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AN INTEGRAL METHOD FOR THE NONEQUILIBRIUM DISSOCIATING LAMINAR FLAT PLATE BOUNDARY LAYER

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Abstract—An integral method of the Pohlhausen-type is derived to calculate the nonequilibrium flat plate boundary layer for a binary mixture consisting of atoms A and molecules A_2. The catalytic activity of the wall can be chosen arbitrarily. The method is based on the Crocco relationship between the enthalpy and velocity profile for Prandtl and Lewis number unity. The velocity profile is assumed to be known and and a trial solution is made for the unknown atom mass-fraction profile. The shape parameter and a characteristic boundary layer thickness of the atom mass-fraction profile are obtained from the integral relations for momentum and diffusion. The influence of the catalytic activity of the wall on the development of the temperature and atom mass-fraction profile as well as on the wall heat flux is discussed.

NOMENCLATURE

A,	atom;
A_2,	molecule;
a_0–a_5,	coefficients of atom mass-fraction profile;
C_b,	constant in equation (2.10);
C_f,	constant in equation (2.9);
$\bar{c}_p$,	frozen specific heat of mixture;
D,	binary diffusion coefficient;
F_1, F_2,	gradient and curvature of atom mass-fraction profile at the wall;
G_1,	defined by equation (3.16);
G_2,	defined by equation (3.17);
G_3,	defined by equation (3.18);
h,	enthalpy;
H,	h/h_δ;
h_t,	total enthalpy, $h_t = h + u^2/2$;
K_c,	equilibrium constant;
K_w,	specific rate coefficient for surface reaction;
k_f,	specific dissociation rate coefficient;
k_b,	specific recombination rate coefficient;
Le,	Lewis number;
M,	molecular weight;
Ma,	Mach-number;
$\dot{m}_A$,	production rate of atoms per unit volume;
n_b,	exponent in equation (2.10);
n_f,	exponent in equation (2.9);
p,	static pressure;
p_D,	characteristic dissociation pressure;
Pr,	Prandtl number;
q,	energy flux;
R,	individual gas constant for molecular component;
T,	absolute temperature;
T_D,	characteristic dissociation temperature;
u, v,	x- and y-components of velocity;
U,	u/u_δ;
X,	catalytic body;
x, y,	co-ordinates parallel and normal to the plate;
Greek symbols	
α,	atom mass-fraction;
Δ,	defined by equation (3.26);
δ,	boundary layer thickness;
δ_α,	diffusion thickness;

δ_u, momentum loss thickness;
η, y/δ;
θ, T/T_δ;
κ, isentropic exponent;
λ, thermal conductivity of mixture;
μ, dynamic viscosity of mixture;
ρ, mass density of mixture;
ρ_D, characteristic dissociation density;
τ, shear stress, $\tau = \mu\, \partial u/\partial y$;
ω, exponent in equation (2.27).

Subscripts
A, denotes atom;
M, denotes molecule;
w, denotes wall conditions;
δ, denotes conditions at outer edge of boundary layer;
1, denotes atom A as catalytic body;
2, denotes molecule A_2 as catalytic body;
*, denotes equilibrium conditions.

1. INTRODUCTION

THE PROBLEM of calculating chemically reacting nonequilibrium boundary layers has a physical and a mathematical aspect. The physical problem is to describe the homogeneous reactions in the gas phase as well as the heterogeneous reactions at the wall and to find good approximations for the transport coefficients. For a binary mixture those questions can be answered sufficiently accurate. On the other hand the mathematical problem is to solve a set of strongly coupled partial differential equations. Because of these difficulties only special cases have been reported in the literature, see e.g. the comprehensive article of Chung [1]. The various cases of nonequilibrium surface reactions are studied assuming that the gas phase reaction is frozen. On the other hand the nonequilibrium gas phase reaction is considered for surfaces either nonreacting or in equilibrium.

About the first problem, viz. the frozen boundary layer with nonequilibrium surface reaction, the reader will find a lot of references in the article by Hayday and McGraw [2].

Chung and Anderson [3] have been first to calculate a flat plate boundary layer with nonequilibrium gas phase reaction using an integral method of the Pohlhausen-type. They assumed the wall to be adiabatic and non-catalytic. The first calculation of a non-equilibrium boundary layer using a finite difference-method has been performed by Blottner [4]. He treated the same example as Chung and Anderson did and in addition considered the case of a strongly cooled catalytic wall. The last example has been treated also by Pallone, Moore and Erdos [5] who employed an integral method of the Dorodnitsyn-type. Further articles are cited in [1].

Recently Peters [6] as well as the author [7] have studied the general problem of a flat plate boundary layer with nonequilibrium gas phase reaction and arbitrary heterogeneous surface reaction. This was done by Peters with a Hermitian difference-method and by the author with an integral-method of the Pohlhausen-type related to that of Chung and Anderson developed for the special case of an adiabatic and non-catalytic wall.

After a short description of the cited integral method [7] the influence of the catalytic activity of the wall on the characteristic boundary layer profiles and on the heat transfer will be discussed in an example.

2. BASIC EQUATIONS

The appropriate boundary layer equations neglecting thermal diffusion are

$$\frac{\partial}{\partial x}(\rho u) + \frac{\partial}{\partial y}(\rho v) = 0 \qquad (2.1)$$

$$\rho u \frac{\partial \alpha}{\partial x} + \rho v \frac{\partial \alpha}{\partial y} = \frac{\partial}{\partial y}\left(\rho D \frac{\partial \alpha}{\partial y}\right) + \dot{m}_A \qquad (2.2)$$

$$\rho u \frac{\partial u}{\partial x} + \rho v \frac{\partial u}{\partial y} = \frac{\partial}{\partial y}\left(\mu \frac{\partial u}{\partial y}\right) \qquad (2.3)$$

$$\rho u \frac{\partial h_t}{\partial x} + \rho v \frac{\partial h_t}{\partial y} = \frac{\partial}{\partial y}(u\tau - q). \qquad (2.4)$$

Here

$$\alpha = \frac{\rho_A}{\rho} \tag{2.5}$$

is the degree of dissociation or atom mass-fraction. Equations (2.1), (2.3) and (2.4) are the well known overall continuity equation, the momentum equation and the energy equation written with the total enthalpy h_t. The energy flux q is due to a conduction and a diffusion term, viz.

$$-q = \lambda \frac{\partial T}{\partial y} + \rho D (h_A - h_M) \frac{\partial \alpha}{\partial y}. \tag{2.6}$$

