DETERMINATION OF HEAT FLUXES IN THE NEIGHBORHOOD OF A DOUBLE CURVATURE STAGNATION POINT IN A FLOW OF DISSOCIATING GAS OF ARBITRARY CHEMICAL COMPOSITION

G. A. Tirskii

Zhurnal prikladnoi mekhaniki i tekhnicheskoi fiziki, No. 1, pp. 45-56, 1965

Numerical solutions are obtained for the equations of a uniform compressible boundary layer with variable physical properties in the vicinity of a stagnation point with different principal curvatures in the presence of an injected gas with the same properties as the incident flow. The results of the numerical solutions are approximated for the heat flux in the form of a relation that depends on the variation of the product of viscosity and density $\mu\rho$ across the boundary layer and on the ratio of the principal radii of curvature.

Using the concepts of effective diffusion coefficients in a multicomponent boundary layer, previously introduced by the author in [1], and the generalized analogy between heat and mass transfer in the presence of injection, together with the numerical solutions obtained, it is always possible, even without additional solutions of the boundary-layer equations, to derive final formulas for the heat fluxes in a flow of dissociating gas of arbitrary chemical composition, provided that we make the fundamental assumption that all recombination reactions take place at the surface.

By way of example, formulas are given for the heat transfer to the surface of a body from dissociating air, regarded as a five-component mixture of the gases O, N, NO, O_2, N_2, and from a dissociating mixture of carbon dioxide and molecular nitrogen of arbitrary composition, regarded as an eleven-component mixture of the gases O, N, C, NO, C_2, O_2, N_2, CO, CN, C_3, CO_2.

In the process of obtaining and analyzing these solutions it was found that, in computing the heat flux, a multicomponent mixture can be replaced with an effective binary mixture with a single diffusion coefficient only when the former can be divided into two groups of components with different (but similar) diffusion properties. In this case the concentrations of one group at the surface must be zero, while the diffusion flows of the second group at the surface are expressible, using the laws of mass conservation of the chemical elements, in terms of the diffusion flows of the first. Then the single effective diffusion coefficient is the binary diffusion coefficient D(A, M), where A relates to one group of components and M to the other.

In view of the small amount of NO($c(NO) < 0.05$), the diffusion transport of energy in dissociated air may be described with the aid of a single binary diffusion coefficient D(A, M) (A = O, N, M = O_2, N_2, NO). However even in the case of complete dissociation into O and C atoms at the outer edge of the boundary layer, the diffusion transport of energy in dissociated carbon dioxide can not be described accurately enough by means of a model of a binary mixture with a single diffusion coefficient, since the diffusion properties of the O and C atoms are distinctly different.

§ 1. Consider the laminar boundary layer in the neighborhood of a double curvature stagnation point when a body is placed in a steady flow of a compressible perfect gas. In particular, this is essentially the problem of the boundary layer in the vicinity of the stagnation point of an axisymmetric body moving at an angle of attack. If we take coordinates along the lines of curvature of the surface as x and z, and direct the y axis along the normal to this surface (Fig. 1), the system of equations of the boundary layer will be

$$\frac{\partial}{\partial x}(\rho u)+\frac{\partial}{\partial y}(\rho v)+\frac{\partial}{\partial z}(\rho w)=0 \qquad (1.1)$$

$$\rho\left(u\frac{\partial u}{\partial x}+v\frac{\partial u}{\partial y}+w\frac{\partial u}{\partial z}\right)=\rho_e\beta_x^2x+\frac{\partial}{\partial y}\left(\mu\frac{\partial u}{\partial y}\right),\quad \beta_x=\left(\frac{\partial U_e}{\partial x}\right)_{x=z=0} \qquad (1.2)$$

$$\frac{\partial p}{\partial y}=0 \qquad (1.3)$$

$$\rho\left(u\frac{\partial w}{\partial x}+v\frac{\partial w}{\partial y}+w\frac{\partial w}{\partial z}\right)=\rho_e\beta_z^2z+\frac{\partial}{\partial y}\left(\mu\frac{\partial w}{\partial y}\right),\quad \beta_z=\left(\frac{\partial W_e}{\partial x}\right)_{x=z=0} \qquad (1.4)$$

$$\rho\left(u\frac{\partial h}{\partial x}+v\frac{\partial h}{\partial y}+w\frac{\partial h}{\partial z}\right)=\frac{\partial}{\partial y}\left(\frac{\lambda}{c_p}\frac{\partial h}{\partial y}\right) \qquad (1.5)$$

$$p=\rho RT \qquad (1.6)$$

where u, v, w, are the projections of the velocity vector on the x, y, and z axes, p pressure, ρ density, T temperature, λ heat conductivity, μ viscosity, U_e, W_e velocity components of the inviscid flow in the x and z directions, respectively, and c_p the specific heat capacity of the gas at constant pressure.

In deriving this system of equations, apart from the usual assumptions of boundary layer theory, we made certain simplifying assumptions connected with the fact that the flow is investigated close to the stagnation point: 1) small terms associated with the dissipation and action of pressure forces were dropped from the energy equation (1.5); 2) in Eqs. (1.2) and (1.4) we used the relation

$$p/\rho_e + {}^1\!/_2\,(\beta_x^2 x^2 + \beta_z^2 z^2) = \text{const}\,.$$

With the same assumptions, the boundary conditions for system (1.1)-(1.6) in the presence of injection independent of the coordinates x and z will be

$$u = U_e = \beta_x x,\ w = W_e = \beta_z z,\ h = h_e \text{ when } y \to \infty\,, \tag{1.7}$$

$$u = w = 0,\ v = v_0 \geqslant 0,\ h = h_0 \text{ when } y = 0\,. \tag{1.8}$$

§ 2. We shall seek a solution of the boundary problem (1.1)-(1.8) in the form:

$$u = \beta_x x f'(\eta), \quad \rho v = -\rho_e \left(\frac{\nu_e \beta_x}{l_e}\right)^{1/2} [f(\eta) + \varphi(\eta)], \quad h = h_e \theta(\eta) \tag{2.1}$$

$$w = \beta_x z \varphi'(\eta), \quad \eta = \left(\frac{\beta_x l_e}{\nu_e}\right)^{1/2} \int_0^y \frac{\rho}{\rho_e}\,dy, \quad \nu_e = \frac{\mu_e}{\rho_e}, \quad l = \frac{\mu\rho}{\mu_0\rho_0}$$

where the subscript 0 relates to conditions at the body surface, and the subscript e to conditions at the outer edge of the boundary layer. The continuity equation is then identically satisfied. Substituting (2.1) in (1.2), (1.4), (1.5) and boundary conditions (1.7), (1.8), we get:

$$(lf'')' + (f + \varphi) f'' = f'^2 - \theta, \qquad l = \mu\rho/\mu_0\rho_0\,, \tag{2.2}$$

$$(l\varphi'')' + (f + \varphi)\varphi'' = \varphi'^2 - k^2\theta, \qquad k = \beta_z/\beta_x\,, \tag{2.3}$$

$$\left(\frac{l}{\sigma}\theta'\right) + (f + \varphi)\theta' = 0, \qquad \sigma = \frac{\mu c_p}{\lambda}\,, \tag{2.4}$$

$$f(0) + \varphi(0) = \alpha \leqslant 0, \quad \theta(0) = \theta_0, \quad f'(0) = \varphi'(0) = 0 \left(\alpha = -\frac{\rho_0 v_0}{\sqrt{\beta_x \mu_0 \rho_0}}\right), \tag{2.5}$$

$$f'(\infty) = \theta(\infty) = 1, \qquad \varphi'(\infty) = k\,. \tag{2.6}$$

a system of eighth-order ordinary differential equations (2.2)-(2.4) with a family of boundary conditions (2.5). However, it is easy to see that boundary problem (2.2)-(2.5) permits the following one-parameter group of transformations:

$$f \to f + A, \qquad \varphi \to \varphi - A \tag{2.7}$$

which enables us to reduce the order of system (2.2)-(2.4) by one. For this purpose we introduce the following functions:

$$f_1(\eta) = f'(\eta), \qquad f_2(\eta) = f''(\eta), \qquad \varphi_1(\eta) = \varphi'(\eta), \qquad \varphi_2(\eta) = \varphi''(\eta)$$

$$\theta_1(\eta) = \theta(\eta), \qquad \theta_2(\eta) = \theta'(\eta), \qquad \psi(\eta) = f(\eta) + \varphi(\eta) \tag{2.8}$$

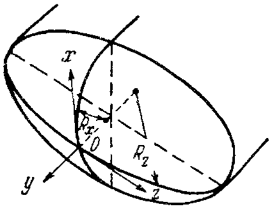

Fig. 1.

