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SLIP CONDITIONS WITH WALL CATALYSIS AND RADIATION
FOR MULTICOMPONENT, NONEQUILIBRIUM GAS FLOW

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16. ABSTRACT The slip conditions for a multicomponent mixture with diffusion, wall-catalyzed atom recombination and thermal radiation are derived, and simplified expressions for engineering applications are presented. The gas mixture may be in chemical nonequilibrium with finite-rate catalytic recombination occurring on the wall. These boundary conditions, which are used for rarefied flow regime flow field calculations, are shown to be necessary for accurate predictions of skin friction and heat transfer coefficients in the rarefied portion of the Space Shuttle trajectory.			
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NOMENCLATURE

$\vec{A}_i, \vec{B}_i, C_i^{(j)},$ $a_i, b_{i0}, c_{i0}^{(j)}$	coefficients in the velocity distribution function for nonuniform mixtures
C_F	skin friction coefficient
C_H	heat transfer coefficient
\vec{d}_j	vector related to diffusion velocity of specie "i"
D_{ij}	diffusion coefficient for species pair "i" and "j"
D_i^T	thermal diffusion coefficient
E	energy flux
$f(\vec{V})$	velocity distribution function
$f^0(\vec{V})$	Maxwellian velocity distribution function
F	net molecular flux of general property such as specie, momentum, or energy
F^i	incident molecular flux
F^r	specularly reflected molecular flux
h	enthalpy
h_i	specific enthalpy of specie "i"
k	Boltzmann constant
K	thermal conductivity
Kn	Knudsen number

NOMENCLATURE Continued

Le_{ij}	Lewis number of species pair "i-j"
m_i	mass of molecule "i"
M	Mach number
n_i	number density of specie "i"
P	pressure
Pr	Prandtl number
q	heat flux
r	normal distance from flow axis
r_b	radius of sphere
R	gas constant
\mathcal{R}	universal gas constant
Re	Reynolds number
T	temperature
u	velocity component along surface of sphere
v	velocity component normal to body
\vec{v}	velocity
\vec{V}	thermal velocity
\vec{W}	nondimensional thermal velocity
W_i	molecular weight

NOMENCLATURE Continued

x	coordinate parallel to body
\vec{X}	external force vector
y	coordinate perpendicular to body
Y_i	mass fraction of specie "i"
α_p	Planck mean absorption coefficient
δ	Knudsen layer thickness, mean free path
ϵ	emission coefficient
γ	ratio of specific heats
γ_i	recombination coefficient
η	viscosity
$\phi(\vec{V})$	general molecular property such as mass, momentum, or energy
ρ	density
σ	Stephan-Boltzmann constant
θ	accommodation coefficient
θ	circumferential angle

Subscripts

i, j	specie indices
0	stagnation condition
R	radiation

NOMENCLATURE Concluded

Subscripts

s	edge of Knudsen layer, slip
w	wall
x	coordinate parallel to body
y	coordinate normal to body
∞	free stream property

SLIP CONDITIONS WITH WALL CATALYSIS AND RADIATION FOR MULTICOMPONENT, NONEQUILIBRIUM GAS FLOW

I. INTRODUCTION

To accurately predict the heat transfer to the Space Shuttle during high altitude flight, the proper slip conditions at the gas-wall interface must be employed. In those cases in which the mean free path is small in comparison with the characteristic length of the body ($Kn \ll 1$), the boundary condition at the surface of a solid body is that the gas velocity relative to the body is zero and that the temperatures of the body and gas are identical. However, these conditions are approximate and, when the Knudsen number is finite, the boundary conditions must be refined. Specifically, the density at the wall is sufficiently rarefied that the velocity, temperature, pressure, and concentration at the wall are different from that of the immediately adjacent gas. These "slip" or "jump" conditions will be derived.

At high altitude-low Reynolds number flight, the Knudsen number is finite and the continuum model of the gas breaks down in regions of large gradients such as near a cold body. Hence, the Navier-Stokes description cannot be used in the region of gas a distance on the order of one mean free path away from the wall [1]. This region of gas is commonly referred to as the Knudsen layer.

Since there are not sufficient collisions between gas molecules for the Navier-Stokes approximation to be valid in the Knudsen layer, the more rigorous Boltzmann equation should be utilized. The boundary conditions for the Boltzmann equation would be such that the solution would match the solution of the Navier-Stokes equations in the bulk flow and satisfy the kinetic boundary conditions at the wall.

Without actually solving the complex Boltzmann equation in the Knudsen layer, Patterson [2] and Shidlovskiy [3] have used a slip model to find an approximate Navier-Stokes solution to the flow in the knudsen layer. This approach will be used herein. Scott [4] extended the approach of Shidlovskiy to include a multicomponent mixture with diffusion and wall-catalyzed atom

recombination; however, second order terms in the velocity and temperature slip equations were neglected and it contained errors. The complete expressions with the effects of radiation are included herein, and simplified results for engineering applications are discussed.

Sample calculations are made with single and multicomponent species gas slip conditions to show the necessity of including the multicomponent species in the slip conditions for catalytic and noncatalytic surfaces.

II. ANALYSIS

By matching the species, momenta, and energy fluxes at the outer edge of the Knudsen layer to the difference between the incident and reflected fluxes at the wall, the jump in properties at the wall are obtained. The fluxes are assumed to be constant across the Knudsen layer. These fluxes are calculated from moments of the distribution function. The distribution function comes from a Chapman-Enskog expansion for a multicomponent mixture obtained through a variational method. The Chapman-Enskog expansion, which for small departures from local translational equilibrium leads from the more exact Boltzmann equation to the approximate Navier-Stokes equation, is used to give solutions for the slip conditions compatible to the order of approximation of the Navier-Stokes equations.

It is assumed that the molecules specularly reflected from the wall are associated with the slip temperature while the molecules diffusely reflected from the wall are associated with the wall temperature. That is, the specularly reflected molecules have no accommodation with the wall while the diffusely reflected molecules are fully accommodated. The accommodation coefficient for specie "i", θ_i , is the fraction of those gas molecules (atoms) colliding with the surface that stick and subsequently leave the surface with the energy associated with the wall temperature. Some of the atoms which stick recombine with other atoms to form molecules. The recombination coefficient for specie "i", γ_i , is the fraction of those incident atoms that recombine at the surface. Changes in the internal energy of reflecting molecules are neglected.

