AN APPROXIMATE ANALYSIS OF THE EFFECTS OF NITROGEN INJECTION INTO THE BOUNDARY LAYER ON A GRAPHITE SURFACE IN A HIGH-TEMPERATURE DISSOCIATED AIRFLOW

by Kenneth C. Weston

Manned Spacecraft Center
Houston, Texas

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ABSTRACT

This study considers the effects of injection of a nonreacting gas (taken to be nitrogen) on the heat and mass transfer of a porous, chemically reacting surface (graphite) at hypersonic speeds. Heat and mass transfer relations are obtained for the carbon surface.

Numerical results are presented for the case of the sphere stagnation point at hypersonic speeds. Reductions in carbon surface mass loss and aerodynamic heating as a result of nitrogen injection are demonstrated. Comparisons with more rigorous digital computer solutions for zero nitrogen injection show the same qualitative trends and numerical differences of about 10 percent.
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SUMMARY

This study considers the effects of injection of a nonreacting gas (taken to be nitrogen) on the heat and mass transfer of a porous, chemically reacting surface (graphite) at hypersonic speeds. All chemical reactions are considered to occur in a reacting sheet adjacent to the wall. Equations for the determination of species mass fractions at the wall are derived under the assumptions of a frozen boundary layer and chemical equilibrium in the flame sheet. Schmidt and Prandtl numbers are taken as unity. Heat and mass transfer relations are obtained for the carbon surface.

Numerical results are presented for the case of the sphere stagnation point at hypersonic speeds. Reductions in carbon surface mass loss and aerodynamic heating as a result of nitrogen injection are demonstrated. Comparisons with more rigorous digital computer solutions for zero nitrogen injection show the same qualitative trends and numerical differences of about 10 percent.

INTRODUCTION

Graphite is considered frequently as a heat-protection material for the leading edges and other high heating-rate areas of lifting reentry vehicles. Its ability to sustain high temperatures and its strength at elevated temperatures make it particularly suitable for such applications. These unusual qualities have motivated considerable analytical study of the ablative behavior of graphite. Moreover, its elemental nature offers substantial analytical simplifications relative to chemically complex organic ablators. The present work utilizes this simplicity to examine the effects on heat and mass transfer of injection of nonreacting nitrogen through porous graphite.

A number of investigators have analyzed the behavior of the flow over an ablating substance within the framework of boundary-layer theory. In 1957, Dennison and Dooley (ref. 1) treated the laminar boundary layer with combustion using a model very much like that employed in the present study. This model assumes all chemical reactions to occur at a surface to which oxygen and fuel are transported by convection and diffusion. Chemical equilibrium is assumed to exist at this surface; combustion
products diffuse in both directions from the surface. As a further simplification, reference 1 utilized constant property boundary-layer solutions for Lewis and Prandtl numbers of unity.

In 1962 and 1964, S. Scala (refs. 2 and 3) presented the results of sophisticated calculations of the ablation of graphite. These digital computer solutions of the reacting gas boundary layer included consideration of nine chemical components and six chemical reactions in the boundary layer. The calculations involved simultaneous integration of coupled boundary-layer equations including calculations of transport properties based on multicomponent diffusion rather than the frequently employed binary model. These calculations show distributed reaction zones within the boundary layer, and are the most detailed results presently available for graphite ablation.

In reference 4, Lees concluded that, for a Lewis number of unity, reaction rates in the boundary layer play a secondary role in determining the mass fractions of chemical species at the surface and transport properties. His analysis also suggests that combustion may be beneficial in reducing heat transfer if the heat of sublimation is comparable to the heat reaction. Lees further stated that these conclusions are independent of the model of chemical reaction assumed.

Dorrance outlined a method in reference 5 for the analysis of the reacting laminar boundary layer on a carbon surface. His analysis considered all reactions to occur at the wall, with the boundary layer treated as nonreacting. The present work extends this analysis, for the case of Prandtl and Schmidt numbers of unity, to the case of nitrogen injected into a porous carbon surface.

This work is based on research documented in a Master's Thesis at Rice University in 1965. Discussions with Dr. Frederic A. Wierum of Rice University are gratefully acknowledged.

SYMBOLS

\[ B \] mass transfer parameter
\[ C \] species mass fractions
\[ \bar{C} \] elemental mass fractions
\[ C_H \] Stanton number
\[ c_p \] specific heat at constant pressure
\[ D \] diffusion coefficient
\[ f \] modified stream function (see equations (59), (60), and (61))
\[ G \] function defined by equation (74)

2
g  dimensionless enthalpy, \( \frac{I}{I_e} \)

(g) gaseous phase

h local static enthalpy

\( h_{\text{eff}} \) effective heat of ablation

\( h_i \) enthalpy of the i'th specie

\( h_i^0 \) heat of reaction of the i'th specie

I stagnation enthalpy

\( J_1, J_2, J_3 \) quantities defined in equations (38) to (40)

\( K_1, K_2, K_3, K_4 \) equilibrium constants defined in equations (1) to (4)

k thermal conductivity

L Lewis number, \( \frac{\rho D_c \rho}{k} \)

\( L_{vc} \) heat of sublimation of graphite

\( \ell \) density-viscosity ratio defined in equation (63)

M molecular weight

\( \bar{M} \) mean molecular weight defined in equation (81)

\( M^* \) Mach number

\( M_a \) molecular weight of undissociated air

\( M_e^* \) Mach number at edge of boundary layer

\( \dot{m}_C \) mass flux of carbon

\( \dot{m}_E \) total mass flux from equilibrium layer defined in equation (10)

\( \dot{m}_N \) mass flux of nitrogen
\( P \)  Prandtl number, \( \frac{\mu c_p}{k} \)

\( p \)  pressure

\( \dot{q} \)  heat flux

\( \dot{q}_h \)  energy absorbed in steady ablation

\( \dot{q}_{\text{rad}} \)  radiative heat flux from surface

\( \dot{q}_s \)  heat flux to graphite surface

\( \dot{q}_w \)  aerodynamic heat flux with mass injection effects included

\( R \)  sphere radius of curvature

\( \sigma \)  universal gas constant

\( R_i \)  gas constant for \( i \)'th specie

\( r \)  radius normal to body axis of symmetry extending to body surface

\( S \)  Schmidt number, \( \mu / \rho D \)

\( s \)  coordinate along body surface

\( (s) \)  solid phase

\( \bar{s} \)  boundary-layer coordinate defined by equation (58)

\( T \)  temperature

\( T^+ \)  reference temperature defined by equation (79)

\( t \)  time

\( u \)  local velocity parallel to wall

\( v \)  local velocity normal to wall

\( \dot{w}_i \)  rate of production of the \( i \)'th specie

\( X \)  \( \left[ \sum_i \rho_i M_i \right]^{-1} \), equation (30)
\( x_i \)  
- mole fraction of the i'th specie

\( y \)  
- coordinate normal to wall

\( Z_i \)  
- dimensionless mass fraction of i'th specie, \( \frac{C_i}{C_i,e} \)

\( \delta \)  
- thickness of equilibrium layer

\( \eta \)  
- boundary-layer coordinate defined in equation (57)

\( \eta^*, \eta^{**} \)  
- dummy variables

\( \lambda \)  
- generalizing variable representing \( f', g, \) or \( Z_i \)

\( \mu \)  
- viscosity coefficient

\( \nu \)  
- index, \( \nu = 0 \) for planar flow, \( \nu = 1 \) for axisymmetric flow

\( \rho \)  
- density

\( \tau \)  
- thickness of graphite layer

\( \phi \)  
- generalizing variable representing \( 1, P, \) or \( S \)