Equation (2.2) is the partial continuity equation for the atoms, often called diffusion equation. The source term $\dot{m}_A$ is the mass rate of formation of atoms per unit volume due to homogeneous chemical reaction. Here we consider the dissociation—recombination reaction

$$A_2 + X \underset{k_b}{\overset{k_f}{\rightleftharpoons}} 2A + X. \tag{2.7}$$

From chemical kinetics the production term $\dot{m}_A$ is given by

$$\dot{m}_A (\rho, T, \alpha) = \frac{\rho^2}{M_A} \left[(1 - \alpha) \left(k_{f1} \alpha + k_{f2} \frac{1 - \alpha}{2} \right) - \frac{2 \rho \alpha^2}{M_A} \left(k_{b1} \alpha + k_{b2} \frac{1 - \alpha}{2} \right) \right], \tag{2.8}$$

see [8]. The reaction rate constants k_f and k_b for the forward (dissociation) and backward (recombination) reaction can be written as

$$k_f(T) = C_f \, T^{n_f} \exp\left(-\frac{T_D}{T} \right) \tag{2.9}$$

$$k_b(T) = C_b \, T^{n_b}, \tag{2.10}$$

where k_b is related to k_f through the equilibrium constant K_c:

$$K_c = \frac{k_f}{k_b}. \tag{2.11}$$

The constants C_f, n_f, C_b and n_b depend on the special reaction considered and on the catalytic body X, which for the binary mixture considered can be an atom A (Index 1) or a molecule A_2 (Index 2).

Further the thermal and caloric equation of state are needed. The mixture is assumed to behave as a Lighthill gas, so that we have

$$p = (1 + \alpha) \rho R T \tag{2.12}$$

$$h = \left[4 + \alpha \left(1 + \frac{T_D}{T} \right) \right] R T. \tag{2.13}$$

Following [1] the boundary conditions of the set of equations (2.1)–(2.4) are at the wall ($y = 0$):

$$u(x, 0) = v(x, 0) = 0 \tag{2.14}$$

$$T(x, 0) = T_w(x) \tag{2.15a}$$

$$q(x, 0) = q_w(x) = -\left[\lambda \frac{\partial T}{\partial y} + \rho D (h_A - h_M) \frac{\partial \alpha}{\partial y} \right]_w \tag{2.15b}$$

$$\left(\rho D \frac{\partial \alpha}{\partial y} \right)_w = K_w \left(\rho \frac{\alpha - \alpha^*}{1 - \alpha^*} \right)_w \qquad \text{for } K_w \neq \infty \tag{2.16a}$$

$$\alpha(x, 0) = \alpha_w(x) = \alpha_w^*(x) \qquad \text{for } K_w \to \infty \tag{2.16b}$$

and at the outer edge of the boundary layer ($y = \delta$):

$$\begin{aligned} u(x, \delta) &= u_\delta(x) = \text{constant} \\ T(x, \delta) &= T_\delta(x) = \text{constant} \\ \alpha(x, \delta) &= \alpha_\delta(x) = \text{constant}. \end{aligned} \tag{2.17}$$

For the energy equation (2.4) the wall temperature $T_w(x)$ or the wall heat flux $q_w(x)$ must be given. The diffusion equation (2.2) also has two alternative boundary conditions. Equation (2.16a) describes the relation between the diffusion of atoms towards the wall and the production of molecules due to the heterogeneous recombination reaction at the wall, this is usually known to be a first-order reaction. The reaction rate coefficient K_w of the heterogeneous wall reaction depends on the surface material as well as on the gaseous reactant and the surface temperature. In the limiting case of a catalytic wall ($K_w \to \infty$) the atom mass-fraction at the wall is equal to its equilibrium value, then equation (2.16b) holds. For a partially or non-catalytic wall ($K_w \neq \infty$) equation (2.16a) holds; then the unknown atom mass fraction at the wall is coupled with its unknown gradient at the wall. If the wall is strongly cooled so that $\alpha_w^* = 0$ the right hand side of equation (2.16a) becomes $K_w(\rho\alpha)_w$. The equilibrium atom mass-fraction α^* follows for the Lighthill gas from

$$\alpha^*(T, p) = \frac{1}{\sqrt{\left[1 + \frac{p}{p_D} \cdot \frac{T_D}{T} \exp\left(\frac{T_D}{T}\right)\right]}}. \quad (2.18)$$

It is useful to introduce into the energy equation (2.4) the Prandtl- and Lewis-number

$$Pr = \frac{\mu \bar{c}_p}{\lambda} \quad (2.19)$$

$$Le = \frac{\rho D \bar{c}_p}{\lambda}. \quad (2.20)$$

The frozen specific heat $\bar{c}_p$ for the Lighthill gas is

$$\bar{c}_p = (4 + \alpha) R. \quad (2.21)$$

For most gases of interest Pr and Le are close to unity. Assuming $Pr = Le = 1$ one obtains for the energy equation

$$\rho u \frac{\partial h_t}{\partial x} + \rho v \frac{\partial h_t}{\partial y} = \frac{\partial}{\partial y}\left(\mu \frac{\partial h_t}{\partial y}\right). \quad (2.22)$$

Now the well known Crocco relationship between enthalpy and velocity field

$$H \equiv \frac{h}{h_\delta} = 1 + (H_w - 1)(1 - U) + \frac{u_\delta^2}{2h_\delta} U(1 - U) \quad (2.23)$$

holds, when the further assumption $H_w =$ constant is made. Equation (2.23) is approximately valid also for variable wall enthalpy.

In the following we are going to assume that the atom mass-fraction at the outer edge of the boundary layer will be zero. This assumption which is not necessary, see [7], but simplifies the following relations, yields $u_\delta^2/2h_\delta = (\kappa - 1) Ma_\delta{}^2/2$ for $\alpha_\delta = 0$.

