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Chemical Nonequilibrium Boundary Layer Behind a Moving Shock Wave

By

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Summary. An analysis is attempted for the boundary layer in a chemical nonequilibrium region behind a moving shock wave into diatomic gases. The rate of mass production of atoms is taken into account for the boundary layer as well as for the external flow. By introducing an appropriate expression for the mass production rate of atoms, the approximate solution for the problem has been obtained. Actual calculations have been worked out for the distributions of mass fraction of atoms, heat transfer rate and temperature rise along the wall. From the results it is found that the dissociative relaxation process for the gas of external flow is appreciably amplified in the relaxing behaviors of surface temperature rise as well as heat-transfer rate. Such an amplification of relaxation process at the wall depends strongly on the catalycity of the surface material, while not strongly on the mass production rate of atoms within the boundary layer.

1. INTRODUCTION

We shall consider the boundary layer which grows along a straight wall of arbitrary catalycity in the nonequilibrium dissociating flow behind a strong plane shock wave moving into a stationary diatomic gas. In general the transitional behavior of diatomic molecules to the equilibrium state in passing through the strong shock wave is so complicated that the rigorous treatment for the problem is anomalously difficult. Therefore we shall take into account only the dissociation mode of gases. That is to say, the dissociative mode is assumed to approach an equilibrium state through an appreciable region behind the shock, while the translational, rotational and vibrational modes are assumed to be in their equilibrium states throughout the entire region behind the shock wave. This simplifying assumption may be permitted when the shock wave is strong enough to produce an appreciable fraction of atoms due to dissociation, so that the chemical state of gas is mostly affected by dissociation process.

So far the boundary layer associated with the equilibrium dissociating external flow has been investigated by several authors [*1*], [*2*]. Recently Chung [*3*] has presented an analysis of the boundary layer in nonequilibrium dissociating flow behind a moving strong shock along a straight wall. In his analysis the chemical reaction within the boundary layer was assumed frozen. This assumption may be approximately valid for the case when the shock speed is extremely high. For cases of finite shock speed, however, the frozen-boundary-layer assumption is not compatible with the conditions of reacting external flow at the edge of the boundary layer. Therefore, we must deal with the problem in taking into account the rate of production of atoms due to chemical reactions in the boundary layer as well as in the external flow. The net mass rate of production of atoms is expressed as a complicated function of the temperature and mass fraction of atoms, so that an appropriate approximation will be looked for to simplify the analysis.

In actual calculations the distributions of mass fraction of atoms, heat transfer rate and surface temperature along the wall will be evaluated for several examples, because these are of significance in the application to the shock-tube diagnostics.

2. MATHEMATICAL FORMULATION

We conveniently choose the coordinate system fixed with respect to the shock. The x-axis is taken along the wall and the y-axis along the shock front (Figure 1).

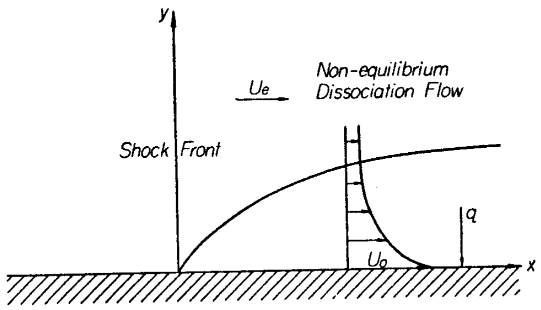

FIGURE 1. Illustrative Sketch of Flow.

In this coordinate system, the boundary layer flow is steady so long as the shock speed is assumed constant.

The steady boundary layer equations for nonequilibrium flow are

$$\frac{\partial(\rho u)}{\partial x}+\frac{\partial(\rho v)}{\partial y}=0 \tag{2-1}$$

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

$$\rho\left(u\frac{\partial H}{\partial x}+v\frac{\partial H}{\partial y}\right)=\frac{\partial}{\partial y}\left[\frac{\mu}{P}\frac{\partial H}{\partial y}+\mu\left(1-\frac{1}{P}\right)\frac{\partial}{\partial y}\left(\frac{u^2}{2}\right)\right]$$
$$-\frac{\partial}{\partial y}\left[\left(\frac{1}{L}-1\right)\rho D h_D\frac{\partial \alpha}{\partial y}\right] \tag{2-3}$$

$$\rho\left(u\frac{\partial \alpha}{\partial x}+v\frac{\partial \alpha}{\partial y}\right)=\frac{\partial}{\partial y}\left(\rho D\frac{\partial \alpha}{\partial y}\right)+\dot{w} \tag{2-4}$$

$$p_e=\rho RT(1+\alpha)$$

In these equations, u and v are the x and y components of the velocity, respectively. The symbols ρ, p, T and α are the density, pressure, temperature and mass fraction of atoms, respectively. The symbols μ, D and R are the viscosity, binary diffusion coefficient and gas constant of molecules, respectively. P and L are the

Prandtl number and Lewis number. The total enthalpy H can be expressed as

$$H=\int c_{PM}dT+\frac{1}{2}u^2+h_D\alpha$$

where h_D and c_{PM} are the specific dissociation energy and the specific heat for molecules, respectively. The term $\dot{w}$ is the net mass rate of production of atoms due to chemical reactions.

It is worthwhile noting that the term $\dot{w}$ in Eq. (2-4) vanishes for the frozen-boundary-layer case which was analyzed in Reference [*3*]. Since, in general, $\dot{w}$ is a complicated function depending on the temperature and mass fraction of atoms, we shall introduce an approximate expression for $\dot{w}$ in order to simplify the analysis. This will be discussed in the succeeding section.

