Nonequilibrium Stagnation Point Boundary Layers with Arbitrary Surface Catalycity

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An approximate theory of nonequilibrium stagnation point boundary layer flow on highly cooled blunt bodies at hypersonic flight speeds, including a finite atom recombination rate on the surface, is presented. The analysis is based on a simplified nonlinear representation of the reaction rate distribution across the boundary layer which is derived from the fact that recombination near the wall dominates the nonequilibrium behavior when the wall is highly cooled. Closed-form solutions for the conditions at the gas/solid interface, such as atom concentration at the wall and heat transfer, are obtained in terms of a universal function of a single, composite Damköhler number. This number represents the combined effects of homogeneous and heterogeneous reaction over a wide range of the various thermochemical parameters involved. The theory is found to be in good agreement with the numerical results for nonequilibrium flow reported by Fay and Riddell.

Nomenclature

C = Chapman-Rubesin constant, $\rho\mu/\rho_s\mu_s$
C_p = specific heat
G = reaction rate distribution function, Eq. (5)
g_z, g_θ = boundary layer distribution functions defined in Eqs. (12) and (14)
H_D = $\alpha_s Le\, h_D/C_{p,M}T_s$
h_D = specific dissociation energy of molecules
I = Pohlhausen boundary layer integral, Eq. (15)
$\mathcal{I}_z, \mathcal{I}_\theta,$ = boundary layer reaction rate integrals, Eq. (16)
$\mathcal{I}_{z,F_1}, \mathcal{I}_{z,F_2}, \mathcal{I}_{z,F_3}$ = reaction rate integrals for frozen flow, Eq. (29) and Fig. 5
K_w = speed of catalytic atom recombination on body surface
k_r' = recombination rate constant
Le = Lewis number, Pr/Sc
Pr = Prandtl number
p = static pressure
Q_w = nondimensional heat transfer rate, Eq. (9)
$\dot{q}_w$ = surface heat transfer rate per unit area
R_b = nose radius of curvature, Fig. 1
R_m = molecular gas constant
R_u = universal gas constant
$\mathcal{R}$ = net reaction rate distribution function ($= \theta^{\omega-2}G$)
r_0 = local body radius, Fig. 1
Sc = Schmidt number
T = absolute temperature
u = velocity component parallel to body
V_∞ = freestream velocity
v = velocity component normal to body
x = distance along body
y = distance normal to body
Z = $z(0)/z_F(0)$, see Eq. (30)
z = α/α_s
α = atom mass fraction
β = inviscid flow stagnation point velocity gradient, $(du/dx)_s$
Γ = Damköhler number for gas-phase recombination, Eq. (4)
Γ^* = composite Damköhler number for combined gas phase surface reaction, Eq. (31)
ϵ = see Eq. (1)
ζ_w = Damköhler number for surface reaction, Eq. (8)
η = boundary layer similarity coordinate, Eq. (1)
θ = T/T_s
θ_D = $h_D/(R_M T_s)$
μ = coefficient of viscosity
ρ = mixture density
ω = recombination rate temperature-dependence exponent, $k_r = k_r' T^\omega$

Subscripts

A = denotes atom
eq = value for equilibrium boundary layer flow
F = value for frozen boundary layer flow
M = denotes molecule
s = inviscid flow conditions at stagnation point
w = conditions on body surface

I. Introduction

Significant departure from chemical equilibrium can occur in the flow around a blunt- or sharp-nosed hypersonic body at high altitudes.[1, 2] Consequently, there is considerable interest in the theory of nonequilibrium-dissociated laminar boundary layer flows, since the chemical state within the boundary layer can have an important bearing on vehicle heat transfer and the observables in the wake. Mathematically, the problem is a formidable one for chemical reactions of practical interest, and exact solutions must be carried out on a digital computer. Unfortunately, the numerical results available from existing solutions[3-7] are confined to a relatively few specific cases and are insufficient to determine the underlying functional dependence of the nonequilibrium boundary layer properties on the important thermochemical parameters. Moreover, the effect of a finite gas-phase recombination-dissociation rate has been treated only for a surface that is either perfectly catalytic or noncatalytic with respect to atom recombination, although it is clear from these limiting cases that intermediate degrees of surface catalycity can have a profound effect on nonequilibrium boundary layer properties, such as heat transfer. In view of these limitations, an approximate theory of nonequilibrium boundary layer flow which yields closed-form solutions over a wide range of parametric conditions and takes into account the simultaneous effects of homogeneous and heterogeneous reaction would be very useful.

It has been shown[8] that the chemical state of the boundary layer (in the absence of significant viscous dissipation) is controlled mainly by the recombination rate near the wall when the wall is highly cooled. Exploiting this fact, Chung and Liu[9] recently have proposed an approximate solution for nonequilibrium stagnation point heat transfer on highly cooled bodies with arbitrary surface catalycity in which the

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boundary layer is considered to be chemically frozen and the gas-phase reaction is treated as an equivalent second-order recombination rate taking place entirely on the surface. Although this theory is very useful and has the virtue of great simplicity, it provides only a gross representation of the effect of the highly nonlinear recombination-dissociation reaction distribution across the boundary layer. Furthermore, this approach remains semiempirical because it involves an arbitrary unknown constant that must be obtained by a matching with existing numerical solutions.

In the present paper, a more detailed study of nonequilibrium stagnation point boundary layers with arbitrarily catalytic, nonablating surfaces is given wherein the actual distribution of the net recombination-dissociation reaction rate across the boundary layer is considered. The basic assumptions and the governing flow equations in the similarity coordinate first are set forth for a gas that is a binary mixture of atoms and molecules. Some very useful general features of the nonequilibrium boundary layer are observed by formally integrating these flow equations across the boundary layer and by examining the nature of the net reaction rate distribution throughout the gas. Physical arguments, supported by previously obtained exact solutions in the limiting case of nearly frozen flow,[10–12] then are advanced to show that the analytical representation of the reaction rate distribution can be simplified conveniently for highly cooled walls with small resultant error in the surface properties. The essential nonlinear features of this distribution are, however, retained. As a result, simple closed-form solutions for all the nonequilibrium boundary layer properties at the wall are obtained with arbitrary surface catalycity. It is shown that this approximate theory, which involves no arbitrary correlation constants, *predicts* very well the numerical results for nonequilibrium flow reported by Fay and Riddell.[4] Finally, on the basis of the theory, the relative sensitivity of stagnation boundary layer properties to the homogeneous and heterogeneous reaction rates will be discussed.

II. Basic Relations

A. Assumptions

Consider laminar boundary layer flow of a nonequilibrium-dissociated gas at the stagnation point of a two-dimensional or axially symmetric body (Fig. 1). The body is taken to be highly cooled and nonablating with a first-order atom recombination rate on the surface. Furthermore, in order to retain only those features that are of primary importance concerning the nonequilibrium behavior, the following simplifying assumptions are made:

1) The gas is, or can be approximated by, a binary gas mixture composed of atoms (mass fraction α) and molecules.

2) The inviscid flow is in dissociation equilibrium at the edge of the boundary layer.

