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# ON LAMINAR BOUNDARY-LAYER FLOWS OF A DISSOCIATED GAS PAST CATALYTIC SURFACES*

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**Abstract**—This paper treats laminar boundary-layer flows of a dissociated gas past catalytic surfaces, particular attention being paid to situations where the surface reaction rates vary as powers of the streamwise coordinate and the reaction orders are different from unity. The gas in the boundary layer is represented by a chemically frozen binary mixture of atoms and molecules, and the usual simplifying assumptions applicable to hypersonic boundary-layer flows are used. Approximate integrals of the diffusion equation are obtained analytically with the aid of the asymptotic method. Herein this method is shown to compare very favorably with others, both with respect to simplicity of application and accuracy of results. In contrast to other approaches, it lends a definite unity of approach, little added difficulty being encountered in treating other than first order reactions or in obtaining boundary-layer profiles. Surface distributions of atoms and heat transfer are exhibited graphically and compared with published theoretical results.

## NOMENCLATURE

| | |
|---|---|
| $c_p$, | specific heat; |
| $D$, | diffusion coefficient; |
| $f, \bar{f}, F$, | dimensionless velocity functions; |
| $h$, | enthalpy; |
| $H, \bar{H}$, | dimensionless enthalpies; |
| $l$, | dimensionless product of density ($\rho$) and viscosity ($\mu$); |
| $L$, | a characteristic length; |
| $Le$, | Lewis number; |
| $k_w$, | specific reaction rate; |
| $p$, | pressure; |
| $Pr$, | Prandtl number; |
| $r$, | radius of a body of revolution; |
| $\bar{s}$, | dimensionless coordinate along surface, equation (6); |
| $Sc$, | Schmidt number; |
| $T$, | temperature; |
| $u, U$, | velocity components along surface; |
| $v, V$, | velocity components normal to surface; |
| $w$, | atom concentration; |
| $W$, | atom concentration ratio $w/w_e$; |
| $x$, | coordinate along surface; |
| $X$, | dimensionless coordinate along surface; |
| $y$, | coordinate normal to surface. |

Greek symbols

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|---|---|
| $\varepsilon$, | parameter related to geometry; |
| $\zeta, \bar{\zeta}$, | Damkohler numbers, equations (17) and (35); |
| $\bar{\eta}, \eta$, | dimensionless coordinates normal to surface, equations (6) and (11); |
| $\lambda$, | thermal conductivity of the mixture; |
| $\mu$, | dynamic viscosity; |
| $\xi$, | dimensionless coordinate along surface, equation (11); |
| $\rho$, | density; |
| $\Psi$, | stream function, equation (7). |

Subscripts

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| $e$, | boundary-layer edge; |

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| $f$, | frozen; |
| $i$, | $i$th component; |
| $tf$, | total frozen; |
| 0, | arbitrary reference condition; |
| $w$, | wall; |
| $\infty$, | conditions upstream of the body. |

Superscripts

| | |
|---|---|
| $N$, | reaction order. |

## 1. INTRODUCTION

THE GAS in the boundary layer enveloping a vehicle moving at hypersonic speed is generally dissociated and, to a good approximation, may often be taken as a binary mixture of atoms and molecules. As is well known, the determination of the boundary-layer structure is nonetheless still complicated through the mutual interaction of flow and chemistry. Now, in certain flight regimes of practical interest, the homogeneous chemical reactions within the gas phase proceed quite slowly in comparison to the heterogeneous reactions at the surface, in fact, slowly enough so that the former may be neglected altogether. The actual conditions in the gas phase may then be represented by the so-called frozen flow, the composition in the boundary layer, apart from the influence of the wall, being controlled by diffusion alone. Chemical activity is confined solely to the gas–solid interface and obviously plays a controlling role in determining surface composition and energy transfer to the vehicle. An important case arises whenever the surface remains structurally intact and acts as a catalyst, promoting thereby the recombination of atoms diffusing from the outer portion of the boundary layer inwards. The reactions proceed generally at a finite rate, the entire process being out of chemical equilibrium. The catalyticity of the surface is considered to be a prescribed function of $x$—the coordinate parallel to the surface.

The problems just mentioned have received considerable attention. The first related papers on the subject, not restricting the hydrodynamic aspects too severely, are apparently due to Chambré [1], Chambré and Acrivos [2] and Acrivos and Chambré [3]. The first work lays a general basis for the formulation of problems involving chemical reactions on solid surfaces for a variety of internal and external flows of the boundary-layer type. Formal solutions describing the (nonsimilar) concentration and temperature fields, say $w$ and $T$, are based on the Volterra equation equivalent to the original linear partial differential equations for $w$ and $T$. The latter two papers, [2, 3] deal with further numerical examples employing power series solutions in the streamwise coordinate and approximate solutions based on the Volterra equation; therein, the reactions are taken as isothermal, for the most part of first order, and the catalyticity is considered constant. In [2, 3], the procedure yielding the power series solutions for the concentration field is the same as that of Chapman and Rubesin [4] who treated convective heat transfer to nonisothermal surfaces.* In fact, the problems are to all practical purposes mathematically identical. A similar remark holds for the approximate results, these being deduced similarly to those given by Lighthill [5]. The work described by Chambré and Acrivos in [2] has recently been extended by Inger [6] who solved the same problem for flat plate and supersonic wedge flows when the catalyticity is a power law function of the streamwise coordinate. His series solutions of the diffusion equation (requiring up to fifteen terms) were compared with those of Chung and Anderson [7, 8] based on the von Kármán–Pohlhausen method, those of Chung, Liu and Mirels [9] using what Inger calls the Lighthill–Volterra approach, and a local similarity approximation.

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* We emphasize that the basic problem in [2, 3], as well as in the other quoted references dealing with flows past catalytic surfaces, amounts to the solution of the diffusion equation. The momentum and energy equations, uncoupled from the latter and appropriately simplified and transformed, are of the same form as those for nonreacting low speed flows of the similarity class. The concentration field is, with the exception of the stagnation point flow, nonsimilar.

The first two agreed very well with the series solutions, but the last was found to be relatively poor, particularly for the more rapid variations of catalyticity with the streamwise coordinate. All of the results were obtained for first order reactions. This includes the examples in [9] and its later version [10] dealing with jump discontinuities in surface catalyticity. The influence of reaction order other than unity was investigated by Rosner [11] for flat plate flows. Assuming constant catalyticity, he solved the problem by an iterative technique based on the von Kármán–Pohlhausen integral method. A more complete bibliography is given in Chung's article [12].

One aim of this paper is to present a number of new results on flows past catalytic surfaces, focusing particular attention on situations where the catalytic efficiency is not constant and the reaction order is different from unity. This has bearing on various practical problems, for example, the construction of catalytic gauges. What is equally important, the paper presents applications of a rather powerful analytical method of integration of the boundary-layer equations that is well deserving of further tests. For the particular class of problems treated herein, the method lends a definite unity of approach; in contrast to other approaches, there is little added difficulty in treating reaction orders other than unity or in obtaining boundary-layer profiles. Moreover, the procedure used herein appears to compare very favorably with other approximate methods, both with respect to simplicity of application and accuracy of results.[*]

## 2. BOUNDARY-LAYER EQUATIONS AND ASSOCIATED BOUNDARY VALUE PROBLEMS

The principles expressing respectively conservation of total mass, momentum, energy, and mass of the individual species for laminar boundary-layer flows of a chemically frozen binary mixture may be written as follows:

$$\frac{\partial}{\partial x}(\rho u r^{\varepsilon}) + \frac{\partial}{\partial y}(\rho v r^{\varepsilon}) = 0, \tag{1}$$

$$\rho u \frac{\partial u}{\partial x} + \rho v \frac{\partial u}{\partial y} = -\frac{\mathrm{d}p}{\mathrm{d}x} + \frac{\partial}{\partial y}\left(\mu \frac{\partial u}{\partial y}\right), \tag{2}$$

$$\rho u \frac{\partial h_{tf}}{\partial x} + \rho v \frac{\partial h_{tf}}{\partial y} = \frac{\partial}{\partial y}\left\{\frac{\mu}{Pr}\left[\frac{\partial h_{tf}}{\partial y} + (Pr - 1)\frac{\partial}{\partial y}\left(\frac{u^2}{2}\right) + \sum_{i=1}^{2}(Le_i - 1)\, h_{if}\, \frac{\partial w_i}{\partial y}\right]\right\}, \tag{3}$$

$$\rho u \frac{\partial w_i}{\partial x} + \rho v \frac{\partial w_i}{\partial y} = \frac{\partial}{\partial y}\left(\rho D \frac{\partial w_i}{\partial y}\right). \tag{4}$$

