathbf{CN}}$$
(17)

$$\mathbf{\tilde{w}}_{c} = \mathbf{\tilde{w}}_{c} + \mathbf{\tilde{w}}_{c_{3}} + \frac{\mathbf{\tilde{m}}_{c}}{\mathbf{\tilde{m}}_{CO}} \mathbf{\tilde{w}}_{CO} + \frac{\mathbf{\tilde{m}}_{c}}{\mathbf{\tilde{m}}_{CO_{2}}} \mathbf{\tilde{w}}_{CO_{2}} + \frac{\mathbf{\tilde{m}}_{c}}{\mathbf{\tilde{m}}_{CN}} \mathbf{\tilde{w}}_{CN}$$
(18)

The expression for the overall conservation of mass is obtained by adding eqs. 16, 17 and 18.

$$\sum_{i} \dot{w}_{i} = 0 \tag{19}$$

To complete the analysis of the gas phase chemistry, it is noted that in addition to eqs. 16, 17, and 18, six relationships are still needed which specify the rates of the chemical reactions. For the assumption of local thermochemical equilibrium, one has the necessary information from the six equilibrium functions for the corresponding chemical reactions given below, (see table III):

$$O_2 \neq 2O;$$
  $K_{P_0} = \frac{(X_0)^{P_0}}{X_{O_2}}$  (20)

.-. .2\_

$$N_2 = 2N;$$
  $K_{P_N} = \frac{(X_N)^P}{X_{N_2}}$  (21)

 $CO+O = CO_2;$   $K_{P_{CO_2}} = \frac{X_{CO_2}}{X_{O}X_{CO}P}$  (22)

C +O = CO; 
$$K_{P_{CO}} = \frac{X_{CO}}{X_{C}X_{O}P}$$
 (23)

C+N = CN; 
$$K_{P_{CN}} = \frac{X_{CN}}{X_{C}X_{N}P}$$
 (24)

$$3C \neq C_3;$$
  $K_{PC_3} = \frac{X_{C_3}}{(X_C)^3 P^2}$  (25)

Now let us turn our attention to the chemical interactions at the gassolid interface. We consider the situation for which the surface mass transfer is caused by chemical rearrangement (combustion) of both the oxygen and nitrogen bearing species in the gas stream with the carbon surface and by sublimation of the solid carbon to form monatomic and triatomic gaseous carbon. We note that, when the gas at the surface is in thermochemical equilibrium with the condensed phase, the six equilibrium functions presented above (equations 20 through 25) may be used. In order to completely define the system, three additional relationships are required. One of these will be an equilibrium function, applicable only at the surface, which when used with the previously defined equilibrium relationships (i.e., eqs. 20 - 25), will specify the rate at which the element carbon is leaving the graphite surface. Another condition is obtained from Dalton's law of partial pressures, and for the final relationship, we make use of the fact that, physically, the surface is impermeable to the mass fluxes of the elements oxygen and nitrogen.

The chemical reaction and the corresponding equilibrium function which applies only at the wall is

$$C(s) \neq C(g); \quad K_{P_{C}} = X_{C}^{P}$$
 (26)

Equation 26, when used in combination with equations 20 through 25, allows one to determine all the possible gas-surface interactions for this system.

From Dalton's law we obtain

$$\sum_{i} X_{i} = 1$$
(27)

For the final condition, which results in a mass flux compatibility constraint, we make use of the following impermeability conditions.

$$\dot{\mathbf{m}} = 0 ; \quad \dot{\mathbf{m}} = 0 \widetilde{\mathbf{N}}_{\mathbf{w}} \qquad \widetilde{\mathbf{O}}_{\mathbf{w}}$$
(28)

where

$$\hat{\mathbf{m}}_{\mathbf{N}_{\mathbf{W}}} = \left( \hat{\mathbf{m}}_{\mathbf{N}} + \hat{\mathbf{m}}_{\mathbf{N}_{2}} + \frac{\mathcal{M}_{\mathbf{N}} \hat{\mathbf{m}}_{\mathbf{CN}}}{\mathcal{M}_{\mathbf{CN}}} \right)_{\mathbf{W}}$$
(29)

and

$$\dot{\mathbf{m}}_{\tilde{O}_{\mathbf{w}}} = \left( \dot{\mathbf{m}}_{O} + \dot{\mathbf{m}}_{O_{2}} + \frac{\dot{\mathcal{m}}_{O}}{\mathcal{M}_{CO_{2}}} \dot{\mathbf{m}}_{CO_{2}} + \frac{\dot{\mathcal{m}}_{O_{2}}}{\mathcal{M}_{CO_{2}}} \dot{\mathbf{m}}_{CO_{2}} - \dot{\mathbf{m}}_{CO_{2}} \right)_{\mathbf{w}}$$
(30)

Using the fact that

$$\dot{\mathbf{m}}_{\mathbf{i}_{\mathbf{W}}} = \mathbf{C}_{\mathbf{i}_{\mathbf{W}}} \dot{\mathbf{m}}_{\mathbf{W}} + \mathbf{j}_{\mathbf{i}_{\mathbf{W}}}$$
(31)

one then obtains

• • --

· ·

$$\begin{bmatrix} \frac{m}{j_{N} + j_{N_{2}} + \frac{m}{m_{CN}} j_{CN}}}{\frac{m}{C_{N} + C_{N_{2}} + \frac{m}{m_{CN}} c_{CN}}} \end{bmatrix}_{W} = \begin{bmatrix} \frac{j_{0} + j_{0_{2}} + \frac{m_{0}}{2m_{CO}} j_{CO} + \frac{m_{0}}{2m_{CO}} j_{CO_{2}}}{\frac{m}{2m_{CO}} c_{O_{2}} - \frac{m_{0}}{2m_{CO_{2}}} c_{O_{2}}} \\ \frac{m_{0} - m_{0}}{m_{O_{2}} - \frac{m_{0}}{2m_{O_{2}}} c_{O_{2}}} \\ \frac{m_{0} - m_{O_{2}} - \frac{m_{O_{2}}}{2m_{O_{2}}} c_{O_{2}}}{\frac{m_{O_{2}} - \frac{m_{O_{2}}}{2m_{O_{2}}} c_{O_{2}}} \\ \frac{m_{0} - m_{O_{2}} - \frac{m_{O_{2}}}{2m_{O_{2}}} c_{O_{2}}} \\ \frac{m_{O_{2}} - \frac{m_{O_{2}}}{2m_{O_{2}}} c_{O_{2}}}{\frac{m_{O_{2}} - \frac{m_{O_{2}}}{2m_{O_{2}}} c_{O_{2}}} \\ \frac{m_{O_{2}} - \frac{m_{O_{2}} - \frac{m_{O_{2}}}{2m_{O_{2}}} c_{O_{2}}}{\frac{m_{O_{2}} - \frac{m_{O_{2}}}{2m_{O_{2}}} c_{O_{2}}} \\ \frac{m_{O_{2}} - \frac{m_{O_$$

which is the mass flux compatibility constraint.