We next proceed to specify the boundary conditions. The particles have no mean motion relative to the wall surface, so that in the present coordinate system

$$u=U_0 \qquad \text{at} \quad y=0 \tag{2-5}$$

where U_0 is the shock speed. The wall temperature may be assumed constant, because the deviation from the room temperature is comparatively small in the concerning region. We thus obtain the condition for the total enthalpy H of gases at the wall as

$$H=H_0+h_D\alpha \qquad \text{at} \quad y=0 \tag{2-6}$$

where H_0 is the total enthalpy of gases ahead of the shock. As regards the mass fraction of atoms, we should take into account the reaction of atoms on the catalytic wall. The rate of diffusion of atoms to the wall should be equal to the rate of recombination of atoms at the wall. For the diatomic gases as oxygen and nitrogen, the rates of recombination of atoms on the solid surfaces have been found to be linear with the mass fraction of atoms [*4*]. If this is the case, we have

$$\frac{L\mu}{P}\frac{\partial\alpha}{\partial y}=k_w\rho\alpha \qquad \text{at} \quad y=0 \tag{2-7}$$

where k_w is the coefficient representing the catalycity of wall. For a limiting case of k_w infinitely large, the condition of Eq. (2-7) reduces to

$$\alpha=0 \qquad \text{at} \quad y=0 \tag{2-8}$$

Using the solution for the inviscid flow behind the plane shock wave, we can derive the conditions at the outer edge of the boundary layer. Since the total enthalpy is conserved across the shock, we have

$$H=H_0 \qquad \text{at} \quad y\to\infty$$

Following the usual way for the steady boundary-layer problem, we introduce the transformations

$$\xi=U_0(\rho\mu)_w x \tag{2-9}$$

$$\eta=\frac{U_0}{\sqrt{2\xi}}\int_0 \rho\, dy \tag{2-10}$$

$$f=\frac{1}{U_0}\int_0 u\, d\eta\,, \qquad \frac{\partial f}{\partial \eta}=\frac{u}{U_0} \tag{2-11}$$

$$g=H/H_0 \tag{2-12}$$

$$z=\alpha/\alpha_{e\infty} \tag{2-13}$$

where the subscript w denotes the quantity at the wall and $\alpha_{e\infty}$ the mass fraction of atoms in the external flow downstream at infinity.

Applying these transformations to Eqs. (2-1) and (2-2), we obtain

$$\frac{\partial}{\partial \eta}\left(C\frac{\partial^2 f}{\partial \eta^2}\right)+f\frac{\partial^2 f}{\partial \eta^2}+2\frac{d\ln u_e}{d\ln \xi}\left(\frac{\rho_e}{\rho}\frac{u_e^2}{U_0^2}\right)=2\xi\left(\frac{\partial f}{\partial \eta}\frac{\partial^2 f}{\partial \xi \partial \eta}-\frac{\partial f}{\partial \xi}\frac{\partial^2 f}{\partial \eta^2}\right) \tag{2-14}$$

where C is defined by

$$C=\rho\mu/(\rho\mu)_w$$

Eq. (2-14) is so complicated for the solution that we introduce the following simplification. Since, in the present paper, we are concerned with the region in which the external flow is in dissociative nonequilibrium, the external flow variables depend on x or ξ. It is however known that no appreciable variation in pressure or velocity occurs across the nonequilibrium region. Therefore the external flow velocity u_e may be assumed constant. In order to simplify the formulation, we assume that Prandtl number P and Lewis number L are constant and that $C=1$. The function f then depends on η alone consistently with the boundary conditions. Then Eq. (2-14) reduçes to

$$f'''+ff''=0 \tag{2-15}$$

With the foregoing simplification, applying the transformations of Eqs. (2-9)–(2-13) to Eqs. (2-3) and (2-4), respectively, we obtain the following equations in terms of g and z.

$$\frac{1}{P}\frac{\partial^2 g}{\partial \eta^2}+f\frac{\partial g}{\partial \eta}+\frac{U_0^2}{H_0}\left(1-\frac{1}{P}\right)[f'f'']'-\beta\frac{L-1}{P}\frac{\partial^2 z}{\partial \eta^2}=2\xi f'\frac{\partial g}{\partial \xi} \tag{2-16}$$

$$\frac{L}{P}\frac{\partial^2 z}{\partial \eta^2}+f\frac{\partial z}{\partial \eta}=2\xi\left(f'\frac{\partial z}{\partial \xi}-\bar{\dot{w}}\right) \tag{2-17}$$

where β and $\bar{\dot{w}}$ are given, respectively, by

$$\beta=\frac{h_D}{H_0}\alpha_{e\infty} \tag{2-18}$$

$$\bar{\dot{w}}=\frac{\dot{w}}{\rho U_0^2(\rho\mu)_w\alpha_{e\infty}} \tag{2-19}$$

The boundary conditions of Eqs. (2-5)–(2-8) become

$$f(0)=0\,, \qquad f'(0)=1 \tag{2-20}$$

$$g(\xi,0)=1+\beta z(\xi,0) \tag{2-21}$$

$$\frac{\partial z}{\partial \eta}(\xi, 0)=K\left(\frac{\xi}{\xi_r}\right)^{1/2} z(\xi, 0) \qquad \text{for} \quad k_w \quad \text{finite} \tag{2-22}$$

$$z(\xi, 0)=0 \qquad \text{for} \quad k_w \quad \text{infinite} \tag{2-23}$$

Here K is defined by

$$K=\sqrt{2}\frac{P}{L}\frac{\sqrt{R}}{M_s}\frac{k_w}{a_0}, \qquad R=\frac{\rho_w U_0 x_r}{\mu_w} \tag{2-24}$$

In this equation M_s is the shock Mach number defined by $M_s=U_0/a_0$, where a_0 is the sound speed of gases ahead of the shock. The ξ_r is the ξ corresponding to the dissociative relaxation distance x_r in the external flow, that is

$$\xi_r=U_0(\rho\mu)_w x_r$$

or, in terms of the dissociative relaxation time t_r,

$$\xi_r=U_0^2(\rho\mu)_w t_r$$

The conditions at the outer edge of boundary layer are given by

$$f'(\infty)=u_e/U_0 \tag{2-25}$$

$$g(\xi, \infty)=1 \tag{2-26}$$

$$z(\xi, \infty)=z_e(\xi/\xi_r) \tag{2-27}$$

We here note that, as is easily shown from Eq. (2-17) and the boundary conditions (2-25) and (2-27), $f'\partial z/\partial\xi-\bar{\dot{w}}$ must vanish at $\eta\to\infty$. This means that the frozen-boundary-layer assumption $\bar{\dot{w}}=0$ is inconsistent with the nonequilibrium external flow conditions for a finite value of u_e/U_0, because then $f'\partial z/\partial\xi$ remains finite at $\eta\to\infty$. Therefore the analysis of Reference [3] based on the frozen-boundary-layer assumption is applicable only to a limiting case of $u_e/U_0=0$ at $\eta\to\infty$. In the present analysis, however, the conditions are specified to satisfy $f'\partial z/\partial\xi-\bar{\dot{w}}=0$ at $\eta\to\infty$. Therefore the analysis is applicable to cases of u_e/U_0 finite.