Herein $i = 1, 2$ refer respectively to atoms and molecules. Since $w_1 + w_2 = 1$, where $w_i \equiv \rho_i/\rho$, only one diffusion equation is needed. Hereafter we shall write $w_1 \equiv w$. The set (1–4) covers both two-dimensional flows ($\varepsilon = 0$) and flows past bodies of revolution ($\varepsilon = 1$), the local radius from the axis of symmetry to the generating curve being $r(x)$. The coordinate system $(x, y)$ is body-oriented and orthogonal; the corresponding velocity components are $u$ and $v$, $p$ stands for the pressure, $D$ is the binary diffusion coefficient and $\rho, \mu$, have their standard meaning. The energy equation (3) is written in the "total form", that is, the total frozen enthalpy

$$h_{tf} = \sum_{i=1}^{2} w_i h_{if} + \frac{u^2}{2} = \sum_{i=1}^{2} w_i \int_0^T c_{p_i}\, \mathrm{d}T + \frac{u^2}{2}$$

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[*] We are indebted to a reviewer for bringing to our attention a recent paper by Fox and Libby dealing with the effects of surface catalysis on laminar boundary layers [13]. The paper presents applications of an approximate method, developed by its authors earlier [14, 15], for solving certain laminar boundary-layer equations. Essentially, the method is a perturbation theory of known similar flows. While perhaps preferable from the mathematical point of view, it is considerably more complicated than the asymptotic method and yields, when applied to some of the problems discussed herein, less accurate results than ours.

is taken as the dependent variable.

$$Le_i = \frac{\rho D_i c_p}{\lambda} = \frac{\rho D_i}{\lambda} \sum_{i=1}^{2} w_i c_{p_i}$$

stands for the $i$th Lewis number and $Pr = \mu c_p/\lambda$ is the Prandtl number where $\lambda$ is the conductivity of the mixture. In all of the subsequent work $Pr$, $Le_i$ and the Schmidt number $Sc = \mu/\rho D$ are specified constants.

We shall be concerned with a particular class of solutions of (1–4), subject to the following:

$$u(x,0) = v(x,0) = 0, \tag{5a}$$

$$h_{tf}(x,0) = h_{tf_w} = \text{const},^* \tag{5b}$$

$$\rho_w D_w \frac{\partial}{\partial y} w(x,0) = k_w(\rho_w w_w)^N; \tag{5c}$$

$$\lim_{y\to\infty} u(x,y) = U_e, \tag{5d}$$

$$\lim_{y\to\infty} h_{tf}(x,y) = h_{tf_e} = \text{const}, \tag{5e}$$

$$\lim_{y\to\infty} w(x,y) = w_e = \text{const}. \tag{5f}$$

Herein, the subscripts $w$, $e$ refer respectively to the wall and "edge" of the boundary layer. The third condition, (5c), where on the right hand side the small term

$$\frac{(\rho_w w_w)^N_{\text{equilibrium}} [\rho_w(1 - w_w)]^M}{[\rho_w(1 - w_w)]^M_{\text{equilibrium}}}$$

has been neglected, expresses the surface balance between diffusion of atoms and their recombination; $k_w$ is the specific reaction rate (a function of $x$, or constant) specifying the catalyticity of the wall, $N$ denotes the order of reaction and $M$ is a specified index. The other conditions are self-explanatory.

The set (1–4) is restated in terms of new independent variables

$$\bar{\eta} = \frac{r^\varepsilon U_e}{(2\bar{s})^{\frac{1}{2}}} \int_0^y \rho \, \mathrm{d}y', \qquad \bar{s} = \int_0^x \rho_e \mu_e U_e r^{2\varepsilon} \, \mathrm{d}x', \tag{6}$$

and new dependent variables

$$\bar{H} \equiv \frac{h_{tf}}{h_{tf_e}}, \qquad \bar{W} \equiv \frac{w}{w_e}, \qquad \bar{f}(\bar{\eta}, \bar{s}),$$

the last being related to the stream function $\Psi$ through $\Psi = (2\bar{s})^{\frac{1}{2}} \bar{f}(\bar{\eta}, \bar{s})$. As usual $\Psi$ is such that

$$\rho u r^\varepsilon = \frac{\partial \Psi}{\partial y}, \qquad \rho v r^\varepsilon = -\frac{\partial \Psi}{\partial x}. \tag{7}$$

Standard procedure yields the set corresponding to (2–4),

$$(l\bar{f}_{\bar{\eta}\bar{\eta}})_{\bar{\eta}} + \bar{f}\bar{f}_{\bar{\eta}\bar{\eta}} = -\frac{2\bar{s}}{U_e}\frac{\mathrm{d}U_e}{\mathrm{d}\bar{s}}\left(\frac{\rho_e}{\rho} - \bar{f}_{\bar{\eta}}^2\right) + 2\bar{s}(\bar{f}_{\bar{\eta}}\bar{f}_{\bar{\eta}\bar{s}} - \bar{f}_{\bar{s}}\bar{f}_{\bar{\eta}\bar{\eta}}), \tag{8}$$

$$(l\bar{H}_{\bar{\eta}})_{\bar{\eta}} + Pr\,\bar{f}\bar{H}_{\bar{\eta}} = -\left\{\frac{U_e^2}{h_{tf_e}}[(Pr - 1)\,l\bar{f}_{\bar{\eta}}\bar{f}_{\bar{\eta}\bar{\eta}}]_{\bar{\eta}} + \left[\sum_{i=1}^{2}(Le_i - 1)\,l\,\frac{w_{ie}h_{if}}{h_{tf_e}}\bar{W}_{i,\bar{\eta}}\right]_{\bar{\eta}}\right\} + 2\bar{s}Pr(\bar{f}_{\bar{\eta}}\bar{H}_{\bar{s}} - \bar{f}_{\bar{s}}\bar{H}_{\bar{\eta}}), \tag{9}$$

$$(l\bar{W}_{\bar{\eta}})_{\bar{\eta}} + Sc\bar{f}\bar{W}_{\bar{\eta}} = 2\bar{s}Sc(\bar{f}_{\bar{\eta}}\bar{W}_{\bar{s}} - \bar{f}_{\bar{s}}\bar{W}_{\bar{\eta}}) \tag{10}$$

where $l = \rho\mu/\rho_e\mu_e$, $Sc = \mu/\rho D$ and the subscripts $\bar{\eta}$, $\bar{s}$ denote partial derivatives.

Assuming now that $l = \text{const.}$ and $Pr = Le_i = 1$, equations (8–10) may be simplified further by introducing new independent variables

$$\eta = l^{-\frac{1}{2}}\bar{\eta}, \qquad \xi = \frac{\bar{s}}{(\rho_e\mu_e)_0 U_\infty L^{2\varepsilon+1}} = \int_0^X \frac{\rho_e\mu_e}{(\rho_e\mu_e)_0}\frac{U_e}{U_\infty}\left(\frac{r}{L}\right)^{2\varepsilon} \mathrm{d}X, \tag{11}$$

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* This boundary condition is physically realistic and implies, under a very mild simplifying assumption, constant surface temperature. We have:

$$h_{tf_w} = \sum_{i=1}^{2} w_{iw} h_{if_w} = h_{mf_w} + w_w(h_{af_w} - h_{mf_w}) = h_{mf_w} + w_w \int^{T_w} (c_{p_{aw}} - c_{p_{mw}})\,\mathrm{d}T \doteq h_{mf_w} \doteq c_{p_{mw}} T_w$$

where $m$ and $a$ refer respectively to molecules and atoms. Now, obviously, if $c_{p_a} = c_{p_m} = \text{const}$, the last two statements follow as strict equalities. But, even when $c_{p_a} \neq c_{p_m}$ and both depend on temperature, the term $w_w(h_{af_w} - h_{mf_w})$ is on the order of 4–10 per cent of $h_{mf_w}$ for most practical flows of dissociated air [16, 17] and hence may be neglected irrespective of the variation of $w_w$.

and new dependent variables

$$f(\eta) = l^{-\frac{1}{2}}\bar{f}(\bar{\eta}), \qquad H(\eta) = \bar{H}(\bar{\eta}),$$
$$W(\eta, \xi) = \bar{W}(\bar{\eta}, \bar{s}).^{*} \qquad (12)$$

The resultant set is

$$\frac{d^3 f}{d\eta^3} + f\frac{d^2 f}{d\eta^2} = 0, \qquad (13)$$

$$\frac{d^2 H}{d\eta^2} + Prf\frac{dH}{d\eta} = 0, \qquad (14)$$

$$W_{\eta\eta} + Scf W_{\eta} = 2\xi Sc\frac{df}{d\eta}W_{\xi}, \qquad (15)$$

subject to conditions corresponding to (5), namely:

$$\frac{df(0)}{d\eta} = 0, \qquad (16a)$$

$$f(0) = 0, \qquad (16b)$$

$$H(0) = H_w = \text{const}, \qquad (16c)$$

$$W_{\eta}(0, \xi) = \zeta(\xi)[W(0, \xi)]^N. \qquad (16d)$$

$$\lim_{\eta\to\infty}\frac{df(\eta)}{d\eta} = 1, \qquad (16e)$$

$$\lim_{\eta\to\infty} H(\eta) = 1, \qquad (16f)$$

$$\lim_{\eta\to\infty} W(\eta, \xi) = 1. \qquad (16g)$$

In (16d), $\zeta(\xi)$ is the well known Damkohler number—a convenient measure of the state of chemical nonequilibrium at the surface. Herein it takes the form

$$\zeta(\xi) = \frac{Sc\,\rho_{w_0}^N W_e^{N-1}\left(\frac{\rho_w}{\rho_{w_0}}\right)^N k_w \xi^{\frac{1}{2}}}{\left[\frac{(\rho_e\mu_e)_0\, l\, U_\infty}{2L}\right]^{\frac{1}{2}} \frac{\rho_e\mu_e}{(\rho_e\mu_e)_0}\frac{U_e}{U_\infty}\left(\frac{r}{L}\right)^{\varepsilon}}. \qquad (17)$$

The Damkohler number may be interpreted as a ratio of characteristic surface reaction rate and surface diffusion rate (see, for example [12], p. 143).