The surface mass transfer is due to the mass flux of the element

carbon.

Contraction of the local division of the loc

$$\dot{\mathbf{m}}_{\mathbf{w}} = \dot{\mathbf{m}}_{\mathbf{C}_{\mathbf{w}}} = \left\{ \dot{\mathbf{m}}_{\mathbf{C}} + \dot{\mathbf{m}}_{\mathbf{C}_{3}} + \mathcal{M}_{\mathbf{C}} \left[ \frac{\dot{\mathbf{m}}_{\mathbf{CO}}}{\mathcal{M}_{\mathbf{CO}}} + \frac{\dot{\mathbf{m}}_{\mathbf{CO}_{2}}}{\mathcal{M}_{\mathbf{CO}_{2}}} + \frac{\dot{\mathbf{m}}_{\mathbf{CN}}}{\mathcal{M}_{\mathbf{CN}}} \right] \right\}_{\mathbf{w}}$$
(33)

which, by use of eq. 31, becomes,

$$\dot{\mathbf{m}}_{w} = \frac{\left\{ \mathbf{j}_{C} + \mathbf{j}_{C_{3}} + \mathcal{M}_{C} \left[ \frac{\mathbf{j}_{CO}}{\mathcal{M}_{CO}} + \frac{\mathbf{j}_{CN}}{\mathcal{M}_{CO_{2}}} + \frac{\mathbf{j}_{CN}}{\mathcal{M}_{CN}} \right] \right\}_{w}}{1 - \left\{ \mathbf{c}_{C} + \mathbf{c}_{C_{3}} + \mathcal{M}_{C} \left[ \frac{\mathbf{c}_{CO}}{\mathcal{M}_{CO}} + \frac{\mathbf{c}_{CO_{2}}}{\mathcal{M}_{CO_{2}}} + \frac{\mathbf{c}_{CN}}{\mathcal{M}_{CN}} \right] \right\}_{w}}$$
(34)

The multicomponent diffusion flux vector  $\mathbf{j}_{\mathbf{i}\mathbf{i}}$  utilized in this study is given as follows

$$\underline{j}_{i} = \rho_{i} \underbrace{V}_{i} = \frac{n_{t}^{2}}{\rho} \sum_{j \neq i} \widehat{\mathcal{M}}_{i} \underbrace{\mathcal{M}}_{j} D_{ij} \nabla X_{j}$$
(35)

Note that in the above equation the effects of thermal diffusion, pressure gradients, and body forces are neglected. For the special case of a binary gas mixture, equation (35) reduces to

$$\mathbf{j}_{i} = \frac{\mathbf{n}_{i}^{2}}{\rho} \mathcal{M}_{i} \mathcal{M}_{j} \mathbf{D}_{ij} \nabla \mathbf{X}_{j}$$
(36)

From which one may easily derive the relationship known as Fick's Law.

$$\underline{j}_{i} = -\rho \, \vartheta_{ij} \, \nabla C_{i} \tag{37}$$

In equations 35 and 36,  $n_t = \rho / \bar{m}$ .

Note that the multicomponent diffusion coefficient (D<sub>ij</sub>), (discussed in reference 19) must be used in equation (35), while equations (36) and (37) require the simpler binary diffusion coefficient given in reference 19. Even though equation (37) (i.e. Fick's Law) has been successfully applied (for special cases) in approximate solutions involving multicomponent gas mixtures (references 13, 15, 17, 18, 21), the rigorous expression for the diffusion flux (i.e. equation 35) is, of course, more desirable and is used in the present study.

# 6. BOUNDARY CONDITIONS

In general, the overall mathematical order of the high Reynolds number, thin boundary layer system is 2n + 3, where n is the number of chemical species in the gas mixture Five boundary conditions are applied to the energy and momentum equations. At the wall, one usually specifies the quantities  $\theta_{w}$ ,  $f_{\eta}$  and  $f_{w}$  as follows:

$$\theta_{w} = T_{w}/T_{e}$$
(38)

$$f_{\eta_w} = u_w / u_e = 0 \tag{39}$$

$$-f_{w} = m_{w} \left( \rho_{w} \mu_{w} - \frac{du}{dx} / \beta \right)^{-1/2}$$
(40)

and at the outer edge of the boundary layer, the temperature and velocity go to their asymptotic limits

$$\lim_{\eta \to \infty} \theta = \lim_{\eta \to \infty} f = 1.0$$
(41)

It is convenient, in the numerical solution of this boundary value problem to treat it as an initial value problem and to employ iterated integration until the outer edge boundary conditions are satisfied. Thus, in order to satisfy equations (41), we introduce the wall eigenvalues  $\theta$  and  $\eta_w$  $f_\eta \eta_w$ , the determination of which constitutes a solution of the energy and momentum equations.

The remaining 2(n-1) boundary conditions deal with the chemical species. Now, one must satisfy certain chemical mass balance relationships at the edge of the boundary layer and mass flux compatibility conditions at the gas-solid interface regardless of the thermochemical state of the gas mixture. For an n component gas mixture in which there are k chemical elements, 2 (k-1) of these chemical mass balance and mass flux relationships must be satisfied. This leaves 2 (n-k) relationships which must (of necessity) deal with the rates at which the chemical reactions are progressing.

If the chemical reaction times are much faster than the flow rate times, then a state of local thermochemical equilibrium exists in the gas phase. For this situation, the chemical equilibrium  $(K_p)$  functions and their derivatives satisfy these 2(n-k) relationships. In a sense, the "equilibrium" assumption reduces the overall mathematical order of the system from (2n + 3) to (2k + 3), where five boundary conditions are applied to the energy and momentum equations and the remaining 2 (k-1) boundary conditions deal with the remaining chemical mass balance and mass flux relationships. For the particular case which we treat here (i.e., equilibrium graphite sublimation), n = 9, k = 3 and the six  $K_p$  functions are given by equations 20 through 25.

Following the notation of references 21, 22 we define the mass fractions of the three chemical elements of the multicomponent gas mixture to be

$$C_{\widetilde{C}} = C_{C} + C_{C_{3}} + \mathcal{M}_{C} \left[ \frac{C_{CO}}{\mathcal{M}_{CO}} + \frac{C_{CN}}{\mathcal{M}_{CN}} + \frac{C_{CO_{2}}}{\mathcal{M}_{CO_{2}}} \right]$$
(42)

$$C_{\widetilde{O}} = C_{O} + C_{O_2} + M_{O} \left[ \frac{C_{CO}}{M_{CO}} + \frac{C_{OO_2}}{M_{CO_2}} \right]$$
(43)

$$C_{\widetilde{N}} = C_{N} + C_{N_{2}} + M_{N} \left[ \frac{C_{CN}}{M_{CN}} \right]$$
(44)

At the outer edge of the boundary layer, the concentrations of the carbon bearing species individually go to zero and the ratio of the masses of the elements oxygen to nitrogen takes on its free stream value.

$$C_{e} = 0 \text{ and } \left(\frac{\widetilde{O}}{C}_{\widetilde{N}}\right)_{e} = 0.3068$$
(45)

Now, within the viscous layer, where diffusion effects cannot be neglected, the lighter weight particles tend to diffuse faster than the heavier ones which results in preferential diffusion. Because of this, one may <u>not</u> insist that the ratio of the mases of the elements oxygen to nitrogen remain constant throughout the boundary layer. Instead, one makes use of the surface impermeability conditions (i.e. equations 28) which result in the surface mass flux compatability constraint given by equation (32).