The present problem has thus been reduced to look for the solutions of Eqs. (2-15)–(2-17) satisfying the conditions (2-20)–(2-23) and the conditions (2-25)–(2-27).

3. Approximate Expression for $\dot{w}$

In this section we shall introduce an approximate expression for the net mass rate of production of atoms $\dot{w}$. Gas molecules with which we are concerned are assumed to follow the reaction

$$A_2+M \underset{k_R}{\overset{k_D}{\rightleftarrows}} A+A+M \tag{3-1}$$

where A_2 and A represent molecules and atoms, respectively, and M the third body which may be either molecules or atoms. The symbols k_D and k_R are the rate constants of dissociation and recombination, respectively.

The net mass rate of production of atoms for the reaction (3-1) can be given in terms of the mass fraction of atoms α and the density ρ as

$$\dot{w}=-\frac{k_D}{2p_e}\frac{\rho^3}{\overline{M}^2}(1+\alpha)\left(\frac{\alpha^2}{\alpha^{*2}}-1\right)$$

where $\overline{M}$ is the molecular weight and α^* represents the local equilibrium value of α. The rate constant k_D can be expressed in the form

$$k_D \propto T^m e^{-\theta/T}$$

where θ is the characteristic temperature of dissociation and m a constant pertinent to the gas.

We introduce a function W as the ratio of the net mass rate of production of atoms $\dot{w}$ to that in the external flow $\dot{w}_e$, that is

$$\dot{w}(x, y)=\dot{w}_e(x)W(x, y)$$

Since $\dot{w}_e$ is given by

$$\dot{w}_e(x)=\rho_e u_e \frac{d\alpha_e}{dx}$$

Eq. (2-19) can be rewritten as

$$\bar{\dot{w}}=\frac{u_e}{U_0}\frac{\rho_e}{\rho}\frac{dz_e}{d\xi}W(\xi, \eta) \tag{3-2}$$

It follows from the definition of W that the function W is equal to unity at the outer edge of boundary layer. On the other hand, $\dot{w}$ decreases from a finite value to zero as proceeding from the shock front towards infinite downstream. Therefore we may expect that the term $\dot{w}$ plays a significant role only in the region close to the shock wave. In view of this fact, we approximate the function $W(x, y)$ by $W(0, y)$, the value immediately behind the shock wave. With this approximation, Eq. (3-2) is written as

$$\bar{\dot{w}}=\frac{u_e}{U_0}\frac{dz_e}{d\xi}\tau^{2-m}e^{-\frac{\theta}{T_{ei}}(\tau-1)} \tag{3-3}$$

where, with the temperature T_{ei} of the external flow immediately behind the shock, τ is given by

$$\tau=\frac{T_{ei}}{T}=\frac{1+\dfrac{2}{(\gamma-1)M_s^2}-\left(\dfrac{u_e}{U_0}\right)^2}{\left\{1+\dfrac{2}{(\gamma-1)M_s^2}\right\}g_i(\eta)-[f'(\eta)]^2}$$

The $g_i(\eta)$ represents the function $g(\eta)$ immediately behind the shock. It should be noted that $g_i(\eta)\simeq 1$ when Prandtl number P is close to one. The expression Eq. (3-3) for $\bar{\dot{w}}$ leads our analysis to a great simplification, because $\bar{\dot{w}}$ given by Eq. (3-3) does not depend on α so that Eq. (2-17) reduces to a linear equation.

We turn to obtain the solution for f, g and z. Eq. (2-15) for f has already been solved numerically by Mirels for several values of u_e/U_0 [1], [5], [6]. If the mass fraction of atoms z_e of the external flow is expressed in the power series of ξ/ξ_r in the form

$$z_e\left(\frac{\xi}{\xi_r}\right)=\sum_{n=0}^{\infty}a_n\left(\frac{\xi}{\xi_r}\right)^n, \tag{3-4}$$

the function z should be written in the following form consistent with the boundary conditions of Eqs. (2-22) and (2-27).

$$z(\xi,\eta)=\sum_0^{\infty}\left[Kz_{n-1}A_n(\eta)+\frac{1+(-1)^n}{2}a_{n/2}B_n(\eta)\right]\left(\frac{\xi}{\xi_r}\right)^{n/2} \tag{3-5}$$

where the constants z_n can be calculated by the relation

$$z_n=Kz_{n-1}A_n(0)+\frac{1+(-1)^n}{2}a_{n/2}B_n(0)$$

For a limiting case of K infinite, we have instead of Eq. (3-5)

$$z(\xi,\eta)=\sum_0^{\infty}a_nC_{2n}(\eta)\left(\frac{\xi}{\xi_r}\right)^n \tag{3-6}$$

Substituting Eq. (3-5) or (3-6) into Eq. (2-17) and equating the terms of the same power in ξ/ξ_r, we obtain the equations for A_n, B_n and C_n as follows:

$$\frac{L}{P}A_n''+fA_n'=nf'A_n \qquad n=0,1,2\cdots \tag{3-7}$$

$$\frac{L}{P}B_n''+fB_n'=n[f'B_n-\overline{W}] \qquad n=0,2,4\cdots \tag{3-8}$$

$$\frac{L}{P}C_n''+fC_n'=n[f'C_n-\overline{W}] \qquad n=0,2,4\cdots \tag{3-9}$$

where $\overline{W}$ is given by

$$\overline{W}=\frac{u_e}{U_0}\tau^{2-m}e^{-\frac{\theta}{T_{ei}}(\tau-1)} \tag{3-10}$$

The boundary conditions reduce to

$$A_n'(0)=1,\quad A_n(\infty)=0,\quad n=0,1,2\cdots \tag{3-11}$$

$$B_n'(0)=1,\quad B_n(\infty)=1,\quad n=0,2,4\cdots \tag{3-12}$$

$$C_n(0)=0,\quad C_n(\infty)=1,\quad n=0,2,4\cdots \tag{3-13}$$

For actual calculations the parameters u_e/U_0, L/P, m and θ/T_{ei} involved must be given.