3) The Prandtl number, the Schmidt number, and the product of density and viscosity are each constant across the boundary layer.

4) The atomic and molecular specific heats are equal and constant: $C_{p,A} = C_{p,M} = \text{const.}$†

5) The stream function given by the self-similar solution to the momentum equation is approximated satisfactorily by the Blasius function.

6) Thermal diffusion effects are negligible.

The binary gas model is exact in the case of pure diatomic gases. Moreover, it is known to be a fairly good representation of high temperature, nonequilibrium-dissociated air in the absence of ablation products or any thermally significant ionization[7] when appropriately averaged thermochemical properties are used.[1, 4, 12] Assumption 2 has been shown to be substantially correct for highly cooled blunt bodies in hypersonic flow throughout the nonequilibrium boundary layer flow regime.[13] That is, the effect of nonequilibrium relaxation in the inviscid flow behind the bow shock is significant only when the boundary layer is almost completely frozen. Assumption 2 was implicit in the analysis of Fay and Riddell. Assumption 3 tends to break down for highly dissociated gases because $\rho\mu$ and Sc both are affected strongly by dissociation through the compressibility term in the thermal equation of state.[14] However, each of the assumptions 3–6 generally appears to be a satisfactory engineering approximation in analyzing nonablating, highly cooled boundary layers in air, unless the finer details of the temperature and composition profiles are of interest.[6, 15–19] Of course, the justification of these approximations actually rests on numerical results given by frozen or equilibrium flow solutions. However, it will be shown subsequently in this paper that the influence of variable $\rho\mu$ and the effect of both the Schmidt number and $C_{p,A} - C_{p,M}$ on the nonequilibrium conditions at the surface, as well as the effect of the velocity gradient term in the momentum equation, are, in fact, negligible for most practical applications.

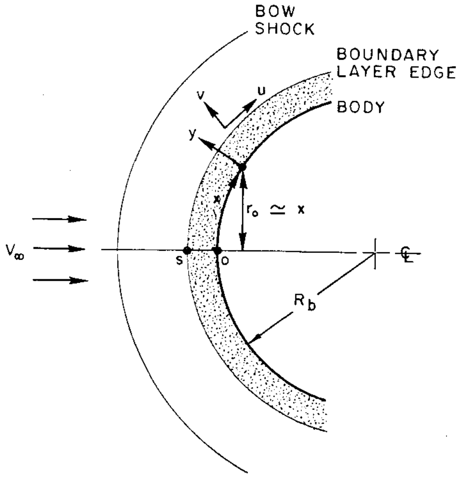

Fig. 1 Flow configuration.

B. Governing Equations

Since the nonequilibrium boundary layer is known to be self-similar at the stagnation point of a symmetric body, it is appropriate to formulate the governing equations in terms of the similarity coordinate:

$$\eta \equiv \left(\frac{\rho_s(1+\epsilon)\beta}{C\mu_s}\right)^{1/2} \int_0^y \frac{\rho}{\rho_s}\,dy \qquad \begin{matrix} \epsilon = 0, \text{ two-dimensional} \\ \epsilon = 1, \text{ axisymmetric} \end{matrix} \tag{1}$$

where $\beta = (du/dx)_s$ and $C = \rho\mu/\rho_s\mu_s = \text{const.}$ Using the foregoing assumptions, the resulting boundary layer equations for conservation of atom mass and energy are[4]

$$Sc\, fz' + z'' = [\alpha_s/(1+\alpha_s)]\Gamma\mathcal{R}(z,\theta) \tag{2}$$

$$Pr\, f\theta' + \theta'' = -[\alpha_s/(1+\alpha_s)]\Gamma H_D\mathcal{R}(z,\theta) \tag{3}$$

where a prime denotes differentiation with respect to η, $f(\eta)$ is the Blasius function, $z \equiv \alpha/\alpha_s$, $\theta \equiv T/T_s$, and $H_D \equiv \alpha_s Le\, h_D/C_{p,M}T_s$, with h_D the dissociation energy. The function $\mathcal{R}(z,\theta)$ is a nondimensional net reaction rate defined below and

$$\Gamma \equiv \frac{4k_r' T_s^{\omega-2} Sc}{(1+\epsilon)B_s}\left(\frac{p_s}{R_u}\right)^2 \tag{4}$$

is a characteristic (flow time/recombination time) ratio or gas-phase Damköhler number for the boundary layer.[4] For

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† This is equivalent to the assumption that the energy in molecular rotation and vibration is negligible compared with the sum of the energies in translation and dissociation.

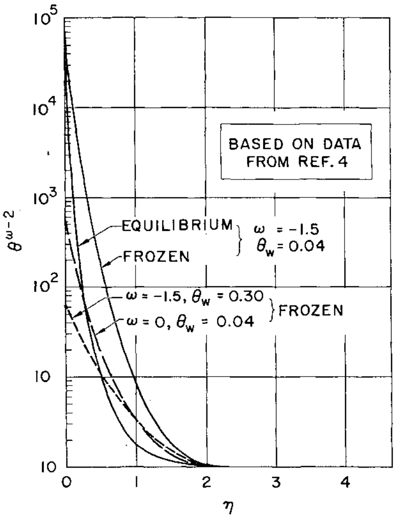


Fig. 2 Typical distribution of temperature-dependent part of recombination rate across the boundary layer.

a mixture of atoms and molecules undergoing the dissociation-recombination reaction

$$A_2 + X \underset{Kr}{\overset{Kd}{\rightleftharpoons}} 2A + X$$

where A_2, A, and X denote a molecule, atom, and any third body, respectively,[‡] and $K_r = k_r' T^{\omega}$ is the recombination rate, $\mathcal{R}(z,\theta)$ can be written as[4]

$$\mathcal{R}(z,\theta) \equiv \theta^{\omega-2} \cdot G(z,\theta) = \theta^{\omega-2} \left(\frac{1+\alpha_s}{1+\alpha_s z}\right) \times \left\{ \underbrace{z^2}_{\text{recombination}} - \underbrace{\left(\frac{1-\alpha_s^2 z^2}{1-\alpha_s^2}\right) \exp\left[\frac{-\theta_D}{\theta}(1-\theta)\right]}_{\text{dissociation}} \right\} \quad (5)$$

with $\theta_D = h_D/R_m T_s$ as the nondimensional dissociation temperature. The function $\theta^{\omega-2}$ in Eq. (5) represents the effect of the varying temperature on the recombination rate (and pre-exponential portion of the dissociation rate). In view of the current evidence that $\omega \simeq -1.5$ for air and most diatomics,[20, 21] this effect has a considerable influence on the nonequilibrium behavior in a highly cooled boundary layer. The function $G(z,\theta)$ represents the composition-dependent part of the net atom reaction rate in the boundary layer and involves a contribution from both the local recombination and dissociation rates, as indicated. Moreover, this function has the important property of vanishing identically when the boundary layer is in complete equilibrium ($\Gamma \to \infty$); it is not zero, however, in the opposite extreme of chemically frozen flow ($\Gamma \to 0$).[§]

