Dissociative Relaxation in Viscous Hypersonic Shock Layers

CHUL PARK*
Imperial College of Science and Technology, London, England

The dissociative relaxation in a viscous shock layer of nonequilibrium dissociating diatomic gas in the stagnation region of a blunt hypersonic body is analyzed. The case in which the maximum local dissociation level is appreciably lower than the inviscid equilibrium value is considered. A simplified atom concentration equation is derived neglecting the recombination term in the reaction, and it is solved for a range of conditions using a digital computer. The procedure for determining the stagnation-point wall concentration for the general case of arbitrary freestream and wall conditions, including air, using the result of these solutions, is described. The approximate solution based on the simplified concentration equation is compared with the exact solutions and shown to agree approximately when the maximum dissociation is less than 80% of the inviscid equilibrium value.

Nomenclature

A_i = constants in Eq. (42a)
B = constant in reduced concentration equation, Eq. (33)
C = constant in reaction rate; see Eq. (5a)
C_p = mean frozen specific heat at constant pressure
D = diffusion coefficient
$(du_s/dx)_0$ = stagnation-point tangential velocity gradient immediately behind the shock
E = constant in B; see Eq. (34)
e = constant in reduced concentration equation, Eq. (33), and defined by Eq. (30)
f = velocity profile function ($f' = df/d\eta = u/u_e$)
g = H_t/H_{t_e}
H_t = $h_t + h_r\alpha$
h_t = $C_pT + \frac{1}{2}(u^2 + v^2)$
h_r = dissociation energy, N_2: 14,450, O_2: 6,610 Btu/lb
K = reaction term in dimensionless concentration equation, Eq. (17)
k = dissociative reaction rate constant, cm^6-mole^{-2}-sec^{-1}
k_w = wall catalytic recombination rate constant, fps
n = $\rho\mu/(\rho_e\mu_e)$
p = pressure
R = radius of curvature
R' = gas constant
R_n = Reynolds number
r = distance from centerline
$(\partial\alpha/\partial t)_r$ = rate of change of atom concentration due to reaction
s = index of temperature in reaction rate; see Eq. (5a)
T = temperature, °K
T_r = characteristic temperature, N_2: 113,200°K, O_2: 59,000°K
u,v = velocity in x and y directions
x,y = distance along and normal to wall
α = atom concentration
β = molar fraction of dissociating gas in the dissociating gas-inert gas mixture, N_2 in air with completely dissociated oxygen: $\frac{2}{3}$, O_2 in air: $\frac{1}{5}$
Δ = shock-layer thickness
θ = T/T_r
λ = frozen thermal conductivity
μ = viscosity
μ_0 = viscosity at 1000°K
ρ = density, cm^{-3}-mole
ρ_r = characteristic density, N_2: 5.4, O_2: 4.1 cm^{-3}-mole
σ = frozen Prandtl number
ω = see Eq. (27)
ξ,η = dimensionless length parameter in x and y direction

Subscripts

E = equilibrium
e = edge of shock layer; see Fig. 1
f = fictitious value
n = noncatalytic wall value
w = wall
$*$ = critical point at which atom concentration becomes maximum
∞ = freestream

Introduction

RECENT research in the field of nonequilibrium real gas carried out by various authors[1] indicates that at the altitudes above 200,000 ft the air density is such that the flow passing through the bow shock wave of a blunt body may not attain chemical equilibrium before it reaches the viscous region near the body surface. The variation of the atom concentration in this regime was first investigated by Chung[2] using the thin viscous shock-layer approximation. He has shown that the boundary-layer-type equations can be used for the relaxing gas throughout the whole shock layer and solved them numerically for a few typical cases with noncatalytic walls, and has shown that the stagnation-point heat-transfer rate is strongly affected by the lack of equilibrium. This computation was, however, extremely tedious, and, because of a number of arbitrary factors affecting the solution, namely, freestream velocity and density, nose radius, dissociative reaction rate, predissociation, wall catalyticity and temperature, the result was in no way extendable to a general case of arbitrary given conditions.

The purpose of the present paper is to investigate the effect of each arbitrary parameter and to derive a simple approximate method for determining the stagnation-point wall atom concentration for the general case of arbitrary freestream and wall conditions. To do this, the basic atom concentration equation is combined with the energy equation to convert it into an equation for temperature and is simplified by neglecting the recombination term and by assuming a profile for the density variation. The resulting equations are solved for a total of 90 conditions using a digital computer, and the resulting wall concentration parameters are correlated approximately with the given simple expressions. The procedure for the determination of the stagnation-point atom concentration under arbitrary given freestream and wall conditions using these expressions is described. The approximate method is compared with the exact solutions of Ref. 2 and three additional cases for a catalytic wall obtained in the present work and is shown to agree within ±10% of the wall concentration

---

Received July 22, 1963; revision received March 20, 1964.

* Research Assistant, Department of Aeronautics.

for those cases where the maximum local atom concentration within the shock layer is less than 80% of the inviscid equilibrium value.