As was mentioned before, the function f has already been solved numerically by Mirels for several values of u_e/U_0. For diatomic perfect gases, u_e/U_0 tends to 1/6 in the limit of shock Mach number infinity. The results of Reference [1] show that the function f indicates no sensitive dependance on u_e/U_0 so long as the shock Mach number is high. Therefore we have chosen $u_e/U_0=1/6$. The characteristic temperature of dissociation θ is equal to 59,000°K for oxygen and 114,-

000°K for nitrogen. We have chosen $\theta/T_{ei}=5$, 10, 15, 20 for actual calculations. Following Wray's recent work [7], an approximate choice for m is suggested to be $m=-1$ for oxygen and $m=-1/2$ for nitrogen for the temperature of 3,000°K $-$8,000°K. We have chosen $m=-1$. As can be seen from Eq. (3-10), $\overline{W}$ is insensitive for the variation in m. Therefore we may expect the results for $m=-1$ is applicable to the case of other diatomic molecules as nitrogen. The parameter L/P has been chosen 1.95 with $L=1.4$ and $P=0.72$.

With these values of parameters u_e/U_0, L/P, m and θ/T_{ei}, Eqs. (3-7)–(3-9) with the respective boundary conditions (3-11)–(3-13) have been numerically solved for A_n, B_n and C_n from $n=0$ up to $n=40$, 20 and 20, respectively, by the use of digital computer OKITAC 5090 A. The values of $A_n'(0)$, $B_n'(0)$ and $C_n(0)$ are given in Table 1. To see the dependence of solution on m, the case for $m=-1/2$ and $\theta/T_{ei}=15$ has been calculated (Table 1). Though the values of $A_n'(0)$ are given up to $n=40$ in Table 1, we can obtain the approximate values for larger n, if necessary, by the relation

TABLE 1.

n	$-A_n(0)$	n	$-A_n(0)$
0	2.2733	21	.3133
1	1.3462	22	.3057
2	1.0176	23	.2987
3	.8435	24	.2921
4	.7332	25	.2860
5	.6560	26	.2802
6	.5983	27	.2747
7	.5531	28	.2695
8	.5165	29	.2646
9	.4862	30	.2599
10	.4605	31	.2555
11	.4383	32	.2512
12	.4190	33	.2472
13	.4020	34	.2434
14	.3868	35	.2397
15	.3732	36	.2362
16	.3609	37	.2328
17	.3497	38	.2295
18	.3395	39	.2264
19	.3300	40	.2234
20	.3213	—	—

m	-1				$-1/2$
θ/T_{ei}	5	10	15	20	15
n	$B_n(0)$				$B_n(0)$
0	1.0000	1.0000	1.0000	1.0000	1.0000
2	.2971	.2506	.2309	.2191	.2298
4	.1588	.1173	.1013	$.9210^{-1}$	.1004
6	.1018	$.6723^{-1}$	$.5489^{-1}$	$.4814^{-1}$	$.5421^{-1}$
8	$.7158^{-1}$	$.4285^{-1}$	$.3329^{-1}$	$.2826^{-1}$	$.3277^{-1}$
10	$.5333^{-1}$	$.2921^{-1}$	$.2169^{-1}$	$.1788^{-1}$	$.2129^{-1}$
12	$.4135^{-1}$	$.2087^{-1}$	$.1487^{-1}$	$.1192^{-1}$	$.1455^{-1}$
14	$.3302^{-1}$	$.1545^{-1}$	$.1058^{-1}$	$.8271^{-1}$	$.1033^{-1}$
16	$.2697^{-1}$	$.1176^{-1}$	$.7763^{-2}$	$.5922^{-1}$	$.7555^{-2}$
18	$.2244^{-1}$	$.9152^{-2}$	$.5835^{-2}$	$.4349^{-2}$	$.5664^{-2}$
20	$.1896^{-1}$	$.7257^{-2}$	$.4475^{-2}$	$.3263^{-2}$	$.4334^{-2}$
n	$C_n'(0)$				$C_n'(0)$
0	.4399	.4399	.4399	.4399	.4399
2	.2920	.2462	.2269	.2153	.2258
4	.2166	.1600	.1381	.1256	.1369
6	.1701	.1124	$.9175^{-1}$	$.8046^{-1}$	$.9061^{-1}$
8	.1386	$.8296^{-1}$	$.6446^{-1}$	$.5472^{-1}$	$.6345^{-1}$
10	.1158	$.6343^{-1}$	$.4711^{-1}$	$.3883^{-1}$	$.4623^{-1}$
12	$.9868^{-1}$	$.4981^{-1}$	$.3548^{-1}$	$.2845^{-1}$	$.3471^{-1}$
14	$.8535^{-1}$	$.3994^{-1}$	$.2736^{-1}$	$.2138^{-1}$	$.2670^{-1}$
16	$.7474^{-1}$	$.3258^{-1}$	$.2151^{-1}$	$.1641^{-1}$	$.2093^{-1}$
18	$.6612^{-1}$	$.2696^{-1}$	$.1719^{-1}$	$.1281^{-1}$	$.1669^{-1}$
20	$.5900^{-1}$	$.2258^{-1}$	$.1393^{-1}$	$.1015^{-1}$	$.1349^{-1}$

$$A_m(0)=\sqrt{\frac{n}{m}}A_n(0)$$

Consistently with the boundary conditions of Eqs. (2-21) and (2-26), g can be expressed in the series of ξ as follows:

$$g(\xi,\ \eta)=g_i(\eta)+\beta\sum_0^\infty g_n(\eta)\left(\frac{\xi}{\xi_r}\right)^{n/2} \tag{3-14}$$