Finally, at the surface, the rate at which the gaseous element carbon is produced from the solid phase is given by equation (26) used inconjunction with the other  $K_{D}$  functions.

Again it is convenient to replace the outer edge boundary conditions on C and (C /C) by initial values at  $\eta = 0$ , and hence we satisfy  $\widetilde{C}_{e}$   $\widetilde{O}$   $\widetilde{N}$   $\widetilde{N}$ 

equations 45 by introducing the eigenvalues  $(C_{\widetilde{O}}^{*}/C_{\widetilde{N}}^{*})_{w}$  and  $-f_{w}$ .

To summarize, the five boundary conditions at the wall for the equilibrium situation are given by equations (26), (32), (38), (39) and (40), and the four eigenvalues at the wall ( $\eta = 0$ ) are  $\theta_{\eta_w}$ ,  $f_{\eta\eta_w}$ ,  $-f_w$  and ( $\binom{C}{C}$ ). The  $\widetilde{C}$   $\widetilde{N}^w$  total number of boundary conditions and eigenvalues at the surface is therefore 2k + 3 = 9, which is the true mathematical order of the system for the "equilibrium" case. The study performed here is applicable to the stagnation regime of axisymmetric bodies. In subsequent work, the graphite ablation process will be investigated with respect to other configurations, in particular cones and wedges. Contraction of the second second

1

1

į t

12 **†** 

## 7. DISCUSSION OF RESULTS

The chemical composition at a graphite surface in a hypersonic air stream is shown in Figure 9 for a range of surface temperatures at a stagnation pressure of one atmosphere. Similar results are obtained at other pressures. Increasing the pressure causes a shift in the composition variation seen here to a higher temperature range, while lower pressures result in a displacement toward lower temperatures. These compositions were obtained by a simultaneous solution of equations (20) through (29) together with the eigenvalue  $(C_{X}/C_{X})$  as determined by the solution of the boundary layer equations subject to the surface compatibility constraint (i.e. eq. 32). The concentrations of the chemical species O, N,  $O_2$  and  $CO_2$  are found to be less than 10<sup>-4</sup> over the full range of surface temperatures at a pressure of one atmosphere. It is seen that nitrogen begins to react with the graphite surface at a surface temperature of approximately 5000°R, while the sublimation process does not become appreciable until temperatures increase beyond  $6000^{\circ}$  R. Note that, the sublimation process yields appreciably greater amounts of triatomic carbon gas than monatomic carbon. Note also that as the sublimation rate increases, the gas at the surface becomes saturated with the sublimation products driving away the oxygen and nitrogen bearing species. It is at this critical temperature and pressure that the sublimation process begins to induce pressure gradients in the gas normal to the gas-solid interface, (See Figure 1).

Figure 10 shows the variation of the effective mass fractions of the elements carbon and nitrogen (defined in equations 42 and 44) with surface

temperature for several given stagnation pressures. As seen in the previous figure, carbon monoxide is the only carbon bearing species present in significant quantity at the surface for the lower temperatures, i.e.  $3000 < T_w < 5000^{\circ}R$ . In this temperature range (i.e. the diffusion controlled oxidation regime)  $C_{ev} = 0.15$ . At higher surface temperatures, nitrogen  $C_w$  reacts with the carbon surface producing the cyano radical CN, sublimation of the solid graphite yields increasing amounts of atomic and triatomic gaseous carbon, and the effective mass fraction of the element carbon  $C_{ev}$ exponentially with surface temperature. The shift in  $C_{ev}$  with stagnation  $C_v$ 

The usefulness of the quantity C in reducing the numerical data  $\widetilde{C}$ and correlating the results will be demonstrated in the ensuing discussion. This physical quantity has the same variation with surface temperature and stagnation pressure as does the sublimation rate. Moreover, the driving force for the mass transfer rate in the diffusion controlled oxidation regime as well as in the diffusion controlled sublimation regime is found to be related to C . The quantitative relationship between C , the surface  $\widetilde{C}$ temperature, and the stagnation pressure has been found to be given by

$$C = 0.15 + 2.4 \times 10^{6} P_{e}^{-0.67} e^{-11.1 \times 10^{7}/T} w$$

$$\widetilde{C}_{w}$$
(46)

where  $P_e$  is in atmospheres, and  $T_w$  in  ${}^{o}R$ .

The ratio of the element nitrogen to the element carbon at the ablating graphite surface, seen in figure 10, decreases as the mass fraction of the

element carbon increases. At the temperature and pressure where this ratio becomes zero, the vaporizing species have driven the oxygen and nitrogen completely away from the surface. Beyond this point, the vapor pressure of the sublimation products exceeds the stagnation gas pressure, a pressure gradient is induced normal to the gas-solid interface, and conventional boundary layer theory is no longer valid.

Figures 11 through 14 show typical boundary layer concentration profiles and variations of the chemical source terms through the viscous layer for surface temperatures of  $6500^{\circ}$ R and  $7500^{\circ}$ R at a stagnation pressure of 5.7 atmospheres. In these figures, 7 is the non-dimensional distance normal to the gas-solid interface. A positive value of the chemical source term  $\dot{w}_i$  indicates that the chemical species is being produced, while a negative value denotes that it is being consumed as a result of the chemical reactions. It is noted that the scaling of the chemical source terms in the stagnation regime must go as  $R_B \dot{w}_i$  since in equations (12) and (14) the stagnation point velocity gradient is assumed to be Newtonian:

$$\frac{du_{e}}{dx} = \frac{1}{R_{B}} \sqrt{\frac{2(P_{e} - P_{\infty})}{\rho_{e}}}$$
(47)

An examination and interpertation of the concentration profiles and chemical source terms shown in figures 11 through 14 enables one to identify the various mass loss mechanisms peculiar to this high surface temperature regime. The surface temperatures quoted in the following discussion are associated with a stagnation pressure of 5.7 atmospheres. However, the shift in characteristic surface temperature with stagnation pressure is predictable via Figures 1, 9, and 10.

At a surface temperature of approximately 5000<sup>°</sup>R, the mass loss mechanism is still one of diffusion controlled oxidation, and the heterogeneous chemical reaction for this case is

$$CO_2 + C(s) \rightarrow 2CO, \quad \Delta Q = 34 \frac{K \text{ cal}}{\text{mole}} (T = 5000^{\circ} \text{R})$$
 (48)

The composition profiles and associated homogeneous combustion reactions for this mechanism are discussed in Ref. (3).

