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THE EQUATIONS OF MOTION
IN A MULTICOMPONENT
CHEMICALLY REACTING GAS



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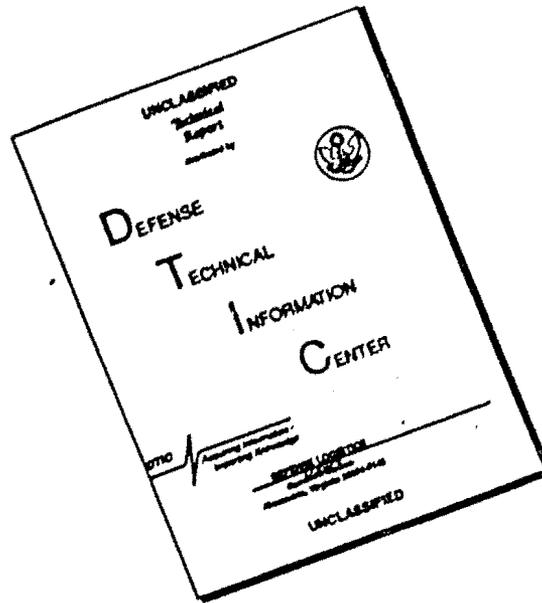
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AEROPHYSICS OPERATION RESEARCH MEMORANDUM NO. 5

THE EQUATIONS OF MOTION IN A MULTICOMPONENT
CHEMICALLY REACTING GAS*

by

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Aerosciences Laboratory
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Summary:

→ The general equations of motion for a multicomponent chemically reacting flow system are introduced. The concept of incompressible flow is presented and the fundamental boundary layer equations appropriate for the analysis of the interaction between a flowing multicomponent chemically reacting gas and a surface are formulated for a typical coordinate system. () ←

*Based on work performed under the auspices of the U. S. Air Force, Ballistic Missiles Division, Contract No. AF 04(645)-24.

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1. INTRODUCTION

In investigating the interaction between a surface and its environment, one is concerned with an analysis of fluid dynamic fields involving the simultaneous transport of mass, momentum and energy. Such problems are described by the equations of change which are a coupled system of nonlinear partial differential equations. The equations of change comprise the conservation laws for the fluid system and consist of the conservation of chemical species, the momentum equation and energy equation. The global form of the conservation of mass, or continuity equation can be obtained directly by summing over all of the equations for the conservation of chemical species.

The presence of chemical reactions in multicomponent gaseous flow systems greatly complicates the analytical formulation and solution of the flow field problem. The complexity of the problem and the relatively small effort expended in this area, as opposed to the voluminous literature and effort dealing with classical nonreacting boundary layers and inviscid flows, have conspired to limit the current state of our knowledge concerning this technically important class of problems. It is therefore of considerable interest to consider the general equations of change appropriate to a multicomponent chemically reacting flow system, and from these to derive the boundary layer equations which describe the phenomena in the immediate vicinity of the surface of a body immersed in such a fluid.

An interesting point is that in the classical treatment of flow fields, the problem is often split into the solution of two problems, inviscid and viscous. An analogous treatment for reacting fields would be to define an "inluscid" flow field as that region where gradients of velocity, temperature, pressure and species concentration are so small that transport processes related to viscosity, thermal conductivity, thermal diffusion, pressure and concentration diffusion may be conveniently neglected. The "fluscid" region is then the boundary layer adjacent to the body, where the aforementioned gradients are so large that coupled transport processes constitute the essential physical phenomena. It is noted that in the case of a reacting flow, in addition to gradients of velocity and temperature, species concentration gradients also appear near the body surface, due to the presence of dissociation, combustion and other forms of chemical reaction. Consequently, one must regard the boundary layer as a multidimensional region.

The inluscid and fluscid fields can then be solved separately, and matching is satisfied by taking the "inner" boundary conditions for the inluscid field as the conditions at "infinity" for the boundary layer. Thus, in simplifying the analysis, by reducing it to the solution of two problems, a complication is introduced in the form of interaction between the inluscid and fluscid fields. In the case of a classical non-reacting gas flow, when the inviscid flow field is irrotational, the interaction appears primarily as a displacement effect at the wall, in the form of a thicker body or equivalent boundary layer displacement thickness. However, when the inviscid flow is

rotational, as for example, when there are entropy gradients in the field due to curved shocks, then in addition to the displacement effect, there is an interaction between the vorticity of the external field and the vortical boundary layer. For the case of weak interaction, it appears that this effect may be included in the boundary layer analysis by modifying the boundary conditions for the velocity gradient at infinity².

In a reacting flow, another type of interaction comes into play in which the concentration gradients must be made to match at the outer junction between the fluid and infusid solutions. And further, one cannot now take the surface conditions independently of the surface mass and energy balance. Intuitively, one would expect that all of these coupling effects could be treated by means of an iterative approach.

In considering the flow of a reacting gas over a surface, it is not correct in general, to treat the environment as a single gas unless at each point the diffusion flux set up by concentration and thermal gradients, and the convective flux set up by pressure gradients, are exactly counterbalanced by the influx of species by convection and the production of species by chemical reactions, so that a stationary equilibrium composition can be maintained in the flow field. Hence, if exact solutions are desired, when chemical components are free to react, especially when a new species is introduced into the boundary layer by means of mass transfer from the surface, due to vaporization, sublimation, heterogeneous reaction, or direct fluid injection, it appears necessary to evaluate the transport

coefficients and thermodynamic properties including viscosity, thermal conductivity, concentration diffusion, thermal diffusion, specific heat and enthalpy at each point in the boundary layer as a function of the local composition, pressure and temperature. Moreover, it is essential that the driving forces for each species be determined by means of the individual equations for the conservation of species, so that the extent of surface reactions can be assessed.