## 3. METHOD OF SOLUTION

We shall deal with the integration of (15) subject to the conditions (16d) and (16g) for high speed flows past plates and wedges. In this section we focus our attention on the method of solution establishing several results valid for various orders of reactions, $N$. Subsequently, we present examples, first for first order reactions and then for reaction orders other than unity.

Equation (15) may obviously be written as

$$W_{\eta\eta} + Scf W_{\eta} = P(\xi, \eta). \qquad (18)$$

A formal integral of (18) is of the form

$$W_{\eta} = e^{-ScF}\,\Phi(\xi, \eta) \qquad (19)$$

where

$$F \equiv \int_0^{\eta} f(\eta')\,d\eta'$$

and $\Phi(\xi, \eta)$ is a "slowly" varying function [19].† The latter is implied by the structure of the boundary-layer equation, in particular by its known asymptotic behavior with respect to $\eta$. Clearly,

$$W(\xi, \eta) = \int_0^{\eta} e^{-ScF}\,\Phi(\xi, \eta')\,d\eta' + W_w. \qquad (20)$$

In the last equation, $W_w \equiv W(\xi, 0)$ stands for the surface concentration ratio of atoms. The latter is evaluated from the associated improper integral

$$\int_0^{\infty} e^{-ScF}\,\Phi(\xi, \eta)\,d\eta$$

and the conditions at infinity, namely:

$$W_w = 1 - \int_0^{\infty} e^{-ScF}\,\Phi(\xi, \eta)\,d\eta. \qquad (21)$$

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* The procedure is essentially that of Lees [18], adopted thereafter by many other authors. The reader may care to note that once $l$ = const. the boundary conditions (5) (see also footnote on p. 966.) immediately admit similarity representations for the momentum and energy equations.

† It may be worthwhile to note that the partial differential equation (18) is nothing but a formal restatement of (15). Thus $P(\xi, \eta)$ and $\Phi(\xi, \eta)$ are implicit functions of $W$. Of course, no approximations whatever are involved at this stage.

The problem effectively reduces then to finding suitable representations for the integrands in (20) and (21) admitting (approximate) evaluation of the integrals by analytical means. To this end, we use a series representation for $f$ valid in a neighborhood of $\eta = 0$; corresponding representations for $W(\xi, \eta)$ and hence $\Phi(\xi, \eta)$ are easily constructed as shown below. Because of the structure of the boundary-layer equation, this information together with procedures used in summing divergent series, [20], suffices for an approximate, yet quite accurate, evaluation of integrals typified by (21), [19]. We turn now to some details.

The series representing $f(\eta)$ in the neighborhood of the origin is that of Blasius,

$$f(\eta) = \sum_{n=2}^{\infty} \frac{a_n}{n!}\eta^n = \frac{a_2}{2!}\eta^2 - \frac{a_2^2}{5!}\eta^5 + \frac{11}{8!}a_2^3\eta^8 - \frac{375}{11!}a_2^4\eta^{11} + \dots \tag{22}$$

where the coefficient $a_2 \equiv \mathrm{d}^2 f(0)/\mathrm{d}\eta^2$ is known. To arrive at a corresponding series representation for $W(\xi, \eta)$ valid near $\eta = 0$ with $\xi$ effectively playing the role of a parameter, we set

$$W(\xi, \eta) = \sum_{n=0}^{\infty} \frac{W_n(\xi)}{n!}\eta^n, \tag{23}$$

substitute (22) and (23) into (15) and read off the results by equating powers of $\eta$. The following are the first few terms obtained in this way:

$$\begin{aligned} &W_2 = 0, \qquad W_3 = 2\xi Sc a_2 W'_0, \\ &W_4 = Sc a_2[4\xi(\zeta(\xi)W_0^N)' - \zeta(\xi)W_0^N], \\ &W_5 = 0, \qquad W_6 = 2\xi Sc a_2^2[8Sc(\xi W'_0)' \\ &\qquad\qquad - (1 + 6Sc)\, W'_0], \dots \end{aligned} \tag{24}$$

where $W_0 = W_w$ and $' \equiv \mathrm{d}/\mathrm{d}\xi$. Together, the boundary condition (16d)—$W_\eta(\xi, 0) = \zeta(\xi)[W(\xi, 0)]^N$—and (23) imply now that

$$W_1 = \zeta(\xi)[W_w]^N. \tag{25}$$

Since both $a_2$ and $\zeta(\xi)$ are given, the set $\{W_n(\xi)\}$ involves as unknowns $W_w$ and its derivatives. In fact, up to the seventh term only $W_w$ and $W'_w$ occur.

We take now

$$\Phi(\xi, \eta) = \sum_{n=0}^{\infty} \frac{\Phi_n(\xi)}{n!}\eta^n.$$

Clearly, members of the required set $\{\Phi_n\}$ are functionally dependent on $\{W_n\}$. A straightforward way for determining the former is to use (19) and the available series (23). The equation generating $\{\Phi_n\}$ is

$$\left[\sum_{n=1}^{\infty} \frac{W_n}{(n-1)!}\eta^{n-1}\right] \exp\left[Sc \sum_{n=2}^{\infty} \frac{a_n}{(n+1)!}\eta^{n+1}\right] = \sum_{n=0}^{\infty} \frac{\Phi_n}{n!}\eta^n. \tag{26}$$

Expanding both sides and equating like powers of $\eta$ yields the results:

$$\begin{aligned} &\Phi_0 = W_1 = \zeta(\xi)W_0^N, \qquad \Phi_1 = W_2 = 0, \\ &\Phi_2 = W_3 = 2\xi Sc a_2 W'_0, \\ &\Phi_3 = W_4 + W_1 Sc a_2 = 4\xi Sc a_2[\zeta(\xi)W_0^N]', \\ &\Phi_4 = 4\Phi_1 Sc a_2 + W_3 = 4Sc a_2 W_2 + W_5 = 0, \\ &\Phi_5 = 10 Sc a_2 W_3 + W_6 \\ &\quad = 2\xi Sc a_2^2[(4Sc - 1)\, W'_0 + 8Sc(\xi W'_0)'], \dots . \end{aligned} \tag{27}$$

In each term, the last equality follows from (24) and (25).

It remains to discuss the procedure for evaluating the integrals entering (20) and (21), namely

$$\int_0^\eta \mathrm{e}^{-ScF}\,\Phi(\xi, \eta')\,\mathrm{d}\eta' \quad \text{and} \quad \int_0^\infty \mathrm{e}^{-ScF}\,\Phi(\xi, \eta)\,\mathrm{d}\eta. \tag{28}$$

Consider the latter. In view of the known behavior of $F$, $\Phi$, and their series representations, the dominant factor in the integrand is the exponential term. Accordingly, one is led to expect that a good approximation to the integral may result if only the leading term in each series is retained, namely:

$$\int_0^\infty e^{-ScF}\,\Phi\,\mathrm{d}\eta \doteqdot \int_0^\infty \exp\,\frac{-Sc\,a_2}{6}\,\eta^3 \times \zeta(\xi)\,[W_w^{[0]}(\xi)]^N\,\mathrm{d}\eta = \tfrac{1}{3}\Gamma(\tfrac{1}{3})\,Sc^{-\frac{1}{3}}\,(6/a_2)^{\frac{1}{3}} \times \zeta(\xi)\,(W_w^{[0]})^N.^*$$

The bracketed superscript 0 is meant to imply that the last expression together with (21) yields the corresponding zeroth approximation to $W_w$. For example, when $N = 1$ we have:

$$W_w^{[0]} = \frac{1}{1 + \frac{1}{3}\Gamma(\frac{1}{3})\,(6/a_2)^{\frac{1}{3}}\,Sc^{-\frac{1}{3}}\,\zeta(\xi)}. \qquad (29)$$

Now, while (29) may indeed prove satisfactory for engineering purposes,† an immediate dilemna arises nonetheless. How are we to assess the accuracy of (29) in a self-consistent manner (not by direct comparison with other results) and how are we to obtain better, "higher order", approximations? For example, including the next term in the $F$ series leads nowhere—the integral does not exist. Apparently for these reasons, Meksyn improved his earlier work [21–23] and evaluated the integrals of the type (28) by what is virtually the method of steepest descent [24]. We shall follow his procedure in the text. An alternate viewpoint that perhaps is more direct is outlined in the footnote.§