Now, at a surface temperature of approximately 5500<sup>°</sup>R, nitrogen begins to undergo heterogeneous reactions directly with the surface to form CN and one has, in addition to the oxidation reaction of eq. 48, the following

$$1/2 N_2 + C(s) \rightarrow CN, \ \Delta Q = 110 \frac{K cal}{mole} (T = 5500^{\circ}R)$$
 (49)

Also, for this surface temperature, one observes multiple flame zones in the gas phase resulting from the following homogeneous reactions.

$$\begin{array}{c} CN + 2O - CO_{2} + 1/2 N_{2}, \ \Delta Q = -326 \ \frac{K \ cal}{mole} \\ CO + O - CO_{2}, \ \Delta Q = -124 \ \frac{K \ cal}{mole} \end{array} \right\} (T = 5500^{\circ} \ (50)$$

Paul Marthan

At a slightly higher surface temperature ( $T_w \sim 6000^{\circ}$ R), one finds that the chemical reaction resulting in the formation of carbon monoxide has moved off from the surface and the heterogeneous reactions at this temperature are those given by equation (49) and the following vaporization reaction

$$3C(s) \sim C_3$$
,  $\Delta Q = 180 \frac{K cal}{mole}$  (T = 6000°R) (51)

Also, one finds that additional CN is being produced by the following homogeneous reaction in the first flame zone nearest the surface

$$2C_3 + 3N_2 - 6CN$$
,  $\Delta Q = 310 \frac{K \text{ cal}}{\text{mole}} (T = 6000^{\circ} \text{R})$  (52)

At this surface temperature, therefore, the formation of CN is due to both a heterogeneous and a homogeneous reaction and the diffusion flux of this species is positive (i.e. away from the surface).

In the second flame zone from the surface, the major chemical reaction results in the formation of carbon monoxide through the exchange reaction

$$CN + O - CO + 1/2 N_2$$
,  $\Delta Q = -203 \frac{K \text{ cal}}{\text{mole}} (T = 6000^{\circ} \text{R})$  (53)

and CO then diffuses back to the surface. In general, at surface temperatures greater than  $6000^{\circ}$ R (for equilibrium chemical reactions), the presence of carbon monoxide gas at the surface is entirely due to the formation of this species in the gas phase and its subsequent diffusion back to the condensed phase. In other words, the net mass flux of carbon monoxide at the surface is zero (i.e.  $\dot{m}_{CO_w} = 0$ ), since its diffusion flux ( $j_{CO_w}$ ) is essentially equal and opposite to its convective flux ( $C_{CO_w}$ , (see eq. 31).

When the surface temperature increases to approximately 6500°R, the chemical reaction which results in the formation of CN begins to move away from the surface and into the gas phase. At this point,  $\dot{m}_{CN_w} \approx 0$ since  $j_{CN_w} \approx -C_{CN_w} \dot{m}_{CN_w}$ , and the mass loss mechanism is therefore entirely that due to the vaporization reaction of equation (51). The concentration profiles for this surface temperature are shown in figure 11 and the zones of chemical interactions (i.e. flame zones) are shown by the chemical source term variations shown in figure 12. One notes that the chemical reaction in the first zone is endothermic as nitrogen is seen to react with
the gaseous carbon species to form CN. In the second flame zone, the following chemical reactions are occuring simultaneously.

$$CN + O - CO + 1/2 N_2 \cdot \Delta Q = -205 \frac{K \text{ cal}}{\text{mole}}$$

$$CN + N - N_2 + C \quad AQ = -57 \frac{K \text{ cal}}{\text{mole}}$$

$$C_3 - 3C \quad AQ = 332 \frac{K \text{ cal}}{\text{mole}}$$

$$CN + O - CO + N \quad AQ = -76 \frac{K \text{ cal}}{\text{mole}}$$

$$K \text{ cal}$$

The overall energy change in this zone is exothermic and one notes that carbon monoxide and atomic gaseous carbon are being formed in this second interaction zone, and subsequently diffuse back to the surface.

Figures 13 and 14 indicate the heterogeneous and homogeneous chemical interactions for a higher surface temperature ( $T_w = 7500^{\circ}R$ ) at the same hypersonic conditions as the two preceeding figures. Here again we see multiple flame fronts (figure 14), but at this higher surface temperature the vaporizing species  $C_3$  has pushed the zones of homogeneous interactions further into the boundary layer. For this situation, CN is evolved in a homogeneous reaction and diffuses back to the condensed phase. Here, as in the case of the lower surface temperature, the interaction zone nearest the surface is endothermic, while the one farther removed is exothermic. Also, as before, CO and C are both produced in the gas phase and diffuse back to the surface.

The corresponding normalized temperature and velocity profiles for these two surface temperatures are shown in figure 15. The temperature variation for  $T_w = 7500^{\circ}R$  clearly shows the effect of the endothermic reaction and associated temperature reduction near the surface as well as the

28

temperature overshoot resulting from the exothermic reaction occuring further out in the gas phase.

Figure 16 shows the variation of the normalized mass loss in the sublimation regime as a function of surface temperature and stagnation pressure. The normalizing factor is the diffusion controlled oxidation mass transfer rate. It is interesting to note that if the gas model utilized for the diffusion controlled oxidation regime in the earlier study (i.e. Ref. 3) had included the chemical species CN in addition to CO and CO<sub>2</sub> as the ablation products, then the diffusion controlled mass loss would not have "fallen off" slightly at the higher temperatures but would have remained at a constant level in this regime. (see Figure 18 of Ref. 3). Essentially, the quantity  $\dot{m}_D(R_B/P_e)^{1/2}$  (in the diffusion controlled oxidation regime) is independent of surface temperature and can be put into the form

$${}^{\circ}m_{\rm D} ({\rm R}_{\rm B}/{\rm P}_{\rm e})^{1/2} = 6.35 \times 10^{-3} \, {\rm LB}_{\bullet}/{\rm FT}_{\bullet}^{3/2} \, {\rm SEC}_{\bullet} - {\rm ATM}_{\bullet}^{1/2}$$
 (55)

Note that  $\dot{m}_S/\dot{m}_D$  in figure 16 ranges over six decades of stagnation pressure, includes surface temperatures up to 10,000°R, and has the same variation with stagnation pressure and surface temperature as does the effective mass fraction (fig. 10) of the element carbon at the surface. In fact, the results of a number of boundary layer solutions covering a wide range of stagnation enthalpies, stagnation pressures, and surface temperatures yielded the relationship

$$\dot{m}_{S}/\dot{m}_{D} \approx 6.67 C$$
 (56)  
 $\tilde{C}_{W}$ 

The limit of conventional boundary layer theory for subliming graphite is given when  $\mathring{m}_S / \mathring{m}_D = 6.67$ . At this point, the pressure of the vaporizing species is equal to the total stagnation gas pressure, since here C is  $\widetilde{C}_w$  equal to unity.