The boundary conditions to be imposed on the solution to Eqs. (2) and (3) are as follows:

$$z(\infty) = \theta(\infty) = 1 \quad (6)$$

$$\theta(0) = \theta_w \text{ (given)} \quad (7)$$

and

$$z'(0) = \underbrace{\frac{Sc\,K_w}{\mu_w}\left(\frac{2C\rho_s\mu_s}{(1+\epsilon)\beta}\right)^{1/2}}_{\zeta_w} z(0) \quad (8)$$

where K_w is the speed of atom recombination on the surface (a known function of the wall temperature and material) with units of velocity and simply is related to the surface catalytic efficiency γ by $\gamma = K_w(\pi/R_m T_w)^{1/2}$. The ζ_w parameter is a characteristic (diffusion time/surface recombination time) or Damköhler number for catalytic surface reaction.[16, 22, 23] The boundary condition (8) expresses the fact that the rate of diffusion of atoms from the gas to the wall is balanced by the rate of recombination on the wall surface due to catalytic reaction.[‖] When $\zeta_w \to \infty$, the surface is completely catalytic [$z(0) = 0$], whereas in the other extreme, $\zeta_w = 0$, the surface is noncatalytic and the atom diffusion into the wall vanishes [$z'(0) = 0$]. In what follows, arbitrary values of ζ_w are considered.

Once Eqs. (2–8) are solved for the atom concentration and temperature distributions, the surface heat transfer rate may be computed from

$$-\frac{Pr\,\dot{q}_w/C_{p,M}T_s}{\{[(1+\epsilon)/2)]C\rho_s\mu_s\beta\}^{1/2}} \equiv Q_w = \underbrace{\theta'(0)}_{\text{conduction}} + \underbrace{H_D z'(0)}_{\text{diffusion}} \quad (9)$$

Clearly, only heat conduction contributes to the heat transfer when the wall is completely noncatalytic or when the energy in dissociation is negligible.

C. Some General Features of the Nonequilibrium Boundary Layer

In view of the highly nonlinear reaction rate terms in Eqs (2) and (3), it is clear that in the presence of dissociation-recombination nonequilibrium the composition and temperature profiles across the boundary layer must be obtained by a numerical solution using a digital computer. However, some very useful information about the nonequilibrium boundary layer behavior can be obtained without actually solving (2) and (3) by performing a purely formal double integration of these two equations with respect to η. (Moreover, these integral relations form the basis of an approximate solution for the conditions at the surface, as will be shown below.) Carrying out this integration, then, and applying boundary conditions (6–8), one obtains, after considerable algebraic rearrangement,

$$z(\eta) = z_F(\eta) - \frac{\alpha_s\Gamma}{1+\alpha_s}[z_F(\eta)\mathcal{J}_z(\infty) - \mathcal{J}_z(\eta)] \quad (10)$$

$$\theta(\eta) = \theta_F(\eta) + \frac{\alpha_s\Gamma H_D}{1+\alpha_s}\left\{\left[\frac{\theta_F(\eta)-\theta_w}{1-\theta_w}\right]\mathcal{J}_\theta(\infty) - \mathcal{J}_\theta(\eta)\right\} \quad (11)$$

where

$$z_F(\eta) = z_F(0) + \frac{z_F'(0)}{0.47\,Sc^{1/3}}\underbrace{\left[\frac{I_z(\eta)}{I_z(\infty)}\right]}_{g_z(\eta)} \quad (12)$$

$$z_F(0) = \frac{z_F'(0)}{\zeta_w} = [1 + \zeta_w I_z(\infty)]^{-1} \quad (13)$$

$$\theta_F(\eta) = \theta_w + (1-\theta_w)\underbrace{\left[\frac{I_\theta(\eta)}{I_\theta(\infty)}\right]}_{g_\theta(\eta)} \quad (14)$$

are the frozen flow solutions ($\Gamma = 0$) for arbitrary surface catalycity obtained by Goulard.[16] Here,

$$I_z(\eta) \equiv \int_0^\eta \exp\left(-Sc\int_0^\eta f d\eta\right) d\eta \quad (15)$$

[‡] Here, the recombination efficiencies of A and A_2 are taken to be equal.

[§] In accordance with assumption 2, note that $G(z,\theta)$ is always zero at the edge of the boundary layer ($z = \theta = 1$), regardless of Γ.

[‖] It should be noted that the rate law used in obtaining (8) neglects the back (dissociation) reaction on the surface, which is consistent with the present restriction to highly cooled walls.[16, 22, 24]

$$\mathcal{J}_z(\eta) \equiv \int_0^\eta \exp\left(-Sc\int_0^\eta f d\eta\right) \times \left[\int_0^\eta \exp\left(Sc\int_0^\eta f d\eta\right) \mathcal{R} d\eta\right] d\eta \qquad (16)$$

whereas I_θ and $\mathcal{J}_\theta$ are obtained from (15) and (16), respectively, simply by replacing Sc by Pr in the exponentials involving $\int f d\eta$.# Evaluating (10) and (11) at the wall, the following general integral relationships are obtained for the nonequilibrium boundary layer with any degree of surface catalycity:

$$\frac{z(0)}{z_F(0)} = \frac{z'(0)}{z_F'(0)} = 1 - \frac{\alpha_s\Gamma}{1+\alpha_s}\mathcal{J}_z(\infty) \qquad (17)$$

$$\theta'(0) = \frac{1-\theta_w + [\alpha_s\Gamma H_D/(1+\alpha_s)]\mathcal{J}_\theta(\infty)}{I_\theta(\infty)} = \frac{1-\theta_w}{I_\theta(\infty)} + \frac{H_D\mathcal{J}_\theta(\infty)}{I_\theta(\infty)\mathcal{J}_z(\infty)}\left[1 - \frac{z(0)}{z_F(0)}\right] \qquad (18)$$

From (9), the heat transfer then may be written as

$$Q_w = \frac{1-\theta_w}{I_\theta(\infty)} + \frac{\mathcal{J}_\theta(\infty)H_D}{I_\theta(\infty)\mathcal{J}_z(\infty)} + H_D\left[z_F'(0) - \frac{\mathcal{J}_\theta(\infty)}{I_\theta(\infty)\mathcal{J}_z(\infty)}\right]\frac{z(0)}{z_F(0)} \qquad (19a)$$

$$= Q_{w,F} + \frac{H_D}{I_\theta(\infty)}\left[\frac{\mathcal{J}_\theta(\infty)}{\mathcal{J}_z(\infty)} - I_\theta(\infty)z_F'(0)\right]\left[1 - \frac{z(0)}{z_F(0)}\right] \qquad (19b)$$

Now, although the reaction rate integrals $\mathcal{J}_z(\infty)$ and $\mathcal{J}_\theta(\infty)$ are unknown implicit functions of Γ and ζ_w, their ratio $\mathcal{J}_\theta(\infty)/\mathcal{J}_z(\infty)$ is exactly unity when $Le = 1 (Sc = Pr)$, regardless of the magnitude of the gas-phase or surface reactions. Therefore, inspection of Eq. (16) suggests that this *ratio* might remain essentially independent of both Γ and ζ_w when the Lewis number is not too far from unity. This conjecture indeed is verified, at least for highly cooled walls, by the numerical results obtained in Refs. 4 and 10. These results show that