Little is known about the actual complex mechanism of gas interaction with the surface of a solid body. Accurate measurements of accommodation coefficients are not available because the physical process is not the same for different materials. For instance, surface adsorption of the gas can be a

factor or the molecules may condense on the surface and then evaporate. The physical shape of a surface can also affect the gas-wall interaction. When the surface is smooth the molecules tend to reflect specularly; however, in reality, the surface is more likely to be rough, having interstices in which the molecules may be temporarily trapped. Reflection of the molecules from a surface of this type is considered diffuse. The molecules strike the boundary with complete loss of the tangential mass velocity and escape after achieving partial or complete accommodation with the wall, the orientation of emission being random. The molecules might also react with other atoms or molecules on the surface before being emitted. Thus until more specific knowledge of gas-wall interaction is obtained, the aforementioned model will be utilized.

Using the notation shown in Figure 1 and denoting $\phi(\vec{v})$ as a convected property such as mass, momentum, or energy, the incident flux of that property normal to the wall is

$$F^{\dagger} = \int_{-\infty}^{\infty} \int_{-\infty}^0 \int_{-\infty}^{\infty} v_y \phi(\vec{V}) f_s(\vec{V}) d^3V, \quad (1)$$

where $f_s(\vec{V})$ is the velocity distribution function at the edge of the Knudsen layer. The specularly reflected flux is proportional to

$$F^{\dagger} = \int_{-\infty}^{\infty} \int_0^{\infty} \int_{-\infty}^{\infty} v_y \phi(\vec{V}) f_s(v_x, -v_y, v_z) d^3V. \quad (2)$$

The diffusely reflected flux is proportional to

$$F_w = \int_{-\infty}^{\infty} \int_0^{\infty} \int_{-\infty}^{\infty} v_y \phi(\vec{V}) f_w(\vec{V}) d^3V, \quad (3)$$

where $f_w(\vec{V})$ is the velocity distribution function at the wall.

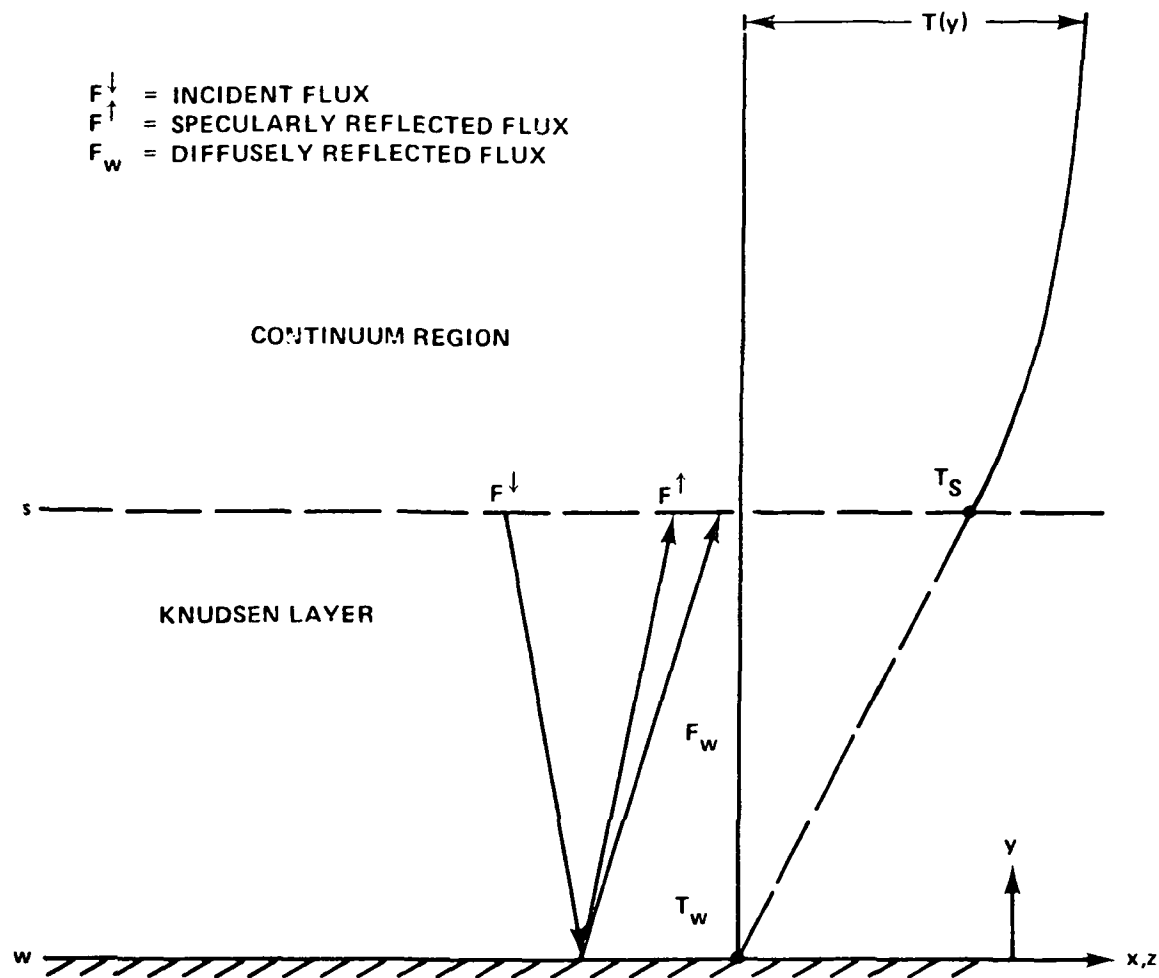


Figure 1. The Knudsen layer showing general fluxes and coordinate axes. The temperature as a function of normal distance is schematically overlayed.

The general flux balance for the convected property is

$$\sum_i F_i = \sum_i F_i^{\downarrow} + \sum_i (1 - \theta_i) F_i^{\uparrow} + \sum_i (\theta_i - \gamma_i) F_{w_i} \quad (4)$$

where the sum over species is not required for the species mass balance. The first term on the right is the incident flux, the second term is the specularly

reflecting flux (incident minus those that stick), and the third term is the diffusely reflecting flux (those that accommodate to the wall minus those that recombine).