With these new results for the graphite mass loss in the sublimation regime, one is now in a position to predict the ablation rate of graphite for <u>all</u> surface temperatures of interest. For example, when one combines the previous results (i.e. Ref. 3) for the low temperature reaction rate controlled regime, the transition regime, and the diffusion controlled oxidation regime with the new solutions given here for the sublimation regime, one obtains the results shown in figure 17. For convenience, the graphite mass transfer rate has again been normalized with respect to the level of the diffusion controlled oxidation mass loss.

In order to relate the low temperature oxidation results to the new work presented here it might be appropriate at this point to summarize briefly the oxidation theories peculiar to the reaction rate controlled and transition regimes. (For the details concerning these regimes see references 3 and 7 to 13.) Examination of the available experimental data indicates that in the reaction rate controlled regime, the oxidation process follows a rate law which may be written in the Arrhenius form shown below.

$$\dot{\mathbf{m}}_{\mathbf{R}}^{-\mathbf{E}/\mathbf{R}\mathbf{T}} \mathbf{e}^{\mathbf{W}} (\mathbf{P}_{\mathbf{O}_{2}})_{\mathbf{W}}^{\mathbf{n}}$$
(57)

In this equation,  $P_{O_{2_w}}$  is the partial pressure of the oxygen at the surface, n is the order of the reaction,  $K_O$  is the effective collision frequency,

30

and E is the activation energy for the chemical reaction. The mass loss in this regime is noted to increase exponentially with surface temperature  $T_w$ . Depending upon the investigator, type of graphite studied, and the test conditions, the order of the reaction n has been reported to vary between zero and unity; the activation energy E falls within the limits 8 to 60 Kcal/ mole; and the effective collision frequency can vary over several orders of magnitude. For our calculations, we have arbitrarily taken the order of the reaction to be one-half, the activation energy to be 44 Kcal/mole, and have chosen two values of K<sub>0</sub> that effectively bracket the existing experimental data (i.e. we arbitrarily choose the "fast" reaction rate and a "slow" reaction rate shown in figure 17). It is noted in passing, that "fast" reaction rates are typical of the performance of ATJ type graphites, while the pyrolytic type graphite reaction rates are orders of magnitude slower.

The different theories which exist for the variation of the mass loss through the transition regime are associated to some degree with the concept of two resistances in series, one chemical and the second gas dynamic. The "double plateau" theory (Ref. 12 and 13) appears to be useful when applied to the situation of fast reaction kinetics associated with the ATJ type graphites. A second theory (Ref. 3, 6,24) superior to the former when considering the slower reaction kinetics of pyrolytic type graphites, is based (in a straight forward manner) on the fact that the diffusion controlled mass transfer,  $\dot{m}_D$ , varies as the square root of the stagnation pressure, and on the assumption that the reaction rate controlled mass loss,  $\dot{m}_R$ , is based on one-half order kinetics. The resulting equation which Scala

31

has derived for the variation of the mass transfer through the transition regime is shown below.

$$\dot{m} = \left[\frac{1}{\dot{m}_{R}^{2}} + \frac{1}{\dot{m}_{D}^{2}}\right]^{-1/2} \text{ or } \frac{\dot{m}}{\dot{m}_{D}} = \left[1 + \left(\frac{\dot{m}_{D}}{\dot{m}_{R}}\right)^{2}\right]^{-1/2}$$
(58)

The normalized mass transfer results for ablating graphite shown in figure 17 may now be represented rather simply (for the entire range of surface temperatures) in terms of the effective mass fraction of the element carbon. Remembering that in the diffusion controlled oxidation regime the plateau is given by  $C_{C_w}^{\sim} = 0.15$ , one has from equation (56)

$$\dot{m}/\dot{m}_{D} = C /0.15$$
 (59)  
 $\tilde{C}_{w}$ 

Therefore, in the low temperature reaction rate and transition regimes

$$\begin{array}{c}
C & \text{is given by} \\
\widetilde{C}_{w} \\
C \\
\widetilde{C}_{w} \\
\end{array} = 0.15 \left[ 1 + \left( \frac{\dot{m}_{D}}{\dot{m}_{R}} \right)^{2} \right]^{-1/2} \\
\left( 60 \right)
\end{array}$$

and in the sublimation regime

$$C = 0.15 + A \cdot P^{B} \cdot e^{-C/T} w$$

$$C_{w}$$
(61)

where the constants A, B, and C have been given previously in equation 46.

Now substitute the value (eq. (55)) of the diffusion controlled mass transfer rate into equation 59 and rearrange to obtain

$$\frac{\dot{m}_{w}}{C}_{\tilde{C}_{w}} \left(\frac{R_{B}}{P_{e}}\right)^{1/2} = 0.04235, \frac{LB}{FT.^{3/2}SEC. ATM^{1/2}}$$
(62)

It is interesting to compare the form of equation (62) with the results of an earlier vaporization study, (Ref. 17). In figure 4 of reference 17 the quantity  $\dot{m}_w \sqrt{R_B}/C_{K_w}$  was represented as a function of the flight velocity, altitude, and surface temperature. Here,  $C_{K_w}$  was defined to be the mass fraction of vaporizing species injected into the boundary layer. Two correlation equations for  $\dot{m}_w \sqrt{R_B}/C_{K_w}$  were offered in this work which represented the data within 15 to 25 percent. Upon a re-examination of these earlier results we now find that equation (62) given above (with a proper interpretation of  $C_{K_w}$ ) represents the data of figure 4, Ref. 17 to within 10 percent. This very important result appears to indicate that the mass transfer rates for arbitrary ablation systems for the hypersonic stagnation region may be closely approximated in a very simple manner (i.e. by the solution of a set of algebraic thermochemical equations which yields the quantity  $C_K$ ).

A set of transport coefficients of interest, and indeed necessary, in determining the relative fluxes of chemical species within the viscous layers and at the surface are the multicomponent Lewis numbers. The Lewis numbers of the gas mixture are defined (Reference 19) in terms of the multicomponent diffusion coefficients,  $D_{ij}$ , which unlike the binary diffusion coefficients,  $\hat{s}_{ij}$ , are not symmetric. Therefore, in addition to being both temperature and composition dependent, the magnitude of the Lewis numbers depends upon the interactions of given pairs of particles in a non-symmetric manner. It is clear that there are generally  $n^2$ -n values of the Lewis numbers; in this case there are 72, of which ten representative values are shown in Figure 18. Up to this point, we have considered only the mass transfer phenomena. Now let us turn our attention to the heat transfer. As an aid to the discussion of the relevant energy changes (and since it has been shown (Refs. 3, 21, 22, 24, 25) that the driving force for the heat transfer is related to the enthalpy difference across the boundary layer), it will be instructive to examine the enthalpies of the individual species produced at the ablating graphite surface, (see Fig. 8).

