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A STUDY OF THE HYPERSONIC LAMINAR BOUNDARY LAYER WITH DISSOCIATION

Part I

T. C. Adamson, Jr.
J. A. Nicholls
P. M. Sherman

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LIST OF SYMBOLS

() \Rightarrow vector quantity

- $C = \rho\mu/\rho_e\mu_e$
- \underline{C}_0 = mass average velocity of gas mixture at any point
- \underline{C}_i = diffusion velocity of molecule of i 'th kind referred to \underline{C}_0
- C_{pi} = specific heat at constant pressure per unit mass, of i 'th species
- \bar{C}_p = specific heat of mixture $\bar{C}_p = \sum_s (\rho_s/\rho) C_{ps}$
- D_{ij} = multicomponent diffusion coefficient
- \mathcal{D}_{ij} = binary diffusion coefficient
- D_i^T = multicomponent thermal diffusion coefficient
- e_i = internal energy of i 'th species per unit mass
- e = internal energy of mixture, $e = \sum (\rho_i/\rho) e_i$
- f = Blasius function
- h_i = enthalpy per unit mass of i 'th species
- h = enthalpy of mixture $h = \sum_i (\rho_i/\rho) h_i$
- k = Boltzmann's constant
- $k_{f,r}$ = forward or reverse reaction-rate constant
- \mathcal{K}_c = equilibrium coefficient in terms of concentration
- \mathcal{K}_p = equilibrium coefficient in terms of partial pressures
- K_i = rate at which molecules of i 'th species are formed per unit volume due to chemical reaction
- m_i = mass of molecule of i 'th kind
- M_i = molecular weight of i 'th species
- \bar{M} = molecular weight of mixture
- n_i = number density = number of molecules of i 'th species per unit volume
- n = number density of mixture, $n = \sum_i n_i$
- N_i = molar density = number of moles of i 'th species per unit volume

LIST OF SYMBOLS (Concl.)

- N = molar density of mixture, $N = \sum_i N_i$
 P = local pressure
 Pr = Prandtl number, $C_p \mu / \lambda$
 \underline{q} = heat-flux vector
 R_0 = universal gas constant
 Sc = Schmidt number, $\mu / \rho D_{12}$
 T = local temperature
 u_0 = component of mass average velocity in X direction
 v_0 = component of mass average velocity in Y direction
 \underline{X}_i = force on ith molecules due to external field
 X_0 = coordinate in physical plane
 Y_0 = coordinate in physical plane
 η = dimensionless coordinate, $\eta = \frac{Y}{Z} \sqrt{\frac{u_e}{\nu_e X}}$
 K_i = dimensionless mass concentration of ith species, $K_i = \rho_i / \rho$
 λ = coefficient of thermal conductivity
 μ = coefficient of dynamic viscosity
 ν = kinematic viscosity, $\nu = \mu / \rho$
 ρ_i = density of ith species
 ρ = density of mixture, $\rho = \sum_i \rho_i$

Subscripts

- e = outer edge of boundary layer
 w = surface of flat plate

ABSTRACT

The general conservation equations for a multicomponent gas mixture with chemical reaction are considered. They are reduced to the boundary-layer equations by the usual order of magnitude analysis, for a two-component and a three-component system. It is shown that a two-component system can be used strictly only for a system following chemical equilibrium. For the case of a nonequilibrium reaction, it is shown that the three-component system can be reduced to a quasi-two-component system by the use of only mildly restrictive assumptions concerning the similarity of the properties of oxygen and nitrogen. The studies indicate that the boundary-layer similarity variable, η , is the sole independent variable only if chemical equilibrium is assumed. Otherwise the variables also depend on the axial coordinate, X .

Arguments for the existence of a buffer layer where no reaction occurs are presented for the case where there is no chemical equilibrium. The thickness of the buffer layer is shown to depend on the wall temperature and the altitude through the pressure.

An outline of the various sources of gas properties at high temperatures and their usefulness is made. A comparative study of the various methods of experimentally studying the hypersonic boundary layer is also carried out. Some consideration is given to the types of instrumentation which have been and might be used.

OBJECTIVE

The purpose of this study is to demonstrate the effects of dissociation on the velocity and temperature distributions in the hypersonic laminar boundary layer, thus indicating the effect of the dissociation on skin friction and heat transfer at the surface.

INTRODUCTION

The analytical problem considered in this report has been simplified considerably from the general problem of the boundary layer in very high speed flow. To emphasize the dissociation effects, extraneous phenomena have been neglected. For example, since there will be shocks in front of or attached to any body traveling at hypersonic Mach numbers, the air entering the boundary layer will have been dissociated to some extent already, and will have begun to recombine to some intermediate concentration of atomic species. Hence, in general, the air entering the boundary layer will have an atomic concentration which varies along the boundary layer (assuming a curved shock). Furthermore, it is known that there is a pressure gradient in the flat-plate hypersonic boundary layer, which is self-induced by the change in thickness of the boundary layer.

Ignoring the above effects for the present, then, one can consider a problem which consists of a typical laminar boundary layer with an external flow of normal air at a very high velocity, and with dissociation occurring within the boundary layer alone. If this flow can be solved, then an attempt can be made to add the above complicating factors, to study their interaction with the dissociation effects.

In conjunction with the analytical studies, a comparative study of real-gas properties has been made, and a chart listing the various properties found in each reference is included in the body of the report.

Consideration has been given to the various experimental facilities being used at the present time in the study of hypersonic flow. It was desired to find what data could be obtained from existing techniques, and to compare these facilities with a shock-detonation tube, where a detonation wave is used to give the gas a high total temperature.

CONSERVATION EQUATIONS

The general equations which hold for a multicomponent gas mixture, either with or without chemical reaction, have been stated in detail by Hirschfelder, *et al.*,¹ through a generalization of the work of Chapman and Cowling.² In particular, the equations modified for the presence of chemical reaction and polyatomic molecules are employed in this report. While the

coefficients of diffusion and viscosity are not changed by considering molecules with internal degrees of freedom, the coefficient of thermal conductivity and the heat-flux vector are affected.

Following the notation as given in the list of symbols, the conservation equations may be written in the following form.

CONSERVATION OF MASS

The continuity equation for each species is

$$\frac{\partial n_i}{\partial t} + \nabla \cdot n_i (\underline{C}_0 + \bar{C}_i) = K_i \quad (1)$$

If this equation is multiplied by m_i , and summed over i , the total continuity equation is obtained. Thus,

$$\frac{\partial \rho}{\partial t} + \nabla \cdot \rho \underline{C}_0 = 0 \quad (2)$$

since $\sum_i n_i m_i = \rho$ by definition, and $\sum_i m_i K_i = 0$, and $\sum_i n_i m_i \bar{C}_i = 0$ from mass conservation considerations.

Finally, if equation (1) is multiplied by m_i and the relative mass concentration $K_i = (n_i m_i) / \rho$ is substituted for $n_i m_i$, then, with the aid of equation (2), it can be shown that equation (1) becomes

$$\rho \left(\frac{\partial K_i}{\partial t} + \underline{C}_0 \cdot \nabla K_i \right) = -\nabla \cdot \rho K_i \bar{C}_i + m_i K_i \quad (3)$$

This latter form of the species continuity equation will be used throughout the remainder of this report. It should be noted that for an r component system, only $r-1$ separate species continuity equations (3) need be used, along with the overall continuity equation, (2), since

$$\sum_{i=1}^r K_i = 1,$$

and $K_i = \rho_i / \rho$. Hence, in a two-component system, knowing K_1 and ρ , for example, would allow one to calculate ρ_1 and ρ_2 .

CONSERVATION OF ENERGY

Summation of the separate energy equations for each species gives the energy equation for the mixture. In terms of the enthalpy, this equation is

$$\rho \left(\frac{\partial h}{\partial t} + \underline{c}_0 \cdot \nabla h \right) = \frac{\partial p}{\partial t} + \underline{c}_0 \cdot \nabla p + p \nabla \cdot \underline{c}_0 - \nabla \cdot \underline{g} - \underline{p} : \nabla \underline{c}_0 - \sum_i n_i \underline{c}_i \cdot \underline{X}_i \quad (4)$$

where

$$\underline{g} = -\lambda \nabla T + \sum_i \rho_i \underline{c}_i h_i + \frac{kT}{n} \sum_{i,j} \frac{n_j}{m_i} \frac{D_i^T}{D_{ij}} (\underline{c}_i - \underline{c}_j) \quad (5)$$

is the heat flux vector, and $h = \sum_i K_i h_i$ is the enthalpy of the mixture.

CONSERVATION OF MOMENTUM

Again, summation of the separate momentum equations for each species gives the overall momentum equation for the mixture:

$$\rho \left(\frac{\partial \underline{c}_0}{\partial t} + (\underline{c}_0 \cdot \nabla) \underline{c}_0 \right) = -\nabla \cdot \underline{p} + \frac{1}{\rho} \sum_i n_i \underline{X}_i \quad (6)$$

DIFFUSION VELOCITY

The diffusion velocity for each component is defined as follows:

$$\underline{c}_i = \underline{c}_i(u_i, v_i) = \frac{n^2}{n_i \rho} \sum_{j \neq i} m_j D_{ij} \underline{d}_j - \frac{1}{n_i m_i} D_i^T \nabla \ln T, \quad (7)$$

where

$$\underline{d}_j = \nabla \left(\frac{n_j}{n} \right) + \left(\frac{n_j}{n} - \frac{n_j m_j}{\rho} \right) \nabla \ln p - \frac{n_j m_j}{\rho} \left(\frac{\rho \underline{X}_j}{m_j} - \frac{1}{\rho} \sum_l n_l \underline{X}_l \right) \quad (8)$$

EQUATION OF STATE

The equation of state of each species is that of a perfect gas: $P_i = n_i kT$, so that the overall equation of state is

$$P = nkT$$

or

$$P = \frac{\rho R_0 T}{\bar{M}}, \quad (9)$$

where

$$\bar{M} = \sum_i \frac{n_i}{n} M_i = \sum_i \frac{N_i}{N} M_i \quad (10)$$

is the molecular weight of the mixture at any given point and R_0 is the universal gas constant.

The above equations are simplified by the assumptions usually made in a boundary-layer study, as well as some assumptions which are necessary only in a multicomponent flow. The assumptions necessary for a general laminar boundary-layer study are as follows:

- a) The flow is a two-dimensional steady flow.
- b) No external forces exist.
- c) Thermal diffusion is negligible.
- d) The usual boundary-layer order of magnitude assumptions apply.

Assumptions c) and d) must be clarified at this point. It is not clear at the present time what role thermal diffusion would play in the case of relatively high temperature gradients such as exist in the hypersonic boundary layer. Some authors³ have included the thermal diffusion term, while others⁴ have disregarded it in view of the fact that not enough is known about the coefficients. Chapman and Cowling⁵ show that for mixtures of hydrogen and nitrogen one can expect the ratio of the thermal diffusion coefficient to the binary diffusion coefficient to be of the order of 0.10 at the most. Furthermore, in most combustion studies where the temperature and concentration gradients are comparable to the hypersonic boundary layer, the thermal diffusion is neglected on the grounds that the mass transferred is negligible compared to that transferred by convection or diffusion due to concentration gradients. The reasoning is that the dimensionless temperature and concentration gradients are of the same order of magnitude while the coefficients are not. In this study, the latter reasons are assumed valid, and thermal diffusion is neglected.

