PRODUCTION TERMS IN CHEMICALLY REACTING EQUILIBRIUM FLOWS, DISCUSSED FOR A BINARY MIXTURE LAMINAR BOUNDARY LAYER FLOW

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Abstract—For a continuously changing flow field of a binary mixture assumed to be in local chemical equilibrium, the concentration of species is uniquely determined by the law of mass-action as a function of any two independent thermodynamic variables such as temperature and pressure. This implies infinite large reaction rates leading to indefinite production rates of species. The partial continuity equation is superfluous being replaced by the law of mass-action. This partial continuity equation on the other hand can be used in connection with the other flow equations as well as the law of mass-action to determine this production rate in equilibrium state. Further on, it is shown that for a flat plate boundary layer flow under certain assumptions the profile $m_A^* \delta^2 / \mu$ is a similar profile which can be put into a nearly closed analytical form. In this expression, m_A^* is the production rate of species A, δ the boundary layer thickness and μ the viscosity. This equilibrium profile as well as the equilibrium profiles of concentration and temperature are compared with corresponding nonequilibrium profiles. The equilibrium profiles appear to be limiting profiles approached asymptotically at infinite distances.

NOMENCLATURE

A, atom;

A_2, molecule;

$\bar{c}_p$, frozen specific heat of mixture;

D, binary diffusion coefficient;

h, enthalpy;

H, h/h_δ;

h_t, total enthalpy, $h_t = h + u^2/2$;

$\vec{J}_A$, diffusion flux of atoms;

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;

m_A, production rate of atoms per unit volume;

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, coordinates parallel and normal to the plate.

Greek symbols

α, atom mass-fraction;

Γ_A, m_A/ρ;

δ_2, momentum loss thickness;

δ, boundary layer thickness;

η, y/δ;

θ, T/T_δ;

λ, thermal conductivity of mixture;

μ, dynamic viscosity of mixture;

ρ, mass density of mixture;

τ, shear stress, $\tau = \mu \, \partial u/\partial y$;

τ, local relaxation time;

χ, defined by equation (2.9).

Subscripts

$A,$ denotes atom or component A resp.;
$w,$ denotes wall conditions;
$\delta,$ denotes conditions at outer edge of boundary layer;
$*,$ denotes equilibrium conditions.

1. INTRODUCTION

CHEMICALLY reacting flows are nonequilibrium flows in general. To reach chemical equilibrium all reactions require molecular collisions and hence a certain characteristic time. From the kinetic viewpoint, the chemical equilibrium state is approached asymptotically. This means that the assumption of local chemical equilibrium can never be realized exactly in a continuously changing flow field. Nevertheless in many cases the concept of equilibrium flow is a valid working approximation. This implies that the characteristic time for a chemical reaction (i.e. the relaxation time defined later) is negligible small compared to a characteristic flow time.

Evidently for the general case of a nonequilibrium flow the chemical kinetics are able to answer the question how the production terms or mass rates of formation of species are influenced by the flow variables (e.g. temperature, density or pressure and concentration). But the so-called collision theory is not able to do this in the limiting case of an equilibrium flow, because this case is unrealistic from the kinetic viewpoint.

In the following the problem determining these equilibrium production terms is discussed. It seems to be evident that the equilibrium production terms do not vanish in a continuously changing flow field, because the local thermodynamic state and therefore the equilibrium concentrations vary from point to point.

For simplicity a binary mixture is chosen for all further considerations. At the end of this article the extension to multicomponent mixtures is briefly discussed.

A fluid flow field containing two components is described by the following set of partial differential equations:

The overall continuity-equation.
the partial continuity-equation for one component,
the momentum-equation and
the energy-equation.

The unknown field variables are the velocity vector, two thermodynamic state variables (e.g. temperature and pressure) and the concentration of one component.

## 2. PARTIAL CONTINUITY EQUATION AND PRODUCTION TERM

The partial continuity-equation written for the component A is

$$\rho \frac{\mathrm{d}\alpha}{\mathrm{d}t} = - \operatorname{div} \vec{j}_A + m_A. \qquad (2.1)$$

This equation describes the total change of the concentration α which is equal to the sum of a diffusion and a production term. Here α is the mass concentration defined by

$$\alpha = \rho_A/\rho. \qquad (2.2)$$

In order to discuss the production term a special reaction is chosen. This reaction shall be the dissociation–recombination reaction of a diatomic gas A_2 (oxygen or nitrogen)

$$A_2 + X \frac{k_f(T)}{k_b(T)} 2A + X, \qquad (2.3)$$
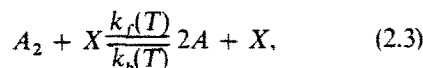
which is used too for an example below. Therein X is a catalytic body, it can be a molecule A_2 or an atom A. The reaction rate constants k_f and k_b for the forward (dissociation) and backward (recombination) reaction are semiempirical functions of the temperature. Both are related to each other by the equilibrium constant

$$K_c(T) = \frac{k_f}{k_b}. \qquad (2.4)$$

This equilibrium constant is defined by the concentrations $[\ldots]^*$ in number of moles per volume (*means equilibrium state) as follows

$$K_c(T) = \frac{[A]^{*2}}{[A_2]^*} = \frac{2\alpha^{*2}}{1 - \alpha^*} \cdot \frac{\rho}{M_A}. \qquad (2.5)$$

whereby the concentration in number of moles per volume is replaced by the atom mass-fraction α (2.2). Equation (2.5) is the so-called law of mass-action. When $K_c(T)$ is given the equilibrium concentration is known as a function of temperature and density or pressure.

For the reaction considered, equation (2.3), the chemical rate equation is given from chemical kinetics by the collision theory. Here the production of atoms in mass per unit volume and time is, see e.g. [1]:

$$m_A(\rho, T, \alpha) = \frac{\rho^2(1 + \alpha)}{M_A}\left[k_f\frac{1 - \alpha}{2} - k_b\frac{\rho}{M_A}\alpha^2\right]$$

$$= \frac{\rho^2(1 + \alpha)}{2M_A}k_f\left[1 - \alpha - \left(\frac{\alpha}{\alpha^*}\right)^2(1 - \alpha^*)\right]. \quad (2.6)$$

In the second form the reaction rate constant k_b is replaced by k_f and K_c through equation (2.4) or α^* through equation (2.5) resp. It has to be noticed that the above chemical rate equation makes no difference between the two possible catalytic bodies A_2 or A. Otherwise the rate equation would contain two different reaction rate constants k_f resp. k_b, see [1]. For the following considerations the simplified equation (2.6) can be used as well as the complete one.

