so that, near the value of $Q = Q_b$ or $Q = Q_c$,

$$B_2/B_1 < (5^*/2)^{1/2} \tag{6.48}$$

The foregoing solutions do not hold in the region where the conditions (3.7, 3.8, 3.8a, 6.16, 6.17, and 6.17a) are not satisfied. A few remarks are added to these conditions. The region where the condition (3.7) does not hold is contained in the region where the OHD-MHD type of solution exists, since it exists in the region $Q < Q_b$, and $5^* - 2\cdot 3^* Q = 0$ means that

$$Q = 5^*/2\cdot 3^* = Q_b - (Q_c - Q_b)/3^*$$

When $Q = 5^*/2\cdot 3^*$, one has

$$\alpha_1 = c_1 \tag{6.49}$$

by (2.10). Namely, when the Alfvén velocity and the sound velocity are the same in the undisturbed flow, the solution may be singular. However, there is no singularity when the Alfvén velocity is equal to the freestream velocity. The condition (3.8) concerns the solution when two shock waves coalesce. When $x = 4^*$, one has $Q = 5^*/2\cdot 3^*$ from (6.26), so that (3.8a) is involved in (3.7) in the region of the MHD-OHD type of solution. This condition is not equal to (3.8a) in $Q > Q_c$. Conditions (6.17) and (6.17a) are always satisfied, which is easily verified in Fig. 4. The regions avoided by the conditions (3.7, 3.8, 3.8a, and 6.16) in the case of small-angle shock waves and the case of general angles of shock waves await further investigation.

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OCTOBER 1963 AIAA JOURNAL VOL. 1, NO. 10

A Solution for the Nonequilibrium Flat-Plate Boundary Layer

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An analytic solution is presented for the boundary-layer flow of a dissociating diatomic gas over a flat plate. Chemical reaction is assumed to be produced solely by viscous heating within the boundary layer. Near the leading edge, where the gas is far from equilibrium, the dominant chemical process is dissociation, whereas the inverse process of recombination is negligible. The dissociation reaction takes place within a rather narrow region centered on the maximum of the frozen temperature profile. By taking advantage of the exponential temperature dependence of the dissociation rate, simple expressions for the temperature and concentration are derived. In particular, the initial rate of accumulation of atoms at a noncatalytic surface is given by the reaction rate at the maximum frozen temperature, modified to account for convection and diffusion. The physical interpretation of these results suggests a simple formula for making predictions in cases where more complicated chemistry occurs. This formula accurately reproduces the results of numerical solutions.

Nomenclature

A_1 = $h_1^{(0)}/u_\infty^2$
c = atom mass fraction
C_P = specific heat at constant pressure
D_{12} = binary diffusion coefficient
$f(\eta)$ = Blasius function
F = function defined by Eq. (36)
$\mathfrak{F}$ = function defined by Eq. (42)
g,G = functions defined by Eq. (29)
h,H = functions defined by Eq. (29)
h_i = perfect-gas enthalpy of ith species
$h_i^{(0)}$ = heat of formation of ith species
k = thermal conductivity
k_d = dissociation rate constant
k_r = recombination rate constant
K = $4k_{r0}/R^2$
l = $\rho\mu/(\rho\mu)_w$
Le = Lewis number, $D_{12}\rho C_P/k$
$m_{1,2}$ = atomic, molecular weight
p = pressure
$P_k(\eta)$ = functions defined by Eq. (18)
Pr = Prandtl number, $\mu C_P/k$
q = heat-transfer rate
Q = dimensionless heat-transfer coefficient, Eq. (14)
r_D = forward reaction rate, $4k_r\rho(p/RT)^2 \times [c_{\text{eq}}^2/(1 - c_{\text{eq}}^2)](1 - c)$
r_R = reverse reaction rate, $4k_r\rho(p/RT)^2[c^2/(1 + c)]$
R = universal gas constant
S = temperature dependence of recombination rate constant, $k_r = k_{r0}T^{-s}$
$s(\eta)$ = function defined by Eq. (26)
T = temperature
T_* = reference temperature, u_∞^2/C_P
T_D = characteristic dissociation temperature, $2h_1^0 m_1/R$
u = x component of velocity

Received April 19, 1963; revision received August 6, 1963. This research was supported by NASA under Contract NAS 5-670. An abridged version of this work[1] was presented at the IAS National Summer Meeting, Los Angeles, Calif., June 19–22, 1962.

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$v(\eta)$ = function defined by Eq. (29)
w_1 = rate of atom production, mass per unit volume, unit time
x,y = coordinates along and normal to the surface
z = $\rho_D h_1^{(0)}\zeta/p$
Γ = catalytic efficiency, Eq. (7)
μ = dynamic viscosity
ν = kinematic viscosity
ψ = dimensionless static enthalpy, $\theta + A_1 c$
ρ = mixture mass density
ρ_D = characteristic dissociation density
θ = dimensionless temperature, T/T_*
ξ,η = boundary-layer coordinates, Eq. (1)
η^* = value of η at which maximum frozen temperature occurs
ζ = dimensionless streamwise coordinate, Eq. (9)
$(\ )'$ = denotes $d/d\eta$
$(\ )_\infty$ = denotes freestream conditions
$(\ )_{eq}$ = denotes chemical equilibrium that would exist at the local temperature and pressure
$(\ )_w$ = denotes wall conditions

Introduction

CHEMICAL nonequilibrium occurs in gas flows whenever reaction rates are finite. Significant effects, due to these finite rates, are encountered in a number of flow situations of current technical interest, notably in connection with hypersonic flight at high altitude and in the case of rocket nozzle flows at relatively low pressures.

In the boundary layers that develop when such flows come in contact with a wall, the relative magnitudes of the convection and reaction rates are changed; their coupling is further complicated by diffusion of chemical species. Thus one may in general expect that the boundary layers associated with these flows will also exhibit varying degrees of chemical nonequilibrium.

The problem considered here is the steady flow of a diatomic gas over a flat plate. One is naturally led to this simple geometry in a first attempt to understand the influence of chemical reaction in boundary-layer flows. Although it allows a relatively simple analysis, the flat plate still displays many of the basic features common to the hypersonic flight situation and to the case of rocket nozzle flows. In the same spirit, the only chemical process considered is a dissociation-recombination reaction. Such a model provides useful results for a wide range of conditions and can also be used as a basis for developing solutions of more complicated problems.

In the present case, a high-speed flow of gas, weakly dissociated, is subjected to a distribution of high temperatures as it enters the boundary layer on a flat plate. This temperature distribution, produced by viscous dissipation, causes dissociation to occur. As atoms begin to appear, their distribution through the boundary layer is then modified by diffusion of the two chemical species, and the final pattern that emerges reflects this interplay of reaction, convection, and diffusion. The present paper presents an approximate description of this pattern.

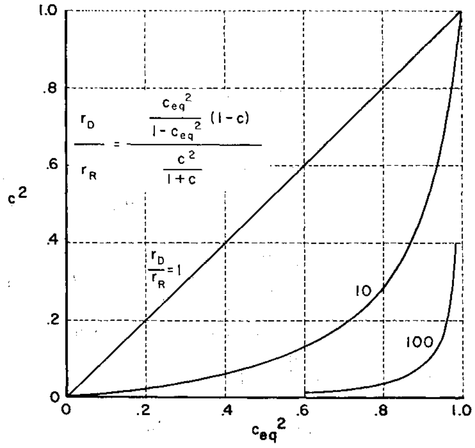

Fig. 1 **Ratio of dissociation rate to recombination rate.**

Except for minor details, the problem posed is the same as that treated by Broadwell,[2] Chung and Anderson,[3] and Jarre,[4] all using integral methods. Broadwell made use of a linearized reaction-rate law, whereas the latter two authors employed more complete expressions for the chemical kinetics. The Rayleigh-problem counterpart of the present study has been examined by Chung[5] and by Moore and Rae,[6] using a linearized reaction-rate law.