Equation (4) must be altered if radiation is included. If radiation stresses and radiation energy density are neglected but one-dimensional radiation heat flux is included, then only the energy flux balance differs from the form of equation (4). Since the gas is rarefied, an optically thin or emission dominated gas is assumed. The Knudsen layer is assumed transparent because of its thickness. This approximation is consistent with assuming constant fluxes across the Knudsen layer. The energy flux balance with radiation is then

$$\sum_i E_i = \sum_i E_i^{\uparrow} + E_R^{\uparrow} + \sum_i (1 - \theta_i) E_i^{\uparrow} + (1 - \epsilon) E_R^{\uparrow} + \sum_i (\theta_i - \gamma_i) E_i^w + E_R^w \quad (5)$$

where

$$E_R^{\uparrow} = -E_R^{\downarrow} = \int_{y=\delta}^{\infty} 4\alpha_p \sigma T^4 dy \quad (5a)$$

and

$$E_R^w = -\epsilon \sigma T_w^4 \quad (5b)$$

The velocity distribution function for a multicomponent mixture perturbed out of equilibrium is

$$f_i(\vec{V}) = f_i^0(\vec{V}) [1 + \psi_i(\vec{V})] \quad (6)$$

where

$$\psi_i(\vec{V}) = -\vec{A}_i \cdot \nabla \ln T - \vec{B}_{i0} : \nabla \vec{v}_0 + n \sum_j \vec{C}_i^{(j)} \cdot \vec{d}_j \quad (6a)$$

and $f_i^0(\vec{v})$ is the Maxwellian velocity distribution for the i th species. The coefficients in equation (6a) are functions of the dimensionless velocity,

$$\vec{W}_i = \sqrt{\frac{m_i}{2kT}} \vec{V}_i, \quad (6b)$$

and contain the constants $a_{i0}, a_{i1}, b_{i0}, c_{i0}^{(j)}$ which are constants determined from the Curtiss and Hirschfelder [5] variation problem in the first approximation for a mixture. These constants are related to the transport properties and functions of the collision integrals [6]. The vector \vec{d}_j is related to the diffusion velocity of the j th species and is defined as

$$\vec{d}_j = \nabla \left(\frac{n_j}{n} \right) + \left(\frac{n_j}{n} - \frac{n_j m_j}{\rho} \right) \nabla \ln P - \left(\frac{n_j m_j}{\rho P} \right) \left[\frac{\rho}{m_j} \vec{X}_j - \sum_i n_i \vec{X}_i \right] \quad (6c)$$

where \vec{X}_j are external forces. The total mass-average velocity, which is to be used later, is

$$\vec{v}_0 = \frac{1}{\rho} \sum_j n_j m_j \vec{v}_j \quad (7)$$

where \vec{v}_j is the sum of the bulk velocity \vec{v}_0 and the thermal velocity \vec{V}_j for species j .

By inserting equations (1), (2), and (3) into equations (4) and (5) with the use of equations (6) and carrying out the triple integrations, the equations for the slip conditions are obtained. All accommodation coefficients θ_i are assumed equal to 0. The slip properties are related to gradients at the outer edge of the Knudsen layer, the properties at the wall and, if radiation is included, the temperature profile.

Concentration slip:

$$\frac{n_i^w}{n_i^s} \left(\frac{T_w}{T_s} \right)^{1/2} = \frac{\theta}{\theta - \gamma_i} \left[1 + \frac{b_{i0}}{6} \left(\frac{\partial v_{0x}}{\partial x} + \frac{\partial v_{0z}}{\partial z} - 2 \frac{\partial v_{0y}}{\partial y} \right) \right]_s - \frac{\sqrt{\pi}}{2} \left(\frac{2 - \theta}{\theta - \gamma_i} \right) \left[a_{i0} \frac{\partial \ln T}{\partial y} - n \sum_j c_{i0}^{(j)} d_{jy} \right]_s \quad (8)$$

Pressure slip:

$$P_s = \left\{ -\frac{\theta}{3} \left(\frac{kT}{2} \sum_i n_i b_{i0} \right) \left(\frac{\partial v_{0x}}{\partial x} + \frac{\partial v_{0z}}{\partial z} - 2 \frac{\partial v_{0y}}{\partial y} \right) + \left[\frac{2 - \theta}{\sqrt{\pi}} k \frac{\partial T}{\partial y} \sum_i \left(a_{i0} - \frac{a_{i1}}{2} \right) n_i \right] + \frac{\theta P^w}{2} - \sum_i \frac{\gamma_i P_i^w}{2} \right\} / \left[\frac{\theta}{2} + \frac{2 - \theta}{\sqrt{\pi}} \sum_i n_{is} \sum_j c_{i0}^{(j)} d_{jy} \right] \quad (9)$$

Velocity slip:

$$v_{0x} = \left\{ \frac{2 - \theta}{2\theta} \sqrt{\pi} \left(\frac{\partial v_{0x}}{\partial y} + \frac{\partial v_{0y}}{\partial x} \right)_s \frac{kT}{2} \sum_i n_i b_{i0} + \sum_i \frac{P_i^s}{2} \left[\left(a_{i0} - \frac{a_{i1}}{2} \right) \frac{\partial \ln T}{\partial x} - n \sum_j c_{i0}^{(j)} d_{jx} \right] \right\} / \left[\sqrt{\frac{m}{2kT_s}} \sum_i P_i^s \left[1 - \frac{2 - \theta}{2\theta} \sqrt{\pi} \left(a_{i0} \frac{\partial \ln T}{\partial y} - n \sum_j c_{i0}^{(j)} d_{jy} \right) + \frac{b_{i0}}{6} \left(\frac{\partial v_{0x}}{\partial x} + \frac{\partial v_{0z}}{\partial z} - 2 \frac{\partial v_{0y}}{\partial y} \right) \right] \right] \quad (10)$$

$$\begin{aligned}
v_{0z} = & \left\{ \frac{2-\theta}{2\theta} \sqrt{\pi} \left(\frac{\partial v_{0z}}{\partial y} + \frac{\partial v_{0y}}{\partial z} \right) \right\}_s \frac{kT}{2} \sum_i n_i b_{i0} + \sum_i \frac{P_i^s}{2} \left[\left(a_{i0} - \frac{a_{i1}}{2} \right) \frac{\partial \ln T}{\partial z} \right. \\
& \left. - n \sum_j c_{i0}^{(j)} d_{jz} \right] \Bigg/ \sqrt{\frac{m}{2kT_s}} \sum_i P_i^s \left[1 - \frac{2-\theta}{2\theta} \sqrt{\pi} \left(a_{i0} \frac{\partial \ln T}{\partial y} \right. \right. \\
& \left. \left. - n \sum_j c_{i0}^{(j)} d_{jy} \right) + \frac{b_{i0}}{6} \left(\frac{\partial v_{0x}}{\partial x} + \frac{\partial v_{0z}}{\partial z} - 2 \frac{\partial v_{0y}}{\partial y} \right) \right] \quad (11)
\end{aligned}$$