In order to discuss the production term m_A for two limiting cases, "equilibrium" and "frozen flow", the diffusion term in equation (2.1) is neglected for simplicity. Then we have

$$\frac{d\alpha}{dt} = \frac{m_A}{\rho} \equiv \Gamma_A. \quad (2.7)$$

That means that to total change of concentration is only affected by the chemical reaction. Following [1] a local characteristic time τ of the rate process is defined by

$$\tau(T, p, \alpha) \equiv -\frac{1}{(\partial\Gamma_A/\partial\alpha)_{T,p}}. \quad (2.8)$$

τ is shortly called the local relaxation time. If we write

$$\Gamma_A = \frac{\chi(T, p, \alpha)}{\tau(T, p, \alpha)} \quad (2.9)$$

a second function is defined by

$$\chi(T, p, \alpha) \equiv -\frac{\Gamma_A}{(\partial\Gamma_A/\partial\alpha)_{T,p}}. \quad (2.10)$$

Generally in equation (2.9) the nominator-function χ describes the departure from the local equilibrium whereas the denominator-function τ, the local relaxation time, renders information about how fast this local equilibrium state is approached. Both values are functions of the thermodynamic state (e.g. temperature and pressure) as well as of the nonequilibrium variable α, the concentration. They depend on the reaction considered, from equation (2.6) it follows in our case

$$\tau = \frac{2M_A}{\rho(1 + \alpha)k_f[1 + 2\alpha(1 - \alpha^*)/\alpha^{*2}]} \quad (2.11)$$

$$\chi = \frac{1 - \alpha - (1 - \alpha^*)(\alpha/\alpha^*)^2}{1 + 2\alpha(1 - \alpha^*)/\alpha^{*2}}. \quad (2.12)$$

Now one notices the important fact that the local relaxation time τ and the reaction rate constant k_f (or k_b, because of $k_f \sim k_b$, see equation (2.4)) are related by $\tau \sim 1/k_f$, which generally holds.

3. EQUILIBRIUM AND FROZEN FLOW

Following [1], two limiting cases $\tau \to 0$ and $\tau \to \infty$ shall be discussed. If the relaxation time τ is vanishingly small, the reaction rate constant k_f becomes infinitely large. This follows from equation (2.11) for finite density. It is physically evident that the production term Γ_A cannot be infinitely large in a reacting and continuously changing flow field. Therefore the assumption of a finite production term Γ_A together with $\tau \to 0$ leads to the result $\chi \to 0$ from equation (2.9). If the nominator-function χ is zero it follows from equation (2.12) that the nonequilibrium concentration α must tend towards its equilibrium value α^*. Generally the statement $\chi(T, p, \alpha) = 0$ defines the equilibrium value α^* (T, p) corresponding to the law of mass-action.

We thus see that the limit $\tau \to 0$ leads to a flow

which is in local chemical equilibrium, we call it an "equilibrium flow". The quotation marks are used because actually the limit of "equilibrium flow" can never be physically realized from the kinetic viewpoint. Nevertheless, this limit is a good approximation when the reaction is very fast and the flow is very slow. The important conclusion is that the production term is indefinite in an "equilibrium flow", because of $\tau = 0$ and $\chi = 0$ in equation (2.9).

It should be noted clearly that "equilibrium flow" is essentially different from simple equilibrium in a closed system at fixed conditions. An "equilibrium flow" is in other words an open system which is locally in chemical equilibrium state. All flow variables change continuously: the equilibrium concentration α^* as well as the indefinite equilibrium production term Γ_A^* are field variables. In a closed system at fixed conditions, on the other hand, there are no changes of the variables, the equilibrium concentration is constant and the production term is zero.

If, on the other hand, the relaxation time τ is infinitely large, the reaction rate constant k_f becomes infinitely small. Therefore the production term vanishes, irrespective of the value of χ. The reaction in the flow is called a frozen reaction, shortly we speak of a "frozen flow". Here the quotation marks indicate just as in the other limit $\tau \to 0$, that a "frozen flow" can never be realized exactly from the molecular viewpoint. Nevertheless it is a good approximation if a very slow reaction takes place in high velocity fluid flow. Neglecting diffusion as in equation (2.6) the fact $\Gamma_A \equiv 0$ leads to constant concentration. Generally in a "frozen flow" the concentration is affected only by diffusion, see equation (2.1).

In the following, we are interested in the limit $\tau \to 0$, the case of "equilibrium flow". Especially the question, how the unknown equilibrium production term can be determined shall be discussed. In order to do this we go back to the system of governing partial differential equations for the fluid flow.

4. THE EQUILIBRIUM PRODUCTION TERM FOR A SPECIAL BOUNDARY LAYER FLOW

Here we restrict our discussion to the special case of a steady, laminar, plane and reacting boundary layer flow along a flat plate. The reason is that using further assumptions this this case leads to a nearly closed form solution for the equilibrium production term. The governing boundary layer equations are:

$$\frac{\partial}{\partial x}(\rho u) + \frac{\partial}{\partial y}(\rho v) = 0 \tag{4.1}$$

$$\rho u \frac{\partial \alpha}{\partial x} + \rho v \frac{\partial \alpha}{\partial y} = \frac{\partial}{\partial y}\left(\rho D \frac{\partial \alpha}{\partial y}\right) + m_A \tag{4.2}$$

$$\rho u \frac{\partial u}{\partial x} + \rho v \frac{\partial u}{\partial y} = \frac{\partial \tau}{\partial y} \tag{4.3}$$

$$\rho u \frac{\partial h_t}{\partial x} + \rho v \frac{\partial h_t}{\partial y} = \frac{\partial}{\partial y}(u\tau - q). \tag{4.4}$$

(4.1) is the overall continuity equation and (4.2) is the partial continuity equation neglecting thermal diffusion. (4.3) is the momentum equation for constant pressure and (4.4) is the energy equation written for the total enthalpy. The energy flux q is due to a conduction and a diffusion term, viz.

$$-q = \lambda \frac{\partial T}{\partial y} + \rho D (h_A - h_M) \frac{\partial \alpha}{\partial y}. \tag{4.5}$$

For given initial and boundary conditions this set of equations has to be solved for nonequilibrium flows. The source term m_A is given from chemical kinetics by an equation like (2.6). The unknown field variables are the velocity components u and v, one thermodynamic variable (h_t or h or T or ρ) and the atom mass-fraction α.