The present results incorporate a realistic description of the chemical kinetics and are obtained without the use of integral methods. The analytical approach is based on the observation that dissociation is the principal reaction near the leading edge, the reverse process of recombination being very weak in that region.† Moreover, this dissociation takes place at the frozen temperature, so that its initial distribution is known. The exponential temperature dependence of the dissociation rate, coupled with the fact that the maximum temperature in the flow is small compared to the characteristic temperature for dissociation, then leads to simple expressions for the first departure from frozen conditions. This leading term is sufficient for practical purposes in a wide range of cases. The development of further terms is indicated, and a simple nonlinear formula for extending the solution downstream is suggested. This formula agrees well with the numerical results of Chung and Anderson.[3]

1. Formulation of the Problem

1.1 Boundary-Layer Equations

A diatomic gas, which may be weakly dissociated, is assumed to flow over a flat plate at sufficiently high speed that considerable viscous heating occurs within the boundary layer. The temperatures of the wall and freestream are taken to be constants, small compared to the temperature produced by viscous dissipation. The external flow is considered to be frozen, so that the dissociation level at the edge of the boundary layer does not change.‡ The wall may be either ideally catalytic or noncatalytic. All interaction effects that might arise from rapid boundary-layer growth near the leading edge are ignored, and the pressure is taken to be constant everywhere.

In the usual boundary-layer coordinates,

$$\xi = \int_0^x \rho_w \mu_w u_\infty dx \qquad \eta = \frac{u_\infty}{(2\xi)^{1/2}} \int_0^y \rho dy \tag{1}$$

the equations for the conservation of momentum, chemical species, and energy have the form

$$(lf_{\eta\eta})_\eta + ff_{\eta\eta} = 2\xi(f_\eta f_{\eta\xi} - f_\xi f_{\eta\eta}) \tag{2}$$

$$\left(\frac{Lel}{Pr} c_\eta\right)_\eta + fc_\eta + \frac{2\xi w_1}{\rho u_\infty^2 \rho_w \mu_w} = 2\xi(f_\eta c_\xi - f_\xi c_\eta) \tag{3}$$

$$\left(\frac{\bar{C}_P}{\bar{C}_{Pw}} \frac{l}{Pr} T_\eta\right)_\eta + \frac{\bar{C}_P}{\bar{C}_{Pw}} fT_\eta - \sum_{i=1,2} \frac{2\xi w_i}{\rho u_\infty^2 \rho_w \mu_w} \frac{h_i + h_i^{(0)}}{\bar{C}_{Pw}} + \frac{u_\infty^2}{\bar{C}_{Pw}} lf_{\eta\eta}^2 + \sum_{i=1,2} \frac{C_{Pi}}{\bar{C}_{Pw}} \frac{lLe}{Pr} c_{i\eta} T_\eta = 2\xi \frac{\bar{C}_P}{\bar{C}_{Pw}} (f_\eta T_\xi - f_\xi T_\eta) \tag{4}$$

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† This approximation was suggested by Walter E. Gibson of the Aerodynamic Research Department, Cornell Aeronautical Laboratory, who has employed an analogous approximation in his studies of inviscid nonequilibrium flows (for example, Ref. 7). The author is indebted to him for his suggestion and for many helpful discussions of the present work.

‡ Reference 1 discusses the special case in which the external flow is undissociated, with wall and freestream temperatures constant and equal.

where c designates the atom mass fraction, w_1 is the mass rate of atom production per unit volume and unit time, h_i is the perfect gas enthalpy, $h_i^{(0)}$ is the heat of dissociation, and where

$$l = \rho\mu/[(\rho\mu)_w] \qquad f_\eta = [u(\xi,\eta)]/u_\infty$$

$$C_{Pi} = dh_i/dT \qquad \bar{C}_P = c(C_{P1} - C_{P2}) + C_{P2}$$

$$Le = \rho D_{12}\bar{C}_P/k \qquad Pr = \mu\bar{C}_P/k$$

where $(\ )_\infty$ denotes freestream conditions, $(\ )_w$ denotes wall conditions, and $(\ )_{1,2}$ refers to the atomic and molecular species, respectively.

1.2 Simplifying Assumptions

A solution of these equations is now sought near the leading edge, where the gas is far from equilibrium, and the principal chemical reaction is dissociation. It will be seen that this approximation to the chemistry is rigorously valid only when the local atom mass fraction c is everywhere small compared with the equilibrium atom mass fraction c_{eq} corresponding to the local temperature and pressure. Because c_{eq} never exceeds unity, this implies that the dissociation level must be low, in the sense that $c \ll 1$. The fact that the gas is weakly dissociated leads to certain simplifications in the transport properties which are outlined in the remainder of this section; in the next section, the approximation to the chemical reaction term is described.

Because c is small, the mass-averaged specific heat $\bar{C}_P$ is approximately that of the molecules. If, in addition, its temperature dependence is neglected, one has

$$\bar{C}_P/\bar{C}_{Pw} = 1 + O(c)$$

The neglect of this temperature dependence amounts to the assumption that the vibrational contribution is constant over the range of interest. The formulas presented below apply for fully excited vibration in order to facilitate a later comparison with some other work that incorporates this assumption. Next, the Lewis and Prandtl numbers are assumed constant, and the density-viscosity product is assumed equal to its wall value, i.e., $l = 1$. If, finally, one neglects the difference of perfect gas enthalpies $h_1 - h_2$ in comparison to the heat of dissociation $h_1^{(0)}$ and uses the fact that $w_1 = -w_2$, the concentration and temperature equations become

$$\frac{Le}{Pr}\, c_{\eta\eta} + fc_\eta + \frac{2\xi}{u_\infty^2\rho_w\mu_w}\,\frac{w_1}{\rho} = 2\xi f' c_\xi \tag{5}$$

$$\frac{1}{Pr}\, T_{\eta\eta} + fT_\eta = \frac{2\xi h_1^{(0)}}{u_\infty^2\rho_w\mu_w C_P}\,\frac{w_1}{\rho} - \frac{u_\infty^2}{C_P}\, f''^2 + 2\xi f' T_\xi \tag{6}$$

where $f(\eta)$ is the Blasius function:

$$f''' + ff'' = 0 \qquad f(0) = f'(0) = 0 \qquad f'(\infty) = 1$$

Because a significant number of atoms may reach the wall, the boundary condition there must allow for the occurrence of a catalytic surface reaction. If this reaction is assumed to be first order, a balance between the flux of atoms arriving at the surface and their rate of disappearance by heterogeneous reaction leads to the boundary condition[8]

$$\frac{Le}{Pr}\,\mu_w u_\infty\left(\frac{\partial c}{\partial\eta}\right)_w = (2\xi)^{1/2}\,\Gamma\left(\frac{RT_w}{2\pi m_1}\right)^{1/2}(c - c_{eq})_w \tag{7}$$

where Γ is the catalytic efficiency, defined as the ratio of the number of atoms recombining on the wall to the total number that reach the wall. Only the limiting cases of a fully catalytic ($\Gamma = \infty$) or a fully noncatalytic wall ($\Gamma = 0$) are considered here, so that one will have either $(c_\eta)_w = 0$ for a noncatalytic wall or $c_w = 0$ for a cold catalytic wall. The boundary values of the temperature profile are the constant wall and freestream temperatures.

1.3 Chemical Reaction Term

The chemical kinetics are taken to follow the reaction[9]

$$\mathcal{A}_2 + X \underset{k_r}{\overset{k_d}{\rightleftarrows}} 2\mathcal{A}_1 + X$$

where $\mathcal{A}_1, \mathcal{A}_2$, and X represent the atoms, molecules, and inert collision partners, respectively. The net mass rate of production of atoms w_1 per unit volume and unit time for this reaction may be written as

$$w_1 = 4k_r\rho\left(\frac{p}{RT}\right)^2\left\{\frac{c_{eq}^2}{1 - c_{eq}^2}\,(1 - c) - \frac{c^2}{1 + c}\right\} \tag{8}$$

The first term inside the braces represents the forward (dissociation) reaction, whereas the second term accounts for the reverse (recombination) process. The approximation made here is to neglect the recombination term. Figure 1 shows the ratio of the forward (dissociation) rate r_D to the reverse (recombination) rate r_R, as a function of c^2 and c_{eq}^2. The main point to be noticed is the wide range in which recombination can be neglected, even in the presence of appreciable concentrations. For example, when the local temperature and pressure are such that $c_{eq} = 0.9$, the ratio of reaction rates will exceed 10, even for local concentrations as high as 0.5. Of course, the approximation will not be uniformly as good as this throughout the whole boundary-layer profile. Near a cold, noncatalytic wall, for example, the dissociation rate is essentially zero, whereas an appreciable rate of recombination may occur. Thus, rigorously speaking, the approximation is valid only in the limit where c is everywhere vanishingly small compared to c_{eq}. From the viewpoint of practical application, however, the nonlinear behavior displayed in Fig. 1 suggests that dissociation will predominate in many situations, even when c is appreciable. The present approximation can be expected to describe the important sections of the reaction profile correctly.