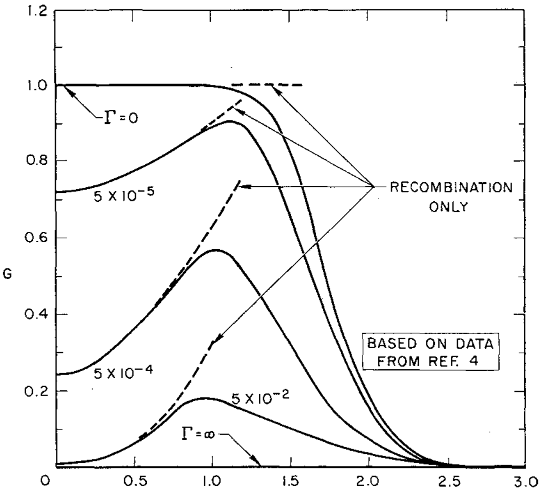
$$\begin{aligned} \mathcal{J}_\theta(\infty)/\mathcal{J}_z(\infty) &\cong Le^{-0.48} \quad \Gamma \to \infty,\ \zeta_w \text{ arbitrary; Ref. 4} \\ &\cong Le^{-0.45} \quad \Gamma \ll 1,\ \zeta_w = 0 \text{ or } \infty\text{; Ref. 10} \end{aligned} \qquad (20)$$

In view of the close agreement of the exponents for these two divergent cases, it appears reasonable to regard $\mathcal{J}_\theta(\infty)/\mathcal{J}_z(\infty)$ as a weak function of Le only in the present analysis. Consequently, since $Z(0)_{\text{eq}} \simeq 0$ for cooled walls,[4] the first two terms on the right sides of Eqs. (18) and (19a) may be identified as the equilibrium wall temperature gradient and heat transfer, respectively. Equations (17–19), therefore, yield a very simple relationship between the following nondimensional ratios:

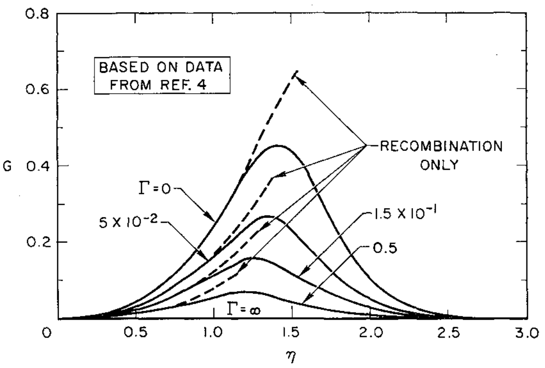
$$1 - \frac{z(0)}{z_F(0)} = 1 - \frac{z'(0)}{z_F'(0)} = \frac{\theta'(0) - \theta_F'(0)}{\theta'_{\text{eq}}(0) - \theta_F'(0)} = \frac{Q_w - Q_{w,F}}{Q_{w,\text{eq}} - Q_{w,F}} \qquad (21)$$

regardless of the values of Sc, Pr, ζ_w, or Γ. Equation (21) indicates that the solution to the species conservation equation (2) is sufficient to determine all the nonequilibrium conditions at the surface once the frozen and equilibrium values are known. The latter properties are available in the literature[4,15–18] or can be computed from Eqs. (13 and 18–20). For a highly cooled wall, Eq. (21) is a direct result of assumptions 1–6. In this connection, it may be noted that the first two equalities in (21) are valid for any $\rho\mu$ law provided that $Le = 1$ and $C_{p,A} = C_{p,M} =$ const, as may be shown readily from the general boundary layer equations. On the other hand, the third equality involving the heat transfer entails the additional assumption $\rho\mu =$ const.

Equations (17–19) show that the effect of nonequilibrium reaction on the boundary layer properties at the surface arises from a double integral of the net reaction rate $\mathcal{R}(z,\theta) = \theta^{\omega-2}\cdot G(z,\theta)$ across the boundary layer. Therefore, a closer examination of this function is indicated in order to determine the relative influence of recombination and dissociation on the nonequilibrium behavior and how this influence depends on the degree of surface cooling and catalycity. Accordingly, some typical distributions of the functions $\theta^{\omega-2}$ and G are plotted in Figs. 2 and 3, respectively.[4] It is seen that, unless the boundary layer is quite close to equilibrium, the contribution of the exponential dissociation term to G is negligible throughout the inner half of the boundary layer for highly cooled walls, regardless of the wall catalycity. Correspondingly, $\theta^{\omega-2}$ increases from unity at the edge of the boundary layer to an extremely large value at the wall, with most of this sharp increase occurring near the wall (Fig. 2). Consequently, for highly cooled walls, the major contribution to the reaction rate integrals $\mathcal{J}_z(\infty)$ and $\mathcal{J}_\theta(\infty)$ throughout most of the nonequilibrium flow regime comes from the magnitude of $\theta^{\omega-2}$ and the function G in the recombination-dominated gas region near the wall.[8] It will be the aim of the present paper to exploit this situation by obtaining simplified yet realistic approximations to the reaction rate function $\mathcal{R}(z,\theta)$ such that the foregoing integral relations can be solved analytically.



a) Noncatalytic wall, $\zeta_w = 0$



b) Catalytic wall, $\zeta_w = \infty$

Fig. 3 Typical distribution of composition-dependent part of net dissociation-recombination reaction rate across nonequilibrium stagnation boundary layer ($\theta_w = 0.04$, $\theta_D = 10$, $\omega = -1.5$, $Pr = 0.70$, $Le = 1.4$, $\alpha_s = 0.536$).

$I_z(\infty) \cong (0.47\ Sc^{1/3})^{-1}$.

III. Approximate Solution for Surface Properties

A. Analysis

As a preliminary step in dealing with the complete nonequilibrium flow regime, it is helpful first to consider the case of small departures from frozen flow ($\Gamma \ll 1$) for which exact solutions to Eqs. (10) and (11) have been obtained.[10, 12] In this nearly frozen limit, the first-order nonequilibrium solution is given by evaluating the reaction rate function $\mathcal{R}$ and the corresponding integrals $\mathcal{I}_z$ and $\mathcal{I}_\theta$ using the frozen flow solutions (12) and (14).

These solutions were carried out for either a completely catalytic or noncatalytic surface over a wide range of values of θ_w, ω, θ_D, Sc, and Le.** A detailed study of the results clearly indicated that the major contribution to the reaction rate integrals $\mathcal{I}_z(\infty)$ and $\mathcal{I}_\theta(\infty)$ comes from the atom recombination rate in the gas near the wall when the wall is highly cooled. Moreover, the magnitude of these integrals was found to be approximately proportional to $[(1+\alpha_s)/(1+\alpha_s z_w)]\theta_w^{\omega-2}$. Correspondingly, it was observed that the contribution of the exponential dissociation term in Eq. (5), although not altogether negligible, is relatively small compared to that of the recombination term and is dependent only weakly on the parameters θ_w and θ_D. These results are in accord with the properties of the function $\mathcal{R}$ previously observed from Figs. 2 and 3.