How does this set of equations change for the two limits discussed? For the "frozen flow" we have to put $m_A \equiv 0$. The convective change of concentration is only influenced by diffusion.

In the limit $\tau \to 0$, the "equilibrium flow", the reaction rates are assumed so fast that the concentration is uniquely determined by any two independent thermodynamic variables such

as pressure and temperature. For this case the partial continuity equation is superfluous, it is replaced by an algebraic equation $\alpha = \alpha^*(T, p)$, the law of mass-action. Of course the partial continuity equation remains valid for "equilibrium flows", since it is a balance-equation for the species. We cannot, however, use this equation to calculate "equilibrium flows", since the production term is indefinite as discussed above. If, on the other hand, the production term were not undetermined the set of equations would be overdetermined. We would have five equations, the fluid flow equations (4.1)–(4.4) and the law of mass-action (2.5), to calculate the four unknowns u, v, h_t (or h or T or ρ) and α^*.

The following conclusion can be drawn from this consideration: The partial continuity equation represents the equation to determine the production term of "equilibrium flows". Hence we write:

$$m_A^* = \rho u \frac{\partial \alpha^*}{\partial x} + \rho v \frac{\partial \alpha^*}{\partial y} - \frac{\partial}{\partial y}\left(\rho D \frac{\partial \alpha^*}{\partial y}\right). (4.6)$$

The equilibrium production term m_A^* therefore depends on the unknown field variables u, v, ρ and α^*. These variables are determined by the other balance equations, the overall continuity equation (4.1), the momentum equation (4.3) and the energy equation (4.4), together with the law of mass-action (2.5). This statement is not only valid for the particular flow considered above, it is generally valid for reacting "equilibrium flows" so long as a binary mixture is considered. Further below the extension to multicomponent mixtures is discussed.

Generally the set of equations (4.1), (4.3), (4.4) and (2.5) must be solved numerically if special initial and boundary conditions are given. With known values u, v, p and $\alpha^* = f(x, y)$ the equilibrium production term then follows from equation (4.6) as $m_A^*(x, y)$. By making some additional assumptions, however, we can simplify the problem considerably. At the end we then find a nearly closed form solution for a characteristic dimensionless parameter containing m_A^*.

From a thermal and a caloric equation of state we obtain relations $\rho(T, p, \alpha)$ and $h(T, p, \alpha)$. The mixture is assumed to behave as a Lighthill gas, so we have

$$p = (1 + \alpha) \rho R T \qquad (4.7)$$

$$h = [4 + \alpha(1 + T_D/T)] R T. \qquad (4.8)$$

The law of mass-action (2.5) yields the equilibrium atom mass-fraction $\alpha^*(T, p)$, here we have for the Lighthill gas

$$\alpha^* = \left[1 + \frac{p}{p_D} \frac{T_D}{T} \exp\left(\frac{T_D}{T}\right)\right]^{-\frac{1}{2}}. \qquad (4.9)$$

For "equilibrium flows" thus follows $\rho = \rho(T, p)$ and $h = h(T, p)$. Using this the variable m_A^* is a function of the velocity and temperature (or enthalpy) field alone. In the next step we eliminate the enthalpy through the velocity field by means of the Crocco-integral, which is a special solution of the energy-equation (4.4). To obtain this solution the Prandtl- and Lewis-number defined by

$$Pr = \frac{\mu \bar{c}_p}{\lambda}; \qquad Le = \frac{\rho D \bar{c}_p}{\lambda} \qquad (4.10)$$

are introduced into the energy equation ($\bar{c}_p = (4 + \alpha) R$ is the frozen specific heat of the mixture). Assuming $Pr = Le = 1$ this leads to

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

(see [2], p. 117). Now the well-known Crocco relationship between enthalpy and velocity field holds, if the further assumption of constant wall enthalpy is made:

$$H = 1 + (H_w - 1)(1 - U) + \frac{u_\delta^2}{2h_\delta} U(1 - U).$$

$$(4.11)$$

We introduced here: $H \equiv h/h_\delta$ and $U \equiv u/u_\delta$. The atom mass-fraction α^* in (4.6) is replaced by T and p, see (4.9), then the temperature is replaced by h and p, see (4.8) and (4.9), and finally the enthalpy is replaced by the velocity field, see (4.11). Then it follows from (4.6):

$$m_A^* = \left(\frac{\partial \alpha^*}{\partial T}\right)_p \left(\frac{\partial T}{\partial h}\right)_p \frac{\partial h}{\partial u} \left[\rho u \frac{\partial u}{\partial x} + \rho v \frac{\partial u}{\partial y}\right]$$

$$- \frac{\partial}{\partial y}\left[\mu \frac{\partial u}{\partial y}\left(\frac{\partial \alpha^*}{\partial T}\right)_p \left(\frac{\partial T}{\partial h}\right)_p \frac{\partial h}{\partial u}\right].$$

After differentiation of the second term this yields by using the momentum equation (4.3):

$$m_A^* = -\mu \frac{\partial u}{\partial y} \frac{\partial}{\partial y}\left[\left(\frac{\partial \alpha^*}{\partial T}\right)_p \left(\frac{\partial T}{\partial h}\right)_p \frac{\partial h}{\partial u}\right].$$

$$(4.12)$$

In the following the equivalent dimensionless form

$$\frac{m_A^* \delta^2}{\mu} = -\frac{\partial U}{\partial \eta} \frac{\partial}{\partial \eta}\left[\left(\frac{\partial \alpha^*}{\partial \Theta}\right)_p \left(\frac{\partial \Theta}{\partial H}\right)_p \frac{\partial H}{\partial U}\right] \quad (4.13)$$

with $\Theta \equiv T/T_\delta$ and $\eta \equiv y/\delta(x)$ is used. Applying (4.7)–(4.11) and after some rearrangement indicated in the appendix the final result is:

$$\frac{m_A^* \delta^2}{\mu} = \left(\frac{\partial U}{\partial \eta}\right)^2 \frac{a(\alpha^*)}{b(\theta, \alpha^*)} \left\{\frac{c(U, \theta, \alpha^*)}{d(\theta, \alpha^*)}\right.$$

$$\left. \times e(\theta, \alpha^*) - f(\theta)\right\}. \quad (4.14)$$

where the following abbreviations are used:

$$a(\alpha^*) = [4 + \alpha_\delta^*(1 + T_D/T_\delta)]\, \alpha^*(1 - \alpha^{*2})$$

$$b(\theta, \alpha^*) = 2\theta^2(4 + \alpha^*) + (\theta + T_D/T_\delta)^2 \alpha^*$$

$$\times (1 - \alpha^{*2})$$

$$c(U, \theta, \alpha^*) = [1 - H_w + (1 - 2U)\, u_\delta^2/(2h_\delta)]$$

$$\times [4 + \alpha_\delta^*(1 + T_D/T_\delta)]\, 2\theta^2$$

$$d(\theta, \alpha^*) = [2\theta^2(4 + \alpha^*) + (\theta + T_D/T_\delta)^2 \alpha^*$$

$$\times (1 - \alpha^{*2})]^2$$

$$e(\theta, \alpha^*) = 2\theta(4 + \alpha^*)(\theta + 2T_D/T_\delta) - (\theta + T_D/$$

$$T_\delta)(4 - \alpha^* - 12\alpha^{*2} - \alpha^{*3})$$

$$f(\theta) = (\theta + T_D/T_\delta)\, u_\delta^2/h_\delta.$$

Adopting equation (4.8) we find

$$H_w = \frac{\theta_w(4 + \alpha_w^*) + \alpha_w^* T_D/T_\delta}{4 + \alpha_\delta^*(1 + T_D/T_\delta)}. \quad (4.15)$$

Thus the expression $m_A^* \delta^2/\mu$ depends on the velocity-, the temperature- and the atom mass-fraction-profile. The last two profiles are uniquely related to each other by the law of mass-action or equation (4.9) resp. and the caloric equation of state (4.8) together with the Crocco-relationship (4.11). So we have

$$\alpha^* = \left[1 + \frac{p}{p_D} \cdot \frac{T_D}{\theta T_\delta} \exp\left(\frac{T_D}{\theta T_\delta}\right)\right]^{-\frac{1}{2}} \quad (4.16)$$

$$\theta = \frac{4 + \alpha_\delta^*(1 + T_D/T_\delta)}{4 + \alpha^*}\left[1 + (H_w - 1)(1 - U)\right.$$

$$\left. + \frac{u_\delta^2}{2h_\delta} U(1 - U)\right] - \frac{\alpha^*}{4 + \alpha^*} \cdot \frac{T_D}{T_\delta} \quad (4.17)$$

with H_w (θ_w, α_w^*) from equation (4.15). Now the only unknown is the velocity-profile $U(x, y)$. If this is known, the α^*- and θ-profiles are given by (4.16) and (4.17) and the $m_A^* \delta^2/\mu$-profile is given by (4.14).

Finally we assume the velocity-profile to be similar and known by a polynomial of the Pohlhausen-type:

$$U(\eta) = 2\eta - 2\eta^3 + \eta^4. \quad (4.18)$$

This is a good approximation for a flat plate boundary layer flow with constant wall conditions. This last assumption leads to the result, that the α^*- and θ-profiles are similar as well as the $m_A^* \delta^2/\mu$-profile. So we have the statement

$$\frac{m_A^* \delta^2}{\mu} = f(\eta) \quad (4.19)$$

for the particular boundary layer flow considered and the assumptions that were made. Because of $\delta \sim \sqrt{x}$ and $\mu = \mu(\eta)$ we find for the equilibrium production term

$$m_A^* = \frac{F(\eta)}{x} \sim \frac{1}{x}. \quad (4.20)$$

The equilibrium production term decreases with increasing distance from the leading edge, for $x \to \infty$ it follows $m_A^* \to 0$.

5. EXAMPLE

It would be interesting to compare in an example the discussed "equilibrium" with corresponding nonequilibrium profiles. The example chosen has been treated first by Chung and Anderson [3] with an integral method. The wall is assumed to be adiabatic and non catalytic, the fluid is oxygen with the characteristic data

$$T_D = 59\,500\,K$$
$$p_D = 2\cdot33 \times 10^7\,bar$$
$$M_A = 16\,g/mol.$$

The boundary conditions are

$$T_\delta = 218\,K$$
$$p_\delta = 1\cdot12 \times 10^{-2}\,bar$$
corresponding to 100000 ft altitude
$$Ma_\delta = 15$$
$$\alpha_\delta = 0.$$

It has to be noticed that the wall temperature is not given explicitly if the wall is adiabatic. The wall temperature follows from equation (4.5) for the condition of zero wall heat flux after some rearrangements and using certain assumptions made in section 4. This leads to

$$\theta_w(q_w = 0) = \frac{1}{4 + \alpha_w} \{[4 + \alpha_\delta(1 + T_D/T_\delta)]$$
$$\times [1 + u_\delta^2/(2h_\delta)] - \alpha_w T_D/T_\delta\}$$

see [4]. With $\theta_w(\alpha_w)$ from the above equation and $\alpha_w(\theta_w)$ by (4.16) the unknowns θ_w and α_w can be determined. For the special case $\alpha_w = \alpha_\delta = 0$ one obtains the well-known relationship $\theta_w = 1 + u_\delta^2/(2h_\delta)$ valid for $Pr = 1$. In the following two different calculations, the "equilibrium" and the nonequilibrium case, are compared with each other. For the "equilibrium flow" considered here the interesting profiles (α^*, θ^* and $m_A^* \delta^2/\mu$) are given by the equations (4.16), (4.17) and (4.14). These are similar profiles as we have discussed.