Gas Model

The gas under consideration is assumed to be a mixture of an ideal dissociating gas[3] and an inert gas. By defining the dilution fraction β by

$$\beta = \frac{\text{molar density of dissociating gas}}{\text{total molar density of mixture}}$$

the thermodynamic and caloric equations for such a mixture are

$$p = \rho R'T(1 + \alpha) \tag{1}$$

$$\frac{\alpha_E^2}{1 - (\alpha_E/\beta)} = \frac{\beta\rho_r}{\rho}\exp\left(-\frac{T_r}{T_E}\right) \tag{2}$$

$$H_t = C_pT + h_r\alpha + \tfrac{1}{2}(u^2 + v^2) \tag{3}$$

For air, nitrogen is treated as the inert gas at low enthalpy levels, i. e., up to the point where oxygen completely dissociates, and atomic oxygen is treated as the inert gas at higher enthalpy levels. The necessary characteristic constants β, T_r, ρ_r, and h_r for oxygen and nitrogen are given in the Nomenclature. This simplified gas model of air is accurate at both low and high dissociation levels but breaks down at around the point where oxygen completely dissociates. The following analysis is applicable for air, therefore, only for cases where the dissociation level is appreciably different from the said condition.

The vibrational relaxation times for oxygen and nitrogen are at least one order smaller than the dissociative relaxation times in the dissociating temperature regime, and therefore the vibrational mode is assumed to be fully excited, so that the approximate relation $C_p = (4.5 + 0.5\alpha_e)R'$ holds behind the shock. As the flow approaches the wall, the temperature falls and therefore the vibrational contribution decreases, but the increase in atom concentration compensates the drop in C_p and maintains it at around $(4.5 + 0.5\alpha_e)R'$. In the present analysis, therefore, the frozen specific heat C_p is approximated by

$$C_p = (4.5 + 0.5\alpha_e)R' \tag{4}$$

The chemical reaction rate equation used is that of Ref. 4:

$$\left(\frac{\partial\alpha}{\partial t}\right)_r = k\rho_r\rho\left\{\left(1 - \frac{\alpha}{\beta}\right)\exp\left(-\frac{T_r}{T}\right) - \frac{\alpha^2}{\beta}\frac{\rho}{\rho_r}\right\} \tag{5}$$

where

$$k = C(T°\text{K}/4500)^{-s}\ \text{cm}^6\text{-mole}^{-2}\text{-sec}^{-1} \tag{5a}$$

The value of s chosen here was 1.5 (derived from Ref. 5). The value of C is left arbitrary throughout the analysis.

The Prandtl and Lewis numbers of a moderately dissociated diatomic gas are shown to vary around 0.7 and 1, respectively,[6, 7] and therefore, in the present paper, they are assumed to be 0.7 and 1 throughout.

Fundamental Equations

At altitudes above 200,000 ft, the boundary-layer thickness at the stagnation region of a blunt hypersonic body becomes very large and almost comparable with the shock-layer thickness. In this region, the flow between the shock wave and the body can be solved by considering the gas to be viscous throughout the whole shock layer.[2, 8] The fundamental equations for such a flow are derived in Refs. 2 and 8. Assuming that 1) the Lewis number is unity and 2) the kinetic energy $\frac{1}{2}(u^2 + v^2)$ may be neglected in comparison with the frozen enthalpy in the stagnation region, the fundamental equations within the stagnation region $\Delta \geq |x|$ are as follows (see Fig. 1):

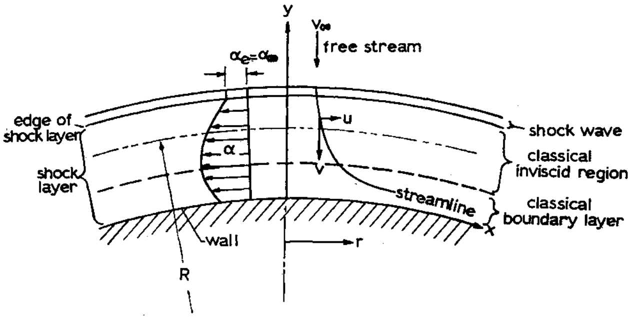

Fig. 1 Sketch of the flow field in the stagnation region of an axisymmetric hypersonic shock layer.

Continuity

$$\frac{\partial}{\partial x}(\rho ur) + \frac{\partial}{\partial y}\left\{\left(1 + \frac{y}{R}\right)\rho vr\right\} = 0 \tag{6}$$

Momentum

$$\rho\left(u\frac{\partial u}{\partial x} + v\frac{\partial u}{\partial y} + Ruv\right) = -\frac{dp}{dx} + \frac{\partial}{\partial y}\left(\mu\frac{\partial u}{\partial y}\right) \tag{7}$$

Energy

$$\rho\left(u\frac{\partial h_t}{\partial x} + v\frac{\partial h_t}{\partial y}\right) = \frac{\partial}{\partial y}\left(\frac{\lambda}{C_p}\frac{\partial h_t}{\partial y}\right) - \rho h_r\left(\frac{\partial\alpha}{\partial t}\right)_r \tag{8}$$