2. SYMBOLS:

a acoustic velocity

$B_i = \frac{X_i}{\bar{m}}$ referred mole fraction of i^{th} species

C_i mass fraction of species i

$$C_i = \frac{\rho_i}{\rho} = \frac{X_i m_i}{\bar{m}} = \frac{n_i m_i}{\rho} \quad \left(\sum_i C_i = 1 \right)$$

C_p specific heat at constant pressure, C_v specific heat at constant volume

\underline{d} driving force

D_{ij} diffusion coefficient, (multicomponent system)

\mathcal{D}_{ij} diffusion coefficient. (binary system)

D_1^T thermal diffusion coefficient

e thermodynamic internal energy per unit mass, including chemical

E stagnation internal energy, $E = e + \frac{1}{2} v^2$

\underline{F}_i external force acting on a unit mass of species i

h static enthalpy, $h = e + \frac{p}{\rho}$

h_i static enthalpy of the i^{th} species, including enthalpy of formation
 $h_i = e_i + \frac{p_i}{\rho_i}$

$\Delta h_{f_i}^{\circ}$ enthalpy of formation of i^{th} species

H stagnation enthalpy, $H = h + \frac{1}{2} v^2$

\underline{I} unit tensor

$\underline{j}_i = \rho_i \underline{V}_i$ relative mass flux of species i

$\underline{J}_i = \rho_i \underline{V}_i$ absolute mass flux of species i

$\underline{g}_i = n_i \underline{V}_i$ relative molar flux of species i

k coefficient of thermal conductivity

k Boltzmann's constant

l linear dimension, cm.

m_i molecular weight of species i

$\bar{m} = \sum_i X_i m_i$ molecular weight of the gas mixture

\dot{M}_i net molar production of species i per unit volume by chemical reaction

n_i moles of i per unit volume

n_t total number of moles per unit volume

N_i number of molecules of i per unit volume

N total number of species

P static pressure

\vec{Q} energy flux vector

R universal gas constant

r_c radius of curvature

r_o radius, measured from the centerline to the surface

t time

T temperature

u x component of velocity

v y component of velocity

\vec{v}_i absolute flow velocity of species i

$\vec{v} = \frac{1}{\rho} \sum_i \rho_i \vec{v}_i$ mass-weighted average velocity of the fluid mixture

$\vec{V}_i = \vec{v}_i - \vec{v}$ diffusion velocity of species i

\dot{w}_i net mass rate of production of species i per unit volume by chemical reaction where $\sum_i \dot{w}_i = 0$

X_i mole fraction of species i , $X_i = \frac{n_i}{n_t}$ $\left(\sum_i X_i = 1 \right)$

x, y, r_0	coordinate system
$\underline{\epsilon}_{ij}$	symmetric rate of strain tensor
$\underline{\tau}_{ij}$	viscous stress tensor
μ	ordinary viscosity coefficient
λ	a quantity related to the second viscosity coefficient
ρ_i	partial density of species i , $\rho_i = n_i m_i$
ρ	density of the fluid mixture, $\rho = n_t \bar{m}$
$\underline{\pi}$	pressure tensor
Φ	dissipation function

Subscripts

i	i^{th} chemical species
t	total

Dimensionless Groups

$$Pr = \frac{\bar{c}_p \mu}{k} \quad \text{Prandtl Number}$$

$$L_{ij} = \frac{\rho \bar{c}_p D_{ij}}{k} \quad \text{Lewis Number}$$

$$L_i^T = \frac{\bar{c}_p D_i^T}{k} \quad \text{Thermal Lewis Number}$$

3. BASIC RELATIONSHIPS

Referring to the list of symbols, we observe that the total number of moles in a unit volume is obtained by summing over all the contributions of each species, i.e.

$$n_t = \sum_i n_i \quad (1)$$

The density of the fluid is given by summation over all the partial densities of all the species.

$$\rho = \sum_i \rho_i = \sum_i n_i m_i = \sum_i \rho c_i \quad (2)$$

The absolute molar flux of species i with respect to fixed spatial coordinates is given by:

$$n_i \underline{v}_i$$

hence the mass flux of species i with respect to fixed spatial coordinates is given by:

$$\underline{J}_i = n_i m_i \underline{v}_i = \rho c_i \underline{v}_i = \rho_i \underline{v}_i \quad (3)$$

We may thus obtain the mass-weighted-average velocity of the fluid by summing over \underline{J}_i

$$\rho \underline{v} = \sum_i \underline{J}_i = \sum_i \rho_i \underline{v}_i \quad (4)$$

This velocity \underline{v} is the macroscopically observed stream velocity, i.e.

$$\underline{v} = \frac{1}{\rho} \sum_i \underline{J}_i = \frac{1}{\rho} \sum_i \rho_i \underline{v}_i = \frac{1}{\rho} \sum_i n_i m_i \underline{v}_i = \sum_i c_i \underline{v}_i \quad (5)$$

The diffusion velocity \underline{V}_i of species i is then defined as the difference between the absolute velocity of species i and the observed stream velocity.

$$\underline{V}_i = \underline{v}_i - \underline{v} \quad (6)$$

It is then possible to define the diffusion flux vector

$$\underline{j}_i = \rho_i \underline{V}_i \quad (7)$$

Note that the mass weighted average of the diffusion velocity is zero.

This may be shown quite easily, by summing equation (6) over all ρ_i and then introducing equations (2) and (4).

$$\begin{aligned} \frac{1}{\rho} \sum_i \rho_i \underline{V}_i &= \frac{1}{\rho} \sum_i \rho_i \underline{v}_i - \frac{1}{\rho} \sum_i \rho_i \underline{v} \\ &= \frac{1}{\rho} (\rho \underline{v}) - \frac{\underline{v}}{\rho} (\rho) = 0 \end{aligned}$$

Consequently we may write:

$$\sum_i \underline{j}_i = \sum_i \rho_i \underline{V}_i = 0 \quad (8)$$

4. CONSERVATION OF SPECIES

The conservation of species i may be written:

$$\frac{\partial n_i}{\partial t} + \nabla \cdot (n_i \underline{v}_i) = \dot{M}_i \quad (9)$$

or equivalently

$$\frac{\partial \rho_i}{\partial t} + \nabla \cdot \underline{J}_i = \dot{W}_i \quad (10)$$

where the chemical source function \dot{W}_i represents the mass rate of production of species i by chemical reaction and may be determined only with great difficulty from chemical kinetics.

Upon eliminating \underline{v}_i , we obtain:

$$\frac{\partial n_i}{\partial t} + \nabla \cdot [n_i (\underline{v} + \underline{V}_i)] = \dot{M}_i \quad (11)$$

$$\frac{\partial \rho_i}{\partial t} + \nabla \cdot [\rho_i (\underline{v} + \underline{V}_i)] = \dot{W}_i \quad (12)$$

If there are N different species in the flow field, only $N-1$ of these equations will be required in addition to the global continuity equation, which follows.

Summing equation (10) over all the species, we find:

$$\frac{\partial}{\partial t} \sum_i \rho_i + \nabla \cdot \sum_i \rho_i \underline{v}_i = \sum_i \dot{W}_i$$

Since mass is neither being created nor destroyed, neglecting relativistic effects,

$$\sum_i \dot{W}_i = 0 \quad (13)$$

and the former becomes:

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \underline{v}) = 0 \quad (14)$$

the familiar global continuity equation. Other forms may also be derived.