Instead of H_w the ratio $\theta_w \equiv T_w/T_\delta$ is commonly used as heat transfer parameter. From equations (2.12) and (2.13) one obtains

$$\frac{\rho}{\rho_\delta} = \frac{1}{\theta(1 + \alpha)} = \frac{\rho}{\rho_\delta}(\theta, \alpha) \quad (2.24)$$

$$\theta \equiv \frac{T}{T_\delta} = \frac{4H - \alpha\, T_D/T_\delta}{4 + \alpha} = \theta(H, \alpha). \quad (2.25)$$

Introducing θ_w instead of H_w equation (2.23) leads to

$$H = 1 + \left[\theta_w \frac{4 + \alpha_w}{4} + \frac{\alpha_w T_D}{4T_\delta} - 1\right](1 - U) + \frac{\kappa - 1}{2} Ma_\delta^2\, U(1 - U) = H(U, \alpha_w). \quad (2.26)$$

The transport coefficients μ, λ and D must be known. However because of $Pr = Le = 1$ only one relation is necessary. Approximately this one is

$$\frac{\mu}{\mu_\delta} = \theta^\omega; \qquad 0 \leqslant \omega \leqslant 1. \quad (2.27)$$

3. INTEGRAL METHOD

Using the coupling relation (2.26) the velocity and atom mass fraction profiles are unknown. The temperature and density profiles will be found from equations (2.24)–(2.26). The velocity profile can be assumed to be given as

$$U(\eta) = 2\eta - 2\eta^3 + \eta^4. \quad (3.1)$$

Then only the atom mass-fraction profile remains unknown. It shall be approximated by the fifth degree profile

$$\alpha(x, \eta) = \sum_{i=0}^{5} a_i(x)\eta^i \quad (3.2)$$

as Chung and Anderson [3] did. The six coefficients $a_i(x)$ of the above polynomial are determined by satisfying the following boundary conditions. At the wall ($\eta = 0$) we have

$$\alpha(x, 0) = \alpha_w(x) \tag{3.3}$$

$$\left(\frac{\partial\alpha}{\partial\eta}\right)_w = \frac{\delta\,\rho_\delta u_\delta}{\mu_\delta} \cdot \frac{K_w}{u_\delta} \cdot \frac{1}{\theta_w{}^{1+\omega}(1+\alpha_w)} \left(\frac{\alpha - \alpha^*}{1 - \alpha^*}\right)_w$$

$$\equiv F_1(\delta, \alpha_w) \qquad \text{for } K_w \neq \infty \tag{3.4a}$$

$$\alpha_w(x) = \alpha_w{}^*(x) \quad \text{for } K_w \to \infty \tag{3.4b}$$

$$\left(\frac{\partial^2\alpha}{\partial\eta^2}\right)_w = -\frac{\delta^2 \dot{m}_{AW}}{\mu_\delta \theta_w^\omega} - \frac{1}{\theta_w \omega}\left(\frac{\partial\mu/\mu_\delta}{\partial\eta}\right)_w \left(\frac{\partial\alpha}{\partial\eta}\right)_w$$

$$\equiv F_2(\delta, \alpha_w). \tag{3.5}$$

Equation (3.4a) follows from the boundary condition (2.16a). Chung and Anderson considered the special case $K_w = 0$, for which $(\partial\alpha/\partial\eta)_w = 0$. If the wall is catalytic ($K_w \to \infty$), the boundary condition (2.16a) or (3.4a) respectively must be replaced by equation (2.16b) and equation (3.4b) holds. The relation (3.5) is obtained from the diffusion equation (2.2) written at the wall. The second term on the right hand side is zero. This follows from the compatibility condition of the momentum equation (2.3) and the given velocity profile (3.1).

At the outer edge of the boundary layer ($\eta = 1$) we have

$$\alpha(x, \delta) = \alpha_\delta = 0 \tag{3.6}$$

$$\left(\frac{\partial\alpha}{\partial\eta}\right)_\delta = 0 \tag{3.7}$$

$$\left(\frac{\partial^2\alpha}{\partial\eta^2}\right)_\delta = -\frac{\delta^2 \dot{m}_{A\delta}}{\mu_\delta} = 0. \tag{3.8}$$

The relation (3.8) follows from the diffusion equation (2.2). It is equal to zero because of $m_{A\delta} = 0$.

From equations (3.3)–(3.8) we get the following relations for the six coefficients $a_i(x)$:

$$\begin{aligned} a_0 &= \alpha_w \\ a_1 &= F_1 \\ a_2 &= \tfrac{1}{2} F_2 \\ a_3 &= -10\,\alpha_w - 6F_1 - \tfrac{3}{2} F_2 \\ a_4 &= 15\,\alpha_w + 8F_1 + \tfrac{3}{2} F_2 \\ a_5 &= -6\alpha_w - 3F_1 - \tfrac{1}{2} F_2. \end{aligned} \tag{3.9}$$

They are functions only of the unknown boundary layer thickness δ and the unknown atom mass-fraction α_w at the wall. The quantity α_w is a useful shape parameter for the non and partially catalytic wall ($K_w \neq \infty$). If the wall is catalytic ($K_w \to \infty$), then $\alpha_w = \alpha_w{}^*$ and the gradient $F_1 \equiv (\partial\alpha/\partial\eta)_w$ can be used as the shape parameter. In the following we restrict ourselves to the case $K_w \neq \infty$: for the case $K_w \to \infty$ see [7]. As we shall se in chapter 4, the (only theoretically existing) limit $K_w \to \infty$ can be approximated by $K_w \gg 1$.

The two unknowns δ and α_w are obtained from the integral relations for momentum and diffusion

$$\frac{d\delta_u}{dx} = \frac{\tau_w}{\rho_\delta u_\delta{}^2} \tag{3.10}$$

$$\frac{d\delta_\alpha}{dx} = -\frac{\left[\mu\left(\frac{\partial\alpha}{\partial y}\right)\right]_w}{\rho_\delta u_\delta} + \frac{\int_0^\delta \dot{m}_A\,dy}{\rho_\delta u_\delta} \tag{3.11}$$

with

$$\delta_u = \delta \int_0^1 \frac{\rho}{\rho_\delta} U(1 - U)\,d\eta \tag{3.12}$$

$$\delta_\alpha = \delta \int_0^1 \frac{\rho}{\rho_\delta} U\,\alpha\,d\eta \tag{3.13}$$

as the well known momentum loss thickness and the so called diffusion thickness. In order to solve the two ordinary differential equations (3.10) and (3.11), the quantities δ_u, δ_α, τ_w, $(\mu\,\partial\alpha/\partial y)_w$ and $\int_0^\delta \dot{m}_A\,dy$ must be expressed as functions of the two unknowns δ and α_w as well as of the given parameters of the problem.