Noting that the recombination rate constant varies inversely with some power of the temperature and that p is constant for this problem, the source term has the form[10]

$$\frac{2\xi}{u_\infty^2\rho_w\mu_w}\,\frac{w_1}{\rho} = \frac{2\xi}{u_\infty^2\rho_w\mu_w}\,\frac{Kp^2}{T_*^{\,s+2}}\left(\frac{T_*}{T}\right)^{s+2}\frac{c_{eq}^2}{1 - c_{eq}^2}\,(1 - c)$$

where T_* is a reference temperature, to be chosen later; c has been retained in this term for the reasons just mentioned, although, strictly speaking, the theory only applies when c is negligible compared to unity.

The quantity $\kappa^* = Kp^2/T_*^{\,s+2}$ can be interpreted as the reciprocal of a characteristic time for the reaction. It is convenient to absorb this quantity into the coordinate system by the change of variable

$$\zeta = \xi\kappa^*/u_\infty^2\rho_w\mu_w \tag{9}$$

The ζ coordinate measures the ratio of a typical flow time to the characteristic time for the chemical reaction, i.e.,

$$\zeta = (x/u_\infty)/(1/\kappa^*)$$

Thus, $\zeta \ll 1$ denotes the range where the reaction is far from completion, whereas $\zeta \gg 1$ corresponds to the near-equilibrium condition.

The final quantity that remains to be specified is the equilibrium concentration. For this, the Lighthill gas[11] representation is chosen. The equilibrium concentration that would exist at the local temperature and pressure is then

$$\frac{c_{eq}^2}{1 - c_{eq}^2} = \frac{\rho_D RT}{2m_1 p}\exp\left\{-\frac{T_D}{T}\right\} \tag{10}$$

Here ρ_D is the characteristic density for dissociation, assumed constant, and T_D is the characteristic dissociation temperature, $2h_1^{(0)}m_1/R$. With this explicit form, one can absorb all remaining effect of the pressure level by introducing the new streamwise coordinate

$$z = (\rho_D h_1^{(0)}/p)\zeta$$

1.4 Final Form of the Equations

Since viscous heating is the mechanism that produces the chemical reaction in this problem, it is appropriate to choose, as a reference temperature, some measure of the temperature rise due to viscous heating. Let $T_* = u_\infty^2/C_P$, $\theta = T/T_*$. Then the final form of the equations to be solved is, using $C_P = (9/2)(R/m_2)$,

$$\frac{Le}{Pr} c_{\eta\eta} + fc_\eta + \frac{2z}{\theta^{s+2}} \frac{2}{9A_1} \theta \exp\left\{-\frac{9A_1}{2\theta}\right\}(1 - c) = 2zf'c_z \tag{11}$$

$$\frac{1}{Pr} \theta_{\eta\eta} + f\theta_\eta = \frac{2z}{\theta^{(s+2)}} \frac{2}{9} \theta \exp\left\{-\frac{9A_1}{2\theta}\right\} (1 - c) - f''^2 + 2zf'\theta_z \tag{12}$$

where the parameter A_1 is defined as $A_1 = h_1^{(0)}/u_\infty^2$. The boundary conditions are

$$c(z, \infty) = c_\infty \qquad c(z,0) = 0 \text{ (catalytic wall)}$$
$$c_\eta(z,0) = 0 \text{ (noncatalytic wall)} \qquad \theta(z, \infty) = \theta_\infty$$
$$\theta(z,0) = \theta_w \tag{13}$$

Thus, the problem has been reduced to the solution of two differential equations, (11) and (12) and, apart from the Lewis and Prandtl numbers, depends only on the parameters A_1 and S.

1.5 Range of Values of A_1

The parameter A_1 is proportional to the ratio of the dissociation energy to the kinetic energy of the main stream, i.e., to the ratio of characteristic temperature for dissociation to viscous temperature rise. Thus, A_1 is expected to be large. Table 1 gives its value for oxygen, nitrogen, and hydrogen.

1.6 Heat-Transfer Formulas

It is useful to express the surface heat-transfer in terms of the dependent variables θ and c. The heat transfer rate q is given by

$$q = \left\{k \frac{\partial T}{\partial y}\right\}_{y=0} + \rho \sum_{i=1,2} (h_i + h_i^{(0)}) \left\{D_{12} \frac{\partial c_i}{\partial y}\right\}_{y=0}$$

Thus, again neglecting $h_1 - h_2$ compared to $h_1^{(0)}$,

$$q = \mu u_\infty^2 \left(\frac{u_\infty}{2\nu_w x}\right)^{1/2} \left\{\frac{\theta_\eta}{Pr} + \frac{Le}{Pr} A_1 c_\eta\right\}_{\eta=0} = \mu u_\infty^2 \left(\frac{u_\infty}{2\nu_w x}\right)^{1/2} Q$$

where the dimensionless heat-transfer coefficient Q is defined as

$$Q = \{(\theta_\eta/Pr) + (Le/Pr)A_1 c_\eta\}_{\eta=0} \tag{14}$$

Table 1 Values of A

	$h_1^{(0)}$, kcal/g	ρ_D, g/cm^3	T_D, °K	A_1
O_2	3.66	150	59,000	$\frac{1.532 \times 10^{11}}{\{u_\infty[\text{cm/sec}]\}^2}$
N_2	8.04	130	113,000	$\frac{3.36 \times 10^{11}}{\{u_\infty[\text{cm/sec}]\}^2}$
H_2	51.2	1.65	52,000	$\frac{2.14 \times 10^{12}}{\{u_\infty[\text{cm/sec}]\}^2}$

2. Analysis for the Case of Equal Diffusivities

In this section, the further restriction is made that the mass, momentum, and thermal diffusivities are all the same. Thus, the Prandtl and Lewis numbers are assumed equal to unity.

2.1 Solution for a Catalytic Wall

For the case where the surface is fully catalytic, the calculation of surface concentration and heat transfer is simplified by the following standard procedure (see, e.g., Ref. 12). If Eq. (11) is multiplied by A_1 and the result added to Eq. (12), the reaction term is eliminated, and the result is

$$\psi_{\eta\eta} + f\psi_\eta = 2zf'\psi_z - f''^2 \tag{15}$$

where $\psi = \theta + A_1 c$. Note that the heat-transfer coefficient, defined by Eq. (14), is the gradient of this function at the wall. In general, the boundary conditions on ψ are not given; however, in the important limiting case where the wall is fully catalytic, the surface concentration vanishes, and so the boundary values of ψ are $\psi(z,0) = \theta_w$, $\psi(z, \infty) = \theta_\infty + A_1 c_\infty$, and the solution is independent of z:

$$\psi = \theta_w + \tfrac{1}{2}(f' - f'^2) + (A_1 c_\infty + \theta_\infty - \theta_w)f'$$

Thus, for a fully catalytic wall, one has the familiar result that the heat-transfer rate is unaffected by the ratio of flow time to reaction time:[12]

$$Q = (\tfrac{1}{2} + A_1 c_\infty + \theta_\infty - \theta_w)f''(0) \tag{16}$$

2.2 Surface Concentration—Heat Transfer Relation for a Noncatalytic Wall

For the case of a noncatalytic wall, where the surface values of ψ are not given, the function ψ does not solve the problem directly. However, it may be used to provide a relation between the surface concentration and heat transfer. This section gives this expression, and Sec. 2.3 presents the series solution for the noncatalytic wall.

