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SOME SIMPLE SURFACE REACTIONS IN LAMINAR BOUNDARY LAYERS

PAUL A. LIBBY and GUIDO BACCAGLINI

Department of the Aerospace and Mechanical Engineering Sciences, and Institute for Radiation Physics and Aerodynamics,* University of California, San Diego, La Jolla, California, U.S.A.

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Abstract—A previously developed analysis for the characteristics of the laminar boundary layer with surface catalysis is extended to a simple, two-step chemical reaction: $\mathcal{M}_1 \rightarrow \mathcal{M}_2 \rightarrow \mathcal{M}_3$. It is shown that an exact numerical solution of the appropriate integral equations may be obtained. Solutions involving discontinuous surface activities may also be systematically treated. In addition with certain further approximations the integral equations provide a convenient basis for solution by series methods. The same techniques may be applied to other simple reactions, e.g. $\mathcal{M}_1 \leftrightarrows \mathcal{M}_2$ and $\mathcal{M}_1 + \mathcal{M}_2 \rightarrow \mathcal{M}_3$.

NOMENCLATURE

$\hat{A}_n$, constants, cf. equation (5);
$\mathscr{A}_{nm}$, constants;
D, diffusion coefficient;
f, modified stream function, cf. equation (1);
k, rate of reaction;
$\mathcal{M}_i$, chemical symbol for species i;
$N_n(\eta)$, eigenfunctions, cf. equation (5);
r, cylindrical radius of surface, cf. equation (2);
s, transformed streamwise coordinate, cf. equation (2);
T, temperature;
u, velocity component in the x-direction;
W_i, molecular weight for species i;
Y_i, mass fraction of species i;
Z_n, function, cf. [2].

Greek symbols

α, series solution parameter;
$\alpha_m, \beta_m, \gamma_m$, constants in series representations, cf. equation (9);
η, transformed normal coordinate, cf. equation (2);
$\varkappa$, ratio of second to first reaction rate, cf. equation (7);
λ_n, eigenvalues, cf. equation (5);
μ, viscosity coefficient;
ν_i, stoichiometric coefficients for species i;
ρ, mass density.

Subscripts

e, conditions at edge of boundary layer;
w, conditons on wall.

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1. INTRODUCTION

THE PROPERTIES of laminar boundary layers with surface catalyzed reactions have been the subject of considerable recent study. Primary motivation in the aerospace community is related to the importance of atom recombination on partially catalytic surfaces in determining heat transfer to vehicles in high-altitude, high-speed flight and to the development of diagnostic probes for experimental gas dynamics [1–4]. Recently [5] appeared and may be referred to for additional relevant references. Furthermore,

the fluid mechanics of such boundary layers is so well-developed that careful laboratory experiments carried out in conjunction with theoretical studies permit determination of fundamental physiochemical data on surface catalysis [6, 7].

Most of the relevant theoretical studies have been concerned either with binary systems, e.g. atom recombination, or with more complex systems involving highly dilute reactants and products. In these cases the surface boundary condition relates the gradient of the concentration of a species i to the concentration of species i. Recently Libby and Liu [6] presented an analysis for a more general class of reactions involving the reaction $\nu'_1\mathcal{M}_1 + \nu'_2\mathcal{M}_2 \rightarrow \nu''\mathcal{M}_3 + \nu''_4\mathcal{M}_4$; following a Langmuir–Hinshelwood mechanism, i.e. one wherein the reactants are all in an adsorbed state; and occurring in a laminar boundary layer on a constant pressure surface. In this case the gradient of species i at the surface depends on the concentration of all species at the surface in a complex manner. Provided certain assumptions concerning the transport and fluid mechanical aspects of the flow are considered acceptable, the analysis of [6] may be readily extended to multistep reactions; to reactions involving Rideal–Ely mechanisms, i.e. some reactants from the gas phase striking other, adsorbed reactants; and to chemical systems with species which are so strongly adsorbed as to be negligibly present in the gas. These extensions are possible because of the availability from the analysis of [6] of solutions for species conservation which permit the gradient of species i at the surface to be computed at a generic streamwise station provided the surface concentration of species i upstream of that station is known. From the boundary conditions involving these gradients there are formed an appropriate number of integral equations which may be solved rapidly by numerical techniques.

To make calculations based on these extensions physically meaningful it is necessary to incorporate within the analysis for the particular chemical system of interest the available physiochemical information concerning adsorption, desorption, chemical mechanisms and chemical kinetics. Indeed interpreting such information in terms of the phenomenology of the boundary layer appears to present the greatest obstacle to such calculations.

It is the purpose of the present paper to demonstrate a further utility of the analysis of [6], namely, for the treatment of some chemical reactions which although simple nevertheless involve boundary conditions more complex than those usually treated. We adopted the point of view which is frequently taken, namely, that the rate of appearance or disappearance of a species is proportional to the gas phase concentrations of the appropriate reactants and which avoids explicit consideration of the surface concentrations (mol/cm^2) of the reactants. Questions concerning reaction mechanisms, reaction inhibition due to strongly adsorbed products, changing orders of reaction and the like do not arise in this point of view. Thus the phenomenology of surface reactions is greatly simplified, hopefully not to such an extent that calculations are devoid of physical content.