Then problem (2.2)-(2.6) can be reduced to a basic system of seventh-order ordinary differential equations with a family of boundary conditions (σ = const)

$$\begin{aligned} &f_1' = f_2, && f_2 = l^{-1}[f_1^2 - \theta_1 - (l' + \psi) f_2] \\ &\varphi_1' = \varphi_2, && \varphi_2 = l^{-1}[\varphi_1^2 - k^2\theta_1 - (l' + \psi)\varphi_2] \\ &\theta_1' = \theta_2, && \theta_2' = -l^{-1}(l' + \sigma\psi)\theta_2, \qquad \psi' = f_1 + \varphi_1 \end{aligned} \tag{2.9}$$

$$\begin{gathered} f_1(0) = \varphi_1(0) = 0, \quad \psi(0) = \alpha \leqslant 0, \quad \theta_1(0) = \theta_0 \\ f_1(\infty) = \theta_1(\infty) = 1, \qquad \varphi_1(\infty) = k \end{gathered} \tag{2.10}$$

The case k = 0 corresponds to flow near a stagnation line (plane case) and then $\varphi \equiv 0$; when k = 1 we get flow near a stagnation point (axisymmetric case) and then $f \equiv \varphi$. If the coordinate x corresponds to the greater principal curvature, then $0 \leq k \leq 1$.

The problem (2.2)-(2.6) has been formulated and numerically solved by Howarth [2] for $\theta_0 = 1$ (incompressible flow) and $l = 1, \alpha = 0$. Reshotko [3] has analyzed the problem for $\theta_0 \ll 1$ and $l = 1$, $\alpha = 0$, when the right sides of Eqs. (2.2) and (2.3) can be neglected and Blasius equations are obtained for the functions $f\sqrt{1+k} \equiv \varphi\sqrt{1+k}$. We have numerically integrated the more general problem (2.9), (2.10) on a BESM-2 computer, using the standard program for solving systems of ordinary differential equations by the Adams method with automatic selection of the increment to a given accuracy. In the process of solving the problem, the parameters $f_1'(0)$, $\varphi_1'(0)$, $\theta_2(0)$ were selected so as to satisfy the conditions at infinity. The accuracy achieved was 10^{-4}. The computations were taken to $\eta = \eta_\infty = 4$. The choice of parameters was automated. Calculations showed that for $\eta_\infty = 4$ all the functions go out to their asymptotics,

$\eta_\infty =$	3	4	6	8
$f''(0) =$	0.556 417 14	0.556 410 22	0.556 410 18	0.556 410 14
$f''(0) =$	0.249 354 88	0.249 352 27	0.249 352 22	0.249 352 18
$\theta'(0) =$	0.333 582 60	0.333 571 21	0.333 571 20	0.333 571 18

Computations were performed for $l = 1$ and for the function $l = \mu\rho/\mu_0\rho_0$; the viscosity coefficient μ was calculated from Sutherland's formula. The parameters k, θ_0, σ, $s = S/T_e$, where S is Sutherland's constant, were varied.

Altogether about 200 variants were analyzed. The results are given in Tables 1 and 2. From these tables it follows that the dependence of $\theta'(0)$ on k is almost linear.

TABLE 1

$l = 1$; $\sigma = 0.71$, $\sigma = 0.7$

α	θ_0	k	$f''(0)$		$\varphi''(0)$		$\theta'(0)$	
			$\sigma = 0.71$	$\sigma = 1$	$\sigma = 0.71$	$\sigma = 1$	$\sigma = 0.71$	$\sigma = 1$
0	0	0	0.6039	0.6489	0	0	0.4391	0.5067
		0.25	0.6565	0.6945	0.1459	0.1507	0.4861	0.5578
		0.50	0.7008	0.7422	0.3235	0.3478	0.5292	0.6006
		0.75	0.7433	0.7884	0.5423	0.6507	0.5703	0.6561
		1.0	0.7837	0.8227	0.7837	0.8227	0.6093	0.6919
	0.5	0	0.9369	0.9547	0	0	0.2362	0.2710
		0.25	0.9652	0.9872	0.1751	0.1771	0.2578	0.2920
		0.50	0.9957	1.0565	0.4176	0.4453	0.2793	0.3220
		0.75	1.0271	1.0413	0.7147	0.7581	0.3005	0.3675
		1.0	1.0587	1.0761	1.0587	1.0761	0.3210	0.3666
	1.0	0	1.2326	1.2326	0	0	0	0
		0.25	1.2476	1.2476	0.2013	0.2013	0	0
		0.50	1.2669	1.2669	0.4990	0.4990	0	0
		0.75	1.2887	1.2887	0.8732	0.8732	0	0
		1.0	1.3119	1.3119	1.3119	1.3119	0	0
—0.5	0	0	0.2985	0.3069	0	0	0.2117	0.2033
		0.25	0.3439	0.3531	0.06941	0.07103	0.2555	0.2481
		0.50	0.3834	0.3942	0.1717	0.1772	0.2936	0.2917
		0.75	0.4235	0.4403	0.3036	0.3151	0.3312	0.3355
		1.0	0.4624	0.4816	0.4624	0.4816	0.3686	0.3779
	0.5	0	0.6614	0.6669	0	0	0.1303	0.1290
		0.25	0.6838	0.6896	0.1034	0.1244	0.1490	0.1484
		0.50	0.7095	0.7166	0.2728	0.2757	0.1682	0.1699
		0.75	0.7374	0.7456	0.4962	0.5018	0.1880	0.1921
		1.0	0.7662	0.7753	0.7662	0.7753	0.2076	0.2144
	1.0	0	0.9692	0.9692	0	0	0	0
		0.25	0.9796	0.9796	0.1319	0.1319	0	0
		0.50	0.9950	0.9950	0.3603	0.3603	0	0
		0.75	1.0135	1.0134	0.6649	0.6649	0	0
		1.0	1.0335	1.0339	1.0339	1.0339	0	0
—1	0	0	0.0794	0.0576	0	0	0.0544	0.0258
		0.25	0.12029	0.09958	0.01974	0.1727	0.09165	0.05402
		0.50	0.1429	0.12612	0.05807	0.05240	0.1117	0.07362
		0.75	0.1714	0.1654	0.1186	0.1116	0.1379	0.1007
		1.0	0.2030	0.1966	0.2030	0.1966	0.1676	0.1320
	0.5	0	0.4555	0.4520	0	0	0.05577	0.0413
		0.25	0.4701	0.4663	0.05373	0.05347	0.06957	0.05279
		0.50	0.4873	0.4849	0.1650	0.1649	0.08312	0.0667
		0.75	0.5082	0.5074	0.3260	0.3257	0.09393	0.08303
		1.0	0.5312	0.5318	0.5312	0.5318	0.1156	0.1002
	1.0	0	0.7566	0.7566	0	0	0	0
		0.25	0.7625	0.7625	0.08149	0.08149	0	0
		0.50	0.7733	0.7733	0.2526	0.2526	0	0
		0.75	0.7872	0.7872	0.4968	0.4968	0	0
		1.0	0.8035	0.8035	0.8035	0.8035	0	0

The derivative of the dimensionless temperature (enthalpy) $\theta'(0)$, required for computing the heat flux, can be approximated, on the basis of these calculations, in the form:

$$\frac{g'(0)}{\sigma l_e^{1/2}} = 0.570\,(1 + 0.34k)\,\sigma^{-0.6}\, l_e^{-0.06-0.04k} + 0.67\,\frac{\alpha}{l_e^{1/2}}\,(1 + 0.20\alpha) \qquad (2.11)$$

$$g'(0)=\frac{\theta'(0)}{1-\theta_0}, \qquad 0{,}7\leqslant\sigma\leqslant 1 . \tag{2.11 cont.}$$

Note that a more exact approximation of the last (second degree with respect to α) term of (2.11) gives in the plane case: 0.213α for $\sigma = 0.7$ and 0.303α for $\sigma = 1$. Therefore formula (2.11) gives more accurate values for σ close to 0.7. In general, formula (2.11) gives a deviation of not more than 3-4% from the numerical solutions for $|\alpha| < 0.5$ and $\theta_0 > 0.3$-0.5. For $-\alpha \sim 1$ and $\theta_0 \sim 0.1$ the discrepancy may amount to 10%.