The specific relation between surface concentration and heat transfer is found by writing

$$\psi = \theta_w + \tfrac{1}{2}(f' - f'^2) + A_1\psi^{(2)}(z,\eta) + [A_1 c_\infty + \theta_\infty - \theta_w]f'$$

where the function $\psi^{(2)}$ satisfies

$$\begin{gathered} \psi_{\eta\eta}^{(2)} + f\psi_\eta^{(2)} - 2zf'\psi_z^{(2)} = 0 \\ \psi^{(2)}(z,0) = c_w(z) \qquad \psi^{(2)}(z, \infty) = 0 \end{gathered} \tag{17}$$

The solution of this problem can be expressed in terms of known thermal boundary-layer solutions. By making use of the expansions

$$c_w(z) = \sum_{k=0}^{\infty} S_k z^k \qquad \psi^{(2)}(z,\eta) = \sum_{k=0}^{\infty} S_k P_k(\eta) z^k$$

where, as will be seen below, $S_0 = c_\infty$, and where

$$\begin{gathered} P_k'' + fP_k' - 2kf'P_k = 0 \\ P_k(0) = 1, P_k(\infty) = 0 \end{gathered} \tag{18}$$

the heat transfer is found as

$$Q_{\text{Noncat}} = f''(0)[\tfrac{1}{2} + A_1 c_\infty + \theta_\infty - \theta_w] + A_1 \sum_{k=0}^{\infty} S_k P_k'(0) z^k \tag{19}$$

The coefficients $P_k'(0)$ have been tabulated, for example, by Tifford and Chu,[13] so that Eq. (19), in principle, relates a given concentration distribution $c_w(z)$ to the corresponding distribution of the heat-transfer coefficient $Q(z)$. However, it is much more instructive (and probably adequate for calculational purposes as well) to invert the series in Eq. (19), so as to display the concentration/heat-transfer relation

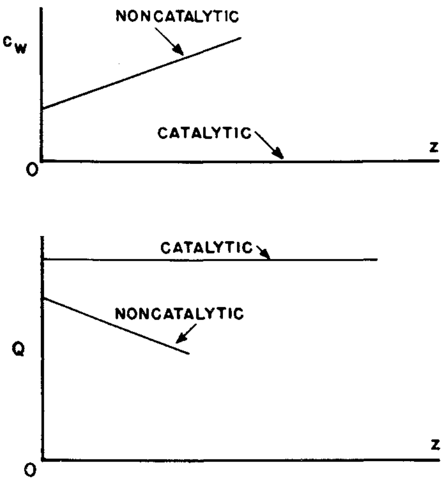


Fig. 2 Sketch of surface concentration and heat-transfer distribution.

explicitly. Using the values $P_0'(0) = -0.470$, $P_1'(0) = -0.765$, $P_2'(0) - P_1'(0) = -0.164$, one finds

$$\frac{Q_{\text{noncat}}}{A_1} = \frac{f''(0)}{A_1}\left[\tfrac{1}{2} + A_1c_\infty + \theta_\infty - \theta_w\right] - 0.470c_\infty - 0.765(c_w - c_\infty) - 0.164\,\frac{S_2}{S_1^2}(c_w - c_\infty)^2 + \ldots \quad (20)$$

The leading term of this expression is recognized as the (constant) value of Q appropriate to a fully catalytic wall. At the leading edge, where $c_w = c_\infty$, the heat-transfer coefficient for the noncatalytic wall is less than that for a catalytic wall. As one moves away from the leading edge, c_w begins to exceed c_∞ (as will be shown in the next section), so that the heat-transfer coefficient falls even further below the catalytic-wall value. The same type of behavior has been noted previously in the Rayleigh analogy[6] of this problem; sufficiently near the leading edge, the heat-transfer reduction achieved by a noncatalytic wall is proportional to the enthalpy frozen at the surface. Figure 2 is a sketch of the distributions that may be expected near the leading edge.

2.3 Series Solution for a Noncatalytic Wall

If the temperature and concentration are written as

$$\begin{aligned} c(z,\eta) &= c_0(\eta) + c_1(\eta)z + \ldots \\ \theta(z,\eta) &= \theta_0(\eta) + \theta_1(\eta)z + \ldots \end{aligned} \quad (21)$$

with boundary conditions

$$\begin{aligned} &c_k'(0) = 0 \qquad c_0(\infty) = c_\infty \qquad c_k(\infty) = 0 \quad k = 1,2,\ldots \\ &\theta_0(0) = \theta_w \qquad \theta_0(\infty) = \theta_\infty \qquad \theta_k(0) = \theta_k(\infty) = 0 \quad k = 1,2,\ldots \end{aligned} \quad (22)$$

then the equations to be satisfied by the first two terms are, from (11) and (12),

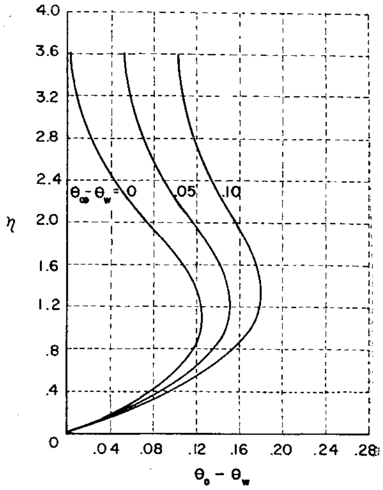
$$\begin{aligned} c_0'' + fc_0' &= 0 \\ \theta_0'' + f\theta_0' &= -f''^2 \end{aligned} \quad (23)$$

$$\begin{aligned} c_1'' + fc_1' - 2f'c_1 &= -\frac{4}{9A_1}\,\frac{\exp\{-9A_1/2\theta_0\}}{\theta_0^{s+1}}\,(1 - c_0) \\ \theta_1'' + f\theta_1' - 2f'\theta_1 &= \frac{4}{9}\,\frac{\exp\{-9A_1/2\theta_0\}}{\theta_0^{s+1}}\,(1 - c_0) \end{aligned} \quad (24)$$

The "frozen" ($z = 0$) solutions are

$$c_0(\eta) = c_\infty \qquad \theta_0(\eta) = \theta_w + \tfrac{1}{2}(f' - f'^2) + (\theta_\infty - \theta_w)f' \quad (25)$$

Fig. 3 Frozen temperature distribution.



This temperature distribution is shown in Fig. 3 for several values of $\theta_\infty - \theta_w$.

The solutions for $c_1(\eta)$ and $\theta_1(\eta)$ can be expressed in terms of any solution of the homogeneous equation:

$$s'' + fs' - 2f's = 0 \quad (26)$$

A convenient choice of boundary conditions is $s(0) = 1$, $s'(0) = 0$, which yields, by standard methods

$$\frac{c_1(\eta)}{s(\eta)} = G(\infty)v(\infty) - G(\eta)v(\eta) - \int_\eta^\infty v(\tau)\,\frac{g(\tau)s(\tau)}{f''(\tau)}\,d\tau \quad (27)$$

$$\frac{\theta_1(\eta)}{s(\eta)} = H(\eta)v(\eta) - \int_0^\eta v(\tau)\,\frac{h(\tau)s(\tau)}{f''(\tau)}\,d\tau - \frac{v(\eta)}{v(\infty)}\left\{H(\infty)v(\infty) - \int_0^\infty v(\tau)\,\frac{h(\tau)s(\tau)}{f''(\tau)}\,d\tau\right\} \quad (28)$$

where

$$\left.\begin{aligned} &G(\tau) = \int_0^\tau \frac{g(t)s(t)dt}{f''(t)} \qquad H(\tau) = A_1G(\tau) \\ &g = \frac{4}{9A_1}\,\frac{\exp\{-9A_1/2\theta_0\}}{\theta_0^{s+1}}\,(1 - c_\infty) \qquad h = A_1g \\ &v(\eta) = \int_0^\eta \frac{f''(t)dt}{[s(t)]^2} \end{aligned}\right\} \quad (29)$$

Numerical values of $s(\eta)$ and $v(\eta)$, found by a Runge-Kutta integration scheme,§ as well as values of $f''(\eta)$, are given in Table 2 and are shown in Fig. 4. By using these functions, the integrals in Eqs. (28) and (29) can be calculated numerically. However, accurate algebraic approximations to these integrals can be derived in the following way: the function g is proportional to the dissociation rate evaluated at the frozen temperature. In many cases, this temperature distribution will exhibit a pronounced maximum in the region where viscous heating is greatest, being relatively cool elsewhere. For such cases, the dissociation rate is exponentially small in the cool parts of the flow and has a significant magnitude only in a narrow band centered around the point $\eta = \eta^*$, where $\theta_0(\eta)$ has its maximum. This behavior is shown in Fig. 5 for the case $A_1 = \frac{20}{9}$, $s = 0$, $\theta_w = 0$, and $\theta_\infty = 0$, 0.05, and 0.10. Because g has this type of variation, the main contribution to the integrals defining $c_1(\eta)$ and $\theta_1(\eta)$ must come from the narrow band in which g reaches its maximum. The quantitative description of this, which is provided by the Laplace method, leads to asymptotic expansions of c_1 and θ_1. For the case of a cold wall, the details

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§ These calculations were programmed for an IBM 704 by Harvey Selib of the Systems Research Department, Cornell Aeronautical Laboratory.

