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SURFACE CATALYSIS IN DISSOCIATED, CHEMICALLY FROZEN AIR BOUNDARY LAYERS WITH VARIABLE TRANSPORT PROPERTIES

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Abstract—This work is concerned with the effects of surface catalysis and variable transport properties on the structure of chemically frozen, dissociated air boundary layers enveloping flat plates and slender wedges. Our main interest is in nonsimilar hypersonic flows past catalytic segments placed aft of leading edges or stagnation points coated with noncatalytic materials. The problems are solved numerically; the method of solution is shown to be reliable and applicable in general to the solution of nonsimilar boundary-layer equations. Local convective heat transfer and heat release due to catalysis of atoms are computed separately. These results show that variable transport properties and non-similarity of the flow field have a significant influence on the heat flux due to catalysis and suggest possible serious errors in available diagnostic formulas for catalytic gauges.

NOMENCLATURE

c_p,	frozen specific heat of the mixture at constant pressure, $$c_p = \sum_{i=1}^{2} w_i c_{p_i};$$
c_v,	specific heat at constant volume;
D,	binary, atom–molecule, diffusion coefficient, $D \equiv D_{ij}$;
$f, \bar{f}$,	dimensionless velocity functions;
h,	enthalpy, $$h = \sum_{i=1}^{2} w_i h_i;$$
$H, \bar{H}$,	dimensionless total frozen enthalpies of the mixture, $$H = (\tfrac{1}{2}u^2 + h_f)(\tfrac{1}{2}U_e^2 + h_{f_e})^{-1} \equiv h_{tf}/h_{tf_e};$$
K,	a constant;
l,	dimensionless product of mixture density and viscosity, $\rho\mu/\rho_e\mu_e$;
Le,	Lewis number, $$Le = \frac{\rho D c_p}{\mu};$$
k_w,	specific surface reaction rate;
p,	static pressure;
Pr,	Prandtl number of the mixture, $$Pr = \frac{\mu c_p}{\lambda};$$
q_c, q_d,	convective heat transfer and heat flux due to catalysis, equations (11) and (12);
q_t,	total heat transfer, $q_c + q_d$;
$q^*_{c\text{-sim}}$,	convective heat transfer for similar flows based on Lees' formula with $l \equiv \mathrm{K} = l_{w,r}{}^{0\cdot 2}$;
$q_{c\text{-sim, E.C.P.}}$, $q_{c\text{-sim, V.P.}}$,	convective heat transfer for similar flows computed, respectively, with equivalent constant properties and variable properties;

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Sc,	Schmidt number, $Sc = \frac{\mu}{\rho D}$;
T,	temperature, [°R];
u, U_e,	velocity components along the surface;
v,	velocity component normal to the surface;
w,	atom concentration;
W,	atom concentration ratio, w/w_e;
x,	coordinate parallel to the surface;
y,	coordinate normal to the surface.

Greek symbols

ζ,	Damkohler number, $\zeta \equiv \frac{Sc_w \rho_w k_w \xi^{\frac{1}{2}}}{l_w(\rho_e \mu_e U_e)^{\frac{1}{2}}}$
$\bar{\zeta}$,	Damkohler number for E.C.P. problems, $\bar{\zeta} = \mathrm{K}^{\frac{1}{2}}\zeta_{ave}, \mathrm{K} = {l_{w,r}}^{0.2}$;
η,	coordinate normal to surface;
$\bar{\eta}$,	coordinate normal to surface (E.C.P.) problems), $\bar{\eta} = \mathrm{K}^{-\frac{1}{2}}\eta, \mathrm{K} = {l_{w,r}}^{0.2}$;
λ,	thermal conductivity of the mixture;
μ,	dynamic viscosity of the mixture;
ξ,	coordinate parallel to the surface;
ρ,	density of the mixture;
ψ,	stream function.

Subscripts

a,	atom;
ave,	average;
e,	"edge" of boundary layer;
f,	frozen;
i,	ith component;
m,	molecule;
o,	refers to $\xi_o = 1$;
r,	reference condition;
t,	total;
tf,	total frozen;
w,	wall;
w, r,	fixed ξ reference condition at the wall.

1. INTRODUCTION

LOW SPEED boundary-layer flows with chemical reactions confined to a bounding surface were discussed by Chambré [1] and Chambré and Acrivos [2, 3]. Shortly thereafter, many aerodynamicists considered analogous problems for hypersonic flows, particular emphasis being placed on dissociated boundary layers with catalytic surface recombinations of the atomic species. These efforts were directed towards reducing heat transfer to vehicles exposed to a high-altitude hypersonic environment and towards utilizing catalysis for diagnostics of high-temperature experimental facilities. The first utilization is possible because at high altitudes chemical reactions in a hypersonic boundary layer comprised of products of shock-dissociated air are often strongly inhibited; hence, local heat transfer may be significantly reduced by preventing surface recombinations of the atomic species [4–17]. Alternately, the theory of a frozen, dissociated, hypersonic boundary layer over a catalytic surface provides a basis for deducing the degree of free stream dissociation from relatively simple heat-transfer measurements [18–25].

Now, most of the quoted theoretical works are based on the assumption of continuously distributed surface reactions and rest on drastically simplified representations for the transport properties of the gaseous mixtures. The justifications are pragmatical. Well known simplifications of the governing equations are thus achieved, the whole procedure presumably leaving computed values of local heat transfer substantially unchanged. Errors commonly quoted are on the order of 5–15 per cent. That

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† These may appear staggered, for example: h_{tf_e} stands for "total frozen enthalpy at the edge of the boundary layer."

such claims are not necessarily valid even for self-similar flows is evident from the recent paper by Janowitz and Libby [26]. They assumed an artificial, continuous distribution of surface catalyticity, isolated the effects due to variations in transport properties, and established alterations in heat transfer close to 60 per cent as well as significant changes in the structure of the boundary layer. Errors of comparable magnitude were also noted by Vidal and Golian [25]. The authors of [25] reported that measured heat transfer to a uniformly catalytic flat plate immersed in a frozen dissociated oxygen stream was about 40 per cent lower than that predicted by a simplified property theory of Inger [13].

Herein we are concerned with the influence of transport properties on boundary layer development and heat transfer when the flows are nonsimilar. We deal with the flow configuration considered by Chung *et al.* [27] in order to re-examine the theoretical basis for the attractive catalytic gauge systems they mention. The problems are attacked numerically.† In a broader sense, our purpose is to further develop and test a numerical method that is applicable, in general, to the solution of nonsimilar boundary-layer flows. In this respect, our aims resemble those of Smith and his co-workers [29, 30].