\( \psi \)  
- stream function

Subscripts:

- \( A \)  air
- \( E \)  condition in equilibrium layer
- \( e \)  condition at outer edge of boundary layer
- \( f \)  frozen
- \( i \)  of i'th specie
- \( \text{in} \)  initial
- \( M \)  arithmetic mean value
- \( \text{N. B.} \)  no mass injection
- \( \text{sp} \)  stagnation point
The ablation of graphite at hypersonic speeds occurs through sublimation and chemical reactions with the surrounding air. At wall temperatures below about 1000° K the rate of mass loss is governed by the rate of oxidation of the graphite surface. At slightly higher temperatures a transition region precedes a third region in which the rate of surface recession is governed by the rate of diffusion of oxygen into the boundary layer. This "diffusion-controlled regime" prevails over a range of wall temperatures from about 1500° to about 3000° K at atmospheric pressure. The present analysis considers the effects of nitrogen injection on graphite ablation in this regime. At temperatures above 3000° K the rate of sublimation of carbon exceeds the rate of diffusion of oxygen, and uncombined gaseous carbon molecules exist at the wall in significant amounts. In this regime nitrogen reactions with graphite yield sizable mass fractions of cyanogen.

The present study considers the ablation of graphite for the diffusion-controlled regime in terms of a model in which the rate of diffusion of oxygen to the chemically active graphite surface is governed by mathematical solutions for a frozen boundary layer. The boundary layer is frequently termed frozen when the rate of generation of species in it is negligible. Such solutions have been successful in predicting heat transfer in dissociated-air boundary layers in which the wall catalyzes atom recombination and the wall temperatures are well below the boundary-layer-edge temperature (refs. 4 to 6). It is therefore assumed that all chemical reactions occur in an infinitesimal layer adjacent to the wall in which chemical equilibrium exists. This "equilibrium layer" is a region where nitrogen and carbon are received from the ablating surface, chemical reactions occur with oxygen from the boundary layer, and the equilibrium mixture is supplied to the boundary layer. In view of the approximation imposed by some of the necessary assumptions, it is reasonable to take advantage of the great simplifications made possible by assuming Prandtl, Schmidt, and, therefore, Lewis numbers to be unity. These assumptions are perhaps best justified by the remarkable agreement of the present calculations with the results of reference 3 which were obtained with state-of-the-art transport properties.

The present analysis is limited to hypersonic conditions for which the species at the edge of the boundary layer are atomic or molecular. Moreover, the boundary-layer-edge composition is assumed to be made up of nitrogen and oxygen only. Boundary-layer-edge conditions are obtained from the normal shock conservation equations, the assumption of isentropic and isoenthalpic flow along the body streamline, and the real air properties of reference 7. Absence of consideration of ions and electrons at the boundary-layer edge limits the applicability of this analysis to boundary-layer-edge temperatures below 10 000° K. This is well beyond the maximum equilibrium-shock-layer temperatures encountered, for example, during the reentry of current manned orbital vehicles.
The thermal decomposition of a graphite surface has been studied by many investigators. While carbon molecules (atomic carbon C and higher mass carbon radicals such as $C_2, C_3, C_4, \ldots, C_n$) may sublime from a hot carbon surface, experimental evidence indicates that $C_3$ and C are most abundant over a wide range of temperatures (refs. 3 and 8). In the present analysis it is assumed that the sole product of carbon mass loss is gaseous $C_3$. Dissociation of $C_3$ to C and subsequent reactions with oxygen to produce carbon monoxide are allowed in the equilibrium layer. Formation of carbon dioxide is not considered since it has been shown in reference 3 to be present only as a trace species in the temperature range of interest. The analysis is therefore based on the assumed heterogeneous surface reaction

$$C_3(s) \rightleftharpoons C_3(g)$$

and the following homogeneous reactions in the equilibrium layer

$$C_3(g) \rightleftharpoons 3C(g)$$

$$2C(g) + O_2(g) \rightleftharpoons 2CO(g)$$

$$C(g) + O(g) \rightleftharpoons CO(g)$$

where (s) and (g) indicate solid and gaseous phases, respectively.

The results of reference 3 show that nitrogen reactions are insignificant in the temperature range of interest. In this case nitrogen acts only as a diluent. Moreover, nitrogen is present in the equilibrium layer in diatomic form only; the range of wall temperatures considered is too low for significant dissociation.

Composition of the Equilibrium Layer

The partial pressures of the species in the four chemical reactions listed may be related through the following expressions for the equilibrium constants:

$$K_1(T) = p_{C_3}$$

$$K_2(T) = \frac{p_C^3}{p_{C_3}}$$
The partial pressure of $C_3$ is given by Thorne and Winslow (ref. 8) in the vicinity of $2400^\circ K$ as

$$\log p_{C_3} = 9.811 - \frac{40.296}{T}$$

where $T$ and $p$ are specified in $^\circ K$ and atmospheres. Thus the partial pressure of $C_3$ at the wall is determined when the wall temperature is specified. The partial pressures of the other species, except diatomic nitrogen $N_2$, may be expressed in terms of the partial pressure of carbon monoxide and the equilibrium constants as follows:

$$p_C = K_1^{1/3} K_2^{1/3}$$

$$p_{O_2} = \left( \frac{1}{K_3} K_1^{2/3} K_2^{2/3} \right) p_{CO}^2$$

$$p_O = \left( \frac{1}{K_4} K_1^{1/3} K_2^{1/3} \right) p_{CO}$$

The pressure at the wall is related to the partial pressures of the above species and nitrogen by Dalton's law of partial pressure

$$p_{N_2} + p_{O_2} + p_O + p_C + p_{C_3} + p_{CO} = p_E = p_w$$

The latter equality follows from the usual assumption of constancy of pressure across a boundary layer. To obtain the expression for the partial pressure of carbon monoxide necessary to determine partial pressures of the other species in the equilibrium layer, the convection and diffusion of species and mass injection at the wall must be considered.
Mass Balance

Consider the flux of mass through the equilibrium layer at the wall as shown in the following sketch. In general, nitrogen and carbon are uniformly injected into the equilibrium layer and a net mass flux $\dot{m}_E$ from the equilibrium layer into the boundary layer is defined. Then for steady flow

$$\dot{m}_E = \dot{m}_{N, w} + \dot{m}_{C, w} \quad (10)$$

Expressions may also be written for the accumulation of mass of each of the elements C, N, and monatomic oxygen O in the infinitesimal equilibrium layer. For a steady flow of each of the elemental mass fractions, the net rate of storage of each element must be zero. The following relations must then be satisfied:

$$\delta \rho \frac{d\bar{C}_C}{dt} = \dot{m}_{C, w} - \dot{m}_E \bar{C}_C, E + \left( \rho D \frac{\partial \bar{C}_C}{\partial y} \right)_E = 0 \quad (11)$$

$$\delta \rho \frac{d\bar{C}_N}{dt} = \dot{m}_{N, w} - \dot{m}_E \bar{C}_N, E + \left( \rho D \frac{\partial \bar{C}_N}{\partial y} \right)_E = 0 \quad (12)$$

$$\delta \rho \frac{d\bar{C}_O}{dt} = -\dot{m}_E \bar{C}_O, E + \left( \rho D \frac{\partial \bar{C}_O}{\partial y} \right)_E = 0 \quad (13)$$
For later reference, equations (11) to (13) may be written

\[ \dot{m}_C, w + \dot{m}_N, w = \dot{m}_N, w + \dot{m}_E \overline{C}_E, E - \left( \rho D \frac{\partial \overline{C}_C}{\partial y} \right)_E \] (14)

\[ \dot{m}_N, w = \dot{m}_E \overline{C}_N, E - \left( \rho D \frac{\partial \overline{C}_N}{\partial y} \right)_E \] (15)

\[ 0 = m_E \overline{C}_O, E - \left( \rho D \frac{\partial \overline{C}_O}{\partial y} \right)_E \] (16)