Table 2 The functions $s(\eta)$, $v(\eta)$, $f''(\eta)$

η	$s(\eta)$	$v(\eta)$	$f''(\eta)$	η	$s(\eta)$	$v(\eta)$	$f''(\eta)$
0.	1.000000	0.	0.46960	2.9	4.945944	0.61121	0.08064
0.1	1.000157	0.04696	0.46956	3.0	5.365708	0.61149	0.06771
0.2	1.001252	0.09385	0.46931	3.1	5.811736	0.61169	0.05631
0.3	1.004227	0.14051	0.46861	3.2	6.284194	0.61183	0.04637
0.4	1.010021	0.18667	0.46725	3.3	6.783178	0.61193	0.03782
0.5	1.019576	0.23198	0.46503	3.4	7.308724	0.61200	0.03054
0.6	1.033840	0.27599	0.46173	3.5	7.860816	0.61205	0.02442
0.7	1.053762	0.31822	0.45718	3.6	8.439400	0.61208	0.01933
0.8	1.080302	0.35817	0.45119	3.7	9.044389	0.61211	0.01515
0.9	1.114429	0.39539	0.44363	3.8	9.675679	0.61212	0.01176
1.0	1.157121	0.42950	0.43438	3.9	10.333152	0.61213	0.00904
1.1	1.209372	0.46021	0.42337	4.0	11.016685	0.61214	0.00687
1.2	1.272191	0.48736	0.41057	4.1	11.726157	0.61214	0.00518
1.3	1.346600	0.51096	0.39599	4.2	12.461451	0.61215	0.00386
1.4	1.433639	0.53110	0.37969	4.3	13.222460	0.61215	0.00285
1.5	1.534358	0.54799	0.36181	4.4	14.009087	0.61215	0.00208
1.6	1.649818	0.56194	0.34249	4.5	14.821246	0.61215	0.00151
1.7	1.781086	0.57327	0.32195	4.6	15.658863	0.61215	0.00108
1.8	1.929224	0.58236	0.30045	4.7	16.521875	0.61215	0.00077
1.9	2.095288	0.58953	0.27825	4.8	17.410231	0.61215	0.00054
2.0	2.280312	0.59514	0.25567	4.9	18.323887	0.61215	0.00037
2.1	2.485301	0.59946	0.23301	5.0	19.262809	0.61215	0.00026
2.2	2.711216	0.60276	0.21058	5.1	20.226971	0.61215	0.00018
2.3	2.958970	0.60526	0.18867	5.2	21.216352	0.61215	0.00012
2.4	3.229407	0.60712	0.16756	5.3	22.230935	0.61215	0.00008
2.5	3.523301	0.60851	0.14748	5.4	23.270708	0.61215	0.00005
2.6	3.841343	0.60953	0.12861	5.5	24.335662	0.61215	0.00003
2.7	4.184138	0.61028	0.11112	5.6	25.425791	0.61215	0.00002
2.8	4.552198	0.61082	0.09511	5.7	26.541089	0.61215	...

of this derivation are given in the Appendix, where it is shown that the surface concentration near the leading edge may be expressed in terms of the homogeneous reaction rate, evaluated at the maximum in the frozen temperature:

$$c_w = c_\infty + \frac{x}{u_\infty}\left(\frac{w_1}{\rho}\right)_{\theta=\theta_0(\eta^*)} \frac{s(\eta^*)}{[f''(\eta^*)]^2}\,[v(\infty) - v(\eta^*)] \times \left(\pi\,\frac{T_0(\eta^*)}{T_D}\right)^{1/2} \tag{30}$$

This formula has a simple physical interpretation: near the leading edge, one may imagine that atoms are being produced only at the maximum of the frozen temperature

$$dc/dt)_{x=0,\eta=\eta^*} = w_1/\rho)_{\theta=\theta_0(\eta^*)} \tag{31}$$

Their distribution in the x direction is then given by multiplying this rate by an effective flow time, proportional to x/u_∞. Finally, the rate of increase of surface concentration is obtained by multiplying this expression by the appropriate factor to account for diffusion to the surface. Equation (30) may be thought of as supplying estimates for these factors. Although Eq. (30) has been derived under the assumption that recombination is negligible, nevertheless its physical interpretation suggests that it might be a useful approximation for any level of dissociation. Thus, one is tempted to reinstate the recombination term, using the full expression, Eq. (8), to calculate w_1/ρ. This idea is taken up again in Sec. 2.4.

The Laplace method may also be used to calculate the concentration and temperature at the point $\eta = \eta^*$. The details of this calculation are given in the Appendix, where it is shown that the initial concentration at $\eta = \eta^*$ is somewhat greater than that at the surface. Thus the concentration profiles have qualitatively the same appearance as that found in the Rayleigh analogy[6] of this problem. This behavior is sketched in Fig. 6.

The solution just described, which consists only of the leading terms in a series expansion from the leading edge, is not without value for practical application. There are many instances where the physical lengths of interest are such that the flow is always nearly frozen, so that the leading terms will suffice. When this is not the case, the leading terms can be used, in conjunction with the equilibrium solution, to estimate the distance required for the flow to equilibrate. Furthermore, a natural extension of these leading terms is developed in the next section, in a manner that accounts for the essential nonlinearity of the problem.

2.4 Extension to Larger Values of *Z*

Sufficiently far from the leading edge, the temperature and atom-concentration profiles approach a state of equilibrium. When this state has been reached, the boundary values for the concentration become constant:

$$c(z,0) = c_{\text{eq}})_w \qquad c(z,\infty) = c_{\text{eq}})_\infty$$

Thus, the solution for the ψ function is given by Eqs. (17) and (18):

$$\psi_{\text{eq}}(\eta) = \theta_w + \tfrac{1}{2}(f' - f'^2) + A_1 c_{\text{eq}})_w(1 - f') + [A_1 c_{\text{eq}})_\infty + \theta_\infty - \theta_w]f'$$

and the equilibrium distributions of concentration and temperature are found by solving the transcendental equation:

$$\theta_{\text{eq}}(\eta) + A_1 c_{\text{eq}}[\theta_{\text{eq}}(\eta)] = \psi_{\text{eq}}(\eta)$$

In order to approach this solution, the series development of the preceding section would have to be expanded to a large number of terms. The fact is that even the term of order z^2 is extremely difficult to obtain, since one must expand the exponential

$$\begin{aligned} z \exp\left\{-\frac{9A_1}{2\theta}\right\} &= z \exp\left\{-\frac{9A_1}{2\theta_0}\left[1 - \frac{\theta_1}{\theta_0}\,z + \ldots\right]\right\} \\ &= z \exp\left\{-\frac{9A_1}{2\theta_0}\right\} \exp\left\{\frac{9A_1}{2\theta_0}\,\frac{\theta_1}{\theta_0}\,z\right\}\ldots \\ &= \exp\left\{-\frac{9A_1}{2\theta_0}\right\}\left\{z + \frac{9A_1}{2\theta_0}\,\frac{\theta_1}{\theta_0}\,z^2 + \ldots\right\} \end{aligned} \tag{32}$$

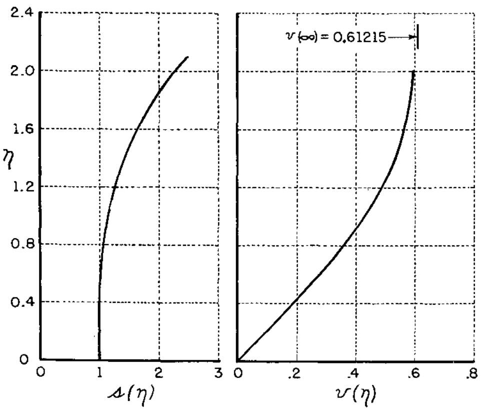


Fig. 4 The functions $s(\eta)$ and $v(\eta)$.

