

BOUNDARY LAYER WITH CHEMICAL REACTIONS

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UDC 517.9:532.533

A numerical solution is shown to the equations of a laminar boundary layer near the critical point of a blunt body with chemical reactions occurring at the surface and in the main stream.

1. For a mixture of gases, the equations of a laminar boundary layer near the critical point of an axially symmetric body are in Dorodnitsyn variables [1-4]:

$$\xi = \int \rho_w \mu_w u_e r^2 dx; \quad \eta = \frac{r u_e}{\sqrt{2\xi}} \int \rho dy; \quad (1)$$

$$(lf'')' + ff'' + \frac{1}{2} \left(\frac{\rho_e}{\rho} - f'^2 \right) = 0; \quad (2)$$

$$\left(\frac{ic_p}{Pr} \theta' \right)' + \left(c_p f + \sum c_{pi} v_i \right) \theta' = \frac{1}{B} \sum \frac{\omega_i h_i}{\rho T_e}; \quad (3)$$

$$v_i - fc_i = \frac{\omega_i}{\rho B}; \quad i = 1, 2, \dots, n-1; \quad (4)$$

$$\sum c_i = 1; \quad \sum v_i = 0;$$

$$l = \frac{\rho \mu}{\rho_w \mu_w}; \quad v_i = \frac{l \rho c_i V_i}{\mu \frac{\partial \eta}{\partial y}}; \quad (5)$$

$$f = \frac{\psi}{\sqrt{2\xi}}; \quad \theta = \frac{T}{T_e}; \quad B = 2 \frac{\partial u_e}{\partial x}, \quad (6)$$

with ψ denoting the flow function; u_e and T_e denoting the velocity and the temperature respectively at the outer edge of the boundary layer; and v_i denoting the dimensionless diffusion currents.

The gas in a boundary layer considered here consists of 10 components: C, O, H, C₂, CO₂, CO, H₂O, OH, H₂, and O₂. The same components, except C and C₂ appear at the outer edge of the boundary layer and in the inviscid stream. The surface layer of the body is made up of graphite which sublimates into the stream and enters into chemical reactions with the other components at the surface.

2. The boundary conditions are defined by the following system of equations.

The mass balance equation for the i -th component is

$$c_i \rho V_i + c_i \rho v = \omega_i; \quad i = 1, 2, \dots, n-1. \quad (7)$$

Since chemical equilibrium reactions occur at the surface, not all equations in (7) are independent. From the equations (7) we set up $(k-1)$ independent continuity equations for the components C, O, H (k denotes the number of elements):

$$\sum_i n_{ij} \frac{M_j}{M_i} (c_i \rho V_i + c_i \rho v) = \sum_i n_{ij} \frac{M_j}{M_i} \omega_i. \quad (8)$$

Institute of Heat and Mass Transfer, Academy of Sciences of the ByelSSR, Minsk. Translated from *Inzhenerno-Fizicheskii Zhurnal*, Vol. 22, No. 5, pp. 866-871, May, 1972. Original article submitted June 22, 1971.

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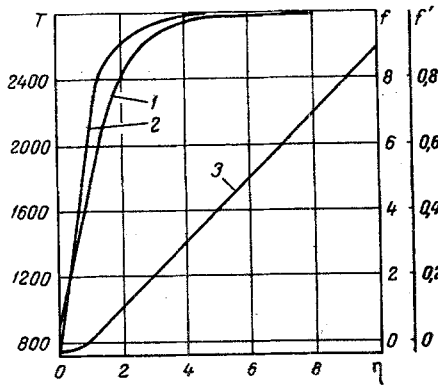


Fig. 1

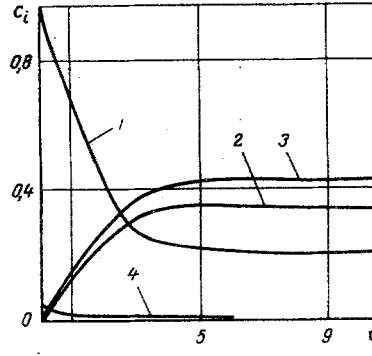


Fig. 2

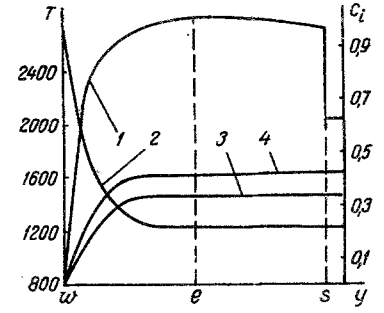


Fig. 3

Fig. 1. Distribution of T ($^{\circ}\text{K}$), f , and f' in the boundary layer: 1) T ; 2) f ; 3) f' .