2. ANALYSIS

(1) *Boundary value problems*

We consider the flow of dissociated air in a hypersonic laminar boundary layer on either a flat plate or a wedge. To avoid excessive complications, we think of air as a binary mixture of atoms and molecules. The transport properties of the mixture are specified functions of local atom concentration and temperature. The boundary layer is chemically frozen; and the ambient conditions—constant speed U_e, constant temperature T_e and constant atom concentration w_e—are given. A section of the surface of the plate or the wedge acts as a catalyst promoting the recombination of atoms diffusing from the outer regions of the boundary layer inward. In all cases, the heterogeneous surface reaction is of first order and takes place aft of a given streamwise location x_0. The surface is non-catalytic from the leading edge up to x_0.

The well known boundary layer equations appropriate to our problems (see, for example, [16] pp. 965–966) may be reduced to the following system:

Momentum:

$$\frac{\partial}{\partial\eta}\left(l\frac{\partial^2 f}{\partial\eta^2}\right)+\frac{1}{2}f\frac{\partial^2 f}{\partial\eta^2} = \xi\left[\frac{\partial f}{\partial\eta}\frac{\partial}{\partial\xi}\left(\frac{\partial f}{\partial\eta}\right)-\frac{\partial f}{\partial\eta}\frac{\partial^2 f}{\partial\eta^2}\right]. \qquad (1)$$

Energy:

$$\frac{\partial}{\partial\eta}\left(\frac{l}{Pr}\frac{\partial H}{\partial\eta}\right)+\frac{1}{2}f\frac{\partial H}{\partial\eta} + \frac{\partial}{\partial\eta}\left[l\left(1-\frac{1}{Pr}\right)\frac{U_e^2}{h_{tf_e}}\frac{\partial f}{\partial\eta}\frac{\partial^2 f}{\partial\eta^2} + \sum_{i=1}^{2}\frac{l}{Pr}\left(Le_i-1\right)\frac{h_{if}}{h_{tf_e}}w_e\frac{\partial W_i}{\partial\eta}\right] = \xi\left[\frac{\partial f}{\partial\eta}\frac{\partial H}{\partial\xi}-\frac{\partial f}{\partial\xi}\frac{\partial H}{\partial\eta}\right]. \qquad (2)$$

Diffusion:

$$\frac{\partial}{\partial\eta}\left(\frac{l}{Sc}\frac{\partial W}{\partial\eta}\right)+\frac{1}{2}f\frac{\partial W}{\partial\eta} = \xi\left[\frac{\partial f}{\partial\eta}\frac{\partial W}{\partial\xi}-\frac{\partial f}{\partial\xi}\frac{\partial W}{\partial\eta}\right]. \qquad (3)$$

Equations (1)–(3) reflect changing the standard independent variables (x, y) to (ξ, η) where

$$\xi \equiv x \text{ and } \eta(x, y) = \left(\frac{U_e}{\rho_e\mu_e x}\right)^{\frac{1}{2}}\int_0^y \rho\,\mathrm{d}y.$$

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† In contrast to Libby and Liu [14], Fox and Libby [15], Hayday *et al.* [16], [28] and Li and Kirk [17] who aim to develop methods yielding approximate solutions to all practical purposes in closed form.

The dependent variables W, H are normalized with respect to free stream quantities,

$$W \equiv \frac{w}{w_e}, \qquad H \equiv \frac{h_{tf}}{h_{tf_e}},$$

and f is related to the stream function Ψ by $f = \Psi(\rho_e \mu_e U_e x)^{-\frac{1}{2}}$. All symbols are listed in the Nomenclature.

The boundary conditions are as follows:

$$\frac{\partial}{\partial \eta} f(\xi, 0) = f(\xi, 0) = 0, \quad \lim_{\eta \to \infty} \frac{\partial}{\partial \eta} f(\xi, \eta) = 1; \tag{4a}$$

$$H(\xi, 0) = H_w, \qquad \lim_{\eta \to \infty} H(\xi, \eta) = 1; \tag{4b}$$

$$W(\xi, 0) = W_w(\xi) = 1 \quad \text{for} \quad \xi \leqslant \xi_o,$$

$$\left.\begin{aligned} \frac{\partial}{\partial \eta} W(\xi, 0) &= \frac{Sc_w \rho_w k_w \xi^{\frac{1}{2}}}{l_w (\rho_e \mu_e U_e)^{\frac{1}{2}}} W(\xi, 0) \text{ for } \xi > \xi_o; \\ \lim_{\eta \to \infty} W(\xi, \eta) &= 1. \end{aligned}\right\} \tag{4c}$$

The statement (4a) is self-explanatory. In (4b), H_w is taken as constant implying, under some mild restrictive assumptions, constant surface temperature (see [16] footnote, p. 966). The first condition in (4c) states that no catalysis takes place for $\xi \leqslant \xi_o$. A glance at equation (3) suffices to show that not only is the initial distribution $W(0, \eta) = 1$ automatically required but that $W(\xi, \eta) = 1$ for all $\xi \leqslant \xi_o$. Aft of ξ_o, catalytic recombination of atoms proceeds at a rate k_w; it is tacitly assumed that the reaction is of first order as reflected in the balance at the surface between the diffusive flux of atoms and their recombination (see [16] and [31], p. 143).

We note in passing that, in the sense of Lees' cold wall approximation, (1)–(3) cover flows with pressure gradients and, with a slight change in η, apply formally to flows past bodies of revolution. The nonsimilarity of the flow field, reflected explicitly in the right-hand sides of (1)–(3), is caused principally by the boundary conditions on the diffusion equation and (one expects) to a lesser degree by the mutual interdependence of the equations through the transport properties of the mixture. For example, if l = const. and $Pr = Le_i = 1$ equations (1) and (2) admit similarity solutions not dependent on the diffusion equation. Approximations of this sort were used in [16], [27] and elsewhere [31]. One aim of this paper is to present sample solutions testing the validity of the approximations just mentioned. For this reason and to provide one of several checks of the accuracy of our numerical results, we not only solve (1)–(4) but also a related system with simplified transport properties described in the next paragraph.