These are listed below for convenience.

$$\frac{d\rho}{dt} + \rho \nabla \cdot \underline{v} = 0 \quad (15)$$

$$\rho \frac{dc_i}{dt} = \dot{w}_i - \nabla \cdot (\rho_i \underline{V}_i) \quad (16)$$

where $\frac{d}{dt} () = \frac{\partial}{\partial t} () + \underline{v} \cdot \nabla ()$

is the streaming derivative. Undoubtedly, we have not exhausted all the possibilities in representing the conservation of mass.

Returning briefly to the flux with respect to the mass average velocity, we note that the flux may be broken down into several parts, i.e.

$$\underline{j}_i = \rho_i \underline{V}_i = \rho_i \left(\underline{V}_i^{(c)} + \underline{V}_i^{(\tau)} + \underline{V}_i^{(p)} + \underline{V}_i^{(F_i)} \right) \quad (17)$$

Here we observe that the mass flux \underline{j}_i contains components due to gradients in concentration, temperature, pressure, and external forces. From the thermodynamics of irreversible processes, if the situation encountered is not too far removed from equilibrium, the flux must be a linear function of the driving forces, and the net flux is then the sum of the individual contributions. Hirschfelder et al² gives:

$$\underline{j}_i = \frac{n_t^2}{\rho} \sum_{j \neq i} m_i m_j D_{ij} \underline{d}_j - D_i^T \nabla \ln T \quad (18)$$

where

$$\begin{aligned} \underline{d}_j = & \nabla X_j + (X_j - c_j) \nabla \ln p \\ & - \frac{c_j}{p} \left[\frac{\rho}{m_j} \underline{F}_j - \sum_k n_k \underline{F}_k \right] \end{aligned} \quad (19)$$

For the case of a binary mixture in which only concentration diffusion and thermal diffusion are significant, equation (18) reduces to:

$$\underline{j}_i = \frac{n_t^2}{\rho} m_i m_j \mathcal{D}_{ij} \nabla X_j - D_i^T \nabla \ln T \quad (20)$$

and it is then not difficult to show that:

$$\underline{V}_i = - \mathcal{D}_{ij} \nabla \ln c_i - \frac{D_i^T}{\rho_i} \nabla \ln T \quad (21)$$

We observe that no simplifications result upon introduction of mass fraction rather than mole fraction, when there are more than two chemical components.

5. THE MOMENTUM EQUATION

The momentum equation in aerothermochemistry is identical with that used in aerodynamics for gases without chemical reactions.

$$\rho \frac{d\mathbf{v}}{dt} = \nabla \cdot \underline{\underline{\Pi}} + \sum_i \rho_i \underline{\underline{F}}_i \quad (22)$$

where $\underline{\underline{F}}_i$ is the external force acting on a unit mass of species i , and $\underline{\underline{\Pi}}$ is the pressure tensor. The pressure tensor may be written:

$$\underline{\underline{\Pi}} = -p \underline{\underline{I}} + \underline{\underline{\tau}}_{ij} \quad (23)$$

where p is the static pressure and $\underline{\underline{\tau}}_{ij}$ is the viscous stress tensor. According to equation (22), the macroscopic velocity of the fluid undergoes a change because of the gradient in static pressure, the internal shear and the external forces which act on the various chemical species present. We may write for $\underline{\underline{\tau}}_{ij}$:

$$\underline{\underline{\tau}}_{ij} = 2\mu \underline{\underline{\epsilon}}_{ij} + \underline{\underline{I}} \lambda \nabla \cdot \mathbf{v} \quad (24)$$

where

μ is the conventional viscosity

λ is related to the second viscosity coefficient

$\underline{\underline{I}}$ is the unit tensor

$\underline{\underline{\epsilon}}_{ij}$ is the symmetric rate of strain tensor where a typical term is given by:

$$\epsilon_{ij} = \frac{1}{2} \left(\frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i} \right) \quad (i, j = 1, 2, 3) \quad (25)$$

such that $\epsilon_{ij} = \epsilon_{ji}$, in cartesian coordinates.

If it is assumed that Stokes' postulate holds which is equivalent to assuming that we are dealing with a process whose characteristic time is much smaller than the viscous characteristic time, then

$$\lambda + \frac{2}{3}\mu = 0 \quad (26)$$

and there follows:

$$\tau_{ij} = 2\mu \left(\underline{\underline{\epsilon}}_{ij} - \frac{1}{3} \underline{\underline{I}} \nabla \cdot \underline{\underline{v}} \right) \quad (27)$$

6. THE ENERGY EQUATION

A quite general form of the energy equation, is given by:

$$\rho \frac{de}{dt} = - \nabla \cdot \underline{Q} + \underline{\Pi} : \nabla \underline{v} + \sum_i \rho_i \underline{v}_i \cdot \underline{F}_i \quad (28)$$

This equation is formally analogous to the first law of thermodynamics, where the internal energy e includes chemical energy. In words, this equation states that the internal energy of the mixture e , following the mean motion, changes due to the combined effects of the energy flux vector \underline{Q} , the work of the pressure tensor $\underline{\Pi}$ and the work done by the external forces \underline{F}_i .

The energy equation may be rewritten in many different equivalent forms, but before we develop some of these other forms, it will be instructive to examine the energy flux and pressure tensor work terms a little more closely. The energy flux with respect to the mass average velocity, denoted by \underline{Q} may be broken down into its component parts, i.e.,

$$\underline{Q} = \underline{Q}^{(\tau)} + \underline{Q}^{(d)} + \underline{Q}^{(c_i)} + \underline{Q}^{(R)} \quad (29)$$

which represent contributions due to temperature gradients, diffusion, concentration gradients and radiation. If the effects of radiation can be separated out, the remaining terms are:

$$\underline{Q} = -k \nabla T + \sum_i \rho_i \underline{v}_i h_i - \frac{RT}{n_t} \sum_i \sum_{j \neq i} \frac{n_j D_i^T}{m_i \mathcal{D}_{ij}} (\underline{v}_j - \underline{v}_i) \quad (30)$$

The name Fourier is associated with the first term on the right hand side, while the third term is related to the Dufour effect. The radiative flux $\underline{Q}^{(R)}$ depends in a detailed manner on the frequency and intensity of the radiation and on the fluid properties. One procedure that may be used at present is to evaluate this term after having solved the flow field. Obviously, such a procedure is approximately valid only if $|\underline{Q}^{(R)}| \ll |\underline{Q}|$.