The function $g_i(\eta)$ should satisfy the equation

$$\frac{1}{P}g_i''+fg_i'+\frac{U_0^2}{H_0}\left(1-\frac{1}{P}\right)[f'f'']'=0$$

and the boundary conditions

$$g_i(0)=g_i(\infty)=1$$

The numerical results for $g_i(\eta)$ have been given by Mirels for $P=0.72$. For $P=1$, we obtain $g=1$. As for $g_n(\eta)$, we seek for the expression for $g_n'(0)$ alone, because we need only $g_n'(0)$ to calculate the heat transfer rate. We obtain the expression for $g_n'(0)$ from the solutions of Eqs. (3-7)–(3-9) by the use of the approximate expression for f, as follows:

for k_w finite

$$g_n'(0)=Kz_{n-1}(2\sqrt{L}-1)+\frac{1+(-1)^n}{2}a_{n/2}\sqrt{L}\frac{B_n(0)}{A_n(0)} \qquad n=0,\ 1,\ 2,\cdots \tag{3-15}$$

and for k_w infinite

$$g_n'(0)=a_{n/2}(\sqrt{L}-1)C_n'(0) \qquad n=0,\ 2,\ 4,\cdots \tag{3-16}$$

The detailed derivations of Eqs. (3-15) and (3-16) are shown in Appendix.

4. Heat Transfer Rate and Surface Temperature Rise

The heat transfer rate $\dot{q}$ to the wall is given by

$$-\dot{q}=\frac{\mu_w}{P}\left(\frac{\partial h}{\partial y}\right)_w+h_D\rho_w D\left(\frac{\partial \alpha}{\partial y}\right)_w \tag{4-1}$$

where h is the static enthalpy of gases. For cases of nondissociating gases, introducing the transformations of Eqs. (2-9)–(2-13) into Eq. (4-1), we obtain

$$-\dot{q}_i=\frac{(\rho\mu)_w}{P}\frac{H_0U_0}{\sqrt{2\xi}}\left[g_i'(0)-\frac{U_0^2}{H_0}f''(0)\right]$$

The values of $g_i'(0)$ and $f''(0)$ for $C=1$ and $P=0.72$ have already been obtained by Mirels [5]. It is convenient to introduce the dimensionless heat-transfer rate $(\dot{q}-\dot{q}_i)/\dot{q}_i$ in order to see the magnitude of deviation of the heat transfer rate from nondissociating case. By the use of Eqs. (3-4), (3-5), (3-14), (3-15) and (3-16), we obtain for k_w finite

$$\frac{\dot{q}-\dot{q}_i}{\dot{q}_i}=\beta\frac{\sum_0^\infty\left\{(L+2\sqrt{L}-2)Kz_{n-1}-\frac{1+(-1)^n}{2}a_{n/2}\frac{\sqrt{L}B_n(0)}{A_n(0)}\right\}\left(\frac{\xi}{\xi_r}\right)^{n/2}}{g_i'(0)-\frac{U_0^2}{H_0}f''(0)} \tag{4-2}$$

for k_w infinite

$$\frac{\dot{q}-\dot{q}_i}{\dot{q}_i}=\beta\frac{(L+\sqrt{L}-2)\sum_0^\infty a_n C_{2n}'(0)\left(\frac{\xi}{\xi_r}\right)^n}{g_i'(0)-\frac{U_0^2}{H_0}f''(0)} \tag{4-3}$$

The surface heat transfer rate can be determined from the measurement of wall temperature by means of surface thermometory. That is, the wall temperature $T(t)$ at a measuring point is related to $\dot{q}$ there as follows [8]:

$$T(t)-T_0=-\frac{1}{\sqrt{\pi(\rho c_P k)_b}}\int_0^t\frac{\dot{q}(\tau)}{\sqrt{t-\tau}}\,d\tau \tag{4-4}$$

where $(\rho c_P k)_b$ signifies the quantity pertinent to the wall material. Here T_0 is the wall temperature ahead of the shock. With $\dot{q}_i$ for the nondissociating gases, Eq. (4-4) gives the surface temperature T_i as

$$T_i-T_0=\sqrt{\frac{\pi}{(\rho c_P k)_b}}\cdot\sqrt{\frac{(\rho\mu)_w}{2}}\,\frac{H_0}{P}\left[g_i'(0)-\frac{U_0^2}{H_0}f''(0)\right]$$

The temperature T_i is constant independently of both time t and location x or ξ. Therefore T_i is identical with the temperature immediately behind the shock wave for the case of dissociating gases. Combining Eqs. (4-2) and (4-3) to Eq. (4-4), we obtain

for k_w finite

$$\frac{T(t)-T_i}{T_i-T_0}=\beta\frac{\sum_0^\infty\left\{(L+2\sqrt{L}-2)Kz_{n-1}-\frac{1+(-1)^n}{2}a_{n/2}\frac{\sqrt{L}B_n(0)}{A_n(0)}\right\}I_n\left(\frac{t}{t_r}\right)^{n/2}}{\pi\left\{g_i'(0)-\frac{U_0^2}{H_0}f''(0)\right\}} \tag{4-5}$$

for k_w infinite

$$\frac{T(t)-T_i}{T_i-T_0}=\beta\frac{(L+\sqrt{L}-2)\sum_0^\infty a_n C_{2n}'(0)I_{2n}\left(\frac{t}{t_r}\right)^n}{\pi\left\{g_i'(0)-\frac{U_0^2}{H_0}f''(0)\right\}} \tag{4-6}$$

where I_n's are the numerical constants given by

$$I_n=\begin{cases}\dfrac{2^{\frac{n}{2}+1}\left(\frac{n}{2}\right)!}{3,\,5\cdots(n+1)} & \text{for even } n\\[2ex] \dfrac{1,\,3\cdots\cdots n}{2^{\frac{n+1}{2}}\left(\frac{n+1}{2}\right)!}\cdot\pi & \text{for odd } n\end{cases}$$