Boundary value problems based on what we shall call "equivalent constant properties" (E.C.P.)† are constructed as follows: let l = K where K is a specified constant; let the specific heats of the components, c_{pi}, be equal and constant and let Sc, Pr, Le_i be constants on the order of one. As mentioned earlier, equations for f and H are then uncoupled from the W equation and, because of the boundary conditions (4a) and (4b), admit similarity solutions. It is natural to introduce now a new independent variable $\bar{\eta} = K^{-\frac{1}{2}}\eta$ and new dependent variables $\bar{f}$, $\overline{W}$ and $\overline{H}$, the first being defined by $\bar{f} = K^{-\frac{1}{2}} f$ and the latter two following from $\overline{W}(\xi, \bar{\eta}) = W[\bar{\eta}(n); \xi]$, $\overline{H}(\bar{\eta}) = H[\eta(\bar{\eta})]$. Equations corresponding to (8)–(10) are

$$\frac{\mathrm{d}^3 \bar{f}}{\mathrm{d}\bar{\eta}^3} + \frac{1}{2} \bar{f} \frac{\mathrm{d}^2 \bar{f}}{\mathrm{d}\bar{\eta}^2} = 0, \tag{5}$$

$$\frac{\mathrm{d}^2 \overline{H}}{\mathrm{d}\bar{\eta}^2} + \frac{1}{2} Pr \bar{f} \frac{\mathrm{d}\overline{H}}{\mathrm{d}\bar{\eta}} = 0, \tag{6}$$

$$\frac{\partial^2 \overline{W}}{\partial \bar{\eta}^2} + \frac{1}{2} Sc \bar{f} \frac{\partial \overline{W}}{\partial \bar{\eta}} = \xi\, Sc \frac{\mathrm{d}\bar{f}}{\mathrm{d}\bar{\eta}} \frac{\partial \overline{W}}{\partial \xi}, \tag{7}$$

subject to

$$\frac{\mathrm{d}}{\mathrm{d}\bar{\eta}} \bar{f}(0) = \bar{f}(0) = 0, \qquad \lim_{\bar{\eta} \to \infty} \frac{\mathrm{d}\bar{f}}{\mathrm{d}\bar{\eta}} = 1; \tag{8a}$$

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† Henceforth, E.C.P. is used consistently. Moreover, V.P. refers in the grammatically appropriate sense to variable properties.

$$\overline{H}(0) = \overline{H}_w = \text{const.} \lim_{\bar{\eta}\to\infty} \overline{H}(\bar{\eta}) = 1; \qquad \text{(8b)}$$

$$\overline{W}(\xi, 0) = \overline{W}_w(\xi) = 1 \quad \text{for} \quad \xi \leqslant \xi_0,$$

$$\frac{\partial}{\partial\bar{\eta}} \overline{W}(\xi, 0) = \bar{\xi}\, \overline{W}(\xi, 0) \quad \text{for} \quad \xi > \xi_0;$$

$$\lim_{\bar{\eta}\to\infty} \overline{W}(\xi, \bar{\eta}) = 1. \qquad \text{(8c)}$$

Problems posed by equations (5)–(8c) are considered "equivalent" to equations (1)–(4c), once a proper choice of K and the Damkohler number $\bar{\xi}$ is made. The choice of the latter is by no means trivial. The difficulty is this. In the V.P. problems, the Damkohler number

$$\zeta \equiv \frac{Sc_w \rho_w k_w \xi^{\frac{1}{2}}}{l_w(\rho_e \mu_e U_e)^{\frac{1}{2}}}$$

(see equation 4c) varies not only as $\xi^{\frac{1}{2}}$ but also in a complicated manner because of the factor $(Sc_w \rho_w k_w)/l_w$; clearly, the latter depends on transport properties. Now, while the formal relationship between $\bar{\zeta}$ and ζ is

$$\bar{\zeta} = \mathrm{K}^{\frac{1}{2}}\zeta, \qquad \text{(9)}$$

in any E.C.P. problem the Damkohler number $\bar{\zeta}$ must be property-independent. The question then is: to what ζ is a given $\bar{\zeta}$ to correspond and vice versa? Herein this correspondence is arbitrarily established by taking an average of the factor $(Sc_w \rho_w k_w)/l_w$ over the entire ξ-range of a given nonsimilar V.P. solution and substituting this average into (9). This yields $\bar{\zeta} = \mathrm{K}^{\frac{1}{2}}\zeta_{ave}$; the factor K is evaluated according $\mathrm{K} = l_w^{0\cdot 2}$ where again we take an average of the $\rho_w \mu_w$ product over the ξ-range. In making these choices, we hope to minimize the difference between the heat transfer computed in the two sets of problems. Final results show that this indeed happens, at least for the solutions presented in this report. Furthermore, our numerical solutions of the E.C.P. diffusion equation are practically the same as the corresponding analytical (series) solutions of Chung ([31], p. 179).

2. *Summary of properties of dissociated air and method of solution*

We represent dissociated air as a binary mixture of atoms and molecules. The molecular specie is considered to have twice the weight of the atoms, the former being assigned an average weight of 30 and the latter 15. In adopting this point of view, we adhere to established procedure exemplified by the works of Fay and Riddell [5] and Scala and Baulknight [32]. The properties of the individual species are based on the better data currently available. To conserve space, we merely list here the pertinent sources of information on transport properties. The formulas representing our curve fits to the various tabulated data, omitted herein, are given in [33] and [40].

Temperature–enthalpy relationship. This is given by a rational function of the form $T = Z_1(h_{mf})/Z_2(h_{mf})$, is valid over the entire h_{mf}, T range, and is based on the analytical properties of the c_{pm} relationship of [32].

Frozen specific heat of the mixture, c_p. This is given by the standard formula of [32] incorporating the value for c_{pa} used therein.

Viscosity of the mixture, μ. The mixture formula is based on Wilke [34]; viscosity for the atomic specie, μ_a, is based on Yun and Mason [35] and viscosity for the molecular specie, μ_m, is based on the earlier work of Amdur and Mason [36]; low temperature data conform to NBS-tables [37].

Conductivity of the mixture, λ. Is calculated as suggested by Mason and Saxena [38] with $\lambda_a \sim \mu_a$; $\lambda_m \sim \mu_m$ incorporates the Eucken relation due to Hirschfelder [39].

Binary, atom–molecule diffusion coefficient, $D_{a-m} \equiv D$. This is presented as pD (a function of temperature) and is based on the data of Yun and Mason [35]. Graphs of the various properties are given in [40].

An attempt to integrate equations that have the structure of equations (1)–(3) goes back to Hartree and Womersley [41]. Their idea is to replace the ξ-derivatives by finite differences and then solve the resultant ordinary differential equations subject to the split boundary conditions (4a)–(4c) as initial value problems. Specifically, the main steps of our procedure are the following. The similar flow field which exists up to $\xi = \xi_o$ is determined first by integrating equation (1) and equation (2) with their right-hand sides set equal to zero. (The solution of equation (3) is $W = 1$ for all $\xi \leqslant \xi_o$.) This is tantamount to solving an initial value problem governed by weakly coupled equations; the guesses $f''(0)$, $H'(0)$ are systematically improved as in our earlier work [42] until the conditions at infinity are satisfied to prescribed accuracy. Best available property information is used at each stage of the iterative procedure. The method is carried over with suitable modifications into the nonsimilar regime and the same procedure applies to the simpler boundary value problems, equations (5)–(8c). For details, in particular our approach to systematic improvements of derivatives at the surface and the so-called interior matching technique, we refer the reader to [33], [40] and [43].