§ 3. Using the results of the preceding section and the concept of effective coefficients of diffusion in a multicomponent mixture, together with the generalized analogy between heat and mass transfer coefficients [1], it is possible to construct a method of deriving formulas for the specific heat fluxes from a dissociated frozen boundary layer to an ideally catalytic surface when a body is exposed to a flow of gas of arbitrary chemical composition with injection of a gas with properties close to those of the incident flow.

TABLE 2

$l \neq 1, \quad \sigma = 0.71$

α	θ_0	k	$f''(0)$		$\varphi''(0)$		$\theta'(0)$	
			$s = 0.2$	$s = 0.02$	$s = 0.2$	$s = 0.02$	$s = 0.2$	$s = 0{,}02$
0	0.05	0	0.6908	0.4583	0	0	0.4455	0.2836
		0.25	0.7374	0.4867	0.1588	0.1028	0.4908	0.3121
		0.50	0.7831	0.5149	0.3607	0.2346	0.5347	0.3398
		0.75	0.8269	0.5421	0.5988	0.3908	0.5764	0.3662
		1.0	0.8688	0.5684	0.8688	0.5684	0.6159	0.3913
	0.5	0	0.9114	0.8898	0	0	0.2255	0.2171
		0.25	0.9371	0.9138	0.1684	0.1631	0.2455	0.2363
		0.50	0.9655	0.9404	0.4029	0.3910	0.2662	0.2661
		0.75	0.9949	0.9681	0.6908	0.6711	0.2865	0.2756
		1.0	1.0244	0.9961	1.0244	0.9961	0.3060	0.2944
	1.0	0	1.2326	1.2326	0	0	0	0
		0.25	1.2476	1.2476	0.2012	0.2012	0	0
		0.50	1.2668	1.2668	0.4990	0.4990	0	0
		0.75	1.2886	1.2886	0.8732	0.8732	0	0
		1.0	1.312	1.312	1.312	1.312	0	0
—0.5	0.05	0	0.3976	0.1950	0	0	0.2459	0.09701
		0.25	0.4327	0.2150	0.08362	0.03608	0.2783	0.1173
		0.50	0.4728	0.2380	0.2068	0.09704	0.3157	0.1400
		0.75	0.5138	0.2614	0.3647	0.1810	0.3542	0.1630
		1.0	0.5540	0.2846	0.5540	0.2846	0.3920	0.1862
	0.5	0	0.6442	0.6284	0	0	0.1231	0.1158
		0.25	0.6628	0.6451	0.0982	0.09392	0.1387	0.1307
		0.50	0.6863	0.6667	0.2612	0.2517	0.15698	0.1483
		0.75	0.7118	0.6904	0.4777	0.4612	0.1759	0.1664
		1.0	0.7384	0.7152	0.7384	0.7152	0.1946	0.1844
	1	0	0.9692	0.9692	0	0	0	0
		0.25	0.9797	0.9797	0.1320	0.1320	0	0
		0.50	0.9950	0.9950	0.3603	0.3603	0	0
		0.75	1·01358	1.01358	0.6650	0.6650	0	0
		1.0	1.03317	1.03317	1.03317	1.03317	0	0
—1	0.05	0	0.1882	0.1134	0	0	0.1077	0.04298
		0.25	0.2054	0.1247	0.03209	0.01644	0.1225	0.05365
		0.50	0.2308	0.1415	0.09134	0.05173	0.1449	0.07007
		0.75	0.2619	0.1604	0.1792	0.1066	0.17297	0.08882
		1.0	0.2955	0.1798	0.2955	0.1798	0.2041	0.1082
	0.5	0	0.4482	0.4395	0	0	0.05381	0.04893
		0.25	0.4577	0.4477	0.05065	0.04831	0.06229	0.05692
		0.50	0.4729	0.4612	0.1578	0.1520	0.07510	0.06901
		0.75	0.4916	0.4780	0.3135	0.3034	0.09007	0.08323
		1.0	0.5123	0.4967	0.5123	0.4967	0.1059	0.09821
	1.0	0	0.7567	0.7567	0	0	0	0
		0.25	0.7626	0.7626	0.08162	0.08162	0	0
		0.50	0.7733	0.7733	0.2526	0.2526	0	0
		0.75	0.7873	0.7873	0.4960	0.4960	0	0
		1.0	0.8035	0.8035	0.8035	0.8035	0	0

§ 3.1. Consider the case where there is no dissociation in the flow. Then, using (2.1), the local specific heat flux to the surface of the body will be

$$q=\lambda\frac{\partial T}{\partial y}=\frac{g'(0)\sqrt{\beta_x\mu_e\rho_e}}{\sigma l_e^{1/2}}\,(h_e-h_0) \tag{3.1}$$

where the value g'(0) must be taken from (2.11).

§ 3.2. We shall find the heat flux for a body in a flow of air which at the outer edge of the boundary layer takes the form of a five-component mixture of the dissociation products, O, N, NO, O_2, N_2. In order to be able to use the results of the preceding calculations, we shall assume that the reactions in the boundary layer are frozen, while at the surface they are infinitely fast, i. e., the surface is an ideal catalyst. This limitation has only a slight effect on the heat flux [4], if the generalized Lewis-Semenov numbers are not very different from unity ($0.5 < L_i < 2$). For mixtures composed of the chemical elements O, N, C, $L_i \sim 0.8$-1.5. The boundary conditions for the components, following from the condition of conservation of O and N at the surface, will be

$$\sum_{k=1}^{N} m_{lk}\,[\rho v\,(c_k - c_k^{(1)}) + I_k]_0 = 0 \qquad (l = \mathrm{O}, \mathrm{N}), \qquad I_i = \rho_i V_i \tag{3.2}$$

where I_i is the mass diffusion flow of the i-th component along the normal to the surface, V_i is the diffusion rate ρ_i, c_i are the density and mass concentration of the i-th component, m_{lk} is the fraction of element l in component k by weight, the subscript 0 denotes conditions at the surface on the boundary layer side, and the superscript (1) conditions at the surface on the body side, and N is the number of components.

If the surface is maintained at a temperature below the dissociation threshold for a given pressure, then

$$c_0(\mathrm{O}) = c_0(\mathrm{N}) = c_0(\mathrm{NO}) = 0 \tag{3.3}$$

where $c_0(\mathrm{O})$ is the concentration of the element O at the surface, and so on. Note that conditions (3.2) are dependent by virtue of the identities:

$$\sum_{k=1}^{N} c_k = 1, \qquad \sum_{k=1}^{N} I_k = 0\,. \tag{3.4}$$

At the surface we get the recombination reactions

$$\begin{aligned} 2\mathrm{O} &\rightleftarrows \mathrm{O}_2 + Q(\mathrm{O}_2), & Q(\mathrm{O}_2) &= 117973 \text{ cal/mole},\\ 2\mathrm{N} &\rightleftarrows \mathrm{N}_2 + Q(\mathrm{N}_2), & Q(\mathrm{N}_2) &= 225072 \text{ cal/mole},\\ \mathrm{O} + \mathrm{N} &\rightleftarrows \mathrm{NO} + Q(\mathrm{NO}), & Q(\mathrm{NO}) &= 150043 \text{ cal/mole}. \end{aligned} \tag{3.5}$$