For k_w finite the mass fraction of atoms at the wall vanishes downstream far from the shock front as $\xi/\xi_r \to \infty$. For k_w finite the surface temperature rise, as $\xi/\xi_r \to \infty$, tends to a constant asymptotic value which is equal to the temperature rise for the case when the wall is fully catalytic and the external flow is uniform, *i.e.* $z_e=1$, $z_w=0$. This asymptotic value T_∞ is given from Eq. (4-6) by

$$\frac{T_\infty - T_i}{T_i - T_0} = \beta \frac{(L+\sqrt{L}-2)C_0'(0)}{g_i'(0) - \dfrac{U_0^2}{H_0} f''(0)} \tag{4-7}$$

It can be easily shown from Eq. (4-3) that the dimensionless heat-transfer rate $(\dot{q}-\dot{q}_i)/\dot{q}_i$ has the same asymptotic value as Eq. (4-7) as $\xi/\xi_r \to \infty$. In quite the same way, for the case when $k_w=0$ the asymptotic value of temperature rise (or dimensionless heat-transfer rate) is given from Eq. (4-5) by

$$\frac{T_\infty - T_i}{T_i - T_0} = \beta \frac{\sqrt{L}/A_0(0)}{g_i'(0) - \dfrac{U_0^2}{H_0} f''(0)}$$

5. Results and Discussion

Following the analysis in the previous section, we can evaluate the surface heat transfer and surface temperature rise, provided that the mass fraction of atoms of the external flow is expressed by the power series in terms of ξ/ξ_r. For actual calculations we assume the form of z_e as follows:

$$z_e = 1 - e^{-\xi/\xi_r}$$

and then a_n's in Eq. (3-4) are given by

$$a_0 = 0, \qquad a_n = \frac{(-1)^{n-1}}{n!} \qquad (n=1, 2, 3\cdots)$$

The mass fraction of atoms z_w at the wall, surface heat transfer $\dot{q}$ and surface temperature rise $T-T_i$ from the temperature just behind the shock have been calculated for $\theta/T_{ei}=5$, 10, 20 and $K=0$, 1, 2, ∞. In Figures 2, 3 and 4 the

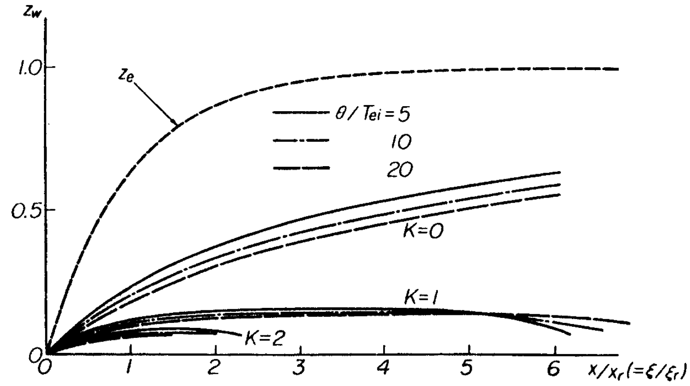

FIGURE 2. Atom Concentration at the Wall.
($u_e/U_0=1/6$, $P=0.72$, $L=1.4$)

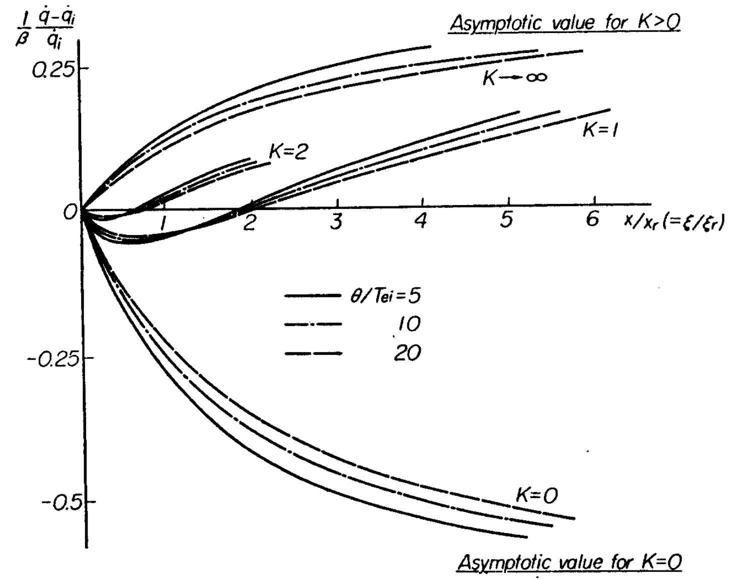

FIGURE 3. Heat Transfer Rate. ($u_e/U_0=1/6$, $P=0.72$, $L=1.4$)

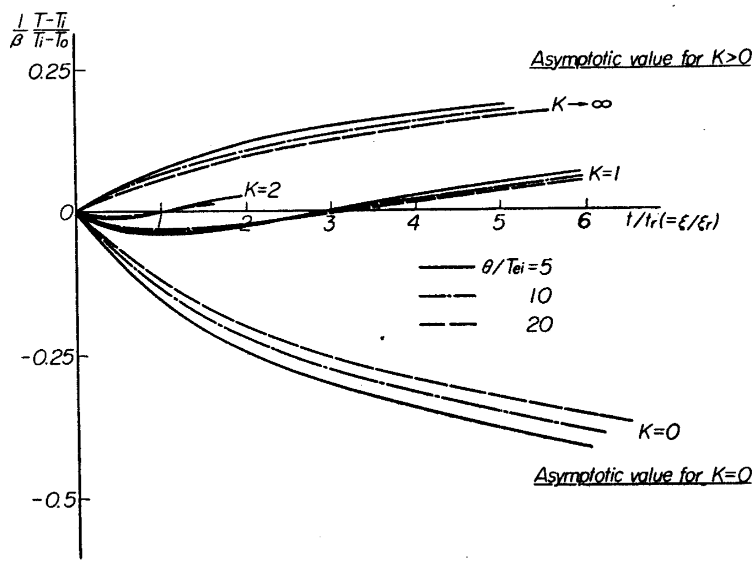

FIGURE 4. Surface Temperature Rise.
($u_e/U_0=1/6$, $P=0.72$, $L=1.4$)

results are plotted against ξ/ξ_r. It can be seen from Figure 2 that, for a fixed K, the mass fraction of atoms z_w at the wall indicates only a weak dependance on θ/T_{ei}. The similar tendencies can be seen from Figures 3 and 4, respectively, for the surface heat transfer rate and surface temperature rise. As can be seen from Eq. (3-3), the rate of mass production of atoms depends mainly on the magnitude of the parameter θ/T_{ei}. Therefore the mass fraction of atoms, surface heat transfer and temperature rise are less sensitive for the variation in the rate of mass production of atoms. This can be expected qualitatively from the fact that in Eq. (3-10) $\overline{W}$, the term for the mass production of atoms, is the order of magnitude of u_e/U_0 which is small for a strong shock wave.