In stating that the usual boundary-layer order of magnitude assumptions hold, one is making a tacit assumption about the reaction rate, which must be clarified. The boundary-layer approximations can be made because, in the boundary layer, a change in any variable in the flow direction is very small compared to the change in this variable in a direction perpendicular to the flow direction. This physical fact is used in stating that the derivative $\partial/\partial x$ is of order $1/L$ while $\partial/\partial y$ is of order $1/\delta$ where L and δ are the length and thickness of the boundary layer, respectively, and $\delta \ll L$. In making the same assumption in the species continuity equation, one is really assuming that not only the rate of diffusion of species but also the rate of creation of species by reaction is small in the flow direction compared to their values in the direction vertical to the flow. While this assumption is very restrictive in combustion problems, it should not introduce any new difficulties in the present problem because the reaction to be considered is a dissociation reaction which is self-damping, i.e., if the temperature is increased, the increased rate of dissociation then lowers the temperature. Hence, any zone of dissociation in the boundary layer will tend to grow with the boundary layer

and become more diffuse, rather than tend to become a thin self-propagating reaction as would occur in an exothermic reaction. Therefore, except at the initiation of the boundary layer where a singularity exists in all the usual boundary-layer solutions, the boundary-layer assumption should hold for the concentration, and thus the changes in x or flow direction should be small compared to the changes in the y or radial direction.

With the above assumptions, equations (2) to (8) become

$$\begin{aligned}
 a) \quad & \frac{\partial \rho u_0}{\partial x_0} + \frac{\partial \rho v_0}{\partial y_0} = 0 \\
 b) \quad & \rho u_0 \frac{\partial K_i}{\partial x_0} + \rho v_0 \frac{\partial K_i}{\partial y_0} = -\frac{\partial (\rho K_i v_i)}{\partial y_0} + m_i K_i \\
 c) \quad & \rho u_0 \frac{\partial h}{\partial x_0} + \rho v_0 \frac{\partial h}{\partial y_0} = u_0 \frac{\partial P}{\partial x_0} - \frac{\partial (\rho y_0)}{\partial y_0} + \mu \left(\frac{\partial u_0}{\partial y_0} \right)^2 \\
 d) \quad & \rho y_0 = -\lambda \frac{\partial T}{\partial y_0} + \sum_i \rho_i v_i h_i \\
 e) \quad & \rho u_0 \frac{\partial u_0}{\partial x_0} + \rho v_0 \frac{\partial u_0}{\partial y_0} = \frac{\partial (\mu \frac{\partial u_0}{\partial y_0})}{\partial y_0} - \frac{\partial P}{\partial x_0} \quad \text{and} \\
 f) \quad & v_i = \frac{n^2}{n_i \rho} \sum_{j \neq i} m_j D_{ij} \frac{\partial (n_j/n)}{\partial y_0}
 \end{aligned} \tag{11}$$

where $(d_j)_{y_0} = \frac{\partial (n_j/n)}{\partial y_0}$ because $\frac{\partial P}{\partial x_0} = 0$

In the above equations u_0 , v_0 , and x_0 , y_0 , are the velocities and coordinates in the physical plane. For the flat plate with no pressure gradient $\partial P / \partial x_0 = 0$, of course.

EQUATIONS FOR A TWO-COMPONENT MIXTURE

The assumption that a dissociating flow consists of two components is often made to simplify the equations. In this case, the two components are molecular and atomic "air." Actually, this assumption can be used only if (a) chemical equilibrium exists at every point or the reaction rate is very slow compared to diffusion across the streamlines (Lees' two cases⁶), or if (b)

enough is known about the rate constants in the dissociation of O_2 and N_2 to provide an average rate which would hold for the dissociation of air. The last condition does not seem feasible since N_2 does not begin to dissociate until most of the O_2 has dissociated, indicating a large difference in the activation energies for each of the reactions. However, when no chemical rate is involved, such as in the case of chemical equilibrium, or rates slow compared to diffusion processes, then a two-component system seems adequate since the molecular weights of N_2 and O_2 and thus N and O are almost equal, and since the transport and thermodynamic properties are also very similar. To write the specific equations for a two-component system, one need only compute the diffusion velocities.

The last of equations (11) is the relation for the diffusion velocity. For a two-component mixture

$$v_1 = \frac{n^2}{n_1 p} m_2 D_{12} \frac{\partial (m_2/n)}{\partial y_0} ,$$

where $D_{12} = D_{21}$ for a binary mixture.

Now
$$\frac{n_2}{n} + \frac{n_1}{n} = 1 ,$$

and

$$\frac{n_1}{n} = \frac{n_1 m_1}{n_1 m_1 + n_2 m_2} = \frac{K_1}{K_1 + \frac{m_1}{m_2} K_2} = \frac{K_1}{K_1 (1 - \frac{m_1}{m_2}) + \frac{m_1}{m_2}} ,$$

since $K_1 + K_2 = 1$.

Therefore,

$$\begin{aligned} \frac{\partial (n_2/n)}{\partial y_0} &= - \frac{\partial (n_1/n)}{\partial y_0} = \frac{-1}{(K_1 (1 - \frac{m_1}{m_2}) + \frac{m_1}{m_2})^2} \frac{m_1}{m_2} \frac{\partial K_1}{\partial y_0} \\ &= \left(\frac{n_1}{n K_1} \right)^2 \frac{m_1}{m_2} \frac{\partial K_1}{\partial y_0} , \end{aligned}$$

and

$$v_1 = - \frac{D_{12}}{K_1} \frac{\partial K_1}{\partial y_0} \tag{12}$$

Likewise, since $\sum_i \rho_i v_i = 0$,

$$\begin{aligned} v_2 &= - \frac{\rho_1}{\rho_2} v_1 = \frac{D_{12}}{K_2} \frac{\partial K_1}{\partial y_0} \\ &= - \frac{D_{12}}{K_2} \frac{\partial K_2}{\partial y_0} , \end{aligned}$$

so that in general, for a binary system,

$$v_i = - \frac{D_{12}}{K_i} \frac{\partial K_i}{\partial y_0} \quad (13)$$

Thus, the condition that Ficks' law be used for the diffusion velocity, as stated by Lees⁷, is unnecessary for a two-component flow. Actually, Ficks' law is written in terms of mole fractions for a system at constant temperature and pressure so that n , the total number density, is a constant. However, it may be used for systems with varying T or P if the concentration of one component is very small compared to the other, or if the molecular weights are equal. These assumptions, made tacitly when Ficks' law is used, are unnecessary for this case.

The equations for a binary system are as follows:

$$\frac{\partial \rho u_0}{\partial x_0} + \frac{\partial \rho v_0}{\partial y_0} = 0$$

$$\rho u_0 \frac{\partial K_1}{\partial x_0} + \rho v_0 \frac{\partial K_1}{\partial y_0} = \frac{\partial}{\partial y_0} (\rho D_{12} \frac{\partial K_1}{\partial y_0}) + m_1 K_1$$

$$\rho u_0 \frac{\partial h}{\partial x_0} + \rho v_0 \frac{\partial h}{\partial y_0} = u_0 \frac{\partial P}{\partial x_0} - \frac{\partial}{\partial y_0} (q_{y_0}) + \mu \left(\frac{\partial u_0}{\partial y_0} \right)^2$$

$$q_{y_0} = - \lambda \frac{\partial T}{\partial y_0} - \rho D_{12} \sum_{i=1}^2 h_i \frac{\partial K_i}{\partial y_0} \quad (14)$$

$$\rho u_0 \frac{\partial u_0}{\partial x_0} + \rho v_0 \frac{\partial u_0}{\partial y_0} = - \frac{\partial P}{\partial x_0} + \frac{\partial}{\partial y_0} \left(\mu \frac{\partial u_0}{\partial y_0} \right)$$

$$P = \frac{\rho R_0 T}{M}$$

$$\bar{M} = \frac{M_1}{K_1 \left(1 - \frac{M_1}{M_2} \right) + \frac{M_1}{M_2}}$$

where M_1 and M_2 are the molecular weights of species one and two. q_{y_0} may be written in the form given by Lees by noting that

$$h = \sum_i \kappa_i h_i$$

and

$$h_i = \int_0^T C_{p_i} dT + h_i^{(0)}$$

where $h_i^{(0)}$ is the heat of formation at zero degrees absolute. Then, since each component is a perfect gas, $C_{p_i} = C_{p_i}(T)$, and

$$\frac{\partial h_i}{\partial y_0} = \frac{dh_i}{dT} \frac{\partial T}{\partial y_0} = C_{p_i} \frac{\partial T}{\partial y_0}$$

and

$$\begin{aligned} \frac{\partial h}{\partial y_0} &= \sum_i \kappa_i C_{p_i} \frac{\partial T}{\partial y_0} + \sum_i h_i \frac{\partial \kappa_i}{\partial y_0} \\ &= \bar{C}_p \frac{\partial T}{\partial y_0} + \sum_i h_i \frac{\partial \kappa_i}{\partial y_0} \end{aligned}$$

Then,

$$\partial y_0 = \frac{-\lambda}{\bar{C}_p} \left[\frac{\partial h}{\partial y_0} + \left(1 - \frac{\rho \alpha_{12} \bar{C}_p}{\lambda}\right) \sum_i h_i \frac{\partial \kappa_i}{\partial y_0} \right] \quad (15)$$

The above equations are essentially those considered by Lees.⁸ As was mentioned previously, they should be used only when chemical equilibrium is assumed (no equation necessary for κ_1), or when $m_1 \kappa_1$ can be considered small compared to the rest of the terms in the equation for κ_1 , since it would be very difficult to evaluate $m_1 \kappa_1$, the rate term, for the decomposition of air rather than its separate components.

One might wonder why a two-component system could not be used where the temperatures stay low enough so that only the decomposition of O_2 need be considered. After all, N_2 and O_2 have transport properties which are very similar, and since only one dissociation reaction is being considered, there should be no confusion in what reaction-rate parameters to use. The reason that this cannot be done is that the rate at which O_2 decomposes depends on the local concentration of O_2 , not on the concentration of O_2 and N_2 . In a two-component system, one can tell only what fraction of the whole concentration is made up of molecular species. One cannot tell the difference between O_2 and N_2 molecules. From the standpoint of diffusion, heat capacity, etc., this information never becomes necessary. However, to know the local reaction rate, one must know the O_2 concentration; that is, one must be able to distinguish between O_2 and N_2 molecules. For this reason, a three-component system should be used. In general, the use of such a system involves more than simply adding another equation to the set. The transport properties become extremely complex, and terms are added to the energy equation and heat-flux vector. However, it is possible to simplify this system of equations in-

to the so-called quasi-two-component system used for the remainder of this study.