From equations (2.24) and (2.25) we obtain

$$\delta_u = \delta \int_0^1 \frac{(4+\alpha)\,U(1-U)}{(1+\alpha)(4H - \alpha\,T_D/T_\delta)}\,d\eta = \delta_u(\delta, \alpha_w) \tag{3.14}$$

$$\delta_\alpha = \delta \int_0^1 \frac{(4+\alpha)\,U\,\alpha}{(1+\alpha)(4H - \alpha\, T_D/T_\delta)}\,\mathrm{d}\eta = \delta_\alpha\,(\delta, \alpha_w). \qquad (3.15)$$

Both integrals can be solved numerically with the coupling relationship (2.26) and the trial solutions (3.1) and (3.2). Using equation (3.1) the wall shear stress is given by

$$\frac{\tau_w}{\rho_\delta u_\delta^2} = \frac{2\mu_\delta \theta_w^{\,\omega}}{\rho_\delta u_\delta\, \delta} \equiv G_1(\delta). \qquad (3.16)$$

Furthermore we find

$$\frac{(\mu\partial\alpha/\partial y)_w}{\rho_\delta u_\delta} = \frac{K_w}{u_\delta}\cdot\frac{1}{\theta_w(1+\alpha_w)}\left(\frac{\alpha-\alpha^*}{1-\alpha^*}\right)_w \equiv G_2(\alpha_w). \qquad (3.17)$$

The integral relation

$$\frac{\delta}{\rho_\delta u_\delta}\int_0^1 \dot{m}_A\,\mathrm{d}\eta \equiv G_3\,(\delta, \alpha_w) \qquad (3.18)$$

can be obtained numerically with the production term given by equation (2.8). For the equations (3.10) and (3.11) we can write in short hand

$$\frac{\mathrm{d}\delta_u\,(\delta, \alpha_w)}{\mathrm{d}x} = G_1\,(\delta) \qquad (3.19)$$

$$\frac{\mathrm{d}\delta_\alpha\,(\delta, \alpha_w)}{\mathrm{d}x} = -\,G_2(\alpha_w) + G_3\,(\delta, \alpha_w). \qquad (3.20)$$

The quantities δ_u, δ_α, G_1, G_2 and G_3 depend on the two unknowns $\delta(x)$ and $\alpha_w(x)$ as well as on the given parameters of the problem. At the outer edge of the boundary layer Ma_δ, T_δ and p_δ are given and α_δ is assumed zero. At the wall the catalytic activity K_w and the wall temperature T_w or alternatively the wall heat flux q_w are given. If q_w is known a relation between T_w and q_w is obtained from boundary condition (2.15b). By aid of the equations (2.21) and (2.25) and with $Pr = Le = 1$ we get

$$\frac{-\,q_w\delta}{RT_\delta\mu_\delta\theta_w^{\,\omega}} = (4+\alpha_w)\left(\frac{\partial\theta}{\partial\eta}\right)_w + \left(\theta_w + \frac{T_D}{T_\delta}\right)\left(\frac{\partial\alpha}{\partial\eta}\right)_w = 4\left(\frac{\partial H}{\partial\eta}\right)_w. \qquad (3.21)$$

The enthalpy gradient at the wall is obtained from equations (2.26) and (3.1) leading to

$$\frac{-\,q_w\delta}{2RT_\delta\mu_\delta\theta_w^{\omega}} = 4\left(1 + \frac{\kappa-1}{2}Ma_\delta^2 - \theta_w\right) - \alpha_w(\theta_w + T_D/T_\delta). \qquad (3.22)$$

This is a relation between the wall heat flux q_w, the wall temperature θ_w and the two unknowns δ and α_w. For the special case of an adiabatic wall it follows

$$\theta_w(q_w = 0) = \frac{1}{4+\alpha_w}\left[4\left(1 + \frac{\kappa-1}{2}Ma_\delta^2\right) - \alpha_w T_D/T_\delta\right] = \theta_w(\alpha_w) \qquad (3.23)$$

In order to solve the two ordinary differential equations (3.19) and (3.20) they are transformed into

$$\frac{\mathrm{d}\delta}{\mathrm{d}x} = \frac{1}{\Delta}\left[G_1\left(\frac{\partial\delta_\alpha}{\partial\alpha_w}\right)_\delta + (G_2 - G_3)\left(\frac{\partial\delta_u}{\partial\alpha_w}\right)_\delta\right] \qquad (3.24)$$

$$\frac{\mathrm{d}\alpha_w}{\mathrm{d}x} = -\frac{1}{\Delta}\left[G_1\left(\frac{\partial\delta_\alpha}{\partial\delta}\right)_{\alpha_w} + (G_2 - G_3)\left(\frac{\partial\delta_u}{\partial\delta}\right)_{\alpha_w}\right] \qquad (3.25)$$

with

$$\Delta \equiv \left(\frac{\partial\delta_u}{\partial\delta}\right)_{\alpha_w}\left(\frac{\partial\delta_\alpha}{\partial\alpha_w}\right)_\delta - \left(\frac{\partial\delta_u}{\partial\alpha_w}\right)_\delta\left(\frac{\partial\delta_\alpha}{\partial\delta}\right)_{\alpha_w} = \Delta\,(\delta, \alpha_w). \qquad (3.26)$$

The partial derivatives of δ_u and δ_α with respect to δ and α_w are given in the appendix as functions of δ and α_w. The integration of the equations (3.24) and (3.25) starts just behind the leading edge at $x = x_0$ (here $x_0 = 1$ mm is chosen). There the initial condition for the shape parameter is

$$\alpha_w(x_0) = \alpha_\delta(x_0) = 0. \qquad (3.27)$$

The initial condition for the boundary layer thickness follows from the integral relation of momentum (3.19). Because of $\alpha(x_0, \eta) = 0$ the quantity δ_u/δ, equation (3.14), is constant and the integration of equation (3.19) leads to

$$\delta(x_0) = 2 \sqrt{\left(\frac{\mu_\delta \theta_w{}^\omega x_0}{\rho_\delta u_\delta \delta_u/\delta}\right)}. \qquad (3.28)$$

With given initial conditions the set of equations (3.24) and (3.25) is solved numerically by a Runge–Kutta procedure. When the quantities $\delta(x)$ and $\alpha_w(x)$ are known, the atom mass-fraction profile is given by equation (3.2) and the enthalpy, temperature and density profiles are obtained by the aid of equations (2.24)–(2.26) and (3.1) respectively.