As is seen from Figures 2, 3 and 4, the atom concentration, heat transfer and temperature rise at the wall depend mainly on the value of K, the parameter defined by Eq. (2-24). The parameter K is proportional to $k_w\sqrt{p_e t_r}$ where k_w is the rate constant for recombination on the wall and t_r the dissociative relaxation time for the gas of the external flow. For oxygen and nitrogen the magnitude of k_w is about 1,000 cm/sec for metal walls and about 1 cm/sec for glass walls [*4*]. If, for example, a combination of oxygen and steel wall is considered, the existing data on k_w [*4*] and t_r [*9*] give $0.5 \lesssim K \lesssim 3$ for M_s from 8 to 15.

For the limiting case of $K=0$ or for the case of noncatalytic wall, the dimensionless surface-temperature rise $(T-T_i)/(T_i-T_0)$ approaches a negative asymptotic value as ξ/ξ_r increases. On the contrast to this, it approaches a posititive asymptotic value for cases of non-zero K, no matter how small. The dimensionless surface-heat-transfer rate $(\dot{q}-\dot{q}_i)/\dot{q}_i$ shows the similar behavior to that of the dimensionless temperature rise. In order to see the behavior of approach to the asymptotic value, we use a characteristic distance ξ_{rT} which is chosen as the value of ξ for the point where the surface temperature rise reaches $1/e$ times the asymptotic value as $\xi/\xi_r \to \infty$. In the similar way we choose the characteristic distance $\xi_{r\dot{q}}$ for the surface-heat-transfer rate. For both limiting cases of $K=0$ and $K \to \infty$, the dimensionless temperature rises monotonically approach the respective asymptotic values. In these cases, the ratios ξ_{rT}/ξ_r and $\xi_{r\dot{q}}/\xi_r$ are estimated roughly about 5 and 2, respectively. For cases of finite K, the dimensionless temperature rise follows a curve close to the values for $K=0$ when ξ/ξ_r is small and then approaches a positive asymptotic value as $\xi/\xi_r \to \infty$. As can be seen from Figure 4, the ratio ξ_{rT}/ξ_r seems to be much greater for smaller K, so long as K is finite. Indeed, if the curves calculated for $K=1$ are extrapolated to the region of larger ξ, the ratio ξ_{rT}/ξ_r is estimated roughly about ten. From the above-obtained results it follows that the dissociative relaxation process for the gas of external flow is appreciably amplified in the relaxing behaviors of surface temperature rise as well as heat transfer rate. Such an amplification of the relaxation process depends strongly on the value of K or the catalycity of surface material, not strongly on the value of θ/T_{ei} or the mass production rate of atoms within the boundary layer.

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References

[*1*] Mirels, H.: Laminar Boundary Layer Behind a Strong Shock Moving into Air, NASA TN D-291, (1960).

[*2*] Hartunian, R.A. and Marrone, P.V.: Viscosity of Dissociated Gases from Shock-Tube Heat-Transfer Measurements, Phys. Fluids, Vol. 4, p. 535 (1961).

[3] Chung, P.M.: Chemically Frozen Boundary Layer with Surface Reactions Behind a Strong Shock Wave, Phys. Fluids, Vol. 6, p. 550 (1963).

[4] Goulard, R.: On Catalytic Recombination Rates in Hypersonic Stagnation Heat Transfer, Jet Propulsion, Vol. 28, p. 737 (1958).

[5] Mirels, H.: Laminar Boundary Layer Behind Shock Advancing into Stationary Fluid, NACA TN 3401 (1955).

[6] Mirels, H.: Boundary Layer Behind Shock or Thin Expansion Wave Moving into Stationary Fluid, NACA TN 3712 (1956).

[7] Wray, K.L.: Chemical Kinetics of High Temperature Air, in "Hypersonic Flow Research" (F. Riddell, ed.) Academic Press, New York (1961).

[8] Rabinowicz, J., Jessey, M.E. and Bartsch, C.A.: Resistance Thermometer for Heat Transfer Measurement in a Shock Tube, GALCIT Hypersonic Research Project, Memo. No. 33 (1956).

[9] Bernstein, L.: Tabulated Solutions of the Equilibrium Gas Properties Behind the Incident and Reflected Normal Shock-Wave in a Shock-Tube. I Nitrogen, II Oxygen, A.R.C. TR C.P. No. 626 (1963).

APPENDIX

Approximate Expression for $g_n'(0)$

We shall derive an approximate expression for $g_n'(0)$. Substituting Eq. (3-14) into g given by Eq. (2-16) and equating the terms of the same power in ξ/ξ_r, we obtain a set of equations for $g_n'(0)$'s as follows:

for k_w finite

$$\frac{1}{P}g_n''+fg_n'-\frac{L-1}{P}\left[Kz_{n-1}A_n''+\frac{1+(-1)^n}{2}a_{n/2}B_n''\right]=nf'g_n \quad (n=0, 1, 2\cdots)$$

for k_w infinite

$$\frac{1}{P}g_n''+fg_n'-\frac{L-1}{P}\,\frac{1+(-1)^n}{2}a_{n/2}C_n''=nf'g_n \qquad (n=0, 2, 4\cdots)$$