It is shown subsequently that when the Prandtl, Schmidt, and Lewis numbers are unity, the velocity, enthalpy, and elemental mass fraction profiles are linearly related. Therefore,

\[ \overline{C} = \overline{C}_E + \frac{\overline{C}_e - \overline{C}_E}{I_e - I_E} \left( I - I_E \right) \] (17)

where

\[ I = \sum_i C_i \left( \int_0^T c_{p_i} dT \right) + \sum_i C_i h_1^{o} + u^2/2 \]

Then

\[ \frac{\partial \overline{C}}{\partial y} = \frac{\overline{C}_e - \overline{C}_E}{I_e - I_E} \frac{\partial I}{\partial y} \]

and the diffusion term in equations (14) to (16) may be expressed in terms of the Stanton number

\[ \left( \rho D \frac{\partial \overline{C}}{\partial y} \right)_E = \left( \overline{C}_e - \overline{C}_E \right) \left( \frac{L_k}{c_p} \frac{\partial I}{\partial y} \right)_E = \left( \overline{C}_e - \overline{C}_E \right) \rho u e C_H \] (18)
where $L = 1$ and the Stanton number $C_H$ is given by

$$
\rho_e u e C_H = \frac{\left( \frac{k}{c} \frac{\partial T}{\partial y} \right)}{T_e - T_E}
$$

The diffusion terms in equations (14) to (16) may be eliminated by using equation (18). The resulting expressions are

\begin{align*}
\dot{m}_E &= \dot{m}_{N, w} + \dot{m}_E \overline{C}_C, E - \left( \overline{C}_C, e - \overline{C}_C, E \right) \rho_e u e C_H \tag{19} \\
\dot{m}_{N, w} &= \dot{m}_E \overline{C}_N, E - \left( \overline{C}_N, e - \overline{C}_N, E \right) \rho_e u e C_H \tag{20} \\
0 &= \dot{m}_E \overline{C}_O, E - \left( \overline{C}_O, e - \overline{C}_O, E \right) \rho_e u e C_H \tag{21}
\end{align*}

where equation (10) has been used to eliminate the injection rate of carbon at the wall.

A mass injection parameter $B$ is defined as

$$
B = \frac{\dot{m}_E}{\rho_e u e C_H} \tag{22}
$$

Equations (19) to (21) become

\begin{align*}
(B + 1) \overline{C}_C, E &= \overline{C}_C, e + B - \frac{\dot{m}_{N, w}}{\rho_e u e C_H} \tag{23} \\
(B + 1) \overline{C}_N, E &= \overline{C}_N, e + \frac{\dot{m}_{N, w}}{\rho_e u e C_H} \tag{24} \\
(B + 1) \overline{C}_O, E &= \overline{C}_O, e \tag{25}
\end{align*}
Throughout the following pages the subscript \( w \) is omitted from the wall nitrogen-injection parameter \( \frac{\dot{m}_{N,w}}{\rho_e u e C_H} \) with the understanding that nitrogen injection through the wall is indicated.

Equations (23) to (25) represent the mass balances on the equilibrium layer in terms of the elemental mass fractions. These expressions may be rewritten in terms of species mass fractions. In so doing, the mass fractions of carbon at the edge of the boundary layer and the mass fraction of monatomic nitrogen at the wall are set equal to zero.

\[
(B + 1) \left[ C_{C_3} E + C_C E \left( \frac{MC}{MCO} \right) C_{CO} E \right] = B - \frac{\dot{m}_N}{\rho_e u e C_H} \tag{26}
\]

\[
(B + 1) \left( C_{N_2} E \right) = \left( C_{N_2} E + C_N E \right) + \frac{\dot{m}_N}{\rho_e u e C_H} \tag{27}
\]

\[
(B + 1) \left( C_O E + C_{O_2} E + \frac{MO}{MCO} C_{CO} E \right) = \left( C_O E + C_{O_2} E \right) \tag{28}
\]

It is desirable to write the mass fractions in the equilibrium layer in terms of partial pressures of the species. The partial pressure and the mass fraction of the \( i \)'th specie are related by

\[
C_i = p_i M_i X \tag{29}
\]

where

\[
X = \frac{1}{\sum p_i M_i} \tag{30}
\]
Equations (26) to (28) become

\[(B + 1) \left( M_{C_3} p_{C_3}, E + M_{C^2} p_{C}, E + M_{C^2} p_{CO}, E \right) x_E = B - \frac{m_N}{\rho u e C_H} \]  \hspace{1cm} (31)

\[(B + 1) \left( M_{N_2} p_{N_2}, E \right) x_E = C_{N_2}, e + C_{N}, e + \frac{m_N}{\rho u e C_H} \]  \hspace{1cm} (32)

\[(B + 1) \left( M_{O^2} O, E + M_{O^2} p_{O_2}, E + M_{O^2} p_{CO}, E \right) x_E = C_{O}, e + C_{O_2}, e \]  \hspace{1cm} (33)

All of the basic relations are now available to solve for the partial pressures of the species in the equilibrium layer. From equation (32) the partial pressure of diatomic nitrogen $N_2$ is given by

\[p_{N_2}, E = \frac{C_{N_2}, e + C_{N}, e + \frac{m_N}{\rho u e C_H}}{(B + 1) x_E M_{N_2}} \]  \hspace{1cm} (34)

Equation (33) may be used to eliminate $(B + 1) x_E$ from equation (34) yielding

\[p_{N_2}, E = \frac{\left( C_{N_2}, e + C_{N}, e + \frac{m_N}{\rho u e C_H} \right) \left( M_{O^2} O, E + M_{O^2} p_{O_2}, E + M_{O^2} p_{CO}, E \right)}{M_{N_2} \left( C_{O}, e + C_{O_2}, e \right)} \] \hspace{1cm} (35)
Using equations (7) and (8) the partial pressure of nitrogen may be expressed in terms of the partial pressure of carbon monoxide

$$\frac{p_{N_2}, E}{M_{N_2}} = \left( \frac{C_{N_2}, e + C_N, e + \frac{\dot{m}_N}{\rho e u e C_H}}{M_{N_2}\left(C_O, e + C_{O_2}, e\right)} \right) \left( \frac{M_O K_4^{-1} K_1^{-1/3} K_2^{-1/3} p_{CO}, E}{M_{N_2} \left(C_O, e + C_{O_2}, e\right)} \right)$$

$$+ \left( \frac{C_{N_2}, e + C_N, e + \frac{\dot{m}_N}{\rho e u e C_H}}{M_{N_2}\left(C_O, e + C_{O_2}, e\right)} \right) \left( \frac{M_O K_3^{-1} K_1^{-2/3} K_2^{-2/3} p_{CO}, E, 2 + M_O p_{CO}, E}{M_{N_2} \left(C_O, e + C_{O_2}, e\right)} \right)$$

(36)