QUASI-TWO-COMPONENT SYSTEM

Consider a three-component gas mixture made up of O_2 (subscript 1), O (subscript 2), and N_2 (subscript 3). This means that the external flow Mach number must be low enough so that only a negligible amount of N_2 dissociates into N . For this range of temperatures, then, there is no reaction involving N_2 . The assumption is also made that the molecular weights of O_2 and N_2 are the same, and that the thermodynamic properties are the same. That is:

$$M_1 = M_3 = \frac{M_{O_2} + M_{N_2}}{2} \quad (16)$$

and

$$\begin{aligned} h_1 &= h_3 \\ c_p &= c_{p3} \end{aligned} \quad (17)$$

The assumption is also made that $D_{13} = D_{31} = 0$; i.e., that O_2 and N_2 , having essentially the same properties, do not diffuse into each other. The gas mixture, then, consists of N_2 and O_2 molecules and O atoms. Within this mixture, one can distinguish between O_2 and N_2 only insofar as calculating the concentration of O_2 for the reaction rate. For all other intents and purposes, O_2 and N_2 are the same gas. With these assumptions, then,

$$\begin{aligned} D_{32} = D_{23} = D_{21} = D_{12} \\ D_{31} = D_{13} = 0 \end{aligned} \quad (18)$$

Using Hirschfelder's⁹ form for the multicomponent diffusion coefficient for a three-component mixture, one can write the following general relation between the multicomponent and binary coefficients:

$$D_{ij} = D_{ij} \Delta_{ij} \quad (19)$$

where

$$\begin{aligned} \Delta_{12} &= 1 + \frac{N_3 \left(\frac{M_3}{M_2} D_{13} - D_{12} \right)}{N_1 D_{23} + N_2 D_{13} + N_3 D_{12}} \\ \Delta_{21} &= 1 + \frac{N_3 \left(\frac{M_3}{M_1} D_{23} - D_{21} \right)}{N_1 D_{23} + N_2 D_{13} + N_3 D_{12}} \end{aligned}$$

with the others being obtained by cyclical permutation of the indices. Next,

if the assumptions involving the D_{ij} and M_i are employed, one obtains the following set of relations:

$$\begin{aligned} \Delta_{12} &= 1 - \frac{N_3}{N_1 + N_3} = \frac{N_1}{N_1 + N_3} = \frac{n_1}{n_1 + n_3} , \\ \Delta_{21} &= 1 , \\ \Delta_{23} &= 1 , \end{aligned} \tag{20}$$

and
$$\Delta_{32} = \frac{N_3}{N_1 + N_3} = \frac{n_3}{n_1 + n_3} .$$

Note that the concentration ratios may be written in terms of moles per unit volume or molecules per unit volume.

The last of Equations (11) may now be used to calculate the diffusion velocities. Thus,

$$\begin{aligned} v_1 &= \frac{n^2}{n_1 \rho} \left\{ m_2 D_{12} \frac{\partial(n_2/n)}{\partial y_0} + m_3 D_{13} \frac{\partial(n_3/n)}{\partial y_0} \right\} \\ &= \frac{n^2}{n_1 \rho} m_2 \Delta_{12} \left(\frac{n_1}{n_1 + n_3} \right) \frac{\partial(n_2/n)}{\partial y_0} , \\ v_2 &= \frac{n^2}{n_2 \rho} m_1 \Delta_{12} \left\{ \frac{\partial(n_1/n)}{\partial y_0} + \frac{\partial(n_3/n)}{\partial y_0} \right\} , \\ v_3 &= \frac{n^2}{n_3 \rho} m_2 \Delta_{12} \left(\frac{n_3}{n_1 + n_3} \right) \frac{\partial(n_2/n)}{\partial y_0} \end{aligned} \tag{21}$$

To convert the number or mole fractions into relative mass fractions, the following relations may be used.

$$\begin{aligned} \frac{n_1}{n} &= \frac{n_1 m_1}{n_1 m_1 + n_2 m_2 \frac{m_1}{m_2} + n_3 m_3 \frac{m_1}{m_3}} \\ &= \frac{K_1}{K_1 \left(1 - \frac{m_1}{m_2} \right) + K_3 \left(\frac{m_1}{m_3} - \frac{m_1}{m_2} \right) + \frac{m_1}{m_2}} \end{aligned} \tag{22}$$

since $K_2 = 1 - K_1 - K_3$.

Likewise,

$$\frac{n_3}{n} = \frac{m_1}{m_3} \frac{K_3}{K_1(1 - \frac{m_1}{m_2}) + K_3(\frac{m_1}{m_3} - \frac{m_1}{m_2}) + \frac{m_1}{m_2}} \quad (23)$$

and

$$\frac{n_2}{n} = 1 - \frac{n_3}{n} - \frac{n_1}{n}$$

The derivatives of the sum of equations (22) and (23) is taken next, and making use of the assumption that $m_1 = m_3$, one may write it as,

$$\frac{\partial}{\partial y_0} \left(\frac{n_1}{n} + \frac{n_3}{n} \right) = - \frac{\partial}{\partial y_0} \left(\frac{n_2}{n} \right) = \frac{1}{[(K_1 + K_3)(1 - \frac{m_1}{m_2}) + \frac{m_1}{m_2}]^2} \frac{m_1}{m_2} \left(\frac{\partial K_1}{\partial y_0} + \frac{\partial K_3}{\partial y_0} \right) \quad (24)$$

where

$$\frac{1}{[(K_1 + K_3)(1 - \frac{m_1}{m_2}) + \frac{m_1}{m_2}]^2} = \frac{n_1^2}{n^2} \frac{1}{K_1^2} = \frac{n_3^2}{n^2} \frac{1}{K_3^2} \left(\frac{m_3}{m_1} \right)^2$$

again from equations (22) and (23).

Finally, to write the diffusion velocities in terms of the desired variables, one must write $(n_1)/(n_1 + n_3)$ and $(n_3)/(n_1 + n_3)$ in terms of the K_i . This can be done as follows:

$$\frac{n_1}{n_1 + n_3} = \frac{n_1 m_1}{n_1 m_1 + n_3 m_3 \frac{m_1}{m_3}} \approx \frac{K_1}{K_1 + K_3} \quad (25)$$

$$\frac{n_3}{n_1 + n_3} \approx \frac{K_3}{K_1 + K_3}$$

since m_1 is assumed equal to m_3 .

Substitution of equations (24) and (25) into equations (21) and a slight rearrangement gives the desired form for the diffusion terms in the continuity equations.

$$\begin{aligned} \rho K_1 v_1 &= - \frac{K_1}{K_1 + K_3} \rho D_{12} \frac{\partial}{\partial y_0} (K_1 + K_3) \\ \rho K_2 v_2 &= - \rho D_{12} \frac{\partial K_2}{\partial y_0} = - \rho D_{12} \frac{\partial}{\partial y_0} (K_1 + K_3) \\ \rho K_3 v_3 &= - \frac{K_3}{K_1 + K_3} \rho D_{12} \frac{\partial}{\partial y_0} (K_1 + K_3) \end{aligned} \quad (26)$$

These relations may be checked by noting that the relation for the conservation of mass by diffusion is satisfied. That is:

$$\sum_i \rho_i v_i = \sum_i \rho K_i v_i = \rho D_{12} \left[1 - \frac{K_1}{K_1 + K_3} - \frac{K_3}{K_1 + K_3} \right] \frac{\partial (K_1 + K_3)}{\partial y_0} = 0$$

With the above relations for the diffusional mass transport, the species continuity equations [equation (11b)] may be written. Also, equation (11d) may be written in terms of the concentration gradients. Thus,

$$q_{y_0} = -\lambda \frac{\partial T}{\partial y_0} + \sum_i \rho_i v_i h_i \quad (11d)$$

But

$$\sum_i \rho_i v_i h_i = -\rho D_{12} \left[h_1 \frac{K_1}{K_1 + K_3} \frac{\partial (K_1 + K_3)}{\partial y_0} + \frac{h_3 K_3}{(K_1 + K_3)} \frac{\partial (K_1 + K_3)}{\partial y_0} + h_2 \frac{\partial K_2}{\partial y_0} \right],$$

and since by assumption $h_1 = h_3$,

$$\begin{aligned} \sum_i \rho_i h_i v_i &= -\rho D_{12} \left[h_1 \frac{\partial (K_1 + K_3)}{\partial y_0} + h_2 \frac{\partial K_2}{\partial y_0} \right] \\ &= -\rho D_{12} \left[h_1 \frac{\partial K_1}{\partial y_0} + h_3 \frac{\partial K_3}{\partial y_0} + h_2 \frac{\partial K_2}{\partial y_0} \right] \\ &= -\rho D_{12} \sum_i h_i \frac{\partial K_i}{\partial y_0} \end{aligned} \quad (27)$$

Therefore, with the assumptions made concerning the O_2 and N_2 , the heat-flux vector can be written in exactly the same form as for the binary system;

$$q_{y_0} = -\frac{\lambda}{c_p} \left[\frac{\partial h}{\partial y_0} - \left(1 - \frac{\rho D_{12} \bar{c}_p}{\lambda} \right) \sum_i h_i \frac{\partial K_i}{\partial y_0} \right], \quad (28)$$

where $\partial T / \partial y_0$ has been written in terms of $\partial h / \partial y_0$ and $\partial K_i / \partial y_0$, as before.

The complete set of equations for this ternary mixture can be written now. As was mentioned before, however, it is necessary to consider only two of the three possible species continuity equations, and the overall continuity equation. Since there is no reaction rate considered for the N_2 , the equation for K_3 , being the simplest of the three, is one choice. The equation in $K_2(0)$, is chosen as the other, since $K_2 = 1 - (K_1 + K_3)$ and $K_1 + K_3$ is a natural grouping in the equations, and since, as will be discussed later, the boundaries

where $K_2 \approx 0$ (limit of dissociation) are very important. The complete set of equations for the three-component, quasi-two-component system are as follows:

$$a) \quad \frac{\partial \mu_0}{\partial x_0} + \frac{\partial p_0}{\partial y_0} = 0$$

$$b) \quad \rho \mu_0 \frac{\partial K_2}{\partial x_0} + \rho v_0 \frac{\partial K_2}{\partial y_0} = \frac{\partial}{\partial y_0} \left(\rho D_{12} \frac{\partial K_2}{\partial y_0} \right) + m_2 K_2$$

$$c) \quad \rho \mu_0 \frac{\partial K_3}{\partial x_0} + \rho v_0 \frac{\partial K_3}{\partial y_0} = -\frac{\partial}{\partial y_0} \left(\frac{K_3}{1-K_2} \rho D_{12} \frac{\partial K_2}{\partial y_0} \right)$$

$$d) \quad \rho \mu_0 \frac{\partial \mu_0}{\partial x_0} + \rho v_0 \frac{\partial \mu_0}{\partial y_0} = \frac{\partial}{\partial y_0} \left(\mu \frac{\partial \mu_0}{\partial y_0} \right) - \frac{\partial T}{\partial x_0}$$

$$e) \quad \rho \mu_0 \frac{\partial h}{\partial x_0} + \rho v_0 \frac{\partial h}{\partial y_0} = -\frac{\partial}{\partial y_0} (c_{y_0}) + \mu_0 \frac{\partial P}{\partial x_0} + \mu \left(\frac{\partial \mu_0}{\partial y_0} \right)^2 \quad (29)$$

$$f) \quad c_{y_0} = -\frac{\lambda}{\bar{C}_p} \left[\frac{\partial h}{\partial y_0} - \left(1 - \frac{\rho D_{12} \bar{C}_p}{\lambda} \right) \sum_{i=1}^3 h_i \frac{\partial K_i}{\partial y_0} \right]$$

$$g) \quad P = \frac{\rho R_0 T}{M}$$

$$h) \quad \frac{\bar{M}}{M_1} = \frac{1}{K_2 + 1}$$

Equation (29h) is written for the specific case where $M_3 = M_1$, and $(M_2)/M_1 = 1/2$. In general,

$$\bar{M} = \sum_{i=1}^3 \frac{N_i}{N} M_i$$

but for the above conditions, this reduces to

$$\begin{aligned} \frac{\bar{M}}{M_1} &= \frac{N_1 + N_3}{N} + \frac{1}{2} \frac{N_2}{N} \\ &= \frac{1}{2} \left[1 + \frac{N_1 + N_3}{N} \right], \end{aligned}$$

and substitution of equations (22) and (23), again with the above conditions on molecular weights, gives the desired results.