Since for five components there are two elements, three specific enthalpies of the components can be expressed in terms of two independent enthalpies and the heats of reaction (3.5); for example,

$$\begin{gathered} h(\mathrm{O}) = h(\mathrm{O}_2) + \frac{Q(\mathrm{O}_2)}{m(\mathrm{O}_2)}, \qquad h(\mathrm{N}) = h(\mathrm{N}_2) + \frac{Q(\mathrm{N}_2)}{m(\mathrm{N}_2)}\\ h(\mathrm{NO}) = \frac{m(\mathrm{O})}{m(\mathrm{NO})}h(\mathrm{O}_2) + \frac{m(\mathrm{N})}{m(\mathrm{NO})}h(\mathrm{N}_2) + \frac{Q(\mathrm{O}_2)}{2m(\mathrm{NO})} + \frac{Q(\mathrm{N}_2)}{2m(\mathrm{NO})} - \frac{Q(\mathrm{NO})}{m(\mathrm{NO})} \end{gathered} \tag{3.6}$$

where m(O) is the molecular weight of the element O, and so on. Then, using (3.2)-(3.5), the specific heat flux to the surface for injection of O_2 and N_2 may be expressed in the form

$$\begin{aligned} q &= \left(\lambda\frac{\partial T}{\partial y}\right)_0 - \sum_{k=1}^{N} h_{k0} I_{k0} - \rho_0 v_0\,(h_0 - h^{(1)}) = \left(\lambda\frac{\partial T}{\partial y}\right)_0 - \sum_{k=1}^{N} h_{k0}\,[I_k + \rho v\,(c_k - c_k^{(1)})]_0 =\\ &= \left(\frac{\lambda}{c_p}\frac{\partial h^T}{\partial y}\right)_0 - \frac{Q(\mathrm{O}_2)}{m(\mathrm{O}_2)}I(\mathrm{O}) - \frac{Q(\mathrm{N}_2)}{m(\mathrm{N}_2)}I(\mathrm{N}) - \left[\frac{Q(\mathrm{O}_2)}{2m(\mathrm{NO})} + \frac{Q(\mathrm{N}_2)}{2m(\mathrm{NO})} - \frac{Q(\mathrm{NO})}{m(\mathrm{NO})}\right] I(\mathrm{NO}) \end{aligned} \tag{3.7}$$

where h^T is the enthalpy of the ideal gas state of the mixture, i. e., $dh^T = c_p dT$, c_i is the mass concentration of the i-th component, h_i is the specific enthalpy of the i-th component, including its heat of formation, h_0 is the enthalpy of the mixture, and $h^{(1)}$ the enthalpy of the injected mixture.

It is easy to see that if the heat capacities of the components are similar, which is true of a dissociating gas, the function h^T satisfies Eq. (1.5). Therefore

$$\left(\frac{\lambda}{c_p}\frac{\partial h^T}{\partial y}\right)_0 = \left(\frac{\lambda}{c_p}\right)_0 \left(\frac{\beta_x l_e}{\nu_e}\right)^{1/2} \frac{\rho_0}{\rho_e} h_e^T \theta'(0) = \sqrt{\beta_x \mu_e \rho_e}\, \frac{g'(0)}{\sigma l_e^{1/2}} (h_e^T - h_0^T) \tag{3.8}$$

where $g'(0)\sigma^{-1} l_e^{-1/2}$ is taken from the numerical solution or formula (2.11).

In order to compute the heat flux (3.7) due to the diffusion of the dissociation products of air and their recombination at the surface, it is necessary to solve, jointly with system (2.2)-(2.4), the diffusion equations of the components, which in the variables of (2.1) are written in the form:

$$(lS_i^{-1}c_i')' + (f+\varphi)\,c_i' = 0, \qquad S_i = \frac{\mu}{\rho D_i} \tag{3.9}$$

where the effective diffusion coefficients D_i are found from the equations [1]:

$$\frac{1}{D_i} = \sum_{j=1}^{N} \frac{x_j}{D_{ij}}\left(1 - \frac{c_i}{c_j}\frac{I_j}{I_i}\right) + \sum_{k=1}^{N} c_k \sum_{j=1}^{N} \frac{x_j}{D_{kj}}\left(\frac{c_i}{c_j}\frac{I_j}{I_i} - \frac{c_i}{c_k}\frac{I_k}{I_i}\right) \tag{3.10}$$

Here x_i is the molar concentration, and D_{ij} the binary diffusion coefficient. If we use the generalized analogy between the processes of heat and mass transfer in a multicomponent boundary layer in the presence of injection [1, 5], it is sufficient to be able to compute the coefficients D_i at the surface. In fact, the generalized analogy between heat and mass transfer may be written in the form [1, 5]:

$$\left(\frac{-I_i}{\lambda \partial T/\partial y}\right)_0 = \left(\rho D_i \frac{\partial C_i}{\partial y}\right)_0 \Big/ \left(\lambda \frac{\partial T}{\partial y}\right)_0 = L_{i0}^{m} \frac{c_{ie} - c_{i0}}{h_e^T - h_0^T}, \qquad L_i = \frac{\sigma}{S_i} \tag{3.11}$$

where

$$\begin{aligned} &m = 0.6 \text{ for } \alpha = 0, && 0.25 < L_{i0} < 5, \\ &m = 1 \text{ for } -\alpha = 0.2 - 0.6, && 0.3 < L_{i0} < 3, \\ &m = 2 \text{ for } -\alpha \approx 1, && 0.6 < L_{i0} < 1.4. \end{aligned}$$

Then, with (3.8) and (3.11), expression (3.7) transforms to

$$q = \sqrt{\beta_x \mu_e \rho_e}\,\frac{g'(0)}{\sigma l_e^{1/2}} \Big\{h_e - h_0 + c_e(\mathrm{O})[L^m(\mathrm{O}) - 1]_0 \frac{Q(\mathrm{O_2})}{m(\mathrm{O_2})} +$$

$$+ c_e(N)\,[L^m(N) - 1]_0 \frac{Q(\mathrm{N_2})}{m(\mathrm{N_2})} + c_e(\mathrm{NO})\,[L^m(\mathrm{NO}) - 1]\left[\frac{Q(\mathrm{O_2})}{2m(\mathrm{NO})} + \frac{Q(\mathrm{N_2})}{2m(\mathrm{NO})} - \frac{Q(\mathrm{NO})}{m(\mathrm{NO})}\right]\Big\} \tag{3.12}$$

where

$$h_e = h_e^T + hd \tag{3.13}$$

$$h_d = c_e(\mathrm{O})\frac{Q(\mathrm{O_2})}{m(\mathrm{O_2})} + c_e(\mathrm{N})\frac{Q(\mathrm{N_2})}{m(\mathrm{N_2})} + c_e(\mathrm{NO})\left[\frac{Q(\mathrm{O_2})}{2m(\mathrm{NO})} + \frac{Q(\mathrm{N_2})}{2m(\mathrm{NO})} - \frac{Q(\mathrm{NO})}{m(\mathrm{NO})}\right] = \\ = 3686 c_e(\mathrm{O}) + 8038 c_e(\mathrm{N}) + 716\, c_e(\mathrm{NO}),\ [h_d] = \text{cal/g}. \tag{3.14}$$

Physically, h_e represents the total enthalpy of the mixture at the outer edge of the boundary layer (stagnation enthalpy), and h_d the dissociation energy of a unit mass of air. In order to compute the generalized Lewis-Semenov numbers $L_{i0} = (\rho c_p D_i/\lambda)_0$ in (3.12), it is necessary to know the effective diffusion coefficients at the surface. From (3.10), using boundary conditions (3.3), we at once get:

$$\left(\frac{1}{D_i}\right)_0 = \frac{x(\mathrm{O_2})}{D(i,\mathrm{O_2})} + \frac{x(\mathrm{N_2})}{D(i,\mathrm{N_2})} \qquad (i = \mathrm{O, N, NO}).$$

Hence, if, for simplicity, we drop the subscript 0, at the surface we have:

$$D_i = \frac{D(i,\mathrm{O_2})}{1 + [D(i,\mathrm{O_2})/D(i,\mathrm{N_2}) - 1]\,x(\mathrm{N_2})} \qquad (i = \mathrm{O, N, NO}). \tag{3.15}$$

