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INVESTIGATION OF
CHEMICAL NONEQUILIBRIUM EFFECTS
IN VISCOUS SHOCK LAYERS

P. Roy Choudhury

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Final Report

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P. Roy Choudhury
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ENGINEERING CENTER
UNIVERSITY OF SOUTHERN CALIFORNIA
LOS ANGELES 7, CALIFORNIA

ABSTRACT

The shock layer about a blunt body in a hypersonic flow field is studied considering both viscous and chemical nonequilibrium effects. An order of magnitude study is conducted to predict flight regimes for chemical equilibrium and for frozen flow. Conservation equations are formulated for the viscous, reacting flow in the shock layer about a sphere using a seven species, six reaction chemical model. A numerical method for solution of these equations is developed and the results of solution attempts discussed.

TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

iv

I. INTRODUCTION

Conversion of the kinetic energy of a hypersonic vehicle to thermal energy through shock waves and viscous effects may result in dissociation and ionization of the gas surrounding the vehicle. A knowledge of the properties and extent of this ionized layer is important in determining energy transfer to the vehicle and methods of communication with it. In order to determine the structure of the reacting layer one must take into account the body shape, shock shape, nonequilibrium dissociation and recombination, rotational and vibrational relaxation, diffusion and viscous effects. Most attempts at an analytic formulation of the problem have assumed that viscosity effects are limited to a relatively thin boundary layer within the shock layer. For bodies at high altitudes this model is inappropriate as viscous effects are significant throughout the entire shock layer. The purpose of this report is to determine the flight regimes, as specified by Mach number and altitude, in which viscosity and nonequilibrium reaction effects are important in the shock layer about a blunt body, and to attempt an analytic or numerical solution to the flow. In order to accomplish this object it is necessary to determine, by a literature search, what reactions would be important and what the reaction rate constants for these reactions should be.

A literature survey of current work in flow about blunt bodies of hypersonic speeds revealed that most authors have considered either an inviscid, nonequilibrium flow or a viscous flow in chemical equilibrium. The analytical models used are for the most part based on a boundary-layer flow, with curvature and normal pressure gradient effects neglected. Chung (Ref. 1) has given solutions for flow in the viscous shock layer with nonequilibrium chemical reactions for an "air atom" and "air molecule" model. His analysis is based on a thin shock layer with boundary-layer type assumptions. A solution for nonreacting flow using the complete Navier-Stokes equations has been obtained by Ho and Probstein (Ref. 2) by assuming forms for the dependent variables in the neighborhood of the stagnation point such that the Navier-Stokes equations reduce to a set of ordinary differential equations.

A more recent review by Cheng (Ref. 3) of hypersonic flow research indicates that no solutions are yet available in which viscous and chemical nonequilibrium effects are accounted for throughout the shock-layer region. Additional references to the literature will not be presented here since the comprehensive survey by Cheng (ibid) is currently available.

II. FORMULATION OF THE PROBLEM

A. A SIMPLE ORDER OF MAGNITUDE STUDY

Before attempting to solve the complete problem of the chemically nonequilibrium viscous shock layer of the reentry body, a simple order of magnitude study based on the characteristic dissociation and convective times has been performed (Ref. 4). From this preliminary analysis it is possible to construct a flight spectrum to indicate the regions in the altitude-Mach number plane where the chemical state of the gas at the stagnation region is expected to be in a near frozen or in a near equilibrium state. This approximate analysis is somewhat similar to those of Pearce et al (Ref. 5) and Grier and Sands (Ref. 6). These studies deal with the recombination of species in the boundary layer and are valid at lower altitudes where the shock layer is inviscid. In the present analysis we consider an altitude range where the shock layer is not inviscid. The entire shock layer is viscous and the chemical state of the gas is governed by the rate of dissociation. The following assumptions are made in order to estimate the characteristic times:

(a) The shock wave is a thin discontinuity and no reaction takes place within the shock thickness.

(b) The temperature of the body, T_B, is constant (1500° K) and the body is noncatalytic.

(c) The average thermodynamic properties in the shock layer determine the chemical state of the gas.

(d) In the shock layer O_2 dissociates first.

(e) The shock layer is essentially frozen if less than 10% O_2 dissociation takes place.

Because of the thin discontinuity, assumption (a) is self-explanatory. A typical temperature of a cooled body (may be ablative) is given by (b). Assumption (c) would be valid if proper averages are taken. Unfortunately, the correct average values may not be known accurately a priori, but a reasonable estimate for the viscous shock layer can be made as a zeroth approximation. The velocity distribution along the stagnation streamline is roughly linear (u_s behind the shock and zero at the stagnation region). Therefore $\bar{u} \sim \dfrac{u_s}{2}$. If, however, we use $\bar{T} \sim \dfrac{T_s + T_B}{2}$, we find that the resulting $\bar{T}$ is lower than that of the actual <u>inviscid</u> value (the subscript s denotes the state just behind the shock). Because of heat conduction, the average temperature of the <u>viscous</u> shock layer, in general, will be lower than the inviscid case. Moreover, due to radiative heat transfer, the temperature may decrease further. Thus $\bar{T} \sim \dfrac{T_s + T_B}{2}$ will be reasonably close to the actual average value in the viscous shock layer with radiative heat transfer.

The upper limiting case is also considered where $\bar{T} \sim T_s$. This is the worst possible condition where the shock layer is subjected to the maximum possible temperature.

For a given M_∞; $\frac{T_s}{T_\infty}$, $\frac{\rho_s}{\rho_\infty}$, $\frac{p_s}{p_\infty}$, $\frac{u_s}{U_\infty}$, etc. can be found easily. From these values $\bar{u}$, $\bar{T}$ and $\bar{\rho}$ corresponding to $\bar{T}$ can be evaluated. During its travel through the shock layer, the fluid will tend to dissociate at the above average conditions.

Assumption (d) is quite accurate for thermodynamic calculations but will not convey the correct physical picture when one is interested in the formation of NO and its subsequent ionization, $NO \rightleftharpoons NO^+ + e^-$. However, for the assumed model, if O_2 dissociation is frozen to start with, the above ionization will not take place. Since in the present simplified analysis we want to know whether the gas is in a near frozen chemical state or in a state of nonequilibrium, assumption (d) is consistent with the other assumptions.

Instead of using 10% O_2 dissociation as the criterion of a near frozen state, [assumption (e),] we can also assume 1% dissociation as the criterion in order to be on the conservative side. That is why Fig. 2 shows both 1% and 10% O_2 dissociation lines.

Using the relationship $\frac{\Delta}{R_B} \sim \frac{\rho_\infty}{\rho_s}$ (Δ = shock standoff distance and R_B = body radius) we can estimate the convective time t_c as $\frac{\Delta}{\bar{u}}$. Thus for a one-step reaction $\sum_j \nu'_j M_j \underset{k_b}{\overset{k_f}{\rightleftharpoons}} \sum_j \nu''_j M_j$, the ratio of the characteristic dissociation and the convective times, $\frac{t_d}{t_c} \sim \wp$ can be given by the following expression

$$\wp \sim \left\{ (\nu''_i - \nu'_i) \, k_f \prod_j \frac{[M_i]^{\nu''_j}}{[M_i]} \right\}^{-1} \quad \frac{1}{R_B \, \frac{\rho_\infty}{\rho_s} \, \frac{M_s}{2} \, a_\infty \sqrt{\frac{\bar{T}}{T_\infty}}}$$

-5-

where k_f = forward reaction rate constant, $\dfrac{(\text{conc.})^{1-(\text{order})}}{\text{sec}}$

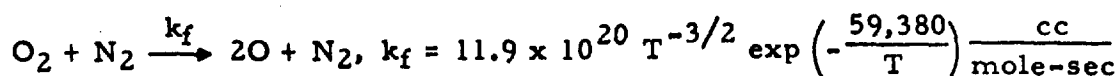k_b = reverse reaction rate constant, $\dfrac{(\text{conc.})^{1-(\text{order})}}{\text{sec}}$

$[\ ]$ = molal concentration, $\dfrac{\text{moles}}{\text{ft}^3}$

a = speed of sound, ft/sec

M = Mach number

For a very large $\wp$ we get a near frozen state and for a very small $\wp$ we get a near equilibrium state of the shock layer.

Eschenroeder, et al (Ref. 7), give the following rate constant for O_2 dissociation.

$$O_2 + N_2 \xrightarrow{k_f} 2O + N_2, \quad k_f = 11.9 \times 10^{20}\, T^{-3/2} \exp\left(-\frac{59,380}{T}\right) \frac{cc}{mole\text{-}sec}$$

It is assumed here that this expression can be extrapolated to temperatures as high as $15,000^\circ$K or higher.

Figure 1 is a plot of $\wp$ vs M_∞ for various altitudes. Figure 2 is the flight spectrum cross plotted from Fig. 1. These are for R_B = 1 ft. In order to be on the conservative side the highest available rate constant for O_2 dissociation is chosen. The expression used for the shock standoff distance also gives somewhat high values. Thus the resulting t_c will be larger than the actual value. The combination of these conservative characteristic times gives higher values of percent O_2 dissociation.