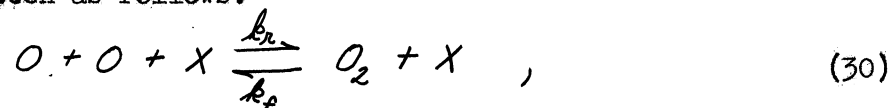
$$\frac{\bar{M}}{M_1} = \frac{1}{2} \left[1 + \frac{k_1 + k_3}{2 - (k_1 + k_3)} \right]$$

$$= \frac{1}{k_2 + 1}$$

For the special case of a flat plate with a uniform exterior flow, the main problem with which this study is concerned, $(\partial P)/(\partial X_0) = 0$. Hence for the remainder of this report, the pressure term will be neglected.

CHEMICAL REACTION-RATE TERM

Before continuing with any revisions or transformations of the boundary-layer equations, the chemical rate term appearing in equation (29b) should be carefully examined. This term, $m_2 \bar{K}_2$, expresses the rate at which mass of species 2 (atomic oxygen) is created by chemical reaction, per unit volume. To write this rate, something must be known about the proper chemical equation for the reaction. According to Hirschfelder,¹⁰ the reaction for the recombination of atomic oxygen depends on a three-body collision, and hence the reaction should be written as follows:



where X is any third body (i.e., another O atom, or an O₂ or N₂ molecule) and k_r and k_f are the reverse and forward reaction-rate constants, respectively. Since the reaction is usually written as a dissociation reaction, the k_r and k_f appear reversed in equation (30). Actually, this equation holds for both the dissociation and recombination of oxygen; depending on the direction in which the reaction happens to be proceeding.

From equation (30), one can find the rate at which atomic oxygen is being formed, making use of the law of mass reaction rates. Thus, the rate at which moles of O are being formed per unit volume, is, using Penners' form of the rate law,¹¹

$$\frac{d(N_2)}{dt} = -2k_r N_2^2 N_x + 2k_f N_1 N_x \quad , \quad (31)$$

where N_2 , N_1 , and N_x are the moles per unit volume of O, O₂, and any third body, respectively. Since X can be any of the constituents of the mixture, $N_x = N$,

and,

$$\frac{d(N_2)}{dt} = -2k_r N [N_2^2 + K_c N_1] \quad (32)$$

where K_c is the equilibrium constant written in terms of concentration. That is,

$$K_c = \frac{k_f}{k_r} \quad (33)$$

The equilibrium constant is usually written in terms of partial pressures. Then,

$$K_c = K_p \frac{1}{R_0 T} = K_p \frac{N}{P} \quad (34)$$

Also, it is desired to calculate $m_2 K_2$ which is $M_2 \frac{d(N_2)}{dt}$. Therefore,

$$\begin{aligned} m_2 K_2 &= M_2 \frac{d(N_2)}{dt} = -2k_r N [M_2 N_2^2 + K_p \frac{N N_1 M_2}{P}] \\ &= -2k_r N \left[\frac{P^2 K_2^2}{M_2} - \frac{K_p}{P} \frac{P^2 K_1 M_2}{M} \right] \end{aligned}$$

where $p = N\bar{M}$.

Next, the equation may be rearranged as follows:

$$m_2 K_2 = -2k_r \frac{NP^2}{M_2} \frac{M_1}{\bar{M}} \left[K_2^2 \frac{\bar{M}}{M_1} - \frac{K_p}{P} K_1 \left(\frac{M_2}{M_1} \right)^2 \right]$$

The term multiplying the bracket can be revised, using the equation of state. Thus,

$$\begin{aligned} \frac{NP^2}{M_2} \frac{M_1}{\bar{M}} &= \frac{P^3}{M_2 (\bar{M})^2} \frac{M_1}{M_2} = \frac{P M_1}{(\bar{M})^2 M_2} \frac{P^2 \bar{M}^2}{(R_0 T)^2} \\ &= \frac{M_1}{M_2} \frac{P^2}{R_0^2} \frac{P}{T^2} \end{aligned}$$

and since $M_1/M_2 = 2$, and $\bar{M}/M_1 = 1/(K_2 + 1)$, the equation for $m_2 K_2$ can be written, finally as

$$\begin{aligned} m_2 K_2 &= M_2 \frac{d(N_2)}{dt} = -(2k_r) 2 \left(\frac{P}{R_0} \right)^2 \frac{P}{T^2} \left[\frac{K_2^2}{K_2 + 1} - \frac{K_p K_1}{4P} \right] \\ &= -PW \end{aligned} \quad (35)$$

so that w is defined as

$$w \equiv (2k_2) z \left(\frac{P}{P_0}\right)^2 \frac{1}{T^2} \left[\frac{k_2^2}{k_2+1} - \frac{K_P k_1}{4P} \right]$$

$$= (2k_2) z \left(\frac{P}{P_0}\right)^2 \frac{1}{T^2} \left[\frac{k_2^2}{k_2+1} - \frac{K_P (1-k_2-k_3)}{4P} \right] \quad (36)$$

According to Hirschfelder,¹² k_r may be approximated by considering the reaction $H_2 \rightleftharpoons 2H$. His calculations give the following results:

$$2k_2 \approx 1.2 \times 10^{16} \left(\frac{T}{300}\right)^{5/2} \frac{cm^6}{(moles)^2 sec} \quad (37)$$

Also, using the values of Fricke for the equilibrium constant, Hirschfelder claims that the following expression gives good accuracy for temperatures up to 5000°K.

$$K_P \approx \text{EXP} \left(15.8 - \frac{60000}{T} \right) \quad (38)$$

Using the above values, an approximation of the reaction rate may be obtained. Note that in the definitions of w , k_r , and K_P , w is a function only of the temperature and concentrations. ρ does not enter into the definition explicitly.

FLAT-PLATE EQUATIONS IN PHYSICAL PLANE

At this point, the equations covered in (29) can be rewritten for the case of a flat plate with uniform external flow, $(\partial P / \partial X_0) = 0$, and using the definition of the rate law. In writing these equations, one new variable is defined to make the equations look more similar. Thus, $K = 1 - K_2$ is used. Equations (29) become, then,

$$a) \quad \frac{\partial P U_0}{\partial x_0} + \frac{\partial P v_0}{\partial y_0} = 0$$

$$b) \quad P U_0 \frac{\partial K}{\partial x_0} + P v_0 \frac{\partial K}{\partial y_0} = \frac{2}{2y_0} \left(P_0 D_{12} \frac{\partial K}{\partial y_0} \right) - P w$$

$$c) \quad P U_0 \frac{\partial K_3}{\partial x_0} + P v_0 \frac{\partial K_3}{\partial y_0} = \frac{2}{2y_0} \left(\frac{K_3}{K} P_0 D_{12} \frac{\partial K}{\partial y_0} \right) \quad (39)$$

$$d) \rho u_0 \frac{\partial u_0}{\partial x_0} + \rho v_0 \frac{\partial u_0}{\partial y_0} = \frac{\partial}{\partial y_0} \left(\mu \frac{\partial u_0}{\partial y_0} \right)$$

$$e) \rho u_0 \frac{\partial h}{\partial x_0} + \rho v_0 \frac{\partial h}{\partial y_0} = \frac{\partial}{\partial y_0} \left[\frac{\lambda}{c_p} \left\{ \frac{\partial h}{\partial y_0} - \left(1 - \frac{\rho \delta_{12} \bar{c}_p}{\lambda} \right) \sum_{i=1}^3 h_i \frac{\partial K_i}{\partial y_0} \right\} + \mu \left(\frac{\partial u_0}{\partial y_0} \right)^2 \right]$$

$$f) P = (2-K) \frac{\rho R_0 T}{M_1} = \text{constant.} \quad (39)$$

(Cont.)

It should be noted that the energy equation (39e) may be written in other forms. If the product of u_0 times the momentum equation is added to the energy equation, one obtains the well-known form where the total enthalpy $h_s = h + (u_0^2/2)$ is involved. If the equation is written in terms of the temperature rather than the enthalpy, then, since the equation of state connects the density with temperature, there is a better connection between the energy and state-equation; however, the energy equation becomes more complicated through the appearance of the reaction-rate term. These two forms are listed at this time for future reference.

$$a) \rho u_0 \frac{\partial h_s}{\partial x_0} + \rho v_0 \frac{\partial h_s}{\partial y_0} = \frac{\partial}{\partial y_0} \left[\frac{\lambda}{c_p} \left\{ \frac{\partial h_s}{\partial y_0} - \left(1 - \frac{\bar{c}_p \mu}{\lambda} \right) \frac{\partial (u_0^2/2)}{\partial y_0} - \left(1 - \frac{\rho \delta_{12} \bar{c}_p}{\lambda} \right) \sum_{i=1}^3 h_i \frac{\partial K_i}{\partial y_0} \right\} \right] \quad (40)$$

$$b) \rho u_0 \frac{\partial T}{\partial x_0} + \rho v_0 \frac{\partial T}{\partial y_0} = \frac{1}{c_p} \frac{\partial}{\partial y_0} \left(\lambda \frac{\partial T}{\partial y_0} \right) + \frac{\mu}{c_p} \left(\frac{\partial u_0}{\partial y_0} \right)^2 - \frac{\rho \delta_{12}}{c_p} \sum_i c_{p_i} \frac{\partial K_i}{\partial y_0} \frac{\partial T}{\partial y_0} + \frac{\rho W}{c_p} (h_1 - h_2)$$

Here $(h_1 - h_2)$ is the heat released due to reaction. In combustion problems this is considered to be a constant, given by some average value. However, in this case the assumption depends on the temperature range involved, and it may not be possible to use a constant value.

TRANSFORMATION OF EQUATIONS

In accordance with usual boundary layer practice, equations (39) can be transformed into a corresponding incompressible plane by means of the

Dorodnitsyn¹³ transformation. Whereas, without dissociation, this transformation effectively decouples the momentum and energy equations since $\rho u \approx$ constant, with dissociation, since $\rho u \neq$ constant, the equations are not completely decoupled, and the new plane is not completely incompressible. However, as other authors have pointed out,^{14,15} the effects due to these variations are small, and can be taken care of by an iterative solution of the momentum equation and energy equation.