Combining equation (36) with equations (1) and (6) to (9) yields a quadratic equation for $p_{CO}, E$

$$\left( \frac{C_{N_2}, e + C_N, e + \frac{\dot{m}_N}{\rho e u e C_H}}{M_{N_2}\left(C_O, e + C_{O_2}, e\right)} \right) \left[ M_O \left( 1 + K_4^{-1} K_1^{-1/3} K_2^{-1/3} \right) p_{CO}, E \right.$$

$$+ M_O K_3^{-1} K_1^{-2/3} K_2^{-2/3} p_{CO}, E, 2 \left. \right] + \left( K_3^{-1} K_1^{-2/3} K_2^{-2/3} \right) p_{CO}, E^2$$

$$+ \left( K_4^{-1} K_1^{-1/3} K_2^{-1/3} \right) p_{CO}, E + K_1^{1/3} K_2^{1/3} + K_1 + p_{CO}, E - p_e = 0$$

(37)

Let

$$J_1 = \frac{C_{N_2}, e + C_N, e + \frac{\dot{m}_N}{\rho e u e C_H}}{M_{N_2}\left(C_O, e + C_{O_2}, e\right)}$$

(38)
\[ J_2 = 1 + K_4^{-1}K_1^{-1/3}K_2^{-1/3} \]  \hspace{1cm} (39)

\[ J_3 = K_3^{-1}K_1^{-2/3}K_2^{-2/3} \]  \hspace{1cm} (40)

Expressed in terms of the \( J \), equation (37) becomes

\[ p_{\text{CO, } E} + 2 J_1 J_2 M_0 + J_2 \frac{J_1}{J_1 J_3 M_0 O_2 + J_3} p_{\text{CO, } E} + \frac{J_1^{1/3} K_2^{1/3} K_3^{1/3} + K_1 - p_e}{J_1 J_3 M_0 O_2 + J_3} = 0 \]  \hspace{1cm} (41)

The complete solution for the partial pressure of carbon monoxide may be shown as

\[ p_{\text{CO, } E} = \frac{1}{2} \left[ \left( \frac{J_1 J_2 M_0 + J_2}{J_1 J_3 M_0 O_2 + J_3} \right)^2 + 4 \left( \frac{p_e - K_1 - K_1^{1/3} K_2^{1/3} K_3^{1/3}}{J_1 J_3 M_0 O_2 + J_3} \right) - \frac{J_1 J_2 M_0 + J_2}{J_1 J_3 M_0 O_2 + J_3} \right] \]  \hspace{1cm} (42)

Over a wide range of wall temperature and pressure, the squared term in the radical of equation (42) is large compared with the other term. Thus numerical difficulties are encountered in attempting to evaluate \( p_{\text{CO, } E} \) using equation (42). Examination of the orders of magnitudes of the terms in equation (41) reveals that while \( p_{\text{CO, } E}^2 \) is of order one, the other two terms are many orders of magnitude larger. In this case \( p_{\text{CO, } E} \) can be accurately calculated by neglecting \( p_{\text{CO, } E}^2 \) in equation (41). The following simpler expression is obtained

\[ p_{\text{CO, } E} = \frac{p_e - K_1 - K_1^{1/3} K_2^{1/3}}{J_1 J_2 M_0 + J_2} \]  \hspace{1cm} (43)

This expression may be accurately employed for the determination of \( p_{\text{CO, } E} \) when

\[ \frac{J_1 J_2 M_0 + J_2}{J_1 J_3 M_0 O_2 + J_3} \gg p_{\text{CO, } E} \]  \hspace{1cm} (44)
Using equation (43) the partial pressures of the species other than CO may be expressed in terms of $J$ as

$$p_{O_2}, E = J_3 \left( \frac{P_e - K_1 - K_1^{1/3} K_2^{1/3}}{J_1 J_2 M_O + J_2} \right)^2$$  \hspace{1cm} (45)$$

$$p_O, E = (J_2 - 1) \left( \frac{P_e - K_1 - K_1^{1/3} K_2^{1/3}}{J_1 J_2 M_O + J_2} \right)$$  \hspace{1cm} (46)$$

$$p_C, E = K_1^{1/3} K_2^{1/3}$$  \hspace{1cm} (47)$$

$$p_{C_3}, E = K_1$$  \hspace{1cm} (48)$$

$$p_{N_2}, E = J_1 \left( M_O J_2 p_{CO, E} + M_{O_2} J_3 p_{CO, E} \right)^2 \right)$$

$$= p_e - p_{CO, E} - p_{O_2, E} - p_O, E - p_C, E - p_{C_3}, E$$  \hspace{1cm} (49)$$

When the wall temperature, nitrogen injection parameter, and boundary-layer-edge conditions are specified, $J$ can be calculated from equations (38) to (40); the equilibrium-layer partial pressures can be evaluated from equations (43) and (45) to (49), and $B$ is determined from equation (32). To evaluate the heat and mass fluxes at the graphite surface the theory of the boundary layer must be considered.

**Boundary Layer**

The present analysis of the boundary layer follows the treatment of Dorrance in reference 5. The basic equations for the reacting gas boundary layer are presented.
Continuity:

\[ \frac{\partial}{\partial s} \left( \rho u \nu \right) + \frac{\partial}{\partial y} \left( \rho v \nu \right) = 0 \quad (50) \]

S-momentum:

\[ \rho u \frac{\partial u}{\partial s} + \rho v \frac{\partial u}{\partial y} = -\frac{dp}{ds} + \frac{\partial}{\partial y} \left( \mu \frac{\partial u}{\partial y} \right) \quad (51) \]

Y-momentum:

\[ p = p_e = p_E \quad (52) \]

Energy:

\[ \rho u \frac{\partial I}{\partial s} + \rho v \frac{\partial I}{\partial y} = \frac{\partial}{\partial y} \left[ \frac{\mu}{P} \frac{\partial I}{\partial y} + \mu \left( 1 - \frac{1}{P} \right) \frac{\partial u^2}{\partial y} \right] - \frac{\partial}{\partial y} \left[ \left( \frac{1}{L} - 1 \right) \rho D \sum_i h_i \frac{\partial C_i}{\partial y} \right] \quad (53) \]

Species:

\[ \rho u \frac{\partial C_i}{\partial s} + \rho v \frac{\partial C_i}{\partial y} = \frac{\partial}{\partial y} \left( \rho D \frac{\partial C_i}{\partial y} \right) + \omega_i \quad (54) \]

State:

\[ p_i = \rho_i R_i T \quad (55) \]

Enthalpy:

\[ I = \sum_i C_i \left( \int_0^T c_{p,i} \, dT + h_i^0 \right) + u^2/2 = h + u^2/2 \quad (56) \]
Equations (50) to (56) apply to the flow of a laminar boundary layer over a plane ($\nu = 0$) or axisymmetric ($\nu = 1$) surface. The gas is assumed to be an ideal gas and the diffusion process is assumed to be represented by binary diffusion according to Fick's law. Equations (50) to (56) are a set of nonlinear partial differential equations which are not generally solvable. A very useful technique for the solution of such equations is to transform the equations into ordinary differential equations. Solutions of this type are termed similar solutions. The transformation of equations (50) to (56) is derived in detail in reference 5. The equations are transformed into an $\eta, \bar{s}$ coordinate system in which

$$
\eta = \frac{\rho \, \mu \, e \, \varepsilon}{(2\bar{s})^{1/2}} \int_0^y \frac{\rho}{\rho_e} \, dy
$$

and

$$
\bar{s} = \int_0^s \rho_e \, \mu \, e \, \varepsilon \, u_e \, ds
$$

A stream function which is the product of separate functions of $\eta$ and $s$ is introduced

$$
\psi(s, \eta) = N(s) \, f(\eta)
$$

The function $f(\eta)$ is defined such that

$$
u = u_e \, f'(\eta)
$$

The modified stream function at the wall $f(0)$ is also related to the mass flow through the wall as

$$
f(0) = \frac{-(\rho \nu)}{\rho_e \, \mu \, e \, \varepsilon} \frac{(2\bar{s})^{1/2}}{\varepsilon}
$$
The dependent variable in the momentum equation becomes \( f \), and \( \psi \) is eliminated. The resulting equation is then considered to be a function of \( \eta \) only. The resulting momentum equation becomes

\[
(l f''')' + ff'' + \frac{2\bar{s}}{u_e} \frac{d u_e}{d\bar{s}} \left( \frac{p_e}{\rho} - (f')^2 \right) = 0
\]  
(62)

where primes denote differentiation with respect to \( \eta \) and

\[
l = \frac{\rho u'}{\rho_e u_e}
\]