The work done by the pressure tensor is given by:

$$\underline{\pi} : \nabla \underline{v} = -p \nabla \cdot \underline{v} + \Phi \quad (31)$$

where Φ , the dissipation function is given by:

$$\begin{aligned} \Phi &= \underline{\tau}_{ij} : \nabla \underline{v} \\ &= \frac{1}{2} \mu \sum_i \sum_j \left(\frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i} \right)^2 + \lambda \left(\frac{\partial v_k}{\partial x_k} \right)^2 \end{aligned} \quad (32)$$

upon having introduced equation (24).

For example, in x, y, z coordinates:

$$\begin{aligned} \Phi &= \lambda \left(\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z} \right)^2 \\ &+ 2\mu \left[\left(\frac{\partial u}{\partial x} \right)^2 + \left(\frac{\partial v}{\partial y} \right)^2 + \left(\frac{\partial w}{\partial z} \right)^2 \right] \\ &+ \mu \left[\left(\frac{\partial w}{\partial y} + \frac{\partial v}{\partial z} \right)^2 + \left(\frac{\partial u}{\partial z} + \frac{\partial w}{\partial x} \right)^2 + \left(\frac{\partial v}{\partial x} + \frac{\partial u}{\partial y} \right)^2 \right] \end{aligned} \quad (33)$$

Setting $\lambda = -\frac{2}{3}\mu$ and rearranging, the dissipation function becomes:

$$\begin{aligned} \Phi &= \frac{2}{3}\mu \left[\left(\frac{\partial v}{\partial y} - \frac{\partial w}{\partial z} \right)^2 + \left(\frac{\partial w}{\partial z} - \frac{\partial u}{\partial x} \right)^2 + \left(\frac{\partial u}{\partial x} - \frac{\partial v}{\partial y} \right)^2 \right] \\ &+ \mu \left[\left(\frac{\partial w}{\partial y} + \frac{\partial v}{\partial z} \right)^2 + \left(\frac{\partial u}{\partial z} + \frac{\partial w}{\partial x} \right)^2 + \left(\frac{\partial v}{\partial x} + \frac{\partial u}{\partial y} \right)^2 \right] \end{aligned} \quad (34)$$

If Stokes' postulate holds, $\Phi \geq 0$. That is, Φ is essentially a positive quantity that vanishes only when the fluid motion consists of a pure dilation. The physical meaning is that viscosity is a method of adding internal energy to the fluid at the expense of other forms of energy. For a non-Stokesian fluid, consisting of complex molecules, it is possible for $\Phi < 0$.

Introducing equations (30) and (31) into the energy equation, the latter becomes:

$$\begin{aligned} \rho \frac{de}{dt} &= -\rho \nabla \cdot \underline{v} + \Phi + \nabla \cdot (K \nabla T) - \nabla \cdot \sum_i \rho_i \underline{V}_i h_i \\ &+ \nabla \cdot \frac{RT}{n_t} \sum_i \sum_{j \neq i} \frac{n_j D_{ij}^T}{m_i \mathcal{D}_{ij}} (\underline{V}_j - \underline{V}_i) + \sum_i \rho_i \underline{V}_i \cdot \underline{F}_i \end{aligned} \quad (35)$$

The energy equation may also be written in terms of the enthalpy.

Taking

$$e = h - \frac{p}{\rho} \quad (36)$$

equation (35) becomes:

$$\rho \frac{dh}{dt} = -\nabla \cdot \underline{Q} + \Phi + \frac{dp}{dt} + \sum_i \rho_i \underline{V}_i \cdot \underline{F}_i \quad (37)$$

or expanded:

$$\begin{aligned} \rho \frac{dh}{dt} = & \nabla \cdot (\kappa \nabla T) - \nabla \cdot \sum_i \rho_i \underline{V}_i h_i + \Phi + \frac{dp}{dt} \\ & + \nabla \cdot \frac{RT}{n_t} \sum_i \sum_{j \neq i} \frac{n_j D_i^T}{m_i \mathcal{D}_{ij}} (\underline{V}_j - \underline{V}_i) + \sum_i \rho_i \underline{V}_i \cdot \underline{F}_i \end{aligned} \quad (38)$$

If we consider that the gaseous system is composed of a mixture of reacting perfect gases, then the caloric equation is simply:

$$\begin{aligned} c_{v_i} &= \left(\frac{\partial e_i}{\partial T} \right)_v & e_i &= e_i(T) \\ \bar{c}_v &= \sum_i c_i c_{v_i} & e &= \sum_i c_i e_i \end{aligned} \quad (39)$$

and hence upon utilizing equation (10), the energy equation may be written:

$$\begin{aligned} \rho \bar{c}_v \frac{dT}{dt} = & - \nabla \cdot \underline{Q} + \underline{\pi} : \nabla \underline{v} + \sum_i \rho_i \underline{V}_i \cdot \underline{F}_i \\ & - \sum_i e_i \dot{w}_i + \sum_i e_i (\nabla \cdot \rho_i \underline{V}_i) \end{aligned} \quad (40)$$

which may be expanded into the form:

$$\begin{aligned} \rho \bar{c}_v \frac{dT}{dt} = & - \rho \nabla \cdot \underline{v} + \Phi + \nabla \cdot (\kappa \nabla T) - \nabla \cdot \sum_i \rho_i \underline{V}_i h_i \\ & + \nabla \cdot \frac{RT}{n_t} \sum_i \sum_{j \neq i} \frac{n_j D_i^T}{m_i \mathcal{D}_{ij}} (\underline{V}_j - \underline{V}_i) + \sum_i \rho_i \underline{V}_i \cdot \underline{F}_i \\ & - \sum_i e_i \dot{w}_i + \sum_i e_i (\nabla \cdot \rho_i \underline{V}_i) \end{aligned} \quad (41)$$

We can also obtain a similar result in terms of the enthalpy.

We take:

$$c_{p_i} = \left(\frac{\partial h_i}{\partial T} \right)_p \quad h_i = h_i(T) \quad (42)$$

$$\bar{c}_p = \sum_i c_i c_{p_i} \quad h = \sum_i c_i h_i$$

and there follows immediately:

$$\rho \bar{c}_p \frac{dT}{dt} = \nabla \cdot (k \nabla T) - \sum_i c_{p_i} \rho_i \underline{V}_i \cdot \nabla T + \Phi$$

$$+ \frac{dp}{dt} + \nabla \cdot \frac{RT}{n_t} \sum_i \sum_{j \neq i} \frac{n_j D_{ij}^T}{m_i \Omega_{ij}} (\underline{V}_j - \underline{V}_i)$$

$$- \sum_i h_i \dot{w}_i + \sum_i \rho_i \underline{V}_i \cdot \underline{F}_i \quad (43)$$

It should be noted that while e and h contain the chemical energy of formation, they don't include either the kinetic energy of the macroscopic motion of the gas, or the potential energy associated with the external forces \underline{F}_i

If we wish to include the kinetic energy, we may do so as follows.