For two given pairs of components the ratios of the binary diffusion coefficients in (3.15) depend only on the temperature, since on the basis of the kinetic theory of gases [6]

$$\frac{D_{ij}}{D_{kl}} = \frac{\sqrt{1/m_i + 1/m_j}\,(\sigma_k + \sigma_l)^2\,\Omega^{(1,1)^*}(\tau_{kl})}{\sqrt{1/m_k + 1/m_l}\,(\sigma_i + \sigma_j)^2\,\Omega^{(1,1)^*}(\tau_{ij})}, \qquad \tau_{ij} = \frac{k^* T}{\sqrt{\varepsilon_i \varepsilon_j}} \tag{3.16}$$

where σ_i is the distance between molecules for which the interaction energy is zero, ε_i is the absolute value of the maximum energy of attraction, k^* is Boltzmann's constant, and $\Omega^{(1,1)^*}(\tau_{ij})$ is the mean reduced collision cross section. Since the function $\Omega^{(1,1)^*}$ is only slightly temperature-dependent [6], for two given pairs of components, ratio (3.16) is practically unaffected by the temperature. In fact, from the tables given in [8], we have for 500, 1000, and 2000°K, respectively:

$$\frac{D(\mathrm{O}, \mathrm{O_2})}{D(\mathrm{O}, \mathrm{N_2})} = 1.038,\ 1.038,\ 1.040; \qquad \frac{D(\mathrm{N}, \mathrm{O_2})}{D(\mathrm{O}, \mathrm{O_2})} = 1.007,\ 1.006,\ 1.006;$$
$$\frac{D(\mathrm{N}, \mathrm{O_2})}{D(\mathrm{N}, \mathrm{N_2})} = 1.035,\ 1.043,\ 1.041; \qquad \frac{D(\mathrm{NO}, \mathrm{O_2})}{D(\mathrm{N}, \mathrm{O_2})} = 0.709,\ 0.716,\ 0.716; \tag{3.17}$$
$$\frac{D(\mathrm{NO}, \mathrm{O_2})}{D(\mathrm{NO}, \mathrm{N_2})} = 0.991,\ 1.020,\ 1.022.$$

Hence for the same surface temperatures

$$\frac{L(\mathrm{N})}{L(\mathrm{O})} = \frac{D(\mathrm{N})}{D(\mathrm{O})} = 1.007\,\frac{1 + 0.038x(\mathrm{N_2})}{1 + 0.035x(\mathrm{N_2})},$$
$$\frac{L(\mathrm{N})}{L(\mathrm{O})} = 1.006\,\frac{1 + 0.038x(\mathrm{N_2})}{1 + 0.043x(\mathrm{N_2})}, \qquad \frac{L(\mathrm{N})}{L(\mathrm{O})} = 1.006\,\frac{1 + 0.040x(\mathrm{N_2})}{1 + 0.041x(\mathrm{N_2})}, \tag{3.18}$$

i.e., the generalized Lewis-Semenov numbers L(O) and L(N) differ by not more than 1%. Therefore we take

$$L(\mathrm{O}) = L(\mathrm{N}) = L(\mathrm{A}) = \frac{\rho c_p D(\mathrm{N}, \mathrm{N_2})}{\lambda}\left[1 + \left(\frac{D(\mathrm{N}, \mathrm{N_2})}{D(\mathrm{N}, \mathrm{O_2})} - 1\right)x(\mathrm{O_2})\right]^{-1} =$$
$$= \frac{\rho c_p D(\mathrm{N}, \mathrm{N_2})}{\lambda\,[1 - 0.040x(\mathrm{O_2})]} = L(\mathrm{N}, \mathrm{N_2}). \tag{3.19}$$

Then, using the data of [7], we get L(A) = 1.315 (500°K); 1.370 (1000°K); 1.485 (2000°K). It is interesting to note that in view of the similarity of the diffusion properties of the molecules O_2 and N_2, separation of the composition of the incident flow at the surface of the body [1] has practically no effect on the values of L(A) at the surface, since $0.040x(O_2) \approx \approx 0.01$.

Finally, at 500, 1000, and 2000°K, respectively, we have:

$$\frac{L(\mathrm{NO})}{L(\mathrm{A})} = \frac{D(\mathrm{NO})}{D(\mathrm{N})} = 0.709\,\frac{1 + 0.035x(\mathrm{N_2})}{1 - 0.009x(\mathrm{N_2})} \approx 0.73$$
$$\frac{L(\mathrm{NO})}{L(\mathrm{A})} = 0.716\,\frac{1 + 0.043x(\mathrm{N_2})}{1 + 0.020x(\mathrm{N_2})} \approx 0.73 \tag{3.20}$$
$$\frac{L(\mathrm{NO})}{L(\mathrm{A})} = 0.716\,\frac{1 + 0.041x(\mathrm{N_2})}{1 + 0.022x(\mathrm{N_2})} \approx 0.73$$

and the heat flux (3.12) can be written in the form:

$$q = \sqrt{\beta_x \mu_e \rho_e}\,\frac{g'(0)}{\sigma l_e^{1/2}}\,\{h_e - h_0 + (L(\mathrm{A})^m - 1)\,h_d - 716c_e(\mathrm{NO})\,L^m(\mathrm{A})\,(1 - 0.73^m)\}. \tag{3.21}$$

The last term in (3.21), proportional to the concentration of NO at the outer edge of the boundary layer, is less than 1% of the remaining terms, since in all cases c(NO) < 0.05. Therefore, although $L_0(NO)$ is considerably different from L(A) [cf. (3.20)], the assumption that the processes of diffusion in dissociated air can be described with the aid of a single coefficient of binary diffusion D(A, M) and thus with the aid of a single Lewis-Semenov number L(A), as for example in [4, 9], does not lead to serious errors. Note that the appearance of nitric oxide reduces the diffusion energy transport effect [cf. (3.21)], since the heavier NO particles diffuse more slowly than the O and N atoms [D(NO) < D(A)]. Thus, of the ten binary diffusion coefficients determining the diffusion processes in the five-component boundary layer of dissociated air, by virtue of boundary conditions (3.3) and the asymptotic dependence of the derivatives on the concentrations at the surface, the mass transfer processes depend on only seven: $D(O, O_2)$, $D(O, N_2)$, $D(N, O_2)$, $D(N, N_2)$, $D(NO, O_2)$, $D(NO, N_2)$, $D(O_2, N_2)$. Moreover, the coefficient $D(O_2, N_2)$ drops out by virtue of boundary conditions (3.2). Of the remaining six binary diffusion coefficients only two: D(A, M) and D(M, M) are essentially different, and these enter into the final expression for the heat flux (3.21). Since c(NO) ≪ 1, in practice the diffusion heat transfer processes in five-component air are determined by the single binary diffusion coefficient D(A, M). In the presence of additional components with diffusion properties similar to those of air molecules, when boundary conditions (3.2) are modified, we get a significant dependence on the binary diffusion coefficient D(M, M) [5].

§ 3.3 Now let us consider the more complicated case of a body in a flow consisting of a mixture of CO_2 and molecular nitrogen in an arbitrary ratio. At sufficiently high speeds in such an atmosphere, on passing through the shock wave formed in front of the body, the flow dissociates and gives an eleven-component mixture of the dissociation products and starting components: O, N, C, O_2, N_2, NO, C_2, C_3, CO, CN, CO_2. In this case, we can take as the independent reactions, for example:

$$
\begin{array}{llll}
2O \rightleftarrows O_2 + Q(O_2), & Q(O_2) = 117\,973; & 3C \rightleftarrows C_3 + Q(C_3), & Q(C_3) = 320\,755; \\
2N \rightleftarrows N_2 + Q(N_2), & Q(N_2) = 225\,072; & C + O \rightleftarrows CO + Q(CO), & Q(CO) = 255\,790; \\
O + N \rightleftarrows NO + Q(NO), & Q(NO) = 150\,043; & C + N \rightleftarrows CN + Q(CN), & Q(CN) = 194\,121; \\
2C \rightleftarrows C_2 + Q(C_2), & Q(C_2) = 143\,170; & C + O_2 \rightleftarrows CO_2 + Q(CO_2), & Q(CO_2) = 263\,570,
\end{array}
\tag{3.22}
$$

where the heats of reaction Q are measured in cal/mole. Since these eleven components are formed by three chemical elements, the partial specific enthalpies of eight of them can be expressed in terms of those of the other three [e.g., $h(O_2)$, $h(N_2)$, and $h(CO_2)$] and the heats of reaction (3.22) as follows:

$$
\begin{aligned}
&h(O) = h(O_2) + \frac{Q(O_2)}{m(O_2)}, \qquad h(N) = h(N_2) + \frac{Q(N_2)}{m(N_2)} \\
&h(NO) = \frac{m(O)}{m(NO)} h(O_2) + \frac{m(N)}{m(NO)} h(N_2) + \frac{Q(O_2)}{2m(NO)} + \frac{Q(N_2)}{2m(NO)} - \frac{Q(NO)}{m(NO)} \\
&h(CO) = -\frac{m(O)}{m(CO)} h(O_2) + \frac{m(CO_2)}{m(CO)} h(CO_2) + \frac{Q(CO_2)}{m(CO)} + \frac{Q(O_2)}{2m(CO)} - \frac{Q(CO)}{m(CO)} \\
&h(CN) = -\frac{m(O_2)}{m(CN)} h(O_2) + \frac{m(CO_2)}{m(CN)} h(CO_2) + \frac{m(N)}{m(CN)} h(N_2) + \\
&\qquad + \frac{Q(CO_2)}{m(CN)} + \frac{Q(N_2)}{2m(CN)} - \frac{Q(CN)}{m(CN)} \\
&h(C) = -\frac{m(O_2)}{m(C)} h(O_2) + \frac{m(CO_2)}{m(C)} h(CO_2) + \frac{Q(CO_2)}{m(C)} \\
&h(C_2) = -\frac{m(O_2)}{m(C)} h(O_2) + \frac{m(CO_2)}{m(C)} h(CO_2) + \frac{Q(CO_2)}{m(C)} - \frac{Q(C_2)}{m(C_2)} \\
&h(C_3) = -\frac{m(O_2)}{m(C)} h(O_2) + \frac{m(CO_2)}{m(C)} h(CO_2) + \frac{Q(CO_2)}{m(C)} - \frac{Q(C_3)}{m(C_3)}.
\end{aligned}
\tag{3.23}
$$

By virtue of the boundary conditions

$$
\sum_{k=2}^{N} m_{lk} [\rho v (c_k - c_k{}^{(1)}) + I_k]_0 = 0, \qquad l = O,\ N,\ C \tag{3.24}
$$

$$
(c_i)_0 = 0, \qquad (I_i)_0 \neq 0, \qquad i \neq N_2,\ CO_2 \tag{3.25}
$$

and relations (3.23), in the presence of heterogeneous recombination reactions of the dissociation products of the incident flow and the injection of N_2 and CO_2 gases the specific heat flux at the surface may be represented in the form:

$$
\begin{aligned}
q &= \left(\lambda \frac{\partial T}{\partial y}\right)_0 - \sum_{k=1}^{N} h_{k0} I_{k0} - \rho_0 v_0 (h_0 - h^{(1)}) = \left(\lambda \frac{\partial T}{\partial y}\right)_0 - \\
&- \sum_{k=1}^{N} h_{k0} [I_k + \rho v (c_k - c_k{}^{(1)})]_0 = \left(\frac{\lambda}{c_p} \frac{\partial h^T}{\partial y}\right)_0 - I(O) \frac{Q(O_2)}{m(O_2)} - \\
&- I(N) \frac{Q(N_2)}{m(N_2)} - I(NO) \left[\frac{Q(O_2)}{2m(NO)} + \frac{Q(N_2)}{2m(NO)} - \frac{Q(NO)}{m(NO)}\right] - \\
&- I(CO) \left[\frac{Q(CO_2)}{m(CO)} + \frac{Q(O_2)}{2m(CO)} - \frac{Q(CO)}{m(CO)}\right] - I(CN) \left[\frac{Q(CO_2)}{m(CN)} + \frac{Q(N_2)}{2m(CN)} - \frac{Q(CN)}{m(CN)}\right] - \\
&- I(C) \frac{Q(CO_2)}{m(C)} - I(C_2) \left[\frac{Q(CO_2)}{m(C)} - \frac{Q(C_2)}{m(C_2)}\right] - I(C_3) \left[\frac{Q(CO_2)}{m(C)} - \frac{Q(C_3)}{m(C_3)}\right].
\end{aligned}
\tag{3.26}
$$

Using (3.11) and (3.8) and introducing the heat of dissociation of unit mass of the external flow

$$
\begin{aligned}
h_d &= c_e(O) \frac{Q(O_2)}{m(O_2)} + c_e(N) \frac{Q(N_2)}{m(N_2)} + c_e(NO) \left[\frac{Q(O_2)}{2m(NO)} + \frac{Q(N_2)}{2m(NO)} - \frac{Q(NO)}{m(NO)}\right] + \\
&+ c_e(CO) \left[\frac{Q(CO_2)}{m(CO)} + \frac{Q(O_2)}{2m(CO)} - \frac{Q(CO)}{m(CO)}\right] + c_e(CN) \left[\frac{Q(CO_2)}{m(CN)} + \frac{Q(N_2)}{2m(CN)} - \frac{Q(CN)}{m(CN)}\right] + \\
&+ c_e(C) \frac{Q(CO_2)}{m(C)} + c_e(C_2) \left[\frac{Q(CO_2)}{m(C)} - \frac{Q(C_2)}{m(C_2)}\right] + c_e(C_3) \left[\frac{Q(CO_2)}{m(C)} - \frac{Q(C_3)}{m(C_3)}\right] = \\
&= 3686 c_e(O) + 8038 c_e(N) + 716 c_e(NO) + 2385 c_e(CO) + 6999 c_e(CN) + 21964 c_e(C) + \\
&+ 15999 c_e(C_2) + 13054 c_e(C_3), \qquad [h_d] = \text{cal/g},
\end{aligned}
\tag{3.27}
$$

we can transform the heat flux (3.26) as follows:

$$q = \sqrt{\beta_x \mu_e \rho_e}\,\frac{g'(0)}{\sigma l_e^{1/2}}\Big\{h_e - h_0 + c_e(\mathrm{O})\,[L^m(\mathrm{O})-1]_0\,\frac{Q(\mathrm{O_2})}{m(\mathrm{O_2})} +$$
$$+ c_e(\mathrm{N})\,[L^m(\mathrm{N})-1]_0\,\frac{Q(\mathrm{N_2})}{m(\mathrm{N_2})} + c_e(\mathrm{NO})\,[L^m(\mathrm{NO})-1]_0\left[\frac{Q(\mathrm{O_2})}{2m(\mathrm{NO})}+\frac{Q(\mathrm{N_2})}{2m(\mathrm{NO})}-\frac{Q(\mathrm{NO})}{m(\mathrm{NO})}\right]+$$
$$+ c_e(\mathrm{CO})\,[L^m(\mathrm{CO})-1]_0\left[\frac{Q(\mathrm{CO_2})}{m(\mathrm{CO})}+\frac{Q(\mathrm{O_2})}{2m(\mathrm{CO})}-\frac{Q(\mathrm{CO})}{m(\mathrm{CO})}\right]+c_e(\mathrm{CN})\,[L^m(\mathrm{CN})-$$
$$-1]_0\left[\frac{Q(\mathrm{CO_2})}{m(\mathrm{CN})}+\frac{Q(\mathrm{N_2})}{2m(\mathrm{CN})}-\frac{Q(\mathrm{CN})}{m(\mathrm{CN})}\right]+c_e(\mathrm{C})\,[L^m(\mathrm{C})-1]_0\,\frac{Q(\mathrm{CO_2})}{m(\mathrm{C})}+$$
$$+ c_e(\mathrm{C_2})\,[L^m(\mathrm{C_2})-1]\left[\frac{Q(\mathrm{CO_2})}{m(\mathrm{C})}-\frac{Q(\mathrm{C_2})}{m(\mathrm{C_2})}\right]+c_e(\mathrm{C_3})\,[L^m(\mathrm{C_3})-1]_0\left[\frac{Q(\mathrm{CO_2})}{m(\mathrm{C})}-\frac{Q(\mathrm{C_3})}{m(\mathrm{C_3})}\right] \qquad (3.28)$$

where $h_e = h_e^T + h_d$ is the total enthalpy of the incident flow (stagnation enthalpy), and numerical values of the heats of reaction must be taken from (3.22). In order to calculate the generalized Lewis-Semenov numbers in (3.28), we first find the effective diffusion coefficients at the surface. From (3.10), using (3.25), we get

$$\left(\frac{1}{D_i}\right)_0 = \frac{x(\mathrm{N_2})}{D(i,\mathrm{N_2})} + \frac{x(\mathrm{CO_2})}{D(i,\mathrm{CO_2})} \qquad (i \neq \mathrm{N_2}, \mathrm{CO_2}) .$$