In pursuing the purpose of the present paper we shall in effect relate much of the previous work on laminar boundary layers with surface catalysis to the analysis of [6] and thereby shall show that it provides an alternative formulation consistent with modern developments in boundary-layer theory. In this formulation many problems can be solved with little computation, the major part of the numerical analysis being provided by the eigenfunction representations which form an integral part of the analysis of [6] and which for most problems may be considered to be presently available. In the interest of brevity we shall consider only one of the reactions treated by Acrivos and Chambré [8] in their application to surface catalysis of Lighthill's method which applies strictly to Schmidt numbers large compared to unity but which even for values thereof close to unity, as are of interest in gases, is known to lead to

reasonably accurate predictions. The present analysis is for a Schmidt number of unity but applies to compressible flows, to either two-dimensional or axisymmetric flows, and to flows with favorable pressure gradients provided "cold-wall" conditions prevail. Other simple reactions are readily studied by the same techniques. The present work must thus be considered an extension of several previous contributions to surface catalysis in laminar boundary layers.

2. BASIS FOR THE ANALYSIS

We consider either two-dimensional or axisymmetric laminar boundary layers with velocity fields given by the Blasius solution, i.e. by solution of the equation

$$\left.\begin{aligned} &f_0''' + f_0 f_0'' = 0 \\ &f_0(0) = f_0'(0) = 0 \\ &f_0'(\infty) = 1 \end{aligned}\right\} \quad (1)$$

where $(\,)'$ denotes differentiation with respect to the independent variable η and where η and s are transformed coordinates related to the Cartesian coordinates x, y along and normal to the planar or cylindrical surface, respectively, according to

$$\left.\begin{aligned} &\eta = \rho_e u_e r^j (2s)^{-\frac{1}{2}} \int_0^y (\rho/\rho_e)\,\mathrm{d}y' = \eta(x, y) \\ &s = \int_0^x \rho_e \mu_e u_e r^{2j}\,\mathrm{d}x' = s(x). \end{aligned}\right\} \quad (2)$$

The index $j = 0$ for two-dimensional cases, $j = 1$ for axisymmetric cases. The velocity components are related to $f(\eta)$ according to

$$\left.\begin{aligned} &u = u_e f_0', \\ &v = -(\rho_e/\rho)\,\mu_e u_e r^j (2s)^{-\frac{1}{2}} [f_0 + \eta_x (2s)^{\frac{1}{2}} f_0']. \end{aligned}\right\} \quad (3)$$

Implicit in the description of the velocity field by $f_0(\eta)$ defined here are the assumptions that the $\rho\mu$ ratio, $\rho\mu/\rho_e\mu_e \simeq 1$, an assumption frequently employed because of the simplification which results, and that the pressure gradient term $(2s/u_e)(\mathrm{d}u_e/\mathrm{d}s)[(\rho_e/\rho) - f'^2]$ and the non-similar terms involving $(\partial/\partial s)$ may be neglected. The neglect of the former implies that the pressure gradient is favorable, i.e. $(2s/u_e)(\mathrm{d}u_e/\mathrm{d}s) > 0$, and that $(\rho_e/\rho_w) \ll 1$ while the neglect of the latter implies that initial and boundary conditions are compatible with flow similarity.

If gas phase reactions are neglected, then the equation describing the conservation of species i in terms of its mass fraction Y_i in a boundary layer whose velocity field is given by $f_0(\eta)$ is

$$(\partial^2 Y_i/\partial\eta^2) + f_0(\partial Y_i/\partial\eta) - 2sf_0'(\partial Y_i/\partial s) = 0 \quad (4)$$

where we have made a second assumption regarding the transport properties of the gas mixture, namely, that there exists a single diffusion coefficient D applicable to all species and that the Schmidt number, namely $(\mu/\rho D)$, based thereon is unity. The initial and boundary condition at infinity applicable to equation (4) and of interest here are

$$Y_i(0, \eta) \equiv Y_{i,0}(\eta)$$

$$Y_i(s, \infty) = Y_{i,e}, \quad \text{given}$$

where $Y_{i,0}(\eta)$ is the initial distribution defined by the Crocco relation $Y_{i,0}(\eta) = Y_{i,w}(0) + [Y_{i,e} - Y_{i,w}(0)]f_0'$. If the surface boundary condition is specified in terms of $Y_i(s, 0) = Y_{i,w}(s)$, arbitrary but given, then [6] following the earlier analysis of [4], has provided the solution

$$Y_i(s, \eta) = Y_{i,e} f_0' + Y_{i,w}\left[(1 - f_0') - \sum_{n=1}^{\infty} \hat{A}_n N_n(\eta)\right] + \sum_{n=1}^{\infty} \hat{A}_n s^{-\frac{1}{2}\lambda_n} (\tfrac{1}{2}\lambda_n) N_n(\eta) \times \int_0^s \xi^{\frac{1}{2}\lambda_n - 1} Y_{i,w}(\xi)\,\mathrm{d}\xi \quad (5)$$

where the $N_n(\eta)$ and λ_n are eigenfunctions and eigenvalues, respectively, and are defined by

$$N_n'' + f_0 N_n' + \lambda_n f_0' N_n = 0$$

subject to $N_n(0) = 0$ and $\lim_{\eta\to\infty} N_n(\eta) \sim \exp[-(\eta - \varkappa)^2/2]$ where $\varkappa = \lim_{\eta\to\infty}(\eta - f_0) = 1{\cdot}21678$. The coefficients $\hat{A}_n$ are related to the square of the norms C_n of the eigenfunctions appropriately

weighted according to $\hat{A}_n = (C_n \lambda_n f''_{0,w})^{-1}$ where $f''_{0,w} = 0{\cdot}469600$. The first ten eigenfunctions, eigenvalues and norms have been given in [9] for the arbitrary but convenient normalization $N'_n(0) = 1$, which we retain in this work.