The improper integral (28) is rewritten as follows:

$$\int_0^\infty e^{-ScF}\,\Phi(\xi,\eta)\,\mathrm{d}\eta = \int_0^\infty e^{-Sc\tau}\,\Phi(\xi,\eta(\tau))\,\frac{\mathrm{d}\eta}{\mathrm{d}\tau}\,\mathrm{d}\tau. \qquad (30)$$

Because the series for $F$ starts with $\eta^3$, the series relating $\eta$ and $\tau$ is of the form

$$\eta = \sum_{m=0}^{\infty} \frac{A_m}{m+1}\,\tau^{\frac{1}{3}(m+1)},$$

([19], p. 53), valid for sufficiently small $\tau$. In turn, since $\eta$ starts with $\tau^{\frac{1}{3}}$, we set

$$\Phi(\xi,\eta)\,\frac{\mathrm{d}\eta}{\mathrm{d}\tau} = \tau^{-\frac{2}{3}} \sum_{m=0}^{\infty} d_m(\xi)\,\tau^{m/3} \qquad (31)$$

and evaluate the coefficient set $\{d_m\}$ in terms of $\{\Phi_n\}$. A somewhat lengthy proof shows that each coefficient $d_m$ equals one-third of the coefficient of $\eta^m$ in the expansion of

$$(c_0 + c_1\eta + c_2\eta^2 + c_3\eta^2 + \ldots)^{-\frac{1}{3}(m+1)} \times (b_0 + b_1\eta + b_2\eta^2 + b_3\eta^3 + \ldots) \qquad (32)$$

where the sets $\{c_n\}$ and $\{b_n\}$ are the following:

$$c_0 = \frac{a_2}{3!}, \qquad c_1 = c_2 = 0, \qquad c_3 = -\frac{a_2^2}{6!},$$

$$c_4 = c_5 = 0, \qquad c_6 = \frac{11}{9!}a_2^3, \qquad c_7 = c_8 = 0,$$

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[*] In essence, this exemplifies the motivating ideas for the asymptotic method developed by Meksyn.

[†] As indicated in the subsequent figures, the simple expression (29) gives more accurate results than those based on the local similarity approximation.

[§] The difficulties just mentioned suggest the use of a new independent variable, $\tau = F(\eta)$. Substituting $\tau$ into the second integral (28) yields

$$\int_0^\infty e^{-Sc\tau} \sum_{n=0}^{\infty} \frac{\Phi_n}{n!}\,\eta^n\,\frac{\mathrm{d}\eta}{\mathrm{d}\tau}\,\mathrm{d}\tau.$$

Now integrating (22), we obtain

$$F(\eta) = \tau = \frac{z}{3!} - \frac{z^2}{6!} + \frac{11}{9!}z^3 - \frac{375}{12!}z^4 + \ldots,$$

where $z \equiv a_2\eta^3$. Inverting this series, ([25], p. 16) gives

$$z = a_2\eta^3 = 6\tau + \frac{3}{10}\tau^2 - \frac{13}{1400}\tau^3 + \frac{1}{61\,600}\tau^4 + \ldots,$$

so that

$$\eta = \left(\frac{z}{a_2}\right)^{\frac{1}{3}} = \left(\frac{6\tau}{a_2}\right)^{\frac{1}{3}}\left(1 + \frac{1}{60}\tau - \frac{1}{1260}\tau^2 + \frac{23}{891\,000}\tau^3 + \ldots\right).$$

We may now express $\eta^n$ in terms of $\tau$ for each $n$. Multiplying each of these by $\Phi_n(\xi)/n!\ \mathrm{d}\eta/\mathrm{d}\tau$, ($\mathrm{d}\eta/\mathrm{d}\tau$ obtained from above expression), and collecting the coefficients of similar powers of $\tau$ yields finally the $d_m$'s given in the text.

$$c_9 = -\frac{375}{12!}a_2^4, \ldots, \qquad b_0 = \Phi_0,$$

$$b_1 = \Phi_1, \qquad b_2 = \frac{\Phi_2}{2!}, \ldots, \qquad b_n = \frac{\Phi_n}{n!}.$$

We omit the algebra and state the results.

$$
\begin{aligned}
d_0 &= \frac{1}{3}\left(\frac{6}{a_2}\right)^{\frac{1}{3}} \zeta(\xi) W_0^N, \qquad d_1 = 0,\\
d_2 &= 2\xi Sc W_0',\\
d_3 &= \frac{1}{3}\left(\frac{6}{a_2}\right)^{\frac{1}{3}} [4\xi Sc(\zeta W_0^N)' + \tfrac{1}{15}(\xi W_0^N)], \qquad (33)\\
d_4 &= 0, \qquad d_5 = \tfrac{4}{5}\xi Sc^2[3W_0' + 2\zeta W_0''], \ldots .
\end{aligned}
$$

Once the set $\{d_m\}$ is established, integrals of the type (30) may be evaluated. The procedure is as follows: formally, from (21) and the $\tau$ transformation, we obtain

$$1 - W_w = \int_0^\infty \mathrm{e}^{-Sc\tau} \tau^{-\frac{2}{3}} \sum_{m=0}^{\infty} d_m \tau^{m/3}\, \mathrm{d}\tau. \quad (34)$$

Now, the right-hand side of (34) is in fact an asymptotic development in terms of the Schmidt number with $W_w$ and its derivatives appearing as a set of parameters. For a fixed $Sc$, we then treat the expansion of (34) as a divergent series and, using Euler's transformation, construct a sequence of "sums" from the truncated expressions.* These "sums", of course, are in general differential equations in $W_w$. Our attention will be confined to the first four "sums", that is, those yielding first order equations for $W_w$ when $m \geqslant 2$ and algebraic equations when $m = 0$ and 1. The differential equations are linear for $N = 1$ but nonlinear otherwise; the algebraic equations are of degree one only when $N = 1$. After combining (20) and (21), the same procedure may be used to calculate boundary-layer profiles of $W(\xi, \eta)$. We turn now to examples.

*First order reactions*

Consider the case $N = 1$. It is convenient to use

$$\bar{\zeta}(\xi) = \tfrac{1}{3}\Gamma(\tfrac{1}{3})\left(\frac{6}{Sca_2}\right)^{\frac{1}{3}} \zeta(\xi) \qquad (35)$$

as a new independent variable replacing $\xi$. The specific reaction rate $k_w(x)$ is assumed to be of the form $k_w = (\mu_w/\mu_{w_0})\, k_{w_0} x^d$ where $\mu_{w_0}$, $k_{w_0}$ are (constant) reference values and $d$ remains to be specified; moreover, $\varepsilon = 0$. For flat plate or high speed wedge flows, $\zeta(\xi)$, given by (17), may also be written as

$$\zeta(\xi(\bar{X})) = \frac{Sc\, \rho_w k_w X^{\frac{1}{2}}}{\left(\dfrac{U_e \rho_e \mu_e l}{2L}\right)^{\frac{1}{2}}}. \qquad (36)$$

Consider first the determination of $W_w$ on the basis of (34) where the $d_m$'s are now functions of $\bar{\zeta}$ obtained by a simple chain rule from (33) and (35). We construct a sequence of successive approximations to $W_w$, namely†:

$$
\begin{gathered}
W_w^{[0]} = W_w^{[0]}(d_0), \qquad W_w^{[1]} = W_w^{[1]}(d_0, d_1),\\
W_w^{[2]} = W_w^{[2]}(d_0, d_1, d_2; E_1),\\
W_w^{[3]} = W_w^{[3]}(\mathrm{d}_0, d_1, d_2, d_3; E_1),\\
W_w^{[4]} = W_w^{[4]}(d_0, d_1, d_2, d_3, d_4; E_{1,2}).
\end{gathered}
$$

This notation suggests that the "order of approximation" depends on the number of $d$'s taken; the letter $E$ means that the partial series is Euler summed and the associated subscripts indicate different types of Euler transformations used. In following the criteria of [26], $W_w^{[3]}$ tests for the effect of including an additional term under a given transformation; $W_w^{[4]}$, apart from taking still another term, verifies that under two different Euler transformations the changes in $W_w$ are practically

---

* Because well defined sums of the associated divergent series are evaluated by using only a small number of terms, we adopt the point of view of [26], namely: no particular result is accepted as valid unless subjected to further checks on internal consistency. For further details, the reader is referred to [26] and references quoted therein. A general discussion on divergent series together with a number of pertinent references may be found in Chapters 13 and 14 of Knopp's book [20].

† It is understood that $W_w^{[i]}$, $i = 1, \ldots 4$, and the members of the set $\{d_m\}$ are now appropriately transformed new functions; the notational changes are suppressed.

nil. Accordingly, either $W_w^{[4]}$ is accepted as the final result. In any case, the changes from $W_w^{[2]}$ to $W_w^{[4]}$ are slight and already $W_w^{[0]}$, as shown in the graphs, provides us with better results than those based on numerical solutions employing the local similarity concept.