In contrast to the "equilibrium flow" the calculations of the nonequilibrium profiles is much more complex. The full set of equations (4.1)–(4.4) has to be solved. This has been done by the author [4] with an integral method

similar to that of Chung and Anderson [3]. This integral method [4], which is also described in [5], is more general with regard to different boundary conditions than the method of [3], which is only applicable for an adiabatic and noncatalytic wall. Further on the assumptions made here correspond to those made in the method of [4, 5]. This integral method is based on the Crocco-relationship between enthalpy and velocity profile for unity Prandtl- and Lewis-number. The velocity profile is assumed to be given by a polynomial like equation (4.18) 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-fraction profile are obtained from integral relations for momentum and diffusion.
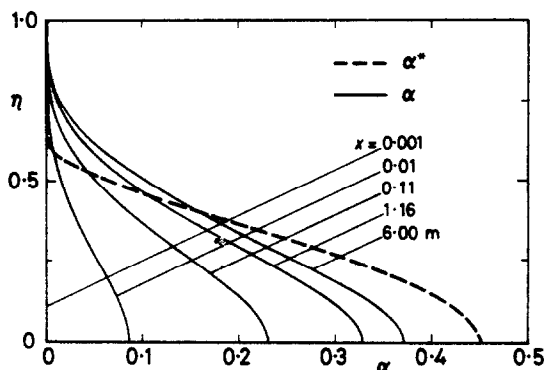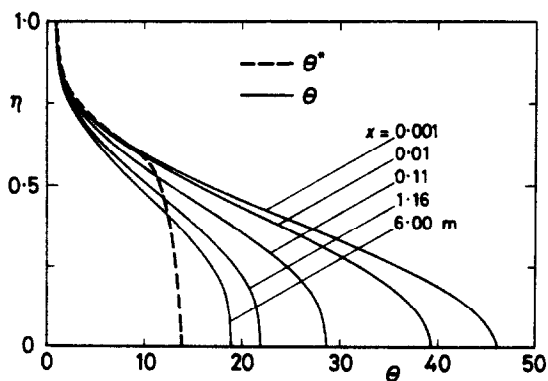

FIG. 1. Atom mass-fraction profiles.

FIG. 2. Temperature profiles.

Figures 1 and 2 show the equilibrium profiles of atom mass-fraction and temperature. Both are compared with the corresponding non-equilibrium profiles, which naturally are non-similar. Near the leading edge the dissociation reaction dominates, the atom mass-fraction profile grows rapidly whereas the temperature profile becomes more slender because energy is absorbed by the reaction. The development of the atom mass-fraction and temperature at the wall with increasing distance from the leading
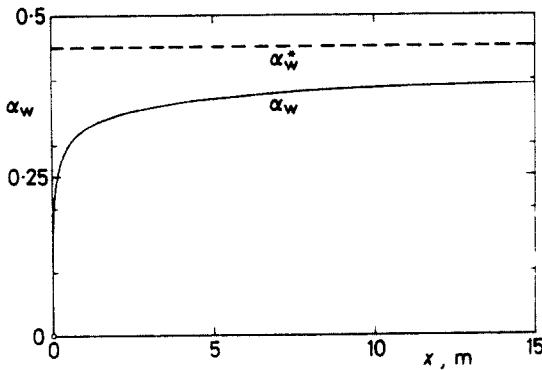

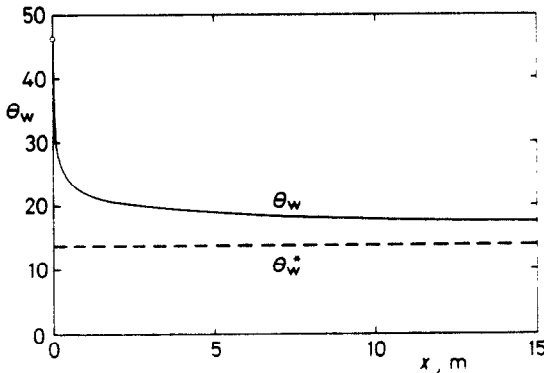FIG. 3. Atom mass-fraction at the wall.

FIG. 4. Wall temperature.

edge is shown in Figs. 3 and 4. First the atom mass-fraction at the wall grows rapidly and it obviously tends asymptotically towards its equilibrium value for very large distances. The decreasing wall temperature shows the analo-gous behaviour. Not only the equilibrium values at the wall but the complete equilibrium profiles appear to be limiting profiles which seem to be approached by the nonequilibrium profiles at infinity. The overlapping of the nonequilibrium profiles with the corresponding equilibrium profile near the outer edge of boundary layer is possibly due to the simple trial solution made for the nonequilibrium atom mass-fraction profile, see [4, 5].

For the example considered the flow evidently is still far from local chemical equilibrium state except for very large distances from the leading edge. The difference of the atom mass-fraction at the wall from its equilibrium value is still about 20 per cent at $x = 5$ m and about 10 per cent at $x = 35$ m. Therefore the assumption of local equilibrium is only approximately valid for even large distances.

Figure 5 shows the actually interesting profiles of the production term in the discussed characteristic dimensionless form. Under the assumptions we have made the equilibrium profile is similar whereas the nonequilibrium profile varies with the distance x. Positive production means that more atoms than mole-cules are produced by the reaction or that the dissociation-reaction predominates. This is the case in regions of high temperature and hence in regions near the wall. Toward the outer edge of boundary layer the temperature decreases and the production term becomes negative. This means that the recombination-reaction pre-dominates there. For the nonequilibrium case the negative part is small compared with the positive one. Only at large distances the recombination-reaction becomes important.

Qualitatively the equilibrium and the non-equilibrium profiles have the same characteristic shape. If we compare them we have to remember the different methods of calculation. The equili-brium profile follows from the partial continuity equation together with the other boundary layer equations and the law of mass action. On the other hand, in the nonequilibrium cal-culation, empirical informations are needed

for the reaction rate coefficients in the rate equation (2.6), which influences the nonequilibrium profiles considerably. Furthermore the relative inaccuracy involved in the integral method used to determine the nonequilibrium profiles has to be taken into consideration.

