

CHEMICAL NONEQUILIBRIUM EFFECTS IN HYPERSONIC AERODYNAMICS*

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ABSTRACT

The influence of chemical nonequilibrium on hypersonic flows is considered in the following cases:

(a) Recombination and dissociation in the boundary layer. It is pointed out that, since in the region of maximum convective heating, the outer inviscid flow is in equilibrium, departures from equilibrium occur only close to the wall, and this makes possible the obtention of a simple analytical solution in which the effects of arbitrary reaction rates, body shapes, and flight regimes are clearly shown.

(b) Chemical reactions between the air constituents and any injected or vaporized material from the wall. In this case the assumption is made that the chemical reaction is so fast that it takes place in a very thin region. This simplifies the obtention of an analytical solution for finite reaction rate. A criterium for flame extinction is given.

INTRODUCTION

At the hypersonic Mach numbers encountered by vehicles reentering the atmosphere, the deceleration of the air gives rise to temperatures so high that dissociation and ionization reactions as well as chemical reactions between the air constituents and injected or vaporizing surface material occur. All these processes have a strong influence on the flow field, and, especially on heat transfer. Heat energy is transported by convection along streamlines, and in addition by thermal radiation, conduction, and mass diffusion of atoms carrying chemical energy.

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However, for those altitudes and flight regimes giving the greatest heat-transfer rates, the Reynolds numbers are sufficiently high that viscous, conduction, and diffusion effects are confined to shock waves and boundary layers with negligible thickness compared to any typical dimension of the flow field.

For the study of chemical effects one or the other of the following assumptions is usually made: (a) chemical equilibrium flow (infinite reaction rate), and (b) frozen flow (zero reaction rate). In this paper we shall be concerned with that part of the Aerothermochemistry¹ dealing with laminar boundary layer flows including the effects of chemical nonequilibrium.

We shall leave aside the study of nonequilibrium inviscid flows on the grounds that it has received considerable attention in the literature,² and in addition, as may be seen in Fig. 1 taken from Ref. 3, the outer flow is in equilibrium in the region of maximum convective heating.

Nonequilibrium shock waves have also been treated in the literature (see, for example, Refs. 4 and 5).

For the relatively cold boundary layer, thermal radiation from the air has not a predominant effect and therefore, it will not be considered. Radiation from the shock layer may represent a very important contribution to heat transfer at high speed (see Fig. 1 and Refs. 6, 7, and 8).

Ionization will not be considered, although it obviously is important at extreme speeds.⁹

In the region of most intense convective heating (see Fig. 2 taken from Ref. 3), the Reynolds numbers of interest are large enough so that the flow is in the continuum regime and, in addition, the concept of classical boundary layer applies (see Ref. 10). Ferri, Zakkay and Lu Ting¹¹ have studied the vorticity interaction regime, while Chung¹² considered the viscous layer regime.

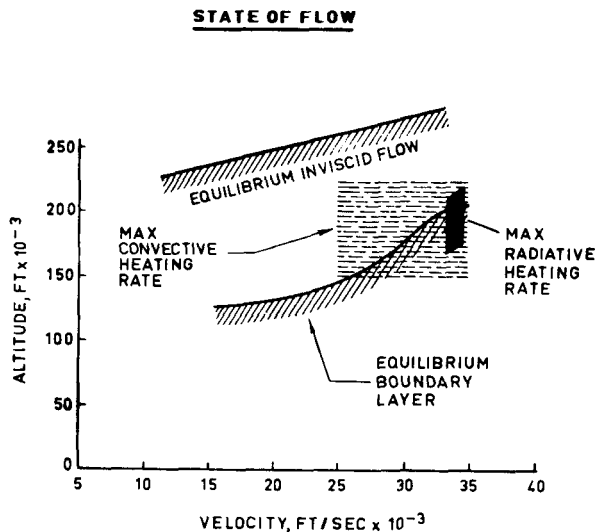


Fig. 1.

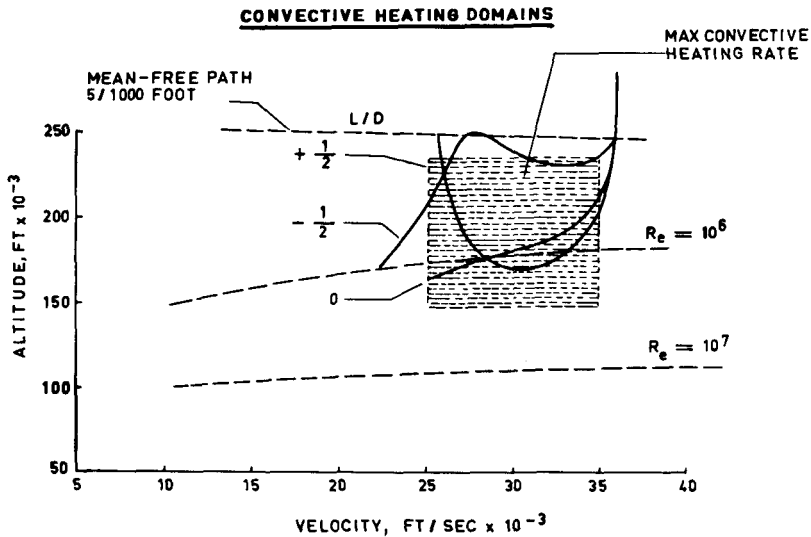


Fig. 2.

Reynolds numbers are, on the other hand, low enough to insure laminar boundary-layer flow over most of the body surface.

Two types of chemical reactions will be considered in this paper:

I. Dissociation and recombination reactions, either in homogeneous or heterogeneous phase.

II. Chemical reactions between the air constituents and any injected or vaporized material from the wall.

We shall make the assumption, when studying the first type of reactions, that they take place mostly in a region close to the wall where the convective effects may be neglected. Whenever the outer flow is in chemical equilibrium, the flow in the outer part of the boundary layer will also be in equilibrium. Actually, as pointed out by Lighthill,¹³ the time scale for convection in the outer part of the boundary layer, or time required for flow past the body, equals the time scale for diffusion across the boundary layer; and whenever this time scale is large compared with the time scale for dissociation or recombination, equilibrium will prevail. But, as it has been shown by Clarke,¹⁴ the characteristic chemical time increases as temperature decreases. Therefore we may expect that, for the highly cooled wall, when the altitude or flight speed increase, departures from equilibrium will at first occur close to the wall and they will later extend to the outer part of the boundary layer, and finally to the outer inviscid flow. This is in agreement with the flow behavior presented in Fig. 1.

Fay and Riddel,¹⁵ Chung,¹⁶ and Chung and Anderson,¹⁷ among others, have already considered the effect of finite recombination rate on heat transfer. Our emphasis will be laid on obtaining simple analytical solutions, clearly showing the influence of arbitrary chemical kinetics, body shape, and flight regime on heat-transfer rate.