Fig. 2. Distribution of mass concentrations c_i of components in the boundary layer: 1) CO ; 2) CO_2 ; 3) H_2O ; 4) H_2 .

Fig. 3. Variation of T ($^{\circ}\text{K}$) and c_i in the region between the shock wave and the body along the y -axis, plotted to different scales [w] wall; e) outer edge of the boundary layer; s) shock wave; unperturbed stream]: 1) T ; 2) CO ; 3) CO_2 ; 4) H_2O .

Since the body consists of graphite, the right-hand side of (8) is equal to ρv for C and equal to zero for O, H:

$$\begin{aligned} \sum n_{iC} \frac{M_C}{M_i} (c_i \rho V_i + c_i \rho v) &= \rho v; \\ \sum n_{iO} \frac{M_O}{M_i} (c_i \rho V_i + c_i \rho v) &= 0; \\ \sum n_{iH} \frac{M_H}{M_i} (c_i \rho V_i + c_i \rho v) &= 0. \end{aligned} \quad (9)$$

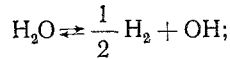
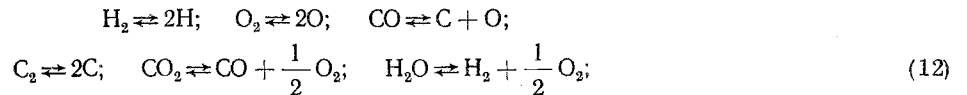
Equations (9) will be supplemented by

$$\sum c_{iw} = 1; \quad \sum c_{iw} V_{iw} = 0. \quad (10)$$

From these relations it is possible to determine the concentration and the diffusion current of one of the components. We have selected CO as such a "last" component. The energy balance will be written as [1-4]

$$\lambda \frac{\partial T}{\partial y} - \sum \rho c_i V_i - \rho v (h_w - h_{10}) - \epsilon \sigma T_w^4 = 0; \quad (11)$$

with h_w denoting the enthalpy of the gas at the surface; h_{10} denoting the enthalpy of cold graphite; and ϵ denoting the emissivity of the graphite body. In addition, to Eqs. (9), (10), and (11) we have also the chemical equilibrium equations for the independent chemical reactions at the surface:



$$\begin{aligned} \frac{p^2(\text{H})}{p(\text{H}_2)} &= K_1; & \frac{p^2(\text{O})}{p(\text{O}_2)} &= K_2; & \frac{p(\text{C})p(\text{O})}{p(\text{CO})} &= K_3; \\ \frac{p^2(\text{C})}{p(\text{C}_2)} &= K_4; & \frac{p(\text{CO})\sqrt{p(\text{O}_2)}}{p(\text{CO}_2)} &= K_5; & \frac{p(\text{H}_2)\sqrt{p(\text{O}_2)}}{p(\text{H}_2\text{O})} &= K_6; \end{aligned} \quad (13)$$

$$\frac{\sqrt{p(\text{H}_2)}p(\text{OH})}{p(\text{H}_2\text{O})} = K_7; \quad p_C + p_{\text{C}_2} = p_{\text{sat}}(T_w).$$

The boundary conditions at the surface, in terms of dimensionless parameters, are

$$f(0) = -\frac{(\rho v)_w}{\sqrt{2\rho_w u_w \frac{\partial u_e}{\partial x}}}; \quad \theta(0) = \frac{T_w}{T_e}; \quad f'(0) = 0. \quad (14)$$

At the outer edge of the boundary layer, where $\eta \rightarrow \infty$, we have

$$u \rightarrow u_e = \frac{\partial u_e}{\partial x} x; \quad f' \rightarrow 1; \quad \theta \rightarrow 1; \quad c_i \rightarrow c_{ie}. \quad (15)$$