Species

$$\rho\left(u\frac{\partial\alpha}{\partial x} + v\frac{\partial\alpha}{\partial y}\right) = \frac{\partial}{\partial y}\left(\rho D\frac{\partial\alpha}{\partial y}\right) + \rho\left(\frac{\partial\alpha}{\partial t}\right)_r \tag{9}$$

where h_t is the total frozen enthalpy not containing the chemical energy of reaction. At the wall, the atom concentration is assumed to obey the simple linear reaction law[9]

$$\rho_w D_w(\partial\alpha/\partial y)_w = \rho_w\alpha_w k_w \tag{10}$$

Multiplying Eq. (9) by h_r and adding to (8), there follows, for unit Lewis number,

$$\rho\left(u\frac{\partial H_t}{\partial x} + v\frac{\partial H_t}{\partial y}\right) = \frac{\partial}{\partial y}\left(\frac{\lambda}{C_p}\frac{\partial H_t}{\partial y}\right) \tag{11}$$

where H_t is the total enthalpy containing the reaction energy.

Introducing the transformation of variables,[10]

$$\xi = \int_0^x \rho_e\mu_e u_e r^2 dx \tag{12}$$

$$\eta = \frac{u_e r}{(2\xi)^{1/2}}\int_0^y \rho\, dy \tag{13}$$

$$\frac{\partial\psi}{\partial y} = \rho ur \qquad \frac{\partial\psi}{\partial x} = -\rho vr \qquad \psi = (2\xi)^{1/2}f(\eta) \tag{14}$$

$$\frac{u}{u_e} = \frac{df}{d\eta} = f' \qquad g = \frac{H_t}{H_{te}} \tag{15}$$

it follows that, in the stagnation region,

$$v = -\{2\rho_e\mu_e(du_e/dx)_0\}^{1/2}f \tag{16}$$

Then Eqs. (6, 7, 9, and 11) are nondimensionalized in the stagnation region as

$$[(n/\sigma)\alpha']' + f\alpha' + K = 0 \tag{17}$$

$$[(n/\sigma)g']' + fg' = 0 \tag{18}$$

$$(nf'')' + ff'' + \tfrac{1}{2}[2(\rho_\infty/\rho) - f'^2] = 0 \tag{19}$$

where

$$K = \frac{1}{2}\frac{(\partial\alpha/\partial t)r}{(du_e/dx)_0} \tag{17a}$$

The governing boundary conditions are as follows: at $\eta = 0$, $f = f' = 0$ and $g = g_w$,

$$\alpha' = \left\{\frac{\rho_e\mu_e}{2(du_e/dx)_0}\right\}^{1/2}\frac{k_w}{\rho_w D_w} = f_e\frac{k_w}{v_e}\frac{\mu_w}{\mu_e}\sigma\alpha_w \tag{20}$$

and at $\eta = \eta_e$, $f = f_e$, $f' = g = 1$, and $\alpha = \alpha_e = \alpha_\infty$, where f_e is given from (16) as

$$f_e = \rho_e v_e\{2\rho_e\mu_e(du_e/dx)_0\}^{-1/2} \tag{21}$$

The parameter f_e is related to the freestream Reynolds number $R_{n\infty}$ and the shock-layer Reynolds number R_{ne},

$$R_{n\infty} \equiv \rho_\infty v_\infty R_e/\mu_\infty \tag{22a}$$

$$R_{ne} \equiv \rho_e v_e R_e/\mu_e = R_{n\infty}(\mu_\infty/\mu_e) \tag{22b}$$

where R_e is the radius of curvature of bow shock wave, by

$$f_e^2 = \tfrac{1}{2}(\rho_\infty\mu_\infty/\rho_e\mu_e)R_{n\infty} \tag{23a}$$

$$= \tfrac{1}{2}(\rho_\infty/\rho_e)R_{ne} \tag{23b}$$

The viscosity is approximated in the present paper by

$$\mu = \mu_0(T°\mathrm{K}/1000)^\omega \tag{24}$$

in which ω is taken as 0.76 to permit the best fit for nitrogen in the data of Ref. 6. The chosen value of ω can also be used with good accuracy for air. The value of ω for oxygen is slightly smaller than that for nitrogen, but the value 0.76 will still be a reasonable approximation for a limited range of temperature by choosing an appropriate value of μ_0.

The viscosity-density parameter n is taken as unity for computation purposes:

$$n = 1 \tag{25}$$

This is based on the approximation

$$\frac{\rho}{\rho_e} = \frac{T_e}{T}\frac{1+\alpha_e}{1+\alpha} = \left(\frac{T_e}{T}\right)^{1-\omega}$$

Because of the relation $\alpha_e \leq \alpha$ (near the shock wave), the foregoing approximation is generally quite acceptable near the shock wave. Near the wall, the approximation of Eq. (25) is not quite accurate, but the effect of a variation in n on the wall atom concentration is quite small, as will be shown later.