Premultiply the momentum equation by \underline{v} and there is obtained:

$$\rho \underline{v} \cdot \frac{d\underline{v}}{dt} = \underline{v} \cdot (\nabla \cdot \underline{\pi}) + \sum_i \rho_i \underline{v} \cdot \underline{F}_i \quad (44)$$

$$= \rho \frac{d}{dt} \left(\frac{1}{2} v^2 \right)$$

Define

$$E = e + \frac{1}{2} v^2$$

$$H = h + \frac{1}{2} v^2 = e + \frac{p}{\rho} + \frac{1}{2} v^2 \quad (45)$$

and then we may write the general expressions:

$$\rho \frac{dE}{dt} = -\nabla \cdot \underline{Q} + \nabla \cdot (\underline{\pi} \cdot \underline{v}) + \sum_i \rho_i \underline{v}_i \cdot \underline{F}_i \quad (46)$$

where

$$\nabla \cdot (\underline{\pi} \cdot \underline{v}) = \underline{\pi} : \nabla \underline{v} + \underline{v} \cdot (\nabla \cdot \underline{\pi}) \quad (47)$$

Also,

$$\begin{aligned} \rho \frac{dH}{dt} = & \nabla \cdot (K \nabla T) - \nabla \cdot \sum_i \rho_i \underline{v}_i h_i + \Phi + \frac{\partial p}{\partial t} \\ & + \underline{v} \cdot (\nabla \cdot \underline{\tau}_{ij}) + \nabla \cdot \frac{RT}{n_t} \sum_i \sum_{j \neq i} \frac{n_j D_i^T}{m_i \delta_{ij}} (\underline{v}_j - \underline{v}_i) \\ & + \sum_i \rho_i \underline{v}_i \cdot \underline{F}_i \end{aligned} \quad (48)$$

We have obviously not exhausted all of the possibilities for representing the energy equation.

7. THE EQUATION OF STATE

A reasonable approximation to the thermal behavior of the gaseous mixture is the assumption that the equation of state is given by:

$$p = \rho \bar{R} T \quad (49)$$

where $\bar{R} = \frac{R}{\bar{m}}$

There also follows:

$$\begin{aligned} \bar{R} &= \frac{1}{\rho} \sum_i \rho_i R_i = \sum_i c_i R_i = R \sum_i \frac{c_i}{\bar{m}_i} \\ \bar{m} &= \frac{1}{n_t} \sum_i n_i m_i = \sum_i X_i m_i = \frac{1}{\sum_i \frac{c_i}{\bar{m}_i}} \end{aligned} \quad (50)$$

Some other useful forms of equation (49) are:

$$\begin{aligned} p_i &= \rho_i R_i T \\ p &= n_t \bar{m} R T = n_t R T \\ p_i &= N_i k T \end{aligned} \quad (51)$$

After a sufficient number of solutions have been obtained in a given type of problem utilizing perfect gas behavior, then it would be well to reconsider the effect of non-ideal thermal equations.

8. THE INFLUSCID EQUATIONS

Up to this point, all of the equations have been rather general.

Let us now obtain the influscid equations by neglecting all transport phenomena.

That is, diffusion, viscosity and thermal conductivity are eliminated

from further consideration in the inviscid flow field and there follows

accordingly:

Conservation of species i

$$\rho \frac{dc_i}{dt} = \dot{w}_i \quad (52)$$

Global Continuity

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \underline{v}) = 0 \quad (53)$$

Momentum Equation

$$\rho \frac{d\underline{v}}{dt} = -\nabla p + \sum_i \rho_i \underline{F}_i \quad (54)$$

Energy Equation

$$\rho \frac{dh}{dt} = \frac{dp}{dt} \quad (55)$$
$$\rho \frac{dH}{dt} = \frac{\partial p}{\partial t} + \sum_i \rho_i \underline{v} \cdot \underline{F}_i$$

which shows that only in the steady state is the stagnation enthalpy

constant when following the macroscopic motion of the gas, (neglecting

external forces).

In the solution of the incompressible equations, further difficulties are introduced when one attempts to satisfy the boundary conditions. This situation very clearly exists in a hypersonic flow field since the governing partial differential equations are of mixed type. We will reserve our discussion until later. Let us now proceed to the boundary layer equations.

9. THE BOUNDARY LAYER EQUATIONS

The first thing we must take cognizance of is that the boundary layer approximation is not invariant with the coordinate system. Stated another way, the form of the boundary layer equations together with their boundary conditions actually depend on the choice of the coordinate system to such an extent that different results may actually be obtained for the same physical body when different coordinate systems are utilized³. Thus, for example, if the boundary layer approximation is made with respect to the coordinate system sketched in figure 1, the boundary layer equations for a reacting multicomponent mixture can be formulated as follows.

The conservation of species i may be written:

$$\frac{\partial \rho_i}{\partial t} + \nabla \cdot [\rho_i (\underline{v} + \underline{V}_i)] = \dot{w}_i \quad (56)$$

where the general form of the molar diffusion flux is given by eq. (18)

$$\underline{g}_i = n_i \underline{V}_i = \frac{n_i}{\rho} \sum_{j \neq i} m_j D_{ij} \underline{d}_j - \frac{D_i^T}{m_i} \nabla \ln T \quad (57)$$

and the driving force \underline{d}_j may be written:

$$\underline{d}_j = \nabla X_j + (X_j - c_j) \nabla \ln p \quad (58)$$

if external forces are neglected. The D_{ij} are the multicomponent diffusion coefficients, of which there are $N^2 - N$ where N is the number of species, and the X_j are the mole fractions.