For present purposes equation (5) is useful in computing

$$(\partial Y_i/\partial\eta)(s,0) = (\partial Y_i/\partial\eta)_w = Y_{i,e} f''_{0,w} - Y_{i,w}\left(f''_{0,w} + \sum_{n=1}^{\infty} \hat{A}_n\right) - \sum_{n=1}^{\infty} \hat{A}_n s^{-\frac{1}{2}\lambda_n} \times \tfrac{1}{2}\lambda_n \int_0^s \xi^{\frac{1}{2}\lambda_n - 1}\, Y_{i,w}(\xi)\, d\xi \qquad (6)$$

which implies that the flux of species i at any station corresponding to s may be computed provided the surface concentration of that species at all upstream stations is known. Equation (6) plays the same role in the present analysis as the integral equation derivable from Lighthill's method for the case of large Schmidt numbers; its form is quite different, involving as it does an infinite series, but its utility is the same.

Before proceeding further we note that in many problems involving surface catalysis the heat transfer to the surface is of interest. Moreover a solution for the energy distribution within the boundary layer for arbitrary surface temperature $T_w(s)$ must frequently be considered. Provided the Prandtl number may be assumed to be unity methods analogous to those leading to equation (5) may be employed and result in the solution for the energy field given in [6]. In the present analysis it will not be necessary to apply explicitly this energy solution so we shall not consider it further but its availability should perhaps be recalled. In this connection we also note that the solution of the energy equation is required for the determination of the properties of the flow within the boundary layer in physical, i.e. x, y coordinates. In particular the inverse transformation $s, \eta \to x, y$ requires the density distribution (ρ_e/ρ) as a function of s, η to be known and this requires in general a solution of the energy equation along with the species equations.

3. THE CASE $\mathscr{M}_1 \overset{k_1}{\to} \mathscr{M}_2 \overset{k_2}{\to} \mathscr{M}_3$

Consider a two-step, unimolecular reaction with negligible backward rates. Let W_1 denote the molecular weight of each of the three participating species which in general we take to be diluted to an arbitrary degree by a background gas so that $Y_1 + Y_2 + Y_3 \neq 1$. We have been unable to find specific examples of catalyzed reactions which follow a mechanism of this sort but it is probable that rearrangement of some hydrocarbons with an intermediate $\mathscr{M}_2$ created may be so described.

In this case the molal fluxes of the three species at the surface are not equal and we must deal with three integral equations; from considerations of diffusive and chemical behavior at the surface under steady-state conditions we find

$$\left(\frac{\partial Y_1}{\partial\eta}\right)_w = \chi(s)\, Y_{1,w}$$
$$\left(\frac{\partial Y_2}{\partial\eta}\right)_w = \chi(s)\,(-Y_{1,w} + \varkappa Y_{2,w}) \qquad (7)$$
$$\left(\frac{\partial Y_3}{\partial\eta}\right)_w = \chi(s)\,(-\varkappa Y_{2,w})$$

where $\chi(s) \equiv (k_1/u_e)(\rho_w/\rho_e)(\mu_0/\mu_e)(L/r)^j [(2s)^{\frac{1}{2}}/\mu_0 L^j]$, where μ_0 is some constant, reference value of viscosity coefficient and L is a reference length, and where $\varkappa \equiv (k_2/k_1)$. The parameter $\varkappa$ determines whether the intermediate species 2 is subject to net creation or destruction; if $\varkappa \ll 1$, then species 2 tends to be created from species 1 faster than it is destroyed in the production of species 3 and its concentration tends to increase with χ. On the contrary if $\varkappa \gg 1$ then species 2 tends to be depleted in the production of species 3.

Equations (7) provide the boundary conditions for the three species equations and when used in connection with equation (6) for $i = 1$, 2, 3 lead to three integral equations. The first of these concerns $Y_{1,w}$ and is coupled to the others only through the nonlinear effect contained in (ρ_w/ρ_e); the second concerns $Y_{2,w}$,

depends directly on $Y_{1,w}$ and is again coupled to the others through (ρ_w/ρ_e); finally, the third equation involves $Y_{3,w}$ within the integrals and $Y_{2,w}$ and $Y_{3,w}$ outside the integrals.