Based on an average temperature $\overline{T} \sim \dfrac{T_s + T_B}{2}$ the analysis shows that O_2 dissociation will be nearly frozen at higher altitudes particularly in the viscous-layer regime. The same basic conclusion
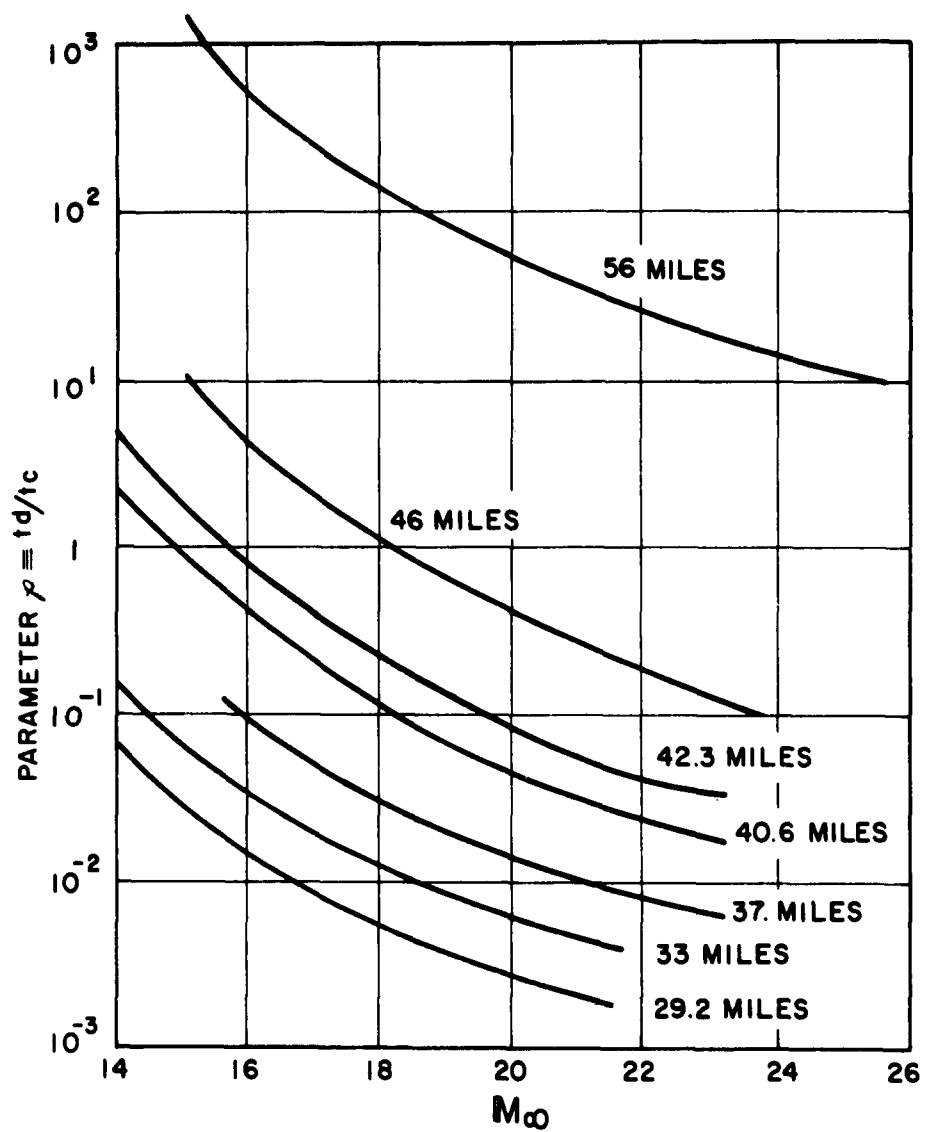
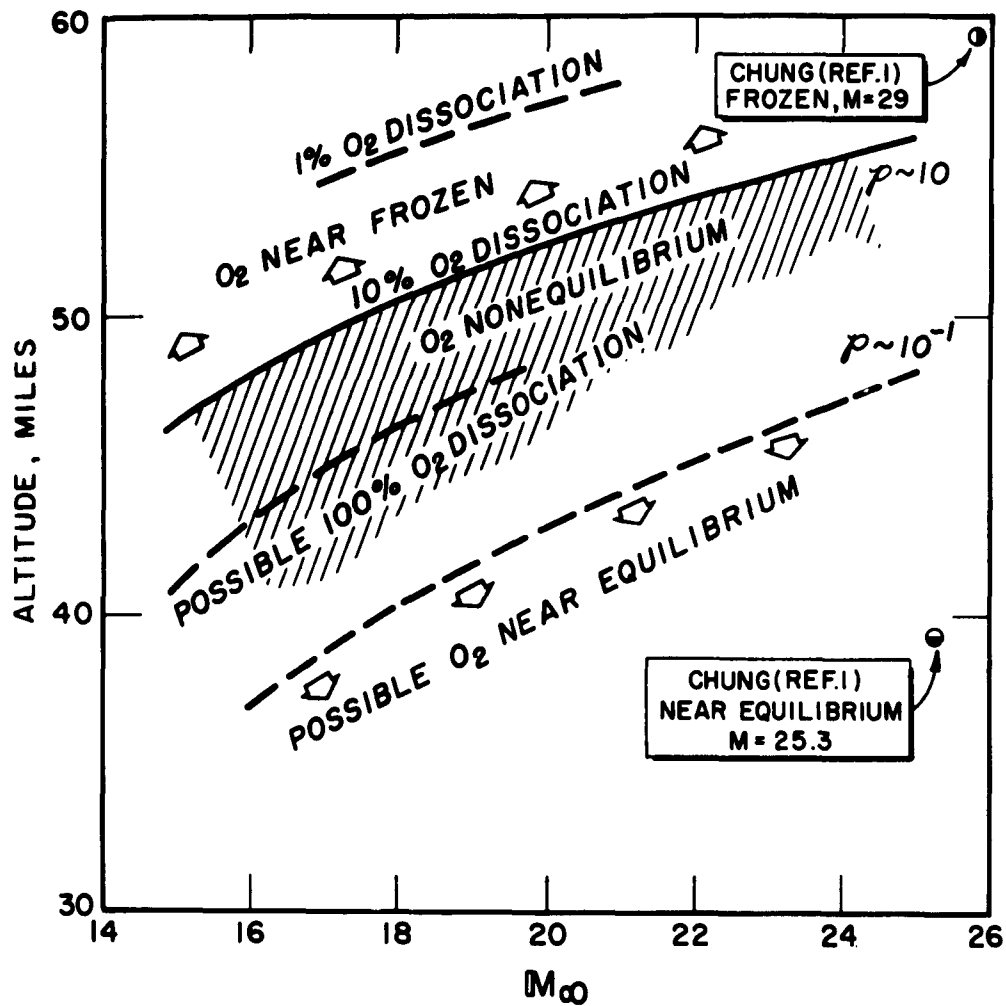Fig. 1   Dissociation Parameter $\mathscr{P}$ For R_B = 1 Foot.

Fig. 2   Chemical State Of The Shock Layer At The Stagnation
Region Of A 1-Foot Radius Noncatalytic Spherical Body
$T_B = 1500^\circ K$, ARDC Model Atmosphere (1959).

is also obtained by considering $\overline{T} \sim T_s$. This case is the upper limit where the average gas temperature in the shock layer is equal to T_s. Obviously this upper limit is physically impossible. The results essentially indicate that in the viscous-layer regime ionization at the stagnation region of a hypersonic 1-foot radius reentry body is unlikely. In view of the extremely high speed of the body this conclusion is contrary to popular belief. However, recent shock tube experiments of Herzberg (Ref. 8) indicated that the impurities such as diaphragm materials are the main sources of ionization. By carefully controlling the impurities he was able to decrease the degree of ionization to a level where the instruments failed to detect any ionized species. The results obtained by Chung (Ref. 1) also indicate that Fig. 2 gives a qualitatively correct picture. Two points from his study are plotted in Fig. 2.

The effect of the presence of atomic oxygen in the free stream is also considered. Assuming that the atomic oxygen is 50 percent of the total oxygen in the free stream, the same basic conclusion is reached.

An order of magnitude study such as ours is inherently approximate. But it shows the correct trend. At lower altitudes the results will be in considerable error. This is because chemical equilibrium will prevail in the inviscid portion of the shock layer. For this reason, the line showing 100% O_2 dissociation will not portray an accurate state of the gas. Possibly N_2 dissociation will also be significant in this region.

B. CONSERVATION EQUATIONS

While the result of the previous section gives the qualitative chemical

nature of the stagnation region of a 1-foot radius body, it fails to give any

information on the structure of the shock layer. It also fails to take into

account the important chemical reactions other than the dissociation of O_2.

The standard conservation equations for a reacting mixture are

written in spherical coordinates for an axisymmetric spherical body shown

in Fig. 3. The assumptions which led to the given form of a particular

equation are listed along with each equation (steady state system).

(i) Conservation of overall mass:

$$\frac{1}{r^2} \frac{\partial}{\partial r} (\rho r^2 u) + \frac{1}{r \sin\theta} \frac{\partial}{\partial\theta} (v \rho \sin\theta) = 0$$
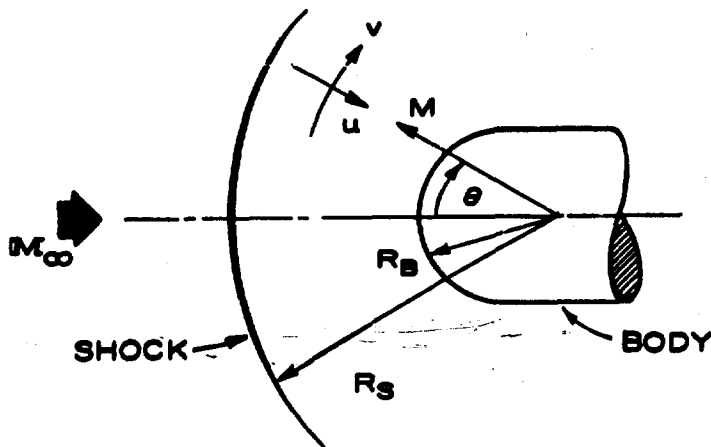

Fig. 3   Coordinate System.

where ρ = mass density

      u = r-component of the velocity

      v = θ-component of the velocity.