Whence, dropping the subscript 0 for simplicity,

$$D_i = \frac{D(i,\mathrm{N_2})}{1+[D(i,\mathrm{N_2})/D(i,\mathrm{CO_2})-1]\,x(\mathrm{CO_2})} \qquad (i \neq \mathrm{N_2}, \mathrm{CO_2}) \qquad (3.29)$$

Thus, for $T_0 = 500, 1000, 2000$°K, respectively, we have:

$$\begin{aligned}
&\frac{D(\mathrm{O},\mathrm{N_2})}{D(\mathrm{N},\mathrm{N_2})} = 0.991,\ 1.000,\ 0.995; && \frac{D(\mathrm{CO},\mathrm{N_2})}{D(\mathrm{CO},\mathrm{CO_2})} = 1.279,\ 1.255,\ 1.262\ ;\\
&\frac{D(\mathrm{N},\mathrm{N_2})}{D(\mathrm{N},\mathrm{CO_2})} = 1.220,\ 1.209,\ 1.215; && \frac{D(\mathrm{NO},\mathrm{N_2})}{D(\mathrm{C_2},\mathrm{N_2})} = 1.040,\ 1.022,\ 1.025\ ;\\
&\frac{D(\mathrm{O},\mathrm{N_2})}{D(\mathrm{O},\mathrm{CO_2})} = 1.245,\ 1.205,\ 1.225; && \frac{D(\mathrm{C_2},\mathrm{N_2})}{D(\mathrm{C_2},\mathrm{CO_2})} = 1.256,\ 1.240,\ 1.243\ ;\\
&\frac{D(\mathrm{O},\mathrm{N_2})}{D(\mathrm{C},\mathrm{N_2})} = 0.895,\ 0.909,\ 0.907; && \frac{D(\mathrm{NO},\mathrm{N_2})}{D(\mathrm{C_3},\mathrm{N_2})} = 1.290,\ 1.258,\ 1.259\ ;\\
&\frac{D(\mathrm{C},\mathrm{N_2})}{D(\mathrm{C},\mathrm{CO_2})} = 1.200,\ 1.190,\ 1.186; && \frac{D(\mathrm{C_3},\mathrm{N_2})}{D(\mathrm{C_3},\mathrm{CO_2})} = 1.320,\ 1.268,\ 1.250\ ;\\
&\frac{D(\mathrm{NO},\mathrm{N_2})}{D(\mathrm{CO},\mathrm{N_2})} = 1.032,\ 1.013,\ 1.013; && \frac{D(\mathrm{NO},\mathrm{N_2})}{D(\mathrm{O},\mathrm{N_2})} = 0.748,\ 0.734,\ 0.735\ ;\\
&\frac{D(\mathrm{NO},\mathrm{N_2})}{D(\mathrm{NO},\mathrm{CO_2})} = 1.315,\ 1.261,\ 1.264, && \frac{D(\mathrm{NO},\mathrm{N_2})}{D(\mathrm{N},\mathrm{N_2})} = 0.741,\ 0.734,\ 0.731\ .
\end{aligned} \qquad (3.30)$$

Therefore, for example, for $T_0 = 500$°K we have:

$$\begin{aligned}
\frac{L(\mathrm{O})}{L(\mathrm{N})} &= \frac{D(\mathrm{O})}{D(\mathrm{N})} = 0.991\,\frac{1+0.22x(\mathrm{CO_2})}{1+0.24x(\mathrm{CO_2})} \approx 0.99-0.97\\
\frac{L(\mathrm{O})}{L(\mathrm{C})} &= \frac{D(\mathrm{O})}{D(\mathrm{C})} = 0.895\,\frac{1+0.20x(\mathrm{CO_2})}{1+0.24x(\mathrm{CO_2})} = 0.89-0.87\\
\frac{L(\mathrm{NO})}{L(\mathrm{CO})} &= \frac{D(\mathrm{NO})}{D(\mathrm{CO})} = 1.032\,\frac{1+0.279x(\mathrm{CO_2})}{1+0.315x(\mathrm{CO_2})} = 1.03-1.00\\
\frac{L(\mathrm{NO})}{L(\mathrm{C_2})} &= \frac{D(\mathrm{NO})}{D(\mathrm{C_2})} = 1.040\,\frac{1+0.256x(\mathrm{CO_2})}{1+0.315x(\mathrm{CO_2})} = 1.04-1.00\\
\frac{L(\mathrm{NO})}{L(\mathrm{C_3})} &= \frac{D(\mathrm{NO})}{D(\mathrm{C_3})} = 1.29\,\frac{1+0.32x(\mathrm{CO_2})}{1+0.315x(\mathrm{CO_2})} = 1.29\\
\frac{L(\mathrm{NO})}{L(\mathrm{O})} &= \frac{D(\mathrm{NO})}{D(\mathrm{O})} = 0.748\,\frac{1+0.245x(\mathrm{CO_2})}{1+0.315x(\mathrm{CO_2})} = 0.75-0.71\\
\frac{L(\mathrm{NO})}{L(\mathrm{N})} &= \frac{D(\mathrm{NO})}{D(\mathrm{N})} = 0.741\,\frac{1+0.22x(\mathrm{CO_2})}{1+0.315x(\mathrm{CO_2})} = 0.74-0.69.
\end{aligned} \qquad (3.31)$$

Here the first values correspond to $x(\mathrm{CO_2}) = 0$ and the second to $x(\mathrm{CO_2}) = 1$. By virtue of (3.30) we also get similar ratios of the L numbers for other surface temperatures. It follows from (3.31) that in this particular case there are really only four significantly different L numbers:

$$L\,(\mathrm{C}),\quad L\,(\mathrm{A}) = L\,(\mathrm{O}) = L\,(\mathrm{N}),\quad L\,(\mathrm{M}) = L\,(\mathrm{NO}) = L\,(\mathrm{CO}) = L\,(\mathrm{CN}) = L\,(\mathrm{C_2})\quad L\,(\mathrm{C_3})\;.$$

In each of these groups the L numbers differ by not more than 3% for any surface temperature. Moreover, upon dissociation of CO_2 the concentration of C_3 molecules is negligible, so that without detriment to accuracy we can combine L (C_3) and L (M). Then the heat flux (3.28) can be reduced to the simpler form:

$$\begin{aligned}
q = {} & \sqrt{\beta_x \mu_e \rho_e}\,\frac{g'(\mathrm{O})}{\sigma l_e^{1/2}}\,\{h_e - h_0 + [L^m(\mathrm{A}) - 1]_0 h_d - \\
& - L^m(\mathrm{A})\left[1 - \frac{L^m(\mathrm{C})}{L^m(\mathrm{A})}\right] c_e(\mathrm{C})\,\frac{Q(\mathrm{CO_2})}{m(\mathrm{C})} - L^m(\mathrm{A})\left[1 - \frac{L^m(\mathrm{M})}{L^m(\mathrm{A})}\right] \times \\
& \times \Big[c_e(\mathrm{NO})\left(\frac{Q(\mathrm{O_2})}{2m(\mathrm{NO})} + \frac{Q(\mathrm{N_2})}{2m(\mathrm{NO})} - \frac{Q(\mathrm{NO})}{m(\mathrm{NO})}\right) + c_e(\mathrm{CO})\left(\frac{Q(\mathrm{CO_2})}{m(\mathrm{CO})} + \frac{Q(\mathrm{O_2})}{2m(\mathrm{CO})} - \frac{Q(\mathrm{CO})}{m(\mathrm{CO})}\right) + \\
& + c_e(\mathrm{CN})\left(\frac{Q(\mathrm{CO_2})}{m(\mathrm{CN})} + \frac{Q(\mathrm{N_2})}{2m(\mathrm{CN})} - \frac{Q(\mathrm{CN})}{m(\mathrm{CN})}\right) + c_e(\mathrm{C_2})\left(\frac{Q(\mathrm{CO_2})}{m(\mathrm{C})} - \frac{Q(\mathrm{C_2})}{m(\mathrm{C_2})}\right) + \\
& + c_e(\mathrm{C_3})\left(\frac{Q(\mathrm{CO_2})}{m(\mathrm{C})} - \frac{Q(\mathrm{C_3})}{m(\mathrm{C_3})}\right)\Big]\Big\} = \sqrt{\beta_x \mu_e \rho_e}\,\frac{g'(\mathrm{O})}{\sigma l_e^{1/2}}\,\{h_e - h_0 + [L^m(\mathrm{A}) - 1]_0 h_d + \\
& + 21\,964\, c_e(\mathrm{C})\, L^m(\mathrm{A})\,(1{,}15^m - 1) - [716 c_e(\mathrm{NO}) + 2385 c_e(\mathrm{CO}) + 6999 c_e(\mathrm{CN}) + \\
& + 15\,999 c_e(\mathrm{C_3}) + 13\,054 c_e(\mathrm{C_3})] + L^m(\mathrm{A})\,(1 - 0.73^m)\}
\end{aligned} \tag{3.32}$$

where the value of $q'(0)/\sigma l_e^{1/2}$ must be taken from (2.11) and that of h_d from (3.27).