Clearly, the expansion indicated by the last step here will have a very small radius of convergence, and there appears to be nothing to be gained by pursuing the development of further terms. Instead, a simple nonlinear formula for estimating the solution at any value of z is derived below.

The nonlinear formula is based on the assumption that Eq. (30), which is rigorously correct only for $x \rightarrow 0$, is in fact that the correct form of the solution at all values of x, provided only that the maximum of the frozen temperature, appearing in Eq. (30), be replaced by the maximum of the local temperature at the station in question:

$$c_w - c_\infty \approx \frac{x}{u_\infty}\left(\frac{w_1}{\rho}\right)_{\theta_{\max}(x)} \frac{s(\eta^*)}{[f''(\eta^*)]^2}\,[v(\infty) - v(\eta^*)] \times \left(\pi\,\frac{T_{\max}(x)}{T_D}\right)^{1/2} \tag{33}$$

Furthermore, it is assumed that the local maximum temperature and the local surface concentration bear the same relation to each other at any value of z as they do near the leading edge, i.e., replace the leading-edge expressions (see the Appendix):

$$\begin{aligned} c(z,\eta^*) &= c_\infty + c_1(\eta^*)z + 0(z^2) = c_\infty + s(\eta^*)c_1(0)z + 0(z^2) \\ &= c_\infty + s(\eta^*)[c_w(z) - c_\infty] + 0(z^2) \\ \theta(z,\eta^*) &= \theta_0(\eta^*) - [v(\eta^*)/v(\infty)]A_1[c(z,\eta^*) - c_\infty] + 0(z^2) \\ &= \theta_0(\eta^*) - [A_1 v(\eta^*)/v(\infty)]s(\eta^*) \times [c_w(z) - c_\infty] + 0(z^2) \end{aligned}$$

by the relations

$$\begin{aligned} \theta_{\max}(z) &= \theta_{\max}(z = 0) - [A_1 v(\eta^*)/v(\infty)]s(\eta^*) \times [c_w(z) - c_\infty] \\ c(z,\eta^*) &= c_\infty + s(\eta^*)[c_w(z) - c_\infty] \end{aligned} \tag{34}$$

Then, Eq. (33) takes the form

$$\frac{x}{u_\infty} = \frac{c_w - c_\infty}{F(c_w - c_\infty)} \tag{35}$$

where

$$F(c_w - c_\infty) = \frac{s(\eta^*)}{[f''(\eta^*)]^2}\,[v(\infty) - v(\eta^*)]\left[\pi \times \frac{T_{\max(x=0)} - (A_1 u_\infty{}^2/C_P)[v(\eta^*)/v(\infty)]s(\eta^*)(c_w - c_\infty)}{T_D}\right]^{1/2} \times \left(\frac{w_1}{\rho}\right) \tag{36}$$

where w_1/ρ is to be evaluated at the concentration and temperature given by (34). Note that, in this formula, the complete expression for w_1/ρ, including recombination, has been used. This reaction rate is a function only of the temperature and concentration at the point $\eta = \eta^*$. Each of these quantities, in turn, depends only on c_w and is given by Eqs. (34). Thus, the usual roles of the dependent and independent variables have been interchanged in Eq. (35); one specifies the surface concentration c_w and calculates the corresponding value of x.

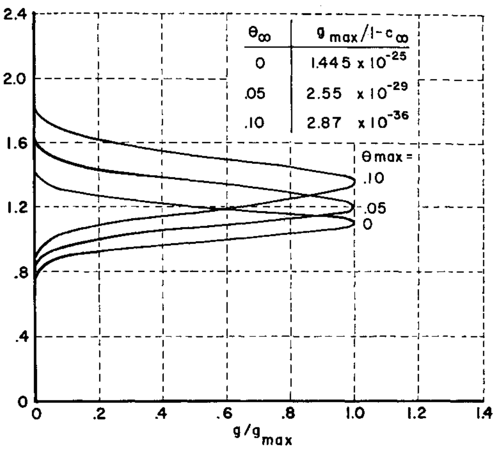


Fig. 5 Distribution of dissociation rate, $\theta_w = 0$, $S = 0$, $A_1 = \frac{20}{9}$.

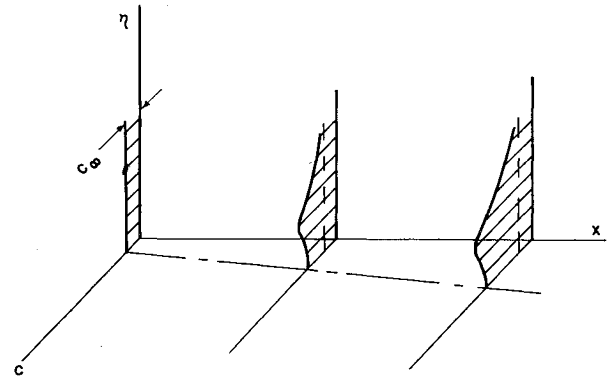


Fig. 6 Concentration profiles near the leading edge (noncatalytic wall).

Unfortunately, there are no exact solutions of the basic partial differential equations which could be used to assess the accuracy of this formulation. However, Chung and Anderson[3] have published some results found by an integral method, for the case of an adiabatic wall and an undissociated stream. The formula, analogous to Eq. (35), that applies for the adiabatic-wall case displays excellent agreement with the numerical results of Chung and Anderson. The remainder of this section derives this analogous formula, presents the comparison, and then returns to a discussion of the agreement that may be anticipated for the cold-wall case.

The boundary conditions appropriate to the adiabatic-wall case of Chung and Anderson are

$$c_\eta(z,0) = \theta_\eta(z,0) = 0 \qquad c(z,\infty) = 0 \qquad \theta(z,\infty) = \theta_\infty \tag{37}$$

Their approximations to the physical model are in all respects identical with those used here, with the exception that they retain the complete expression, Eq. (8), for the chemical production term.

In view of the boundary conditions, Eq. (37), their problem has the exact solution

$$\psi = \theta + A_1 c = \theta_w + \tfrac{1}{2}(f' - f'^2) \tag{38}$$

Thus, at the wall, the counterpart of Eq. (34) is, with no approximation,

$$\theta_w + A_1 c_w = \theta_w(z = 0) \tag{39}$$

For this case, the leading terms in the expansions of c and θ are readily found to be

$$c_0(\eta) = 0 \qquad \frac{c_1(\eta)}{s(\eta)} = \int_\eta^\infty \frac{f''(\tau)P(\tau)}{[s(\tau)]^2}\,d\tau$$

$$\theta_0(\eta) = \theta_\infty + \tfrac{1}{2}(1 - f'^2) \qquad \theta_1(\eta) = -A_1c_1(\eta)$$

where

$$P(\tau) = \int_0^\tau \frac{p(t)s(t)dt}{f''(t)} \qquad p = \frac{4}{9A_1}\,\frac{\exp\{-9A_1/2\theta_0\}}{\theta_0{}^{s+1}}$$

In this case, the dissociation rate is large at the wall and decreases rapidly as one moves away from the wall. Thus the Laplace method may again be used to estimate the surface concentration, which is found to be

$$c_w \approx \frac{x}{u_\infty}\left(\frac{w_1}{\rho}\right)_{\eta=z=0} \frac{v(\infty)}{[f''(0)]^2}\left[\pi\,\frac{T(0,0)}{T_D}\right]^{1/2} \tag{40}$$

The revision of this formula, analogous to that suggested in the cold-wall case, is to write

$$x/u_\infty = c_w/\mathfrak{F}(c_w) \tag{41}$$

where

$$\mathfrak{F}(c_w) = \frac{v(\infty)}{[f''(0)]^2}\left(\frac{w_1}{\rho}\right)_{\substack{c=c_w\\ \theta=\theta_\infty+(1/2)-A_1c_w}} \times \left[\pi\,\frac{T_{\max}(x=0) - A_1T{*}c_w}{T_D}\right]^{1/2} \tag{42}$$

This formula has been applied to the numerical cases presented by Chung and Anderson; the comparison, shown in Fig. 7, indicates that Eq. (41) agrees within 5% of the momentum integral result, at least for this special case. The calculations, of course, used the complete expression for the chemical reaction, including recombination, and Chung and Anderson's values were used for all the basic parameters.