If $x, y, u,$ and v are the coordinates and velocities in the corresponding quasi-incompressible flow, then they are connected to the physical variables with the following relations.

$$\begin{aligned}
 a) \quad y &= \int_0^y \frac{\rho}{\rho_e} dy_0 \\
 b) \quad x &= x_0 \\
 c) \quad \frac{\partial C}{\partial x_0} &= \frac{\partial C}{\partial x} + \frac{\partial C}{\partial y} \frac{\partial y}{\partial x_0} \\
 d) \quad \frac{\partial C}{\partial y_0} &= \frac{\rho}{\rho_e} \frac{\partial C}{\partial y} \\
 e) \quad u &= u_0 \\
 f) \quad v_0 &= -\frac{\rho_e}{\rho} \left(-v + u \frac{\partial y}{\partial x_0} \right)
 \end{aligned} \tag{41}$$

Here ρ_e is the density along the edge of the boundary layer. The velocity relations are found by defining the stream function in the usual way:

$$\begin{aligned}
 \rho u_0 &= \rho_e \frac{\partial \psi}{\partial y_0} \\
 \rho v_0 &= -\rho_e \frac{\partial \psi}{\partial x_0}
 \end{aligned} \tag{42}$$

and performing the given transformation of variables. That is:

$$\begin{aligned}
 \rho u_0 &= \rho_e \frac{\rho}{\rho_e} \frac{\partial \psi}{\partial y} \\
 \text{or, } u_0 &= \frac{\partial \psi}{\partial y} \\
 \text{Also, } \rho v_0 &= -\rho_e \left(\frac{\partial \psi}{\partial x} + \frac{\partial \psi}{\partial y} \frac{\partial y}{\partial x_0} \right)
 \end{aligned}$$

Now, defining $u = \frac{\partial \psi}{\partial y}$, and

$$v = -\frac{\partial \psi}{\partial x} \quad (43)$$

in the transformed planes, one obtains the relations given in equations (41e) and (41f).

With the definitions given in equations (41), and defining

$$C = \frac{\rho \mu}{\rho_e \mu_e} \quad (44)$$

one can write equations (39) in the following manner.

$$\begin{aligned} a) \quad & u \frac{\partial u}{\partial x} + v \frac{\partial u}{\partial y} = 0 \\ b) \quad & u \frac{\partial \kappa}{\partial x} + v \frac{\partial \kappa}{\partial y} = \nu_e \frac{\partial}{\partial y} \left(\frac{C}{S_c} \frac{\partial \kappa}{\partial y} \right) - w \\ c) \quad & u \frac{\partial \kappa_3}{\partial x} + v \frac{\partial \kappa_3}{\partial y} = \nu_e \frac{\partial}{\partial y} \left(\frac{C}{S_c} \kappa \frac{\partial \kappa}{\partial y} \right) \\ d) \quad & u \frac{\partial u}{\partial x} + v \frac{\partial u}{\partial y} = \nu_e \frac{\partial}{\partial y} \left(C \frac{\partial u}{\partial y} \right) \\ e) \quad & u \frac{\partial h}{\partial x} + v \frac{\partial h}{\partial y} = \nu_e \frac{\partial}{\partial y} \left[\frac{C}{P_r} \left\{ \frac{\partial h}{\partial y} - \left(1 - \frac{P_r}{S_c} \right) \sum_{i=1}^3 h_i \frac{\partial \kappa_i}{\partial y} \right\} \right] + \\ & + \nu_e \left(\frac{\partial u}{\partial y} \right)^2 \end{aligned} \quad (45)$$

ν_e is the kinematic viscosity along the edge of the boundary layer, and P_r and S_c are the Prandtl number and Schmidt number, respectively. They are defined as

$$P_r = \frac{\bar{C}_p \mu}{\lambda}$$

and,

$$S_c = \frac{\mu}{\rho D_{12}} \quad (46)$$

where all quantities are for the mixture at a given point.

The forms of the energy equation given in equations (40) can also be written in terms of the new variables. Thus,

$$a) \quad u \frac{\partial h_s}{\partial x} + v \frac{\partial h_s}{\partial y} = \gamma_e \frac{\partial}{\partial y} \left[\frac{c}{P_r} \left\{ \frac{\partial h_s}{\partial y} - (1-P_r) \frac{\partial (u^2/2)}{\partial y} - (1-\frac{P_r}{S_c}) \sum_{i=1}^3 h_i \frac{\partial K_i}{\partial y} \right\} \right]$$

$$b) \quad u \frac{\partial T}{\partial x} + v \frac{\partial T}{\partial y} = \frac{\gamma_e}{C_p} \frac{\partial}{\partial y} \left(\frac{c}{P_r} \bar{C}_p \frac{\partial T}{\partial y} \right) + \frac{c}{C_p} \frac{\gamma_e}{S_c} \left(\frac{\partial u}{\partial y} \right)^2 - \frac{c}{S_c} \frac{\gamma_e}{C_p} \sum_{i=1}^3 C_{p_i} \frac{\partial K_i}{\partial y} \frac{\partial T}{\partial y} + \frac{u}{C_p} (h_1 - h_2) \quad (47)$$

At this point, it is instructive to write the equations in one more different form. This form involves the use of the so-called boundary-layer variable, η . However, instead of assuming immediately all variables are functions of η alone, as is usually done, one can transform the equations, instead of from x and y , to s and η , say, where

$$s = x \quad \text{and} \quad \eta = \left(\frac{\gamma_e}{\nu_e x} \right)^{1/2} \frac{y}{z} \quad (48)$$

Also, a dimensionless stream function is defined in the usual way, except that f is now a function of x and η .

$$\psi = (\nu_e \gamma_e x)^{1/2} f(\eta, x) \quad (49)$$

With these definitions, a straightforward change of variables leads to the following set of equations, from equations (45):

$$\begin{aligned} a) \quad & \frac{\partial}{\partial \eta} \left(\frac{c}{S_c} \frac{\partial K}{\partial \eta} \right) + f \frac{\partial K}{\partial \eta} = x \left[\frac{4u}{\gamma_e} + 2 \left\{ \frac{\partial f}{\partial \eta} \frac{\partial K}{\partial x} - \frac{\partial f}{\partial x} \frac{\partial K}{\partial \eta} \right\} \right] \\ b) \quad & \frac{\partial}{\partial \eta} \left(\frac{c}{S_c} \frac{K_3}{K} \frac{\partial K}{\partial \eta} \right) + f \frac{\partial K_3}{\partial \eta} = 2x \left\{ \frac{\partial f}{\partial \eta} \frac{\partial K_3}{\partial x} - \frac{\partial f}{\partial x} \frac{\partial K_3}{\partial \eta} \right\} \\ c) \quad & \frac{\partial}{\partial \eta} \left(c \frac{\partial^2 f}{\partial \eta^2} \right) + f \frac{\partial^2 f}{\partial \eta^2} = 2x \left\{ \frac{\partial f}{\partial \eta} \frac{\partial^2 f}{\partial x \partial \eta} - \frac{\partial f}{\partial x} \frac{\partial^2 f}{\partial \eta^2} \right\} \\ d) \quad & \frac{\partial}{\partial \eta} \left(\frac{c}{P_r} \left[\frac{\partial h_s}{\partial \eta} - (1-P_r) \frac{\gamma_e^2}{8} \frac{\partial}{\partial \eta} \left(\left(\frac{\partial f}{\partial \eta} \right)^2 \right) - (1-\frac{P_r}{S_c}) \sum_i h_i \frac{\partial K_i}{\partial \eta} \right] \right) + f \frac{\partial h_s}{\partial \eta} = 2x \left\{ \frac{\partial f}{\partial \eta} \frac{\partial h_s}{\partial x} - \frac{\partial f}{\partial x} \frac{\partial h_s}{\partial \eta} \right\} \end{aligned} \quad (50)$$

where the energy equation has been written in terms of the total enthalpy.

The boundary conditions for the above equations are, in general,

$$\begin{aligned}
 @ \eta = 0 & \quad f = f' = 0 \\
 & \quad \kappa = \kappa_w(x) \\
 & \quad \kappa_3 = \kappa_{3w}(x) \\
 & \quad h_s = h_w(x) \\
 @ \eta = \infty & \quad f' = 2 \\
 & \quad \kappa = \kappa_e(x) \\
 & \quad \kappa_3 = \kappa_{3e}(x) \\
 & \quad h_s = h_{se}(x)
 \end{aligned} \tag{51}$$

Of course, if the incoming air has no dissociation, then κ_e , κ_{3e} , and h_{se} are not functions of x .

The important thing to notice about equations (50) is the dependence of the dependent variables on x . In the usual boundary layer analysis, these variables are assumed to be functions of η alone. In terms of the momentum equation, this means, for instance, that $\partial f / \partial x = \partial^2 f / \partial x \partial \eta = 0$. Now, the resulting equation must be independent of x , or the assumption cannot be made. Looking at equation (50a), then, it is clear that κ is not independent of x unless chemical equilibrium exists. This is true since even if one assumed $\kappa = \kappa(\eta)$ and $f = f(\eta)$ so that $\partial f / \partial x = \partial \kappa / \partial x = 0$, there would be a term $4xw/U_e$ on the right-hand side of the equation, so that x would appear explicitly in the equation. If chemical equilibrium exists, however, the net rate of production of O by chemical reaction is zero at every point, and $w \equiv 0$. Then, however, equations involving κ and κ_3 are unnecessary, since all concentrations may be calculated from equilibrium considerations.

Equation (50b) is the only equation which has a term multiplied by x , which is not of the form where an assumption about the dependence of the variables on η would remove the explicit x . However, if κ depends on x as well as η , then κ_3 , h_s , and even f , through c , depend implicitly on x since κ appears in the equation. Actually, C depends on h_s and κ , but, as Probstein showed,¹⁶ the dependence of f on C is not very pronounced, so the assumption that f depends on η alone should not be too inaccurate. However, as mentioned above, the assumption is strictly true only in the case of chemical equilibrium, or no reaction at all, of course.

METHODS OF SOLUTION

Before considering any actual methods of solution, it is instructive to picture the temperature distribution through a high external velocity boundary layer with heat transfer into the wall, with no dissociation. The temperature profile is shown in Fig. 1.

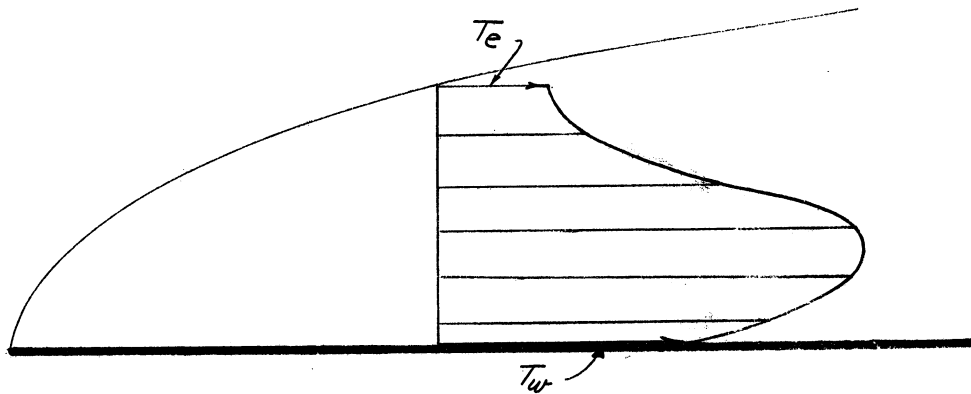


Fig. 1. Temperature distribution with no dissociation.