For the second type of chemical reactions we shall assume, following the usual procedure in the study of diffusion flames,¹⁸⁻²² the chemical reactions to be so fast that they take place only in a very thin zone. We shall neglect in this region convection effects compared with conduction, diffusion and chemical effects; then, the equations, giving the temperature and concentration distributions in the reaction zone are solved and a parameter is obtained giving the criterium for flame extinction.

NOMENCLATURE

- c_p = Specific heat at constant pressure
- c_i = Mass fraction of species i
- D = Binary diffusion coefficient
- f = Dimensionless stream function, defined in text
- $g = h_s/h_{se}, g_T = h_f/h_{fe}$
- h = Specific enthalpy, including chemical enthalpy
- h_i^0 = Heat of formation of species i
- $h_f = \sum c_i \int c_{p,i} dT + u^2/2$, "frozen" total specific enthalpy
- $h_s = \sum c_i h_i + u^2/2$, total specific enthalpy
- h_T = Thermal specific enthalpy
- $Le = Pr/Sc$, Lewis number
- M = Mean molecular weight
- M_i = Molecular weight of species i
- M_∞ = Freestream Mach number
- p = Pressure
- Pr = Prandtl number
- qs = Heat flux to the wall
- r = Cross-sectional radius of body of revolution
- R = Universal gas constant
- R_0 = Nose radius
- Re = Reynolds number
- $Sc = \mu/\rho D$, Schmidt number
- t_c = Chemical time, defined by Eq. (31)
- t_m = Mechanical time, defined in text
- T = Absolute temperature
- u, v = Components of velocity parallel and normal to body surface
- w_i = Mass production rate of species i
- x, y = Boundary layer coordinates along and normal to body surface
- z = Defined by Eq. (15)
- α = Defined by Eq. (10)
- β = Pressure gradient parameter, defined in text
- ∂ = Catalytic efficiency of the wall
- η = Dimensionless distance from wall, defined in text
- θ = Angle between normal to body surface and flight direction
- μ = Coefficient of viscosity
- ν = Stoichiometric ratio species 1 to species 2

- ξ = Dimensionless coordinate along body surface, defined in text
 ρ = Density
 φ = Defined by Eq. (15)

Subscripts

- e = Denotes conditions at the outer edge of the boundary layer
 E = Chemical equilibrium conditions
 f = Frozen conditions
 i = Corresponding to the i th species
 r = Conditions at the flame for the infinitely fast reaction rate
 w = Conditions at the wall
 z = Derivatives with respect to z

Primes denote derivatives with respect to η

LAMINAR BOUNDARY LAYER EQUATIONS

BASIC EQUATIONS

We shall begin by writing the laminar boundary-layer equations for the steady two-dimensional or axially symmetric flow of a reacting gas mixture. For the details of the arguments and basic assumptions leading to these equations see Refs. 23, 15, and 19.

When using a boundary-layer coordinate system these equations take the following form:

CONTINUITY EQUATION

$$\frac{\partial}{\partial x} (\rho u r^k) + \frac{\partial}{\partial y} (\rho v r^k) = 0 \quad (1)$$

where $k = 0$ for two-dimensional flow and $k = 1$ for axially symmetrical flow.

MOMENTUM EQUATION

$$\rho u \frac{\partial u}{\partial x} + \rho v \frac{\partial u}{\partial y} = - \frac{dp_e}{dx} + \frac{\partial}{\partial y} \left(\mu \frac{\partial u}{\partial y} \right) \quad (2)$$

ENERGY EQUATION

$$\rho u \frac{\partial h_s}{\partial x} + \rho v \frac{\partial h_s}{\partial y} = \frac{\partial}{\partial y} \left(\frac{\mu}{Pr} \frac{\partial h_s}{\partial y} \right) + \frac{\partial}{\partial y} \left(\mu \left(1 - \frac{1}{Pr} \right) \frac{\partial u^2}{\partial y} \right) + \frac{\partial}{\partial y} \left[\rho D \left(1 - \frac{1}{Le} \right) \sum h_i \frac{\partial c_i}{\partial y} \right] \quad (3)$$

CONTINUITY EQUATION FOR EACH OF THE SPECIES

$$\rho u \frac{\partial c_i}{\partial x} + \rho v \frac{\partial c_i}{\partial y} - \frac{\partial}{\partial y} \left[\rho D \frac{\partial c_i}{\partial y} \right] = w_i \quad (4)$$

EQUATION OF STATE

$$\frac{p}{\rho} = \frac{R}{M} T \quad \text{where} \quad M^{-1} = \sum c_i M_i^{-1} \quad (5)$$

For the evaluation of the diffusion velocities the gas has been considered as an effective binary mixture so that Fick's law applies. Thermal diffusion has been neglected. The diffusion stress tensor has also been neglected.

The total enthalpy, that includes both the thermal and chemical enthalpies, is defined by the relation $h_s = u^2/2 + \sum h_i c_i$, where

$$h_i = \int_0^T c_{p,i} dT + h_i^0$$

The transport coefficients and the mass rate of formation of the i th species w_i are functions of the local thermodynamic variables ρ , T and c_i .

Equations (1) to (5) together with the appropriate boundary conditions constitute the set of equations whose solution is required.

LOCAL SIMILARITY FORM AND BOUNDARY CONDITIONS

To facilitate the approximate solution of the boundary-layer equations we shall write them in the so-called "local similarity" form by introducing the change of variables, proposed by Lees,²³ in the form used in Ref. 15, that combines the Levy and Mangler and the Howarth-Dorodnitsyn transformations.

Let

$$\eta = \frac{u_e r^k}{\sqrt{2\xi}} \int_0^y \rho dy$$

and

$$\xi = \int_0^x \rho_w \mu_w u_e r^{2k} dx$$

With the introduction of the stream function ψ such that:

$$\rho u r^k = \frac{\partial \psi}{\partial y} \quad \text{and} \quad \rho v r^k = - \frac{\partial \psi}{\partial x}$$

the continuity equation is automatically satisfied.

Letting $\psi = \sqrt{2\xi} f(\eta, \xi)$, we may write $u/u_e = f'(\eta, \xi)$ and the boundary-layer equations take the following form:

MOMENTUM EQUATION

$$(Cf'')' + ff'' + \frac{2\xi}{u_e} \frac{du_e}{d\xi} \left[\frac{\rho_e}{\rho} - (f')^2 \right] = \text{t.i.d.} \quad (6)$$

CONTINUITY EQUATION FOR EACH OF THE SPECIES

$$\left(\frac{C}{S_c} c_i' \right)' + f c_i' + \frac{2\xi}{\rho_w \mu_w u_e^2 r^{2k}} \frac{w_i}{\rho} = \text{t.i.d.} \quad (7)$$

ENERGY EQUATION

$$\left(\frac{C}{Pr} g'\right)' + fg' + \frac{u_e^2}{2h_{se}} \left[2C \left(1 - \frac{1}{Pr}\right) ff''\right]' + \left[\frac{C}{Pr} (Le - 1) \Sigma \frac{h_i c_i'}{h_{se}}\right]' \quad (8)$$

= t.i.d.

where the primes denote differentiation with respect to η . We have written $h_s/h_{se} = g(\eta, \xi)$ and $C = \rho\mu/\rho_w\mu_w$. The t.i.d.'s in the right-hand side of the equations mean terms involving derivatives of f , g , or c_i with respect to ξ .