From the condition Eqs. (2-21) and (2-26), we have

for k_w finite

$$g_n(0)=Kz_{n-1}A_n(0)+\frac{1+(-1)^n}{2}a_{n/2}B_n(0), \qquad g_n(\infty)=0$$

for k_w infinite

$$g_n(0)=0, \qquad g_n(\infty)=0$$

Let us introduce the functions $G_n(\eta)$, $H_n(\eta)$, $J_n(\eta)$ and $K_n(\eta)$ which are the solutions of the following equations,

$$\frac{1}{P}G_n''+fG_n'=nf'G_n' \qquad n=0, 1, 2\cdots \tag{A-1}$$

$$\frac{1}{P}H_n''+fH_n'=nf'H_n \qquad n=0, 1, 2\cdots \tag{A-2}$$

$$\frac{1}{P}J_n''+fJ_n'=n[f'J_n-\overline{W}] \qquad n=0, 2, 4\cdots \tag{A-3}$$

$$\frac{1}{P}K_n''+fK_n'=n[f'K_n-\overline{W}] \quad n=0, 2, 4\cdots \tag{A-4}$$

satisfying the respective boundary conditions

$$G_n(0)=A_n(0), \qquad G_n(\infty)=0 \tag{A-5}$$

$$H_n(0)=B_n(0), \qquad H_n(\infty)=0 \tag{A-6}$$

$$J_n(0)=B_n(0), \qquad J_n(\infty)=1 \tag{A-7}$$

$$K_n(0)=0 \qquad K_n(\infty)=1 \tag{A-8}$$

We then obtain the following expression for $g_n(\eta)$ in terms of the above-defined functions,

for k_w finite

$$g_n(\eta)=Kz_{n-1}[2G_n(\eta)-A_n(\eta)]+\frac{1+(-1)^n}{2}a_n[H_n(\eta)+J_n(\eta)-B_n(\eta)] \quad n=0, 1, 2, \cdots \tag{A-9}$$

and for k_w infinite

$$g_n(\eta)=a_{n/2}[K_n(\eta)-C_n(\eta)] \qquad n=0, 2, 4\cdots \tag{A-10}$$

Comparing Eqs. (A-1)–(A-4) with Eqs. (3-7)–(3-9) for A_n, B_n and C_n, the following transformations are conveniently introduced,

$$\bar{\eta}=\sqrt{L}\,\eta \tag{A-11}$$

$$F(\bar{\eta})=\sqrt{L}f(\eta) \tag{A-12}$$

Since f is proportional to η either in the region of η small or in the region of η large, we have the approximate relation as follows:

$$F(\bar{\eta})\simeq f(\bar{\eta}) \tag{A-13}$$

Indeed the validity of this relation has been checked for the case of $u_e/U_0=1/6$ and $L=1.4$ (see Figure 5). With this approximation Eq. (A-1) for $G_n(\eta)$ is rewritten as

$$\frac{L}{P}\frac{d^2G_n}{d\bar{\eta}^2}+f(\bar{\eta})\frac{dG_n}{d\bar{\eta}}=n\frac{df(\bar{\eta})}{d\bar{\eta}}G_n \qquad n=0, 1, 2\cdots \tag{A-14}$$

The boundary conditions given by Eqs. (A-5)–(A-8) are invariant through the transformations (A-11) and (A-12). The solution G_n for Eq. (A-14) satisfying the condition (A-5) is quite the same as the solution A_n for Eq. (3-7) satisfying Eq. (3-11). That is,

$$\left.\frac{dG_n}{d\bar{\eta}}\right|_{\bar{\eta}=0}\simeq 1$$

and hence

$$\left.\frac{dG_n}{d\eta}\right|_{\eta=0}\simeq\sqrt{L} \tag{A-15}$$

In the same way we obtain

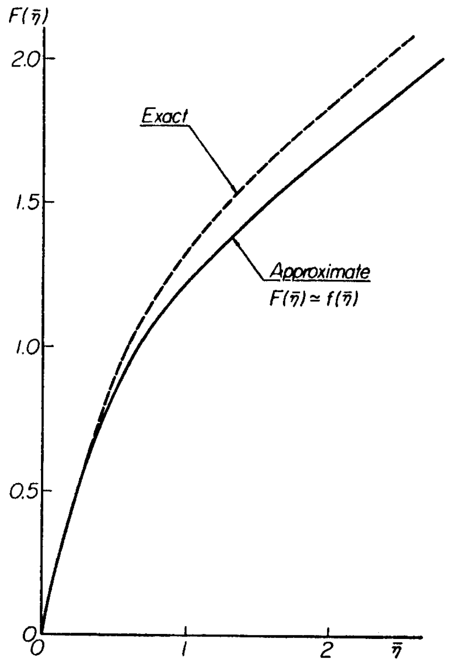

FIGURE 5. The Function $F(\bar{\eta})$ versus $\bar{\eta}$. ($u_e/U_0=1/6$, $L=1.4$)

$$\left.\frac{dH_n}{d\eta}\right|_{\eta=0} \simeq \sqrt{L}\frac{B_n(0)}{A_n(0)} \tag{A-16}$$

The function $\overline{W}$ involved in Eqs. (A-3) and (A-4) has a form of Eq. (3-10). Since $dF/d\bar{\eta}=df/d\eta$ and $g_i(\eta)\simeq 1$ for the Prandl P close to one, we have the approximate relation as follows:

$$\overline{W}(\eta)\simeq\overline{W}(\bar{\eta}) \tag{A-17}$$

By the use of the transformations Eq. (A-11) and (A-12) with the approximate relations (A-13) and (A-17), Eqs. (A-3) and (A-4) reduce approximately to the same as the equations for B_n and C_n, respectively. Therefore we obtain

$$\left.\frac{dJ_n}{d\eta}\right|_{\eta=0} \simeq 0 \tag{A-18}$$

$$\left.\frac{dK_n}{d\eta}\right|_{\eta=0} \simeq \sqrt{L}C_n'(0) \tag{A-19}$$

We can thus determine $g_n'(0)$ from Eqs. (A-9) and (A-10) by the use of $G_n'(0)$, $H_n'(0)$, $J_n'(0)$ and $K_n'(0)$ which are given by Eqs. (A-15), (A-16), (A-18) and (A-19), respectively.