At least for the wall heat flux q_w an analytic expression can be derived. It follows from equation (3.22) as

$$\frac{-q_w}{\rho_\delta u_\delta h_\delta} = 2\theta_w{}^\omega \frac{\mu_\delta}{\rho_\delta u_\delta \delta}\left[1 + \frac{\kappa - 1}{2} Ma_\delta^2 - \theta_w - \frac{\alpha_w}{4}\left(\theta_w + \frac{T_D}{T_\delta}\right)\right]. \qquad (3.29)$$

4. RESULTS AND DISCUSSION

Results obtained by the integral method presented in this paper have been compared with two special examples given in the literature, see [7]. The first one was that of Chung and Anderson [3], who treated an adiabatic and non catalytic wall by an integral method, and the second one that of Blottner [4], who treated a strongly cooled and catalytic wall by a finite difference method. In both examples good agreement is found.

The most interesting problem is that of arbitrary catalytic activity at the wall. Then the full boundary condition (2.16a), which couples the atom mass-fraction and its gradient at the wall, holds. Such an example has been recently calculated by Peters [6] by a Hermitian difference method. He used the following data

$$\left.\begin{aligned} T_\delta &= 218^\circ\,\mathrm{K} \\ p_\delta &= 1{\cdot}207\,.\,10^{-2}\,\mathrm{atm} \end{aligned}\right\}\ \text{corresponding to 100 000 ft altitude}$$

$$Ma_\delta = 23{\cdot}8$$

$$\theta_w = 3.$$

The fluid may be oxygen with the characteristic data

$$T_D = 59\,500^\circ\mathrm{K}$$

$$p_D = 2{\cdot}3\,.\,10^7\,\mathrm{atm}$$

$$M_A \doteq 16\,\mathrm{g/mol}.$$

The viscosity of molecular oxygen is $\mu_\delta = 1{\cdot}59\,.\,10^{-5}$ kg/m·s at $T_\delta = 218^\circ$K. For the relationship (2.27) $\omega = 0{\cdot}7$ is chosen. The reaction rate constants in the production term (2.8) are given by Camac and Vaughan and by Byron, see [7, 8].

The reaction rate constant K_w of the heterogeneous surface reaction is taken as a variable parameter. Realistic values of K_w lie between about 0·05 m/sec for Pyrex (nearly non catalytic) and about 50 m/s for silver (nearly catalytic), see [2]. In the following the influence of the wall catalycity on the boundary layer profiles is discussed.

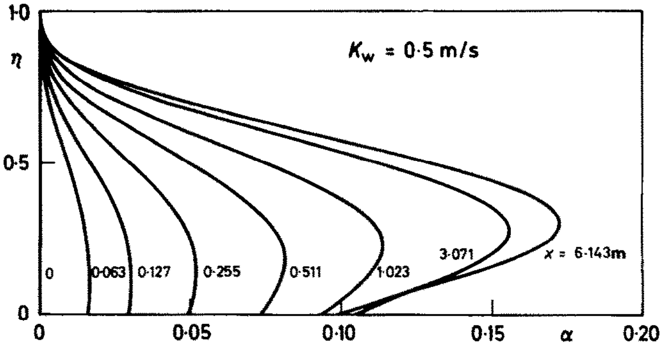

FIG. 1. Atom mass-fraction profiles for a partially catalytic wall.

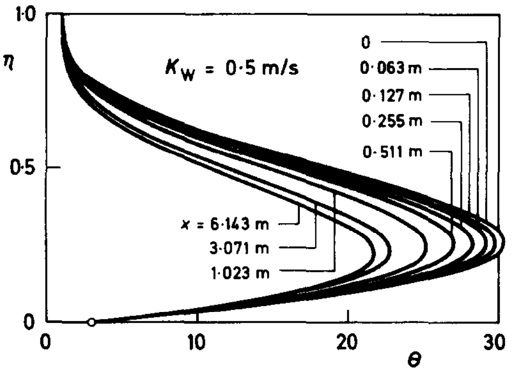

FIG. 2. Temperature profiles for a partially catalytic wall.

Figure 1 shows the development of the atom mass-fraction profile for a partially catalytic wall ($K_w = 0{\cdot}5$ m/s) and Fig. 2 shows the temperature profiles. At the beginning of the plate the dissociation reaction is dominating, the atom mass-fraction profile grows rapidly and the temperature profile becomes more slender with increasing distance from the leading edge.

Figures 3 and 4 show the profiles of interest at a constant distance ($x = 0{\cdot}511$ m) but for different values of the catalytic activity of the wall. High values of K_w mean high assistance of the gas phase recombination near the wall; for

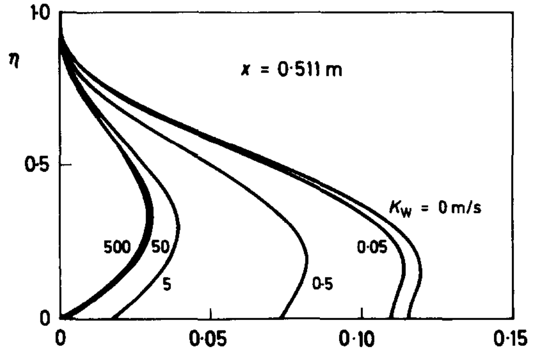

FIG. 3. Atom mass-fraction profiles for various values of K_w.

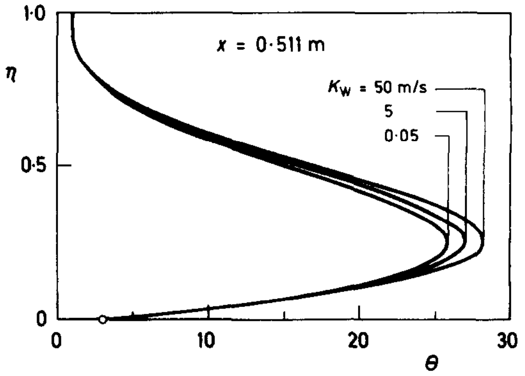

FIG. 4. Temperature profiles for various values of K_w.