If we neglect the differences in thermal enthalpy between components, compared to the heats of formation, the term $\Sigma h_i c_i'$ of the energy equation may be written

$$\Sigma h_i c_i' = \Sigma h_i^0 c_i'$$

If we define $g_T = h_f/h_{fe}$, where

$$h_f = h_T + \frac{u^2}{2} = h_s - \Sigma c_i h_i^0$$

and by multiplying Eq. (7) by h_i^0/h_{fe} , summing over all species, and subtracting the result from Eq. (8) multiplied by h_{se}/h_{fe} , we obtain¹⁹

$$\left(\frac{C}{Pr} g_T'\right)' + fg_T' + \frac{u_e^2}{2h_{fe}} \left[2C \left(1 - \frac{1}{Pr}\right) ff''\right]' - \frac{2\xi}{\rho_w\mu_w u_e^2 r^{2k}} \frac{\Sigma w_i h_i}{\rho h_{fe}} = \text{t.i.d.} \quad (9)$$

as an alternative form of the energy equation.

The boundary conditions are as follows:

$$f(0, \xi) = f_w = -\frac{1}{\sqrt{2\xi}} \int_0^x (\rho v)_w r^k dx, \quad f'(0, \xi) = 0$$

$$f'(\eta, \xi) \rightarrow 1 \quad \text{as} \quad \eta \longrightarrow \infty$$

$$g(0, \xi) = g_w \quad \text{and} \quad g(\eta, \xi) \longrightarrow 1 \quad \text{as} \quad \eta \longrightarrow \infty$$

$$g_T(0, \xi) = g_{Tw} \quad \text{and} \quad g_T(\eta, \xi) \longrightarrow 1 \quad \text{as} \quad \eta \longrightarrow \infty$$

We shall suppose the temperature at the wall to be a known function of ξ . Then if we neglect as above the differences in thermal enthalpy of the components compared to the heats of formation, that is true at elevated temperatures where the c_{p_i} 's are very nearly all the same and constant,²⁴ g_{Tw} shall be a known function of ξ , while g_w depends strongly on the values of c_{iw} .

Boundary conditions on the mass fractions at the wall depend on whether there is mass injection or not at the wall, and on the details of the surface reaction.

We may generally write this condition in the form

$$c_i'(0) = F(c_i(0), \xi)$$

We shall assume the outer flow to be in thermodynamic equilibrium and write

$$c_i(\eta, \xi) \longrightarrow c_{ie}(\xi) \quad \text{as} \quad \eta \longrightarrow \infty$$

LOCAL SIMILARITY APPROXIMATION

For the simple case of stagnation point flow a similarity solution of the above written system of equations exists such that f , c_i , and g are functions only of the similarity variable η . For finite recombination rate this appears to be the only case in which a similarity variable can be found. The functions f , c_i/c_{ie} , and g will depend on the variable ξ due to the variation along the body surface of the parameters

$$\beta = \frac{2\xi}{u_e} \frac{du_e}{d\xi}, \quad \frac{u_e^2}{2h_{se}}, \quad \frac{h_i^0}{h_{se}}, \quad t_m = \frac{2\xi}{\rho_w \mu_w u_e^{2\gamma-2k}}$$

and of the boundary conditions.

For the flat plate and cone, the conditions at the outer edge of the boundary layer are constant along the surface, and therefore, exact similarity solutions can be found when the flow in the boundary layer is either frozen or in chemical equilibrium.

At hypersonic flight speeds, for highly cooled wall, $\rho_w/\rho_e \gg 1$ and, as suggested by Lees,²² the pressure gradient term in Eq. (6) should be small; therefore, the neglecting of this term should have a fairly small effect on the velocity profile and an even smaller effect on the concentration and enthalpy profiles.

For Lewis number close to one or for small h_i^0/h_{se} , the last term in the left-hand side of the energy Eq. (8) may be neglected when compared to the other terms of the equation.

The third term in Eqs. (8) and (9) is numerically small for blunt-nosed bodies at high speeds and may also be neglected.

If all the above mentioned terms are dropped, a similarity solution may be obtained, as was done by Lees,²³ giving heat transfer rates at the wall in good quantitative agreement with experiments and more exact solutions, for both frozen and chemical equilibrium flow.

In order to approximately solve the boundary-layer equations for finite recombination rate, the so called "local similarity approximation" will be used, as it seems a logical extension of Lees' method of solution of the frozen and chemical equilibrium cases.

In this approximation, suggested by Lees and used by Kemp, Rose, and Detra²⁵ for the study of the chemical equilibrium case, the above mentioned parameters β , u_e^2/h_{se} , etc., and the boundary conditions are supposed to be slowly varying functions of ξ . Then the terms involving derivatives with respect to ξ may be neglected compared to the other terms in Eqs. (6), (7), (8), and (9). However, the numerically small terms, responsible for the lack of similarity in the frozen and chemical equilibrium cases, are retained.

In order to assess the validity of this approximation, the terms neglected when obtaining the local similarity solution may be approximately evaluated

with the use of this solution, and then compared with the other terms of the equations.

As shown by Kemp, Rose, and Detra, the local similarity approximation works quite well, at least for chemical equilibrium flow, except at regions where rapid expansions take place.

The assumption is made here that the mass-production terms do not have a large influence on the local similarity approximation. This assumption is supported by the fact that near the stagnation point, where the mass production term may be very important, exact similarity exists, and, at regions far from the stagnation point (large ξ), the mass production term tends to be numerically small.

In solving Eqs. (6) to (9) with the terms involving derivatives with respect to ξ neglected, we shall use a constant value for C . By choosing $C = C_0 = (\rho_w \mu_w / \rho_e \mu_e)^{0.8}$ we shall obtain Fay and Riddell's heat-transfer rates for the air boundary layer at the stagnation point. The use of the stagnation point value of C is supported by the fact that Kemp, Rose, and Detra, by numerical integration of Eqs. (6) and (8) in the limiting case of chemical equilibrium, found that, so far as the calculation of $g_w'/(1 - g_w)$ is concerned, the dissipation term which appears in Eq. (8) could be neglected, provided the stagnation point $\rho\mu$ ratio is used all along the surface.

Following Moore's suggestion²⁶ we shall approximate the pressure gradient term by $\alpha\beta ff''$ on the grounds that ff'' and $\rho_e/\rho - f'^2$ have certain similarities, and choosing α so that the difference of the pressure gradient term and its approximation have a vanishing average across the boundary layer; that is,

$$\alpha \int_0^\infty ff'' d\eta = \int_0^\infty (\rho_e/\rho - f'^2) d\eta$$

Moore found that

$$\alpha \simeq 1 + 2.6 \frac{T_w}{T_e} \quad (10)$$

We shall in addition assume the Prandtl and Lewis numbers to be constants.