Now, (34) clearly gives the general result,

$$W_w = 1 - \sum_{m=0}^{\infty} \frac{d_m}{Sc^{(m+1)/3}} \Gamma\left(\frac{m+1}{3}\right). \tag{37}$$

Our sequence of approximations, based on equations obtained from (37); takes the form

$$W_w^{[0]} = 1 - T_0 = W_w^{[1]}, \tag{38a}$$

$$W_w^{[2]} = 1 - [\tfrac{1}{2}T_0 + \tfrac{1}{4}(T_0 + T_1) + \tfrac{1}{8}(T_0 + 2T_1 + T_2)], \tag{38b}$$

$$W_w^{[3]} = 1 - [\tfrac{1}{2}T_0 + \tfrac{1}{4}(T_0 + T_1) + \tfrac{1}{8}(T_0 + 2T_1 + T_2) + \tfrac{1}{16}(T_0 + 3T_1 + 3T_2 + T_3)], \tag{38c}$$

$$W_w^{[4]} = 1 - [\tfrac{1}{2}T_0 + \tfrac{1}{4}(T_0 + T_1) + \tfrac{1}{8}(T_0 + 2T_1 + T_2) + \tfrac{1}{16}(T_0 + 3T_1 + 3T_2 + T_3) + \tfrac{1}{32}(T_0 + 4T_1 + 6T_2 + 4T_3 + T_4)], \tag{38d}$$

$$W_w^{[4]} = 1 - [\tfrac{1}{2}T_0 + \tfrac{1}{4}(T_0 + T_1) + \tfrac{1}{8}(T_0 + 2T_1 + T_2) + \tfrac{1}{16}(T_0 + 3T_1 + 3T_2 + T_3) + \tfrac{1}{64}(T_0 + 4T_1 + 6T_2 + 4T_3 + T_4)], \tag{38e}$$

where we have compressed the notation in writing

$$T_m \equiv \frac{d_m}{Sc^{(m+1)/3}} \Gamma\left(\frac{m+1}{3}\right).$$

The differential equation determining $W_w^{[2]}$ is the following:

$$\frac{\mathrm{d}W_w^{[2]}}{\mathrm{d}\bar\zeta} + \frac{192 + 168\bar\zeta}{48(d + \frac{1}{2})\bar\zeta} W_w^{[2]} = \frac{192}{48(d + \frac{1}{2})\bar\zeta}, \tag{39}$$

subject to the conditions $W_w^{[2]}(0) = 1$. Closed form solutions are possible when $d = (8 - n)/2n$ where $n$ is any positive integer. For example, taking $n = 1, 2, 4$ and $8$ ($d = \frac{7}{2}, \frac{3}{2}, \frac{1}{2}, 0$), we have the results:

$$W_w^{[2]} = \frac{8}{7\bar\zeta}(1 - e^{\frac{7}{2}\bar\zeta}), \qquad d = \tfrac{7}{2}; \tag{40a}$$

$$W_w^{[2]} = \frac{2}{\bar\zeta^2}\left[\frac{4}{7}\bar\zeta - \frac{16}{49}(1 - e^{-\frac{7}{4}\bar\zeta})\right], \qquad d = \tfrac{3}{2}; \tag{40b}$$

$$W_w^{[2]} = \frac{4}{\bar\zeta^4}\left[\frac{2}{7}\bar\zeta^3 - \frac{12}{49}\bar\zeta^2 + \frac{48}{343}\bar\zeta - \frac{96}{2401}(1 - e^{-\frac{7}{4}\bar\zeta})\right], \qquad d = \tfrac{1}{2}; \tag{40c}$$

$$W_w^{[2]} = \frac{8}{\bar\zeta^8}\left[\frac{1}{7}\bar\zeta^7 - \frac{1}{7}\bar\zeta^6 + \frac{6}{49}\bar\zeta^5 - \frac{30}{343}\bar\zeta^4 + \frac{120}{2401}\bar\zeta^3 - \frac{360}{16807}\bar\zeta^2 + \frac{720}{117649}\bar\zeta - \frac{720}{823543}(1 - e^{-7\bar\zeta})\right], \qquad d = 0. \tag{40d}$$

Otherwise, numerical solutions are apparently required, in spite of the fact that the differential equations are linear.

The differential equations for $W_w^{[3]}$ and $W_w^{[4]}$ [corresponding to (38c), (38d) and (38e)] may be written as follows:

$$\frac{\mathrm{d}W_w^{[3]}}{\mathrm{d}\bar\zeta} + \frac{192 + \bar\zeta\{180 + 8[(1/30Sc) + 2(\mathrm{d} + \frac{1}{2})]\}}{(d + \frac{1}{2})\bar\zeta(120 + 16\bar\zeta)} W_w^{[3]} = \frac{192}{(d + \frac{1}{2})\bar\zeta(120 + 16\bar\zeta)}, \tag{41a}$$

$$\frac{\mathrm{d}W_w^{[4]}}{\mathrm{d}\bar\zeta} + \frac{192 + \bar\zeta\{186 + 24[(1/30Sc) + 2(d + \frac{1}{2})]\}}{(d + \frac{1}{2})\bar\zeta(192) + 48\bar\zeta)} W_w^{[4]} = \frac{192}{(d + \frac{1}{2})\bar\zeta(192 + 48\bar\zeta)}, \tag{41b}$$

$$\frac{\mathrm{d}W_w^{[4]}}{\mathrm{d}\bar\zeta} + \frac{192 + \bar\zeta\{183 + 16[(1/30Sc) + 2(d + \frac{1}{2})]\}}{(d + \frac{1}{2})\bar\zeta(156 + 32\bar\zeta)} W_w^{[4]} = \frac{192}{(d + \frac{1}{2})\bar\zeta(156 + 32\bar\zeta)}. \tag{41c}$$

These were integrated numerically subject to $W_w^{[3]}(0) = W_w^{[4]}(0) = 1$.* Solutions of (41b) and (41c), testing the influence of two different Euler transformations, agreed generally to three decimal places. Typical results are presented in Figs. 1–4. Figure 1 gives a comparison of $W_w^{[4]}$ with the "exact" results of Inger [6] for $d = 0, \frac{1}{2}$, 1 and $\frac{3}{2}$. The agreement is very good.† The dashed curve represents results based on the local similarity approximation. The latter were taken from [6] and, to the accuracy presented herein, found to fall on a single curve for all the $d$'s considered. An enlarged version of Fig. 1 is given in Fig. 2 where several results due to Chung *et al.* are also included. The latter were carefully replotted from the graphs presented in [6]. The largest deviations occur when $d = 1$ where the results of [9] appear generally closer to the $d = \frac{1}{2}$ curve than to the $d = 1$ curve. Figures 3 and 4 indicate respectively the "best" and "poorest" convergence of the successive approximations to $W_w$. The former is obtained for $d = 0$ where already the second approximation is indistinguishable from $W_w^{[3]}$ and $W_w^{[4]}$ for $\bar{\zeta} < 2{\cdot}25$. The circles represent local similarity results. Figure 3 also shows the first and final iterates obtained by Fox and Libby [13] with their perturbation method. Their results are for $Sc = 1$ (in contrast to ours and Inger's taking $Sc = 0{\cdot}72$) but, as the authors of [13] point out, the influence of the Schmidt number is not strong and therefore

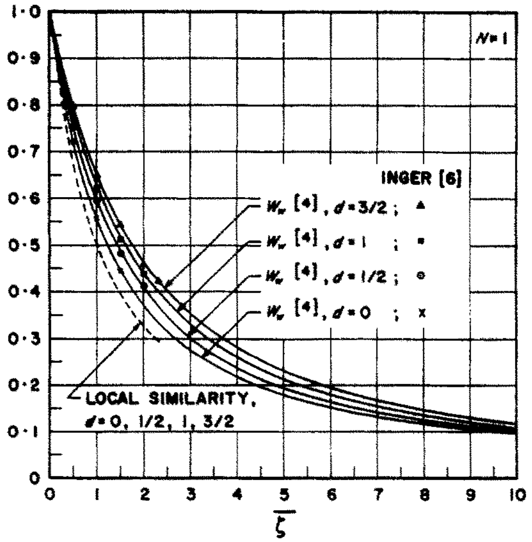

FIG. 1. Influence of streamwise variation of reaction rates on surface atom concentration, $N = 1$.

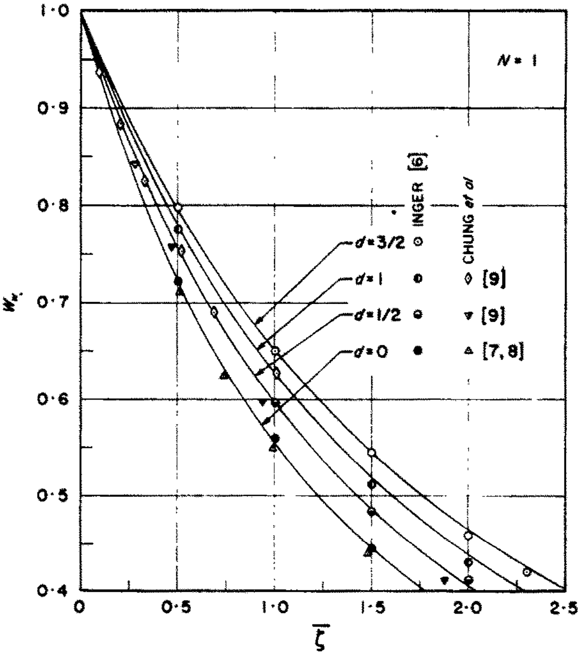

FIG. 2. Influence of streamwise variation of reaction rates on surface atom concentration, $N = 1$.