Defining a referred mole fraction $B_i = x_i / \bar{m}$ the diffusion equation may be written:

$$\rho \frac{dB_i}{dt} + \nabla \cdot \vec{J}_i = \dot{M}_i \quad (59)$$

On introducing eqs. (57) and (58), eq. (59) becomes:

$$\rho \frac{dB_i}{dt} + \nabla \cdot \left\{ \sum_{j \neq i} \frac{\rho}{\bar{m}^2} [m_j D_{ij} \{ \nabla x_j + (x_j - c_j) \nabla \ln p \}] - \frac{D_i^T \nabla T}{m_i T} \right\} = \dot{M}_i \quad (60)$$

When the boundary layer approximation is made with respect to a body-oriented axially-symmetric coordinate system, the diffusion equation becomes:

$$\rho \left(\frac{\partial B_i}{\partial t} + u \frac{\partial B_i}{\partial x} + v \frac{\partial B_i}{\partial y} \right) + \frac{\partial}{\partial y} \left[\frac{\mu}{Pr} \left\{ \sum_{j \neq i} \frac{m_j}{\bar{m}^2} L_{ij} \frac{\partial}{\partial y} (\bar{m} B_j) - \frac{L_i^T}{m_i T} \frac{\partial T}{\partial y} \right\} \right] = \dot{M}_i \quad (61)$$

The energy equation may be written:

$$\rho \bar{c}_p \frac{dT}{dt} = \frac{dp}{dt} + \Phi + \nabla \cdot (K \nabla T) - \sum_i c_{p_i} \rho \vec{V}_i \cdot \nabla T - \sum_i h_i \dot{w}_i \quad (62)$$

where the Dufour effect has been neglected and the following notation has been introduced,

$$h_i = \Delta h_{f_i}^0 + \int_0^T c_{p_i} dT; \quad c_{p_i} = \left(\frac{\partial h_i}{\partial T} \right)_p; \quad \bar{c}_p = \sum_i c_i c_{p_i} \quad (63)$$

On making the boundary layer approximation there is obtained:

$$\rho \bar{c}_p \left(\frac{\partial T}{\partial t} + u \frac{\partial T}{\partial x} + v \frac{\partial T}{\partial y} \right) = \frac{\partial p}{\partial t} + u \frac{\partial p}{\partial x} + \mu \left(\frac{\partial u}{\partial y} \right)^2 + \frac{\partial}{\partial y} \left(K \frac{\partial T}{\partial y} \right) - \sum_i c_{p_i} m_i \frac{\mu}{Pr} \left\{ \sum_{j \neq i} \frac{m_j}{\bar{m}^2} L_{ij} \frac{\partial}{\partial y} (\bar{m} B_j) - \frac{L_i^T}{m_i T} \frac{\partial T}{\partial y} \right\} \frac{\partial T}{\partial y} - \sum_i h_i m_i \dot{M}_i \quad (64)$$

It is again noted that equation (62) merely represents one of several convenient forms, since the energy equation can be written in many equivalent forms. Global continuity becomes:

$$\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial x} (\rho u r_0) + \frac{\partial}{\partial y} (\rho v r_0) = 0 \quad (65)$$

Finally upon neglecting external forces the momentum equation yields the following x and y scalar equations:

$$\rho \left(\frac{\partial u}{\partial t} + u \frac{\partial u}{\partial x} + v \frac{\partial u}{\partial y} \right) = - \frac{\partial p}{\partial x} + \frac{\partial}{\partial y} \left(\mu \frac{\partial u}{\partial y} \right) \quad (66)$$

$$\rho \left(\frac{\partial v}{\partial t} - \frac{u^2}{r_c} \right) = - \frac{\partial p}{\partial y} \quad (67)$$

The behavior of the above equations, under the influence of suitable constraints, forms the basis for studies of the interaction between a surface and a reacting stream.

It is noted that under certain circumstances, it may be permissible to lump the gaseous components whose thermal and chemical behavior is similar so that although the gas is actually a multicomponent mixture, its behavior may be approximated by a binary mixture. Further, in formulating the governing equations for a two-component chemically reacting boundary layer, it may be convenient to utilize mass fractions rather than mole fractions in representing the composition of the gas.

For a binary mixture we can introduce eq. (21) so that the diffusion

and energy equations become respectively:

$$\rho \left(\frac{\partial c_i}{\partial t} + u \frac{\partial c_i}{\partial x} + v \frac{\partial c_i}{\partial y} \right) = \frac{\partial}{\partial y} \left(\rho \mathcal{D}_{ij} \frac{\partial c_i}{\partial y} + \frac{D_i^T}{T} \frac{\partial T}{\partial y} \right) + \dot{w}_i \quad (68)$$

$$\rho c_p \left(\frac{\partial T}{\partial t} + u \frac{\partial T}{\partial x} + v \frac{\partial T}{\partial y} \right) = \frac{\partial p}{\partial t} + u \frac{\partial p}{\partial x} + \mu \left(\frac{\partial u}{\partial y} \right)^2 + \frac{\partial}{\partial y} \left(k \frac{\partial T}{\partial y} \right) \quad (69)$$

$$+ \sum_i \left[c_{p_i} \left(\rho \mathcal{D}_{ij} \frac{\partial c_i}{\partial y} + \frac{D_i^T}{T} \frac{\partial T}{\partial y} \right) \right] \frac{\partial T}{\partial y} - \sum_i h_i \dot{w}_i$$

while the global continuity and momentum equations remain unchanged. Here again, all possible forms of the energy equation have not been exhausted.

For example, another useful form is obtained from eq. (38)

$$\rho \left(\frac{\partial h}{\partial t} + u \frac{\partial h}{\partial x} + v \frac{\partial h}{\partial y} \right) = \frac{\partial p}{\partial t} + u \frac{\partial p}{\partial x} + \mu \left(\frac{\partial u}{\partial y} \right)^2 \quad (70)$$

$$+ \frac{\partial}{\partial y} \left(k \frac{\partial T}{\partial y} \right) + \frac{\partial}{\partial y} \left[\sum_i h_i \left(\rho \mathcal{D}_{ij} \frac{\partial c_i}{\partial y} + \frac{D_i^T}{T} \frac{\partial T}{\partial y} \right) \right]$$

Note that the Dufour effect and all external forces have been taken negligible above.

We have also assumed that we have a sufficient number of auxiliary relations for the determination of the transport properties of the gaseous mixture. For example, to a good approximation the viscosity of a mixture in terms of the viscosities of the pure components, the binary diffusion coefficients and the mole fractions is given by⁴:

$$\mu_{mix} = \sum_i \frac{X_i^2}{\frac{X_i^2}{\mu_i} + 1.385 \sum_{k \neq i} \frac{X_i X_k RT}{P \eta_i \mathcal{D}_{ik}}} \quad (71)$$

10. BOUNDARY CONDITIONS

The unknown dependent variables in a reacting flow field are the three velocity components, (this reduces to two for axially symmetric flow), the pressure, the temperature and the composition. Once these have been determined, the problem may be considered solved. Thus, in general, the mathematical problem consists of solving for $N + 5$ unknowns, where N is the total number of chemical species. To accomplish this end, we have at our disposal the following system of equations, $N + 5$ in total;

$N - 1$	conservation of species
1	global continuity
3	momentum equations
1	energy
1	state

In addition, we must also provide a set of boundary conditions which is in agreement with the overall order of the mathematical system. Examination shows that the order of the system and hence its mathematical character depends on whether the flow field is fluscid or influscid. In general, when the flow field is influscid, the system is of the $N + 4^{\text{th}}$ order, however, when the flow is fluscid, the overall order of the system is $2N + 7$, and hence the fluscid system requires $N + 3$ more boundary conditions than the influscid flow system, in order to properly define the mathematical problem.