The nature of the solution of the problem is dependent greatly on the magnitude of K in Eq. (17). When K is very large, the flow is almost in equilibrium; when it is very small, there is no appreciable chemical reaction within the shock layer. In the present work, the intermediate case of finite values of K is considered, i.e., for flow in which an appreciable relaxation is taking place, a condition that can be expressed as

$$K_{\max} \doteqdot 0(1) \tag{26}$$

Approximating air by a mixture of a dissociating gas and an inert gas (see section on gas model) is justified on the basis of a large difference between the K values for oxygen and nitrogen. It is possible to write down two concentration equations of the form of Eq. (17) separately for oxygen and nitrogen, and, as expected from the difference in dissociation energies, nitrogen dissociation contributes approximately twice as much energy absorption as oxygen. But the value of K, which is maximum at the edge of shock layer, differs for the two gases by a ratio approximately equal to $\exp(-T_r/T_e)$, which is a very small value when $T_e < 30{,}000°\mathrm{K}$. (The argument here refers to nitrogen values.) At low enthalpy levels, therefore, the dissociation of nitrogen is negligible when the oxygen dissociation rate is such as to satisfy Eq. (26); at high enthalpy levels where K for nitrogen satisfies (26), the value for oxygen is so large that one can assume that the oxygen is fully dissociated before nitrogen starts dissociating.

Reduction of Concentration Equation

The relaxation term K in Eq. (17) is positive in an underdissociated condition, i.e., when the local atom concentration is smaller than the local equilibrium atom concentration as determined from the temperature and density by Eq. (2), and it is negative in an overdissociated condition. From the nature of the atom concentration profile, therefore, one sees that K cannot be negative at the point where atom concentration reaches the maximum value. The ratio of the first and second term in K, representing dissociation and recombination, respectively, is

$$\frac{\text{recombination term}}{\text{dissociation term}} = \exp\left(\frac{T_r}{T} - \frac{T_r}{T_1}\right) \tag{27}$$

where T_1 is a fictitious equilibrium temperature satisfying the condition

$$\frac{\alpha^2}{1-(\alpha/\beta)} = \frac{\beta\rho_r}{\rho}\exp\left(-\frac{T_r}{T_1}\right)$$

In an undissociated flow,

$$T_1 < T_E \tag{27a}$$

where T_E is the equilibrium temperature for the given enthalpy and pressure, and also

$$T_E < T \tag{27b}$$

where T is the local temperature corresponding to the underdissociated condition. Combining Eqs. (27a) and (27b), one sees that, in an appreciably underdissociated flow in which T_E is appreciably less than T, $T_E < 0.9T$, say, the ratio of the two terms [Eq. (27)] is very small when T is in the practical range of interest, e.g., $T/T_r < 0.3$. Defining the critical point η_* as the point where α reaches the maximum, then, in the "outer region" $\eta_e > \eta > \eta_*$, $K \doteqdot K$ due to dissociation alone is greater than zero. For the first approximation, therefore, the recombination term may be neglected in the "outer region."

The factor $\rho(1 - \alpha/\beta)$ can be approximated, when $\alpha - \alpha_e$ is appreciably smaller than β, by

$$\rho\left(1-\frac{\alpha}{\beta}\right) = \frac{p}{R'T}\frac{1-(\alpha_e/\beta)-[(\alpha-\alpha_e)/\beta]}{1+\alpha_e+(\alpha-\alpha_e)} \doteqdot$$

$$\frac{p}{R'T}\frac{1-(\alpha_e/\beta)}{1+\alpha_e}\exp\left\{-(\alpha-\alpha_e)\left(\frac{1}{\beta-\alpha_e}+\frac{1}{1+\alpha_e}\right)\right\} \tag{28}$$

Since in this region

$$(4.5+0.5\alpha_e)\theta_e + \alpha_e \doteqdot (4.5+0.5\alpha_e)\theta + \alpha$$

where $\theta = T/T_r$, Eq. (28) is reduced further to

$$\rho\left(1-\frac{\alpha}{\beta}\right) \doteqdot \frac{p}{R'T}\frac{1-(\alpha_e/\beta)}{1+\alpha_e}\times$$

$$\exp\left\{-(4.5+0.5\alpha_e)\left(\frac{1}{\beta-\alpha_e}+\frac{1}{1+\alpha_e}\right)(\theta_e-\theta)\right\} \tag{28a}$$

Thus, in the "outer region," the relaxation term is approximated by

$$K = \frac{Cp_e\rho_r T_r{}^{-s-1}}{2(du_e/dx)_0 R'}\frac{1-(\alpha_e/\beta)}{1+\alpha_e}\exp(-e\theta_e)\theta^{-s-1}\times$$

$$\exp\left(-\frac{1}{\theta}+e\theta\right) \tag{29}$$

where

$$e = (4.5+0.5\alpha_e)\left(\frac{1}{\beta-\alpha_e}+\frac{1}{1+\alpha_e}\right) \tag{30}$$

The function $\theta^{-s-1} \exp(-1/\theta + e\theta)$ takes the maximum value at the edge of the shock layer and decreases very rapidly as temperature falls toward the wall, i.e., by several orders of magnitude. Considering the original assumption, Eq. (26), therefore, it is seen that the relaxation term is negligibly small in comparison with other terms at the critical point $\eta = \eta_*$.