3. RESULTS

(1) *Heat transfer*

We assess the influence of variable transport properties and the induced nonsimilarity of the flow field on local heat transfer. To exhibit this influence clearly, the local convective heat flux, q_c, and the diffusive heat flux, q_d, are computed separately. The latter equals the heat released in the recombination reaction of atoms.

Now, in accord with boundary layer theory, the total heat transferred to the wall, q_t, may be expressed as the sum

$$q_t = q_c + q_d \tag{10}$$

where

$$q_c = \lambda_w \frac{\partial}{\partial y} T(x, 0)$$

and

$$q_d = \sum_{i=1}^{2} \rho_w D_w \frac{\partial}{\partial y} w_i(x, 0)\, h_{iw}.$$

A simple computation shows that in terms $\partial h_{tf}/\partial_y$

$$q_c = \frac{\mu_w}{Pr_w}\left[\frac{\partial}{\partial y} h_{tf}(x, 0) - (h_{af_w} - h_{mf_w})\frac{\partial}{\partial y} w(x, 0)\right] \tag{11}$$

and

$$\begin{aligned} q_d &= \sum_{i=1}^{2} \rho_w D_w \frac{\partial}{\partial y} w_i(x, 0)\, h_{iw} \\ &= \sum_{i=1}^{2} \rho_w D_w \frac{\partial}{\partial y} w_i(x, 0)\,(h_{if_w} + h_i^{\circ}) \\ &= \frac{\mu_w}{Sc_w}\frac{\partial}{\partial y} w(x, 0)\,(h_{af_w} - h_{mf_w}) \\ &\qquad + \frac{\mu_w}{Sc_w}\frac{\partial}{\partial y} w(x, 0)\, h_a^{\circ}; \end{aligned} \tag{12}$$

h_i° stands for the heat of formation of the *i*th specie.

The sum of (11) and (12) gives

$$\begin{aligned} q_t = \frac{\mu_w}{Pr_w}&\left[\frac{\partial}{\partial y} h_{tf}(x, 0) - (Le_w - 1)(h_{af_w} - h_{mf_w})\frac{\partial}{\partial y} w(x, 0)\right] \\ &+ Le_w \frac{\mu_w}{Pr_w}\frac{\partial}{\partial y} w(x, 0)\, h_a^{\circ}. \end{aligned} \tag{13}$$

In equation (13), the term with the square brackets and the remainder still correspond to q_c and q_d providing all terms having $(h_{af_w} - h_{mf_w})$ as a factor are negligible. Now, $(h_{af} - h_{mf})$ was consistently neglected both in solving the system (1)–(4c) and in calculating the transport properties. Consistency demands, therefore, that the same assumption also be introduced into the various heat transfer formulas.

Consider first the influence of transport properties on q_c as reflected in the ratios

$$\frac{q_c}{q^*_{c\text{-sim}}} = \frac{l(\xi, 0)\, Pr^{-1}(\xi, 0)\, h_{tf_e} \dfrac{\partial}{\partial\eta} H(\xi, 0)}{\dfrac{0{\cdot}47}{\sqrt{2}} Pr_{w,r}{}^{-\frac{2}{3}} (l_{w,r})^{0{\cdot}1} (h_{tf_e} - h_w)}, \tag{14}$$

$$\frac{q_c}{q_{c\text{-sim, E.C.P.}}} = \frac{l(\xi, 0)\, Pr^{-1}(\xi, 0) \dfrac{\partial}{\partial\eta} H(\xi, 0)}{(l_{w,r})^{0{\cdot}1}\, Pr_{w,r}{}^{-1} \dfrac{\mathrm{d}}{\mathrm{d}\bar{\eta}} \bar{H}(0)}, \tag{15}$$

and

$$\frac{q_c}{q_{c\text{-sim, V.P.}}} = \frac{l(\xi, 0)\, Pr^{-1}(\xi, 0) \dfrac{\partial}{\partial\eta} H(\xi, 0)}{l(1, 0)\, Pr^{-1}(1, 0) \dfrac{\partial}{\partial\eta} H(1, 0)}. \tag{16}$$

("sim" stands for "similar"). The first of these, (14), gives a comparison of the nonsimilar, variable properties, conductive heat transfer q_c with $q^*_{c\text{-sim}}$—the heat flux at a corresponding ξ-location computed according to a modified Lees formula used in [27]†. The second ratio, (15), yields the same sort of comparison with results based on the numerical solution of the E.C.P. energy equation. In (16), the effect of the nonsimilarity of the flowfield is isolated in the sense that $q_{c\text{-sim, V.P.}}$ (obtained from solutions of (2) with zero right hand side) rests on the same property assumptions as q_c. Both (14) and (15) require reference states r for the evaluation of the Prandtl number and l. We choose $\xi_r = \xi_o = 1$ and the largest ξ-value of the corresponding nonsimilar solution, namely $\xi_r = 4{\cdot}15$. These choices appear to be most practical because they tend to bracket the variations induced by changes in transport properties. We emphasize that l which appeared formally in (15) was replaced with $(l_{w,r})^{0{\cdot}2}$. Consequently, (14) and (15) are practically the same and yield numerical results differing by no more than $\frac{1}{2}$ per cent. (The denominator of equation (14) differs from its counterpart in (15) only in that the transformed $\partial h_{tf}/\partial y$ is approximated with $f''(0) \cdot Pr_{w,r}{}^{\frac{1}{3}}$.) Representative calculations were based on the following conditions: $U_e = 8000$ ft/sec, $w_e = 0{\cdot}5$, $T_e = 10{,}800$°R, $T_w = 1260$°R, $p = 0{\cdot}1$ atm. and $\xi_o = 1$ ft. The effectiveness of the surface as a catalyst was expressed in terms of the parameter $k_w\xi_o/U_e$ and examined in the range $3 \times 10^{-6} \leqslant k_w\xi_o/U_e \leqslant 3 = 10^{-1}$. The parameter $k_w\xi_o/U_e \sim \zeta_o$ is more convenient than ζ_o because it does not depend on transport properties.