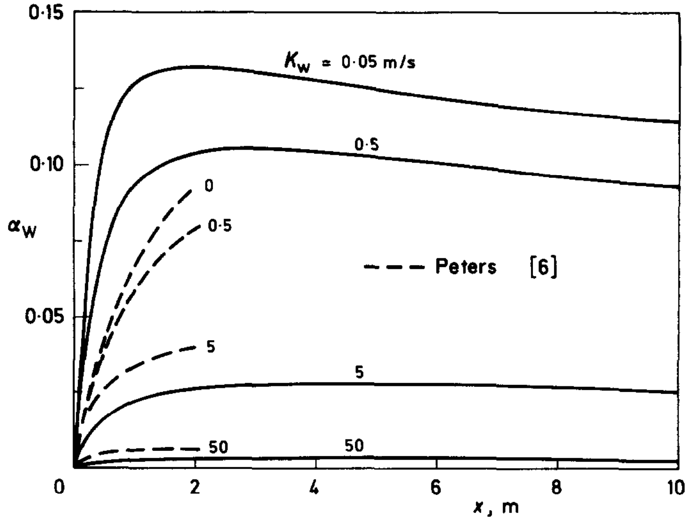

FIG. 5. Atom mass-fraction at the wall for various values of K_w.

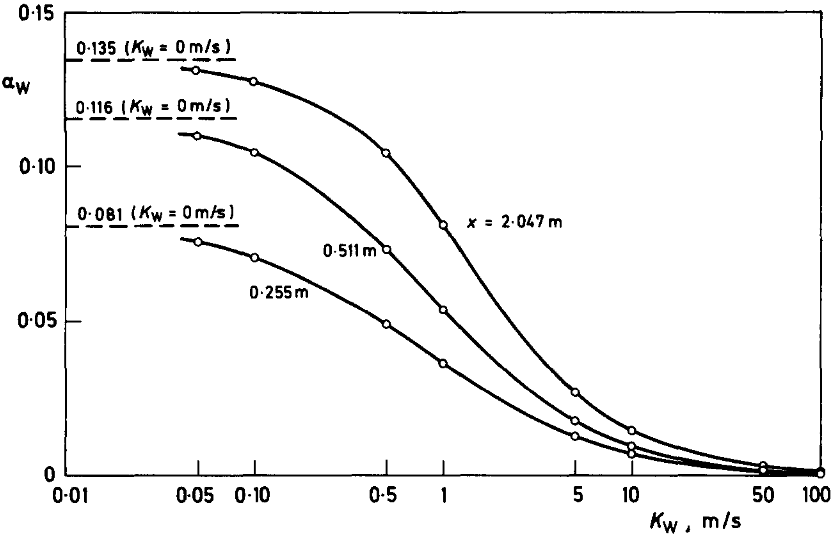

FIG. 6. Atom mass-fraction at the wall at different distances.

$K_w \gg 1$ the atom mass-fraction at the wall changes into its equilibrium value which is zero in our case of the strongly cooled wall. For the non catalytic wall ($K_w = 0$) on the other hand the atom mass-fraction at the wall has a maximum; then there is no assistance of recombination by the wall.

Figure 5 shows the development of the atom mass-fraction at the wall for various values of K_w compared with results of Peters [6]. Peters used more complete relations for the transport properties and the caloric equation of state. For large distances all curves must reach asymptotically the equilibrium value $\alpha_w^* = 0$. Figure 6

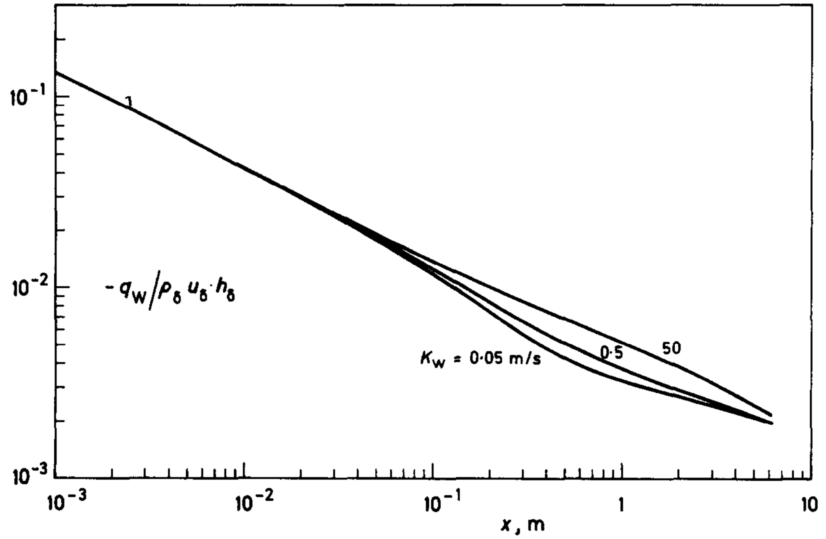

FIG. 7. Wall heat flux for various values of K_w.

gives the same information as Fig. 5, the circles indicate calculated values. From Fig. 6 it is evident, that the wall is nearly non catalytic for values $K_w < 0{\cdot}05$ m/s and nearly catalytic for values $K_w > 50$ m/s.

Finally Fig. 7 shows the wall heat flux for a nearly non catalytic ($K_w = 0{\cdot}05$ m/s), partially catalytic ($K_w = 0{\cdot}05$ m/s) and nearly catalytic ($K_w = 50$ m/s) wall. The heat flux, equation (2.6), depends on two terms. The conduction term is proportional to the temperature gradient and the diffusion term is proportional to the gradient of the atom mass-fraction. Near the leading edge there is no influence of the wall catalycity on the wall heat flux, because the diffusion term is negligible there. At large distances the boundary layer is near its equilibrium state; there the influence of the wall catalycity vanishes too. In general the wall heat flux can be reduced when a surface material with low catalytic activity is chosen.

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APPENDIX

From equations (3.14) and (3.15) we have

$$\delta_u(\delta, \alpha_w) = \delta \int_0^1 f(\eta, \delta, \alpha_w)\, d\eta$$

$$\delta_\alpha(\delta, \alpha_w) = \delta \int_0^1 g(\eta, \delta, \alpha_w)\, d\eta$$

where

$$f \equiv \frac{(4 + \alpha)U(1 - U)}{(1 + \alpha)(4H - \alpha T_D/T_\delta)}$$

$$g \equiv \frac{(4 + \alpha)U\alpha}{(1 + \alpha)(4H - \alpha T_D/T_\delta)}.$$

Thus

$$\left(\frac{\partial \delta_u}{\partial \delta}\right)_{\alpha_w} \equiv \frac{\partial \delta_u}{\partial \delta} = \delta \int_0^1 \frac{\partial}{\partial \delta} f(\eta, \delta, \alpha_w)\, d\eta + \frac{\delta_u}{\delta}$$

$$\left(\frac{\partial \delta_u}{\partial \alpha_w}\right)_\delta \equiv \frac{\partial \delta_u}{\partial \alpha_w} = \delta \int_0^1 \frac{\partial}{\partial \alpha_w} f(\eta, \delta, \alpha_w)\, d\eta$$