It should be noted that the retention of the recombination term, in arriving at Eq. (41), insures that the solution will have the proper behavior for large values of x: as the concentration increases toward its equilibrium value, the factor w_1/ρ approaches zero, and thus x tends to infinity. Consequently, the nonlinear extrapolation formula that is derived incorporates the correct behavior at both small and large values of x, and it is hardly surprising that it accurately describes the variation of a smooth, monotonic function between these two limits. From the point of view of general application, it would appear that such an approach will be useful in many problems, provided that the leading terms of the series for one limit can be revised in such a way as to contain the proper behavior at the other limit. Indeed, Inger[14,15] has successfully adapted this idea to problems dealing with the chemically frozen flow over a surface of variable catalycity and with the nonequilibrium stagnation-point boundary layer. In both cases, the formulas developed by Inger display remarkable agreement with exact solutions.

Returning to the nonlinear extrapolation formula suggested for the cold-wall case, Eq. (35), it is well to note the limitations suggested by these general considerations. In particular, Eq. (35) does not correctly predict the surface concentration far downstream. The results of the Rayleigh problem treated in Ref. 6 indicate that the surface concentration on a cold, noncatalytic wall is not monotonic. Rather, it rises to a maximum value and then decays to zero. This is attributed to the fact that atoms, which are produced near the middle of the boundary layer and diffuse to the wall continue to accumulate until their concentration is sufficient to make recombination an important process, and the final equilibrium occurs in a thin sublayer of the type described by Hirschfelder.[17] However, Eq. (35) predicts a nonzero value of the wall concentration at $x = \infty$.

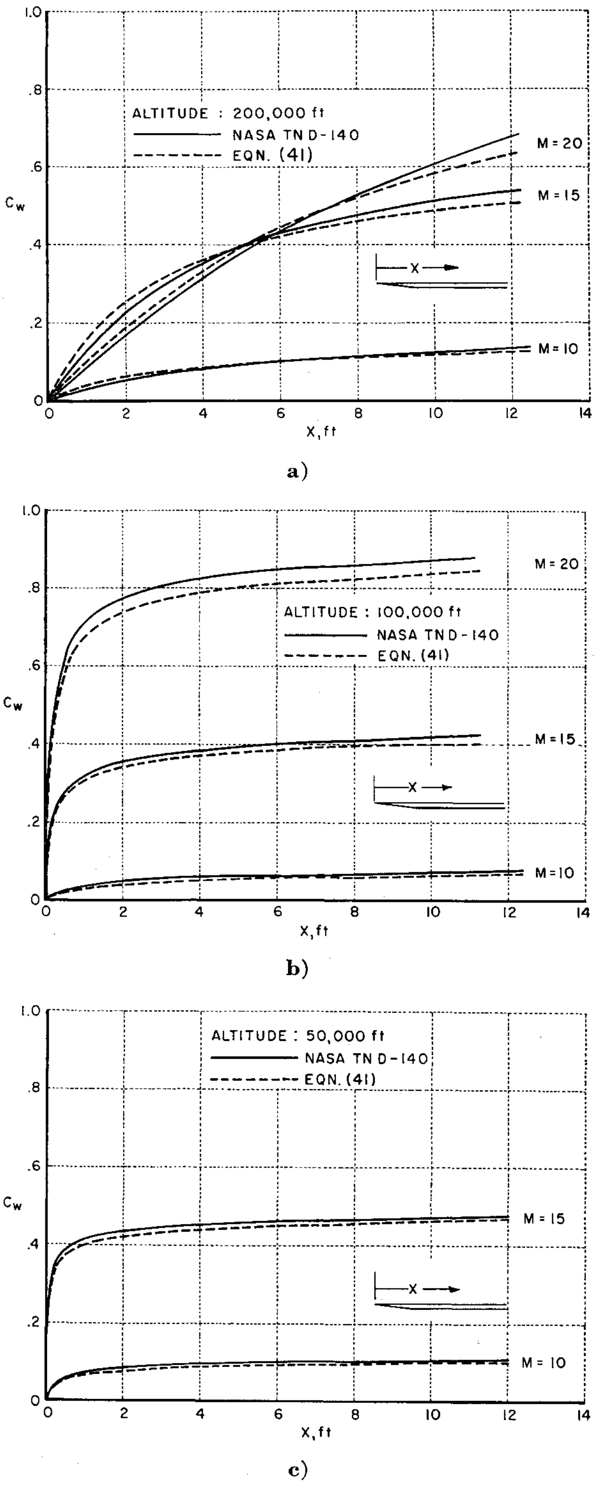
Furthermore, the relation between concentration and temperature given in Eq. (34), namely,

$$\theta(z,\eta^*) = \theta_{\max}(z = 0) - [v(\eta^*)/v(\infty)]A_1[c(z,\eta^*) - c_\infty]$$

does not, in general, satisfy the equilibrium condition

$$\theta_{\text{eq}}(\eta^*) + A_1c_{\text{eq}}[\theta_{\text{eq}}(\eta^*)] = \psi_{\text{eq}}(\eta^*)$$

Thus, although the approach used to derive Eq. (35) could also be used to derive a similar formula for $c(\eta^*)$ [Eq. (34) gives the necessary relations], the result would not agree with the correct equilibrium solution. This deficiency was not present in the adiabatic-wall case of Fig. 7, since the con-



a)

b)

c)

Fig. 7 Nonlinear extrapolation formula compared with momentum-integral method for an adiabatic wall.

centration-temperature relation used there, Eq. (38), does hold at equilibrium.

In general, then, the nonlinear extrapolation formula recommended for the cold, noncatalytic-wall case will serve to extend the leading-edge result downstream but will not be valid all the way to equilibrium. The exact location at which it ceases to be a useful approximation remains to be determined by comparison with exact solutions.

3. Concluding Remarks

The preceding analysis has led to a simple solution for the atom concentration in, and heat transfer from, a diatomic gas that is being dissociated by the heat of viscous dissipation in the boundary layer of a flat plate. The solution incorporates a realistic model for the chemical kinetics and applies for constant values of the wall temperature and catalycity, constant pressure, and constant values of the freestream temperature and atom concentration. The transport properties are approximated by assuming that the density-viscosity product is everywhere equal to its wall value, that the Lewis and Prandtl numbers are unity, and that the specific heat is constant. The solution deals only with the limiting cases of zero and infinite catalycity and consists of the first two terms in a series expansion from the leading edge. These terms may be used for practical application in cases where departures from frozen conditions are not too great. When they are too great, the same terms can be used in conjunction with the equilibrium solution to calculate the distance required for equilibrium to be achieved.

A natural extension of the leading-edge results, which accounts for the essential nonlinearity of the problem, is presented. The predictions of this formula display remarkable agreement with numerical solutions for the case of an adiabatic, noncatalytic wall. The success of this formula is apparently a consequence of the fact that it incorporates the proper behavior at both limits, near the leading edge and far downstream, and of the fact that the true solution varies monotonically between these limits. The analogous solution for the cold, noncatalytic wall does not have the proper behavior far downstream, and the upper bound to its range of usefulness remains to be determined by exact solutions.