Results presented in Table 1 typify conditions for efficient catalysts and consequently reflect the largest variations in transport properties. Nevertheless, convective heat transfer computed on the basis of an approximate theory is subject to relatively mild errors. The last column shows that the isolated effect of non-similarity, as defined by equation (16), is to increase q_c by not more than 11 per cent and that this effect is slightly larger for the larger value of $k_w\xi_o/U_e$. Changes in transport properties alone tend to have the opposite effect in the sense that $q_{c\text{-sim, V.P.}} < q^*_{c\text{-sim}}$. Consequently, the combined influence is to make q_c very close to $q^*_{c\text{-sim}}$ for all $\xi > 1$ irrespective of the choice of the reference

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† The formula applicable to flows past bodies of revolution as well as two-dimensional flows, is

$$q^*_{c\text{-sim}} = 0{\cdot}47\, Pr_{w,r}^{-\frac{2}{3}} (\rho_e\mu_e)_s{}^{\frac{1}{2}} K^{\frac{1}{2}} U_\infty^{\frac{1}{2}} (h_{tf_e} - h_w)\, \Omega(x)$$

where

$$\Omega(x) \equiv \frac{\dfrac{1}{\sqrt{(2)}} \dfrac{\rho_e\mu_e}{(\rho_e\mu_e)_s} \dfrac{U_e}{U_\infty} r^\varepsilon}{\left[\displaystyle\int_0^x \frac{\rho_e\mu_e}{(\rho_e\mu_e)_s} \frac{U_e}{U_\infty} r^{2\varepsilon} \mathrm{d}x'\right]^{\frac{1}{2}}}$$

and the subscripts e, ∞, and s refer, respectively, to the edge of the boundary layer, conditions upstream of the bow shock wave and a reference state. For flow past a flat plate, $U_e = U$, $\rho_e\mu_e = (\rho_e\mu_e)_s$ and $\varepsilon = 0$. Hence Ä(x) $= 1/\sqrt{(2x)}$; $q^*_{c\text{-sim}}$ differs from that given by Lees only by the factor $\sqrt{(\mathrm{K})}$ which is set equal to $(l_{w,r})^{0{\cdot}1}$. This procedure apparently leads to the best agreement with variable property theories, [26].

Table 1. Effect of variable properties and nonsimilarity of the flow field on convective heat transfer

			$(k_w\xi_o/U_e = 0{\cdot}3)$			
ξ	$l(\xi, 0)$	$Pr(\xi, 0)$	$\partial/\partial\eta\ H(\xi, 0)$	$\frac{q_c}{q^*_{c\text{-sim}}\mid\xi_r = 1}$	$\frac{q_c}{q^*_{c\text{-sim}}\mid\xi_r = 4{\cdot}15}$	$\frac{q_c}{q_{c\text{-sim, V.P.}}}$
1·00	1·7121	0·6816	0·1607	0·9286	0·9084	1·0000
1·05	2·4619	0·6943	0·1255	1·0240	1·0017	1·1027
1·11	2·4638	0·6943	0·1249	1·0196	0·9974	1·0980
1·45	2·4654	0·6943	0·1238	1·0115	0·9805	1·0899
2·61	2·4660	0·6943	0·1228	1·0033	0·9814	1·0804
4·15	2·4663	0·6943	0·1223	0·9997	0·9779	1·0765
			$k_w\xi_o/U_e = 0{\cdot}003$			
1·00	1·7121	0·6816	0·1607	0·9296	0·9106	1·0000
1·05	2·1547	0·6914	0·1374	0·9849	0·9657	1·0606
1·11	2·2270	0·6923	0·1340	0·9916	0·9723	1·0678
1·45	2·3245	0·6934	0·1293	0·9972	0·9777	1·0738
2·61	2·3801	0·6938	0·1262	0·9962	0·9767	1·0727
4·15	2·4025	0·6940	0·1248	0·9940	0·9751	1·0708

Table 2. Effect of variable properties and nonsimilarity of the flow field on heat flux due to catalysis

				$k_w\xi_o/U_e = 0{\cdot}3$				
ξ	$Sc(\xi, 0)$	$\partial/\partial\eta\ W(\xi, 0)$	$\partial/\partial\bar{\eta}\ \overline{W}(\xi, 0)$	W_w	$W_{w\text{-E.C.P.}}$	$\frac{q_d}{q_{d\text{-E.C.P.}}\mid\xi r = 1}$	$\frac{q_d}{q_{d\text{-E.C.P.}}\mid\xi r = 4{\cdot}15}$	q_d/q_c
1·00	0·7618	—	—	1·0000	1·0000	—	—	—
1·05	0·4892	0·4917	1·2618	0·0047	0·0114	1·4160	0·8746	6·9659
1·11	0·4886	0·3172	0·8111	0·0029	0·0063	1·4232	0·9791	4·5209
1·45	0·4883	0·1839	0·4910	0·0015	0·0038	1·3653	0·8433	2·6459
2·61	0·4881	0·1416	0·3799	0·0009	0·0022	1·3597	0·8398	2·0548
4·15	0·4880	0·1296	0·3491	0·0006	0·0016	1·3545	0·8367	1·8887
				$k_w\xi_o/U_e = 0{\cdot}003$				
1·00	0·7618	—	—	1.0000	1·0000	—	—	—
1·05	0·5792	0·4057	0·6225	0·3319	0·5123	1·7500	1·1211	4·4154
1·11	0·5559	0·2991	0·5181	0·2470	0·4174	1·6697	1·0696	3·4823
1·45	0·5266	0·1854	0·3902	0·1406	0·2734	1·5144	0·9701	2·3652
2·61	0·5110	0·1444	0·3369	0·0838	0·1759	1·4409	0·9230	1·9461
4·15	0·5049	0·1323	0·3225	0·0616	0·1335	1·4097	0·9031	1·8253
				$k_w\xi_o/U_e = 0{\cdot}0003$				
1·05	0·7189	0·1254	0·1313	0·8419	0·8971	1·7273	1·3591	0·9981
4·15	0·6107	0·1138	0·1727	0·4463	0·5938	1·6065	1·2640	—
				$k_w\xi_o/U_e = 0{\cdot}00003$				
1·05	0·7569	0·0154	0·0161	0·9819	0·9874	1·5686	1·5091	0·1122
4·15	0·7352	0·0273	0·0302	0·9019	0·9331	1·5667	1·5073	—

state. While the above comments apply to specific cases and while a generalization of these to other flow conditions ought to be based on further numerical results, it is expected that the changes in q_c remain slight in general.

Consider next the influence of transport properties on the heat flux q_d released in the recombination reaction of atoms. The pertinent formula is

$$\frac{q_d}{q_{d\text{-E.C.P.}}} = \frac{l(\xi,0)\,Sc(\xi,0)^{-1}\,\dfrac{\partial}{\partial\eta}\,W(\xi,0)}{(l_{w,r})^{0{\cdot}1}\,(Sc_{w,r})^{-1}\,\dfrac{\partial}{\partial\bar{\eta}}\,\overline{W}(\xi,0)}, \qquad (17)$$

an easy consequence of (12) with $(h_{af_w} - h_{mf_w}) \equiv 0$, and our definition of E.C.P. problems. The factor $(l_{w,r})^{0{\cdot}1}$ appears in (17) for the same reasons as in (16).