Finally we are interested in the actual production term profile. This follows from the dimensionless expression $m_A^* \delta^2/\mu$ if $\mu(\eta)$ and $\delta(x)$ are known. We obtain the boundary layer thickness from the well-known integral relation of momentum, which for constant pressure has the form:

$$\frac{d\delta_2}{dx} = \frac{\tau_w}{\rho_\delta u_\delta^2}.$$

There δ_2 is the momentum loss thickness defined by

$$\frac{\delta_2}{\delta} = \int_0^1 \frac{\rho}{\rho_\delta} U(1 - U) \, d\eta.$$

Using the thermal and caloric equation of state. (4.7) and (4.8), we find for $\alpha_\delta = 0$ in our example:

$$\frac{\delta_2}{\delta} = \int_0^1 \frac{(4 + \alpha)U(1 - U)}{(1 + \alpha)(4H - \alpha T_D/T_\delta)} \, d\eta.$$

The H-profile is given by the Crocco relationship (4.11). Then the ratio δ_2/δ is constant and known for the considered "equilibrium flow" (the U-, α^*- and θ^*-profiles are similar). Using equation (4.18) for $U(\eta)$ the integration of the above integral relation leads to

$$\delta(x) = 2 \sqrt{\left(\frac{\mu_w x}{\rho_\delta u_\delta \delta_2/\delta} \right)}.$$

This result and the assumption $\mu \sim T^\omega$ ($\omega = 0, 7$) corresponding to [4,5] yield, together with $m_A^* \delta^2/\mu = f(\eta)$ from equation (4.14), the information shown on Fig. 6. Here we see that the
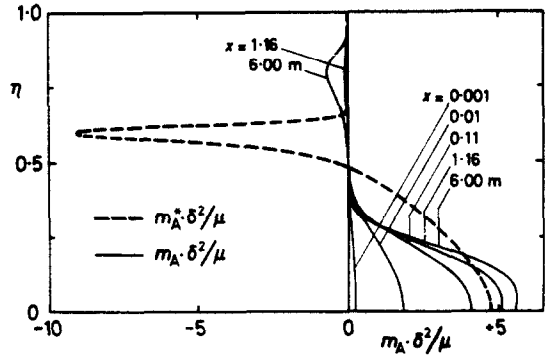
FIG. 5. Profiles of production term in characteristic dimensionless form.

equilibrium as well as the nonequilibrium profile change with the distance x. The difference between the two profiles decreases with increasing distance from the leading edge, both profiles vanish as x goes to infinity.

Another example where the wall is assumed strongly cooled was discussed in a previous paper [6].
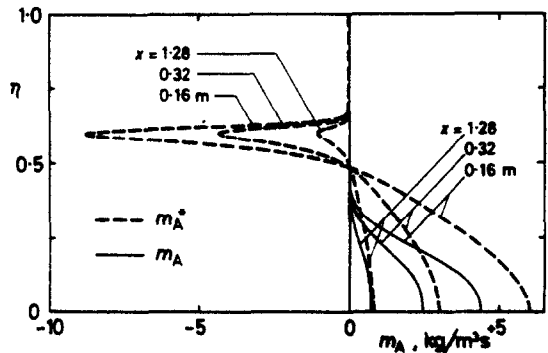
FIG. 6. Profiles of production term.

6. CONCLUSIONS

Figure 7 shall serve to summarize the results. On the left hand side the boundary layer flow in local chemical equilibrium for finite distance from the leading edge is shown qualitatively. All variables of the "equilibrium flow" are field-variables, the production term is finite.

H

In the limit as x goes to infinity all gradients vanish, the variables become constant and the production term goes to zero. Therefore the open system with gradients changes, for $x \to \infty$, into a uniformly moving open system without gradients, which after a velocity transformation is equivalent to a closed system.
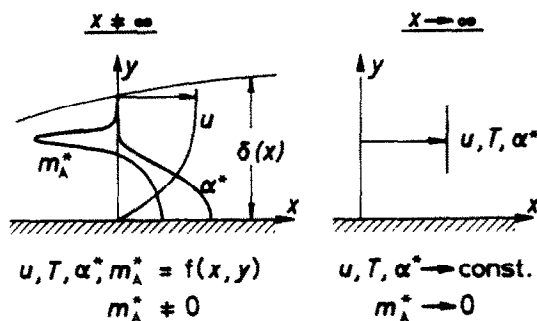

FIG. 7. Comparison between "equilibrium flow" with and without gradients.

On the left hand side we have the case of local chemical equilibrium in an open system with continuously changing state whereas on the right hand side we have simple equilibrium in a closed system at fixed conditions. In other words, on the left hand side the state of equilibrium is assumed to exist only with respect to the chemical reaction whereas all other dissipating nonequilibrium processes such as the transport of mass, heat and momentum do occur. On the right hand side we have equilibrium in general, all gradients and thus all transport processes have vanished. This latter case only leads to a vanishing production term!

Finally some related questions shall be discussed. First let us discuss the wall boundary condition of the partial continuity equation. At the wall the diffusion flux, neglecting thermal diffusion, is given by

$$-(j_A)_w = \left(\rho D \frac{\partial \alpha}{\partial y}\right)_w = K_w \left(\rho \frac{\alpha - \alpha^*}{1 - \alpha^*}\right)_w.$$

Here the heterogeneous reaction at the wall is usually assumed to be a first order reaction. K_w is the specific rate coefficient for the surface reaction, it essentially depends on the surface material. In reality all materials are partially catalytic, which means that K_w is finite and non zero. We call the limiting case $K_w = 0$ a non-catalytic wall, the wall reaction is then frozen and the diffusion flux at the wall is zero. For the other limiting case $K_w \to \infty$ the wall is called catalytic, the heterogenous wall reaction is in equilibrium. In such a case the above boundary condition (which only holds for $K_w \neq \infty$) has to be replaced by the boundary condition $\alpha_w = \alpha_w^*$. Consequently for an "equilibrium flow" (i.e. a flow where the homogeneous reaction is in equilibrium) the further assumption of a catalytic wall (i.e. a wall where the heterogeneous reaction is in equilibrium) has to be made. This leads to an indefinite equilibrium diffusion flux at the wall (because of $K_w \to \infty$ and $\alpha_w \to \alpha_w^*$) corresponding to the indefinite equilibrium production term m_A^* in the flow (because of $\tau \to 0$ and $\chi \to 0$ resp. $k_f \to \infty$ and $\alpha \to \alpha^*$) we have discussed in section 3. Both, the equilibrium diffusion flux at the wall as well as the equilibrium production term in the flow, follow from the boundary layer equations in connection with the law of mass-action.

Next we can discuss the "Thermodynamics of Irreversible Processes". If we neglect the chemical viscosity (of which we know the existence only but nothing else) the production term is proposed to be a product of essentially the chemical affinity (which corresponds to our function χ and which is zero for equilibrium) and a phenomenological coefficient. This coefficient, which only can be determined by chemical kinetics, is proportional to the reaction-rate coefficient, which goes to infinity for equilibrium flows.