Temperature slip:

$$\begin{aligned}
(2kT_s)^{3/2} = & \left\{ (2kT_s)^{3/2} \sum_i \left(\frac{2-\theta}{\theta} \right) \sqrt{\pi} \frac{n_i^s}{\sqrt{m_i}} \left[\frac{5}{8} \left\{ (a_{i0} - a_{i1}) \frac{\partial \ln T}{\partial y} - n \sum_j c_{i0}^{(j)} d_{jy} \right\} \right. \right. \\
& + \sqrt{\frac{m}{2kT_s}} \frac{b_{i0}}{2} \left\{ v_{0x} \left(\frac{\partial v_{0x}}{\partial y} + \frac{\partial v_{0y}}{\partial x} \right) + v_{0z} \left(\frac{\partial v_{0z}}{\partial y} + \frac{\partial v_{0y}}{\partial z} \right) \right\} \\
& + \frac{m}{2kT} \left(\frac{v_{0x}^2 + v_{0z}^2}{4} \right) \left\{ a_{i0} \frac{\partial \ln T}{\partial y} - n \sum_j c_{i0}^{(j)} d_{jy} \right\} \Bigg]_s \\
& + (2kT_w)^{3/2} \sum_i \frac{\theta - \gamma_i}{\theta} \frac{n_i^w}{\sqrt{m_i}} - \frac{2\epsilon}{\pi\theta} \left[\sigma T_w^4 - 4\alpha_p \sigma \int_{\delta}^{\infty} T^4 dy \right] \Bigg\} \\
& \div \left\{ \sum_i \frac{n_i^s}{\sqrt{m_i}} \left[1 + \frac{b_{i0}}{4} \left(\frac{\partial v_{0x}}{\partial x} + \frac{\partial v_{0z}}{\partial z} - 2 \frac{\partial v_{0y}}{\partial y} \right) \left[1 - \frac{\sqrt{\pi}}{3} (v_{0x}^2 \right. \right. \right.
\end{aligned}$$

(12)

$$\begin{aligned}
& + v_{0z}^2) \frac{m}{2kT} \Big] + \frac{m}{8kT} (v_{0x}^2 + v_{0z}^2) - \frac{1}{2} \sqrt{\frac{m}{2kT}} \left(a_{i0} - \frac{a_{i1}}{2} \right) \\
& \left(v_{0x} \frac{\partial \ln T}{\partial x} + v_{0z} \frac{\partial \ln T}{\partial z} \right) + \frac{n\sqrt{\pi}}{2} \sqrt{\frac{m}{2kT}} \sum_j c_{i0}^{(j)} (v_{0x} d_{jx} \\
& + v_{0z} d_{jz}) \Big] \Big\} \quad . \quad (12) \\
& \text{(concluded)}
\end{aligned}$$

III. BOUNDARY CONDITIONS

By equating the net mass flux of atoms to the surface to the rate of consumption of atoms at the wall from surface recombination, Scott [4] established the wall recombination rate constant in terms of the recombination coefficient and the thermal velocity as follows:

$$k_{wi} = \gamma_i \left(\frac{kT_w}{2\pi m_i} \right)^{1/2} \quad . \quad (13)$$

Thus the thermal velocity at the wall limits the maximum rate constant for a fully catalytic ($\gamma_i = 1$) wall. However the rate constant for a fully catalytic wall is often assumed, for simplicity, to approach infinity.

The net mass flux-rate of consumption balance just described can be solved to obtain

$$n_i^s = \frac{- \left(\frac{2 - \gamma_i}{2\gamma_i} \right) \left(\frac{2\pi m_i}{kT_s} \right)^{1/2} \frac{\rho}{nm_i} \left(n_i^s \vec{V}_{y_i} \right)}{1 + \frac{b_{i0}}{6} \left(\frac{\partial v_{0x}}{\partial x} + \frac{\partial v_{0z}}{\partial z} - 2 \frac{\partial v_{0y}}{\partial y} \right)} \quad (14a)$$

where \vec{V}_{yi} is the diffusion velocity defined as

$$n_i^s \vec{V}_{yi} = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} V_{yi} \phi(\vec{V}) f_{is}(\vec{V}) d^3V \quad , \quad (14b)$$

Equations (8) through (12) and (14) form a coupled set of slip conditions to be utilized with flow field calculations. They are applicable to a multicomponent, nonequilibrium gas reacting catalytically on a surface with radiation and diffusion.

IV. SIMPLIFICATION

The constants a_{i0} , a_{i1} , b_{i0} and $c_{i0}^{(j)}$ in the slip conditions, equations (8) through (12) and (14), can be determined from the collision integrals by a variational technique in which they are solutions to sets of simultaneous equations [5]. Due to the complexity of the collision integrals, a great simplification results if one relates these constants directly to the transport properties [5]. This simplification amounts to using: (1) the relation for a_{i0}

$$D_i^T = \frac{n_i m_i}{2} \sqrt{\frac{2kT}{m_i}} a_{i0} \quad (15a)$$

where D_i^T is the thermal diffusion coefficient, (2) the relation for a_{i1}

$$K = \sum_i \frac{n_i K_i}{n} = - \frac{5}{4} k \sum_i n_i \sqrt{\frac{2kT}{m_i}} a_{i1} \quad (15b)$$

where K is the thermal conductivity, (3) the relation for b_{i0}

$$\eta = \sum_i \frac{n_i \eta_i}{n} = \frac{1}{2} k T \sum_i n_i b_{i0} \quad (15c)$$

where η is the viscosity coefficient, and (4) the relation for $c_{i0}^{(j)}$

$$D_{ij} = \frac{\rho n_i}{2nm_j} \sqrt{\frac{2kT}{m_i}} c_{i0}^{(j)} \quad (15d)$$

where D_{ij} is the diffusion coefficient. The diffusion velocity can also be written in terms of transport properties as

$$\vec{V}_{yi} = - \left[\frac{n^2}{\rho n_i} \sum_j m_j D_{ij} d_{jy} - \frac{1}{n_i m_i} D_i^T \frac{\partial \ln T}{\partial y} \right] \quad (16)$$

Substituting equations (15) and (16) into the slip conditions yields the slip conditions in terms of transport properties. Second order terms in the velocity and temperature slip expressions are now dropped.

Concentration slip:

$$\begin{aligned} \frac{n_i^w}{n_i^s} \left(\frac{T_w}{T_s} \right)^{1/2} &= \frac{\theta}{\theta - \gamma_i} \left[1 + \frac{\eta_i}{3kTn} \left(\frac{\partial v_{0x}}{\partial x} + \frac{\partial v_{0z}}{\partial z} - 2 \frac{\partial v_{0y}}{\partial y} \right) \right]_s \\ &- \sqrt{\pi} \left(\frac{2 - \theta}{\theta - \gamma_i} \right) \left(\frac{1}{n_i} \sqrt{\frac{m_i}{2kT}} \right) \left[\frac{D_i^T}{m_i} \frac{\partial \ln T}{\partial y} \right. \\ &\left. - \frac{n^2}{\rho} \sum_j m_j D_{ij} d_{jy} \right]_s \quad (17) \end{aligned}$$