We write the three integral equations in a form suitable for solution by numerical iteration; we find

$$Y_{1,w} = \frac{Y_{1,e} f''_{0,w} + \sum_{n=1}^{\infty} \hat{A}_n (s/\mu_0^2 L^{2j})^{-\frac{1}{2}\lambda_n} (\frac{1}{2}\lambda_n) \int_0^{s/\mu_0^2 L^{2j}} \xi^{\frac{1}{2}\lambda_n - 1} Y_{1,w}(\xi)\, d\xi}{(f''_{0,w} + \sum_{n=1}^{\infty} \hat{A}_n) + \chi(s)}$$

$$Y_{2,w} = \frac{Y_{2,e} f''_{0,w} + \chi(s) Y_{1,w} + \sum_{n=1}^{\infty} \hat{A}_n (s/\mu_0^2 L^{2j})^{-\frac{1}{2}\lambda_n} (\frac{1}{2}\lambda_n) \int_0^{s/\mu_0^2 L^{2j}} \xi^{\frac{1}{2}\lambda_n - 1} Y_{2,w}(\xi)\, d\xi}{(f''_{0,w} + \sum_{n=1}^{\infty} \hat{A}_n) + \varkappa\chi(s)}$$

$$Y_{3,w} = \frac{Y_{3,e} f''_{0,w} + \varkappa\chi(s) Y_{2,w} + \sum_{n=1}^{\infty} \hat{A}_n (s/\mu_0^2 L^{2j})^{-\frac{1}{2}\lambda_n} (\frac{1}{2}\lambda_n) \int_0^{s/\mu_0^2 L^{2j}} \xi^{\frac{1}{2}\lambda_n - 1} Y_{3,w}(\xi)\, d\xi}{(f''_{0,w} + \sum_{n=1}^{\infty} \hat{A}_n)}. \quad (8)$$

A scheme for numerical iteration involving successive solution of these three equations can be readily established along the lines used in [6]. The system of equations is completed by an equation of state which allows the density ratio (ρ_w/ρ_e) appearing in $\chi(s)$ to be expressed in terms of $Y_{1,w}$, $Y_{2,w}$ and $Y_{3,w}$ and by specified distributions of (T_w/T_e), of $(k_1/u_e)(\mu_0/\mu_e)(L/r)^j$, and of $\varkappa$. We note that discontinuous distributions of $\varkappa$ and of $\chi(s)$, are admissible within the framework of this numerical treatment; suppose, for example, there is a discontinuity at $s = s_L$. Then, in general, there will be a discontinuity in $Y_{i,w}$ at $s = s_L$ so that $Y_{i,w}(s_L^-)$ and $Y_{i,w}(s_L^+)$ must be identified for $s > s_L$. However, no further special considerations apply for this case, the iteration carrying through without alteration.

Series solution

Suppose we follow the spirit of the series solution of [2] used for the reaction $\mathscr{M}_1 \rightarrow \mathscr{M}_2$ and assume that (ρ_w/ρ_e) is known *a priori*, that $\varkappa$ is a constant* and that $\chi(s)$ is representable to sufficient accuracy by a series

$$\chi = \sum_{m=0}^{\infty} b_m (s/\mu_0^2 L^{2j})^{m/\alpha}$$

where α is a positive constant and where the b_m coefficients are given.

We note that from a physical viewpoint the independence of (ρ_w/ρ_e) from $Y_{1,w}$ can be achieved if the reactants are highly diluted by the background gas and that the b_0 coefficient is retained in the series since for stagnation point flows, either two-dimensional or axisymmetric, the series would start with a constant term. In fact, it is perhaps appropriate at this point to comment on the reasonable values for α for some common flows of interest; assume that k_f is described by a power series in integer powers of the streamwise coordinate x. Then if (ρ_w/ρ_e) is either constant or roughly so, we find that for flat-plate or wedge flows ($j = 0$, u_e = constant), $\alpha = 2$, $b_0 = 0$; for cones ($r \sim x$, u_e = constant), $\alpha = 6$, $b_0 = 0$; for two-dimensional stagnation points ($j = 0$, $u_e \sim x$), $\alpha = 2$, $b_0 \neq 0$; and finally for axisymmetric stagnation points ($r \sim x$, $u_e \sim x$), $\alpha = 4$, $b_0 \neq 0$. This is

* The extension to the case wherein $\varkappa$ is represented by a series expansion in $(s/\mu_0^2 L^{2j})^{m/\alpha}$ is straightforward.

not to state that these values of α are essential for these cases but only that these are the values which are likely to be of physical significance.

We seek solutions in the form

$$Y_{1,w} = \sum_{m=0}^{\infty} \alpha_m (s/\mu_0^2 L^{2j})^{m/\alpha}$$

$$Y_{2,w} = \sum_{m=0}^{\infty} \beta_m (s/\mu_0^2 L^{2j})^{m/\alpha}$$

$$Y_{3,w} = \sum_{m=0}^{\infty} \gamma_m (s/\mu_0^2 L^{2j})^{m/\alpha}$$

where α_m, β_m and γ_m, $m = 0, 1, 2\ldots$, are to be determined. Substitution into equations (8) and collection of like powers of $(s/\mu_0^2 L^{2j})$ lead to the following:

$$\left.\begin{aligned}
\alpha_0 &= \frac{Y_{1,e} f''_{0,w}}{f''_{0,w} + b_0} \\
\alpha_1 &= -\frac{\alpha_0 b_1}{f''_{0,w} + b_0 + \sum_{n=1}^{\infty} \hat{A}_n[(\alpha\lambda_n/2) + 1]^{-1}} \\
\alpha_2 &= -\frac{\alpha_0 b_2 + \alpha_1 b_1}{f''_{0,w} + b_0 + \sum_{n=1}^{\infty} \hat{A}_n[(\alpha\lambda_n/4) + 1]^{-1}} \\
\alpha_3 &= -\frac{\alpha_0 b_3 + \alpha_1 b_2 + \alpha_2 b_1}{f''_{0,w} + b_0 + \sum_{n=1}^{\infty} \hat{A}_n[(\alpha\lambda_n/6) + 1]^{-1}} \\
\beta_0 &= \frac{Y_{2,e} f''_{0,w} + \alpha_0 b_0}{f''_{0,w} + \varkappa b_0} \\
\beta_1 &= \frac{\alpha_0 b_1 + \alpha_1 b_0 - \beta_0 \varkappa b_1}{f''_{0,w} + \varkappa b_0 + \sum_{n=1}^{\infty} \hat{A}_n[(\alpha\lambda_n/2) + 1]^{-1}} \\
\beta_2 &= \frac{\alpha_0 b_2 + \alpha_1 b_1 + \alpha_2 b_0 - \varkappa(\beta_0 b_2 + \beta_1 b_1)}{f''_{0,w} + \varkappa b_0 + \sum_{n=1}^{\infty} \hat{A}_n[(\alpha\lambda_n/4) + 1]^{-1}} \\
\beta_3 &= \frac{\left[\begin{array}{l}\alpha_0 b_3 + \alpha_1 b_2 + \alpha_2 b_1 + \alpha_3 b_0 \\ \qquad - \varkappa(\beta_0 b_3 + \beta_1 b_2 + \beta_2 b_1)\end{array}\right]}{f''_{0,w} + \varkappa b_0 + \sum_{n=1}^{\infty} \hat{A}_n[(\alpha\lambda_n/6) + 1]^{-1}} \\
\gamma_0 &= \frac{Y_{3,e} f''_{0,w} + \varkappa\beta_0 b_0}{f''_{0,w}}
\end{aligned}\right\} (9)$$

$$\left.\begin{aligned}
\gamma_1 &= \frac{\varkappa(\beta_0 b_1 + \beta_1 b_0)}{f''_{0,w} + \sum_{n=1}^{\infty} \hat{A}_n[(\alpha\lambda_n/2) + 1]^{-1}} \\
\gamma_2 &= \frac{\varkappa(\beta_0 b_2 + \beta_1 b_1 + \beta_2 b_0)}{f''_{0,w} + \sum_{n=1}^{\infty} \hat{A}_n[(\alpha\lambda_n/4) + 1]^{-1}} \\
\gamma_3 &= \frac{\varkappa(\beta_0 b_3 + \beta_1 b_2 + \beta_2 b_1 + \beta_3 b_0)}{f''_{0,w} + \sum_{n=1}^{\infty} \hat{A}_n[(\alpha\lambda_n/6) + 1]^{-1}}.
\end{aligned}\right\} (9)$$

Additional coefficients may be either calculated or deduced.

We thus see that the integral equations developed from [6] provide a convenient means of obtaining series solutions applicable to limited regions of χ. Note also that the series solution for $Y_{1,w}$ is directly applicable to a unimolecular, unidirectional, one-step reaction and is thus directly comparable to [2] provided that the difference in Schmidt numbers is taken into account. In this regard it may be of interest to note that our eigenfunctions provide a direct calculation for the functions Z_n in [2] for $Sc = 1$; this may be shown as follows: Let $Z_n = \sum_{m=1}^{\infty} \mathscr{A}_{nm} N_m + (1 - f'_0)$. Then a straightforward calculation utilizing the orthogonal properties of the N_m function leads to

$$\mathscr{A}_{nm} = -\{[(\alpha\lambda_m/2n) + 1]\, C_m \lambda_m f''_{0,w}\}^{-1}.$$

We have computed the summations appearing in the denominators of equation (9) from the ten terms given by [6] and have estimated from the sequence of partial sums the value of the infinite sum. The results for $\alpha = 2$ are given in Table 1.

Application to flat-plate flows

To illustrate application of this series solution we consider explicitly the case of flat-plate flows with all the b_n coefficients except b_1 equal to zero and with $\alpha = 2, j = 0$. In this case the general series for $Y_{1,w}$, $i = 1, 2, 3$ can be recast into a series of integer powers of $(b_1 s^{\frac{1}{2}}/\mu_0)$. It does not

appear possible to recast the dependent variables so as to remove all of the parameters except $\varkappa$; we can find the solution for $Y_{1,w}$ free of parameters if it is written in terms of $(Y_{1,w} - Y_{1,e})/Y_{1,e}$. The second and third of equations (8), and the series solution for $Y_{2,w}$ and $Y_{3,w}$ may be reformed to yield, respectively, $Y_{2,w}$ and $Y_{3,w}$ in the combinations $(Y_{2,w} - Y_{2,e})/Y_{1,e}$ and $(Y_{3,w} - Y_{3,e})/Y_{1,e}$ but there remains the parameter $(Y_{2,e}/Y_{1,e})$ as well as $\varkappa$.