Thirdly the extension to multicomponent mixtures shall be discussed briefly. In the binary mixture considered a single reaction takes place and therefore we have one equilibrium constant which determines the equilibrium-fraction of one component. The fraction of the second

component follows from the condition that the sum of all fractions must be zero. If a mixture of N components is considered we are only able to determine the necessary number of $(N - 1)$ equilibrium-fractions if $(N - 1)$ independent reactions take place. In order to illustrate this let us consider the frequently used 5-components model for air (O_2, N_2, O, N, NO), where only three independent reactions ($O_2 = 2O$, $N_2 = 2N$, $N + O = NO$) occur. Here we need a further equation to determine the five equilibrium-fractions. This equation, which fixes the ratio of oxygen to nitrogen in the initial state, can only be used if no diffusion takes place. This condition is fulfilled if, for instance, we want to determine the equilibrium values behind a shock, but it is not in the boundary-layer flow considered here. In conclusion we may say that the extension of the proceeding described here to multicomponent mixtures is possible only if $(N - 1)$ independent reactions take place.

Finally two papers have to be mentioned [7, 8], in which an opposite conclusion about the same subject is drawn. Straub et al. [8] pointed out that the production terms for "equilibrium flows" vanish. They argue as follows: If a fluid flow is assumed to be in local chemical equilibrium the chemical affinity of the reaction is zero; on the other hand the reaction rate constants are always finite from the molecular viewpoint. This leads to the result of vanishing production terms for "equilibrium flows". But if we agree to this argumentation it follows a contradiction between the partial continuity equation for vanishing production term and the law of mass-action on the other side as Schönauer et al. [7] have proposed. The set of equations would be overdetermined.

In the author's opinion it seems to be reasonable to argue as follows: If we assume a fluid flow to be in local chemical equilibrium state, then the chemical affinity (which is proportional to our function χ) of each reaction is zero. As a consequence of local equilibrium state it follows

for a fluid flow that the reaction rate constants of each reaction must go to infinity (resp. the relaxation times go to zero), as we have discussed in section 3 for the case of a binary mixture. It seems evident that the reaction rate constants must be infinitely large if local chemical equilibrium is required for a continuously changing flow field. If, on the other hand, the reactions are not assumed to be infinitely fast, the condition of local chemical equilibrium state cannot be fulfilled.

The conclusions drawn here for the special case of a binary mixture lead to the following results:

1. The production term of "equilibrium flows" is indefinite from the viewpoint of chemical kinetics.
2. Using the law of mass-action as well as the other flow equations this indefinite equilibrium production term is given by the (superfluous) partial continuity equation.

If "equilibrium flows" are considered, we must always bear in mind that the name "equilibrium flow" is in reality a contradiction in terms, as Vincenti and Krüger ([1], p. 252) point out. Actually this limit can never be physically realized. Nevertheless it is a frequently used approximation which is more or less valid. A fluid flow can never be in local equilibrium state but it can be very close to it. Then the chemical affinities become very small (but not zero) and the reaction rate constants become very large (but not infinite).

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APPENDIX

In the following the step leading from equation (4.12) or (4.13) resp. to equation (4.14) is described. It follows from the law of mass-action (4.9):

$$\left(\frac{\partial \alpha^*}{\partial \theta}\right)_p = \frac{\theta + T_D/T_\delta}{2\theta^2} \alpha^*(1 - \alpha^{*2}),$$

from the caloric equation of state (4.8):

$$\frac{1}{R}\left(\frac{\partial h}{\partial T}\right)_p = 4 + \alpha^* + (T + T_D)\left(\frac{\partial \alpha^*}{\partial T}\right)_p \quad \text{resp.}$$

$$\left(\frac{\partial H}{\partial \theta}\right)_p = \frac{4 + \alpha^* + \frac{1}{2}\left(\dfrac{\theta + T_D/T_\delta}{\theta}\right)^2 \alpha^*(1 - \alpha^{*2})}{4 + \alpha_\delta^*(1 + T_D/T_\delta)}$$

and from the Crocco relationship (4.11):

$$\frac{\partial H}{\partial U} = 1 - H_w + \frac{u_\delta}{2h_\delta}(1 - 2U).$$

Then equation (4.13) becomes, after substitution of these expressions:

$$\frac{m_A^{*\delta^2}}{\mu} = -[4 + \alpha_\delta^*(1 + T_D/T_\delta)]\frac{\partial U}{\partial \eta}$$

$$\times \frac{\partial}{\partial \eta}\left\{\frac{(\theta + T_D/T_\delta)\alpha^*(1 - \alpha^{*2})[1 - H_w + (1 - 2U)u_\delta^2/(2h_\delta)]}{2\theta^2(4 + \alpha^*) + (\theta + T_D/T_\delta)^2\alpha^*(1 - \alpha^{*2})}\right\}$$

Differentiation leads to

$$\frac{m_A^*\delta^2}{\mu} = -[4 + \alpha_\delta^*(1 + T_D/T_\delta)]\frac{\partial U}{\partial \eta}$$

$$\times \left\{\frac{1 - H_w + (1 - 2U)u_\delta^2/(2h_\delta)}{[2\theta^2(4 + \alpha^*) + (\theta + T_D/T_\delta)^2\alpha^*(1 - \alpha^{*2})]^2}\right.$$

$$\times \left[(\theta + T_D/T_\delta)4\theta^2(2 - 6\alpha^{*2} - \alpha^{*3})\frac{\partial \alpha^*}{\partial \eta} - \alpha^*(1 - \alpha^{*2})\right.$$

$$\times (2\theta(4 + \alpha^*)(\theta + 2T_D/T_\delta) + (\theta + T_D/T_\delta)^2\alpha^*(1 - \alpha^{*2}))$$

$$\left.\times \frac{\partial \theta}{\partial \eta}\right] - \frac{(\theta + T_D/T_\delta)\alpha^*(1 - \alpha^{*2})u_\delta^2/h_\delta}{2\theta^2(4 + \alpha^*) + (\theta + T_D/T_\delta)^2\alpha^*(1 - \alpha^{*2})}\frac{\partial U}{\partial \eta}\right\}$$