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* A closer look at equations (41) and (39) shows that, while they have a perfectly well defined limiting behavior at $\bar{\zeta} = 0$, the equations are nonetheless indeterminate, as they stand, with respect to $\mathrm{d}W_w^{[i]}/\mathrm{d}\bar{\zeta}$ at $\bar{\zeta} = 0$, $i = 2, 3, 4$. The latter fact is important from the standpoint of numerical integration. Accordingly, to avoid loss of significant figures, we find values of $W_w$ from its power series expansion near $\bar{\zeta} = 0$, beginning the numerical integration only with $\bar{\zeta}$ sufficiently large; but, because the power series itself possesses a small radius of convergence, $\bar{\zeta}$ must still be small enough to assure good accuracy. Herein, the power series were generally applied up to $\bar{\zeta} = 0{\cdot}1$. This procedure is easily checked for $W_w^{[2]}$ where closed form solutions are also available. It is worthwhile to note that if more $d_m$'s are used the indeterminacy becomes "more severe". For example: including $d_5$, $d_6$, $d_7$ results in a second order differential equation that has a $\bar{\zeta}^2$ indeterminacy at $\bar{\zeta} = 0$ for $\mathrm{d}^2W_w^{[i]}/\mathrm{d}\bar{\zeta}^2$, $i \geqslant 2$.

† Inger required solutions of fifteen differential equations for the power series representation of $W_w$ in the range shown, roughly, $0 \leqslant \bar{\zeta} < 2{\cdot}3$. Results for $d = \frac{3}{2}$ based on a ten term representation diverged already at $\bar{\zeta} \doteqdot 1{\cdot}1$.

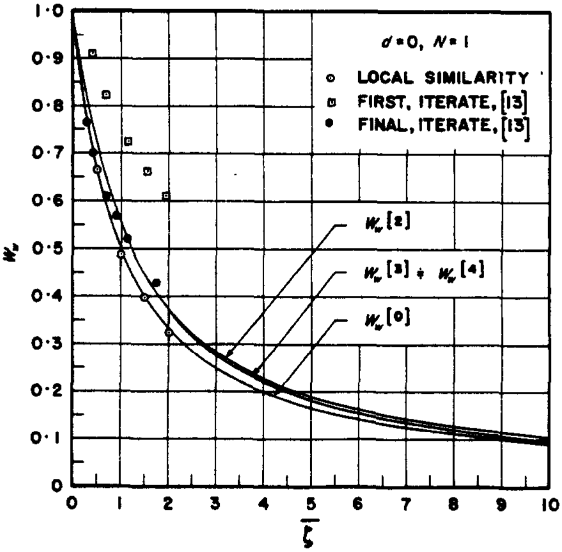

FIG. 3. Influence of order of approximation on surface atom concentration, $d = 0$, $N = 1$.

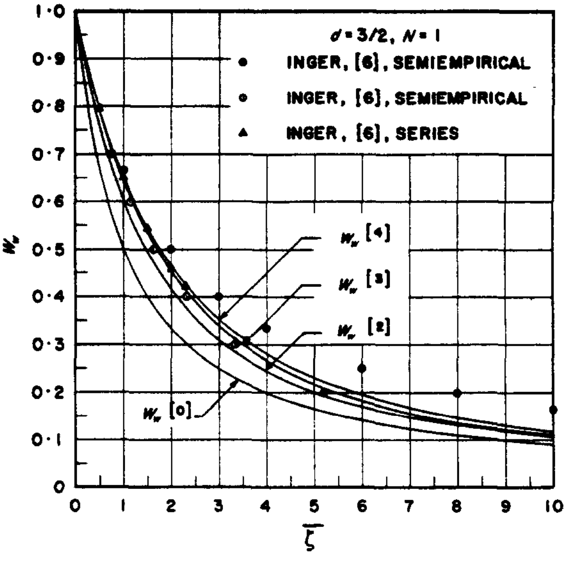

FIG. 4. Influence of order of approximation on surface atom concentration, $d = \frac{3}{2}$, $N = 1$.

we regard the deviations as relatively large. It is interesting to note that in terms of $\bar{\zeta}$ our zeroth approximation $W_w^{[0]}$, roughly corresponding to the first iterate of [13], is in fact independent of the Schmidt number. This is obvious from (29) and (35). The poorest convergence is found for the highest $d$, Fig. 4. This is as expected because $W_w^{[0]}$ is, as an analytical result, independent of $d$ but $W_w$, for any given $\bar{\zeta}$, increases with increasing $d$. The circles and dots give the results of [6] based on semi-empirical approaches. The triangles represent the "exact" series results.

We sketch now the procedure for calculating the $\bar{\zeta}$-history of boundary-layer profiles of the atom mass fraction ratio $W$, choosing as an illustrative example the case $d = 0$. The starting point is the basic equation

$$W(\xi,\eta) = 1 - \int_{\tau}^{\infty} e^{-Sc\tau}\,\tau^{-\frac{2}{3}} \sum_{m=0}^{\infty} d_m \tau^{m/3}\,d\tau, \tag{42}$$

an easy consequence of (20), (21) and the $\tau$-transformation; it is obviously identical to (34) when $\tau = 0$. In establishing the $\eta$–$\tau$ correspondence we have made use of the available Blasius' solution and the definition of $\tau$. (Of course, it is always possible to use the series relationship between $\eta$ and $\tau$ as done for example by Meksyn [19].) The procedure now is somewhat different. The "zero" problem [(42) with $\tau = 0$] is solved, members of the set $\{d_m\}$ (up to $d_5$) are known functions of $W_0(\xi)$, $W_0(\bar{\zeta})$, $dW_0/d\xi$, $dW_0/d\bar{\zeta}$ and, therefore, it remains only to evaluate directly the integral in (42). In terms of $\bar{\zeta}$ and following our notational convention (see footnote† on p. 970) we write

$$W(\bar{\zeta},\eta) = 1 - \int_{\tau}^{\infty} \exp(-Sc\,\tau)\,\tau^{-\frac{2}{3}} \times \sum_{m=0}^{\infty} d_m\,\tau^{m/3}\,d\tau.$$

Consistently with (38), we apply now the Euler transformation to the partial sum

$$\sum_{m=0}^{m} d_m\,\tau^{m/3}$$

that replaces the series in the integrand. A simple computation corresponding to $(38)_4$ gives the result

$$W(\bar{\zeta}, \eta) = 1 - \bar{\zeta} W_0 \left[\frac{31}{32} \frac{\Gamma(\frac{1}{3}, Sc\,\tau)}{\Gamma(\frac{1}{3})} + \frac{\Gamma(\frac{4}{3}, Sc\,\tau)}{\Gamma(\frac{4}{3})} \left(4 + \frac{2}{15\,Sc}\right)\right] - \tfrac{1}{8}\bar{\zeta} \frac{\mathrm{d}W_0}{\mathrm{d}\bar{\zeta}} \left[\frac{4\Gamma(\frac{3}{3}, Sc\,\tau)}{\Gamma(\frac{1}{3})} + \bar{\zeta} \frac{\Gamma(\frac{4}{3}, Sc\,\tau)}{\Gamma(\frac{4}{3})}\right]; \tag{43}$$

$$\Gamma(m/n + 1, Sc\,\tau) = \int_{Sc\tau}^{\infty} \mathrm{e}^{-p} p^{m/n}\,\mathrm{d}p.$$

Graphs based on (43) are shown in Fig. 5. As expected, the largest changes in the concentration profiles occur at large value of $\bar{\zeta}$. The accuracy of the results is comparable to those of $W_w^{[4]}$ when $\eta \leqslant 1$ but poorer when $\eta > 1$. The reason for this lies mainly in the structure of the Euler transformed series. If we allow the conjecture that the same sort of estimates on internal consistency and accuracy of results apply here as before then the results for $\eta > 1$ ought nonetheless be within 8 per cent of the corresponding numerical solutions obtained by direct integration of the partial differential equations. Such will be published in the near future.

### *Reaction orders other than unity*

Herein we investigate the influence of various reaction orders on $W_w$ and the associated diffusive heat flux, $\dot{q}_{w_D}$. To better exhibit this influence we shall treat the same cases here as discussed previously under the assumption $N = 1$. But, because the solution technique is the same, only the main steps need be mentioned and the results summarized.