In Table 2, the first two sets of tabulations are based on the representative flow conditions used in constructing Table 1. The remaining subtables contain selected results that typify conditions for noncatalytic materials. (An example of a "noncatalyst" is pyrex with $0{\cdot}033$ ft/s $\leqslant k_w \leqslant 0{\cdot}34$ ft/s in the temperature range $570°\text{R} \leqslant T_w \leqslant 1420°\text{R}$. In contrast, k_w for a good silver catalyst is about $1{\cdot}7 \,.\, 10^2$ ft/s). The tabulated ratios $q_d/q_{d\text{-E.C.P.}}$ indicate that, unlike for the case of convective heat transfer, large errors in q_d are possible. Moreover, the deviations of q_d from $q_{d\text{-E.C.P.}}$ depend on the choice of the reference state. This is also contrary to what was found to be the case for convective heat transfer. Evidently, the departures of the q_d values from $q_{d\text{-E.C.P.}}$ arise partly because of the significant variations in $Sc(\xi, 0)$ and partly because the product $(l_{w,r})^{0{\cdot}1}\,\partial/\partial\bar{\eta}\,\overline{W}(\xi, 0)$ does not agree well with $l(\xi, 0)\,\partial/\partial\eta\,W(\xi, 0)$. The latter effect must be attributed to the strong nonsimilarity of the concentration field near the discontinuity which is not insignificant even for the extremely low value of $k_w\xi_o/U_e = 0{\cdot}00003$ with practically constant $Sc(\xi, 0)$. The reader may care to contrast the behaviour of the aforementioned products with their counterparts appearing in (14) and particularly (15). The relative magnitudes of q_d and q_c are determined from the ratio

$$\frac{q_d}{q_c} = \frac{Sc^{-1}(\xi,0)\,\dfrac{\partial}{\partial\eta}\,W(\xi,0)\,h_a^o w_e}{Pr^{-1}(\xi,0)\,\dfrac{\partial}{\partial\eta}\,H(\xi,0)\,h_{tf_e}}. \qquad (18)$$

The tabulated values are based on $h_a^o = 2{\cdot}6509 \cdot 10^8\ \text{ft}^2/\text{s}^2$—arithmetic average of the heats of formation for oxygen and nitrogen; $h_\text{O}^0 = 1{\cdot}6656 \cdot 10^8\ \text{ft}^2/\text{s}^2$ and $h_\text{N}^0 = 3{\cdot}6363 \cdot 10^8\ \text{ft}^2/\text{s}^2$. In more detailed computations, one ought to use a properly mass-averaged h_O^0 that identifies the actual amounts of dissociation due to oxygen and nitrogen molecules. In such case, the values in the q_d/q_c column need be multiplied by a constant, not too different from 1. Because q_c tends to change relatively little, the deviations of the ratio q_d/q_c follow those of $q_d/q_{d\text{-E.C.P.}}$. The same is true for $q_t/q_c = 1 + q_d/q_c$. The right-hand limits at $\xi = 1$ are not tabulated because the numerical program does not compute these. Such limits are otherwise determined.

It is worthwhile to consider briefly what implications the tabulated results have in connection with catalytic gauges and the associated diagnostic formulas[†]. Now, one candidate for a diagnostic formula for w_e is implied by (18), namely

$$\begin{aligned} w_e &= \frac{Sc(\xi,0)\,\dfrac{\partial}{\partial\eta}\,H(\xi,0)\,h_{tf_e}}{Pr(\xi,0)\,\dfrac{\partial}{\partial\eta}\,W(\xi,0)\,h_a^o}\,\frac{q_d}{q_c} \\ &= \frac{Sc(\xi,0)\,\dfrac{\partial}{\partial\eta}\,H(\xi,0)\,h_{tf_e}}{Pr(\xi,0)\,\dfrac{\partial}{\partial\eta}\,W(\xi,0)\,h_a^o}\left(\frac{q_t}{q_c} - 1\right) \qquad (19) \end{aligned}$$

[†] A catalytic gauge system consists of two heat transfer gauges; one is a noncatalyst (say glass) and the other is a catalyst for the recombination of atoms (say silver). Now, in a frozen hypersonic boundary layer, the first measures convective heat transfer, but the second measures additionally the heat released in the recombination reaction of atoms. Having these two measurements, it is then possible to deduce from the theory the atom concentration at the edge of the boundary layer. The latter is locally the same as the free-stream concentration.

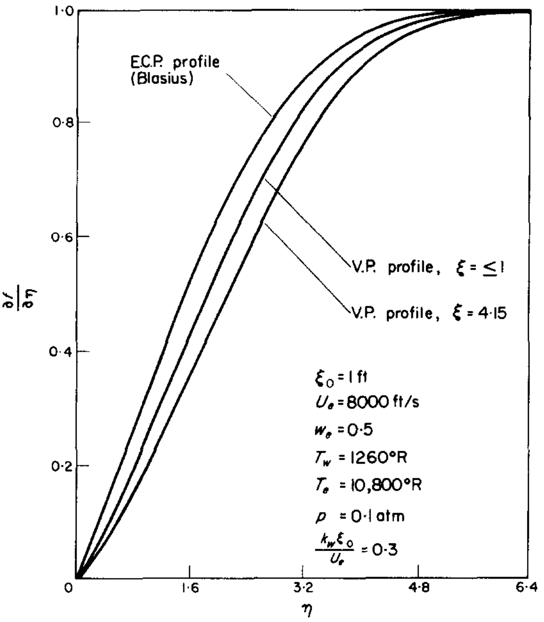

FIG. 1. Velocity profiles, $u/U_e = \partial f/\partial\eta$, for $0 < \xi \leqslant 4{\cdot}15$.

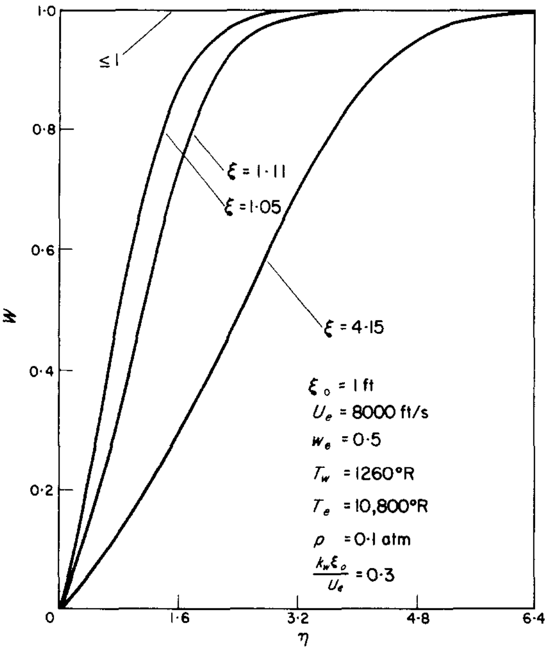

FIG. 3. Atom concentration profiles $W = w/w_e$, for $0 < \xi \leqslant 4{\cdot}15$.