The relevant boundary conditions or compatibility relations for a reacting boundary layer must be developed individually for each problem. It is remarked that the difficulty at the surface usually lies in the coupled mass-energy transport. Typical treatments of the surface boundary conditions for a reacting boundary layer appear in references 4 and 5. The boundary conditions at the outer edge of the boundary layer must be obtained from the inviscid solution. It is therefore of the greatest importance that solutions be obtained for the non-equilibrium inviscid flow field, since unless one knows the conditions at the outer edge of the boundary layer, one cannot predict the state of affairs inside the viscous layer.

11. CONCLUSIONS

Our major interest here has been in formulating the boundary layer equations and not in determining heat and mass transfer which will be considered elsewhere.

From our brief discussion, it is clear that the analytical treatment of flow fields in which chemical reactions are present requires a major effort with regard to the solution of the governing equations, subject to the appropriate boundary conditions.

While general techniques for obtaining closed form solutions of the partial differential equations are desirable, the advent of high speed digital and analog computers has made it more likely that particular numerical solutions will be obtained, and hence it is anticipated that experiments will have to be carefully designed to detect the effects which can be treated theoretically.

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COORDINATE SYSTEM FOR AN AXIALLY SYMMETRIC BODY

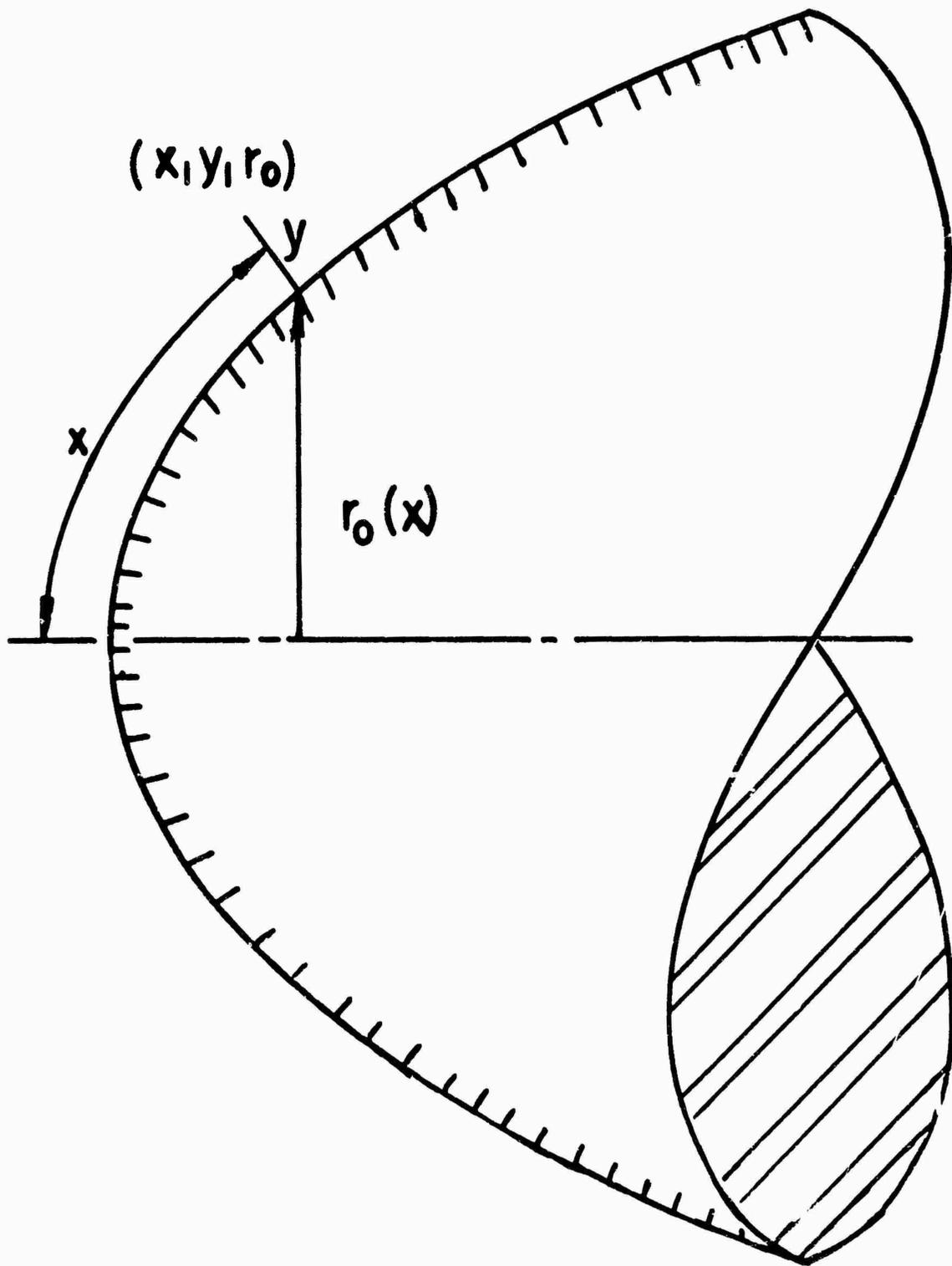
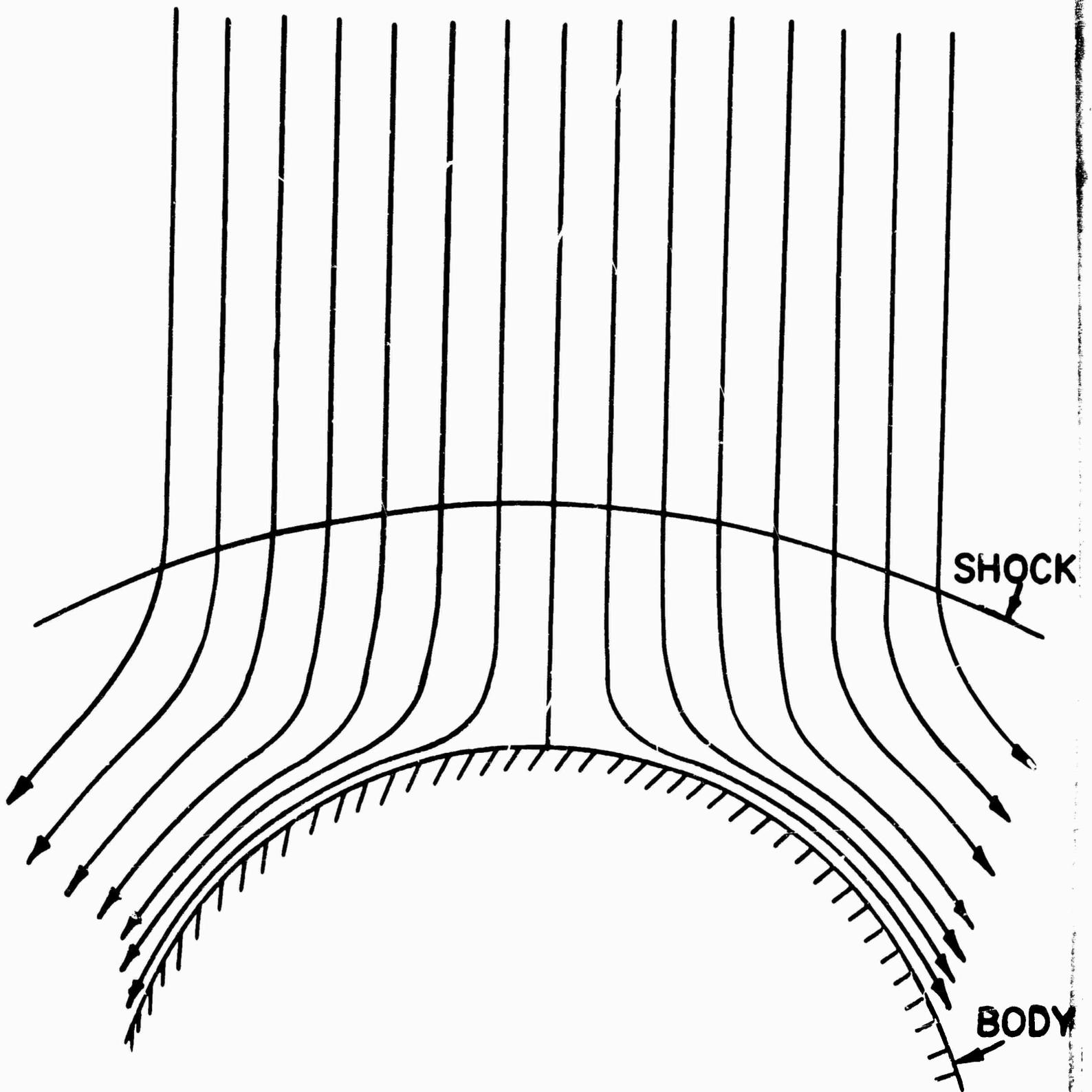
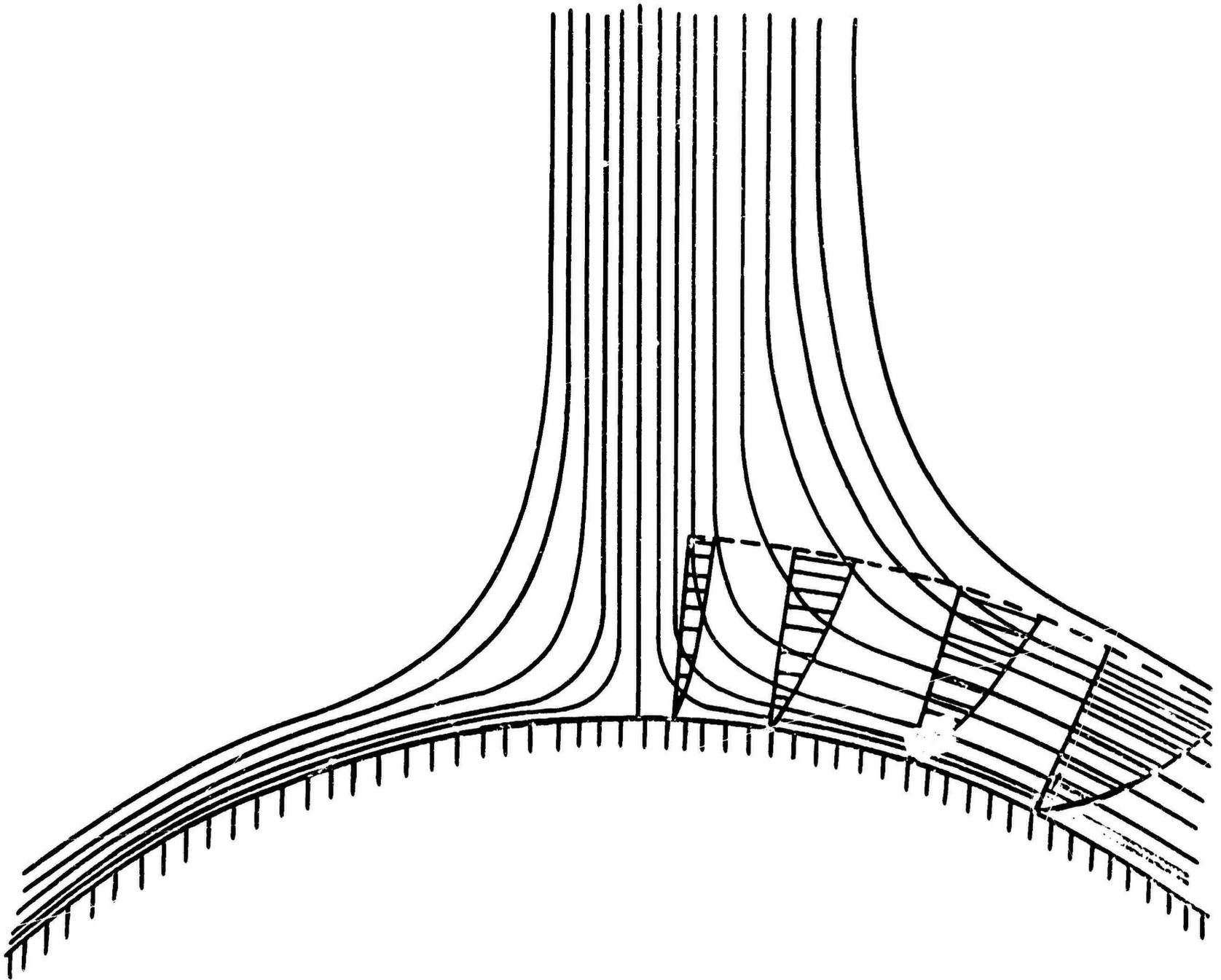


Figure 1



**SCHEMATIC OF INVISCID FLOW FIELD IN
HYPERSONIC FLOW**

Figure 2



**SCHEMATIC OF STAGNATION POINT BOUNDARY
LAYER**

Figure 3