In the "inner region" $\eta_* > \eta > 0$, the recombination term in K becomes greater than the dissociation term, but the magnitude of this recombination term is, at most, the same order as the dissociation term at the critical point, i.e.,

$$|K| \gtreqqless K(\eta_*) \text{ dissociation term only} \qquad \eta_* \geq \eta \geq 0 \quad (31)$$

Thus one sees that the relaxation term is again negligibly small in the "inner region" in the appreciably underdissociated shock-layer flow under consideration. In this region, therefore, the error caused by neglecting the recombination term and retaining the dissociation term in K does not affect the solution appreciably.

The preceding argument thus leads one to use Eq. (29) as the basis for the relaxation term used in Eq. (17) throughout the whole shock-layer region. Using Eq. (29), Eq. (17) is reduced to

$$\left(\frac{1}{\sigma}\alpha'\right)' + f\alpha' + \frac{Cp_e\rho_r T_r{}^{-s-1}}{2(du_e/dx)_0 R'}\,\frac{1-(\alpha_e/\beta)}{1+\alpha_e} \times \exp(-e\theta_e)\theta^{-s-1}\exp\left(-\frac{1}{\theta} + e\theta\right) = 0 \quad (32)$$

Neglecting the kinetic energy term, multiplying Eq. (32) by h_r, and subtracting from Eq. (18) gives

$$(\theta')' + \sigma f\theta' - B\theta^{-s-1}\exp[-(1/\theta) + e\theta] = 0 \quad (33)$$

where

$$B \equiv E f_e{}^2 \theta_e{}^{\omega} \exp(-e\theta_e)\,\frac{1-(\alpha_e/\beta)}{1+\alpha_e} \quad (34)$$

and

$$E \equiv \sigma C\rho_r{}^2 \left(\frac{T_r}{4500}\right)^{-s} \left(\frac{T_r}{1000}\right)^{\omega} \left(\frac{h_r}{C_pT_r}\right)\left(\frac{\mu_0}{C_pT_r\rho_r}\right)\left(\frac{C_pT_e}{v_e{}^2}\right) = \text{const (function of gas property only)} \quad (34a)$$

The values of the constant E for oxygen and nitrogen are, respectively,

$$E = 2.9 \times 10^{-16}C \quad (34b)$$

$$E = 0.80 \times 10^{-16}C \quad (34c)$$

Available data on dissociation rate constants show that the rate constant C for nitrogen is somewhat greater than for oxygen, the ratio of the two being somewhere between 2 and 4. By taking this ratio as 3.6, the factor E becomes a constant common to both oxygen and nitrogen. With this ratio taken as 3.6, for example, and the C values for oxygen and nitrogen as 3.5×10^{14} and 1.24×10^{15}, respectively, the value of E is 0.10 common to both gases.

Instead of solving Eqs. (17–19), it is now possible to obtain an approximate solution to this problem for solving Eqs. (18) and (19) and the reduced concentration equation, Eq. (33). The density ratio ρ_∞/ρ in the momentum equation (19), however, requires the knowledge of both the temperature and the atom concentration. Since the atom concentration is affected by the surface condition, the velocity profile is, in general, dependent on the wall condition. This dependence is, however, very weak, because of the small magnitude of the density term in the momentum equation (19) which is at most $\frac{1}{4}$ compared with the unit value of f' in the same brackets. Since the dependence of atom concentration on the f profile is only to the first order, error in the density ratio does not affect the final concentration profile very much. For this reason, the density ratio is approximated by

$$\rho_\infty/\rho = (\rho_\infty/\rho_e)(\rho_e/\rho) = \tfrac{1}{8}(0.8f' + 0.2) \quad (35)$$

i.e., the density ratio across the shock is approximately equal to 8, which corresponds to the specific heat ratio of $\frac{9}{7}$, and the density at the wall is approximately equal to five times that at the edge.

Solving the reduced equation (33) and the momentum equation (19) with the simplification of Eq. (35) is straightforward. The integration is started from the wall with arbitrarily chosen values of B, e, f_w'', θ_w, and θ_w' and is terminated where $f' = 1$. From the values of f and θ at this terminated point, the corresponding value of $E(1 - \alpha_e/\beta)/(1 + \alpha_e)$ is determined by using Eq. (34). The present method thus has the advantage that, for each arbitrarily chosen set of initial values, a useful result is obtained after one integration.