When all these approximations are introduced into Eqs. (6) to (9), these take the following form:

$$f''' + \frac{1 + \alpha\beta}{C_0} ff'' = 0 \quad (11)$$

$$c_i'' + \frac{S_c}{C_0} fc_i' = - \frac{S_c}{C_0} t_m \frac{w_i}{\rho} \quad (12)$$

$$g'' + \frac{P_r}{C_0} fg' + (L_e - 1) \Sigma \frac{h_i^0 c_i''}{h_{se}} = 0 \quad (13)$$

$$g_T'' + \frac{P_r}{C_0} fg_T' = \frac{P_r}{C_0} t_m \frac{\Sigma w_i h_i^0}{\rho h_{fe}} \quad (14)$$

These equations may be written in a more convenient form by utilizing the following change of variables:

$$f = \sqrt{\frac{C_0}{1 + \alpha\beta}} \varphi(z) \quad \text{where} \quad z = \sqrt{\frac{1 + \alpha\beta}{C_0}} \eta \quad (15)$$

Then Eqs. (11) to (14) may be written

$$\varphi_{zzz} + \varphi\varphi_{zz} = 0 \quad (16)$$

$$c_{izz} + \frac{S_c}{1 + \alpha\beta} \varphi c_{iz} = \frac{S_c}{1 + \alpha\beta} t_m \frac{w_i}{\rho} \quad (17)$$

$$g_{zz} + \frac{P_r}{1 + \alpha\beta} \varphi g_z + (L_e - 1) \Sigma \frac{h_i^0 c_{izz}}{h_{se}} = 0 \quad (18)$$

$$g_{Tzz} + \frac{P_r}{1 + \alpha\beta} \varphi g_{Tz} = \frac{P_r}{1 + \alpha\beta} t_m \frac{\Sigma w_i h_i^0}{h_{fe}} \quad (19)$$

Equations (16), (17), and (18) or (19) must be solved with the following boundary conditions.

$$\text{At } z = 0, \varphi = \varphi_w, \varphi_z = 0, T = T_w, c_{iz} = F(c_i, T_w, p, \varphi_w)$$

$$\text{and for } z \rightarrow \infty, \varphi_z = g = g_T = 1 \quad \text{and} \quad c_i = c_{ie}$$

where φ_w depends on the injection rate at the wall and the function F depends on the details of the chemical reactions at the wall.

BOUNDARY LAYER WITH CHEMICAL REACTION, WITHOUT INJECTION

SOLUTION OF THE EQUATIONS

Equation (16) is the well-known Blasius equation of the boundary layer flow past a semi-infinite plane.

The solution of this equation may be written in power series form as follows:

$$\varphi(z) = a \frac{z^2}{2!} - a^2 \frac{z^5}{5!} + 11a^3 \frac{z^8}{8!} \dots \quad (20)$$

It was suggested by Meksyn²⁷ that Eqs. (16) to (19) can be solved by inserting the expansion (20) in (16)–(19) instead of φ only, leaving φ_{zzz} and φ_{zz} unchanged. The assumption, suggested by Fage and Falkner and used by Lighthill,²⁸ that, so far as the evaluation of convection effects is concerned, the velocity in the boundary layer increases linearly with the distance to the surface is equivalent to retaining only the first term in the power series expansion (20).

Equations (16), (17), and (19) can be expressed in the following form:

$$\varphi_z(z) = \varphi_{zz}(0) \int_0^z e^{-[\varphi_{zz}(0)z^{3/6} - \dots]} dz \quad (21)$$

$$c_i(z) - c_i(0) = c_{iz}(0) \int_0^z e^{-[S_c/(1+\alpha\beta)] [\varphi_{zz}(0)z^{3/6} + \dots]} e^{-[S_c/(1+\alpha\beta)] t_m \int_0^z w_i/(p c_{iz}) dz} dz \quad (22)$$

$$g_T(z) - g_T(0) = g_{Tz}(0) \int_0^z e^{-[P_r/(1+\alpha\beta)] [\varphi_{zz}(0)z^{3/6} + \dots]} e^{-[P_r/(1+\alpha\beta)] t_m \Sigma (h_i^0/h_{fe}) \int_0^z w_i/(p g_{Tz}) dz} dz \quad (23)$$

Equation (21) gives, when making $z \rightarrow \infty$, $\varphi_{zz}(0) = 0.47$.

In the cases under consideration, w_i/ρ is a rapidly decreasing function of z . Assuming that the thickness of the zone, that w_i/ρ needs to "fade out," is much smaller than the thermal boundary layer thickness, we can write Eqs. (22) and (23) in the following approximate form:

$$c_i(z) - c_i(0) = c_{iz}(0) \int_0^z e^{-[S_c/(1+\alpha\beta)] [\varphi_{zz}(0)z^{3/6} + \dots]} \left(1 - \frac{S_c}{1+\alpha\beta} t_m \int_0^z \frac{w_i}{\rho} dz \right) dz \quad (22a)$$

$$g_T(z) - g_T(0) = g_{Tz}(0) \int_0^z e^{-[P_r/(1+\alpha\beta)] [\varphi_{zz}(0)z^{3/6} + \dots]} \left(1 + \frac{P_r}{1+\alpha\beta} t_m \Sigma \frac{h_i^0}{h_{fe}} \int_0^z \frac{w_i}{\rho} dz \right) dz \quad (23a)$$

For the evaluation of the second of the exponentials in Eqs. (22) and (23), advantage has been taken of the fact that, in the region near the wall where they differ from their limiting values, convection effects may be neglected and the following relations hold:

$$c_{iz} = c_{iz}(0) - \frac{S_c}{1+\alpha\beta} t_m \int_0^z \frac{w_i}{\rho} dz$$

$$g_{Tz} = g_{Tz}(0) + \frac{P_r}{1+\alpha\beta} t_m \Sigma \frac{h_i^0}{h_{fe}} \int_0^z \frac{w_i}{\rho} dz$$

The conditions at the wall which appear in Eqs. (22a) and (23a) can be easily computed as follows:

1. If terms of the order of z^5 in the power expansion of φ , are disregarded and conditions at the outer edge of the boundary layer are taken into account, we have:

$$\frac{1}{\varphi_{zz}(0)} = \int_0^\infty e^{-\varphi_{zz}(0)z^{3/6}} dz \quad (24)$$

2. The chemical "source" term may be written in the form:

$$\frac{w_i}{\rho} = \left(\frac{w_i}{\rho}\right)_w e^{-(\Lambda_{i1}z + \Lambda_{i2}z^2 + \dots)} \quad (25)$$

where

$$\Lambda_{i1} = - \left\{ \frac{(w_i/\rho)_z}{w_i/\rho} \right\}_w, \text{ etc.}$$

Under the present status of knowledge of chemical reaction rates, a sufficiently good approximation is obtained by keeping only the first term in the power series of Eq. (25) and disregarding, in what follows, terms of the order of Λ_{i1}^{-2} . Accordingly

$$c_{ie} - c_i(0) = \frac{1}{\varphi_{zz}(0) \left(\frac{S_c}{1 + \alpha\beta}\right)^{1/3}} \left[c_{iz}(0) - \frac{S_c}{1 + \alpha\beta} t_m \left(\frac{w_i}{\rho}\right)_w \frac{1}{\Lambda_{i1}} \right] \quad (26)$$

$$1 - g_T(0) = \frac{1}{\varphi_{zz}(0) \left(\frac{P_r}{1 + \alpha\beta}\right)^{1/3}} \left[g_{Tz}(0) + \frac{P_r}{1 + \alpha\beta} t_m \Sigma \frac{h_i^0}{h_{fe}} \left[\frac{w_i}{\rho}\right]_w \frac{1}{\Lambda_{i1}} \right] \quad (27)$$

Equation (26) may be used for the determination of the concentrations at the wall. The influence of the heterogeneous reaction appears in this equation through the first term in the brackets while the homogeneous reaction influence appears in the last one.