Table 1

$\frac{\partial U}{\partial \delta}$	0
$\frac{\partial H}{\partial \delta}$	0
$\frac{\partial \alpha}{\partial \delta}$	$\frac{\partial a_0}{\partial \delta} + \frac{\partial a_1}{\partial \delta}\eta + \frac{\partial a_2}{\partial \delta}\eta^2 + \frac{\partial a_3}{\partial \delta}\eta^3 + \frac{\partial a_4}{\partial \delta}\eta^4 + \frac{\partial a_5}{\partial \delta}\eta^5$
$\frac{\partial a_0}{\partial \delta}$	0
$\frac{\partial a_1}{\partial \delta}$	$\frac{\partial F_1}{\partial \delta}$
$\frac{\partial a_2}{\partial \delta}$	$\frac{1}{2}\frac{\partial F_2}{\partial \delta}$
$\frac{\partial a_3}{\partial \delta}$	$-6\frac{\partial F_1}{\partial \delta} - \frac{3}{2}\frac{\partial F_2}{\partial \delta}$
$\frac{\partial a_4}{\partial \delta}$	$8\frac{\partial F_1}{\partial \delta} + \frac{3}{2}\frac{\partial F_2}{\partial \delta}$
$\frac{\partial a_5}{\partial \delta}$	$-3\frac{\partial F_1}{\partial \delta} - \frac{1}{2}\frac{\partial F_2}{\partial \delta}$
$\frac{\partial F_1}{\partial \delta}$	$\frac{F_1}{\delta}$
$\frac{\partial F_2}{\partial \delta}$	$2\frac{F_2}{\delta}$

Table 2

		θ_w = const.; b.c. (2.15a)	$q_w = 0$; b. c. (2.15b) $\theta_w = \theta_w(\alpha_w)$ equation (3.23)
	$\frac{\partial U}{\partial \alpha_w}$	0	
	$\frac{\partial H}{\partial \alpha_w}$	$\frac{1}{4}\left[(4+\alpha_w)\frac{\partial \theta_w}{\partial \alpha_w} + \theta_w + \frac{T_D}{T_\delta}\right]$	
with	$\frac{\partial \theta_w}{\partial \alpha_w}$	0	$-\frac{\theta_w + T_D/T_\delta}{4+\alpha_w}$
then	$\frac{\partial H}{\partial \alpha_w}$	$\frac{1}{4}(\theta_w + T_D/T_\delta)$	0
	$\frac{\partial \alpha}{\partial \alpha_w}$	$\frac{\partial a_0}{\partial \alpha_w} + \frac{\partial a_1}{\partial \alpha_w}\eta + \frac{\partial a_2}{\partial \alpha_w}\eta^2 + \frac{\partial a_3}{\partial \alpha_w}\eta^3 + \frac{\partial a_4}{\partial \alpha_w}\eta^4 + \frac{\partial a_5}{\partial \alpha_w}\eta^5$	
	$\frac{\partial \alpha_0}{\partial \alpha_w}$	1	
	$\frac{\partial a_1}{\partial \alpha_w}$	$\frac{\partial F_1}{\partial \alpha_w}$	
	$\frac{\partial a_2}{\partial \alpha_w}$	$\frac{1}{2}\frac{\partial F_2}{\partial \alpha_w}$	
	$\frac{\partial a_3}{\partial \alpha_w}$	$-10 - 6\frac{\partial F_1}{\partial \alpha_w} - \frac{3}{2}\frac{\partial F_2}{\partial \alpha_w}$	
	$\frac{\partial a_4}{\partial \alpha_w}$	$15 + 8\frac{\partial F_1}{\partial \alpha_w} + \frac{3}{2}\frac{\partial F_2}{\partial \alpha_w}$	
	$\frac{\partial a_5}{\partial \alpha_w}$	$-6 - 3\frac{\partial F_1}{\partial \alpha_w} - \frac{1}{2}\frac{\partial F_2}{\partial \alpha_w}$	
	$\frac{\partial F_1}{\partial \alpha_w}$	$\frac{\delta \rho_\delta u_\delta}{\mu_\delta} \cdot \frac{K_w}{u_\delta}\frac{1}{(1+\alpha_w)^2}\left\{\left(\frac{1+\alpha}{1+\alpha^*}\right)_w - \left(\frac{\alpha-\alpha^*}{1-\alpha^*}\right)_w \left[1 + (1+\alpha_w)\frac{1+\omega}{\theta_w} \cdot \frac{\partial \theta_w}{\partial \alpha_w}\right]\right\}$	
	$\frac{\partial F_2}{\partial \alpha_w}$	$-\frac{\delta^2}{\mu_\delta \theta_w{}^\omega}\left\{\frac{\partial \dot{m}_{AW}}{\partial \alpha_w} - \frac{\dot{m}_{AW} \cdot \omega}{\theta_w} \cdot \frac{\partial \theta_w}{\partial \alpha_w}\right\}$	
	$\frac{\partial \theta_w}{\partial \alpha_w}$	see above	
	$\frac{\partial \dot{m}_{AW}}{\partial \alpha_w}$	$\frac{\rho_\delta{}^2}{M_A \theta_w{}^2 (1+\alpha_w)^2}\left[k_{f1w}\left\{\frac{\alpha_w}{\theta_w} \cdot \frac{\partial \theta_w}{\partial \alpha_w}\left[(1-\alpha_w)\left(n_{f1} + \frac{T_D}{\theta_w T_\delta}\right) - 2(1-\alpha_w)\right] + \frac{1-3\alpha_w}{1+\alpha_w}\right\}\right.$ $+ k_{f2w}\left[\frac{(1-\alpha_w)^2}{2\theta_w} \cdot \frac{\partial \theta_w}{\partial \alpha_w}\left(n_{f2} - 2 + \frac{T_D}{\theta_w T_\delta}\right) - 2\frac{1-\alpha_w}{1+\alpha_w}\right]$ $-\frac{k_{b1w} 2\rho_\delta \alpha_w{}^2}{M_A \theta_w (1+\alpha_w)}\left[\frac{\alpha_w}{\theta_w} \cdot \frac{\partial \theta_w}{\partial \alpha_w}(n_{b1} - 3) + \frac{3}{1+\alpha_w}\right]$ $\left.-\frac{k_{b2w} \rho_\delta \alpha_w}{M_A \theta_w (1+\alpha_w)}\left[\frac{(1-\alpha_w)\alpha_w}{\theta_w} \cdot \frac{\partial \theta_w}{\partial \alpha_w}(n_{b2} - 3) + \frac{2(1-2\alpha_w)}{1+\alpha_w}\right]\right]$	