For the purpose of determining the conditions at the surface, the foregoing conclusions suggest that one can make some convenient simplifications in the reaction function G when the wall is highly cooled, regardless of the surface catalycity. Specifically, it was found that the approximations

$$\frac{1+\alpha_s}{1+\alpha_s z} \simeq \frac{1+\alpha_s}{1+\alpha_s z(0)} \tag{22}$$

$$z^2 - \left(\frac{1-\alpha_s{}^2 z^2}{1-\alpha_s{}^2}\right)\exp\left[-\frac{\theta_D(1-\theta)}{\theta}\right] \simeq z^2\left\{1-\exp\left[-\frac{\theta_D(1-\theta)}{\theta}\right]\right\} \tag{23}$$

when used in (5), yield values of $\mathcal{I}_{z,F}(\infty)$ and $\mathcal{I}_{\theta,F}(\infty)$ within 15% or less of the exact solutions for a completely catalytic surface provided that $\theta_w \lesssim 0.30$.†† These approximations permit the effect of arbitrary surface catalycity to be treated explicitly in the presence of nonequilibrium homogeneous reaction. [Moreover, (23) proves a key simplification in subsequently extending the near-frozen solution to arbitrary values of Γ.] Now, approximations (22) and (23) rest on the fact that the chemical behavior in the boundary layer is controlled by the large recombination rate in the cold gas near the wall and is relatively insensitive to the detailed shape of the dissociation rate distribution. Therefore, since it was shown previously that this situation holds true for most of the nonequilibrium flow regime, (22) and (23) need not be restricted to small values of Γ as far as the determination of surface properties is concerned. Furthermore, since it is the recombination rate distribution near the surface which chiefly determines the magnitude of the overall reaction rate integrals, an accurate representation of the function G needs to be made only in the neighborhood of the wall. Thus, to carry the nearly frozen solution forward (approximately) to arbitrary Γ, one may in conjunction with (22) and (23) conveniently take

$$z(\eta) \simeq z(0) + [z'(0)/0.47\ Sc^{1/3}]g_z(\eta) \tag{24}$$

$$\exp[-(\theta_D/\theta)(1-\theta)] \simeq \exp[-(\theta_D/\theta_F)(1-\theta_F)] \tag{25}$$

for the purpose of approximating $G(\eta)$, where $z(0)$ and $z'(0)$ are the unknown surface properties to be found. Equation (24) is exact at sufficiently small η when Γ is arbitrary; it also becomes exact at all η in the limit of nearly frozen flow. Equation (25) is a fairly good approximation to the nonlinear dissociation rate distribution across the boundary layer for all Γ, because the error involved occurs mainly in the outer portion of the boundary layer, where $\theta(\eta) - \theta_F(\eta)$ is small. Finally, a convenient approximation to the highly nonlinear recombination rate temperature-dependence term for a cooled wall can be taken as

$$\theta^{\omega-2}(\eta) \simeq \theta_F{}^{\omega-2}(\eta) \tag{26}$$

This approximation is suggested by Fig. 2, where it is seen that much of the contribution of $\theta^{\omega-2}$ to $\mathcal{I}_z(\infty)$ comes from the very large value of $\theta_w{}^{\omega-2}$ rather than from the finer details of the distribution across the boundary layer. To be sure, some of the effect of $\theta^{\omega-2}$ near the wall derives from $\theta'(0)$ as well as θ_w. Since $\theta'(0)$ is affected significantly by gas-phase reaction, (26) *by itself* therefore becomes a progressively poorer approximation with increasing Γ and is unsatisfactory for nearly equilibrium flow (Fig. 2). However, as shown below, this error is suppressed to a great extent by the corresponding approximation for the function G, such that the resulting approximation for the *net* reaction rate $\mathcal{R}$ is actually quite good throughout the entire nonequilibrium flow regime. Moreover, it has been shown that approximation (26) leads to a good correlation of wall temperature effect on nonequilibrium heat transfer to noncatalytic surfaces.[8]

The foregoing approximations lead to a vastly simplified solution for the nonequilibrium conditions at the gas/solid interface. Substituting Eqs. (22–26) into (5), the net reaction rate distribution may be written (approximately) as

$$\mathcal{R} \simeq \left[\frac{1+\alpha_s}{1+\alpha_s z(0)}\right]\theta_F{}^{\omega-2}\left\{z^2(0) + \frac{2z(0)z'(0)}{0.47\ Sc^{1/3}}\cdot g_z + \left[\frac{z'(0)g_z}{0.47\ Sc^{1/3}}\right]^2\right\}\left\{1-\exp\left[-\frac{\theta_D}{\theta_F}(1-\theta_F)\right]\right\} \tag{27}$$

which correctly vanishes at the edge of the boundary layer.‡‡ This approximation also preserves the correct value of $z''(0)$, which has been shown to be essential for a proper analysis of the nonequilibrium boundary layer.[6, 25] Now, using Eq. (27) in (16), the overall reaction rate integral $\mathcal{I}_z(\infty)$ becomes

$$\mathcal{I}_z(\infty) \cong \left[\frac{1+\alpha_s}{1+\alpha_s z(0)}\right]\left\{z^2(0)\mathcal{I}_{z,F_1} + \frac{2z(0)z'(0)}{0.47\ Sc^{1/3}}\cdot\mathcal{I}_{z,F_2} + \left[\frac{z'(0)}{0.47\ Sc^{1/3}}\right]^2\mathcal{I}_{z,F_3}\right\} \tag{28}$$

Table 1 Tabulation of the reaction rate integrals vs θ_w for $\theta_D = 5$, $\omega = -1.5$, and $Sc = 0.50$

θ_w	I_{z,F_1}	I_{z,F_2}	I_{z,F_3}
0.04	8.2×10^3	1.8×10^2	1.4×10
0.10	8.4×10^2	5.2×10	6.5
0.15	3.2×10^2	2.7×10	4.6
0.20	1.6×10^2	1.7×10	3.5
0.25	9.4×10	1.13×10	2.8
0.30	6.2×10	8.2	2.35

** A discussion of these solutions and the highly cooled wall approximations that they suggested also may be found in Ref. 11.

†† Equations (22) and (23) are exact for nearly frozen flow on a noncatalytic wall. On the other hand, (23) only slightly underestimates the contribution of the dissociation term to $G(z,\theta)$ for highly cooled catalytic surfaces (Fig. 3).