The wall value of atom concentration α_w is determined from relations (3) and (20) as

$$\alpha_w = (4.5 + 0.5\alpha_e) \times \frac{\theta_e - \theta_w + [\alpha_e/(4.5 + 0.5\alpha_e)] - (\theta_w'/g_{w0}')}{f_e(k_w/v_e)(\mu_w/\mu_e)(\sigma/g_{w0}') + 1} \quad (36)$$

where g_{w0}' is the value of g_w' corresponding to the boundary condition $g_w = 0$. For the case of undissociated freestream flow over a noncatalytic wall, (36) gives

$$\begin{aligned}\alpha_{wn} &= (4.5 + 0.5\alpha_e)[\theta_e - \theta_w - (\theta_w'/g_{w0}')] + \alpha_e \\ &= 4.5(\theta_e - \theta_f) \end{aligned} \quad (37)$$

in which θ_f is a fictitious frozen temperature (dimensionless) at the shock-layer edge, which is attained by the gas at the edge of shock layer in the absence of chemical reaction:

$$\theta_f = \theta_w + (\theta_w'/g_{w0}') \quad (37a)$$

In terms of α_{wn}, Eq. (36) can be written as

$$\alpha_w = (1 + \tfrac{1}{9}\alpha_e)[(\alpha_{wn} + \alpha_e)/(1 + \Gamma)] \quad (38)$$

where Γ is the catalyticity factor

$$\Gamma \equiv f_e(k_w/v_e)(\mu_w/\mu_e)(\sigma/g_{w0}') \quad (39)$$

Equation (33) can be integrated formally as

$$\begin{aligned}\theta &= \int_0 \exp\left(-\sigma\int f d\eta\right)\int_0 \exp\left(\sigma\int f d\eta\right) K d\eta d\eta + \theta_w + \theta_w'\int_0 \exp\left(-\sigma\int f d\eta\right) d\eta \\ &= \int_0 \exp\left(-\sigma\int f d\eta\right)\int_0 \exp\left(\sigma\int f d\eta\right) K d\eta d\eta + \theta_f\end{aligned}$$

so that

$$\alpha_{wn} = 4.5\int_0^{\eta_e} \exp\left(-\sigma\int f d\eta\right)\int_0 \exp\left(\sigma\int f d\eta\right) K d\eta d\eta \quad (40)$$

The quantity K in the integrand still contains θ and hence cannot be evaluated. Equation (40), however, enables one to estimate the effect of wall temperature on α_{wn}. K takes the maximum value at the edge of shock layer and decreases very rapidly toward the wall, and therefore the integral (40) is determined mainly by the value of K at and near the shock wave. The possible range of variation of wall temperature for a cooled wall is $0 < \theta_w < 0.03$, or of the order $\frac{1}{10}$ of the edge temperature θ_e, and has little effect on the variation of θ near the shock wave. (Note also that, within the present approximation, f is uniquely determined once the edge condition is specified.) To the accuracy intended here, therefore, the wall concentration for the case of undissociated freestream flow over a noncatalytic wall α_{wn} is independent of wall temperature θ_w, i.e.,

$$\partial\alpha_{wn}/\partial\theta_w = 0 \quad (41)$$

Table 1 Comparison of exact and approximate solutions

Case→ Exact solution by→	1 Chung	2 Chung	3 Chung	4 Park	5 Park	6 Park
$\theta_e = T_e/T_r$	0.227	0.227	0.227	0.180	0.198	0.0993
$f_e = [\frac{1}{2}R_{ne}(\rho_\infty/\rho_e)]^{1/2}$	8.3	5.5	2.3	7.8	4.0	13.0
$E(1 - \alpha_e/\beta)/(1 + \alpha_e)$	0.11	0.11	0.11	0.0229	0.1	0.025
e	9	9	9	11.25	11.25	27
k_w/v_e	0	0	0	0.0237	0.0237	0.0237
$\alpha_\infty = \alpha_e$	0	0	0	0.2	0	0
α_w, exact	0.63	0.51	0.16	0.412	0.203	0.0530
α_{wn}, approx.	0.60	0.49	0.24[a]	0.473	0.198	0.069
α_w, approx.	0.60	0.49	0.24[a]	0.429	0.189	0.0560
α_{wn}/α_E	0.84	0.67	0.20	0.72[b]	0.51[b]	0.32[b] 6
Δ/R_w	0.059[c]	0.063[c]	0.065[c]	0.067	0.065	0.078

[a] This case lies out of applicable range of Eq. (42a). The value here is obtained by straight extrapolation of Eq. (42a).

[b] Inviscid equilibrium dissociation level α_E taken at the edge of shock layer.

[c] Definition of Δ/R_W by Chung[2] is R_W/R_e times that of the present work.

for a cooled wall. Equation (40) also shows that the variation of n in the "inner region" does not affect the wall concentration very much and therefore that the assumption of Eq. (25) which applies mainly to the "outer region" can be used throughout the whole shock layer.

Results and Discussion

The exact solutions of the Eqs. (17–21) are obtained numerically for three typical cases by an iterative method similar to that described in Ref. 2 for finite wall catalyticities. The results are summarized in Table 1, and one result is compared with the approximate solution in Fig. 2. It is seen from these solutions that, despite the relatively large wall catalyticity values assumed ($k_w/v_e = 0.0237$ corresponds approximately to $k_w = 50$ fps for nitrogen flow), the decrease in wall concentration due to recombination at the surface is not great. This is a result of small Γ value [see Eq. (39)]. For the wall catalyticity k_w of the order of 10 fps, Eqs. (38) and (39) show that the wall concentration is reduced only by the order of 10%.