For this case the surface composition far downstream in the sense $(b_1 s^{\frac{1}{2}}/\mu_0) \to \infty$ can be obtained from equations (8); we find, as might be expected on physical grounds, that provided $\varkappa > 0$

$$Y_{1,w},\ Y_{2,w} \to 0$$

$$Y_{3,w} \to Y_{1,e} + Y_{2,e} + Y_{3,e}.$$

This corresponds of course to conversion of all molecules of species 1 and 2 capable of diffusing to the surface into final product. If $\varkappa = 0$, then, again as might be expected on physical grounds,

$$Y_{1,w} \to 0$$

$$Y_{2,w} \to Y_{1,e} + Y_{2,e}$$

$$Y_{3,w} \equiv Y_{3,e}.$$

We show in Fig. 1 the comparison with [2] for the case $\varkappa = 0$, i.e. when there is no production of $\mathscr{M}_3$ from $\mathscr{M}_2$; it may be seen despite the differences in Schmidt number, 0·72 in [2], unity here, that our series solution with ten terms agrees well with the fifteen-term series given by [2] and that both agree well with the exact solution for $0 \leqslant \chi \leqslant 0{\cdot}5$.

We also show the results in Fig. 1 for $(Y_{2,e}/Y_{1,e}) = 0,\ 0{\cdot}1$, respectively, for $\varkappa = 1$ as given by the series solution and by exact numerical solution of equations (8) specialized for this case of $\chi = (b_1 s^{\frac{1}{2}}/\mu_0)$. The agreement between the two calculations is seen to be satisfactory for $\chi \simeq 0{\cdot}5$; the limited range of accuracy of the series solution is of course to be expected. In this regard the exact numerical solution, although requiring programming and machine computation, is superior.

Table 1. Estimates for the infinite sums $\sum_{n=1}^{\infty} \hat{A}_n[(\alpha\lambda_n/m) + 1]^{-1}$

m	$\alpha = 2$	m	$\alpha = 2$
2	0·165	12	0·510
4	0·265	14	0·545
6	0·353	16	0·568
8	0·420	18	0·588
10	0·479	20	0·620

Results for an axisymmetric stagnation point

We briefly discuss the implications of the series solution given by equation (9) for an axisymmetric stagnation point, $\alpha = 4$. The parameters in this case are b_0 and $\varkappa$; the composition at the surface is given for $s \to 0$ as

$$Y_{1,w} = \frac{Y_{1,e} f''_{0,w}}{f''_{0,w} + b_0}$$

$$Y_{2,w} = \left(\frac{f''_{0,w}}{f''_{0,w} + \varkappa b_0}\right)\left[Y_{2,e} + \left(\frac{b_0 Y_{1,e}}{f''_{0,w} + b_0}\right)\right]$$

$$Y_{3,w} = Y_{3,e} + \left(\frac{\varkappa b_0}{f''_{0,w} + \varkappa b_0}\right) \times \left[Y_{2,e} + \left(\frac{b_0 Y_{1,e}}{f''_{0,w} + b_0}\right)\right].$$

This result could be obtained from Crocco integrals relating f'_0 and Y_1 if the boundary conditions at $f'_0 = 1,\ 0$ corresponding to the external stream and to equations (7) are imposed. Higher order terms in powers of s can readily be obtained.

4. CONCLUDING REMARKS

We have shown that the analysis of [6] can be generalized to the case of a two-step, unimolecular reaction $\mathscr{M}_1 \to \mathscr{M}_2 \to \mathscr{M}_3$ so as to lead to three simultaneous integral equations which may be solved by numerical iteration.

The nonlinear effect of the density ratio (ρ_w/ρ_e) and the effect of discontinuities in surface properties may be readily taken into account in this numerical iteration. It is also shown that the integral equations provide a convenient means for obtaining the series solutions which apply in limited regions of the dependent variable, which involve additional assumptions but which provide estimates of catalytic behavior with little computation.

The same analysis both in terms of exact numerical and series solutions can be carried through for a variety of simple reactions, e.g. for $\mathcal{M}_1 \rightleftarrows \mathcal{M}_2$ and $\mathcal{M}_1 + \mathcal{M}_2 \rightarrow \mathcal{M}_3$.

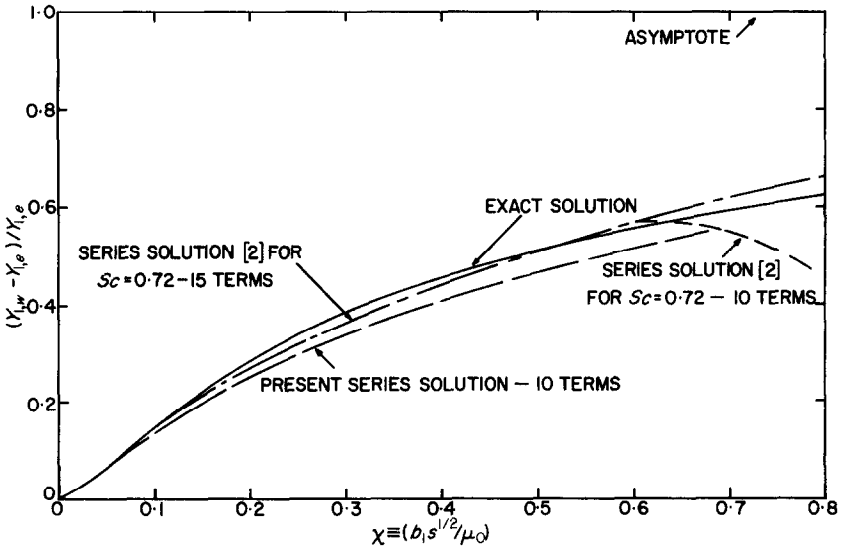

FIG. 1. Solutions for $\mathcal{M}_1 \rightarrow \mathcal{M}_2 \rightarrow \mathcal{M}_3$.