Pressure slip:

$$\begin{aligned}
P_s = & \left\{ -\frac{\theta}{3} \eta_s \left(\frac{\partial v_{0x}}{\partial x} + \frac{\partial v_{0z}}{\partial z} - 2 \frac{\partial v_{0y}}{\partial y} \right) + \left[\frac{2-\theta}{\sqrt{\pi}} k \frac{\partial T}{\partial y} \sum_i \sqrt{\frac{m_i}{2kT}} \left(\frac{2D_i^T}{m_i} \right. \right. \right. \\
& + \left. \left. \frac{2n_i K_i}{5nk} \right) \right] + \frac{\theta P^w}{2} - \sum_i \frac{\gamma_i P_i^w}{2} \left. \right\} / \left[\frac{\theta}{2} \right. \\
& + \left. \left(\frac{2-\theta}{\sqrt{\pi}} \sum_i \frac{2n}{\rho} \sqrt{\frac{m_i}{2kT}} \sum_j m_j D_{ij} d_{jy} \right) \right] \quad (18)
\end{aligned}$$

Velocity slip:

$$\begin{aligned}
v_{0x} = & \frac{1}{\sqrt{\frac{m}{2kT}} P^s} \left\{ \sqrt{\pi} \left(\frac{2-\theta}{2\theta} \right) \eta_s \left(\frac{\partial v_{0x}}{\partial y} + \frac{\partial v_{0y}}{\partial x} \right) + \sum_i \left(\frac{P_i}{n_i} \sqrt{\frac{m_i}{2kT}} \right) \right. \\
& \left. \left[\frac{\partial \ell n T}{\partial x} \left(\frac{D_i^T}{m_i} + \frac{n_i K_i}{5nk} \right) - \frac{n^2}{\rho} \sum_j m_j D_{ij} d_{jx} \right] \right\} \quad (19)
\end{aligned}$$

$$\begin{aligned}
v_{0z} = & \frac{1}{\sqrt{\frac{m}{2kT}} P^s} \left\{ \sqrt{\pi} \left(\frac{2-\theta}{2\theta} \right) \eta_s \left(\frac{\partial v_{0z}}{\partial y} + \frac{\partial v_{0y}}{\partial z} \right) + \sum_i \left(\frac{P_i}{n_i} \sqrt{\frac{m_i}{2kT}} \right) \right. \\
& \left. \left[\frac{\partial \ell n T}{\partial z} \left(\frac{D_i^T}{m_i} + \frac{n_i K_i}{5nk} \right) - \frac{n^2}{\rho} \sum_j m_j D_{ij} d_{jz} \right] \right\} \quad (20)
\end{aligned}$$

Temperature slip:

$$\begin{aligned}
 (2kT_s)^{3/2} = & \left\{ \sqrt{\pi} \frac{2-\theta}{\theta} k T_s \frac{5}{2} \left\{ \frac{\partial \ln T}{\partial y} \left(\sum_i \frac{D_i^T}{m_i} + \frac{2}{5} \frac{K}{k} \right) \right. \right. \\
 & \left. \left. - \sum_i \frac{2n^2}{\rho} \sum_j m_j D_{ij} d_{jy} \right\} + (2kT_w)^{3/2} \sum_i \frac{\theta - \gamma_i}{\theta} \frac{n_i^w}{\sqrt{m_i}} \right. \\
 & \left. - \frac{2\epsilon}{\pi\theta} \left[\sigma T_w^4 - 4\alpha_p \sigma \int_0^\infty T^4 dy \right] \right\} / \sum_i \frac{n_i^s}{\sqrt{m_i}} \left[1 + \frac{\eta_i}{2nkT} \left(\frac{\partial v_{0x}}{\partial x} \right. \right. \\
 & \left. \left. + \frac{\partial v_{0z}}{\partial z} - 2 \frac{\partial v_{0y}}{\partial y} \right) \right] \quad (21)
 \end{aligned}$$

where

$$n_i^s = \frac{\frac{2-\gamma_i}{2\gamma_i} \sqrt{\frac{2\pi m_i}{kT}} \frac{\rho}{nm_i} \left[-\frac{D_i^T}{m_i} \frac{\partial \ln T}{\partial y} + \frac{n^2}{\rho} \sum_j m_j D_{ij} d_{jy} \right]}{1 + \frac{\eta_i}{3nkT} \left(\frac{\partial v_{0x}}{\partial x} + \frac{\partial v_{0z}}{\partial z} - 2 \frac{\partial v_{0y}}{\partial y} \right)} \quad (22)$$

Before any further simplifications are made, it is interesting to note what effects influence the magnitude of the slip conditions. The concentration slip, from equation (22), is directly proportional to the net normal mass flux of species i and inversely proportional to the thermal slip velocity of species i . The velocity slip is related to the tangential shear stress, plus a thermal creep term over species i due to thermal diffusion and heat conduction in the tangential direction, minus a diffusion term in the tangential direction, all divided by the pressure over the thermal slip velocity. The pressure slip is proportional to the pressure at the wall, minus the normal shear stress, plus a term containing normal thermal diffusion and normal thermal conductivity, all divided by one plus a normal diffusion term. The temperature slip is proportional to the diffusely reflected energy flux, minus the normal flux of energy (including radiation), all divided by a term proportional to the density times the thermal slip velocity.

Further simplifications can be made by making the assumptions consistent with Fick's law of diffusion: (1) thermal diffusion is negligible, (2) diffusion due to pressure gradients and external forces is neglected, and (3) a binary mixture of atoms and molecules is assumed so that $D_{ij} = D_{12}$. By assuming that the normal shear stress for species i is the same as that of the bulk mixture ($\tau_{yyi} = \tau_{yy}$ or $n_i \eta_i = n\eta$), the concentration slip and temperature slip are simplified. By assuming that the energy conducted for species i is the same as that of the bulk mixture, the velocity slip and pressure slip are simplified. The above assumptions do not significantly influence the slip conditions.

With these assumptions equations (17) through (22) become

$$\begin{aligned} \frac{n_i^w}{n_i^s} \left(\frac{T_w}{T_s} \right)^{1/2} = \frac{\theta}{\theta - \gamma_i} \left[1 + \frac{\eta}{3n_i kT} \left(\frac{\partial v_{0x}}{\partial x} + \frac{\partial v_{0z}}{\partial z} - 2 \frac{\partial v_{0y}}{\partial y} \right) \right]_s \\ + \sqrt{\pi} \left[\left(\frac{2 - \theta}{\theta - \gamma_i} \right) \frac{n^2 D_{12}}{\rho n_i} \sqrt{\frac{m_i}{2kT}} \sum_j m_j \frac{\partial}{\partial y} (n_j/n) \right]_s, \end{aligned} \quad (23)$$