Next, if one allows dissociation to occur, it is evident that as the temperature increases (coming from T_e toward the wall), a temperature will finally be reached where dissociation becomes important. From this point on toward the wall, the temperature will decrease from the value it would have with no dissociation. In Fig. 2, the dotted line represents the actual temperature distribution with dissociation; the full line, the temperature without dissociation, as in Fig. 1.

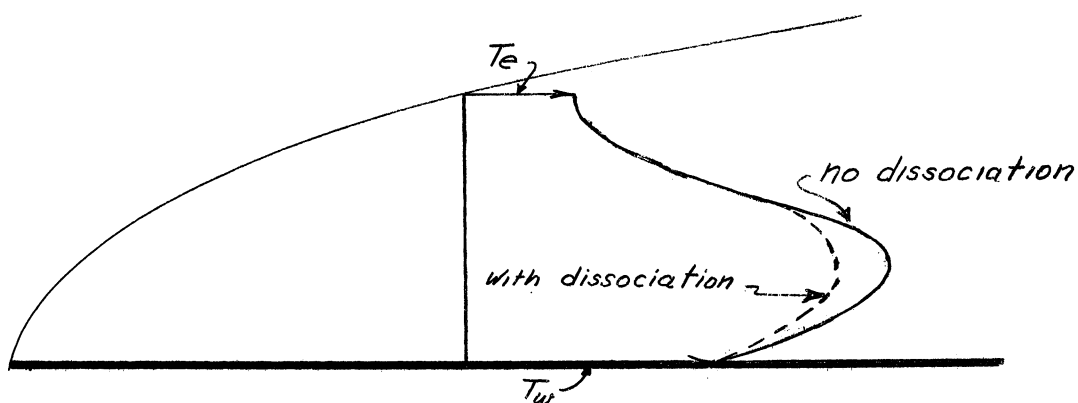


Fig. 2. Effects of dissociation on temperature profile.

The profiles are drawn with the maximum temperature much greater than the wall temperature so that there is heat transfer into the wall, because

in the practical case, the wall temperature must not rise over approximately 1000°K, which is much less than the stagnation temperature at the flight Mach numbers envisaged. Hence in any practical problem, there will be heat transfer into the surface. The effect of dissociation, as can be seen by the sketch in Fig. 2, is to reduce the heat transfer by reducing the temperature gradient at the body surface.

It is evident if chemical equilibrium is assumed, that the temperature at which dissociation begins to have an appreciable effect, as the temperature is increasing, is also the temperature at which dissociation ceases to have any effect as the temperature is decreasing. That is, there is a buffer layer next to the plate where no dissociation occurs. This situation is pictured in Fig. 3.

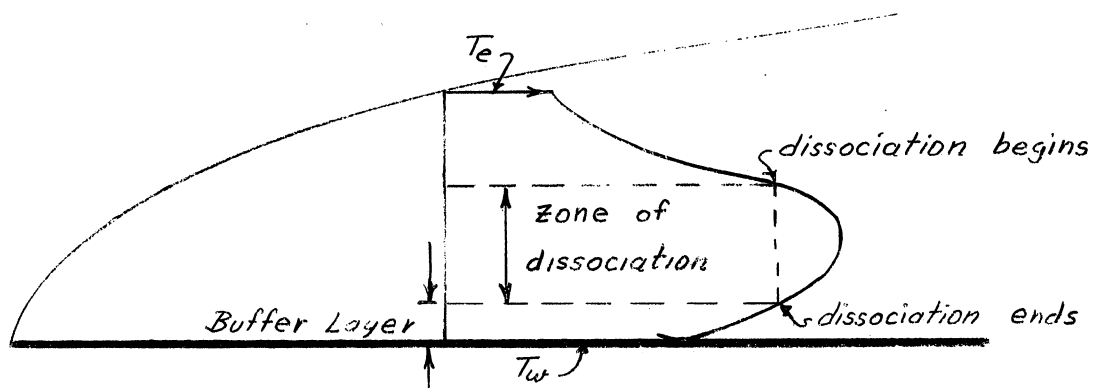


Fig. 3. Buffer layer for case of chemical equilibrium.

Now, this situation is sure to be altered when an actual chemical rate exists. Chemical equilibrium will probably not exist. Since, however, according to equilibrium figures, the temperature at which the relative weight concentration of atomic oxygen is 1% is 2500°K, and since the wall temperature is only about 1000°K, it seems evident that there still should be a layer at the plate surface where no dissociation or recombination takes place. This is because at these temperatures the recombination rate is extremely fast, there being a zero activation energy, and because the fluid is moving slowly compared to the external velocity. Hence the relaxation time must be very small compared to the residence time. This ratio could be expressed, for example, by

$$R_t = \frac{\rho U \frac{\partial K_2}{\partial x}}{(m_2 K_2)_{\text{recombination}}}$$

that is, by the ratio of the nitrogen convected to the atomic oxygen which disappears due to chemical reaction.* This ratio may be written in terms of

*Note that the diffusion terms, in the boundary-layer equations, are of the same order as the convection terms, so that this ratio should hold for the time associated with the cross stream diffusion of mass as well as the time associated with the convection of mass.

Hirschfelder's values (equations 36, 37) and an order of magnitude found.

$$R_t = \frac{\rho U \frac{\partial K_3}{\partial x}}{(2k_r) 2\left(\frac{P}{R_0}\right)^2 \frac{\rho}{T^2} \left(\frac{K_2^2}{K_2+1}\right)}$$

$$\sim \frac{U \frac{K_3}{L}}{1.2 \times 10^{16} \left(\frac{T}{300}\right)^{5/2} 2\left(\frac{P}{R_0}\right)^2 \frac{1}{T^2} \left(\frac{K_2^2}{K_2+1}\right)}$$

where L is the distance from the leading edge. This ratio may be simplified to

$$R_t \sim \frac{\frac{U}{L} K_3}{2.6 \times 10^{11} \left(\frac{T}{300}\right)^{5/2} \left(\frac{P}{R_0}\right)^2 \left(\frac{K_2^2}{K_2+1}\right)}$$

Finally, if K_2 and K_3 are taken to be of order 1, T is taken to be about 2000°K, and P is assumed to be approximately 1/10 of an atmosphere, then

$$R_t \sim \frac{U/L}{5 \times 10^5}$$

or $R_t \sim 2 \times 10^{-6} U/L$, and for $R_t \ll 1$ no significant reaction occurs.

Thus, except at or very near the leading edge, where singularities exist in all the functions, U/L can be of the order 10^4 before the ratio is significantly affected. Of course, all the values used are approximations, but they indicate a general order of magnitude, and show that there should be a buffer layer even when a reaction rate is considered. The concentration profiles would then look something like those pictured in Fig. 4.

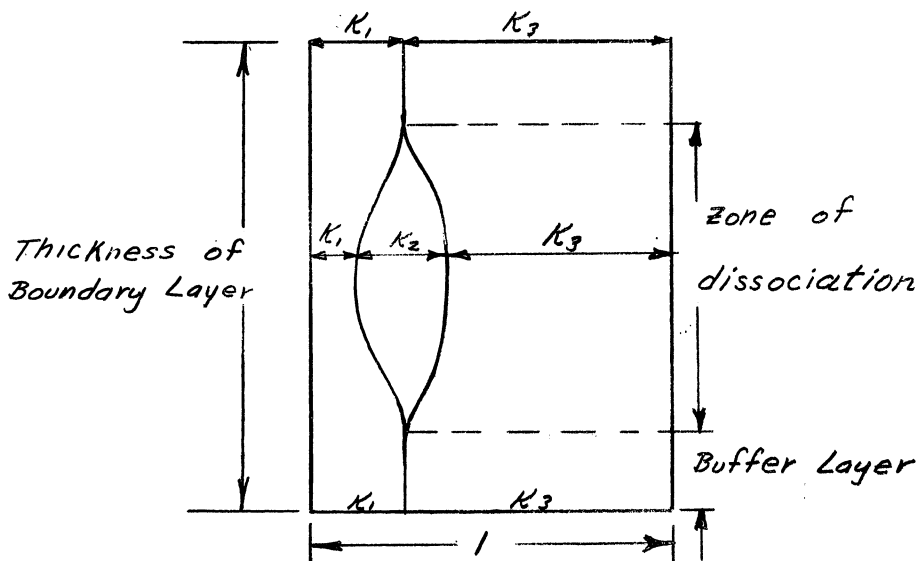


Fig. 4. Concentration profiles in boundary layer.

PROPOSED FUTURE WORK

With the above arguments in mind, the following method of attack is proposed. First, with the assumption of chemical equilibrium, the boundaries of the zone of reaction may be found. They are arbitrarily defined as those lines along which the relative mass concentration of atomic oxygen is 1%, i.e., $K_2 = 0.01$. Next, to see what the effects of a reaction rate are, a perturbation analysis will be made with the net rate of reaction, w , being the small parameter. This will indicate the changes in both the boundaries of the reaction zone, and the profile of the temperature to be expected from a chemical reaction rate. Finally, a numerical analysis can be made, using the best available reaction-rate data. This should be performed with the idea of finding the effects of a 10% or 20% change in any of the chemical parameters, so as to take account of any later more accurate determination of these parameters. The end result of these calculations will be to calculate the heat transfer and skin friction at the plate surface. For this first problem, the parameters are Mach number and external flow density and temperature (altitude).

It is interesting to note that, for the case of chemical equilibrium, the boundaries of the reaction zone are lines of $\eta = \text{const.} = \eta^*$, say. Hence, once these lines are found, i.e., the reaction zone solved, and the temperature and slope of the temperature profile are known, the problem resolves itself into finding the heat transfer in a fictitious boundary layer with no reaction, which has the given value of temperature and temperature derivative, at the given η^* closest to the plate surface. This means, physically, that the new problem consists of a regular boundary-layer problem with a new external stream temperature and a new thermal boundary-layer thickness, these being set by the temperature and temperature derivative at the $\eta = \eta^*$ closest to the surface of the plate. Since the thickness of the thermal boundary layer is associated with the Mach number or the Prandtl number, this indicates that the solution of the boundary layer with dissociation following chemical equilibrium can be found by considering a boundary layer with no dissociation with a new stream temperature, and with either a new stream Mach number, or perhaps a new Prandtl number (i.e., different fluid). This implies that a type of similarity exists between high speed flows with dissociation, and those without dissociation, which involves changing the external conditions to take account of the dissociation. It may be that a change of working fluid can be accounted for; this would mean that testing could be done with a nondissociating medium which would mean a great saving in time and effort. This should be investigated more fully.

Finally, the above studies can be carried out for the case of a dissociated free stream, where the dissociation is caused by a normal shock in front of the flat plate and also for the stagnation-point region of a blunt body, where there must be some surface reaction. In the latter case, an at-

tempt can be made to calculate the extent of such surface reaction, the end of such a region being the beginning of the buffer-layer region as described above.