(ii) Conservation of individual species (assume uncoupled concentration diffusion only):

$$\frac{1}{r^2} \frac{\partial}{\partial r} (\rho\, c_i\, r^2 u) + \frac{1}{r \sin\theta} \frac{\partial}{\partial\theta} (\rho\, c_i v \sin\theta)$$

$$- \frac{1}{r^2} \frac{\partial}{\partial r} \left(\frac{\mu}{Sc}\, r^2 \frac{\partial c_i}{\partial r} \right) - \frac{1}{r \sin\theta} \frac{\partial}{\partial\theta} \left(\frac{\mu}{Sc}\, \frac{\sin\theta}{r}\, \frac{\partial c_i}{\partial\theta} \right) = \left[\dot{M_i} \right] \mathbf{M_i}$$

where c_i = mass fraction of species i

    Sc = Schmidt number

    μ = viscosity coefficient

   $\left[\dot{M_i} \right]$ = rate of change of the molal concentration of species i

   $\mathbf{M_i}$ = molecular weight of species i.

The expression for the volumetric production rate of species i, $\left[\dot{M_i} \right]$ can be written only when the reaction equations are specified. For $\left[\dot{M_i} \right]$, one essentially writes the law of mass action for a given set of reaction equations which affect M_i. These equations are given later in another section.

(iii) Conservation of r-momentum (assume linear stress-strain relationship, negligible second viscosity coefficient):

$$\rho\left[u\frac{\partial u}{\partial r} + \frac{v}{r}\frac{\partial u}{\partial \theta} - \frac{v^2}{r}\right] = \frac{\partial}{\partial r}\left[-p + 2\mu\frac{\partial u}{\partial r}\right]$$

$$+ \frac{1}{r}\frac{\partial}{\partial \theta}\left[\mu\, r\frac{\partial}{\partial r}\left(\frac{v}{r}\right) + \frac{\mu}{r}\frac{\partial u}{\partial \theta}\right]$$

$$+ \frac{\mu}{r}\left[4\frac{\partial u}{\partial r} - 4\frac{u}{r} - \frac{2}{r}\frac{\partial v}{\partial \theta} + \left\{r\frac{\partial}{\partial r}\left(\frac{v}{r}\right) - 2\frac{v}{r} + \frac{1}{r}\frac{\partial u}{\partial \theta}\right\}\cot\theta\right]$$

where p = pressure.

(iv) Conservation of θ-momentum (assume linear stress-strain relationship, negligible second viscosity coefficient):

$$\rho\left[u\frac{\partial u}{\partial r} + \frac{v}{r}\frac{\partial v}{\partial \theta} + \frac{uv}{r}\right] = \frac{\partial}{\partial r}\left[\mu\left\{r\frac{\partial}{\partial r}\left(\frac{v}{r}\right) + \frac{1}{r}\frac{\partial u}{\partial \theta}\right\}\right]$$

$$+ \frac{1}{r}\frac{\partial}{\partial \theta}\left[-p + 2\mu\left(\frac{1}{r}\frac{\partial v}{\partial \theta} + \frac{u}{r}\right)\right]$$

$$+ \frac{1}{r}\left[\left\{2\mu\left(\frac{1}{r}\frac{\partial v}{\partial \theta} - \frac{v}{r}\cot\theta\right)\cot\theta\right\} + 3\mu\left\{r\frac{\partial}{\partial r}\left(\frac{v}{r}\right) + \frac{1}{r}\frac{\partial u}{\partial \theta}\right\}\right]$$

(v) Conservation of energy (assume diffusive enthalpy flux is small compared to the convective flux and no radiation heat transfer):

$$\rho\left[u\frac{\partial}{\partial r}(\overline{c}_p T) + \frac{v}{r}\frac{\partial}{\partial \theta}(\overline{c}_p T)\right] = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 k\frac{\partial T}{\partial r}\right)$$

$$+ \frac{1}{r\sin\theta}\frac{\partial}{\partial \theta}\left(\frac{k}{r}\frac{\partial T}{\partial \theta}\sin\theta\right) + \sum Q_{reaction} + u\frac{\partial p}{\partial r} + \frac{v}{r}\frac{\partial p}{\partial \theta} + \Phi$$

where k = thermal conductivity

$\bar{c}_p$ = mean specific heat of the mixture at constant pressure = $\sum\limits_i c_i c_{p_i}$

$\sum Q_{reaction}$ = net heat released due to reaction

Φ = dissipation function.

The expression for $\sum Q_{reaction}$ can be written for a given set of reaction equations. This will be given later after the particular reaction equations are specified. The dissipation function Φ is given by
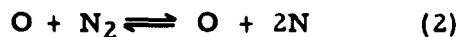
$$\Phi = \mu \left[2\left\{ \left(\frac{\partial u}{\partial r}\right)^2 + \left(\frac{1}{r}\frac{\partial v}{\partial \theta} + \frac{u}{r}\right)^2 + \left(\frac{u}{r} + \frac{v \cot \theta}{r}\right)^2 \right\} + \left\{ r\frac{\partial}{\partial r}\left(\frac{v}{r}\right) + \frac{1}{r}\frac{\partial u}{\partial \theta} \right\}^2 \right]$$

C. REACTION MODEL AND RATE EXPRESSIONS

Atallah (Ref. 9) has surveyed the existing literature on the chemical kinetics of air after a hypersonic shock. He gives the important reactions and their appropriate rate expressions based on the best known experimental data. There seems to be a wide agreement in the literature as to which chemical species should be abundant due to a hypersonic shock in air. However, a great deal of uncertainty exists in the expressions for the rate constants. In general, the experimental values are applicable within a temperature range of $2000^\circ K$ to $6000^\circ K$. The temperature after the shock in front of the reentry body may exceed the upper limit by a large margin. Thus, one is forced to use the rate constants in a temperature range where their validity is questionable. Any error in the reaction rate

will introduce a considerable amount of error in the solution of the shock layer. Bortner (Ref. 10) discusses this very point. Nawrocki (Ref. 11) among others gives an excellent review of the state of knowledge of reaction rates. Since reviews such as this are already available in the published literature, no attempt will be made here to survey the existing experimental data.

The following six chemical reactions involving seven different species are assumed to play an important part in the behavior of the shock layer.

$$O_2 + N_2 \rightleftharpoons 2O + N_2 \qquad (1)$$

$$O + N_2 \rightleftharpoons O + 2N \qquad (2)$$

$$N_2 + O \rightleftharpoons NO + N \qquad (3)$$

$$O_2 + N \rightleftharpoons NO + O \qquad (4)$$

$$2N + O \rightleftharpoons NO + N \qquad (5)$$

$$N + O \rightleftharpoons NO^+ + e^- \qquad (6)$$

Ionization reactions $O \rightleftharpoons O^+ + e^-$ and $N \rightleftharpoons N^+ + e^-$ have not been included in the above set of reaction equations. These two reactions take place at extremely high temperatures and are important in calculating transport coefficients, specific heats, etc. But since we are interested in finding out if we have ionization in the shock layer our investigation should be centered around NO ionization, $NO \rightleftharpoons NO^+ + e^-$. This reaction occurs at a relatively lower temperature and is not as vital for thermodynamic calculations as for locating the position of antenna for communication.

Having established the pertinent reaction equations we are in a position to write expressions for $[\dot{M}_i]$ for each of the seven species. Using the notations of the previous section and applying the law of mass action for each of the six equations we get the following results:

$$\frac{d[O_2]}{dt} = -k_{f_1}[O_2][N_2] + k_{b_1}[O]^2[N_2] - k_{f_4}[O_2][N] + k_{b_4}[NO][O]$$

$$\frac{d[O]}{dt} = 2k_{f_1}[O_2][N_2] - 2k_{b_1}[O]^2[N_2] - k_{f_3}[N_2][O] + k_{b_3}[NO][N]$$

$$+ k_{f_4}[O_2][N] - k_{b_4}[NO][O] - k_{f_3}[N]^2[O] + k_{b_5}[NO][N]$$

$$- k_{f_6}[N][O] + k_{b_6}[NO^+][e^-]$$

$$\frac{d[N_2]}{dt} = -k_{f_2}[O][N_2] + k_{b_2}[O][N]^2 - k_{f_3}[N_2][O] + k_{b_3}[NO][N]$$

$$\frac{d[N]}{dt} = 2k_{f_2}[O][N_2] - 2k_{b_2}[O][N]^2 + k_{f_3}[N_2][O] - k_{b_3}[NO][N]$$

$$-k_{f_4}[O_2][N] + k_{b_4}[NO][O] - k_{f_5}[O][N]^2 + k_{b_5}[NO][N]$$

$$-k_{f_6}[N][O] + k_{b_6}[NO^+][e^-]$$

$$\frac{d[NO]}{dt} = k_{f_3}[N_2][O] - k_{b_3}[NO][N] + k_{f_4}[O_2][N] - k_{b_4}[NO][O]$$

$$+ k_{f_5}[N]^2[O] - k_{b_5}[NO][N]$$

$$\frac{d[NO^+]}{dt} = k_{f_6}[N][O] - k_{b_6}[NO^+][e^-]$$

$$\frac{d[e^-]}{dt} = k_{f_6}[N][O] - k_{b_6}[NO^+][e^-]$$

The subscripts f and b refer to the forward and the reverse reaction rate constants respectively. The number in the subscript refers to the reaction equation. For example, k_{f_3} refers to the forward reaction rate constant for reaction 3.

Now $\sum Q_{reaction}$ in the energy equation is the net heat released or absorbed due to reaction. It can be evaluated either by summing up all the heats of reaction for individual reaction products or by summing up each molecular species multiplied by its heat of formation.

$$\sum Q_{reaction} = - \left\{ k_{f_1}[O_2][N_2] - k_{b_1}[O]^2[N_2] \right\} \Delta h_1$$

$$- \left\{ k_{f_2}[O][N_2] - k_{b_2}[O][N]^2 \right\} \Delta h_2$$

$$- \left\{ k_{f_3}[N_2][O] - k_{b_3}[NO][N] \right\} \Delta h_3 + \left\{ k_{f_4}[O_2][N] - k_{b_4}[NO][O] \right\} \Delta h_4$$

$$+ \left\{ k_{f_5}[N]^2[O] - k_{b_5}[NO][N] \right\} \Delta h_5 - \left\{ k_{f_6}[N][O] - k_{b_6}[NO^+][e^-] \right\} \Delta h_6$$

where Δh's are molal heats of reaction.