where

$$n_i^s = \frac{\left[\left(\frac{2 - \gamma_i}{2\gamma_i} \right) \frac{n D_{12}}{m_i} \sqrt{\frac{2\pi m_i}{kT}} \sum_j m_j \frac{\partial}{\partial y} (n_j/n) \right]}{\left[1 + \frac{\eta}{3n_i kT} \left(\frac{\partial v_{0x}}{\partial x} + \frac{\partial v_{0z}}{\partial z} - 2 \frac{\partial v_{0y}}{\partial y} \right) \right]_s} \quad (24)$$

and

$$\begin{aligned}
 P_s = & \left\{ \frac{\theta P^w}{2} \sum_i \frac{\gamma_i P_i^w}{2} - \frac{\theta \eta_s}{3} \left(\frac{\partial v_{0x}}{\partial x} + \frac{\partial v_{0z}}{\partial z} - 2 \frac{\partial v_{0y}}{\partial y} \right) \right. \\
 & \left. + \frac{2}{5} \left[\frac{2-\theta}{\sqrt{\pi}} K \frac{\partial T}{\partial y} \sum_i \sqrt{\frac{m_i}{2kT}} \right] \right\}_s \\
 & / \frac{\theta}{2} \left[1 + \frac{4n}{\rho \theta} \frac{(2-\theta)}{\sqrt{\pi}} D_{12} \sum_i \sqrt{\frac{m_i}{2kT}} \sum_j m_j \frac{\partial}{\partial y} (n_j/n) \right]_s, \quad (25)
 \end{aligned}$$

$$\begin{aligned}
 v_{0x}^s = & \left[\frac{1}{P} \sqrt{\frac{2kT}{m}} \right]_s \left\{ \sqrt{\pi} \left(\frac{2-\theta}{2\theta} \right) \eta \left(\frac{\partial v_{0x}}{\partial y} + \frac{\partial v_{0y}}{\partial x} \right) \right. \\
 & \left. + \sqrt{\frac{kT}{2}} \sum_i \sqrt{m_i} \left[\frac{K}{5k} \frac{\partial \ln T}{\partial x} - \frac{n^2 D_{12}}{\rho} \sum_j m_j \frac{\partial}{\partial x} (n_j/n) \right] \right\}_s, \quad (26)
 \end{aligned}$$

$$\begin{aligned}
 v_{0z}^s = & \left[\frac{1}{P} \sqrt{\frac{2kT}{m}} \right]_s \left\{ \sqrt{\pi} \left(\frac{2-\theta}{2\theta} \right) \eta \left(\frac{\partial v_{0z}}{\partial y} + \frac{\partial v_{0y}}{\partial z} \right) \right. \\
 & \left. + \sqrt{\frac{kT}{2}} \sum_i \sqrt{m_i} \left[\frac{K}{5k} \frac{\partial \ln T}{\partial z} - \frac{n^2 D_{12}}{\rho} \sum_j m_j \frac{\partial}{\partial z} (n_j/n) \right] \right\}_s, \quad (27)
 \end{aligned}$$

and

$$\begin{aligned}
(2kT_s)^{3/2} = & \left\{ \frac{2-\theta}{\theta} \sqrt{\pi} k T_s \left[\frac{K}{k} \frac{\partial \ln T}{\partial y} - \frac{5 n^2}{\rho} D_{12} \sum_j m_j \frac{\partial}{\partial y} (n_j/n) \right] \right. \\
& + (2kT_w)^{3/2} \sum_i \frac{\theta - \gamma_i}{\theta} \frac{n_i^w}{\sqrt{m_i}} - \frac{2\epsilon}{\pi\theta} \left[\sigma T_w^4 - 4\alpha_p \sigma \int_0^\infty T^4 dy \right] \Bigg\} \\
& / \left\{ \sum_i \frac{n_i^s}{\sqrt{m_i}} \left[1 + \frac{\eta}{2n_i k T} \left(\frac{\partial v_{0x}}{\partial x} + \frac{\partial v_{0z}}{\partial z} - 2 \frac{\partial v_{0y}}{\partial y} \right) \right] \right\}_s.
\end{aligned} \tag{28}$$

These expressions simplify to those presented by Shidlovskiy [3] for a single species if one assumes that the jump conditions are small and radiation is neglected. These jump conditions with radiation for a single species gas are as follows:

$$\frac{\rho_w}{\rho_s} = \sqrt{\frac{T_s}{T_w}} \left\{ 1 + \frac{5}{24} \sqrt{\frac{\pi}{2}} \frac{\delta_s}{\sqrt{RT_s}} \left(\frac{\partial v_{0x}}{\partial x} + \frac{\partial v_{0z}}{\partial z} - 2 \frac{\partial v_{0y}}{\partial y} \right)_s \right\} \tag{29}$$

$$\frac{P_s}{P_w} = 1 + \frac{2-\theta}{\theta} \frac{15}{16} \left(\frac{\delta}{T} \frac{\partial T}{\partial y} \right)_s - \frac{5}{12} \sqrt{\frac{\pi}{2}} \frac{\delta_s}{\sqrt{RT_s}} \left(\frac{\partial v_{0x}}{\partial x} + \frac{\partial v_{0z}}{\partial z} - 2 \frac{\partial v_{0y}}{\partial y} \right)_s \tag{30}$$

$$v_{0x}^s = \frac{2-\theta}{\theta} \frac{5\pi}{16} \delta_s \left(\frac{\partial v_{0x}}{\partial y} + \frac{\partial v_{0y}}{\partial x} \right)_s + \frac{15}{32} \sqrt{\frac{\pi RT_s}{2}} \left(\frac{\delta}{T} \frac{\partial T}{\partial x} \right)_s \tag{31}$$

$$v_{0z}^s = \frac{2-\theta}{\theta} \frac{5\pi}{16} \delta_s \left(\frac{\partial v_{0z}}{\partial y} + \frac{\partial v_{0y}}{\partial z} \right)_s + \frac{15}{32} \sqrt{\frac{\pi RT_s}{2}} \left(\frac{\delta}{T} \frac{\partial T}{\partial z} \right)_s \tag{32}$$

and

$$\frac{T_s}{T_w} = 1 + \frac{2-\theta}{\theta} \frac{75\pi}{128} \left(\frac{\dot{\delta}}{T} \frac{\partial T}{\partial y} \right)_s - \frac{5}{48} \sqrt{\frac{\pi}{2}} \frac{\delta_s}{\sqrt{RT_s}} \left(\frac{\partial v_{0x}}{\partial x} + \frac{\partial v_{0z}}{\partial z} - 2 \frac{\partial v_{0y}}{\partial y} \right) - \frac{\epsilon \left[\sigma T_w^4 - 4 \alpha_p \sigma \int_{\dot{\delta}}^{\infty} T^4 dy \right]}{\pi \theta P_s \sqrt{2RT_s}} \quad (33)$$

where an elastic sphere molecular model has been assumed such that

$$\eta = \frac{5}{8} P \sqrt{\frac{\pi}{2}} \frac{\delta}{\sqrt{RT}} \quad (34a)$$

and

$$K = \frac{15}{4} \frac{k}{m} \eta \quad (34b)$$

Note from equation (33) that the radiation being absorbed at the wall causes T_s to be larger than that without gas emission. This term can also be interpreted in effect as an increase in the wall temperature.