(63)

It should be noted that similar solutions may be obtained for equation (62) only if the third term is a constant or a function of \( \eta \) only. This is the case for a stagnation point where

\[
\frac{2\bar{s}}{u_e} \frac{d u_e}{d\bar{s}} = \text{a constant}
\]

or for a flat plate where

\[
\frac{d u_e}{d\bar{s}} = 0
\]

If dimensionless enthalpy and species functions are defined as

\[
g(\eta) = \frac{I}{I_e}
\]

(64)

\[
Z_i(\eta) = \frac{C_i}{C_{i,e}}
\]

(65)
transformations of the energy and species equations may be written

\[
\left( \frac{\ell'}{P} \frac{g'}{g} \right) + fg' = \frac{2\xi f' g'}{\lambda} \frac{d}{ds} + \left[ \frac{\ell f}{s} \frac{1}{L} - 1 \right] \sum \frac{h_i}{1 - e} Z_i \right] + \frac{u_e^2}{1 - e} \left( \frac{1}{P} - 1 \right) \ell f'' f'''
\]  

(66)

and

\[
\left( \frac{\ell}{s} Z_i \right)' + fZ_i' = \frac{2\xi Z_i}{C_i, e} \frac{dC_i}{ds} - \frac{2\xi \psi_i}{\rho e u_e^2 \mu e^2 \nu C_i, e}
\]  

(67)

The boundary conditions on these equations are

\[
f(0) = f_E = \frac{-(\rho \nu)_E (2\psi)^{1/2}}{\rho e u_e \mu e^2 \nu}
\]

\[f'(0) = 0 \quad \quad \quad \quad \quad \quad \quad \quad \quad f'(\infty) = 1\]

\[Z_i(0) = Z_{iE} = \frac{C_i, E}{C_i, e} \quad \quad \quad \quad \quad \quad \quad \quad \quad Z_i(\infty) = 1\]

\[g(0) = g_E \quad \quad \quad \quad \quad \quad \quad \quad \quad g(\infty) = 1\]

At this point it is desirable to attempt to simplify equations (62), (66), and (67). Lees (ref. 9) has pointed out that, in the presence of extreme cooling, the third term in equation (62) has only a weak effect on solutions of the stagnation-point problem. Therefore, it is assumed that this term is negligible compared with the first and second terms. On a flat plate with no pressure gradient \( \frac{d\psi}{ds} = 0 \) and the third term is identically zero. In the present case the momentum equation is adequately represented by

\[(\ell f''')' + ff'' = 0\]  

(68)
The external flow at the edge of the boundary layer is considered to be isoenergetic. This leads to \[ \frac{dI_e}{ds} = 0 \] and the removal of the first term on the right-hand side of equation (66). The external flow at the boundary-layer edge is evaluated from equilibrium calculations. The species mass fractions are assumed to be frozen at these equilibrium values in the case of both the flat plate and stagnation point. This leads to the elimination of the first term on the right-hand side of equation (67). As discussed in the analysis section, this report considers the case in which no chemical reactions occur in the boundary layer and all reactions are at equilibrium in an infinitesimal layer at the wall. The rate of generation of the various chemical species in the boundary layer is then zero; hence \( \dot{w}_i = 0 \). Finally, with the assumption of Prandtl, Schmidt, and Lewis numbers equal to unity, equations (66) and (67) may be written

\[
\left( \frac{f}{g} \right)' + fg' = 0
\]  
\[ (69) \]

\[
\left( \frac{f}{S} Z_i' \right)' + fZ_i' = 0
\]  
\[ (70) \]

It is evident that equations (68) to (70) are of identical form and may be written

\[
\left( \frac{\ell}{\phi} \lambda' \right)' + f\lambda' = 0
\]  
\[ (71) \]

where \( \lambda \) is \( f', g, \) or \( Z_i \) and \( \phi \) is 1, \( P, \) or \( S. \) It is clear that \( f', g, \) and \( Z_i \) are linearly related when \( P = S = 1 \) since they all satisfy the same differential equation. The functions \( f' \) and \( g \) are also linearly proportional to the elemental mass fractions because the latter are proportional to \( Z_i. \) The boundary conditions associated with equation (71) are

\[
\lambda(0) = \lambda_E^*, \quad \lambda'(0) = \lambda_E^{*'}, \quad \lambda(\infty) = 1
\]

Equation (71) is readily integrated with \( \phi \) and \( \ell \) as constants to yield

\[
\lambda' = \lambda'(0) \exp \left( - \int_0^\eta \frac{\phi}{\ell} f \, d\eta^{**} \right)
\]  
\[ (72) \]
and

\[ \lambda = \lambda(0) + \lambda'(0) \int_0^\eta \exp \left( - \int_0^\eta \frac{\phi}{k} f \, d\eta^{**} \right) \, d\eta^{*} \]  \hspace{1cm} (73)

Let

\[ G(\eta, \phi) = \int_0^\eta \frac{\phi}{k} \exp \left( - \int_0^\eta \frac{\phi}{k} f \, d\eta^{**} \right) \, d\eta^* \]  \hspace{1cm} (74)

so that using equation (73) and the boundary conditions \( \lambda'(0) \) and \( \lambda(\eta) \),

\[ \lambda'(0) = \frac{1 - \lambda(0)}{\frac{k}{\phi} G(\infty, \phi)} \]  \hspace{1cm} (75)

and

\[ \lambda(\eta) = \lambda(0) + [1 - \lambda(0)] \frac{G(\eta, \phi)}{G(\infty, \phi)} \]  \hspace{1cm} (76)

It is evident from equation (75) that if \( G(\infty, \phi) \) is known, \( g'(0) \) and \( Z_1'(0) \) and, therefore, the convective heat transfer can be determined, since

\[ g'(0) = \frac{1 - g(0)}{\frac{k}{p} G(\infty, P)} \]  \hspace{1cm} (77a)

and

\[ Z_1'(0) = \frac{1 - Z_1(0)}{\frac{k}{S} G(\infty, S)} \]  \hspace{1cm} (77b)
Constant property solutions of equation (71) are available in references 10 and 11. Results from these references are presented in figure 1 which relates $G(\propto, \phi)$ to $f(0)$. The mass injection parameter $B$ may be related to these functions using

$$f(0) = \frac{B}{G(\propto, \phi)} \quad (78)$$

which follows from equations (22), (61), and (92).

Thus, given $P = S = 1$, $\ell$, and $B$, the heat transfer parameters $g'$ and $Z'$ are readily obtained from figure 1 and equation (77).