Appendix

Because the dissociation rate has such a pronounced maximum near the leading edge, the integrals defining $c_1(\eta)$ and $\theta_1(\eta)$, Eqs. (27) and (28), may be approximated by the Laplace method. The quantitative description of this method states that (see, e.g., Ref. 16, p. 85), if in the integral

$$J = \int_a^b u(t) \exp\{-Bw(t)\} dt \tag{A1}$$

$u(t)$ is bounded over the interval from a to b and there exists a point $t = \alpha$ in this interval, at which $w'(\alpha) = 0$, $w''(\alpha) > 0$, then, for $B \gg 1$, the integral is asymptotic to

$$J \sim \exp\{-Bw(\alpha)\} \left[u(\alpha) \left(\frac{2\pi}{Bw''(\alpha)} \right)^{1/2} + O(B^{-3/2}) \right] \tag{A2}$$

If α is equal to either a or b, the value of J given in Eq. (A2) is reduced by $\frac{1}{2}$. Asymptotic expressions for $c_1(\eta)$ and $\theta_1(\eta)$ can now be found at $\eta = 0$ and also at the value of η where the frozen temperature reaches its maximum. To do so, note that

$$\frac{1}{\theta_0} = \frac{1}{\theta_w + \frac{1}{2}(f' - f'^2) + (\theta_\infty - \theta_w)f'}$$

$$\left(\frac{1}{\theta_0}\right)' = - \frac{[\frac{1}{2}(1 - 2f') + \theta_\infty - \theta_w]f''}{[\theta_w + \frac{1}{2}(f' - f'^2) + (\theta_\infty - \theta_w)f']^2}$$

Thus, $(1/\theta_0)' = 0$ at the point where $f' = \frac{1}{2} + \theta_\infty - \theta_w$; the location of this point varies from $\eta^* = 1.0918$ when $\theta_\infty - \theta_w = 0$ to $\eta^* = \infty$ when $\theta_\infty - \theta_w = \frac{1}{2}$. Thus $\theta_\infty - \theta_w$ must be less than $\frac{1}{2}$ in order for the Laplace method to apply for the evaluation of Eqs. (27) and (28). At $\eta = \eta^*$,

$$(1/\theta_0)''_{\eta=\eta^*} = \{f''(\eta^*)/\theta_0(\eta^*)\}^2$$

$$\theta_0(\eta^*) = \tfrac{1}{8} + \theta_\infty - \tfrac{1}{2}(\theta_\infty - \theta_w) + \tfrac{1}{2}(\theta_\infty - \theta_w)^2$$

In evaluating $c_1(0)$, note that the integrands of $G(\tau)$ and the third term of Eq. (27) differ only by the factor $v(t)$; thus, the Laplace method gives

$$c_1(0) \sim G(\infty)[v(\infty) - v(\eta^*)]$$

where

$$G(\infty) = \frac{4}{9A_1}(1 - c_\infty) \int_0^\infty \frac{s(t)}{f''(t)} \frac{\exp[-9A_1/2\theta_0(t)]}{[\theta_0(t)]^{s+1}} dt$$

$$\sim \frac{4}{9A_1}(1 - c_\infty) \frac{s(\eta^*)}{f''(\eta^*)} \frac{\exp[-9A_1/\theta_0(\eta^*)]}{[\theta_0(\eta^*)]^{s+1}} \times \left\{ \frac{2\pi}{9A_1} \cdot 2 \left[\frac{\theta_0(\eta^*)}{f''(\eta^*)} \right]^2 \right\}^{1/2} + O\left(\frac{1}{A_1}\right)^{3/2} \tag{A3}$$

Recalling that $2\theta/9A_1 = T/T_D$, this may be arranged as

$$G(\infty) \sim \frac{s(\eta^*)}{[f''(\eta^*)]^2} \frac{2(1 - c_\infty)}{9A_1} \frac{\exp[-9A_1/2\theta_0(\eta^*)]}{[\theta_0(\eta^*)]^{s+1}} \times \left[\pi \frac{T_0(\eta^*)}{T_D} \cdot 8\theta_0(\eta^*) \right]^{1/2} \tag{A4}$$

The factor $8\theta_0(\eta^*)$ is replaced by unity in the formulas below, because θ_∞ and θ_w must be small compared to $\frac{1}{8}$ in order for a pronounced maximum to occur.

Using these results, the early rate of accumulation of atoms at a noncatalytic surface is given by

$$c_w(z) = c_\infty + c_1(0)z + \ldots$$

$$= c_\infty + \frac{s(\eta^*)}{[f''(\eta^*)]^2} [v(\infty) - v(\eta^*)] \frac{2z}{9A_1}(1 - c_\infty) \times \frac{\exp[-9A_1/2\theta_0(\eta^*)]}{[\theta_0(\eta^*)]^{s+1}]} \left[\pi \frac{T_0(\eta^*)}{T_D} \right]^{1/2}$$

But from Eqs. (8) and (9), and the definition of z given in Sec. 1.3,

$$\frac{2z}{9A_1}(1 - c_\infty) \frac{\exp[-9A_1/2\theta_0(\eta^*)]}{[\theta_0(\eta^*)]^{s+1}} \approx \left. \frac{x}{u_\infty} \frac{w_1}{\rho} \right)_{\eta=\eta^*} \tag{A5}$$

if recombination can be neglected. Thus the surface concentration near the leading edge may be expressed in terms of the homogeneous reaction rate, evaluated at the maximum in the frozen temperature

$$c_w = c_\infty + \frac{x}{u_\infty} \left(\frac{w_1}{\rho} \right)_{\theta=\theta_0(\eta^*)} \frac{s(\eta^*)}{[f''(\eta^*)]^2} [v(\infty) - v(\eta^*)] \times \left[\pi \frac{T_0(\eta^*)}{T_D} \right]^{1/2} \tag{A6}$$

It is of interest to calculate the concentration and temperature at the point $\eta = \eta^*$. The asymptotic expressions for the integrals are then multiplied by $\frac{1}{2}$; for example, $G(\eta^*) \sim \frac{1}{2}G(\infty)$, so that

$$c_1(\eta^*)/s(\eta^*) \sim G(\infty)v(\infty) - \tfrac{1}{2}G(\infty)v(\eta^*) - \tfrac{1}{2}v(\eta^*)G(\infty) \sim G(\infty)[v(\infty) - v(\eta^*)]$$

Thus, the concentration at $\eta = \eta^*$ grows more quickly than that at the wall

$$c_1(\eta^*)/c_1(_0) \sim s(\eta^*) > 1$$

Note that

$$
\begin{aligned}
c(z,0) &= c_\infty + c_1(0)z + \ldots \\
c(z,\eta^*) &= c_\infty + c_1(\eta^*)z + \ldots = c_\infty + s(\eta^*)c_1(0)z + \ldots \\
&= c_\infty + s(\eta^*)[c(z,0) - c_\infty] + \ldots
\end{aligned}
$$

Finally, the initial departure from the frozen temperature maximum is given by

$$
\begin{aligned}
\frac{\theta_1(\eta^*)}{s(\eta^*)} &\sim H(\eta^*)v(\eta^*) - \frac{1}{2}\, v(\eta^*)H(\infty) - \frac{v(\eta^*)}{v(\infty)} \times \\
&\qquad [H(\infty)v(\infty) - H(\infty)v(\eta^*)] \\
&\sim -H(\infty)v(\eta^*) \times \\
&\qquad \left[1 - \frac{v(\eta^*)}{v(\infty)}\right] \sim -A_1G(\infty)v(\eta^*)\left[1 - \frac{v(\eta^*)}{v(\infty)}\right] \qquad \text{(A7)}
\end{aligned}
$$

Thus, as noted in Sec. 2.4, the frozen temperature maximum and the surface concentration are related by

$$
\begin{aligned}
\theta(z,\eta^*) &= \theta_0(\eta^*) + \theta_1(\eta^*)z + \ldots \\
&= \theta_0(\eta^*) - A_1G(\infty)\frac{v(\eta^*)}{v(\infty)} \times \\
&\qquad [v(\infty) - v(\eta^*)]s(\eta^*)z + \ldots \\
&= \theta_0(\eta^*) - A_1\frac{v(\eta^*)}{v(\infty)}\, s(\eta^*)c_1(0)z + \ldots \\
&= \theta_0(\eta^*) - A_1\frac{v(\eta^*)}{v(\infty)}\, s(\eta^*)(c_w - c_\infty) + \ldots
\end{aligned}
$$

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