The other way of expressing the net heat release is $\sum Q_{reaction} = \sum [\dot{M}_i] h_i^\circ$; where h_i° is the molal heat of formation of species i. Because of the definition of the heat of formation only the molecular species, O_2 and N_2 need not be considered.

-16-

Bortner (Ref. 12) gives the following heats of reaction for the six reaction equations we have:

$$\Delta h, \frac{\text{kg-cal}}{\text{g-mole}}$$

$$O_2 + N_2 \longrightarrow 2O + N_2 \qquad 117.7$$

$$O + N_2 \longrightarrow O + 2N \qquad 226.0$$

$$N_2 + O \longrightarrow NO + N \qquad 76.1$$

$$O_2 + N \longrightarrow NO + O \qquad -32.3$$

$$2N + O \longrightarrow NO + N \qquad -150.0$$

$$N + O \longrightarrow NO^+ + e^- \qquad 64.5$$

$-\Delta h$ signifies an exothermic reaction.

The rate constants for all the reactions except the fifth reaction are taken from Ref. 9. The rate constants for the fifth reaction are taken from AVCO Report 104.

$$k_{f_1} = 2.36 \times 10^{20} \, T^{-3/2} \, \exp\left(-\frac{59,380}{T}\right) \quad \frac{\text{cc}}{\text{mole-sec}}$$

$$k_{b_1} = 1.86 \times 10^{17} \, T^{-1} \quad \frac{\text{cc}^2}{\text{mole}^2\text{-sec}}$$

$$k_{f_2} = 7.35 \times 10^{20} \, T^{-3/2} \, \exp\left(-\frac{113,340}{T}\right) \quad \frac{\text{cc}}{\text{mole-sec}}$$

$$k_{b_2} = 3.9 \times 10^{19} \, T^{-3/2} \quad \frac{\text{cc}^2}{\text{mole}^2\text{-sec}}$$

$$k_{f_3} = 5.5 \times 10^{11} \ T^{1/2} \exp\left(-\frac{36,245}{T}\right) \frac{cc}{mole\text{-}sec}$$

$$k_{b_3} = 2 \times 10^{11} \ T^{1/2} \ \frac{cc}{mole\text{-}sec}$$

$$k_{f_4} = 8.9 \times 10^{11} \ T^{1/2} \exp\left(-\frac{3940}{T}\right) \frac{cc}{mole\text{-}sec}$$

$$k_{b_4} = 1.21 \times 10^{11} \ T^{1/2} \exp\left(-\frac{19,750}{T}\right) \frac{cc}{mole\text{-}sec}$$

$$k_{f_5} = 2.0 \times 10^{21} \ T^{-3/2} \ \frac{cc^2}{mole^2\text{-}sec}$$

$$k_{b_5} = 7.9 \times 10^{21} \ T^{-3/2} \exp\left(-\frac{75,000}{T}\right) \frac{cc}{mole\text{-}sec}$$

$$k_{f_6} = 6.4 \times 10^{9} \ T^{1/2} \exp\left(-\frac{36,650}{T}\right) \frac{cc}{mole\text{-}sec}$$

$$k_{b_6} = 1.78 \times 10^{19} \ T^{-1} \ \frac{cc}{mole\text{-}sec}$$

The temperature T is in degrees Kelvin.

D. AUXILIARY EQUATIONS AND BOUNDARY CONDITIONS

The conservation equations listed in Section B do not constitute a soluble set unless other auxiliary equations are known. In this section, the other necessary equations are listed.

(a) Equation of state:

Perfect gas for individual species $p_i = \rho c_i \dfrac{R}{M_i} T$

Perfect gas for the ambient air $p_\infty = \rho_\infty \dfrac{R}{M_\infty} T_\infty$

Real gas for the shock layer $p = \rho Z \dfrac{R}{M_\infty} T = \rho \dfrac{R}{\overline{M}} T$

where Z = compressibility factor, $\dfrac{M_\infty}{\overline{M}}$

$\overline{M}$ = mean molecular weight $\sum \dfrac{1}{(c_i/M_i)}$

(b) Transport coefficients and properties:

In the absence of detailed knowledge of the transport coefficient in a nonequilibrium chemical system the following assumptions are made as a zeroth approximation

$$\frac{\mu}{\mu_\infty} = \frac{T}{T_\infty}; \quad \frac{k}{k_\infty} = \frac{T}{T_\infty}; \quad Pr = 1; \quad Sc = 1; \quad c_p = \text{const.}$$

For a gaseous mixture in chemical equilibrium, reasonably accurate estimates of the transport coefficients are available in the literature (NACA TN 4150, for example). It is quite possible that the above assumptions of the behavior of the transport coefficients do not correctly describe our system. However, their choice is dictated by their simpler form. Other available relationships will neither provide more accuracy nor will they help us better understand the

problem. If our solution shows a trend toward near equilibrium chemical state then we plan to use appropriate known transport properties.

(c) The state behind the shock:

T_s, ρ_s, p_s, M_s, etc. can be found from the shock tables for a given T_∞, p_∞, M_∞, etc. We must remember in this connection that no reaction takes place in the shock thickness (thin discontinuity). Thus, we have air at a very high temperature at $r = R_s$.

(d) Shock radius, R_s:

We shall assume $\dfrac{\Delta}{R_B} \sim 0.1$. Therefore, $R_s \sim R_B + \Delta \sim 1.1 R_B$ where Δ = shock standoff distance at the stagnation region. We shall also assume that the shock is spherical for small θ. Choosing Δ arbitrarily eliminates the free-boundary nature of the problem and consequently the number of boundary conditions which may be satisfied by the solution will be reduced by one. If in the solution of the equations, it appears impossible to satisfy the specified boundary conditions at the body using $\Delta \sim 0.1 R_B$ this assumption may be varied.

(e) **Boundary conditions:**

(i) Noncatalytic body:

(At $r = R_B$ and any θ); $u = 0$; $v = 0$; $T = T_B$; $\left.\dfrac{\partial c_i}{\partial r}\right|_{R_B} = 0.$

(At $r = R_s$ and any θ); $u = -u_s$; $v = v_s$; $T = T_s$; $p = p_s$

$$\left[r \frac{\partial}{\partial r}\left(\frac{v}{r}\right) + \frac{1}{r} \frac{\partial u}{\partial \theta} \right]_{r = R_s} = 0 \qquad \begin{array}{c}\text{(no shearing stress}\\ \text{at the shock)}\end{array}$$

$c_i / = 0.$
 atomic
 species

Also $\left.\dfrac{\partial c_i}{\partial \theta}\right|_{r = R_s} = 0$

(ii) Catalytic body:

(At $r = R_B$ and any θ); $u = 0$; $v = 0$; $T = T_B$

c_i other than c_{O_2} and c_{N_2} are zero (complete
           recombination)

At $r = R_s$ the boundary conditions are the same as (i).

From the set of equations shown in the preceding sections we find that we have two independent variables, r and θ. The numbers of dependent variables and equations are as follows:

Dependent variables $\underbrace{u, \ v, \ p, \ \rho, \ T,}_{5} \ \underbrace{c_i}_{7} = 12$

Number of equations:

Conservation of mass (overall)	1
Conservation of species	7
Conservation of momentum	2
Conservation of energy	1
Equation of state	1
Total	12

Thus, we have twelve equations and twelve unknowns, and the system of equations is soluble.

Three altitudes, 175,000 feet, 250,000 feet and 295,000 feet and three M_∞, 20, 25 and 30 are to be investigated. These altitudes will span the "viscous-layer regime" and come down to the fringe of the "boundary-layer regime" as defined by Probstein (Ref. 13).

An analytical solution of these equations was attempted by a method similar to that used by Probstein and Kemp (Ref. 14) in their solution for nonreacting, constant density viscous flow in the shock layer about a sphere. Functional forms for the dependent variables were assumed in an attempt to reduce the partial differential equations to a set of simultaneous ordinary differential equations valid in the stagnation region. Both this method and a series solution method involving expansion in θ about the stagnation line were unsuccessful.

Since no similarity parameters valid beyond the stagnation point are available, a relaxation scheme for the shock layer has been developed in the next chapter. The equations we have are elliptic in nature and are suitable for relaxation solution.

III. NUMERICAL PROCEDURE

The boundary-value problem consists of twelve nonlinear partial differential equations of the second order, with twelve dependent variables and two independent ones. These may be written in the form:

$$P_k(v_i, v_{i_r}, v_{i_{rr}}, v_{i_\theta}, v_{i_{\theta\theta}}, v_{i_{r\theta}}, r, \theta) = 0 \tag{7}$$

$$i = 1, 2 \ldots 12$$

$$k = 1, 2 \ldots 12$$

with boundary values at the shock ($r = R_s$) and the body ($r = R_B$).

In general, the approach to this problem is based on two ideas; first, that the differential equations can be replaced by finite difference equations which are algebraic in the dependent variables at a point; and second, that systems of simultaneous nonlinear algebraic equations can be solved by Newton's Method. Thus, a solution consists of sets of the dependent variables which satisfy Eq. (7) at a finite number of points (r, θ) between the shock and the body, with spacing $\Delta r, \Delta \theta$. If a solution also satisfies boundary values at the body, it is assumed to be a physical solution of the differential equations.