Property Determination

Dorrance (ref. 5) recommends the use of the reference temperature in evaluating $\ell$. The concept of a reference temperature has been utilized for some time in simulating the results of variable property solutions of the boundary-layer equations. Eckert (ref. 12) defines a reference temperature as follows

$$T^+ = 0.5T_e + 0.038T_e M_e^2 + 0.5T_e \quad (79)$$

The evaluation of $\ell$ using the reference temperature is straightforward for air or pure gases whose properties are well known. In the present case, however, the question arises as to the proper method of evaluating $\ell$ for a mixture of gases. The following approach is adopted:

(1) The viscosity is taken as the viscosity of air at the temperature $T^+$ using the Sutherland equation

$$\mu = 3.06 \times 10^{-8} \frac{T^{3/2}}{T + 112} \quad (80)$$
where \( T \) is in \(^\circ\text{K} \) and \( \mu \) in \( \frac{\text{lb-sec}}{\text{ft}^2} \).

(2) The molecular weight \( \bar{M} \) is calculated using the arithmetic mean of the species mass fractions at the wall and the boundary-layer edge as

\[
\bar{M} = \left[ \sum_i \left( \frac{C_i, M}{M_i} \right) \right]^{-1}
\]

(81)

where

\[
C_i, M = \frac{C_i, e + C_i, E}{2}
\]

(82)

(3) The density may then be calculated from the perfect gas law

\[
\rho(T^+) = \frac{p_e \bar{M}}{\rho T^+}
\]

(83)

This approximate approach for evaluating \( t(T^+) \) was compared with a more detailed calculation for the stagnation-point boundary layer in which species mass fractions were obtained at the point in the frozen boundary layer where the temperature is \( T^+ \). These species mass fractions were then used to evaluate the molecular weight and viscosity. No significant difference was obtained between the results of this tedious calculation and the simple method presented herein. In view of existing uncertainties in parameters necessary for detailed calculations of transport properties at high temperatures and the approximate nature of the present analysis, it is thought that more sophisticated approaches are unwarranted.

Convective Heat Transfer

Heat transfer at the carbon surface is assumed to be the result of thermal conduction and the transport of chemical energy which is released or absorbed at the wall.
because of chemical reaction. The wall heat flux is assumed proportional to the gradients of temperature and species mass fraction at the edge of the equilibrium layer

\[-q_w = \left( K \frac{\partial T}{\partial y} + \rho D \sum_i h_i \frac{\partial C_i}{\partial y} \right)_E \]  

(84)

The temperature gradient may be related to the enthalpy gradient by

\[ \left( \frac{\partial I}{\partial y} \right)_E = \left( \sum_i \int_0^T c_{p,i} \frac{dT}{\partial y} + \sum_i C_i c_{p,i} \frac{\partial T}{\partial y} + \sum_i h_i \frac{\partial C_i}{\partial y} \right)_E \]  

(85)

The frozen specific heat \( c_{p,f} \) may now be introduced where

\[ c_{p,f} = \sum_i C_i c_{p,i} \]  

(86)

so that

\[ \left( \frac{\partial T}{\partial y} \right)_E = \left[ \frac{1}{c_{p,f}} \left( \frac{\partial I}{\partial y} - \sum_i h_i \frac{\partial C_i}{\partial y} \right) \right]_E \]  

(87)

where

\[ \sum_i \int_0^T c_{p,i} \frac{dT}{\partial y} + \sum_i h_i \frac{\partial C_i}{\partial y} = \sum_i \left( \int_0^T c_{p,i} \frac{dT}{\partial y} + h_i \frac{\partial C_i}{\partial y} \right) = \sum_i h_i \frac{\partial C_i}{\partial y} \]  

(88)

Thus equation (84) becomes

\[-q_w = \left( K \frac{\partial T}{\partial y} + \rho D \sum_i h_i \frac{\partial C_i}{\partial y} \right)_E \]  

(89)
It is seen that, when the Lewis number is unity, the heat-transfer rate is proportional to the enthalpy gradient at the edge of the equilibrium layer. Rather than setting the Lewis number equal to 1 at this point, the term explicitly displaying the gradient of the mass fraction is retained.

The heat-transfer equation may be transformed into the \( \eta \) coordinate using equations (57), (64), and (65)

\[
-q_w = \frac{\ell \rho e u e r^\nu}{(2\delta)^{1/2} P} \left[ g_E' + (L - 1) \frac{\sum C_i, e h_i, E Z_i, E}{I_e} \right]
\]  

(90)

where the Prandtl number \( P = \frac{\mu E c_p, f, E}{k_E} \) is also not set equal to unity at this point.

Using equation (77), \( g'_E \) and \( Z'_i, E \) are eliminated yielding

\[
-q_w = \rho e u e C_H \left[ 1 + \frac{G(\infty, P)}{G(\infty, S)} \frac{L - 1}{L} \frac{\sum h_i, E (C_i, e - C_i, E)}{I_e - I_E} \right]
\]  

(91)

where

\[
\rho e u e C_H = \frac{\rho e u e r^\nu}{(2\delta)^{1/2} G(\infty, P)}
\]  

(92)

It is evident that, if the Lewis number is set equal to 1, the term in brackets in equation (91) becomes unity. For the case of \( L = 1 \), two implicit effects of mass injection on the heat flux are evident. First, mass injection causes an increase in \( G(\infty, 1) \) and a resultant decrease in the Stanton number \( C_H \). Secondly, variations in the enthalpy of the equilibrium layer, \( I_E' \), will be caused by species variations. It is seen also that, when \( L > 1 \), an additional term is obtained which increases the heat transfer due to increased diffusion of chemical potential energy.

Heat Balance on Fluid-Solid Interface

In order to determine the net heat transferred from the boundary layer to the surface, it is necessary to examine the various energy fluxes crossing the gas-solid.
The following sketch schematically indicates the components of the energy balance at the interface.

It is assumed that the gases flowing over the surface are nonradiating and transparent to the surface radiation $\dot{q}_{\text{rad}}$. The heat balance may be written

$$\dot{q}_s = -\dot{q}_w - \dot{q}_{\text{rad}} + \dot{m}_{N} h_{N_2} + \dot{m}_{C} h_{C} - \dot{m}_E h_{E}(g)$$

(93)

The enthalpy of carbon in the solid phase is related to the enthalpy of carbon in the gaseous phase at the same temperature by the heat of sublimation of carbon as follows

$$h_{C}(s) + L_{vc} = h_{C}(g)$$

(94)

Therefore, combining equations (93) and (94), the heat flux to the surface becomes

$$\dot{q}_s = -\dot{q}_w - \dot{q}_{\text{rad}} + \dot{m}_{N} h_{N_2} + \dot{m}_{C} h_{C} - \dot{m}_E h_{E}(g)$$

(95)

The mass flux $\dot{m}_E$ can be eliminated from equation (95) by using equation (10) to obtain

$$\dot{q}_s = -\dot{q}_w - \dot{q}_{\text{rad}} + \dot{m}_{N} h_{N_2} + \dot{m}_{C} h_{C} - \dot{m}_C L_{vc} - \left(\dot{m}_N + \dot{m}_C\right) h_{E}(g)$$

(96)
Finally, by using equation (91), the surface heat flux can be expressed as

\[ q_s = \rho_e u_e C_H \left[ \frac{I_e - I_{E}}{G(\infty, P)} \left( \frac{L - 1}{L} \right) \sum h_i, E \left( C_i, e - C_i, E \right) - \frac{q_{rad}}{\rho_e u_e C_H} \right] 
+ \frac{m_N}{\rho_e u_e C_H} \left( h_{N2, E} - h_{E}(g) \right) 
+ \frac{m_C}{\rho_e u_e C_H} \left( h_{C, E}(g) - h_{E}(g) \right) - \frac{m_C}{\rho_e u_e C_H} L_{vc} \]  

(97)

It is seen from the enthalpy terms that the injection of nitrogen, in addition to those effects discussed previously, modifies the net energy flux to the surface.