‡‡ Moreover, since $z(0)_{\text{eq}}$ and $z'(0)_{\text{eq}}$ are both essentially zero at a highly cooled wall, Eq. (27) correctly vanishes throughout the boundary layer when $\Gamma \to \infty$. Consequently, (27) should yield reasonable solutions for the properties at the surface, even when $\Gamma \gg 1$.

where

$$\vartheta_{z,F_1} \equiv \int_0^\infty \exp\left(-Sc\int_0^\eta f d\eta\right) \times \left[\int_0^\eta \exp\left(Sc\int_0^\eta f d\eta\right) \theta_F^{\omega-2} \times \left\{1 - \exp\left(-\frac{\theta_D}{\theta_F}(1-\theta_F)\right)\right\} d\eta\right] d\eta \tag{29a}$$

$$\vartheta_{z,F_2} \equiv \int_0^\infty \exp\left(-Sc\int_0^\eta f d\eta\right) \times \left[\int_0^\eta \exp\left(Sc\int_0^\eta f d\eta\right) \theta_F^{\omega-2} \times \left\{g_z(\eta) - \exp\left(-\frac{\theta_D}{\theta_F}(1-\theta_F)\right)\right\} d\eta\right] d\eta \tag{29b}$$

$$\vartheta_{z,F_3} \equiv \int_0^\infty \exp\left(-Sc\int_0^\eta f d\eta\right) \times \left[\int_0^\eta \exp\left(Sc\int_0^\eta f d\eta\right) \theta_F^{\omega-2} \times \left\{g_z^2 - \exp\left(-\frac{\theta_D}{\theta_F}(1-\theta_F)\right)\right\} d\eta\right] d\eta \tag{29c}$$

are reaction rate integrals that depend only on the frozen flow solution (values are given below). Substitution of (28) into Eq. (17) now yields a simple quadratic equation for the nonequilibrium atom concentration (and diffusion) at the wall with any degree of surface catalycity:

$$Z \equiv \frac{z(0)}{z_F(0)} = \frac{z'(0)}{z_F'(0)} = 1 - \frac{\Gamma^* Z^2}{1 + \alpha_s z_F(0) Z} \tag{30}$$

where

$$\Gamma^* \equiv \alpha_s \left[\frac{\vartheta_{z,F_1} + (2\zeta_w \vartheta_{z,F_2}/0.47\,Sc^{1/3}) + (\zeta_w/0.47\,Sc^{1/3})^2 \vartheta_{z,F_3}}{[1 + (\zeta_w/0.47\,Sc^{1/3})]^2}\right] \cdot \Gamma \tag{31}$$

is a composite Damköhler number representing the simultaneous effects of the finite gas-phase and surface reaction rates, as well as the influence of wall temperature and all the thermochemical properties of the gas. With the solution to (30) known, the remaining conditions at the surface can be computed from Eq. (21). The solution to (30) is

$$Z = \frac{\{[1 + \alpha_s z_F(0)]^2 + 4\Gamma^*\}^{1/2} - [1 - \alpha_s z_F(0)]}{2[\alpha_s z_F(0) + \Gamma^*]} \tag{32}$$

and is plotted vs $\alpha_s z_F(0)$ and Γ^* in Fig. 4. It may be seen from this graph that the $\alpha_s z_F(0)$ term (which depends on ζ_w) has a very small effect on the variation of Z with Γ^*. Hence, to a good approximation, the ratios (21) may be considered to be a universal function of the single parameter Γ^* regardless of the individual homogeneous or heterogeneous reaction rates when the surface is highly cooled. In the limit $\Gamma \ll 1$, Eq. (32) reduces to

$$Z = 1 - \{\Gamma^*/[1 + \alpha_s z_F(0)]\} \tag{33}$$

which can be shown to agree exactly with the nearly frozen nonequilibrium solution for a completely noncatalytic wall and to be within 15% or less of the exact nearly frozen solution for a catalytic wall when $\theta_w \lesssim 0.3$.[10–12] On the other hand, when $\Gamma \gg 1$, Eq. (32) yields

$$Z = (\Gamma^*)^{-1/2} \sim \Gamma^{-1/2} \tag{34}$$

which has been shown to be the correct dependence on Γ in the asymptotic approach to equilibrium of a highly cooled boundary layer.[10]

Numerical values of the three frozen reaction rate integrals (29) have been computed and are presented in Figs. 5a–5c, respectively, as a function of θ_w, θ_D, and ω for $Sc = 0.50$. (Tabular values for $\theta_D = 5$, $\omega = -1.5$, and $Sc = 0.5$ are given as a function of θ_w in Table 1.) The corresponding Schmidt number dependence, which is weak, also is indicated. These integrals increase rapidly with either decreasing ω or θ_w but are relatively insensitive to large changes in θ_D when $\omega < 0$ and $\theta_w \ll 1$. However, for $\theta_w \gtrsim 0.30$, they become increasingly sensitive to θ_D, particularly ϑ_{z,F_3}. This indicates a growing influence of the dissociation rate distribution relative to the effect of recombination in the gas. Since it is implicit in the present analysis that the effect of dissociation (θ_D) is relatively small, Eq. (28) becomes a progressively poorer approximation for highly catalytic surfaces ($\zeta_w > 1$) when $\theta_w \gtrsim 0.3$ and $\theta_D \lesssim 10$. On the other hand, for slightly catalytic surfaces ($\zeta_w < 1$), this approximation appears to be a satisfactory one up to wall temperatures as high as $\theta_w = 0.50$ provided that $\theta_D \gtrsim 5$ and $\omega < 0$.

B. Application of the Approximate Theory

The individual effects of the gas-phase and surface reaction rates on nonequilibrium boundary layer properties at the surface for any combination of the physical parameters are calculated easily from Eqs. (31) and (32) and Fig. 5. A typical result is illustrated in Fig. 6, where the ratio Z is plotted as a function of Γ and ζ_w for the case $\alpha_s = 0.536$, $\theta_w = 10$, $\theta_w = 0.04$, $Le = 1.4$, $Pr = 0.70$, and $\omega = -1.5$. This particular example enables a comparison with the numerical results for nonequilibrium flow in the two extremes of surface catalycity reported by Fay and Riddell, which also are shown in Fig. 6. It is seen that the simplified theory lies within 5 to 25% of Fay and Riddell's solutions for either $\zeta_w = 0$ or $\zeta_w = \infty$ throughout the nonequilibrium flow regime, the best agreement being for the atom concentration at a noncatalytic wall. The present theory predicts a slightly smaller spread between the curves for $\zeta_w = 0$ and $\zeta_w = \infty$ than does the Fay and Riddell theory. However, in view of the additional analytical simplifications that have been used here, namely, assumptions 3–5 and the highly cooled wall reaction rate approximations previously discussed, the agreement is quite satisfactory from an engineering standpoint.

In contrast to the present theory, the individual heat transfer, temperature gradient, atom concentration gradient, and atom concentration ratios obtained by Fay and Riddell generally are not equal, particularly in the case of a noncatalytic wall. This is a direct consequence of the effects due to variable $\rho\mu$ and $C_{p,A} - C_{p,M}$ and to the pressure gradient term in the momentum equation, all of which were taken into account in Ref. 4. However, it is evident from Fig. 6 that these effects are not large and can indeed be neglected in obtaining engineering solutions for highly cooled nonequilibrium boundary layer surface properties, regardless of the surface catalycity.