The reduced equations, Eqs. (18, 19, 33, and 35), are solved numerically using the Ferranti Mercury digital computer for the following range of conditions:

$$0.08 < \theta_e < 0.5$$

$$2 < f_e < 15$$

$$E\frac{1 - (\alpha_e/\beta)}{1 + \alpha_e} = 0.025,\ 0.05,\ \text{and}\ 0.1$$

$$e = 11.25\ \text{(value for nitrogen in air) and}$$

$$= 27\ \text{(value for oxygen in air)}$$

$$\theta_w = 0.02$$

The total of 60 solutions was obtained for $e = 11.25$ and 30 solutions for $e = 27$, through interpolation from 200 basic solutions that gave random values of $E(1 - \alpha_e/\beta)/(1 + \alpha_e)$. It was found from these solutions that all the results are correlated by the formulas

$$\alpha_{wn} = \left(\frac{A_3 \log_e\theta_e + A_4 \log_e f_e + A_5}{1 - A_1 \log_e\theta_e - A_2 \log_e f_e}\right)^2 \qquad 3 < f_e < 15 \tag{42a}$$

$$\log_e f_w'' = -0.645 - 0.479(\log_e f_e) + 0.00785(\log_e fe)^2 + 0.00829(\log_e f_e)^3 \tag{42b}$$

$$\log_e g_{w0}' = 0.237(\log_e f_e - 0.637)^{1/2} - 0.879 \tag{42c}$$

The constants A_1 to A_5 are the functions of $E(1 - \alpha_e/\beta)/(1 + \alpha_e)$ and e and are given in Table 2, along with the associated errors in approximating by Eq. (42a). Twenty solutions corresponding to the case $e = 11.25$ and $E(1 - \alpha_e/\beta)/(1 + \alpha_e) = 0.1$ are shown in Fig. 3 and are compared with the approximate formula, Eq. (42a). Shown also in the figure is the variation of f_w'' and g_{w0}' as functions of f_e, which are determined by the simplified method of solution. As seen from Fig. 3, the correlation formula (42a) agrees approximately with the computed solutions (within ±2.5% in this case) within the range $3 < f_e < 15$.

The result of the solution of the simplified concentration equation, Eqs. (42a–42c), can be used to calculate the stagnation-point wall atom concentration and heat-transfer rate for a general case of arbitrary freestream and wall conditions. The procedure for such a calculation is as follows.

Procedure for Calculating the Stagnation-Point Wall Atom Concentration

1) Obtain the following information: velocity, density, and predissociation level in the freestream, dilution fraction β, dissociative reaction rate constant C, nose radius, and wall catalyticity. For air, use the value of β given in the Nomenclature. Wall temperature is immaterial because of relation (41).

2) Determine the condition at the edge of the shock layer, i.e., just behind the normal shock wave, using the Rankine-

Table 2 Constants in Eq. (42a)

e	E	A_1	A_2	A_3	A_4	A_5	Error in Eq. (42a) ±%, max
11.25	0.1	−0.0312	0.632	−0.110	0.299	1.213	2.5
11.25	0.05	0.0251	0.625	−0.132	0.315	1.158	2.5
11.25	0.025	0.0514	0.619	−0.0154	0.329	1.007	2.5
27[a]	0.1	0.0538	0.537	−0.224	0.275	0.989	5.0
27[a]	0.05	−0.0810	0.525	−0.241	0.285	0.931	5.0
27[a]	0.025	0.0036	0.515	−0.265	0.295	0.897	5.0

[a] Applicable range of Eq. (42a) for this case, $\alpha_{wn} < 0.2$.

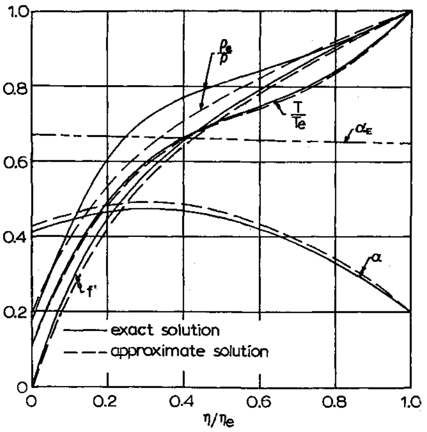

Fig. 2 Typical variation of properties in viscous hypersonic shock layer; $\theta_e = 0.180, f_e = 7.80, k_w/v_e = 0.0237, e = 11.25, E(1 - \alpha_e/\beta)/(1 + \alpha_e) = 0.0229$.

Hugoniot relation with an appropriate specific heat ratio or, for nitrogen dissociation in air with already fully dissociated oxygen behind the shock wave, by solving the caloric and state equations simultaneously.

3) Calculate $\theta_e = T_e/T_r$, f_e by Eq. (21), e by (30), E by (34a) or, if the gas under consideration is either nitrogen or oxygen, by (34b) or (34c).