A. DIFFERENCE EQUATIONS

All partial derivatives are replaced by their corresponding forward difference quotients;

$$\frac{\partial}{\partial r} \, v_i = \frac{v_i(r, \theta) - v_i(r - \Delta r, \theta)}{\Delta r}$$

$$\frac{\partial^2}{\partial r^2} \, v_i = \frac{\frac{\partial}{\partial r}\left(v_i(r, \theta)\right) - \frac{\partial}{\partial r}\left(v_i(r - \Delta r, \theta)\right)}{\Delta r}$$

$$\frac{\partial}{\partial \theta} \, v_i = \frac{v_i(r, \theta) - v_i(r, \theta - \Delta \theta)}{\Delta \theta}$$

$$\frac{\partial^2}{\partial \theta^2} \, v_i = \frac{\frac{\partial}{\partial \theta}\left(v_i(r, \theta)\right) - \frac{\partial}{\partial \theta}\left(v_i(r, \theta - \Delta \theta)\right)}{\Delta \theta}$$

$$\frac{\partial^2}{\partial r \, \partial \theta} \, v_i = \frac{\frac{\partial}{\partial r}\left(v_i(r, \theta)\right) - \frac{\partial}{\partial r}\left(v_i(r, \theta - \Delta \theta)\right)}{\Delta \theta}$$

If $v_i(r - \Delta r, \theta)$ and $v_i(r, \theta - \Delta \theta)$ are known, the problem is reduced to twelve nonlinear simultaneous algebraic equations in twelve unknowns v_i at any point (r, θ).

$$F_k(v_i)\Big|_{r, \theta} = 0 \tag{8}$$

B. NEWTON'S METHOD

Assume that for fixed r, θ a set $\{v_{i_1}\}$ has somehow been estimated which is "sufficiently close" to the solution set $\{v_i\}$. Expand each of the F_k in Taylor's Series about the point $\{v_{i_1}\}$, neglecting all except the first order terms. We have twelve linear equations

$$F_k(v_{i_1} + \Delta v_i) = F_k(v_{i_1}) + \frac{\partial F_k}{\partial v_1} \Delta v_1 + \dots + \frac{\partial F_k}{\partial v_{12}} \Delta v_{12}$$

Assume that $\{v_{i_1} + \Delta v_i\}$ is a solution set, so that $F_k(v_{i_1} + \Delta v_i) = 0$. Then in matrix form

$$\begin{bmatrix} -F_1(v_{i_1}) \\ \vdots \\ -F_{12}(v_{i_1}) \end{bmatrix} = \begin{bmatrix} \frac{\partial F_1}{\partial v_1} & \cdots & \frac{\partial F_1}{\partial v_{12}} \\ & \vdots & \\ \frac{\partial F_{12}}{\partial v_1} & \cdots & \frac{\partial F_{12}}{\partial v_{12}} \end{bmatrix} \begin{bmatrix} \Delta v_1 \\ \vdots \\ \Delta v_{12} \end{bmatrix}$$

or

$$\begin{bmatrix} -F \end{bmatrix} = \begin{bmatrix} J \end{bmatrix} \begin{bmatrix} \Delta v_i \end{bmatrix}$$

Then

$$\begin{bmatrix} \Delta v_i \end{bmatrix} = \begin{bmatrix} J \end{bmatrix}^{-1} \begin{bmatrix} -F \end{bmatrix}$$

and the set

$$v_{i_2} = v_{i_1} + \Delta v_i$$

will be an improved estimate if the process is convergent. This procedure is used repeatedly, giving

$$v_{i_n} = v_{i_{n-1}} + \Delta v_{i_{n-1}}$$

until all the $F_k(v_{i_n})$ are sufficiently close to zero simultaneously.

C. JACOBIAN ELEMENTS

The 144 $\dfrac{\partial F_k}{\partial v_i}$ of the J-matrix may be determined by differentiating each F_k twelve times and writing 144 equations; however it is more efficient to find these numerically. An arbitrary increment δv_i is chosen for each v_i and the derivatives found from the difference quotients:

$$\frac{\partial}{\partial v_i} F_k(v_i) = \frac{F_k(v_1, \dots, v_{i-1}, v_i + \delta v_i, v_{i+1} \dots, v_{12}) - F_k(v_1 \dots v_i \dots v_{12})}{\delta v_i}$$

D. BOUNDARY VALUES

For any numerical solution of a differential equation it is necessary to replace a boundary-value problem with an equivalent initial-value problem. Some of the initial values will be chosen arbitrarily. Each choice will give a solution which may or may not match the known conditions on the final boundary. The arbitrary initial values are then varied until a solution is found which satisfies all boundary conditions.

In this problem the dependent variables v_i are known at the shock from free-stream conditions and the oblique shock relations. Thus all $\frac{\partial}{\partial \theta}\bigg|_{r=R_s} v_i$ and $\frac{\partial^2}{\partial \theta^2}\bigg|_{r=R_s} v_i$ are also known. To get approximate values for $\frac{\partial}{\partial r} v_i$ the inviscid equations are solved at the shock. These values can then be substituted into the viscous equations (7) to find values of $\frac{\partial^2}{\partial r^2} v_i$ so that Eqs. (8) are actually satisfied at the shock.

Values on the stagnation line ($\theta = 0$, $R_B < r < R_s$) must also be known. Originally these were estimated from boundary values and an attempt to improve the estimate was made. It is now felt that the stagnation line must be solved as a separate problem (see Section IV Results).

E. EXTRAPOLATION

To start the Newton's Method iteration at an unknown point (r, θ) an initial estimate of v_i and all derivatives is required. This is done by assuming constant second derivatives and using second order extrapolation from known points $(r - \Delta r, \theta)$ $(r, \theta - \Delta \theta)$

$$\frac{\partial^2}{\partial r^2} v_i(r, \theta) = \frac{\partial^2}{\partial r^2} v_i(r - \Delta r, \theta)$$

$$\frac{\partial}{\partial r} v_i(r, \theta) = \frac{\partial}{\partial r} v_i(r - \Delta r, \theta) + \Delta r \frac{\partial^2}{\partial r^2} v_i(r - \Delta r, \theta)$$

$$v_i(r, \theta) = v_i(r-\Delta r, \theta) + \frac{\partial}{\partial r} v_i(r-\Delta r, \theta)\Delta r + \frac{1}{2\Delta r^2} \frac{\partial^2}{\partial r^2} v_i(r-\Delta r, \theta)$$

and similarly for the θ-derivatives.

F. SEQUENCE OF OPERATIONS

For an individual point (r, θ);

1. Extrapolate initial estimates from points $(r-\Delta r, \theta)$ and $(r, \theta-\Delta\theta)$.

2. Evaluate $F_k(v_i)$ and test for zero. If a solution has been found proceed to next point.

3. If the F_k are not zero, set up and solve the Jacobian matrix for the Δv_i. Modify the v_i and go to step 2.

This procedure is started from the shock and carried along a radial line θ = const. until the body is reached, and repeated for increasing θ until the supersonic region is reached. If the solution does not match the boundary values along the body, the slopes at the shock $\left(\dfrac{\partial v_i}{\partial r}\right)$ are adjusted and another solution is obtained.

G. SUMMARY OF ASSUMPTIONS MADE

1. That a unique solution of the differential equations exists, and that solutions of the corresponding difference equations will converge to this as net size $(\Delta r, \Delta\theta)$ decreases.

2. That the functions $F_k(v_i)$ are well-behaved enough to allow linear representation by Taylor Series in some neighborhood of the $\{v_i\}$.

3. That initial estimates of the v_i can be made which will fall within this region of convergence so that Newton's Method can be used.

4. That unknown boundary values can be estimated with enough accuracy to permit assumption 3 to be made.

IV. RESULTS

The complete flow-field problem was programmed for the WDPC 7090 Computer. The boundary line $\theta = -\Delta\theta$, $R_s > r > R_B$ was assumed to be known and the solution was attempted along the stagnation line. Although many different sets of initial values were tried, none was accurate enough to fall within the region of convergence of Newton's Method. In addition, since the Navier-Stokes equations in spherical coordinates become indeterminant on the stagnation line and a limiting process must be resorted to, it was decided to attempt to solve the stagnation line separately.

This has two advantages; first, a stagnation line solution would serve as a boundary for the flow-field problem; second, it provides a simpler way to study the operation of the numerical techniques used. It was decided to further simplify the problem by approaching it in parts;

that is, to solve the frozen flow problem (three equations, three unknowns) first and then use this solution as a starting point for the reacting flow stagnation line problem.

A. EFFECT OF ERROR ACCUMULATION

A program to solve for (u, ρ, T) in cgs units was written for the Honeywell 800 Computer. This program converges and gives solutions for about one-half the distance from the shock to the body. It was felt that part of the difficulty with convergence of this program was caused by the loss of numerical significance. All computations are floating point, to eight significant digits, but change in the last place of $u, \rho,$ or T affects the higher order digits of the functions.

In an effort to eliminate this difficulty the frozen flow problem was reprogrammed in dimensionless form.[*] This improved the results in degree but not in kind. Although the Newton's Method solution at a point is self-correcting, errors accumulate from point to point, as with any marching procedure. It seems that the increasing error degrades the quality of the initial estimate at a point until it finally falls outside the region of convergence of the Newton's Method. Values of the functions of the initial estimates are plotted versus radius for a typical case in

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[*] The nondimensional equations for frozen flow on the stagnation line are given in the Appendix.

Fig. 4. Thus, this technique can always be expected to fail to converge at some point. The usefulness of the technique depends on whether or not the body is reached before convergence fails.

To attempt to make the solution reach the assumed body position, many sets of initial values of slopes of u, ρ, T at the shock were tried. Sample plots are shown in Figs. 5, 6 and 7. These figures also show that the effect of changing the point spacing is small, indicating that Δr has been chosen small enough. At points where convergence was obtained, the procedure generally decreased the values of the functions by an order of magnitude with each iteration. Convergence at a typical point is shown in Figs. 8, 9 and 10. All figures shown are for $\left(M_{\infty} = 20 \right)^{*}$ altitude of 295,000 feet, and body radius of 1 foot.