FIG. 1 (a). Distribution of $(Y_{1,e} - Y_{1,w})/Y_{1,e}$

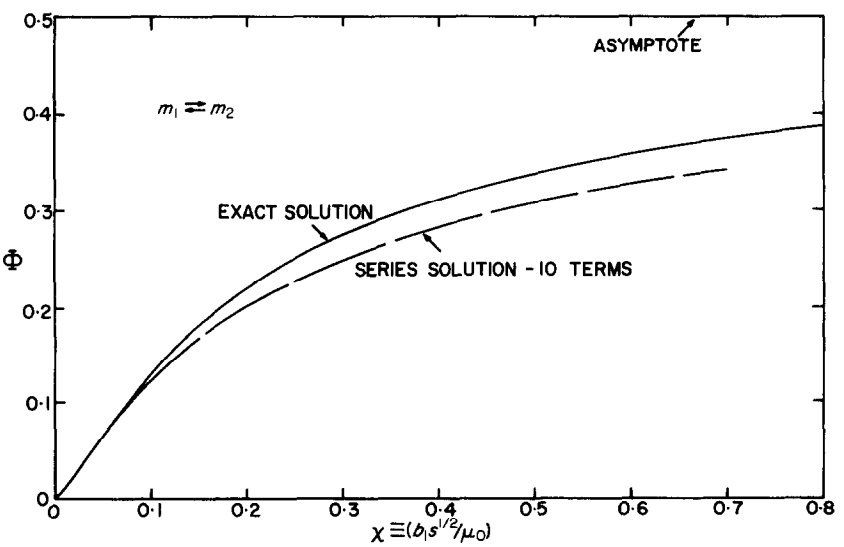

FIG. 1 (b). Distribution of $[(Y_{2,w} - Y_{2,e})/Y_{1,e}]$ for $\kappa = 1, (Y_{2,e}/Y_{1,e}) = 0$.

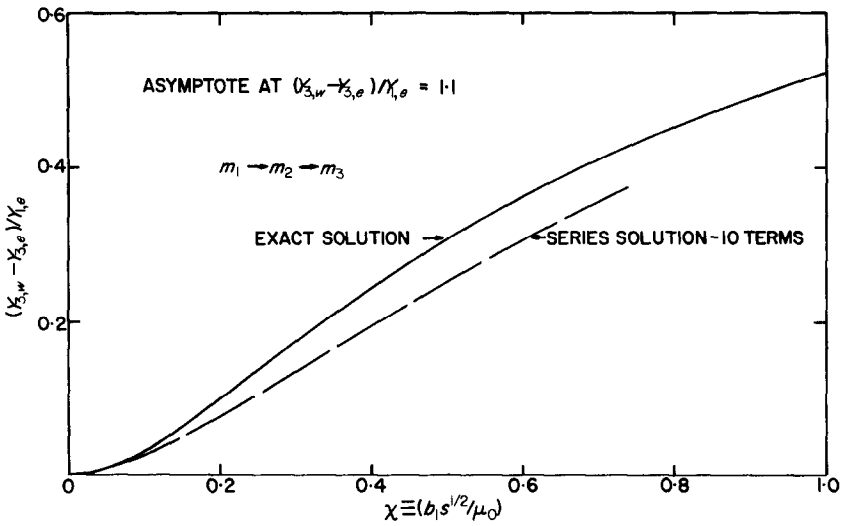

FIG. 1 (c). Distribution of $[(Y_{3,w} - Y_{3,e})/Y_{1,e}]$ for $\kappa = 1, (Y_{2,e}/Y_{1,e}) = 0$.