It should be pointed out that much of the difference between the present theory and that of Ref. 4 for the case $\zeta_w =$

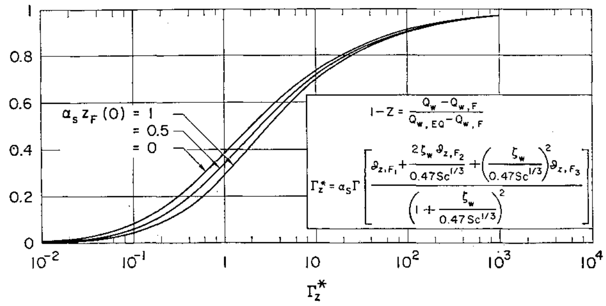
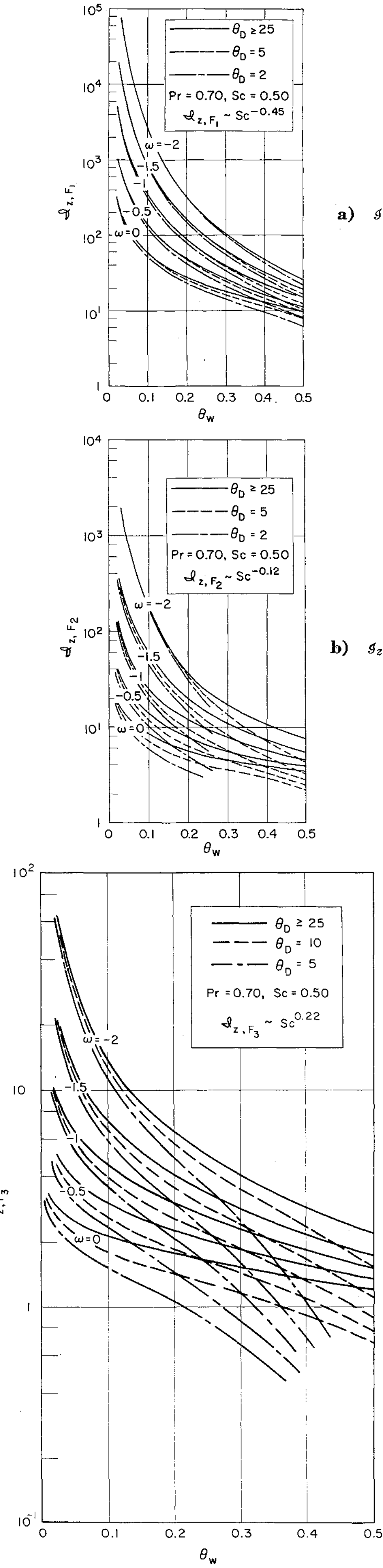


Fig. 4 Universal solution for nonequilibrium stagnation point boundary layer surface properties including arbitrary surface catalycity.



a) $\mathcal{I}_{z,F_1}$

b) $\mathcal{I}_{z,F_2}$

c) $\mathcal{I}_{z,F_3}$

Fig. 5 Reaction rate integrals, $\mathcal{I}_{z,F_{1,2,3}}$.

0 is due to assumptions 3–5 and should not be attributed to the highly cooled wall reaction rate approximations used herein (which are expected to be quite accurate for noncatalytic surfaces; see Figs. 3 and 5). This contention is corroborated further by the exact solutions for nearly frozen flow.[10, 11] On the other hand, for a completely catalytic surface $\zeta_w = \infty$, where the various surface property ratios obtained by Fay and Riddell are nearly equal, a far greater portion of the difference between their results and the present theory can be attributed to the highly cooled reaction rate approximations. Indeed, from Figs. 3 and 5, these approximations are seen to be the least accurate for large ζ_w (although still satisfactory for engineering purposes).

The relative sensitivity of the surface properties with respect to the homogeneous and heterogeneous reaction rates may be observed also in Fig. 6. As implied by Eqs. (31) and (32), these properties are dominated completely by the homogeneous dissociation-recombination rate when the surface catalycity is either very small ($\zeta_w \lesssim 0.1$) or very large ($\zeta_w \gtrsim 20$). However, when $\zeta_w \sim 0(1)$, the heterogeneous (catalytic surface) reaction rate has a profound effect unless the boundary layer is extremely close to dissociation equilibrium throughout. This is because the effect of the nonequilibrium homogeneous reaction rate is influenced strongly by a finite atom recombination rate on the surface through the boundary condition (8). Thus, increasing the surface catalycity substantially enhances the departure from equilibrium (or, equivalently, retards departure from frozen flow to larger Γ) by reducing the atom concentration near the wall and, hence, the gas-phase recombination rate. The sensitivity to surface reaction persists throughout most of the nonequilibrium flow regime, because the gas near the outer edge of the boundary layer comes into equilibrium first, with the region of equilibration extending inward toward the wall with increasing Γ. Therefore, the gas state near the wall, which primarily controls the boundary layer properties at the surface, approaches equilibrium rather slowly and remains influenced by the surface reaction rate up to rather large values of Γ.

The corresponding effect of homogeneous and heterogeneous reactions on the absolute stagnation heat transfer difference $Q_w - Q_{w,\text{eq}}$, as calculated from Fig. 6 and Eqs. (17, 19, and 20), is presented in Fig. 7. As expected, nonequilibrium heat transfer is very sensitive to the heterogeneous recombination rate at the surface when $\zeta_w \sim 0(1)$ unless the boundary layer is very close to equilibrium throughout. Heat transfer is also very sensitive to the gas-phase recombination rate when the wall is noncatalytic. However, this sensitivity decreases markedly as ζ_w increases and becomes negligible at large ζ_w since $(Q_{w,F} - Q_{w,\text{eq}})_{\zeta_w=\infty} \sim Le^{0.63} - Le^{0.52}$; thus, for $\zeta_w \gg 1$, heat transfer is controlled completely by the surface reaction rate unless $\Gamma \gg 1$. It may be concluded, then, that, when either one of the two reaction rates, homogeneous or heterogeneous, is very large, the heat transfer becomes independent of the remaining reaction rate. On the other hand, it is seen that a fiftyfold decrease in ζ_w produces the same overall decrease in heat transfer as does a thousandfold reduction of Γ for a noncatalytic wall. Consequently, the heat transfer is much more sensitive to changes in the surface reaction rate than to changes in the homogeneous dissociation-recombination rate. It may be noted that these conclusions are in qualitative agreement with the results of an earlier study of nonequilibrium Couette flow.[26]

IV. Conclusion

An approximate theory of nonequilibrium-dissociated stagnation boundary layers on highly cooled blunt bodies in hypersonic flow, including a finite first-order atom recombination rate on the surface, has been presented. A binary gas mixture model was employed. Closed-form relations for atom concentration, temperature and concentration

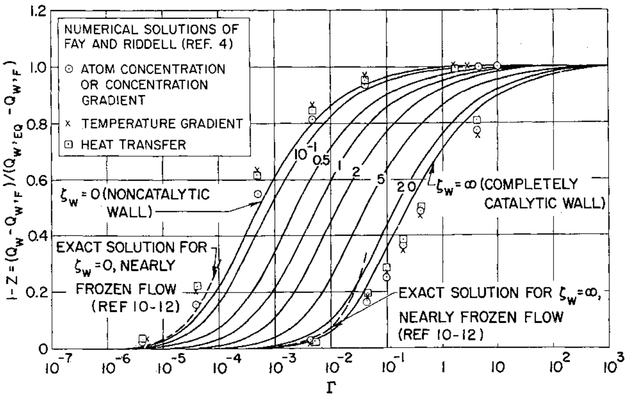


Fig. 6 Relative effect of gas-phase and catalytic surface reaction on nonequilibrium boundary layer properties ($\theta_w = 0.04, \theta_D = 10, \omega = 1.5, Pr = 0.70, \alpha_s = 1.4, \alpha_s = 0.536$).

gradients, and heat transfer at the wall were obtained through certain simplifying approximations in the analytical representation of the net dissociation-recombination rate distribution across the boundary layer. These approximations, which are supported by exact solutions obtained in the limiting case of nearly frozen flow, are derived from the fact that the nonequilibrium effect on boundary layer surface properties is controlled primarily by the gas-phase recombination near the wall when the wall is highly cooled ($\theta_w \lesssim 0.30$). Physical arguments appropriate to this situation yield an approximation for the boundary layer reaction rate distribution which reduces the nonlinear integral equations governing the surface properties to simple quadratic equations. The essential nonlinear features of the dissociation-recombination rate chemistry across the boundary layer are, however, retained.