V. SLIP CONDITIONS NEAR A STAGNATION POINT

Using spherical coordinates, nondimensionalizing by defining $u = \bar{u}/\bar{v}_\infty$, $v = \bar{v}/\bar{v}_\infty$, $\rho = \bar{\rho}/\bar{\rho}_\infty$, $T = \bar{T}/\bar{T}_0$, $\eta = \bar{\eta}/\bar{\eta}_0$, $P = \bar{P}/\bar{\rho}_\infty \bar{v}_\infty^2$ and $r = \bar{r}/\bar{r}_b$, and rearranging terms, the expressions needed to determine slip conditions near a stagnation point for a chemically reacting gas are as follows:

$$\begin{aligned}
\frac{Y_i^w}{Y_i^s} \sqrt{\frac{T_w}{T_s}} &= \frac{\theta}{\theta - \gamma_i} \left[1 + \frac{M_\infty^2}{Re_0} \left(\frac{\eta}{3T\rho Y_i} \right)_s \left(\frac{\gamma RW_i}{R} \right) \frac{\bar{T}_\infty}{\bar{T}_0} \left(\frac{1}{r} \frac{\partial u}{\partial \phi} - 2 \frac{\partial v}{\partial r} \right)_s \right] \\
&+ \sqrt{\pi} \left(\frac{2 - \theta}{\theta - \gamma_i} \right) \frac{M_\infty}{Re_0} \frac{Le}{Pr} \left[w_i \sum_i \left(\frac{Y_i}{w_i} \right)_s \right] \frac{\eta_s}{\rho_s} \sqrt{\frac{\gamma RW_i}{2RT_s}} \frac{\bar{T}_\infty}{\bar{T}_0} \sum_j \left(\frac{\partial Y_j}{\partial r} \right)_s
\end{aligned} \tag{35}$$

where

$$Y_i^s = \frac{\frac{2 - \gamma_i}{2\gamma_i} \frac{M_\infty}{Re_0} \frac{Le}{Pr} \frac{\eta_s}{\rho_s} \sqrt{\frac{2\pi\gamma RW_i}{RT_s}} \frac{\bar{T}_\infty}{\bar{T}_0} \sum_i \left(\frac{\partial Y_i}{\partial r} \right)_s}{1 + \frac{M_\infty^2}{Re_0} \left(\frac{\eta}{3\rho T Y_i} \right)_s \frac{\gamma RW_i}{R} \frac{\bar{T}_\infty}{\bar{T}_0} \left(\frac{1}{r} \frac{\partial u}{\partial \phi} - 2 \frac{\partial v}{\partial r} \right)_s} \tag{36}$$

and

$$\begin{aligned}
P_s &= \left[P^w - \sum_i \frac{\gamma_i P_i^w}{\theta} - \frac{2}{3} \frac{\eta_s}{Re_0} \left(\frac{1}{r} \frac{\partial u}{\partial \phi} - 2 \frac{\partial v}{\partial r} \right)_s \right. \\
&+ \left. \frac{4}{5\sqrt{\pi}} \frac{1}{\gamma - 1} \left(\frac{2 - \theta}{\theta} \right) \frac{\eta_s}{M_\infty Re_0 Pr} \left(\frac{\partial T}{\partial r} \right)_s \sum_i \sqrt{\frac{\gamma RW_i}{2RT_s}} \frac{\bar{T}_0}{\bar{T}_\infty} \right] \\
&/ \left[1 + \frac{2(2 - \theta)}{\sqrt{\pi} \theta} \frac{M_\infty}{Re_0} \frac{Le}{Pr} \sqrt{\frac{\bar{T}_\infty}{\bar{T}_0}} \left(\frac{\eta}{\rho} \right)_s \sum_j \left(\frac{\partial Y_j}{\partial r} \right)_s \sum_i \sqrt{\frac{\gamma RW_i}{2RT_s}} \right] , \tag{37}
\end{aligned}$$

$$\begin{aligned}
u_s = & \frac{\eta_s}{P_s \text{Re}_0 M_\infty} \left[\sqrt{\pi} \left(\frac{2-\theta}{2\theta} \right) \sqrt{\frac{2T_s \bar{T}_0}{\gamma \bar{T}_\infty}} \left(\frac{\partial u}{\partial r} + \frac{1}{r} \frac{\partial v}{\partial \phi} \right) \right. \\
& + \frac{1}{5(\gamma-1) M_\infty \text{Pr}} \left(\frac{\bar{T}_0}{\bar{T}_\infty} \right) \sqrt{\frac{R}{\theta}} \left(\frac{1}{r} \frac{\partial T}{\partial \phi} \right) \sum_i \sqrt{W_i} \\
& \left. - \frac{P_s M_\infty \text{Le}}{\rho_s \text{Pr}} \sqrt{\frac{R}{\theta}} \sum_j \left(\frac{1}{r} \frac{\partial Y_j}{\partial \phi} \right) \sum_i \sqrt{W_i} \right] \quad , \quad (38)
\end{aligned}$$

$$\begin{aligned}
T_s = & \left(T_w \sum_i \left\{ \frac{Y_i \rho}{\left[W_i \sum_i \frac{Y_i}{W_i} \right]^{3/2}} \left[1 + \frac{\eta}{3 P_i \text{Re}_0} \left(\frac{1}{r} \frac{\partial u}{\partial \phi} - 2 \frac{\partial v}{\partial r} \right) \right. \right. \right. \\
& + \left. \left. \frac{\sqrt{\pi}}{Y_i} \left(\frac{2-\theta}{\theta} \right) \frac{M_\infty \text{Le}}{\text{Re}_0 \text{Pr}} W_i \sum_i \left(\frac{Y_i}{W_i} \right) \frac{\eta}{\rho} \sqrt{\frac{\gamma R W_i \bar{T}_\infty}{2\theta T \bar{T}_0}} \sum_j \frac{\partial Y_j}{\partial r} \right] \right\} \right)_s \\
& + \left\{ \frac{2-\theta}{\theta} \sqrt{\pi} \left[\frac{M_\infty}{\text{Pr Re}_0} \frac{\gamma}{\gamma-1} \frac{\eta}{2} \sqrt{\frac{\gamma \bar{T}_\infty}{2T \bar{T}_0}} \frac{\partial T}{\partial r} \right. \right. \\
& \left. \left. - \frac{5P}{2\rho} \eta \frac{M_\infty^3 \gamma \bar{T}_\infty}{\text{Re}_0 \bar{T}_0} \sqrt{\frac{\gamma \bar{T}_\infty}{2T \bar{T}_0}} \frac{\text{Le}}{\text{Pr}} \sum_j \frac{\partial Y_j}{\partial r} \right] \right\}_s \\
& - \frac{\epsilon \gamma M_\infty}{(\gamma-1) \text{Bo}_0 \rho_s \pi \theta} \sqrt{\frac{\gamma \bar{T}_\infty}{2T \bar{T}_0}} \left[T_w^4 - 4 \alpha_p \bar{r}_b \int_{1+\delta}^{\infty} T^4(r) dr \right] \Bigg) /
\end{aligned}$$