In the diffusion controlled regime, the oxidation of graphite results in the formation of both CO and CO<sub>2</sub>. The enthalpies of these species are negative with respect to those of undissociated air. The resulting energy change due to combustion is therefore exothermic, giving a positive contribution to the heat transferred to the surface. However, the thickening of the boundary layer due to the mass addition process tends to reduce the heat transfer. The net effect is to give a resultant energy flux into the solid which is nearly the same as the hypersonic aerodynamic heating in the absence of both combustion and mass transfer.

At higher surface temperatures (i.e. the sublimation regime) the products of ablation include the species C,  $C_3$  and CN. As noted in Figure 8, the formation of these species necessitates an endothermic reaction causing a substantial reduction in the surface heating rate.

These observations are indicated in the heat transfer correlation shown in Figure 19. Here, the heat conducted into the solid ablating graphite  $\left(K \quad \frac{\partial T}{\partial y}\right)_{s,w}$  is normalized by the heat transfer rate in the diffusion controlled oxidation regime,  $Q_0$ , and plotted as a function of the effective mass fraction of the element carbon C . The relationship between the dif- $\widetilde{C}$ fusion controlled heat transfer, the stagnation pressure, the nose radius and the enthalpy difference across the boundary layer which was given in Ref. 3 is shown below.

$$Q_{o} (R_{B}/P_{e})^{1/2} = 33.3 + 0.0333 \left[ H_{e} - h_{w_{air}} \right], BTU/FT^{3/2}SEC. - ATM^{1/2}$$
(63)

From an energy balance at the surface of ablating graphite, including, in addition to the gas phase conduction, diffusion and convection, the energy conducted into the surface layer of the condensed phase  $\left(K \frac{\partial T}{\partial y}\right)_{s,w}$  is defined as

$$\left(K\frac{\partial T}{\partial y}\right)_{s,w} = \left(K\frac{\partial T}{\partial y} - \sum_{i} \rho_{i} \vec{v}_{i} h_{i}\right)_{g,w} - \dot{m}_{w} \left(h_{w} - h_{C(s)}\right)$$
(64)

and as such does not include the effects of the forward radiation from the hot gas cap or the surface reradiation. However, both of these quantities can be accounted for rather simply.

Now, when CO is the primary combustion product (as is the case in the diffusion controlled oxidation regime),  $C_{\widetilde{C}} = 0.15$  and  $\left(K \frac{\partial T}{\partial y}\right)_{s,w} \equiv Q_{o}$ . As the surface temperature rises, and sublimation begins, the quantity  $C_{\widetilde{C}}$  increases exponentially with surface temperature as seen in Figure 10. This is accompanied by the dramatic decrease in the heating rate shown on Figure 19. Since this decrease is linear with  $C_{\widetilde{C}}$ , the heat transfer cor- $C_{w}$  relation equation for graphite ablation may be written as follows

$$\frac{\left(K\frac{\partial T}{\partial y}\right)_{s,w}}{Q_{o}} = 1.0 - S (C_{a} - 0.15)$$
(65)

where the slope S decreases with increasing stagnation enthalpy. The quantity S, shown in figure 20, has been curve fitted as a fifth degree polynomial in stagnation enthalpy shown below.

$$S = a + b H_{e} + c H_{e}^{2} + d H_{e}^{3} + e H_{e}^{4} + f H_{e}^{5}$$
  

$$a = 1.868 \times 10^{2} \qquad d = 1.146 \times 10^{-12}$$
  

$$b = -4.418 \times 10^{-3} \qquad e = -2.057 \times 10^{-15}$$
  

$$c = 3.945 \times 10^{-7} \qquad f = 8.333 \times 10^{-20} \qquad (65)$$

A dimensionless quantity of interest in energy transfer phenomena is the Prandtl number. The Prandtl number of the gas mixture at the surface, defined (Reference 19) in terms of the specific heat, the viscosity and the thermal conductivity of the gas, is shown in figure 21. The relationship between  $\Pr_w$  and  $C_i$  is seen to be a single curve. However, since  $C_i$ is a function of both surface temperature and stagnation pressure (i.e. surface composition), the relationship shown in figure 21 represents the magnitude of the Prandtl number of the gas at the surface of the subliming graphite over a wide range of hypersonic conditions.

A correlation parameter for the skin friction coefficient in the presence of subliming graphite has been found which effectively reduces all the data for a wide range of stagnation pressure, stagnation enthalpy, and surface temperature to a single curve. This parameter, shown in figure , was obtained by combining the Stanton number, the skin iriction coefficient, and non-dimensional mass transfer parameter and plotting the resulting non-dimensional group as a function of the effective mass fraction of the element carbon at the vaporizing surface. This skin friction correlation parameter may be expressed in a number of ways as shown below.

$$\frac{C_{H}^{B}}{C_{f}} = \left[\frac{Q_{w}}{\rho_{e}^{u}e^{(H_{e}^{-h}_{w})}}\right] \cdot \left[\frac{\rho_{e}^{u}e^{2}}{2\tau_{w}}\right] \cdot \left[\frac{\dot{m}_{w}(H_{e}^{-h}_{w})}{Q_{w}}\right] = \frac{\dot{m}_{w}^{u}e}{2\tau_{w}} = \left(\frac{\dot{m}}{C_{f}}\right)_{w} / (\rho_{u})_{e} = \left(\frac{\dot{m}}{C_{f}}\right)_{w} / \rho_{e}^{x} \left(\frac{du_{e}}{dx}\right)_{s} = \left(\frac{\dot{m}_{w}^{R}}{C_{f}_{w}^{x}}\right) / \sqrt{2\rho_{e}^{P}}_{e}$$
$$\approx \left(\frac{\dot{m}_{w}}{C_{f}_{w}}\right) \left(\frac{R_{B}}{x}\right) \left(\frac{\sqrt{\frac{\epsilon}{2}}}{\rho_{w}^{v}v_{w}}\right) \qquad (67)$$

where  $\epsilon$  is the normal shock density ratio.

In order to ascertain the relative importance of the chemical species present in the model representing the graphite sublimation process, additional computations were performed in which the magnitude of the mole fractions for CN and  $C_3$  were arbitrarily reduced from their equilibrium values. This was done by reducing the equilibrium  $K_p$  function for CN (i. e. equation 24) one order of magnitude and by reducing the  $K_p$  function for  $C_3$  (i. e. equation 25) three orders of magnitude. The resulting non-dimensional velocity and temperature profiles for these two solutions are compared with the corresponding equilibrium solution in figure 23. The resulting changes in the heat and mass transfer for these two solutions are also noted in the figure. Note that reducing  $X_{CN}$  one order of magnitude reduced the mass transfer by 24 percent but increased the heat transfer rate by 146 percent. A reduction in  $X_{C_3}$  of three orders of magnitude, resulted in a 32 percent reduction in the mass loss and an increase of 120 percent in the heat transfer. Interestingly enough, the relationships given by equations 56 and 62 were still satisfied for these two "non-equilibrium" solutions. This would appear to suggest that  $\begin{pmatrix} \dot{m}_W \\ C \\ C \\ C \\ W \end{pmatrix}_{EOUILIB}$   $\cong \begin{pmatrix} \dot{m}_W \\ C \\ C \\ C \\ W \end{pmatrix}_{NON-}$ 

EQUILIB.