Making use of the values of $c_i(0)$ computed from Eq. (26), it is possible to find the heat transfer to the wall through the following equation:

$$q_w = 0.47P_r^{-2/3} \sqrt[6]{1 + \alpha\beta} \left(\frac{\rho_e\mu_e}{\rho_w\mu_w}\right)^{0.4} \frac{\rho_w\mu_w\mu_e\tau^k}{\sqrt{2\xi}} \left[h_{se} - h_w + [L_e^{2/3} - 1] \Sigma h_i^0 (c_{ie} - c_i(0)) \right] \quad (28)$$

As we have used Moore's approximation for the pressure gradient term, the factor $\sqrt[6]{1 + \alpha\beta}$ appears in Eq. (28) instead of the value $1 + 0.096\sqrt{\beta}$ given in Ref. 25. Both are approximately equal, for the range of β of interest and for low T_w/T_e ; however, the former value gives better results for T_w/T_e close to one.

Prandtl number influence on the heat transfer is here $P_r^{-2/3}$ instead of $P_r^{-0.6}$ obtained in Ref. 15 when correlating numerical results.

Lewis number influence is given by the factor

$$1 + \left[L_e^{2/3} - 1 \right] \sum_i \frac{h_i^0 [c_{ie} - c_i(0)]}{h_{se} - h_w}$$

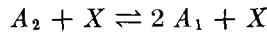
It is of interest to point out that the Lewis number exponent is here 0.67 instead of the values 0.63 (for frozen flow) or 0.52 (for chemical equilibrium) obtained by Fay and Riddell by correlating their numerical results.

Assuming the Prandtl number influence to be given by $P_r^{-0.6}$, Lewis number exponent in Eq. (28) would be 0.6.

In addition, the Lewis number has an indirect influence on the values of $c_i(0)$ and therefore on h_w .

REACTION RATES

As an application of the above method of solution we shall consider the flow of a dissociating and recombining gas. We shall assume it to consist of diatomic molecules A_2 . The equation describing the homogeneous reaction is:



We shall assume that the reaction rate constants are those corresponding to the recombination-dissociation reactions for oxygen.†

The rate of atomic oxygen mass production is:

$$\frac{w_1}{M} = k_d \left(\frac{p}{RT} \right)^2 \frac{1 - c_1}{2} - k_r \left(\frac{p}{RT} \right)^3 \frac{2c_1^2}{1 + c_1} \quad (29)$$

Considerable uncertainty exists about the values of the rate constants. We shall use the values quoted by Demetriades and Farber.²⁹

$$k_r = 3.10^{16} \left(\frac{300}{T} \right)^{1.5} \text{ cm}^6 \text{ mol}^{-2} \text{ sec}^{-1}$$

$$\frac{k_d}{k_r} = 24.5e^{59,000/T} \text{ mol cm}^{-3}$$

By taking relation Eq. (29) into Eq. (12) the following equation is obtained:

$$c_{1zz} + \frac{S_c}{1 + \alpha\beta} \varphi c_{1z} = \frac{S_c}{1 + \alpha\beta} \frac{t_m}{t_e} (c_1 - c_{1E}) \quad (30)$$

† Although ozone is present as an intermediate species in the oxygen production, and the chemical kinetics is not so simple as the one described in the above equation, the ozone mass fraction is, however, negligible. The reason lies in the fact that ozone is in chemical equilibrium except at a very thin layer close to the wall, and the equilibrium concentration of ozone is very small.

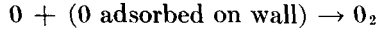
where

$$t_c = \frac{(1 + c_1)(1 - c_{1E}^2)}{c_1 + c_{1E}} \left(\frac{RT}{p} \right)^2 \frac{1}{2k_r} \quad (31)$$

is a characteristic chemical time, that due to the factor $(1 - c_{1E}^2)$, decreases very rapidly when the temperature increases. Then, as pointed out in the Introduction, the ratio t_m/t_c , appearing in Eq. (30), increases with increasing separation from the wall, and c_1 will approach its equilibrium value. This will not be the case for that region close to the wall where the mechanical to chemical time ratio may be small, and departures from equilibrium will occur.

For the heterogeneous reaction rate for oxygen, we shall use the values given in Ref. 29.

The two following mechanisms for surface recombination are proposed:



The total mass rate of production m_2 of oxygen per unit surface is given by

$$\frac{m_2}{M_2} = k_1 \rho^2 \frac{c_1^2}{M_1^2} T^{0.5} + k_2 \partial \rho \frac{c_1}{M_1} T^{0.5}$$

where $k_1 = 15 \times 10^5$ and $k_2 = 9 \times 10^2$ (cgs units).

The factor ∂ appearing in the last term, which measures the efficiency of the second mechanism, ranges from values as low as 10^{-5} , for "poisoned" glass, to values close to one for noble metals and metallic oxides.

The poisoning of the wall decreases the heat transfer to the body; however, it does not have any effect on the first mechanism, which may be predominant for low values of ∂ .

The boundary condition for c_1 at the wall will be:

$$\begin{aligned} c_{1z}(0) \sqrt{1 + \alpha\beta} \left(\frac{\rho_e \mu_e}{\rho_w \mu_w} \right)^{0.4} \frac{\rho_w \mu_w u_e r^k}{\sqrt{2\xi}} \\ = Sc M_2 \left(\frac{p}{RT_w} \right)^2 T_w^{0.5} \frac{2c_1(0)}{[1 + c_1(0)]^2} \cdot \left\{ \frac{k_2 RT_w}{p} \partial \right. \\ \left. + \left(k_1 + \frac{k_2 RT_w}{p} \partial \right) c_1(0) \right\} \end{aligned} \quad (32)$$

DISCUSSION

As shown in relation (28), heat-transfer rates depend on mass fractions at the wall. These may be deduced from Eq. (26) once the parameters α , β , and t_m are found from the inviscid flow. For their evaluation the procedure outlined in Ref. 23 may be used.