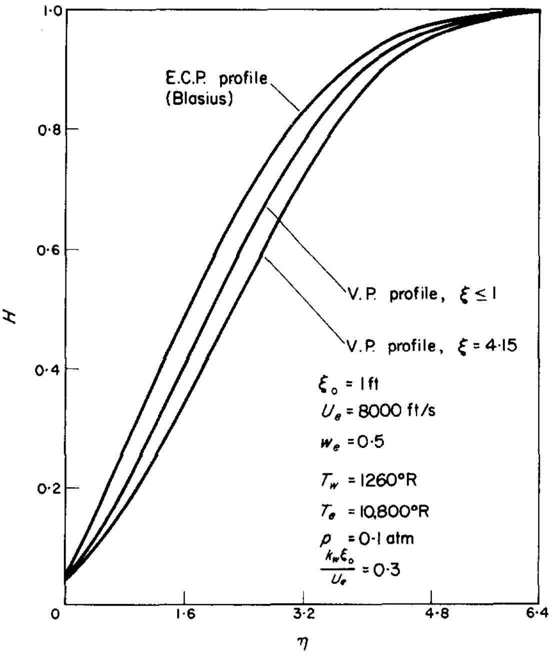

FIG. 2. Total frozen enthalpy profiles, $H = h_{tf}/h_{tf_e}$, for $0 < \xi \leqslant 4{\cdot}15$.

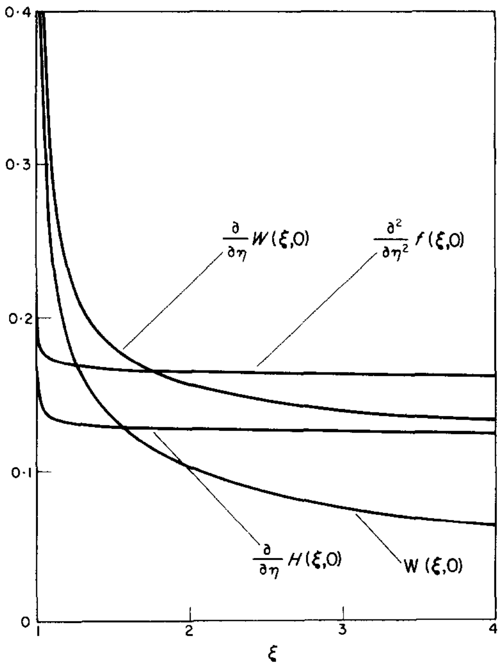

FIG. 4. ξ-history of the derivatives $\partial^2/\partial\eta^2 f(\xi, 0)$, $\partial/\partial\eta\ H(\xi, 0)$ and $\partial/\partial\eta\ W(\xi, 0)$.

It is at once clear from equation (19) that the error in w_e is proportional to q_d/q_c or, what amounts to the same thing, to $(q_t/q_c - 1)$. The ratio $\partial/\partial\eta\, H(\xi, 0)/\partial/\partial\eta\, W(\xi, 0)$ is presumably correlated and appears finally as a function of known ambient and wall conditions. We emphasize that it is not the error in q_c or q_d but the error in the ratio q_d/q_c that matters. Moreover, we are mainly interested in such errors when ξ is slightly larger than 1 (because that is the location of heat-transfer measurements) and, *a fortiriori*, for very low and very high values of $k_w\xi_o/U_e$ (because these correspond, respectively, to an almost perfect noncatalyst and a perfect catalyst). Now, when $k_w\xi_o/U_e = 0{\cdot}3$—implying a value of k_w greater than that for silver—q_d/q_c at $\xi = 1{\cdot}05$ is more than 40 per cent higher than $q_{d\text{-E.C.P.}}/q_{c\text{-E.C.P.}}|\xi_r = 1$. This error is slightly smaller than that reflected in the values of $q_d/q_{d\text{-E.C.P.}}|\xi_r = 1$ because $q_{c\text{-E.C.P.}} \doteq q^*_{c\,\text{sim}}$ underestimates q_c. The choice of the reference state $\xi_r = 1$ seems logical since the E.C.P. transport properties correspond more closely to the actual local conditions. From a practical standpoint such errors seem hardly tolerable. The situation remains substantially the same when $k_w\xi_o/U_e = 0{\cdot}00003$. Of course, the errors here are not too important because q_d is only 11 per cent of q_c. The general increase in heat transfer following the step discontinuity is noreworthy.

2. *Flow field*

Sample profiles of velocity, total frozen enthalpy, and atom concentration, showing the effects of variable transport properties and non-similarity of the boundary layer, are presented, respectively, in Figs. 1, 2, and 3; $k_w\xi_o/U_e = 0{\cdot}3$. The profiles are dimensionless. Evidently, the aforementioned effects are more or less as important to the structure of the velocity field as to the structure of the enthalpy field. Figure 3 shows a partial ξ-history of the concentration field $W = w/w_e$. Note that w_w is very close to zero. Figure 4 presents the ξ-history of the derivatives $\partial^2/\partial\eta^2\, f(\xi, 0)$, $\partial/\partial\eta\, H(\xi, 0)$, $\partial/\partial\eta\, W(\xi, 0)$ and $W(\xi, 0)$ for a less effective catalyst corresponding to $k_w\xi_o/U_e = 0{\cdot}003$. The three derivatives are proportional, respectively, to the skin friction, convective heat transfer, and heat flux due to catalysis. The very rapid approach of $\partial^2/\partial\eta^2\, f(\xi,0)$ and $\partial/\partial\eta H(\xi,0)$ to its ξ-asymptotic behavior is noteworthy. These two curves show explicitly the induced non-similarity effect on the two derivatives just mentioned. Fortunately, the variations of the transport properties tend to smooth the induced non-similarity of $\partial/\partial\eta\; H(\xi,0)$ and result in the relatively small errors in q_c. Figure 5 presents the normalized convective heat-transfer parameter $\partial/\partial\eta\; H(\xi,0)/\partial/\partial\eta\; H(1, 0)$ in a wide range of catalytic efficiencies. The dashed curves depict the results for flat plates and wedges that are catalytic for all ξ. Analogous results for the surface concentration ratio $W(\xi, 0)$ are shown in Fig. 6. We note the significant deviation of a typical E.C.P. curve from its exact counterpart.

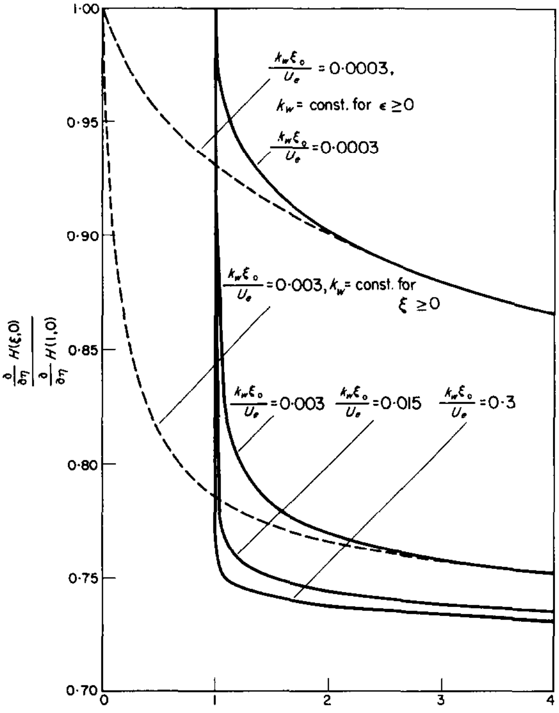

FIG. 5. ξ-history of the convective heat transfer parameter $\partial/\partial\eta\, H(\xi, 0)/\partial/\partial\eta\, H(1, 0)$.