The derivations $\partial \alpha^*/\partial \eta$ and $\partial \theta/\partial \eta$ can be expressed by $\partial U/\partial \eta$ as follows. From equation (4.9) we have for constant pressure

$$\left(\frac{\partial \alpha^*}{\partial \eta}\right) = \left(\frac{\partial \alpha^*}{\partial \theta}\right)_p \frac{\partial \theta}{\partial \eta}.$$

where $(\partial \alpha^*/\partial \theta)_p$ is given above. Equation (4.8) leads to

$$(4 + \alpha^*)^2 \frac{\partial \theta}{\partial \eta} = [4 + \alpha_\delta^*(1 + T_D/T_\delta)](4 + \alpha)^*\frac{\partial H}{\partial \eta}$$

$$- \{4T_D/T_\delta + H[4 + \alpha_\delta^*(1 + T_D/T_\delta)]\}\frac{\partial \alpha^*}{\partial \eta}.$$

Elimination of $\partial \alpha^*/\partial \eta$ by the given expression leads to

$$\frac{\partial \theta}{\partial \eta} = [4 + \alpha_\delta^*(1 + T_D/T_\delta)](4 + \alpha^*)\frac{\partial H}{\partial \eta}\{(4 + \alpha^*)^2$$

$$+ (4T_D/T_\delta + H[4 + \alpha_\delta^*(1 + T_D/T_\delta)])\alpha^*(1 - \alpha^{*2})$$

$$\times (\theta + T_D/T_\delta)/(2\theta^2)\}^{-1}$$

From equation (4.11) we obtain

$$\frac{\partial H}{\partial \eta} = \left[1 - H_w + \frac{u_\delta^2}{2h_\delta}(1 - 2U)\right]\frac{\partial U}{\partial \eta}.$$

If we substitute $\partial H/\partial \eta$, $\partial \theta/\partial \eta$ and $\partial \alpha^*/\partial \eta$ into the expression for $m_A^*\delta^2/\mu$ written above the final equation (4.14) is obtained.

TERMES DE PRODUCTION DANS DES ECOULEMENTS AVEC REACTION D'EQUILIBRE, CAS D'UNE COUCHE LIMITE LAMINAIRE D'UN MELANGE BINAIRE

Résumé—Pour un écoulement de mélange binaire en changement continu et supposé en équilibre chimique local, la concentration des espèces est uniquement déterminée par la loi d'action de masse comme une fonction de chacune des deux variables thermodynamiques indépendantes telles que température et pression. Ceci implique des vitesses de réaction infiniment grandes qui conduisent à des vitesses indéfinies de production d'espèces. L'equation de continuité est superflue étant remplacée par la loi d'action de masse. Cette équation de continuité peut par ailleurs être utilisée en relation avec les autres équations aussi bien que la loi d'action de masse pour déterminer cette vitesse de production en état d'équilibre. On

montre que pour une couche limite sur plaque plane, sous certaines conditions, le profil $m_A^* \delta^2 / \mu$ est un profil en similitude qui peut être mis sous une forme analytique. Dans cette expression m_A^* est la vitesse de production de l'espèce A, δ l'épaisseur de la couche limite et μ la viscosité. Ce profil d'équilibre, les profils d'équilibre de concentration et de température sont comparés avec les profils correspondants hors équilibre. Les profils d'équilibre semblent être des profils limites, approchés asymptotiquement à des distances infinies.

DIE PRODUKTIONSDICHTEN CHEMISCH REAGIERENDER GLEICHGEWICHTSSTRÖMUNGEN, DISKUTIERT FÜR DIE LAMINARE GRENZSCHICHTSTRÖMUNG EINES BINÄREN GEMISCHES

Zusammenfassung—Befindet sich ein strömendes Binärgemisch im lokalen chemischen Gleichgewicht, so ist dessen Konzentration durch das Massenwirkungsgesetz als Funktion zweier thermodynamischer Variabler wie Temperatur und Druck bestimmt. Dies bedeutet unendlich grosse Reaktionsgeschwindigkeiten, die Produktionsdichten sind unbestimmt. Das Massenwirkungsgesetz tritt an die Stelle der partiellen Kontinuitätsgleichung, die ihrerseits zusammen mit den anderen Bilanzgleichungen und dem Massenwirkungsgesetz die Produktionsdichte im Gleichgewicht festlegt. Es wird gezeigt, dass unter gewissen Annahmen das Profil $m_A^* \delta^2 / \mu$ für die Grenzschichtströmung entlang einer ebenen Platte ähnlich ist. Darin bedeuten m_A^* die Produktionsdichte der Teilchensorte A, δ die Grenzschichtdicke und μ die Viskosität. Dieses Gleichgewichtsprofil wie auch das der Konzentration und das der Temperatur werden mit entsprechenden Nichtgleichgewichtsprofilen verglichen. Die Gleichgewichtsprofile scheinen Grenzprofile darzustellen, die nach unendlich grosser Lauflänge asymptotisch erreicht werden.

СКОРОСТЬ ОБРАЗОВАНИЯ ПРОДУКТА РЕАКЦИИ В ХИМИЧЕСКИ РЕАГИРУЮЩИХ РАВНОВЕСНЫХ ПОТОКАХ В СЛУЧАЕ ТЕЧЕНИЯ БИНАРНОЙ СМЕСИ В ПОГРАНИЧНОМ СЛОЕ

Аннотация—В случае непрерывно изменяющегося поля течения бинарной смеси, находящейся в состоянии локального химического равновесия, концентрация реагентов однозначно определяется законом действующих масс как функция любых двух независимых термодинамических переменных, как, например, температура и давление. Это означает бесконечно большие скорости реакции, вызывающие бесконечные скорости образования продукта. Уравнение неразрывности для отдельных реагентов заменяется выражением закона действующих масс. С другой стороны, это уравнение может быть использовано вместе с другими уравнениями движения, а также с выражением закона действующих масс для определения скорости образования продукта в равновксном состоянии. Далее показано, что для течения в пограничном слое на плоской пластине при определенных допущениях профиль $m_A^* \delta^2 / \mu$ является автомодельным и может быть приближенно представлен в аналитическом замкнутом виде. В этом выражении m_A^*—скорость образования компонента A, δ—толщина пограничного слоя и μ—вязкость. Проводится сравнение этого равновесного профиля, а также равновесных профилей концентрации и температуры с соответствующими неравновесными профилями. Из сравнения видно, что равновесные профили являются пределом, к которому приближаются неравновесные профили при устремлении координаты к бесконечности.