The pressure gradient parameter β will be a function of the surface inclination with respect to free stream, while the mechanical time is found to be

$$t_m = \beta R_0 / \left(\frac{du_e}{d\theta} \right) \theta = 0$$

Figures 3 to 5 show the atom mass fraction distribution along the wall (in terms of u_e) for different wall temperatures, at two altitudes and flight Mach numbers.

Relation (26) may be used to obtain the atom mass fraction c_1 at the wall:

$$c_{1e} - c_1 = A \frac{c_1}{1 + c_1} + B \frac{c_1^2}{1 + c_1} \left[1 - \frac{A}{Le^{1/3}} \left\{ \frac{h_1^0}{h_{se}} + \frac{c_p T_w}{3.5 h_{se}} \frac{2 + c_1}{c_1(1 + c_1)} \right\} \frac{c_1}{1 + c_1} \right]^{-1} \quad (33)$$

where

$$A = 2k_2 \vartheta \frac{S_c}{\sqrt{1 + \alpha\beta}} \left(\frac{\rho_w \mu_w}{\rho_e \mu_e} \right)^{0.4} \frac{\sqrt{2\xi}}{\rho_w \mu_w u_e r^k} \frac{p M_2}{R T_w^{0.5}}$$

$$B = 2.6 k_r t_m \left(\frac{P_r}{1 + \alpha\beta} \right)^{1/3} L_e^{-2/3} \frac{c_p T_w}{h_{se}} \left(\frac{p}{R T_w} \right)^2$$

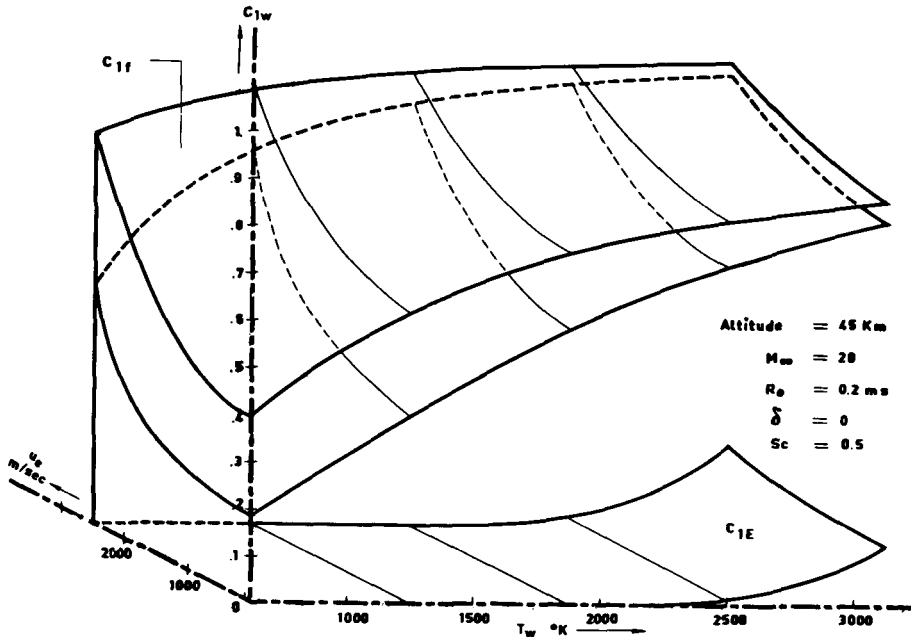


Fig. 3.

In writing this relation, the triple collision mechanism of wall recombination and the homogeneous dissociation reaction have not been taken into account.

The homogeneous reaction rate is represented by the parameter B , while A represents the catalytic activity of the wall. Parameter B is similar to the recombination rate parameter used by Fay and Riddell.¹⁵

When B is put equal to zero, results very similar to those given by Goulard³⁰ for the frozen stagnation flow are obtained.

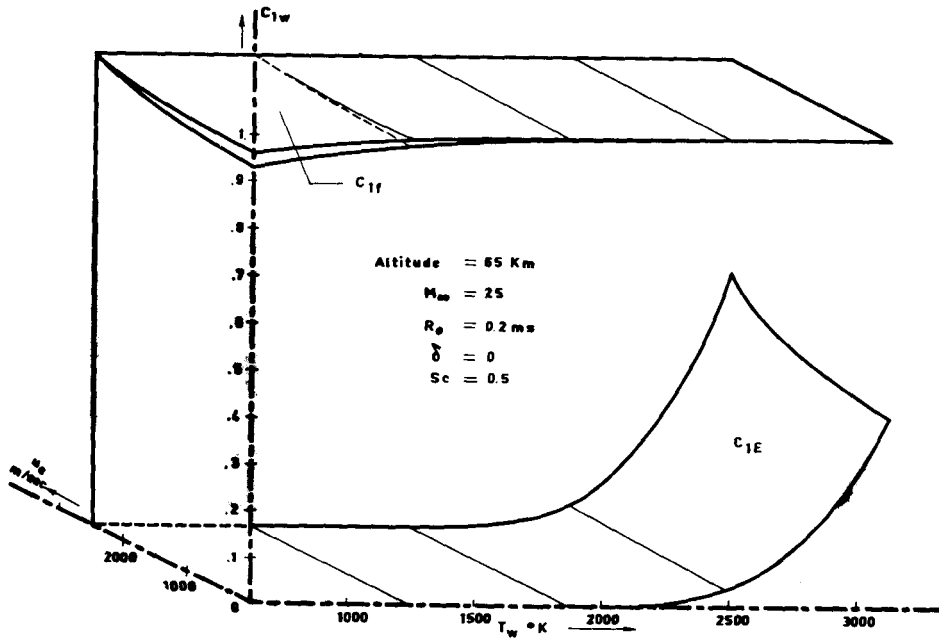


Fig. 4.

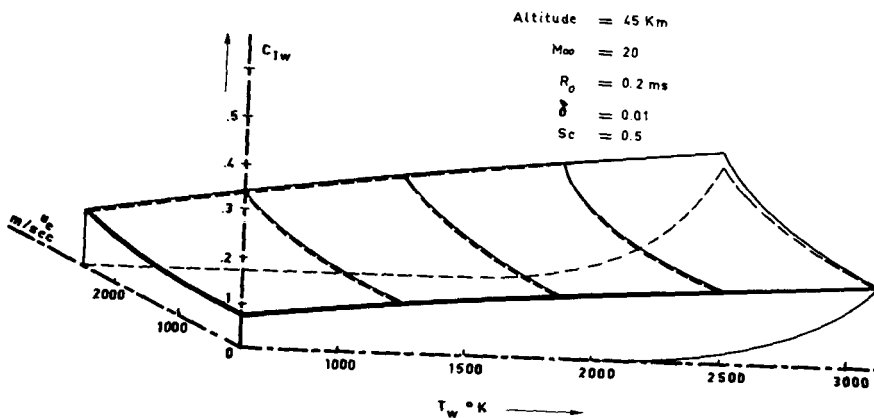


Fig. 5.