PHYSICAL PROPERTIES OF AIR

Information about the physical properties of air is necessary for the solution of aerodynamic problems. These properties will change at high temperatures. The oxygen in air at normal pressure begins to dissociate ($\sim 1\%$ atomic oxygen) at $\sim 2500^\circ\text{K}$ and is completely dissociated at $10,000^\circ\text{K}$. Nitrogen starts dissociating at $\sim 3500^\circ\text{K}$. Ionization of NO starts at about 6000°K , and $\sim 50\%$ of air at $25,000^\circ\text{K}$ is made up of ionized particles.

The earliest computations of thermodynamic properties of air in thermal equilibrium were presented by Bethe.¹⁸ He obtained the properties of air from the quantum mechanical partition functions based on the rigid rotator—harmonic oscillator with a correction for nonrigidity and anharmonicity. Kreiger and White,²⁰ Gilmore,³² and Logan³⁵ employed essentially the same approach, combining constituents into a mixture based on the ideal-gas law. Bethe neglected the effects of NO formation and Kreiger and White neglected ionization. Logan used spectroscopic data instead of the rigid rotator—harmonic oscillator model for the energies.

A different approach is that of Hirschfelder and Curtiss,¹⁹ who employed the Beattie-Bridgeman equations of state for high pressures and the Virial equation of state for lower pressures. The second Virial coefficient was computed from the Lennard-Jones 6-12 potential. Hall and Ibell²⁴ also used the Virial equation of state and computed the second, third, and fourth Virial coefficients from the Lennard-Jones 6-12 potential, but did not consider dissociation. Hilsenrath, *et al.*,³³ employed a similar method also making use of PVT and other experimental data. Hilsenrath and Beckett³⁷ computed thermodynamic properties from ideal-gas thermal functions of constituents and equilibrium concentrations. Their work is being continued to include more than just a mixture of nitrogen and oxygen. They assumed an ideal-gas mixture of oxygen and nitrogen increased proportionately to compensate for other constituents not included at the time.

Only References 31 through 39 include the presently accepted energy of dissociation for nitrogen (9.759 eV). All earlier references employed the lower energy of dissociation (7.37 eV).

Tabulations of transport properties of air are rather limited. Viscosities, conductivities, and Prandtl numbers have been computed based on empirical expressions (References 30, 33) or the Lennard-Jones 6-12 potential and the Eucken relationship (References 19, 21, 23, 26).

For the most part transport properties are unknown at high temperatures due to the lack of experimental data and the unknown aspects of atom-molecule interactions. A discussion of interaction parameters for atom-molecule mixtures is presented in Reference 38. Some predictions have been made (Reference 39) which indicate that the Prandtl number and viscosity do not vary much from the predicted by simple models at temperatures below 9000°K.

Computations based on the Lennard-Jones 6-12 potential have given relatively (at moderate temperatures) usable results. Many of the data, such as force constants and collision integrals, necessary for such computations, are tabulated in Reference 1. It would seem, then, that the use of the Lennard-Jones potential would at least be a consistent and reasonable approach to the problem of computing physical properties.

Table I presents a summary of results of computations available. The basis of the method employed is indicated.

EXPERIMENTAL TECHNIQUES FOR THE STUDY OF HYPERSONIC FLOWS

A great deal has been written about the difficulty encountered in attempts to simulate hypersonic flow problems in the laboratory. The wide array of similarity parameters to be matched (ratio of specific heats, Mach number, Reynolds number, Nusselt number, Schmidt number, etc.) presents a formidable task. In addition, it now becomes imperative to consider the effects of dissociation, vibrational excitation, electronic excitation, and ionization along with the attendant relaxation times. These effects are not scalable but rather depend on local temperatures and pressures. Instrumentation that might be utilized in assessing these effects is greatly limited and obtains but questionable accuracy.

In view of the complicated fluid-mechanic and chemical interrelationships, it is not surprising that different experimental techniques lend themselves more readily to specific areas of experimental interest. Accordingly, it is intended to review briefly those techniques currently being used in the study of hypersonic flow as well as some of the newer techniques suggested by various scientists. Some consideration will also be given to the instrumentation available for these studies, limited though it is. As of this time the authors are not prepared to specify one particular research tool as the optimum for studies of the hypersonic laminar boundary layer.

Pertinent references to the above area are included in the bibliography.

TABLE I

Reference No.:	18	19	20	21	22	23	24*	25	26	27	28	29*	30	31	32	33	34	35	36	37	38	39	
Temperature	5000°K to 25,000°K	273°K to 5000°K	500°K to 8000°K	1500°K to 300°K	40°C	0 to 2000°K	0 to 5000°K	0°K to 6000°K	300°K to 3000°K	0°R to 14,000°R	300°K to 7000°K	298°K to 5000°K	100-1500°K to 2000°K	50°K to 5000°K	1000°K to 3000°K	50°K to 3000°K	1000 to 12,000°K	2000 to 10,000°K	2000 to 8000°K	2000 to 15,000°K	250 to 3560°K	0 to 9000°K	
Density	1 to 20 x std. 27° std.	.008 to 27° std.	1 to 20 x std. 27° std.	0.02-0.0 lb/ft ³																			
Gases	Air, O ₂ , H ₂	Air, O ₂ , H ₂ , NO, H ₂ O, CO, CO ₂ , H ₂ , H ₂ O, H ₂ , H ₂ O, H ₂	Air, O ₂ , H ₂ , NO, H ₂ O, CO, CO ₂ , H ₂ , H ₂ O, H ₂ , H ₂ O, H ₂	Air, O ₂ , H ₂ , NO, H ₂ O, CO, CO ₂ , H ₂ , H ₂ O, H ₂ , H ₂ O, H ₂	Air, O ₂ , H ₂ , NO, H ₂ O, CO, CO ₂ , H ₂ , H ₂ O, H ₂ , H ₂ O, H ₂	Air, O ₂ , H ₂ , NO, H ₂ O, CO, CO ₂ , H ₂ , H ₂ O, H ₂ , H ₂ O, H ₂	Air, O ₂ , H ₂ , NO, H ₂ O, CO, CO ₂ , H ₂ , H ₂ O, H ₂ , H ₂ O, H ₂	Air, O ₂ , H ₂ , NO, H ₂ O, CO, CO ₂ , H ₂ , H ₂ O, H ₂ , H ₂ O, H ₂	Air, O ₂ , H ₂ , NO, H ₂ O, CO, CO ₂ , H ₂ , H ₂ O, H ₂ , H ₂ O, H ₂	Air, O ₂ , H ₂ , NO, H ₂ O, CO, CO ₂ , H ₂ , H ₂ O, H ₂ , H ₂ O, H ₂	Air, O ₂ , H ₂ , NO, H ₂ O, CO, CO ₂ , H ₂ , H ₂ O, H ₂ , H ₂ O, H ₂	Air, O ₂ , H ₂ , NO, H ₂ O, CO, CO ₂ , H ₂ , H ₂ O, H ₂ , H ₂ O, H ₂	Air, O ₂ , H ₂ , NO, H ₂ O, CO, CO ₂ , H ₂ , H ₂ O, H ₂ , H ₂ O, H ₂	Air, O ₂ , H ₂ , NO, H ₂ O, CO, CO ₂ , H ₂ , H ₂ O, H ₂ , H ₂ O, H ₂	Air, O ₂ , H ₂ , NO, H ₂ O, CO, CO ₂ , H ₂ , H ₂ O, H ₂ , H ₂ O, H ₂	Air, O ₂ , H ₂ , NO, H ₂ O, CO, CO ₂ , H ₂ , H ₂ O, H ₂ , H ₂ O, H ₂	Air, O ₂ , H ₂ , NO, H ₂ O, CO, CO ₂ , H ₂ , H ₂ O, H ₂ , H ₂ O, H ₂	Air, O ₂ , H ₂ , NO, H ₂ O, CO, CO ₂ , H ₂ , H ₂ O, H ₂ , H ₂ O, H ₂	Air, O ₂ , H ₂ , NO, H ₂ O, CO, CO ₂ , H ₂ , H ₂ O, H ₂ , H ₂ O, H ₂	Air, O ₂ , H ₂ , NO, H ₂ O, CO, CO ₂ , H ₂ , H ₂ O, H ₂ , H ₂ O, H ₂	Air, O ₂ , H ₂ , NO, H ₂ O, CO, CO ₂ , H ₂ , H ₂ O, H ₂ , H ₂ O, H ₂	Air, O ₂ , H ₂ , NO, H ₂ O, CO, CO ₂ , H ₂ , H ₂ O, H ₂ , H ₂ O, H ₂	Air, O ₂ , H ₂ , NO, H ₂ O, CO, CO ₂ , H ₂ , H ₂ O, H ₂ , H ₂ O, H ₂
Pressure					150 mm Hg	.2-20 x atm.				1-10 ⁻⁴ atm.	10 ⁻¹ atm.		1-200 atm.	10 ⁻⁸ -100 x atm.		.01-100 atm.							
Enthalpy	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	
Internal Energy	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	
Entropy	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	
Composition	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	
Compressibility F.	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	
Specific Heat	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	
Specific Heat Ratio	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	
Velocity of Sound	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	
Viscosity	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	
Thermal Conductivity	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	
Free Energy	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	
Prandtl No.	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	
Dissec. Energy	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	
Ionisation Energy	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	
Fraction of Diatomic Molecules in Each Electronic State	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	
Diffusion Coefficient	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	
Equilibrium Constant	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	
Schmidt No. ($\mu/\rho D$)	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	
Lewis No. ($\lambda/\rho c_p D$)	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	
Ideal Gas	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	
Partition Functions	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	
Virial Eq. of State	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	
Lennard-Jones (6-12)	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	

Wrong energy of dissociation for Hg used before Reference 31.
* No dissociation.

HYPERSONIC WIND TUNNELS

Some work has been done toward extending the Mach number range of conventional blowdown supersonic wind tunnels by increasing the reservoir conditions of pressure and temperature. Noteworthy among these types are the installations at NACA Langley Field and at Brooklyn Polytechnic Institute. The former utilizes a zirconium pebble-type heat exchanger that has anticipated capabilities in the order of 4500°K stagnation temperature. The Brooklyn facility utilizes a pebble-type heat exchanger to charge an adiabatic compression tower that drives a hypersonic tunnel at anticipated temperatures up to 8000°K and pressures of 3500 psi. Even so, such schemes do not simulate flight conditions in the high Mach number range (15-20).

A modification of the methods above is to use a monatomic gas, rather than air, as the working medium. In this way much lower test conditions of temperature and pressure may be utilized without the danger of component liquefaction. The experimental results are also more readily evaluated as there are no dissociation effects to assess. The latter consideration presents a strong objection to this technique. However, many tests can be made at high Mach numbers to study the Mach number effect without the complication of dissociation. Toward this end, Bogdanoff and co-workers at Princeton University have developed a hypersonic tunnel which utilizes helium as the working gas.

SHOCK TUBES AND SHOCK TUNNELS

Probably the greatest source of experimental information in the hypersonic range to date has been the shock tube and its modifications. In essence the technique is simple and inexpensive and lends itself to a wide range of experimental investigations.