The discussion of the last subsection preceding equation (39) is equally applicable here. The notable consequence of taking $N \neq 1$ is that the differential equations determining $W_w^{[i]}, i \geqslant 2$, are now nonlinear and the algebraic equation for $W_w^{[0]}$ is no longer of first degree. Thus $W_w^{[0]}$ is determined from

$$1 - W_w^{[0]} = \bar{\zeta}(W_w^{[0]})^N, \tag{44}$$

an easy consequence of (37). Explicit formulae for $W_w^{[0]}$ are obvious for $N = \frac{1}{2}$ and 2. The differential equations determining $W_w^{[2]}$, $W_w^{[3]}$, and $W_w^{[4]}$ are:

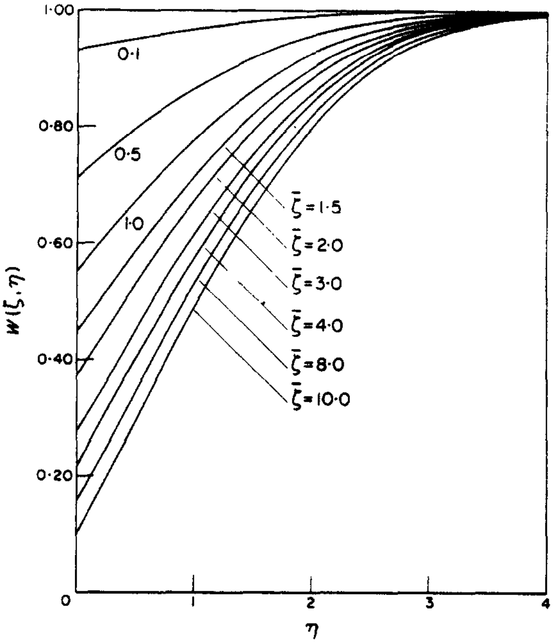

FIG. 5. Typical boundary-layer profiles of atom concentration, $d = 0$, $N = 1$.

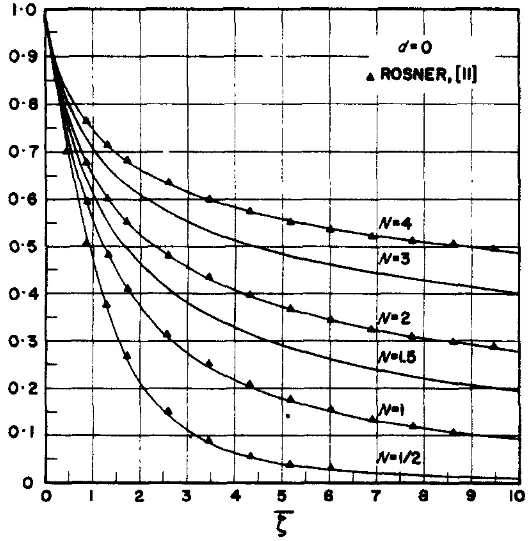

FIG. 6. Influence of order of reaction on surface atom concentration, $d = 0$.

$$\frac{\mathrm{d}W_w^{[2]}}{\mathrm{d}\bar{\zeta}} + \frac{168\bar{\zeta}(W_w^{[2]})^N}{48(d+\frac{1}{2})\bar{\zeta}} = \frac{192(1-W_w^{[2]})}{48(d+\frac{1}{2})\bar{\zeta}}, \tag{45a}$$

$$\frac{\mathrm{d}W_w^{[3]}}{\mathrm{d}\bar{\zeta}} + \frac{\bar{\zeta}\{180+8[(1/30Sc)+2(d+\frac{1}{2})]\}(W_w^{[3]})^N}{(d+\frac{1}{2})\bar{\zeta}[120+16N\bar{\zeta}(W_w^{[3]})^{N-1}]} = \frac{192(1-W_w^{[3]})}{(d+\frac{1}{2})\bar{\zeta}[120+16N\bar{\zeta}(W_w^{[3]})^{N-1}]} \tag{45b}$$

$$\frac{\mathrm{d}W_w^{[4]}}{\mathrm{d}\bar{\zeta}} + \frac{\bar{\zeta}\{186+24[(1/30Sc)+2(d+\frac{1}{2})]\}(W_w^{[4]})^N}{(d+\frac{1}{2})\bar{\zeta}[192+48N\bar{\zeta}(W_w^{[4]})^{N-1}]} \quad \frac{192(1-W_w^{[4]})}{(d+\frac{1}{2})\bar{\zeta}[192+48N\bar{\zeta}(W_w^{[4]})^{N-1}]}, \tag{45c}$$

$$\frac{\mathrm{d}W_w^{[4]}}{\mathrm{d}\bar{\zeta}} + \frac{\bar{\zeta}\{183+16[(1/30Sc)+2(d+\frac{1}{2})]\}(W_w^{[4]})^N}{(d+\frac{1}{2})\bar{\zeta}[156+32N\bar{\zeta}(W_w^{[4]})^{N-1}]} \quad \frac{192(1-W_w^{[4]})}{(d+\frac{1}{2})\bar{\zeta}[156+32N\bar{\zeta}(W_w^{[4]})^{N-1}]}. \tag{45d}$$

Equations (45a–d) correspond respectively to (39), (41a–c) and reduce to the latter when $N = 1$. Integrals of (45) were obtained numerically. Figure 6 shows $W_w^{[4]}$ in the range $\frac{1}{2} \leqslant N \leqslant 4$ when $d = 0$. The triangles represent results due to Rosner, [11], who used an iterative, Kármán–Pohlhausen type approach. The agreement is excellent. Figure 7 presents results similar to those of Fig. 6 but for $d = \frac{3}{2}$. The largest increases in $W_w$ due to $d$ are found for $N = \frac{1}{2}$, the smallest at $N = 4$. Qualitatively, the influence of $d$ on $W_w$ is not very different from the case $N = 1$. In Fig. 8 we show various lower order approximations to $W_w$ for $d = 0$. It is noteworthy that for high values of $N$ already the zeroth approximation is within 5 per cent of $W_w^{[4]}$. The poorest convergence results at $N = \frac{1}{2}$ but even there the values of $W_w^{[i]}$, $i = 2, 3, 4$ are practically identical.

The last four figures summarize results on surface heat transfer due to diffusion. The total surface heat flux $\dot{q}_{w_{tot}} = \dot{q}_{w_{cond}} + \dot{q}_{w_D}$ where the first term denotes the part due to conduction and the second represents the contribution due to diffusion. The latter may be expressed as

$$\dot{q}_{w_D} = \frac{\mu_w h_D w_e}{Sc} \frac{\partial}{\partial y} W(0, \xi)$$

where $h_D$ stands for the specific dissociation energy. Using (5) and the definition of $W$ we obtain an alternate expression,

$$\dot{q}_{w_D}\, Sc/w_e h_D = k_w\, Sc \rho_w^N w_e^{N-1} W_w^N.$$

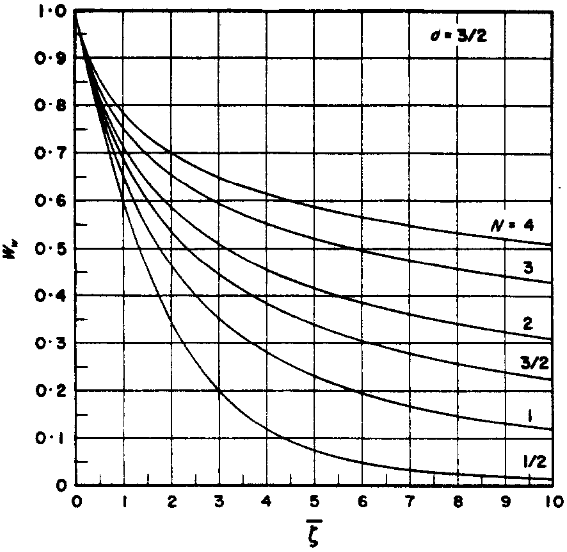

FIG. 7. Influence of order of reaction on surface atom concentration, $d = \frac{3}{2}$.

The results, presented in the form

$$\frac{Sc\,\dot{q}_{w_D}}{w_e h_D}[(\tfrac{1}{2} l \rho_e \mu_e U_e)^{\frac{1}{2}} \xi^{1/(2d+1)} x^{-\frac{1}{2}}]^{-1} \text{ vs. } \xi^{2/(2d+1)}$$

are shown in Figs. 9–12 for four different reaction orders, each figure corresponding to a fixed catalytic efficiency parameter. This particular form of presentation was chosen to facilitate the comparison with the series results of [6] for first-order reactions. All of our results are based on $W_w^{[4]}$. Generally, the agreement is quite good. We are unable to account for the relatively large discrepancies found at low values of the independent variable when $d = 1$, Fig. 11. However, we wonder, in view of the excellent agreement for $d = \frac{1}{2}$ and $\frac{3}{2}$ (bracketing $d = 1$), whether the computations of [6] might not be in error in this special case; particularly, because Inger's $W_w$ vs. $\zeta^{2/(2d+1)}$ curve exhibits a peculiar irregularity. The slight deviations at the tail end of the curves may be due to an insufficient number of terms taken in [6], particularly for $d = \frac{3}{2}$ where the series used in [6] shows the poorest convergence.