Stagnation-Point Problem

Up to this point the analysis has been applicable to flat plate and stagnation-point boundary-layer problems, and to other configurations in the context of local similarity and negligible pressure gradient. Inasmuch as the stagnation-point problem is of greatest interest in current technology, this case is developed in more detail here.

The velocity in the vicinity of a stagnation point is of the form

\[ u_e = \left( \frac{du_e}{dS} \right)_{sp} S \]  

(98)

where \( \left( \frac{du_e}{dS} \right)_{sp} \) is evaluated using the familiar Newtonian velocity gradient formula

\[ \left( \frac{du_e}{dS} \right)_{sp} = \frac{1}{R} \left( 2 \frac{\rho_e - \rho_\infty}{\rho_e} \right)^{1/2} \]  

(99)

From equation (58), \( \bar{s} \) can be evaluated as

\[ \bar{s} = \int_0^S \rho_e u_e e^{2\nu} u_e dS = \rho_e \nu \left( \frac{du_e}{dS} \right)_{sp} \frac{S^{2(\nu+1)}}{2(\nu + 1)} \]  

(100)
Equation (92) then yields

\[ \rho_e u_e C_H = \rho_e u_e \frac{1/2}{\left( \frac{d\rho_e}{ds} \right)_{sp}} \frac{(\nu + 1)^{1/2}}{G(\infty, P)} \]

(101)

The mass fluxes of nitrogen and carbon across the gas-solid interface are then

\[ \dot{m}_N = \left( \frac{\dot{m}_N}{\rho_e u_e C_H} \right) \left( \rho_e u_e \right)^{1/2} \left( \frac{d\rho_e}{ds} \right)_{sp} \frac{(\nu + 1)^{1/2}}{G(\infty, P)} \]

(102)

\[ \dot{m}_C = \left( B - \frac{\dot{m}_N}{\rho_e u_e C_H} \right) \left( \rho_e u_e \right)^{1/2} \left( \frac{d\rho_e}{ds} \right)_{sp} \frac{(\nu + 1)^{1/2}}{G(\infty, P)} \]

(103)

The convective and diffusive heat fluxes at the wall for Lewis and Prandtl numbers of 1 are given by

\[ -d_w = \left( \rho_e u_e \right)^{1/2} \left( \frac{d\rho_e}{ds} \right)^{1/2} \frac{(\nu + 1)^{1/2}}{G(\infty, 1)} \left( I_e - I_E \right) \]

(104)

and the heat flux penetrating the surface of the material is

\[ d_s = \left( \rho_e u_e \right)^{1/2} \left( \frac{d\rho_e}{ds} \right)_{sp} \frac{(\nu + 1)^{1/2}}{G(\infty, 1)} \left[ I_e - I_E + \left( \frac{\dot{m}_N}{\rho_e u_e C_H} \right) h_{N_2} E \right. \\
+ \left. \left( B - \frac{\dot{m}_N}{\rho_e u_e C_H} \right) h_C, E(g) - \left( B - \frac{\dot{m}_N}{\rho_e u_e C_H} \right) L_{vc} - B h_E(g) - \frac{d_{rad}}{\rho_e u_e C_H} \right] \]

(105)

The mass flux of carbon across the interface is proportional to the rate of surface recession since

\[ \dot{m}_C = \rho_C \frac{dr}{dt} \]

(106)
where \( \tau \) is the thickness of the carbon material at the stagnation point. The surface ablation rate is then determined from

\[
\frac{d\tau}{dt} = \frac{1}{\rho_C} \left( B - \frac{\dot{m}_N}{\rho_e u e H} \right) \left( \rho_e u e \right)^{1/2} \left( \frac{du_e}{ds} \right)^{1/2} \frac{(\nu + 1)^{1/2}}{G(\infty, 1)}
\]  

(107)

The thickness of carbon ablated during an arbitrary heating period is given by integration of equation (107)

\[
\tau = \int_0^t \frac{\dot{m}_N}{\rho_C u e H} \left( \rho_e u e \right)^{1/2} \left( \frac{du_e}{ds} \right)^{1/2} \frac{(\nu + 1)^{1/2}}{G(\infty, 1)} dt
\]  

(108)

RESULTS AND DISCUSSION

Calculations have been performed to demonstrate the accuracy of the approximation of the present work in comparison with existing results for the case of no nitrogen injection and to evaluate the effects of nitrogen injection. All calculations pertain to the stagnation-point boundary layer. The method of determination of boundary-layer-edge properties and composition has been outlined. Properties and species mass fractions, so obtained, are tabulated in table I. It is seen that at these flight conditions oxygen is completely dissociated and significant nitrogen dissociation has occurred.

TABLE I. - FREE-STREAM AND STAGNATION-POINT CONDITIONS

<table>
<thead>
<tr>
<th>Case</th>
<th>Altitude, kft</th>
<th>( I_{e'} ), Btu/lb</th>
<th>( p_{e'} ), atm</th>
<th>( T_{e'} ), ( ^\circ \text{K} )</th>
<th>( M_{e'/Ma} )</th>
<th>( \rho_{e'}lbf/ft^3 )</th>
<th>( C_{N, e} )</th>
<th>( C_{N_2, e} )</th>
<th>( C_{O, e} )</th>
<th>( C_{O_2, e} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>115</td>
<td>7864</td>
<td>2.985</td>
<td>6750</td>
<td>1.379</td>
<td>7.070 ( \times 10^{-3} )</td>
<td>0.19</td>
<td>0.58</td>
<td>0.23</td>
<td>( &lt;10^{-3} )</td>
</tr>
<tr>
<td>b</td>
<td>150</td>
<td>7875</td>
<td>.605</td>
<td>6220</td>
<td>1.402</td>
<td>1.530</td>
<td>.21</td>
<td>.56</td>
<td>.23</td>
<td>( &lt;10^{-3} )</td>
</tr>
<tr>
<td>c</td>
<td>180</td>
<td>7877</td>
<td>.2026</td>
<td>5900</td>
<td>1.418</td>
<td>.535</td>
<td>.21</td>
<td>.56</td>
<td>.23</td>
<td>( &lt;10^{-3} )</td>
</tr>
<tr>
<td>d</td>
<td>200</td>
<td>7872</td>
<td>.0966</td>
<td>5750</td>
<td>1.425</td>
<td>.260</td>
<td>.24</td>
<td>.53</td>
<td>.23</td>
<td>( &lt;10^{-3} )</td>
</tr>
<tr>
<td>e</td>
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<td>.0458</td>
<td>5560</td>
<td>1.431</td>
<td>.126</td>
<td>.25</td>
<td>.52</td>
<td>.23</td>
<td>( &lt;10^{-3} )</td>
</tr>
</tbody>
</table>
Table II presents calculations of enthalpy, mass injection parameters, and species mass fractions in the equilibrium layer for a wall temperature of 2000° K. Equilibrium constants for equations (2) to (4) and species properties in the equilibrium layer were obtained from reference 13. In the diffusion-controlled regime it is found that only molecular nitrogen and carbon monoxide exist in significant amounts in the equilibrium layer. This is in agreement with the findings of reference 3 for no nitrogen injection. At 2000° K, for instance, the ratios of the partial pressure of other species to the total pressure were found to be on the order of 10^{-10} or less. It was also found from equation (43) that the relative proportions of nitrogen and carbon monoxide in the equilibrium layer depend only on the nitrogen injection parameter \( \frac{m_N}{\rho_e u C_H} \).