4) From Eq. (42a), determine the corresponding value of α_{wn}. When $E(1 - \alpha_e/\beta)/(1 + \alpha_e)$ and e are not the values presented in Table 2, use logarithmic interpolation. (Because of the exponential nature of the problem, logarithmic interpolation is preferable to the straight interpolation.)

5) Calculate the inviscid equilibrium dissociation level in the stagnation region. Either the value just behind the shock or that at the stagnation point (inviscid flow value) can be used, because they are closely equal to each other.

6) Compare α_{wn} with the inviscid equilibrium value. If α_{wn} is appreciably smaller than the inviscid value ($\alpha_{wn} < 0.8\alpha_E$), the approximate equation (42a) is valid. Proceed to determine α_w by Eq. (38) and the heat-transfer rate using Eq. (42c). If it is not so, the approximate method cannot be used.

The preceding approximate method was tried for the sample cases chosen for exact solution, and the results are presented in Fig. 2 and Table 1. As seen from the table, the approximate method agrees within ±10% when the maximum concentration reached is less than 85% of the inviscid equilibrium value. Such a good agreement supports the use of the simplification and assumptions adopted in the derivation of the reduced concentration equation (33).

The reduced concentration equation (33), along with the accompanying equations (34, 37–39, and 41), clearly shows the role of each arbitrary parameter in the determination of wall concentration: the edge temperature θ_e and the constant f_e that is connected to the Reynolds number by Eq. (23) are the main variables for which a "similar" solution is to be found; the predissociation contributes to decreasing the effective reaction rate and also adds to the wall concentration as shown by Eq. (38), as well as playing a minor role in the "similar" solution through e; the wall catalyticity reduces the wall atom concentration in exactly the same way as in the frozen flow; and wall temperature does not effect the wall concentration.

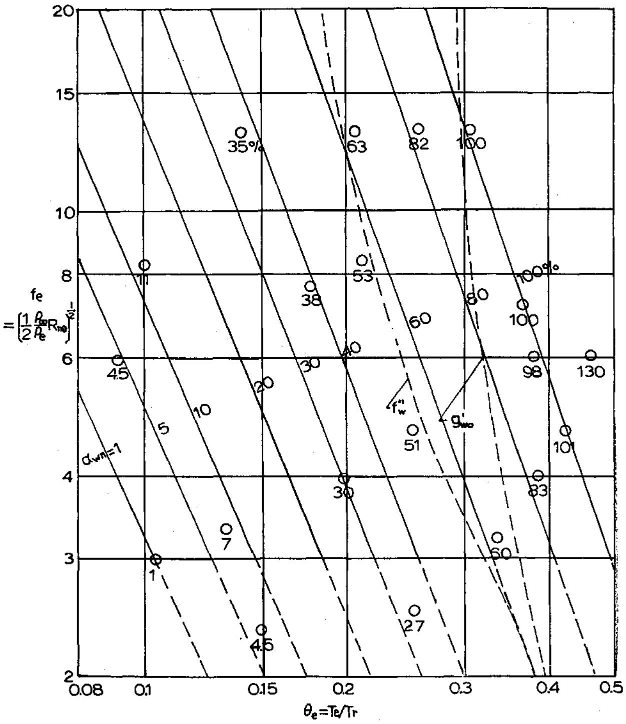

Fig. 3 Typical plot of solutions of approximate concentration equation, Eq. (33); $e = 11.25$, $E(1 - \alpha_e/\beta)/(1 + \alpha_e) = 0.1$. Circles denote the computed points, number below each circle denoting the α_{wn} value in percent. True lines denote the constant α_{wn} points as determined by Eq. (42a).

References

[1] Cheng, H. K., "Recent advances in hypersonic flow research," AIAA J. 1, 295–309 (1963).

[2] Chung, P. M., "Hypersonic viscous shock layer of nonequilibrium dissociating gas," NASA TR R-109 (1961).

[3] Lighthill, M. J., "Dynamics of a dissociating gas, Part 1, Equilibrium flow," J. Fluid Mech. 2, 1–32 (1957).

[4] Freeman, N. C., "Nonequilibrium flow of an ideal dissociating gas," J. Fluid Mech. 4, 407–425 (1958).

[5] Wray, K., Teares, J. D., Kivel, B., and Hammerling, P., "Relaxation processes and reaction rates behind shock fronts in air and component gases," Avco-Everett RR-83 (1959).

[6] Hansen, C. F., "Approximations for the thermodynamic and transport properties of high-temperature air," NASA TR R-50 (1959).

[7] Yos, J. M., "Transport properties of nitrogen, hydrogen, oxygen and air to 30,000°K," Avco-RAD TM 63-7 (1963).

[8] Howe, J. T. and Viegas, J. R., "Solutions of ionized radiating shock layer including reabsorption and foreign species effects and stagnation region heat transfer," NASA TR R-159 (1963).

[9] Goulard, R. J., "On catalytic recombination rates in hypersonic stagnation heat transfer," Jet Propulsion 28, 737–745 (1958).

[10] Lees, L., "Laminar heat transfer over blunt nosed bodies at hypersonic flight speeds," Jet Propulsion 26, 256–269, 274 (1956).