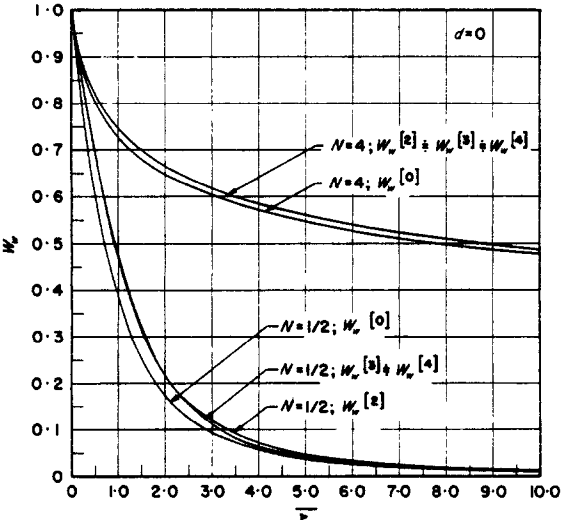

FIG. 8. Influence of order of approximation on surface atom concentration, $N = 1$.

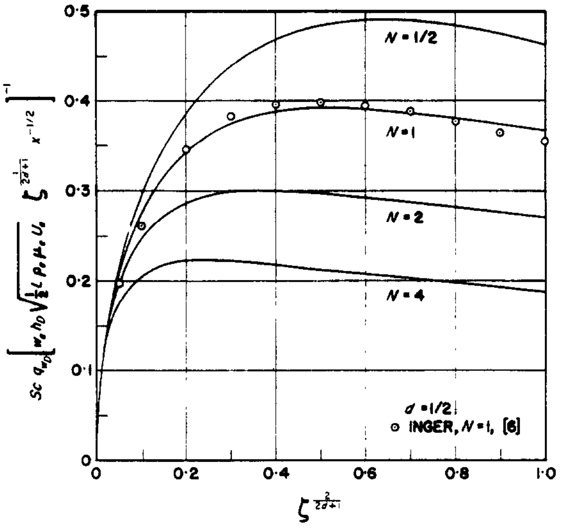

FIG. 10. Influence of reaction order on local diffusive heat flux, $d = \frac{1}{2}$.

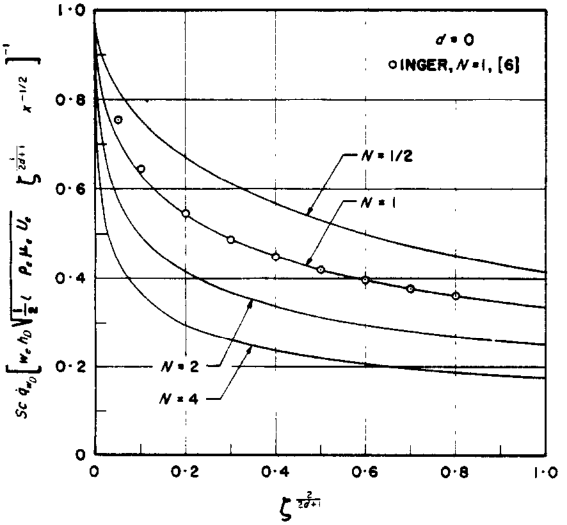

FIG. 9. Influence of reaction order on local diffusive heat flux, $d = 0$.

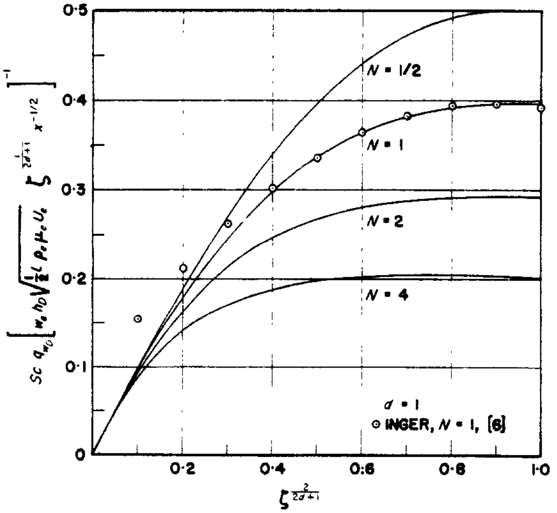

FIG. 11. Influence of reaction order on local diffusive heat flux, $d = 1$.

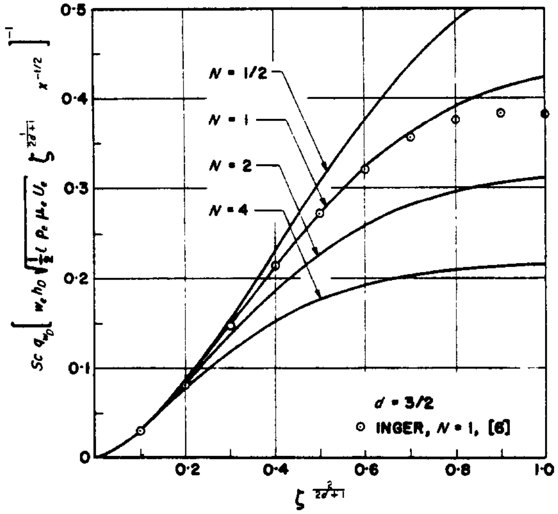

FIG. 12. Influence of reaction order on local diffusive heat flux. $d = \frac{3}{2}$.

In closing, we note that the largest relative changes due to reaction order $N$ occur in the region $\frac{1}{2} \leqslant N \leqslant 1$.

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**Résumé**—Cet article traite des écoulements de couche limite laminaire d'un gaz dissocié le long de surfaces catalytiques, en attachant une attention plus particulière aux cas dans lesquels les vitesses de réaction superficielle varient comme des puissances de la coordonnée longitudinale et les ordres de réaction sont différents de l'unité. Le gaz dans la couche limite est représenté par un mélange binaire figé chimiquement d'atomes et de molécules et l'on emploie les hypothèses simplificatrices habituelles qui s'appliquent aux couches limites hypersoniques. Des intégrales approchées de l'équation de la diffusion sont obtenues analytiquement à l'aide de la méthode asymptotique. On montre ici que cette méthode se compare très favorablement avec d'autres, du point de vue à la fois de la simplicité de l'application et de la précision des résultats. En contraste avec d'autres méthodes, elle donne une unité définie de traitement, et il y a peu de difficulté supplémentaire pour traiter d'autres réactions que celle du premier ordre ou pour obtenir des profils de couche limite. Les distributions superficielles d'atomes et de transport de chaleur sont exposées graphiquement et comparées avec des résultats théoriques publiés.

**Zusammenfassung**—Dieser Aufsatz behandelt die laminare Grenzschichtströmung eines dissoziierten Gases über katalytische Oberflächen, wobei besondere Aufmerksamkeit auf solche Fälle gerichtet ist, in welchen sich Oberflächenreaktionsgeschwindigkeiten nach Potenzen der Strömungskoordinaten ändern, und sich die Reaktionsordnungen von Eins unterscheiden. Das Gas in der Grenzschicht wird dargestellt durch ein chemisch eingefrorenes Zweikomponentengemisch aus Atomen und Molekülen, und es werden die gewöhnlichen vereinfachenden Annahmen für hypersonische Grenzschichtströmungen gemacht. Näherungsweise Integrationen der Diffusionsgleichung wurden analytisch mit Hilfe der Asymptoten-Methode erhalten. Dabei erweist sich diese Methode als sehr günstig im Vergleich zu anderen, sowohl in Hinsicht auf die Einfachheit der Anwendung, als auch im Hinblick auf die Genauigkeit der Ergebnisse. Im Gegensatz zu anderen Näherungen führt diese Methode zu einer in sich geschlossenen Einheit der Näherung, wobei man auf kleine zusätzliche Schwierigkeiten stösst bei der Behandlung von anderen Reaktionsordnungen als Eins oder bei der Berechnung der Grenzschichtprofile. Die Verteilungen der Atome auf die Oberfläche und der Wärmeübergang wurden graphisch dargestellt und mit veröffentlichten theoretischen Ergebnissen verglichen.

**Аннотация**—В данной статье рассматриваются ламинарные пограничные слои диссоциированного газа на каталитических поверхностях, причем особое внимание уделялось случаям, когда скорости реакции на поверхности изменялись как степени продольной координаты и порядок реакции отличается от единицы. Газ в пограничном слое представляет собой химически замороженную бинарную смесь атомов и молекул. Используются обычные упрощающие допущения, применимые к гиперзвуковым пограничным слоям. С помощью асимптотического метода аналитически получены приближенные интегралы уравнения диффузии. По сравнению с другими одметами этот метод точнее и проще в употреблении. По сравнению с другими подходами в данном случае добавляется небольшая трудность при рассмотрении реакций с порядком не равном единице или при получении профилей пограничного слоя. Поверхностные распределения атомов и теплообмен показаны графически и сравнены с опубликованными теоретическими результатами.