B. EFFECT OF SHOCK STANDOFF DISTANCE

It was felt at this point that the main difficulty in reaching the body where $u = 0$ was probably due to the choice of a fixed value of the shock standoff distance. The actual shock standoff distance is a physical parameter and it should be obtained as a part of the solution. For a given body traveling at a specified speed, the shock standoff distance is a unique distance. However, it is not easy to determine the exact value of this

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[*]Free-stream Mach number of 20.

distance for a given body and Mach number combination. The available order of magnitude value of $\frac{\Delta}{R_B}$ is not accurate enough for a problem of this kind.

In our problem, one way of determining this distance as a part of the solution will be to start the iteration from the shock and proceed toward the body through the shock layer. When the solution gives us $u = 0$ and matches the rest of the physical boundary conditions we have actually reached the body. Thus, we get both the structure of the shock layer and Δ from the solution.

Initially a value of $\frac{\Delta}{R_B} \sim 0.1$ was chosen based on the order of magnitude study. Once this ratio was fixed we had twelve equations with twelve unknowns which, in theory at least, are soluble. As a consequence, the solution failed to reach the hypothetical body located at a known distance from the shock. In order to surmount this difficulty, the shock standoff distance was treated as an additional dependent variable. A comparison of values of $\frac{\Delta}{R_B}$ is shown in Figs. 11, 12 and 13. It was found that our initial guess of $\frac{\Delta}{R_B} \sim 0.1$ gave too large a standoff distance. On the other hand, the second guess $\frac{\Delta}{R_B} \sim 0.06$ resulted in a much smaller value of Δ . The actual value of $\frac{\Delta}{R_B}$ will lie between these two limits provided the solution converges.

Since a solution which satisfies the boundary conditions for the chemically frozen flow on the stagnation streamline was not obtained, no attempt was made to solve the reacting case.

V. CONCLUSIONS AND RECOMMENDATIONS

Even though no valid solution was obtained we can conclude the following:

1. The Newton-Raphson iterative method is applicable for problems of this kind provided the initial estimates of the functions and their derivatives are fairly good. As mentioned in the text, if the initial estimates are not close to the actual values no convergence will be reached.

2. In numerically computing the elements of the Jacobian, one cannot neglect the second order terms. If they are neglected the problem will fail to converge.

3. The value of the shock standoff distance cannot be specified a priori. It has to be obtained as a part of the solution.

It is recommended that future work be carried on in an attempt to solve the whole problem. This should be done step by step utilizing the equations in a nondimensional form. First, the stagnation streamline should be solved for a frozen case and then following the same method attempts should be made to solve the reacting case with pertinent reaction equations. The solution of the stagnation streamline will constitute an additional boundary from which the iteration for the whole flow field can be attempted.

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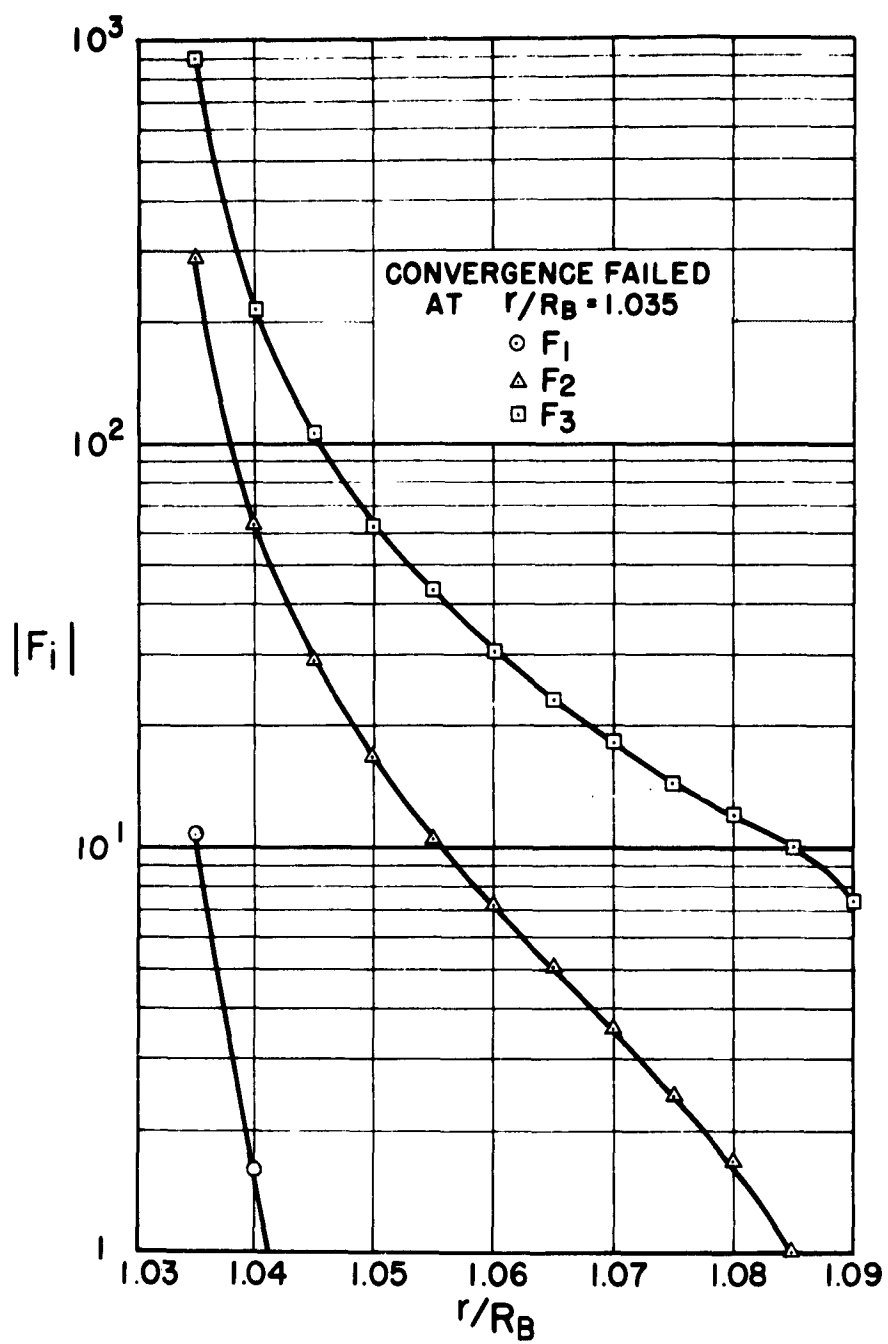
Fig. 4 Values Of Functions Of Initial Estimates Vs. r/R_B.

du/dr/s	dρ/dr/s	dT/dr/s	Δr
———	-.298 x 10⁴	-.5 x 10⁸	204 x 10⁴	5%
□	-.298 x 10³	-.5 x 10⁸	204 x 10⁴	5%
◇	-.298 x 10⁴	+.5 x 10⁸	204 x 10⁴	5%
△	-.298 x 10⁴	-.5 x 10⁸	200 x 10⁴	5%
⊙	-.298 x 10⁴	-.5 x 10⁸	204 x 10⁴	2.5%
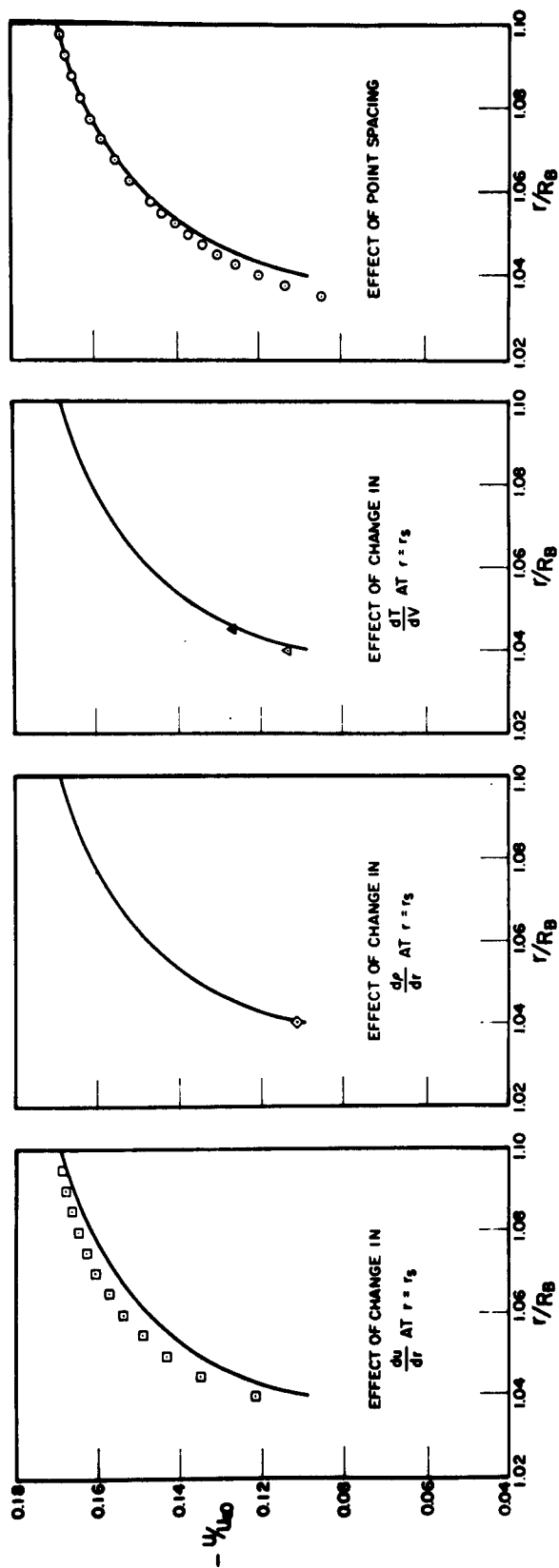
NOTE: POINTS NOT PLOTTED FALL ON COMPARISON CURVE.