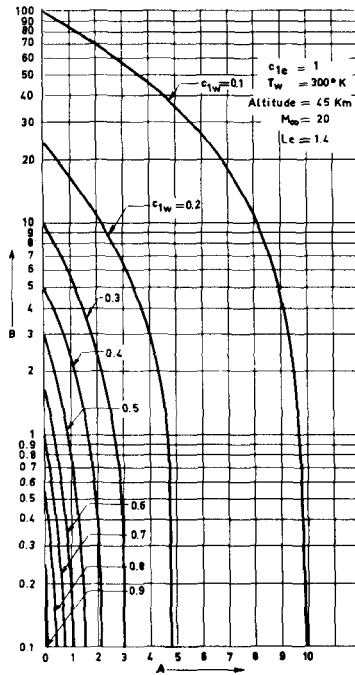


Fig. 6.

For large values of A the atom mass fraction at the wall approaches zero. This same limiting value is obtained for low wall temperatures when the gas phase recombination rate parameter B is large (chemical equilibrium flow).

Whenever the atom mass fraction at the outer edge of the boundary layer is small the same occurs at the wall.

Relation (33) has been plotted in Fig. 6 for $c_{1e} = 1$. A 10^2 fold increase in A is needed to change $c_1(0)$ from 0.9 to 0.1, while the increase in B necessary to obtain the same result is larger, as was pointed out by Chung.¹⁶

The c_1/c_{1e} ratio, when $L_1 = 1$, coincides with the ratio, $(q_{wE} - q_w)/(q_{wE} - q_{wf})$, of the heat-transfer reduction due to nonequilibrium effects to that obtained in the limiting case of frozen flow and noncatalytic wall. This relation has been plotted in Fig. 7 in terms of B , for the noncatalytic wall ($A = 0$) and different c_{ie} values.

BOUNDARY LAYER WITH CHEMICAL REACTION AND MASS ADDITION

STATEMENT OF THE PROBLEM AND INFINITE REACTION RATE SOLUTION

Due to the "blocking effect" of mass addition, large decreases in heat transfer will be produced when some gas is injected in the boundary layer or when the processes of vaporization or sublimation occur. Since chemical reactions may take place between injected or ablated material and air constituents (usually

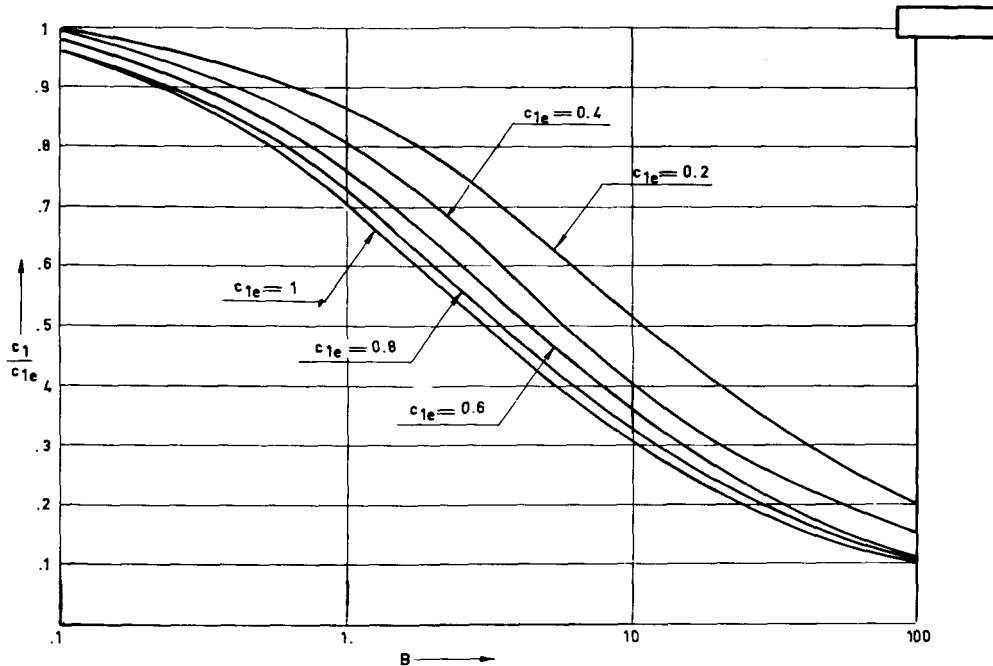


Fig. 7.

oxygen), the heat released by these chemical reactions will modify heat transfer rates to the body surface.

For Lewis number equal to one and whenever the chemical reactions go to completion, heat transfer rates may be obtained without a knowledge of the chemical kinetics of the reactions.^{19,21} If, following Burke and Schumann,¹⁸ the assumption is made that the reaction rate is infinite, flame position, temperature, and concentration distributions may also be evaluated.^{20,22}

In the following we shall study the structure of the reaction zone and the degree of completeness of the chemical reactions by considering finite reaction rate effects.

We shall assume species 2 is injected in the boundary layer, it reacts with species 1 of the air, and species 3 is produced. Inert gases will constitute species 4. We shall use constant values for $\rho\mu$, and $L_c = 1$.

In addition, the injection rate will be supposed to be small so that Eqs. (11) to (14) or (16) to (19) apply. In these equations the w_1 's are as follows:

$$\nu w_2 = w_1, \quad w_3 = -(1 + \nu)w_2, \quad w_4 = 0$$

and

$$w_2 = -K\rho^2 c_1 c_2 e^{-E/RT}$$

where ν is the stoichiometric ratio of species 2 to 1.

An Arrhenius type reaction with second order chemical kinetics has been assumed.

Boundary conditions will be (Fig. 8):

$$c_2 = c_3 = 0, \quad c_1 = c_{1e}, \quad c_4 = c_{4e} \quad \text{as } \eta \rightarrow \infty$$

and

$$(\rho v c_i)_w = \frac{1}{S_c} c_i'(0) \frac{\rho_e \mu_e u_e t^k}{\sqrt{2\xi}}, \quad i = 1, 3, \text{ and } 4$$

when ablation occurs, f_w is determined by a heat balance at the wall.

By assuming f_w and g_w to be known, Eqs. (11) and (13) may be solved by using the methods proposed in Ref. 27. The detailed calculations will be published elsewhere. For low f_w we may in particular write:

$$g'(0) = 0.47 P_r^{1/3} \sqrt[6]{1 + \alpha\beta} (1 - g_w) \cdot \Gamma \quad (34)$$