$$\left\{ \sum_i \frac{Y_i \rho}{\left[W_i \sum_i \frac{Y_i}{W_i} \right]^{3/2}} \left[1 + \frac{\eta}{2 P_i \text{Re}_0} \left(\frac{1}{r} \frac{\partial u}{\partial \phi} - 2 \frac{\partial v}{\partial r} \right) \right] \right\}_s \quad (39)$$

Equations (35) through (39) with the equation of state form a complete set of boundary conditions for a multicomponent, nonequilibrium gas reacting catalytically on a surface. Knowing the wall temperature and thus the recombination rate at the wall, the recombination coefficient (γ_i) can be obtained from equation (13). The accommodation coefficient, θ , can be assumed equal to one until better experimental values are obtained.

For a completely noncatalytic wall, γ_i equals zero and equation (36) reduces to the radial gradient of the mass fraction of species "i" equal to zero. For a completely catalytic wall, γ_i equals one. Using values of γ_i of one and zero gives simplified expressions which show the effect of catalyticity.

VI. SAMPLE CALCULATIONS

To determine whether or not there is any significant difference in using the single species gas slip conditions or the multicomponent reacting gas slip conditions presented here, an accurate stagnation point solution is utilized. The full Navier-Stokes equations are solved from the free stream through the merged shock layer to the body using the concept of local similarity [7]. A rarefied portion of the Space Shuttle orbiter reentry trajectory with catalytic and non-catalytic walls is used as an example. The flight conditions are shown in Table 1.

Since the pressure and mass fraction at the wall are not specified A PRIORI, equations (35) and (37) will not be utilized. This is equivalent to assuming that the pressure slip is the same as the pressure at the wall and that the mass fraction slip is the same as the mass fraction at the wall.

Table 2 presents a summary of the effect of using the more realistic multicomponent gas slip conditions. Results are presented for a spherical nose the same size as the Space Shuttle orbiter and for a typical reentry flight condition.

It is evident from Table 2 that erroneous results would be obtained using the single species slip expressions in lieu of the multicomponent expressions. Using the multicomponent species boundary conditions, the velocity slip is only 52 percent as much and the temperature slip is only 33 percent as much as that using the single species boundary conditions at the highest altitude considered for either type wall. The heat transfer coefficient rises the most (14 percent) at 96.2 km using the multicomponent species expressions and a noncatalytic wall. The heat transfer coefficient continues to rise with altitude over the single species expressions with the use of the more exact boundary conditions for a catalytic wall. For the catalytic and noncatalytic wall conditions, the multicomponent species slip conditions show a reduction of approximately 15 percent in the skin friction coefficient at the highest altitude. From Table 2 it is evident that the use of the more exact multicomponent slip conditions causes a rise of approximately 15 percent in the heat transfer coefficient and a drop of approximately 15 percent in the skin friction coefficient at the highest altitudes when compared with results using the single species slip conditions. Other trajectories may well show even stronger variations in C_H and C_F .

Since this is not necessarily the most severe example, it appears that the more complex multicomponent reacting gas slip conditions must be used for accurate prediction of heat transfer and skin friction coefficients.

TABLE 1. FLOW FIELD FREE STREAM PROPERTIES

	Case 1	Case 2	Case 3	Case 4
Altitude, km	87.43	91.5	96.2	100
Mach Number	29.4	30.7	28.0	27.3
Reynolds Number	1111.	450.	204.	110.
Velocity, km s ⁻¹	7.93	7.93	7.93	7.93
Temperature, K	181.	164.	199.	210.
Density, kg m ⁻³	5.565×10^{-6}	2.130×10^{-6}	1.116×10^{-6}	6.260×10^{-6}
Wall Temperature, K	1640.	1640.	1640.	1640.
Radius of Sphere, cm	30.5	30.5	30.5	30.5

TABLE 2. EFFECTS OF SINGLE SPECIES AND MULTICOMPONENT SPECIES
SLIP EQUATIONS FOR ORBITER TRAJECTORY

	$u_{\text{slip}} v_{\infty}$		T_{slip}/T_w		C_H		C_F	
	Multi- component Species	Single Species	Multi- component Species	Single Species	Multi- component Species	Single Species	Multi- component Species	Single Species
I. Noncatalytic Wall Altitude (km)								
87.43	.02930sin θ	.03030sin θ	1.712	1.359	.1794	.1780	.3559sin θ	.3647sin θ
91.50	.05677sin θ	.07057sin θ	2.017	2.974	.4038	.3743	.6408sin θ	.6746sin θ
96.2	.07169sin θ	.1132sin θ	1.820	4.069	.6099	.5360	.8757sin θ	.9618sin θ
100.	.07337sin θ	.1414sin θ	1.572	4.741	.7779	.6915	1.033sin θ	1.230sin θ
II. Catalytic Wall Altitude (km)								
87.43	.03002sin θ	.03046sin θ	1.627	1.075	.2718	.2741	.3682sin θ	.3701sin θ
91.50	.05076sin θ	.06967sin θ	1.933	2.313	.4446	.4273	.6438sin θ	.6795sin θ
96.2	.07139sin θ	.1117sin θ	1.795	3.912	.6256	.5792	.8747sin θ	.9651sin θ
100.	.07397sin θ	.1400sin θ	1.573	4.651	.7814	.7133	1.082sin θ	1.240sin θ

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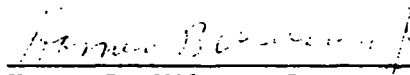
APPROVAL

SLIP CONDITIONS WITH WALL CATALYSIS AND RADIATION FOR MULTICOMPONENT, NONEQUILIBRIUM GAS FLOW

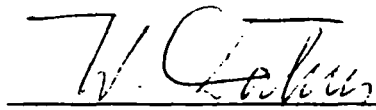
By Dr. William L. Hendricks

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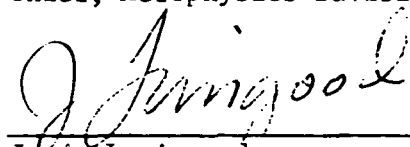
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