In the simple shock tube (a low-pressure test gas separated by a single diaphragm from a high-pressure, high-temperature reservoir gas), the usable testing region is that uniform zone immediately behind the shock wave and preceding the contact surface which separates the original test-section gas from the reservoir gas. Although high stagnation temperatures may be realized in this zone (and hence some meaningful experiments may be conducted), the maximum obtainable Mach number is in the low supersonic range. Furthermore, the time duration of this uniform flow condition is extremely short, about 100 microseconds being the greatest realized to date.

To circumvent these limitations, Cornell Aeronautical Laboratory and the Naval Ordnance Laboratory have modified the simple tube by using an expansion nozzle on the downstream end of the tube which serves to accelerate the low supersonic gases to extremely high Mach numbers. Further performance increases are achieved by using the hot combustion products of hydrogen and oxygen as the reservoir gas.

ARC DISCHARGE TUNNEL

A novel hypersonic tunnel, now in operation at the Arnold Engineering Development Center, consists of a conical-shaped nozzle wherein extremely high stagnation conditions are realized by discharging stored electrical energy across a gap in an air-filled container. Using such techniques, stagnation temperatures of approximately 15,000°K and stagnation pressures of 20,000 psi have been obtained so that test Mach numbers of 15 still yield essentially the correct static temperature desired for simulation. Furthermore, the run time is greatly extended over that of shock tubes. The difficulty lies in the fact that the test-section conditions of pressure and temperature are continually changing with time due to the blowdown-type operation. Furthermore, Mach number changes somewhat with time as the throat of the nozzle is gradually enlarged due to vaporization. A further disadvantage is incurred by vaporization of the discharge terminals, which serves to contaminate the air stream.

Preliminary results that are available to date lead the associated tunnel personnel to believe that chemical equilibrium is attained throughout the nozzle and that the flow is approximately isentropic. It appears that a larger volume of reservoir gas and a prolonged spark duration could make this method very promising.

HYPERVELOCITY PELLETS

Considerable progress has been made toward firing bullets or pellets at extremely high velocities. Such a technique is especially attractive in that the free stream conditions for high speed flight can be duplicated quite accurately and thus lend credence to the results obtained. Shaped charges, hydrogen guns, helium guns, nylon pellets, in addition to the innovations, have been utilized (chiefly by personnel of the Naval Ordnance Laboratory at White Oak, Maryland, and of the Naval Ordnance Test Station at Inyokern) to attain these extremely high velocities.

The chief disadvantage to these techniques is the limited instrumentation that can be applied profitably. To be sure, the pellets' path can be photographed at a number of stations and the velocity and shock patterns determined. Different gases can be used to eliminate or vary the dissociation effects as evidenced in changes in the shock-wave stand-off distance and the characteristics of the wake. However, any measurements on the skin of the pellet or on the boundary-layer characteristics would appear to be extremely difficult, if not impossible. The shape of the pellet would also be quite limited.

OTHER METHODS

In addition to the above outlined techniques that can be applied to the study of hypersonic flows, several variations and new methods have been

suggested and are in the process of experimentation. Among these are the application of an electromagnetic field to the acceleration of an ionized gas and electromagnetic fields applied to the acceleration of small missiles in a tube. Some of these methods show great promise, although the equipment becomes quite prohibitive in cost. No authentic flight data have been obtained in such devices to date as far as the authors know.

A possible variation of the shock tube for purposes of hypersonic research and which to the authors' knowledge has not been tried as yet, is to use a gaseous detonation wave as the reservoir gas and to test in the detonation products immediately behind the contact surface. Preliminary idealized calculations indicate that this zone is typified by high Mach numbers and stagnation temperatures (the latter because of the detonation process as well as the increase in stagnation temperature due to the unsteady expansion). Even if the predicted high Mach numbers could not be obtained (as is the case in conventional shock tubes for the gases in this zone), the stagnation temperature should be extremely high and hence an expansion nozzle could be utilized on the end of the tube. Admittedly, the test gases are not air but combustion products of water vapor, carbon dioxide, monatomic and atomic oxygen, hydroxyl radical, etc. This would, of course, limit the area of application of this technique. However, it may find unique applications for specific experimental studies.

Several other modifications of the shock tube have been suggested. One method is the use of the nonsteady expansion region behind the contact surface as mentioned above in the description of the detonation tube arrangement. The difference here is the use of a second diaphragm in an additional driver section (air in the section between diaphragms) so that the stagnation temperature in back of the second diaphragm would be increased. There is evidence, however, that the theoretical conditions behind this interface may be difficult to achieve experimentally. The use of a shock tube with a contracted low pressure region to make use of reflected shock waves for increasing stagnation temperature is another possibility. In general, there are many possibilities of employing expanded or contracted sections at various initial conditions combined with one or more diaphragms to obtain a variety of test conditions. Strong shocks may also be produced by means of other drivers such as spark discharges or high explosive charges. Of course, simplicity is advantageous, but may have to be sacrificed to obtain desired Reynolds numbers and static temperatures at high Mach numbers.

INSTRUMENTATION

The tests of interest in hypersonic flow studies involve extreme temperatures and complicated chemical changes in the composition of the air. This consideration, along with the extremely short running times available in hypersonic facilities, seriously restricts the type of transducers that can be employed. In shock-tube applications the thin film resistance thermometer has

been of some value and response times in the order of one microsecond are reported. One limitation for its use in the shock tub is its fragility. As a result Rose and Stark at Avco have been developing a calorimeter gage which is based on an "infinitely thick" sensing elements. Hot wires were also found to be too fragile. An additional problem in the case of the hot wire is the necessity of knowing the density to determine the temperature. Optical methods for the determination of density such as interferometry and x-ray absorption techniques are affected by the composition of the gas employed. Dissociation would therefore be a problem. Determinations of shock-wave positions by schlieren or shadowgraph as a measure of real-gas effects is a possibility. Spectroscopy also offers some hope.

High response pressure transducers are also available but again are subject to many doubts. Usually these transducers are subject to temperature or a temperature gradient and it becomes difficult to obtain a valid dynamic calibration at the high temperatures.

APPENDIX

VISCOSITY OF THE MIXTURE

The viscosity of a mixture has been formulated analytically by Bromley and Wilke.¹⁷ Following their development, one defines the mixture viscosity as follows:

$$\mu = \sum_{i=1}^n \frac{\mu_i}{1 + \frac{1}{X_i} \sum_{\substack{j=1 \\ j \neq i}}^n X_j \phi_{ij}} \quad , \quad (A-1)$$

where

$$X_i = \frac{N_i}{N} = \text{mole fraction} \quad (A-2)$$

and

$$\phi_{ij} = \frac{\left[1 + \left(\frac{\mu_i}{\mu_j} \right)^{1/2} \left(\frac{M_j}{M_i} \right)^{1/4} \right]^2}{\frac{4}{\sqrt{2}} \left[1 + \frac{M_i}{M_j} \right]^{1/2}}$$

For the present case, $n = 3$ with $M_1 = M_3$, and $\mu_1 = \mu_3$, with $M_2/M_1 = M_2/M_3 = 1/2$. With these simplifications,

$$\begin{aligned} \phi_{13} &= 1 \\ \phi_{31} &= 1 \\ \phi_{12} &= \frac{1}{4} \sqrt{\frac{2}{3}} \left[1 + \left(\frac{\mu_1}{\mu_2} \right)^{1/2} \left(\frac{1}{2} \right)^{1/4} \right]^2 \\ \phi_{21} &= \frac{1}{2\sqrt{3}} \left[1 + \left(\frac{\mu_2}{\mu_1} \right)^{1/2} (2)^{1/4} \right]^2 = 2 \frac{\mu_2}{\mu_1} \phi_{12} \\ \phi_{23} &= \phi_{21} \\ \phi_{32} &= \phi_{12} \end{aligned} \quad (A-3)$$

Hence, all the ϕ_{ij} can be written in terms of ϕ_{12} or a constant. Substituting for the ϕ_{ij} , one can find the viscosity of the given mixture in terms of the viscosity of the molecular oxygen or nitrogen, μ_1 , and the atomic oxygen, μ_2 .

$$\mu = \mu_1 \left[\frac{X_1 + X_3}{X_1 + X_3 + X_2 \phi_{12}} \right] + \mu_2 \left[\frac{X_2}{X_2 + (X_1 + X_3) \phi_{21}} \right] \quad (A-4)$$

In terms of mass concentrations, (A-4) becomes

$$\mu = \mu_1 \left[\frac{\kappa_1 + \kappa_3}{\kappa_1 + \kappa_3 + 2(1 - \kappa_1 - \kappa_3) \phi_{12}} \right] + \mu_2 \left[\frac{2(1 - \kappa_1 - \kappa_3)}{2(1 - \kappa_1 - \kappa_3) + (\kappa_1 + \kappa_3) \phi_{21}} \right] \quad (A-5)$$

And finally, in terms of the variables used in the text, where $\kappa = 1 - \kappa_2 = \kappa_1 + \kappa_3$, equation (A-4) is as follows:

$$\mu = \mu_1 \left[\frac{\kappa}{\kappa + 2(1 - \kappa) \phi_{12}} \right] + \mu_2 \left[\frac{2(1 - \kappa)}{2(1 - \kappa) + \kappa \phi_{21}} \right] \quad (A-6)$$

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Dorodnitsyn¹³ transformation. Whereas, without dissociation, this transformation effectively decouples the momentum and energy equations since $\rho \mu \approx$ constant, with dissociation, since $\rho \mu \neq$ constant, the equations are not completely decoupled, and the new plane is not completely incompressible. However, as other authors have pointed out,^{14,15} the effects due to these variations are small, and can be taken care of by an iterative solution of the momentum equation and energy equation.

If x , y , u , and v are the coordinates and velocities in the corresponding quasi-incompressible flow, then they are connected to the physical variables with the following relations.

$$\begin{aligned}
 a) \quad y &= \int_0^y \frac{\rho}{\rho_e} dy_0 \\
 b) \quad x &= x_0 \\
 c) \quad \frac{\partial C}{\partial x_0} &= \frac{\partial C}{\partial x} + \frac{\partial C}{\partial y} \frac{\partial y}{\partial x_0} \\
 d) \quad \frac{\partial C}{\partial y_0} &= \frac{\rho}{\rho_e} \frac{\partial C}{\partial y} \\
 e) \quad u &= u_0 \\
 f) \quad v_0 &= -\frac{\rho_e}{\rho} \left(-v + u \frac{\partial y}{\partial x_0} \right)
 \end{aligned} \tag{41}$$

Here ρ_e is the density along the edge of the boundary layer. The velocity relations are found by defining the stream function in the usual way:

$$\begin{aligned}
 \rho u_0 &= \rho_e \frac{\partial \psi}{\partial y_0} , \\
 \rho v_0 &= -\rho_e \frac{\partial \psi}{\partial x_0} ,
 \end{aligned} \tag{42}$$

and performing the given transformation of variables. That is:

$$\begin{aligned}
 \rho u_0 &= \rho_e \frac{\rho}{\rho_e} \frac{\partial \psi}{\partial y} \\
 \text{or, } u_0 &= \frac{\partial \psi}{\partial y} \\
 \text{Also, } \rho v_0 &= -\rho_e \left(\frac{\partial \psi}{\partial x} + \frac{\partial \psi}{\partial y} \frac{\partial y}{\partial x_0} \right)
 \end{aligned}$$