Fig. 5   Effect Of Initial Slopes On Velocity Ratio.

-37-

du/dr/s	dp/dr/s	dT/dr/s	Δr
—	$-.296 \times 10^4$	$-.5 \times 10^8$	204×10^4	5%
□	$-.296 \times 10^3$	$-.5 \times 10^8$	204×10^4	5%
◇	$-.296 \times 10^4$	$+.5 \times 10^8$	204×10^4	5%
△	$-.296 \times 10^4$	$-.5 \times 10^8$	200×10^4	5%
⊙	$-.296 \times 10^4$	$-.5 \times 10^8$	204×10^4	2.5%

EFFECT OF CHANGE IN $\frac{du}{dr}$ AT $r=r_s$

EFFECT OF CHANGE IN $\frac{dp}{dr}$ AT $r=r_s$

EFFECT OF CHANGE IN $\frac{dT}{dv}$ AT $r=r_s$

EFFECT OF POINT SPACING

P/P_0

r/R_B
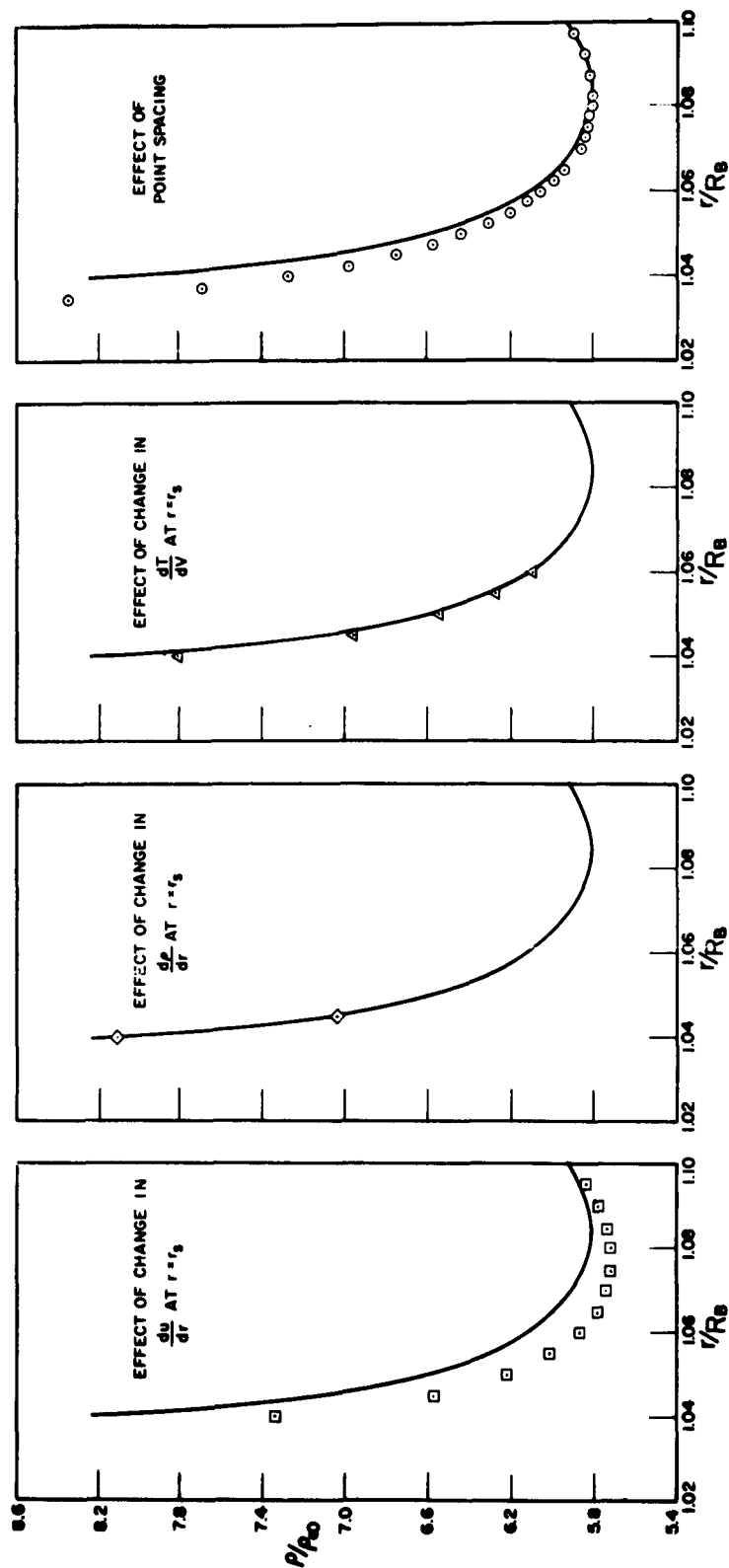
NOTE: POINTS NOT PLOTTED FALL ON COMPARISON CURVE.

Fig. 6   Effect Of Initial Slopes On Density Ratio.
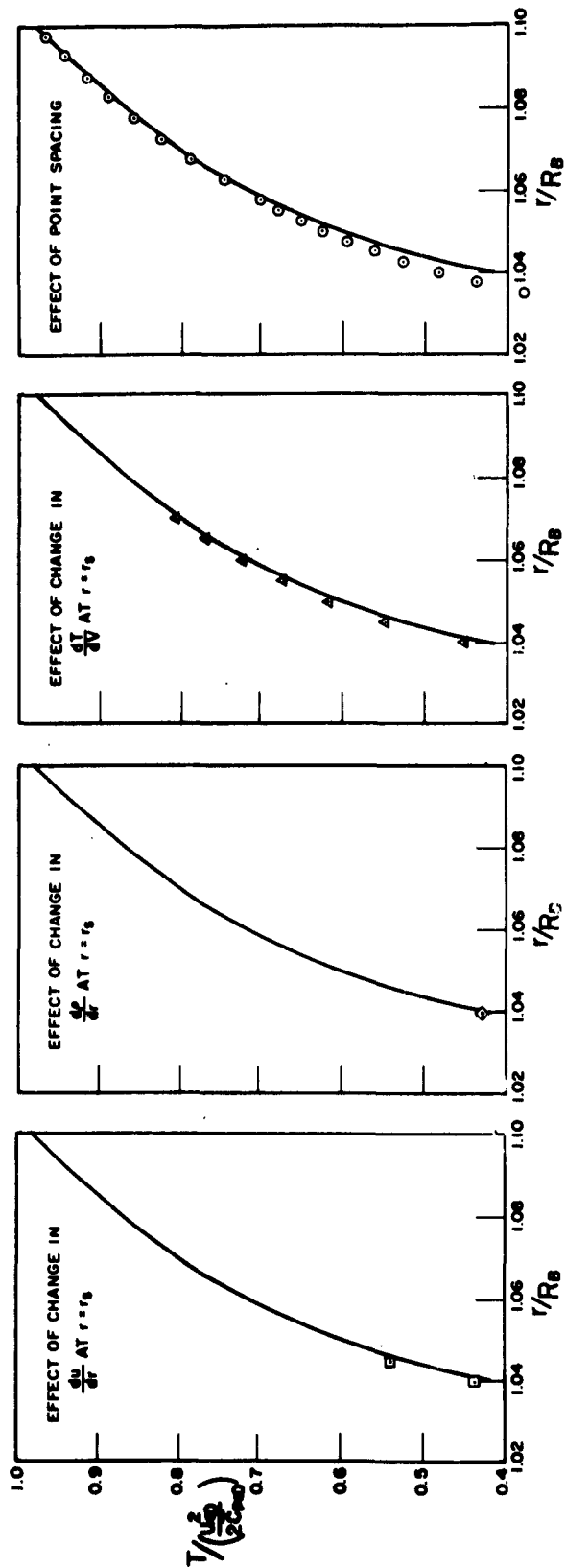
Fig. 7   Effect Of Initial Slopes On Temperature Ratio.
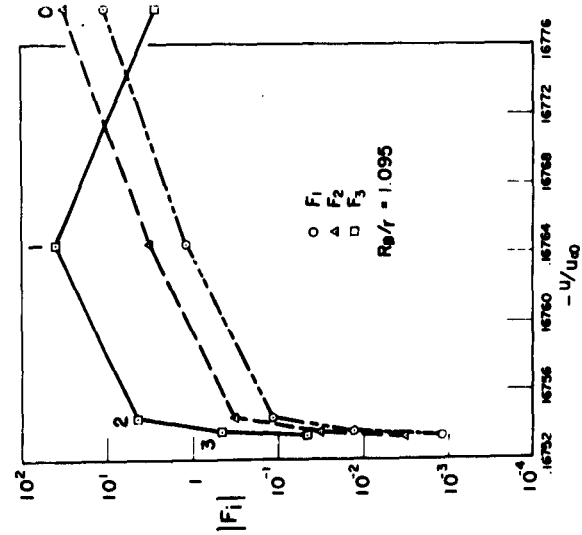
Fig.8 Convergence With Respect To $-u/u_\infty$.
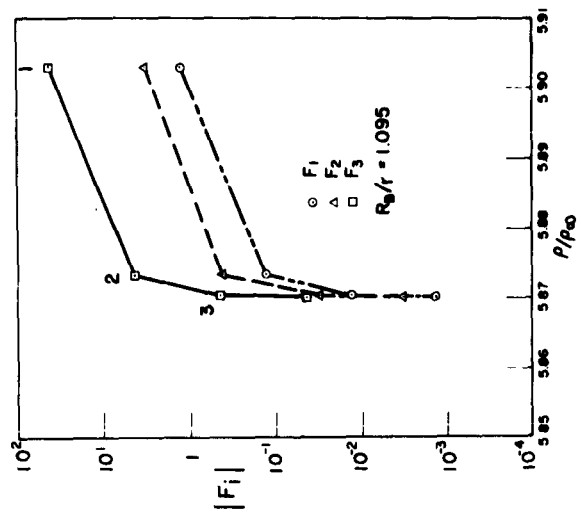
Fig.9 Convergence With Respect To ρ/ρ_∞.
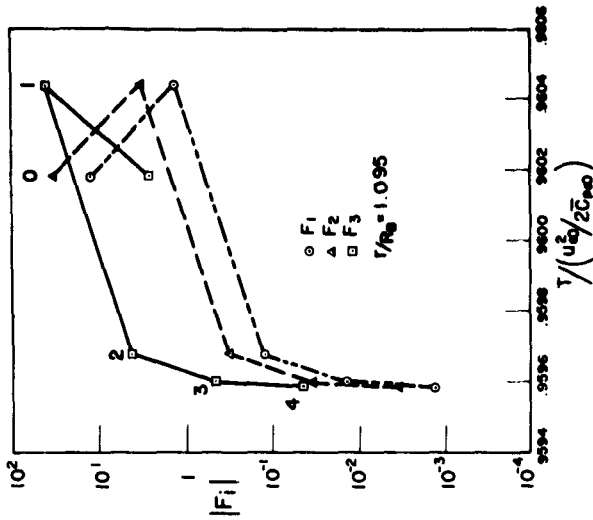
Fig.10 Convergence With Respect To $T/\left(\dfrac{u_\infty^2}{2C_{p\infty}}\right)$.
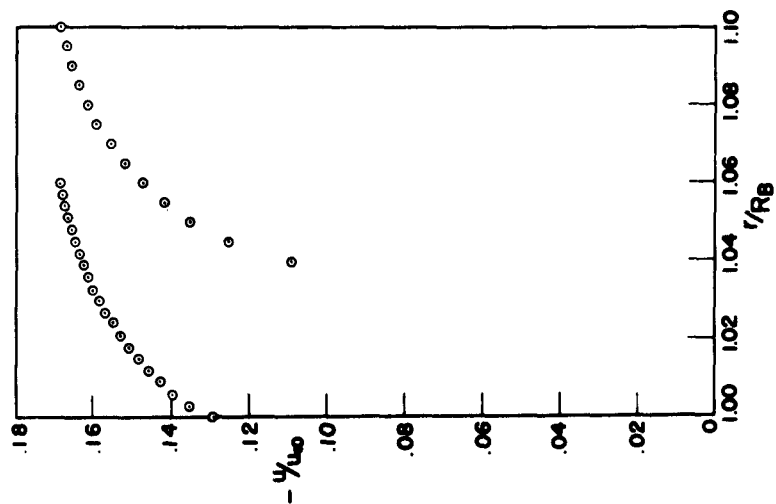
Fig.13