According to the present analysis, all of the nondimensional ratios $(P - P_F)/(P_{eq} - P_F)$ (where P is any one of the forementioned surface properties) can be expressed to a good approximation in closed form as a common universal function of a single composite Damköhler number Γ^* that accounts for combined effects of homogeneous and heterogeneous reactions. A comparison of the present theory with the numerical results of Fay and Riddell in the two extremes of surface catalycity showed satisfactory agreement throughout the nonequilibrium flow regime. Moreover, it appears that much of the 5 to 25% discrepancy between the two theories can be ascribed to the effects of variable $\rho\mu$ and atom-molecule specific heat inequality included in Fay and Riddell's calculations. However, these effects are not large and can be neglected for the purpose of obtaining engineering-accuracy solutions for nonequilibrium boundary layer surface properties on highly cooled walls.

The present theory also provides a quantitative description of the effect of an arbitrary surface catalycity on nonequilibrium-dissociated stagnation boundary layer flows. It was found, for example, that, when either one of the two reaction rates (homogeneous or heterogeneous) is very large, the heat transfer becomes independent of the remaining rate. On the other hand, the heat transfer is more sensitive to changes in the catalytic reaction on the surface than to changes in the homogeneous dissociation-recombination rate.

The approximate, closed-form theory developed herein provides reasonably accurate engineering estimates of dissociated stagnation boundary layer surface properties for arbitrary rates of either the surface catalycity or the gas-phase dissociation-recombination rate provided that Lewis number is not too far from unity and that the wall is sufficiently highly cooled ($\theta_w \lesssim 0.30$). In this connection, it may be noted that the limitation $\theta_w \lesssim 0.30$ in fact does permit fairly high wall temperatures ($T_w \lesssim 1000°$ to 1500°K), so that the theory would serve a large number of anticipated hypersonic flight conditions.

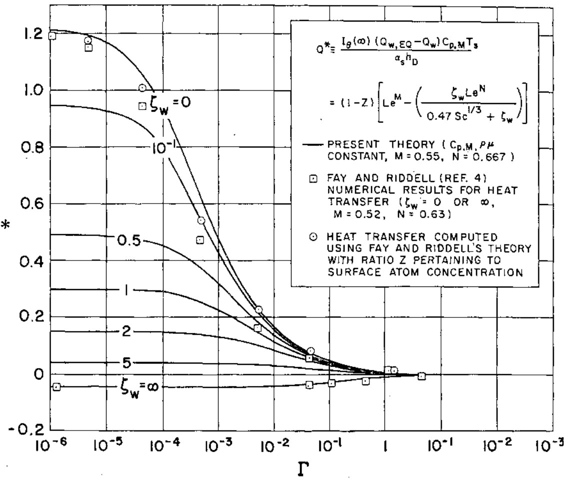


Fig. 7 Effect of surface catalycity on nonequilibrium stagnation heat transfer ($\theta_w = 0.04, \theta_D = 10, \omega = 1.5, Pr = 0.70, \alpha_s = 1.4, \alpha_s = 0.536$).

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Nonequilibrium Dissociating Flow over a Cusped Body

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Exact solutions are obtained for a nonequilibrium dissociating flow of a calorically imperfect, diatomic gas over a cusped body that supports a plane, oblique shock. Numerical examples are presented for N_2 at an altitude of 250,000 ft with M_∞ ranging from 13 to 26, and a shock angle of 80°. Comparison of the results obtained from the models of the simple harmonic oscillator and the Lighthill ideal dissociating gas is made. Variations of the pressure, density, temperature, and degree of dissociation along the streamline are obtained.

Nomenclature

a = sound speed
c_p, c_v = specific heat at constant pressure and volume, respectively
D = dissociation energy per unit mass at 0°K
f = partition function
h = enthalpy
k_r = recombination rate parameter
l_D = $h_1 - h_2$, heat of dissociation per unit mass
M = Mach number
m = gram mass per mole
n, s = natural coordinates, distance normal and along the streamline, respectively
p = pressure
Q = heat added
q = flow speed
R = gas constant, $R_1 = 2R_2$ for diatomic gas
S = specific entropy
T = temperature
T_v = characteristic vibrational temperature
v = $1/\rho$, specific volume
t = time
α = degree of dissociation
β = shock angle
Γ = c_{p0}/c_{v0}, ratio of specific heats at frozen condition
θ = streamline angle
μ = chemical potential
ξ, η = shock-oriented coordinates, distance normal and along the shock, respectively
ρ = density
ψ = stream function
$\omega(T)$ = a thermal function, as shown in Eq. (9)

Subscripts

1,2 = for atomic and molecular species, respectively
∞ = freestream values
e = equilibrium values
0 = frozen values
s = values immediately behind the shock

Introduction

For hypersonic vehicles traveling in air, the gas temperature behind the shock may be high enough to excite the vibrational modes of a diatomic gas and the chemical reactions between the different species in the gas. Since the shock layer is usually very thin, this high-temperature energy, obtained almost instantaneously behind the shock, is absorbed rather gradually by the gas vibrational excitation and gas dissociation. These gradual processes with a finite rate of vibrational relaxation and chemical reaction cause the phenomenon of thermodynamic nonequilibrium behind the shock.

In order to gain some insight into the physics of the nonequilibrium flow, it is advantageous first to investigate this flow over some simple bodies of the sharp or pointed nose type, such as the cusped body, the wedge, and the cone. It is of basic interest to see how in these cases the simple, classical, supersonic flows are modified due to departure from thermodynamic equilibrium. Sedney[1–3] has studied successfully the problems of nonequilibrium vibrational flow over such bodies. Epstein[4] has treated the problem of nonequilibrium dissociating flow behind a plane, oblique shock (or over a cusped body) by using Lighthill's ideal dissociating gas. Capiaux and Washington[5] recently have treated the problem of nonequilibrium dissociating flow past a wedge by using the method of characteristics and assuming also Lighthill's ideal dissociating gas.

The mechanism of vibrational oscillation for a diatomic gas is quite complicated. For simplicity, the assumption of Lighthill's[6] ideal dissociating gas commonly is used, i.e., to

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