Usually, however, not the conditions (15) are known but the conditions p_∞ , T_∞ , u_∞ , and $c_{i\infty}$ in the unperturbed stream sufficiently far away from the body. If $u_\infty > c_\infty$ (c denotes the acoustic velocity), then the boundary-layer equations (1)-(14) and the equations of gas flow in the region from the outer edge of the boundary layer to the shock wave must be solved simultaneously. If the Reynolds number is high and the Mach number $M \sim 2-3$, however, then the thickness of the boundary layer may be considered much smaller than the distance from the body to the shock wave and the effect of the boundary layer on the inviscid flow may be disregarded. In this case one can first solve the inviscid flow problem and then the boundary-layer problem. The system of flow equations for an inviscid and thermally nonconducting gas in the region bounded by the shock wave, the body, the axis of symmetry, and the particular $u = c$ line is as follows [5]:

$$\begin{aligned} \frac{\partial(r\rho u)}{\partial x} + \frac{\partial(Ar\rho v)}{\partial y} &= 0; \\ u \frac{\partial u}{\partial x} + Av \frac{\partial u}{\partial y} + Kuv + \frac{1}{\rho} \cdot \frac{\partial p}{\partial x} &= 0; \\ u \frac{\partial v}{\partial x} + Av \frac{\partial v}{\partial y} - Ku^2 + \frac{A}{\rho} \cdot \frac{\partial p}{\partial y} &= 0; \\ T ds &= dh - \frac{dp}{\rho}; \quad A = 1 + Ky; \\ h &= h(p, T, c_i); \quad \rho = \rho(p, T, c_i). \end{aligned} \quad (16)$$

System (16) was solved by the integral ratios method [5]. The boundary conditions for (16) at the body, at the shock wave, at the axis of symmetry, and at the $u = c$ line were formulated as usually [5]. With chemical equilibrium reactions occurring in the stream, Eqs. (16) had to be supplemented by equations of the gas composition as a function of p and T . The gas in the unperturbed main stream contains O, H, CO, CO₂, H₂O, OH, O₂, and H₂ so that the equations for calculating its components are

$$\begin{aligned} \frac{p^2(\text{H})}{\rho(\text{H}_2)} = K_1; \quad \frac{p^2(\text{O})}{\rho(\text{O}_2)} = K_2; \quad \frac{p(\text{OH})p(\text{H})}{p^2(\text{H})p(\text{O})} = K_8; \\ \frac{p(\text{H}_2\text{O})p(\text{H})}{\rho(\text{H}_2)p(\text{OH})} = K_9; \quad \frac{p(\text{CO})p(\text{O})}{\rho(\text{CO}_2)} = K_{10}; \\ \frac{\sum n_{iC} p_i}{\sum n_{iO} p_i} = \frac{\sum n_{iC} p_{i\infty}}{\sum n_{iO} p_{i\infty}}; \quad \frac{\sum n_{iH} p_i}{\sum n_{iO} p_i} = \frac{\sum n_{iH} p_{i\infty}}{\sum n_{iO} p_{i\infty}}. \end{aligned} \quad (17)$$

After having solved system (16)-(17), we obtained the values of the parameters for an inviscid flow near the blunt body. The values of these at the wall were used as the boundary conditions at the outer edge of the boundary layer (15).

The gradients of concentrations c_i and the diffusion rates V_i are interrelated according to the Stefan-Maxwell equations

$$c_i V_i = -\frac{1-x_i}{\sum_{j \neq i} \frac{x_j}{D_{ij}}} \cdot \frac{\partial c_i}{\partial y} + \left[\sum_{j \neq i} \frac{x_j}{D_{ij}} \sum_{l \neq i} \left(\frac{M}{M_j D_{lj}} c_j V_j + \frac{M}{M_j} \frac{\partial c_j}{\partial y} \right) \right] \quad (18)$$

or, if the concentration gradients of the remaining components (the terms inside the square brackets) are omitted, according to the Wilke equations

$$c_i V_i = -\frac{1-x_i}{\sum_{j \neq i} \frac{x_j}{D_{ij}}} \cdot \frac{\partial c_i}{\partial y}; \quad i = 1, 2, \dots, n-1. \quad (19)$$