Increasing values of \( \frac{m_N}{\rho_e u C_H} \), of course, reduce the mass fraction of carbon monoxide at the wall.

**TABLE II. - EQUILIBRIUM LAYER PROPERTIES**

\( [T_w = 2000° K] \)

<table>
<thead>
<tr>
<th>( \frac{m_N}{\rho_e u C_H} )</th>
<th>( C_{CO, E} )</th>
<th>( C_{N_2, E} )</th>
<th>( \frac{m_C}{\rho_e u C_H} )</th>
<th>B</th>
<th>( I_{E'} ) Btu/lb</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.344</td>
<td>0.656</td>
<td>0.173</td>
<td>0.173</td>
<td>284</td>
</tr>
<tr>
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<td>0.242</td>
<td>0.758</td>
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<td>455</td>
</tr>
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<td>0.186</td>
<td>0.814</td>
<td>0.173</td>
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<td>548</td>
</tr>
<tr>
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<td>0.872</td>
<td>0.173</td>
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<td>646</td>
</tr>
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<td>0.903</td>
<td>0.173</td>
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<td>698</td>
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<td>0.922</td>
<td>0.173</td>
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<td>731</td>
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<tr>
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<td>0.056</td>
<td>0.944</td>
<td>0.173</td>
<td>6.173</td>
<td>769</td>
</tr>
</tbody>
</table>

It can be demonstrated that the carbon mass flux parameter \( \frac{m_C}{\rho_e u C_H} \) is independent of the nitrogen mass injection parameter as shown in table II. Elimination of
While \( \frac{\dot{m}_C}{\rho e u e C_H} \) is invariant with increases in the nitrogen injection parameter, it is evident that the carbon mass loss is reduced due to the decreased Stanton number resulting from the increased total mass injection. The reduction in carbon mass loss with increasing \( \frac{\dot{m}_N}{\rho e u e C_H} \) and increasing altitude is demonstrated in figure 2. Increasing the altitude reduces the carbon mass loss due to the decreasing flux of oxygen available from the free stream for reaction.

As discussed previously, perhaps the most accurate and sophisticated analysis for the ablation of graphite appears in reference 3. For the special case of \( \frac{\dot{m}_N}{\rho e u e C_H} = 0 \), the results of the present analysis are compared with the carbon mass loss obtained from reference 3. It is seen that the present results are consistently lower by about 10 to 15 percent. Differences of this magnitude are not surprising in view of the vast differences between the present model and that of reference 3.

The variation of total mass flux from the equilibrium layer is shown in figure 3 as a function of the nitrogen injection parameter. It is seen that the total mass flux increases rapidly for small values of the injection parameter. At larger values of \( \frac{m_N}{\rho e u e C_H} \), the increase is less marked. This behavior results from the fact that \( C_H \)
decreases rapidly for large values of mass injection, resulting in small increases in total mass flux as \( \frac{\dot{m}_N}{\rho_e u_e C_H} \) is increased.

A comparison of the aerodynamic heat flux with carbon ablation from the present analysis and reference 3 is shown in figure 4. Differences of about 10 percent are evident. In view of the close correspondence of the present results to those of the sophisticated work of reference 3, it is felt that considerable confidence may be placed in the present analysis. It is also evident from figure 4 that nitrogen injection provides substantial reductions in heat flux. This is attributable primarily to large reductions in the Stanton number due to blowing.

The heat flux absorbed by the graphite surface as calculated by equation (97) is shown in figure 5 as a function of the injection parameter for an altitude of 115 000 feet. It is seen that nitrogen injection strongly reduces the heat flux absorbed.

The results presented have all assumed that an unidentified mechanism controlled the surface temperature at a fixed value. Usually, at a given flight condition, the wall temperature will be determined by the rate of radiation cooling, mass loss, and internal conduction. It is of interest to estimate the nitrogen injection required to maintain the wall at a specified wall temperature. In the case of steady ablation the surface temperature is determined by a balance of the net heat flux crossing the solid-gas interface and of the enthalpy transport of carbon and nitrogen from the initial temperature \( T_{in} \)

\[
q_h = m_C \int_{T_{in}}^{T_w} c_p \, C(s) \, dT + m_N \int_{T_{in}}^{T_w} c_p \, N_2 \, dT
\]

(110)
This expression is plotted in figure 5 for $T_{in} = 300^\circ$ K and $T_w = 2000^\circ$ K. The intersection of the two curves shows that a wall temperature of $2000^\circ$ K is obtained at the listed flight conditions with a nitrogen mass injection parameter $rac{m_N}{\rho e u C_H} = 3.5$. Figures 2 and 3 show that this corresponds to graphite and nitrogen expenditures of 0.0029 and 0.056 lb/ft$^2$-sec, respectively.

A widely used parameter in evaluating the merit of a heat-protection system is the effective heat of ablation. It is a measure of the thermal energy accommodated per unit mass loss of the heat-protection system. The effective heat of ablation as conventionally defined is

$$h_{eff} = \frac{(-q_w)_{N.B.}}{m_C}$$

(111)

where $(-q_w)_{N.B.}$ is the aerodynamic heat transfer without mass injection. Using equations (103) and (104) with $I_E = I_A$, the effective heat of ablation becomes

$$h_{eff} = \frac{(I_e - I_A)}{\left(B - \frac{m_N}{\rho e u C_H}\right)} \frac{C_H}{C_H}$$

(112)

The effective heat of ablation is plotted in figure 6 as a function of the enthalpy difference $I_e - I_A$, where $I_A$ is the enthalpy of air at wall temperature and pressure. Again comparison with the results of reference 3 shows satisfactory agreement for the case of no nitrogen injection. It is seen that, as judged by $h_{eff}$, substantial gains are made in ablation efficiency as a result of mass injection. This result demonstrates that, if mass loss of graphite is critical, nitrogen injection may be employed to reduce surface ablation substantially. Clearly, other parameters, which show less favorable comparisons, may be defined to represent the ablation efficiency. Care
should be taken, therefore, in judging heat-protection-system efficiency based on parameters such as $h_{\text{eff}}$.

**CONCLUDING REMARKS**

The effects of nitrogen injection on the heat and mass transfer of an ablating surface have been analyzed based on a model which considers all chemical reactions to occur in an infinitesimal region adjacent to the surface. Diffusion of oxygen through a frozen boundary layer and chemical equilibrium in the equilibrium layer have been assumed to control the rate of mass loss of carbon. Equations have been derived for the species mass fractions and mass injection parameters as well as for the heat and mass transfer rates. It has been demonstrated that:

1. The carbon mass injection parameter is independent of nitrogen injection in the diffusion-controlled regime and, in fact, depends only on the mass fraction of oxygen at the boundary-layer edge.

2. The only species present at the wall in significant quantities are nitrogen and carbon monoxide. Injection of nitrogen increases the wall mass fraction of nitrogen at the expense of the carbon monoxide mass fraction.

3. The injection of nitrogen affects heat transfer by reducing the heat transfer coefficient as a result of increased blowing into the boundary layer and through modifications of the enthalpy of gases at the wall.

4. When minimization of carbon surface recession is important, injection of nitrogen can substantially reduce the carbon mass loss.

Manned Spacecraft Center
National Aeronautics and Space Administration
Houston, Texas, March 23, 1967
914-50-10-01-72
REFERENCES


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—NATIONAL AERONAUTICS AND SPACE ACT OF 1958

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