Figure 7 tests and verifies the appropriateness of the E.C.P. definition. The dots are taken from Chung ([31], p. 179, Fig. 12). The solid curve is based on our E.C.P. definition of a corresponding flat plate of uniform catalyticity.

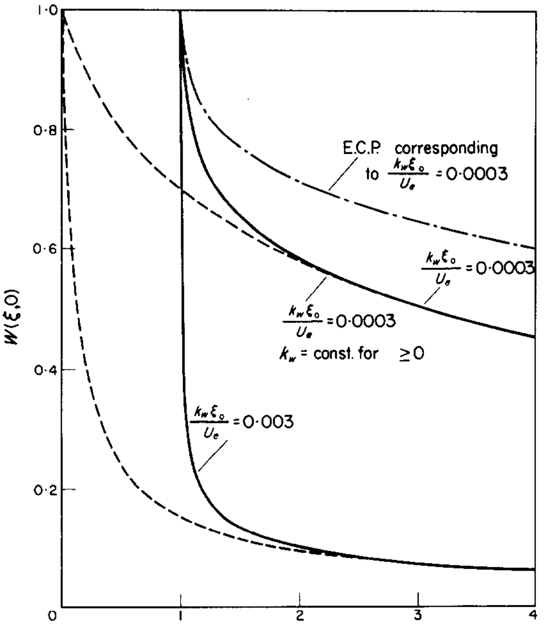

FIG. 6. ξ-history of surface atom concentration $W_w = w_w/w_e$.

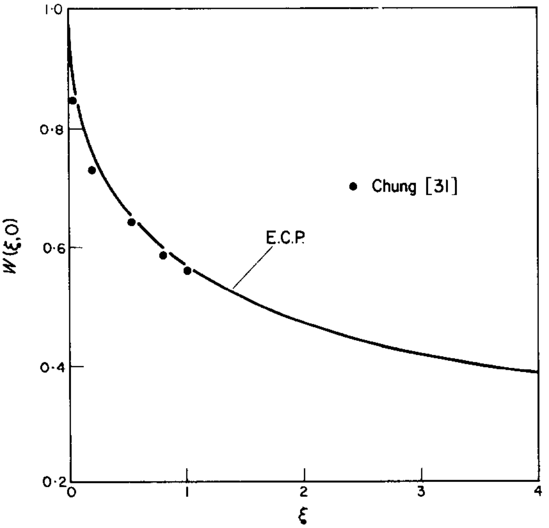

FIG. 7. ξ-history of surface atom concentration $W_w = w_w/w_e$; E.C.P.

4. CONCLUSIONS

The paper shows that variable transport properties and nonsimilarity of the flow field have a significant influence on the surface heat flux released in the recombination reaction of atoms. The same effect on convective heat transfer is considerably smaller. The results suggest that diagnostic formulas based on the simpler (E.C.P.) theories may be in serious error. The main reason is that while the step discontinuity in surface catalyticity causes a large (and from the standpoint of diagnostics often beneficial) increase in total heat transfer it apparently also increases the errors of the E.C.P. analyses. The numerical method of solution is reliable and general. Chemical reactions in the gas phase and other effects may be included with relative ease.

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Résumé—Cette étude se rapporte aux effets de catalyse de surface et des propriétés de transport variables sur la structure de couches limites d'air dissocié figé chimiquement entourant des plaques planes et des dièdres élancés. Notre principal intérêt est l'écoulement hypersonique sans similitude le long de segments catalytiques placés à l'aval des bords d'attaque ou des points d'arrêt revêtus de matériaux noncatalytiques. Les problèmes sont résolus numériquement; on montre que la méthode de résolution est fiable et appliquable en général à la solution des équations de la couche limite sans similitude. Le transport de chaleur local par convection et le dégagement de chaleur dû à la catalyse des atomes sont calculés séparément. Ces résultats montrent que les proprétés de transport variables et la non-similitude du champ d'écoulement ont une influence sensible sur le flux de chaleur dû à la catalyse et suggèrent la possibilité d'erreurs sérieuses dans les formules disponibles de diagnostic pour les jauges catalytiques.

Zusammenfassung—Die Arbeit befasst sich mit den Auswirkungen von Oberflächen-Katalyse und variablen Transporteigenschaften auf die Struktur der Grenzschicht an ebenen Platten und flächen Keilen in chemisch eingefrorener, dissoziierter Luft. Das Hauptinteresse gilt dabei nichtähnlichen hypersonischen Strömungen über Katalysatorsegmenten, die hinter den Anströmkanten oder den Staupunkten angebracht und mit nichtkatalytischen Materialien abgedeckt sind. Die Probleme wurden numerisch gelöst, es wird gezeigt, dass die Lösungsmethode zuverlässig ist und allgemein zur Lösung von nichtähnlichen Grenzschicht-Gleichungen verwendet werden kann. Der lokale konvektive Wärmetransport und die lokale Wärmeausbeute aufgrund der Katalyse wurden einzeln berechnet. Die Ergebnisse zeigen, dass die variablen Transporteigenschaften und die Nicht-Ähnlichkeit des Strömungsfeldes einen erheblichen Einfluss auf den Wärmestrom aufgrund der Katalyse haben. Die Ergebnisse weisen auf mögliche Fehler bei den verfügbaren Rechenformeln für katalytische Abschätzungen hin.

Аннотация—В данной работе рассматривается влияние катализа поверхности и переменных свойств переноса на структуру химически замороженных диссоциированных пограничных слоев воздуха, обтекающих плоские пластины и тонкие клинья. В основном нас интересуют неавтомодельные гиперзвуковые потоки, обтекающие каталитические участки на передних кромках или в критических точках, покрытые некаталитическими материалами. Задачи решаются численно; показано, что метод решения надежен и, в общем, применим к решению неавтомодельных уравнений пограничного слоя. Рассчитаны локальный конвективный теплообмен и выделение тепла за счет катализа атомов. Эти результаты показывают, что переменные свойства переноса и неавтомодельность поля потока значительно влияют на тепловой поток за счет катализа и указывают на возможные серьзные погрешности в имеющихся расчетных формулах для каталитических приборов.