$$\left(\frac{\partial \delta_\alpha}{\partial \delta}\right)_{\alpha_w} \equiv \frac{\partial \delta_\alpha}{\partial \delta} = \delta \int_0^1 \frac{\partial}{\partial \delta} g(\eta, \delta, \alpha_w)\,\mathrm{d}\eta + \frac{\delta_\alpha}{\delta}$$

$$\left(\frac{\partial \delta_\alpha}{\partial \alpha_w}\right)_{\delta} \equiv \frac{\partial \delta_\alpha}{\partial \alpha_w} = \delta \int_0^1 \frac{\partial}{\partial \alpha_w} g(\eta, \delta, \alpha_w)\,\mathrm{d}\eta$$

with

$$\frac{\partial f}{\partial \delta} = f\,\frac{\partial \alpha}{\partial \delta}\left[\frac{T_D/T_\delta}{4H - \alpha T_D/T_\delta} - \frac{3}{(4 + \alpha)(1 + \alpha)}\right]$$

$$\frac{\partial f}{\partial \alpha_w} = f\,\frac{\partial \alpha}{\partial \alpha_w}\left[\frac{T_D/T_\delta}{4H - \alpha T_D/T_\delta} - \frac{3}{(4 + \alpha)(1 + \alpha)}\right] - \frac{\partial H}{\partial \alpha_w}\cdot\frac{4f}{4H - \alpha T_D/T_\delta}$$

$$\frac{\partial g}{\partial \delta} = \frac{\partial \alpha}{\partial \delta}\left[\frac{U(4 + \alpha)}{(1 + \alpha)(4H - \alpha T_D/T_\delta)} - \frac{3g}{(4 + \alpha)(1 + \alpha)} + \frac{gT_D/T_\delta}{4H - \alpha T_D/T_\delta}\right]$$

$$\frac{\partial g}{\partial \alpha_w} = \frac{\partial \alpha}{\partial \alpha_w}\left[\frac{U(4 + \alpha)}{(1 + \alpha)(4H - \alpha T_D/T_\delta)} - \frac{3g}{(4 + \alpha)(1 + \alpha)} + \frac{gT_D/T_\delta}{4H - \alpha T_D/T_\delta}\right] - \frac{\partial H}{\partial \alpha_w}\,\frac{4g}{4H - \alpha T_D/T_\delta}$$

For $\partial\alpha/\partial\delta$, $\partial\alpha/\partial\alpha_w$ and $\partial H/\partial\alpha_w$ see Tables 1 and 2. Note that in the above equations we already made use of $\partial U/\partial\delta$, $\partial H/\partial\delta$ and $\partial H/\partial\alpha_w = 0$.

UNE MÉTHODE INTÉGRALE POUR UNE COUCHE LIMITE LAMINAIRE SUR PLAQUE PLANE AVEC DISSOCIATION HORS D'ÉQUILIBRE

Résumé—On utilise une méthode intégrale du type Polhausen pour calculer la couche limite de plaque plane hors d'équilibre pour un mélange binaire composé d'atomes A et de molécules A_2. L'activité catalytique de la paroi peut être choisie arbitrairement. La méthode est basée sur la relation de Crocco entre les profils d'enthalpie et de vitesse pour des nombres de Prandtl et de Lewis unitaires. Le profil de vitesse est supposé connu et une solution est obtenue pour le profil inconnu de concentration massique en atomes. Le paramètre de forme et une épaisseur de couche limite caractéristique à partir du profil de concentration massique en atomes sont obtenus à partir des relations intégrales pour la quantité de mouvement et la diffusion. On discute l'influence de l'activité catalytique de la paroi sur le développement des profils de température et de concentration massique en atomes aussi bien que sur le flux thermique pariétal.

EINE INTEGRALMETHODE FÜR LAMINARE GRENZSCHICHTEN AN DER EBENEN PLATTE MIT DISSOZIATION IM NICHTGLEICHGEWICHT.

Zusammenfassung—Es wurde eine Integralmethode vom Pohlhausen-Typ abgeleitet, um die Grenzschicht an einer ebenen Platte für ein binäres Gasgemisch, bestehend aus Atomen A und Molekülen A_2, im Nichtgleichgewicht auszurechnen. Die katalytische Aktivität der Wand kann willkürlich gewählt werden. Die Methode beruht auf der Crocco-Beziehung zwischen dem Enthalpie- und Geschwindigkeitsprofil für $Pr = 1$ und $Le = 1$. Das Geschwindigkeitsprofil wurde als bekannt vorausgesetzt. Dann wurde ein Ansatz für das unbekannte Profil des Massenanteils der Atome gemacht. Der Formparameter und die charakteristische Dicke des Profils des Massenanteils an Atomen wurde mit Integralbeziehungen für Impuls und Masse vermittelt. Der Einfluss der katalytischen Aktivität der Wand auf die Ausbildung des Temperaturprofils und des Profils des Massenanteils an Atomen und auf die Wärmestromdichte an der Wand wurde diskutiert.

ИНТЕГРАЛЬНЫЙ МЕТОД ДЛЯ НЕРАВНОВЕСНОГО ДИССОЦИИРУЮЩЕГО ЛАМИНАРНОГО ПОГРАНИЧНОГО СЛОЯ НА ПЛОСКОЙ ПЛАСТИНЕ

Аннотация—Выведен интегральный метод типа метода Польгаузена для расчёта неравновесного пограничного слоя на плоской пластине бинарной смеси, состоящей из атомов A и молекул A_2. Каталитическая ективность стенки может выбираться произвольно. Метод основан на соотношении Крокко между энтальпией и профилем скорости для чисел Прандтля и Льюиса, равных единице. Предполагается, что профиль скорости известен, и методом проб получается решение для неизвестного профиля массовой концентрации атомов. Форм-параметр и характерная толщина пограничного слоя профиля массовой концентрации атома получены из интегральных соотношений для количества движения. Рассмотрено влияние каталитической активности на развитие профиля температуры и массовой концентрации атома, а также на поток тепла на стенке.