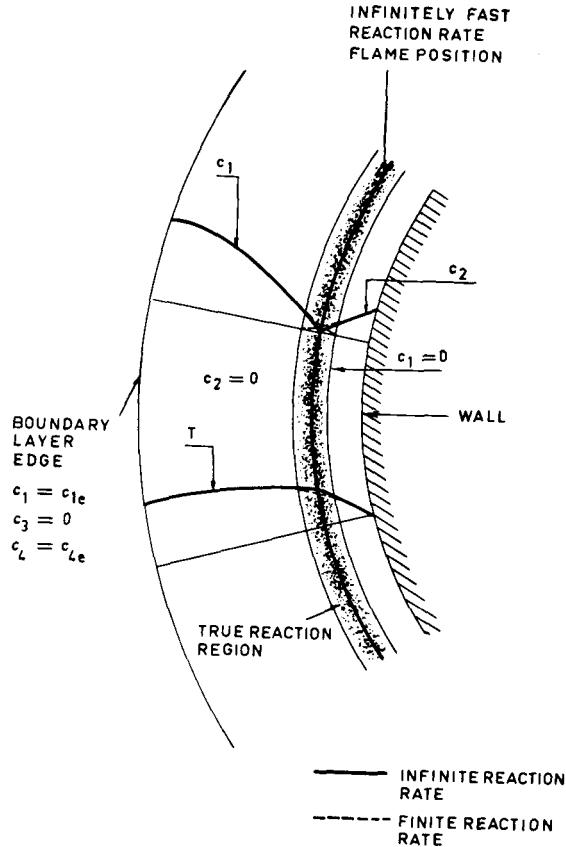


Fig. 8.

where

$$\Gamma = 1 + 1.18 \left(\frac{P_r}{1 + \alpha\beta} + 0.5 \right) \sqrt{1 + \alpha\beta} f_w$$

is equal (except for the small variation in the factor $1 - g_w$) to the ratio of heat transfer with injection to that without injection.

For $L_e = 1$, complete similarity exists between the functions g , c_4 , $c_1 - \nu c_2$, $c_3 + (1 + \nu)c_2$ and $g_T + (q/h_{fe})c_2$, where $q = \nu h_1^0 + h_2^0 - (1 + \nu)h_3^0$ is the heat of reaction per unit mass of species 2.

Now if the reaction rate is sufficiently large, species 1 and 2 may coexist only in a very thin zone or flame front. Therefore, on one side of the reaction zone $c_1 = 0$, while $c_2 = 0$ on the other side. Both c_1 and c_2 will be very small on the reaction zone (zero for infinite reaction rate) (Fig. 8).

Therefore, flame position may be determined putting $c_1 = \nu c_2$.

For sufficiently large values of f_w the reaction zone will be within the boundary layer; and a relation similar to Eq. (34) may be written:

$$- \nu c_2'(0) = 0.47 S_c^{1/3} \sqrt[6]{1 + \alpha\beta} \Gamma [c_{1e} + \nu c_2(0)] \quad (35)$$

This relation, together with the boundary conditions, determines $c_2(0)$. The reaction will take place at the wall for values of f_w larger than

$$f_w = \frac{-0.47 S_c^{-2/3} \frac{c_{1e}}{\nu} \sqrt[6]{1 + \alpha\beta}}{1 + 1.18 \left(\frac{S_c}{1 + \alpha\beta} + 0.5 \right) 0.47 S_c^{-2/3} \frac{c_{1e}}{\nu} (1 + \alpha\beta)^{2/3}}$$

where

$$f_w = - \sqrt{\frac{2x}{\rho_e \mu_e u_e}} (\rho v)_w$$

for the flat plate, and

$$f_w = - \frac{(\rho v)_w}{\sqrt{2\rho_e \mu_e \left(\frac{du_e}{dx} \right)_0}}$$

for the stagnation point.

The values obtained for the flat plate case are in very good agreement with the numerical results given in Ref. 31.

INTERNAL STRUCTURE OF THE REACTION ZONE

For sufficiently fast reaction rates the concentrations and temperature gradients vary rapidly on the very thin reaction zone. Hence, convection effects may be neglected there as compared with the much more important conduction, diffusion and chemical effects.³²

As an example, we shall write, within the reaction zone, Eqs. (12) and (14) as follows:

$$g_{Tzz} = t_m \frac{P_r}{1 + \alpha\beta} \frac{q}{h_{fe}} \frac{w_2}{\rho} \quad (36)$$

$$c_{2zz} = - t_m \frac{P_r}{1 + \alpha\beta} \frac{w_2}{\rho} \quad (37)$$

hence

$$\frac{h_{fe}}{q} g_T + c_2 = A_{22} + A_{21}z_1$$

and similarly

$$\frac{h_{fe}}{q} \nu g_T + c_1 = \nu A_{22} + A_{12}z_1$$

where $z_1 = z - z_r$; z_r gives the flame position for the infinitely fast reaction rate, and the constants A are chosen so that these expressions coincide with the similar relations obtained for the infinitely fast reaction rate. (These relations are valid whenever the chemical reaction has gone to completion before reaching the boundary-layer edges.) For example, $A_{22} = h_{fe}g_{Tr}/q$.

If the reaction rate is large, the concentrations shall be small in the reaction zone and the temperature will also be close to its limiting value T_r . We may accordingly substitute Eq. (36) by:

$$g_{Tzz} = - G \left(1 + \frac{A_{21}}{A_{22}} z_1 - \frac{h_{fe}}{qA_{22}} g_T \right) \left(1 + \frac{A_{12}}{\nu A_{22}} - \frac{h_{fe}}{qA_{22}} g_T \right) \quad (38)$$

where

$$G = t_m \frac{P_r}{1 + \alpha\beta} \frac{q}{h_{fe}} B \rho_r e^{-(E/RT_r)} \nu A_{22}^2$$

Introducing the variables:

$$\psi = \sqrt[3]{A} \left[1 - \frac{h_{fe}}{qA_{22}} g_T + \frac{A_{21}\nu + A_{12}}{2\nu A_{22}} z_1 \right]$$

$$\zeta = \sqrt[3]{A} \frac{A_{21}\nu - A_{12}}{2\nu A_{22}} z_1$$

where

$$A = 4t_m \frac{P_r}{1 + \alpha\beta} B \rho_r e^{-(E/RT_r)} \frac{\nu^3 A_{22}^3}{(A_{21}\nu - A_{12})^2}$$

Equation (38) takes the form

$$\frac{d^2\psi}{d\zeta^2} = \psi^2 - \zeta^2 \quad (39)$$

This equation has been solved in Ref. 32; its solution can be approximately written in the following form:

$$\psi = \left[\zeta^2 + 0.76e^{-(0.67\zeta)^2} \right]^{1/2}$$

In particular, for $z_1 = 0$, that is, at the ideal flame front, we may write

$$g_T = g_{T_r} \left[1 - \frac{0.87}{\sqrt[3]{A}} \right] \quad (40)$$

or

$$c_p T + \frac{1}{2} u_r^2 = \left[c_p T_r + \frac{1}{2} u_r^2 \right] \left(1 - \frac{0.87}{\sqrt[3]{A}} \right) \quad (41)$$

This relation between T and A is valid for such large values of A making T close to T_r . Actually, T decreases very rapidly, and flame extinction occurs, when A becomes smaller than the value corresponding to $T \simeq 0.8T_r$, due to the large values of the activation energy.

Therefore an approximate value of the parameter A for which extinction occurs is obtained by putting in relation (41), $T = T_r$. If u_r^2 is neglected, $A_{\text{ext}} \simeq 80$.

The above solution gives the temperature and concentration distributions within the reaction zone, and it approaches the infinite reaction rate solution at the outer edges of the reaction zone.

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