Fig.12

Fig.11
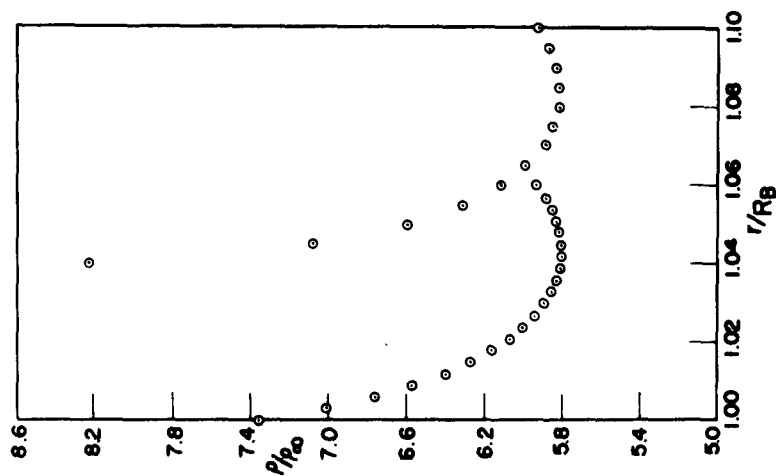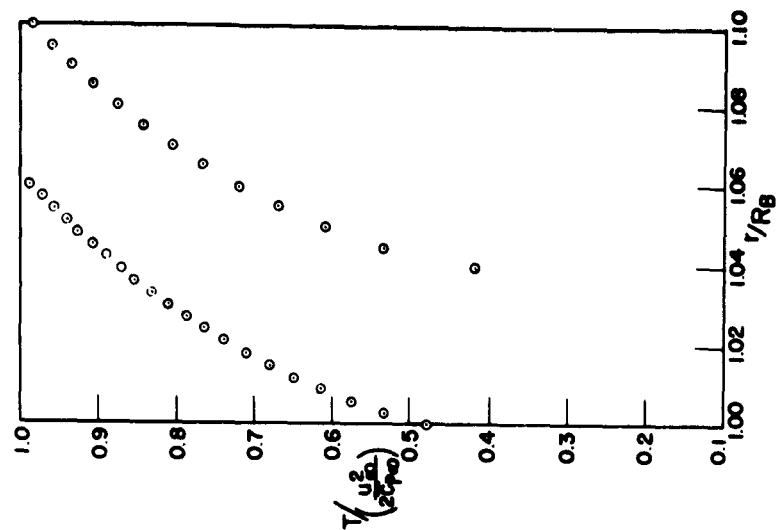
Effect Of Shock Standoff Distance 0.06 R_B And 0.10 R_B.

-41-

APPENDIX

NONDIMENSIONAL EQUATIONS FOR FROZEN FLOW

ON THE STAGNATION LINE

Conservation of Mass

$$F_1 = r'u' \frac{\partial \rho'}{\partial r'} + 2\rho'u' + r'\rho' \frac{\partial u'}{\partial r'} + \rho' \frac{\partial v'}{\partial \theta} = 0$$

Conservation of r-Momentum

$$F_2 = T_\infty' N_R \left\{ \rho'u' \frac{\partial u'}{\partial r'} + \frac{1}{2} \frac{\partial P'}{\partial r'} \right\} - 2 \left\{ T' \frac{\partial^2 u'}{\partial r'^2} + \frac{\partial T'}{\partial r'} \frac{\partial u'}{\partial r'} \right\}$$

$$- \frac{T'}{r^2} \left\{ r' \frac{\partial^2 v'}{\partial r' \partial \theta} - 3 \frac{\partial v'}{\partial \theta} + \frac{\partial^2 v'}{\partial \theta^2} + 4r' \frac{\partial u'}{\partial r'} - 4u' \right\} = 0$$

Conservation of Energy

$$F_3 = T_\infty' N_R \frac{\overline{C_p}}{C_{p\infty}} \rho'u' \frac{\partial T'}{\partial r'} - \frac{1}{N_P} \left\{ 2 \frac{T'}{r'} \frac{\partial T'}{\partial r'} + \left(\frac{\partial T'}{\partial r'} \right)^2 \right.$$

$$\left. + T' \frac{\partial^2 T'}{\partial r'^2} + \frac{T'}{r'^2} \frac{\partial^2 T'}{\partial \theta^2} \right\} - T_\infty' N_R u' \frac{\partial p'}{\partial r'}$$

$$- 4T' \left\{ \left(\frac{\partial u'}{\partial r'} \right)^2 + \left(\frac{\frac{\partial v'}{\partial \theta} + u'}{r'} \right)^2 + \left(\frac{u'}{r'} \right)^2 \right\} = 0$$

where

$$\text{REYNOLDS NUMBER} \quad N_R = \frac{u_\infty \rho_\infty R_B}{\mu_\infty}$$

$$\text{PRANDTL NUMBER} \quad N_P = \frac{\overline{C_{p\infty}} \mu_\infty}{k_\infty}$$

$$\frac{\partial P'}{\partial r'} = \left(\frac{R_0}{C_{p\infty}} \right) \left\{ T' \frac{\partial \rho'}{\partial r'} + \rho' \frac{\partial T'}{\partial r'} \right\}$$

$$R_0 = \frac{R}{M} \quad \text{GAS CONSTANT FOR THIS GAS}$$

$$r' = \frac{r}{R_B} \quad u' = \frac{u}{u_\infty} \quad v' = \frac{v}{u_\infty} \quad \rho' = \frac{\rho}{\rho_\infty}$$

$$T' = T \Big/ \left(\frac{u_\infty^2}{2\overline{C}_{p_\infty}} \right) \qquad T'_\infty = T_\infty \Big/ \left(\frac{u_\infty^2}{2\overline{C}_{p_\infty}} \right)$$

and the θ-derivatives are assumed to have the forms:

$$\frac{\partial v'}{\partial \theta} = \frac{R_B(1-r')}{R_B - R_S} \quad \frac{\partial^2 v'}{\partial r' \partial \theta} = \frac{-R_B}{R_B - R_S}$$

$$\frac{\partial^2 T'}{\partial \theta^2} = \frac{\overline{C}_{p_\infty}}{\overline{C}_p} \left(\frac{1}{\rho_s'^2} - 1 \right) \frac{2 R_B(1-r')}{R_B - R_S}$$

$$\frac{\partial^2 u'}{\partial \theta^2} = \frac{R_B(1-r')}{\rho_s'(R_B - R_S)}$$

University of Southern California Engineering Center, AFCRL 63-154. INVESTIGATION OF CHEMICAL NONEQUILIBRIUM EFFECTS IN VISCOUS SHOCK LAYERS, USCEC 86-101 May 1963, 43 pp. Unclassified Report

The shock layer about a blunt body in a hypersonic flow field is studied considering both viscous and chemical nonequilibrium effects. An order of magnitude study is conducted to predict flight regimes for chemical equilibrium and for frozen flow. Conservation equations are formulated for the viscous, reacting flow in the shock layer about a sphere using a seven species, six reaction chemical model. A numerical method for solution of these equations is developed and the results of solution attempts discussed.