If this is the case, the non-equilibrium mass transfer may be estimated quite readily through an evaluation of the non-equilibrium surface concentrations. A general discussion of the theory of non-equilibrium vaporization processes as applied to hypersonic laminar boundary layers is given in reference 17.

The effect of a change in the chemical model evidently produces a stronger net effect on the heat transfer rate than on the mass transfer rate. This occurs because not only is  $\widetilde{C}_{C_w}$  itself affected by the choice of the chemical model but so is  $h_w$ , the enthalpy of the gas mixture at the surface, which depends critically on the gas composition through the heats of formation of the chemical species present. This in turn alters the driving enthalpy potential,  $H_e - h_w$ , which produces a profound change in the heat transfer rate.

. .

#### 8. CONCLUSIONS

In a theoretical treatment of the vaporization of graphite in a hypersonic environment, it has been established that one must begin with a realistic chemical model in which one includes the contributions of dominant species such as  $C_3$  and CN. If either of these species is not included in the model the results would be seriously in error.

The mass transfer rate has been uniquely correlated to  $C_{\widetilde{C}_w}$ , the effective mass fraction of the element carbon at the surface. It has been shown that over the complete range of surface temperatures, stagnation enthalpies and stagnation pressures of interest, the mass loss increases linearly with  $C_{\widetilde{C}_w}$ . In addition, it has been found that the heat transfer rate into the surface also correlates with  $C_{\widetilde{C}_w}$ . In fact, at each value of the stagnation enthalpy, the heat transfer rate decreases linearly with  $C_{\widetilde{C}_c}$ .

The skin friction coefficient has likewise been correlated, and has been shown to vary inversely with  $C_{\widetilde{C}}$ .

Finally, the range of validity of the present results has been established by determining the combination of surface temperatures and stagnation pressures for which the pressure gradient normal to the surface is significant and the boundary layer approximation is invalid.

### 9. ACKNOW LEDGMENTS

The authors are pleased to acknowledge the discussions of surface kinetics held with Dr. Peter Zavitsanos and Dr. Bernard Hamel of the General Electric Company Space Sciences Laboratory. PERSONAL PROPERTY IN

The differential equations were programmed for digital computation on the IBM 7094 by Messers Frank Bosworth and James Massey.

This paper is based on work performed under the auspices of the United States Air Force, Ballistic Systems Division, Contracts No. AF 04(647)-269 and AF 04(694)-222.

#### 10. REFERENCES

- 1. Scala, S. M., "Surface Combustion in Dissociated Air," Jet Propulsion, Vol. 28, 1958, pp. 340-341.
- 2. Scala, S. M., "A Study of Hypersonic Ablation", <u>Proceedings of</u> the Tenth I.A.F. Congress, London, 1959, Springer Verlag.
- 3. Scala, S. M., "The Ablation of Graphite in Dissociated Air, Part I -Theory", IAS Paper No. 62-154, Thirtieth National Summer Meeting, June 1962; also G.E. Co., MSD, TIS R62SD72, September 1962.
- 4. Scala, S. M., "The Thermal Protection of a Re-Entry Satellite", <u>ARS Journal</u>, Vol. 29, No. 9, pp. 670-672, September 1959.
- Scala, S. M. and Nolan, E. J., "Aerothermodynamic Feasibility of Graphite for Hypersonic Glide Vehicles", Re-entry and Vehicle Design, Vol. 4, Proc. of the Fifth Symposium on Ballistic Missile and Space Technology, Academic Press, New York, 1960, pp. 31-63.
- 6. Nolar, E. J. and Scala, S. M., "Aerothermodynamic Behavior of Pyrolytic Graphite During Sustained Hypersonic Flight", ARS Journal Vol. 32, No. 1, January 1962, pp. 26-35.
- 7. Gulbransen, E. A. and Andrew, K. F., "Reactions of Artificial Graphite", Ind. Eng. Chem., Vol. 44, No. 5, 1952, pp. 1034-1044.
- 8. Parker, A. S., and Hottel, H. C., "Combustion Rate of Carbon," Ind. Eng. Chem., Vol. 28, No. 11, Nov. 1936, pp. 1334-1341.
- 9. Horton, W. S., "Oxidation Kinetics of Pyrolytic Graphte", General Electric Co., G. E. L. Report No. 60GL218, Jan. 1961.
- 10. Henning, G. R., Proceedings of the Fifth Conf. on Carbon, Vol. 1, p. 143, 1962.
- 11. Arthur, J. R., Trans. Faraday Soc. 47, 164 (1951).
- 12. Golovina, E. S. and Khaustovich, G. P., "The Interaction of Carbon with Carbon Dioxide and Oxygen at Temperatures up to 3000 K", <u>Eighth Symposium on Combustion</u>, Williams and Wilkins Co., 1962, pp. 784-792.
- 13. Welsh, W. E., Jr. and Chung, P. M., "A Modified Theory for the Effect of Surface Temperature on the Combustion Rate of Carbon Surfaces in Air", Proceedings of the 1963 Heat Transfer and Fluid Mechanics Institute, California Institute of Technology, Calif., June 1963, Stanford Univ. Press, pp. 146-159.

#### **REFERE NCES (Cont'd)**

- 14. Vidale, G. L., "The Vaporization of Graphite, TiC, ZrC, and HfC", G.E. Co., MSD, TIS R61SD010, January 1961.
- 15. Denison, M. R. and Dooley, D. A., "Combustion in the Laminar Boundary Layer of Chemically Active Sublimators", Aeronutronic Systems Report U-110, Sept., 1957.
- 16. Emmons, H. W., and Leigh, D., "Tabulation of the Blasius Function with Blowing and Suction", Div. of Applied Sci., combustion Aero. Lab., Interim Tech. Rept. No. 9, Harvard Univ. Nov. 1953.
- Scala, S. M. and Vidale, G. L., "Vaporization Processes in the Hypersonic Laminar Boundary Layer", Int. J. Heat and Mass Transfer, Vol. 1, No. 1, pp. 4-22, Pergamon Press, 1960.
- Scala, S. M., "Vaporization of a Refractory Oxide During Hypersonic Flight", <u>1959 Heat Transfer and Fluid Mechanics Institute</u>, p. 181, Stanford University Press, 1959.
- 19. Hirschfelder, J. O., Curtiss, C. F., and Bird, R. B., "Molecular Theory of Gases and Liquids", John Wiley and Sons, 1954.
- 20. Scala, S. M., "The Equations of Motion in a Multicomponent Chemically Reacting Gas", G.E. Co., MSD, TIS R58SD205, December 1957.
- 21. Lees, L., "Convective Heat Transfer with Mass Addition and Chemical Reactions", <u>Third AGARD Colloquium on Combustion and</u> <u>Propulsion</u>, Palermo, Sicily, Pergamon Press, 1959.
- 22. Scala, S. M. and Gilbert, L. M., "Theory of Hypersonic Laminar Stagnation Region Heat Transfer in Dissociating Gases", General Electric Co., MSD, TIS Document No. R63SD40, April 1963. To be published in the <u>Proceedings of the Eighth Midwestern Mechanics</u> Conference, Cleveland, Ohio, April 1963.
- 23. Cook, C.A., Gilbert, L. M., and Scala, S. M., "Normal Shock Waves in Air at Flight Speeds up to 25,000 ft./sec.", G.E. Co., MSD TIS R62SD76, November 1962.
- 24. Scala, S. M., and Gilbert, L. M., "Aerothermochemical Behavior of Graphite at Elevated Temperatures", G. E. Co., MSD, TIS R63SD89, November 1963.