$$L\,(\mathrm{A}) = \frac{\rho C_p D\,(\mathrm{A})}{\lambda} = \frac{\rho c_p D\,(\mathrm{N},\ \mathrm{N_2})}{\lambda\,[1 + (D\,(\mathrm{N},\ \mathrm{N_2})/D\,(\mathrm{N},\ \mathrm{CO_2}) - 1)\,x\,(\mathrm{CO_2})]} = \frac{\rho c_p D\,(\mathrm{N},\ \mathrm{N_2})}{\lambda\,[1 + 0.22x\,(\mathrm{CO_2})]}\;. \tag{3.33}$$

Using the data of [7] on the parameters of the interaction forces for the Lennard-Jones potential, we find from (3.33) that for a given surface temperature the dependence of L (A) on x (CO_2) is practically linear (Fig. 2).

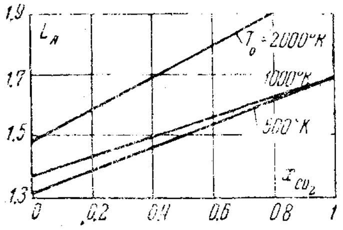

Fig. 2.

In view of the low degree of separation of the starting composition of the incident flow at the surface and the relatively weak dependence of L (A) on x (CO_2), in computing L (A) from (3.33) or Fig. 2 the value of x (CO_2) at the surface may be taken equal to its value in the incident flow (ahead of the shock wave).

Thus, taking values of L (A) from Fig. 2, we can compute the heat flux to the surface from (3.32) for any value of the injection parameter and for any degree of dissociation of the incident flow. For example, for the case of a flow consisting only of CO_2 completely dissociated to C and O atoms ($T_e > 6000$ °K), from (3.32) we get:

$$\begin{gathered}
q = \sqrt{\beta_x \mu_e \rho_e}\,\frac{g'(0)}{\sigma l_e^{1/2}}\,\{h_e - h_0 + [L^m(\mathrm{A}) - 1]\,h_d + 21964 c_e(\mathrm{C})\,L^m(\mathrm{A})[1.15^m - 1], \\
h_d = 3686 c_e(\mathrm{O}) + 21\,964 c_e(\mathrm{C}) = 8671\ \mathrm{cal/g},\ L\,(\mathrm{A}) = 1.69,\ T_0 < 1000°\ \mathrm{K}\;.
\end{gathered} \tag{3.34}$$

We shall now compare the specific heat flux at the stagnation point of a body flying in CO_2 with the heat flux to the same body flying in air. For simplicity we shall assume that there is no injection and, for comparison, that for both atmospheres T_0 = const, h_e = const, p_e = const. Dividing (3.34) by (3.21), we get:

$$\begin{gathered}
\frac{q_{\mathrm{CO_2}}}{q_*} = \frac{\gamma_{\mu\rho}\gamma_h}{\gamma_\sigma\gamma_l}\,,\quad \gamma_{\mu\rho} = \frac{(\sqrt{\beta_x \mu_e \rho_e})_{\mathrm{CO_2}}}{(\sqrt{\beta_x \mu_e' \rho_c})_*}\,,\quad \gamma_\sigma = \left(\frac{\sigma_{\mathrm{CO_2}}}{\sigma^*}\right)^{0.6},\quad \gamma_l = \left(\frac{l_{e\mathrm{CO_2}}}{l_{e_*}}\right)^{0.10} \\
\gamma_h = \frac{\{h_e - h_0 + [L^{0.6}(\mathrm{A}) - 1]\,h_d + 21964\,c_e(\mathrm{C})\,L^{0.6}(\mathrm{A})\,(1.15^{0.6} - 1)\}_{\mathrm{CO_2}}}{\{h_e - h_0 + [L^{0.6}(\mathrm{A}) - 1]\,h_d - 716\,c_e(\mathrm{NO})\,L^{0.6}(\mathrm{A})\,(1 - 0{,}73^{0.6})\}_*}\,.
\end{gathered}$$

For $10^{-3} < p < 10^2$ bar, we have:

$h_e =$	500	1000	5000	10 000	15 000	cal/g
$\dfrac{\gamma_{\mu\rho}}{\gamma_\sigma\gamma_l} =$	1.17	1.16	1.08	1.02	1	

$$L(A)_* = 1.31, \quad L(A)_{CO_2} = 1.69 \quad \text{for} \quad T_0 \leqslant 500°\text{K} .$$

We assume that at the outer edge of the boundary layer there is complete dissociation to C and O atoms in the carbon dioxide and to O and N atoms in the air. Then

$$(h_d)_* = 7037 \text{cal/g}, \qquad (h_d)_{CO_2} = 8670 \text{cal/g}, \qquad \gamma_h = (h_e + 3950)/(h_e + 1223) .$$

For example,

$$\gamma_h = 1.27 \quad \text{for} \quad h_e = 900 \text{ cal/g}, \quad \gamma_h = 1.24 \quad \text{for} \quad h_e = 50\,000 \text{ cal/g}.$$

This increase in heat flux in CO_2 as compared with air is primarily associated with the higher values of the energy of dissociation of unit mass of CO_2 and the Lewis-Semenov number and the somewhat greater mobility of the C and O atoms as compared with the O and N atoms, and, to a lesser extent, with the difference in the values of $\mu\rho$ at the outer edge of the boundary layer.

Using the generalized analogy between the heat and mass transfer coefficients obtained in [10] for a boundary layer with an arbitrary pressure gradient, it is easy to conclude that the specific heat flux for flight in CO_2 gas will always be greater than that for flight in air for any point on the exposed surface.

REFERENCES

1. G. A. Tirskii, "Determination of effective diffusion coefficients in a laminar multicomponent boundary layer," DAN SSSR, vol. 155, p. 1278-1281, 1964.
2. L. Howarth, "The boundary layer in three dimensional flow, Part II, The flow near a stagnation point," Philos. Mag., vol. 75, no. 42, p. 1433-1440, 1951.
3. E. Reshotko, "Heat transfer to a general three dimensional stagnation point," Jet Propuls., vol. 28, no. 1, p. 58-60, 1958.
4. L. Lees, "Convective heat transfer in the presence of a supply of matter and chemical reactions," Collection: Gas Dynamics and Heat Transfer in the Presence of Chemical Reactions [Russian translation], IL, Moscow, p. 13, 1962.
5. G. A. Tirskii, "Laminar multicomponent boundary layer on a chemically active surface," DAN SSSR, vol. 156, no. 4, p. 756, 1964.
6. J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, Molecular Theory of Gases and Liquids [Russian translation], IL, 1961.
7. A. Poger and A. Svehe, "Estimated viscosities and thermal conductivities of gases at high temperatures," NASA TR, R - 132, 1963.
8. G. A. Tirskii, "Analysis of the chemical composition of a multicomponent boundary layer at the surface of burning plastics," Kosmicheskie issledovaniya, no. 4, 1964.
9. D. Fey and F. Riddell, "Theoretical analysis of heat transfer at a forward stagnation point in a flow of dissociated air," Collection: Gas Dynamics and Heat Transfer in the Presence of Chemical Reactions [Russian translation], IL, Moscow, p. 190, 1962.
10. B. I. Reznikov and G. A. Tirskii, "Generalized analogy between the coefficients of heat and mass transfer in a multicomponent boundary layer with an arbitrary pressure gradient," DAN SSSR, vol. 158, no. 4, p. 798-802, 1964.

11 July 1964 Moscow