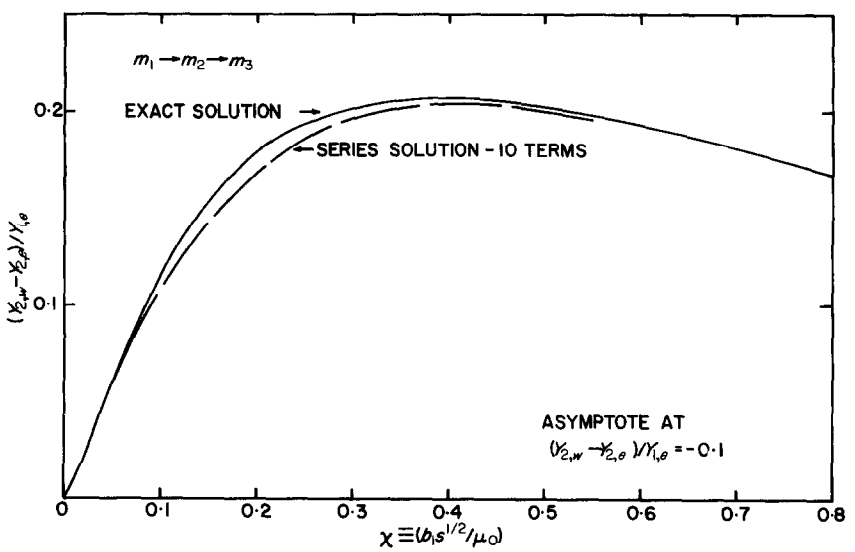

FIG. 1 (d). Distribution of $[(Y_{2,w} - Y_{2,e})/Y_{1,e}]$ for $\kappa = 1, (Y_{2,e}/Y_{1,e}) = 0{\cdot}1$.

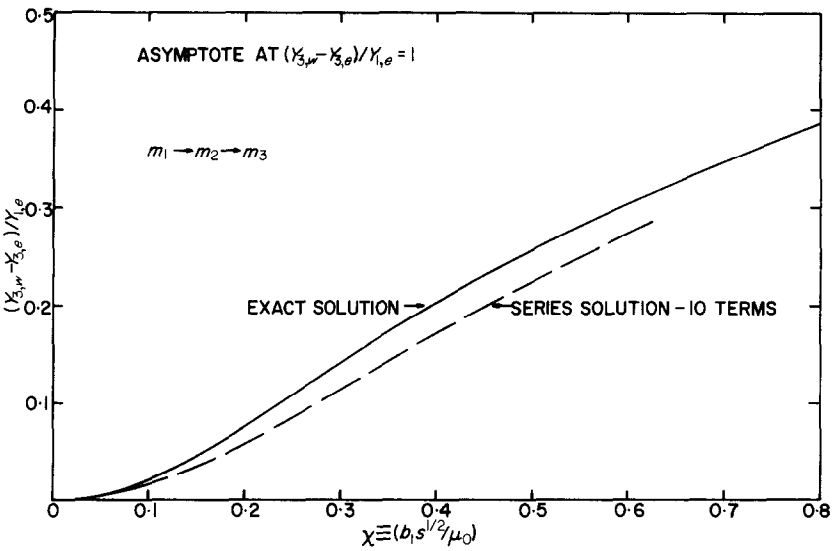

FIG. 1 (e). Distribution of $[(Y_{3,w} - Y_{3,e})/Y_{1,e}]$ for $\chi = 1$, $(Y_{2,e}/Y_{1,e}) = 0{\cdot}1$.

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Résumé—Une théorie exposée auparavant pour les caractéristiques de la couche limite laminaire avec catalyse à la surface est étendue à une réaction chimique simple à deux étapes : $\mathcal{M}_1 \rightarrow \mathcal{M}_2 \rightarrow \mathcal{M}_3$. On montre qu'une solution numérique exacte des équations intégrales appropriées peut être obtenue. Des solutions impliquant des activités discontinues de surface peuvent aussi être traitées de façon systématique. En plus de certaines approximations supplémentaires, les équations intégrales fournissent une base convenable pour la solution par des méthodes de séries. Les mêmes techniques peuvent être appliquées à d'autres réactions simples, par exemple, $\mathcal{M}_1 \rightarrow \mathcal{M}_2$ et $\mathcal{M}_1 + \mathcal{M}_2 \rightarrow \mathcal{M}_3$.

Zusammenfassung—Eine kürzlich entwickelte Analyse der Charakteristika laminarer Grenzschichten mit Oberflächenkatalyse wird auf eine einfache chemische Reaktion mit zwei Schritten $\mathcal{M}_1 \rightarrow \mathcal{M}_2 \rightarrow \mathcal{M}_3$ angewandt. Es wird gezeigt, dass eine exakte numerische Lösung der entsprechenden Integralgleichung möglich ist. Lösungen mit Ungleichförmigkeiten in der Oberflächenaktivität lassen sich auch systematisch behandeln. Daneben geben die Integralgleichungen mit einigen weiteren Näherungen eine bequeme Grundlage für Lösungen nach Reihenmethoden. Das gleiche Verfahren lässt sich auch auf andere einfache Reaktionen wie $\mathcal{M}_1 \rightarrow \mathcal{M}_2$ und $\mathcal{M}_1 + \mathcal{M}_2 \rightarrow \mathcal{M}_3$ anwenden.

Аннотация—Ранее разработанный метод анализа характеристик ламинарного пограничного слоя при катализе на поверхности распространен на случай простой двухстадийной химической реакции: $\mathcal{M}_1 \rightarrow \mathcal{M}_2 \rightarrow \mathcal{M}_3$. Показана возможность получения точного численного решения соответствующих интегральных уравнений. Могут быть также рассмотрены решения, включающие в себя прерывные поверхностные активности. Кроме того, при определенных дальнейших аппроксимациях интегральные уравнения являются хорошей базой для решения методами рядов. Эту же методику можно применить к другим простым реакциям: $\mathcal{M}_1 \rightarrow \mathcal{M}_2$ и $\mathcal{M}_1 \rightarrow \mathcal{M}_2 \rightarrow \mathcal{M}_3$.