### **REFERENCES** (Continued)

25. Fay, J. A., and Riddell, F. R., "Theory of Stagnation Point Heat Transfer in Dissociated Air", J. Aero. Sci., Vol. 25, 1958, pp. 78-85.

٠

# TABLE I. GAS CONSTANTS

				<b>Tref.</b> = $540^{\circ}$ R
SPECIES	σ <sub>i</sub> , A	אר i	(€/k) <sub>i</sub> , <sup>°</sup> K	$\Delta h_{f_i}^{o}$ , BTU/LB
ō	2.96	16		6654
0 <sub>2</sub>	3.54	32	88.0	0
N	2.88	14		14, 527
N <sub>2</sub>	3.749	28	79.8	0
со	3.59	28	110.0	-1698
co2	3.897	44	213.0	-3848
с	3.42	12		25, 755
C3	3.6	36	150	9517
CN	3,5	26	115	7689

man and an a

1

Real Property in

### TABLE II

## COMPARISON OF "CONSTANT" PROPERTY AND VARIABLE PROPERTY SOLUTIONS FOR GRAPHITE SUBLIMATION

ALT. = 100,000 FT.,  $V_{\infty} = 20,000 \text{ FT.}/\text{SEC.}, T_{w} = 6500^{\circ}\text{R},$ 

 $R_B = 1.0 FT.$ 

QUANTITY	"CONSTANT" PROPERTY	VARIABLE PROPERTY	
<sup>f</sup> ηη <sub>w</sub>	0.5835	0.5825	
-f w	0.09954	0.1022	
<sup>θ</sup> n <sub>w</sub>	0.5733	0.5618	
(C /C ) Õ Ñ <sup>w</sup>	0.2842	0.2819	
Q <sub>w</sub> , BTU/Ft. <sup>2</sup> SEC	418.8	396.3	
m <sub>w</sub> , LB/FT <sup>2</sup> SEC	0.01775	0.01822	
C <sup>u</sup> <sub>f</sub> FT./SEC.	16.02	15.99	
c <sub>H</sub> /c <sub>f</sub>	0.3531	0.3390	
m <sup>*</sup> <sub>w</sub> (H <sub>e</sub> -h <sub>w</sub> )/Q <sub>w</sub>	0.2416	0.2619	
Pr	0.6889	0.6890	

•

# TABLE III

.

EQUILIBRIUM CONSTANTS, $\log_{10} K_p = a - b/T (^{\circ}R)$						
Reaction	Equilibrium Constant P <sub>i</sub> is in atm.	a	$b \ge 10^{-4}$			
0 <sub>2</sub> ≠ 20	$K_{p_0} = P_0^2 / P_{0_2}$	6.80	4.68			
N <sub>2</sub> ≠ 2N	$K_{P_{N}} = P_{N}^{2}/P_{N_{2}}$	7.00	9.00			
$CO + O \neq CO_2$	$K_{P_{CO_2}} = P_{CO_2}/P_{CO_2}P_{O}$	-8.00	-5.04			
C + O ≠ CO	$K_{P_{CO}} = P_{CO}/P_{C}P_{O}$	-7.43	-10.29			
C + N ≠ CN	$K_{P_{CN}} = P_{CN} / P_{C} P_{N}$	-6.63	-7.59			
3C ≠ C <sub>3</sub>	$K_{PC_3} = P_{C_3} / P_C^3$	-14.77	-12.83			
C(S) ≠ C	$K_{p_{C}} = P_{C}$	8,12	6.69			

46

مرورين والعب ووعد من ا

.



Figure 1. Mass Transfer Regimes for Ablating Graphite





Figure 3. Coordinate System



Figure 4. Viscosity



(P = 1.0 ATM.)



.....



•

.

Figure 7. Specific Heat vs. Temperature





Figure 9. Chemical Composition at a Graphite Surface





ارو هامهری هاده در از از از از از از میکوه هم ۱۹۹۵ مربع



Figure 11. Concentration Profiles (Equilibrium Graphite Sublimation)





Figure 13. Concentration Profiles ( Equilibrium Graphite Sublimation)





.





Figure 17. Normalized Hypersonic Ablation Rate of Graphite Over the Entire Range of Surface Temperature




Figure 18. Typical Multicomponent Lewis Numbers at the Surface of Subliming Graphite

ł



















Figure 23. Comparison of Temperature and Velocity Profiles (Graphite Sublimation)



SPACE SCIENCES LABORATORY MISSILE AND SPACE DIVISION

## TECHNICAL INFORMATION SERIES

AUTHOR S. M. Scala	UTHOR SUBJECT CLASSIFICATION	
L. M. Gilbert	Aerothermochemistry	August 1964
THE SUBLIMATION OF GRAPHITE AT HYPERSONIC SPEEDS*		g. e. class I gov. class None
REPRODUCIBLE COPY FILED AT MSD LIBRARY. DOCUMENTS LIBRARY UNIT. VALLEY FORGE SPACE TECHNOLOGY CENTER, KING OF PRUSSIA, PA.		no. pages 76

summary In this paper, a new theoretical model is presented for the sublimation of graphite at hypersonic flight speeds. The aerothermochemical interactions between discociated air and graphite are treated by means of a nine component model, including O,  $O_2$ , N,  $N_2$ , CO,  $CO_2$ , C,  $C_3$  and CN. The mass transfer rate, the heat transfer rate, and the skin friction coefficient are determined numerically and are then correlated by means of algebraic equations, as a function of stagnation pressure, stagnation enthalpy and wall temperature in the high Reynolds number laminar flow regime.

\*To be presented at the AIAA Entry Technology Conference, NASA Langley Research Center, October 12-14, 1964.

KEY WORDS

Graphite; Ablation; Sublimation; Hypersonic Flight; Dissociated Air; Laminar Boundary Layer

BT CUTTING OUT THIS BECTANDLE AND FOLDING ON THE CENTEE LINE THE ABOVE INFORMATION CAN BE FITTED INTO A STANDARD CARD FILE

COUNTERSIGNED

L. M. Gilbert