Such an approximation is entirely satisfactory, according to [2], when graphite interacts chemically with the main gas stream. The viscosity, the thermal conductivity, and the binary-diffusion coefficients were calculated by the following formulas:

$$\begin{aligned} \mu &= \sum \frac{c_i}{\mu_i}; \quad \lambda = 0.5 \left[\sum x_i \lambda_i + \left(\sum \frac{x_i}{\lambda_i} \right)^{-1} \right]; \\ \mu_i &= 2.721 \cdot 10^{-7} \frac{(MT)^{0.5}}{\sigma_i^2 \Omega_v}; \quad \lambda_i = 0.875 \mu_i \left(\frac{1}{M_i} + 1.55 c_{T_i} \right); \\ D_{ij} &= 1.858 \cdot 10^{-7} \frac{T^{1.5} [(M_i + M_j)/M_i M_j]^{0.5}}{\rho [(\sigma_i + \sigma_j)/2]^2 \Omega_D}. \end{aligned} \quad (20)$$

The impact integrals Ω_V and Ω_D have been defined here assuming that intermolecular forces are determined by the Lennard-Jones potential [6].

3. The boundary-value problem (1)-(14) was solved by the elimination method with iterations. In order to make the computation schedule applicable to any gas composition and chemical reactions at the surface, the boundary conditions at the surface were replaced by boundary conditions of the first kind, namely: T_w , c_{iw} , and $(\rho v)_w$ were specified for each iteration and were then refined after each iteration with the aid of relations (9)-(13) and

$$\lambda T_y = \alpha (T_e - T_w); \quad \rho c_i V_i = \beta_i (c_{ie} - c_{iw}), \quad (21)$$

with α denoting the transfer coefficient and β_i denoting the mass transfer coefficients. For conditions in an unperturbed stream with $R = 0.06$ m, $u_\infty = 2010$ m/sec, $p_\infty = 1$ atm, $T_\infty = 2060^\circ\text{K}$, and a specified gas composition, the boundary conditions were determined at the outer edge of the boundary layer at the critical point:

$$\begin{aligned} P_e &= 5,7 \text{ atm}; \quad T_e = 2785^\circ\text{K}; \quad u_{ex} = 136682 \frac{1}{\text{sec}}; \\ c(\text{CO}_2) &= 0.342; \quad c(\text{CO}) = 0.211; \quad c(\text{H}_2\text{O}) = 0.42; \quad c(\text{O}_2) = 0.005; \\ c(\text{O}) &= 0.0009; \quad c(\text{OH}) = 0.013; \quad c(\text{H}_2) = 0.006; \quad c(\text{H}) = 0.0003. \end{aligned} \quad (22)$$

4. The solution for conditions (22) is shown in Figs. 1-3. Owing to the chemical reactions, there is an appreciable drop in T_w relative to T_e . This is explained by the large quantity of H_2O in the mixture and by the absorption of heat during the heterogeneous reaction $\text{C}_{\text{graph}} + \text{H}_2\text{O} \rightarrow \text{CO} + \text{H}_2$. The concentrations of C and C_2 are very low at $T_w = 868^\circ\text{K}$ and, under these conditions and with such a composition, most of the carbon of the body is converted into CO. This can be explained by the large quantity of O in the H_2O , CO_2 , O_2 , O, OH components and by a diffusion rate comparable to the rate of chemical reactions at the surface. For this reason, the rate of surface reactions must be taken into account within this range of T_w temperatures. The y -distributions of T and c_i in the boundary layer (w, e), from the outer edge of the boundary layer to the shock wave (e, s), and also in the unperturbed stream (s, ∞) have been plotted in Fig. 3 to different scales. The results of calculations indicate that, assuming a chemical equilibrium at the surface, one can estimate the wear of the body material and the corresponding drop in the body temperature relative to T_∞ , but that a more precise evaluation must take into account the finite rate of reactions within this range of T_w temperatures.

NOTATION

x, y	are the coordinates tied to the body generatrix;
u, v	are the velocity components along x and y respectively;
f	is the dimensionless flow function;
c_i	is the mass concentration of i -th component;
x_i	is the molal concentration of i -th component;
ω_i	is the mass rate of i -th component in chemical reactions;
V_i	is the diffusion rate of i -th component;
h_i	is the specific enthalpy of i -th component;
μ_i	is the dynamic viscosity of i -th component;
λ_i	is the thermal conductivity of i -th component;
D_{ij}	are binary-diffusion coefficients,

- K_j is the equilibrium constant of j -th reaction;
 p_i is the partial pressure of i -th component;
 ρ is the density;
 M is the molecular weight;
 K is the curvature of body contour;
 S is the entropy of mixture;
 h is the enthalpy of mixture;
 n_{ij} is the number of j -element atoms in i -th component.

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