THEORETICAL ANALYSIS OF STEADY, NONADIABATIC PREMIXED LAMINAR FLAMES*

BY

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Abstract. A one-dimensional, steady, non-adiabatic, premixed laminar flame is assumed semi-infinite with the burner at the origin, and the investigation centers on the asymptotic behavior of the temperature and species mass fractions in the burned region near infinity. After a consideration of the general N-species problem, specific results are obtained for the global two-step reaction $v_r R \to \mu_i I$, $v_i I \to \mu_p P$, where R, I, P denote reactant, intermediate, and product species, respectively, and v_r, v_i, μ_i, μ_p are stoichiometric coefficients. Assuming Arrhenius kinetics, it is shown that the classical linearized asymptotic theory is not applicable unless $v_r = v_i = 1$, in which case the approach to burned equilibrium is an exponential decay. Consequently, a nonlinear theory applicable to arbitrary v_r and v_i is presented which shows that in general the asymptotic decay is algebraic. It is further shown that boundedness of the solution at infinity permits the arbitrary specification of only three boundary conditions on the original sixth-order differential system. This result is illustrated by a comprehensive analytical example and the computational implications for the general N-species problem are discussed.

1. Introduction. This paper is concerned with the theoretical determination of the steady-state structure (i.e., profiles of the temperature and species mass fractions) of a general semi-infinite, nonadiabatic, premixed laminar flame. Fig. 1 illustrates the physical problem, which is meant to represent a flame sitting on a porous plug burner from which emerges a premixed combustible mixture. Since there is in general a positive temperature gradient at the origin $x = 0$ due to heat transfer from the burning mixture back to the burner, the flame is nonadiabatic. In the limit that the incoming fluid velocity approaches the adiabatic flame speed, the flame sits infinitely far away from the burner and the temperature gradient is zero at $x = 0$. Hence, the adiabatic case, which can be regarded as the limit of a sequence of nonadiabatic problems, is imbedded in the general non-adiabatic configuration described by Fig. 1.

This problem, especially the ideal adiabatic case, has had a long history [1]. Being set in a particularly simple flow configuration (usually approximated as one-dimensional), it was one of the first combustion problems to be attacked via both analytical and numeri-
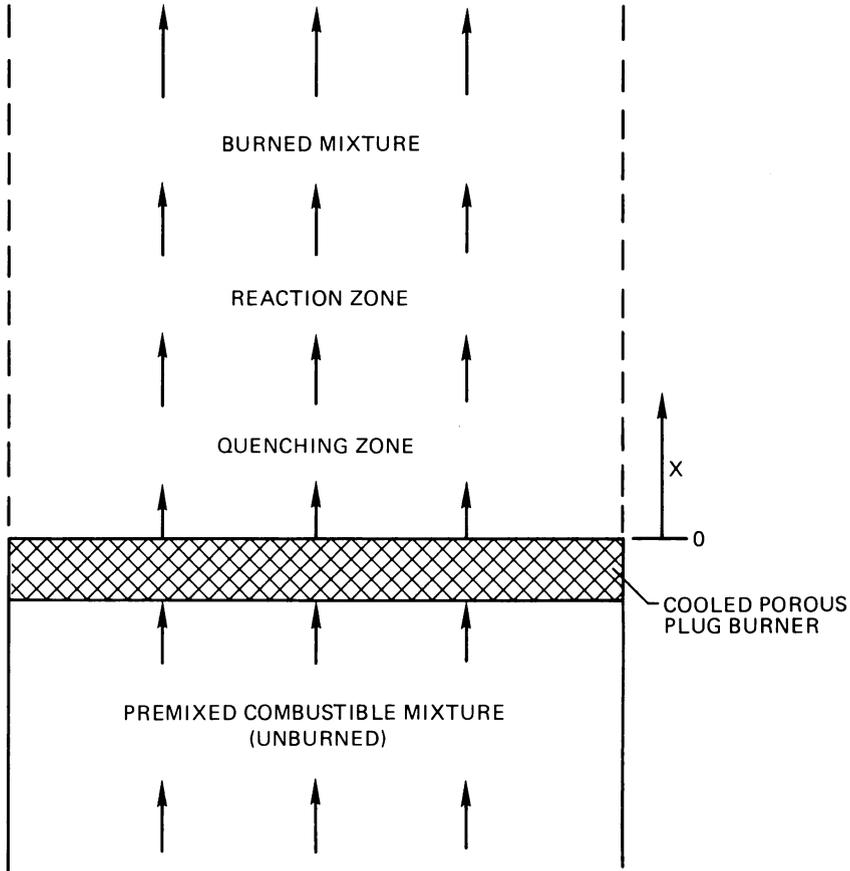
FIG. 1. Physical description of a nonadiabatic premixed laminar flame.

cal approaches. However, this simplicity is deceptive, for the problem has proven to be extremely complex and is still being actively pursued. One of the earliest yet most comprehensive analytical treatments is that due to Hirschfelder et al. [2]. The major contributions in that paper were the presentation of a linearized asymptotic $(x \to \infty)$ analysis of the flame structure in the burned region and a detailed calculation of a simple flame characterized by a single *unimolecular* reversible reaction. However, it is shown in the present work that the linearized analysis is not applicable in general (assuming Arrhenius kinetics) when the chemical reactions are of higher order, and one of the major thrusts of this paper is the development of a nonlinear asymptotic theory valid for even fractional reaction orders. Another interesting result which one obtains from [2] is that there exist nonphysical (i.e., unbounded) solutions of the time-independent flame equations. It is shown here that this has major implications for both the analytical and computational treatments of the problem, since the number of unphysical solutions which must be filtered out determines the number of arbitrary boundary conditions which is consistent with the semi-infinite problem. More recent works [3, 4, 5] have exploited large activation energy asymptotics to further characterize the solution of one-step flames (i.e., flames governed by a single chemical reaction) as a function of

Lewis number, stoichiometry, and burner characteristics. In contrast, the emphasis in the present work is on flames which are modelled by multi-step reaction mechanisms.

Much work has also gone into the development of computational techniques to solve the flame equations numerically. Consequently, several distinct methods have emerged, the time-dependent approach originated by Spalding [6, 7] and at least two types of direct steady-state approaches [8, 9]. The first has met with the greatest success, although Dixon-Lewis [10] has shown that a combination of the first with one of the steady-state methods can produce noteworthy results. A strong motivation for considering the premixed flame problem and one of the major accomplishments of the present work is a critical explanation of the mathematical distinction between these various methods in light of the analytical results obtained here.

An outline of this paper is as follows. In Sec. 2 the steady-state problem is formulated in a Lagrangian coordinate which permits a direct comparison with the usual time-dependent equations. Following an appropriate nondimensionalization (Sec. 3), a conservation law is derived in Sec. 4 which analytically reduces the order of the system. In Sec. 5 the linearized asymptotic analysis is applied, after which explicit consideration is restricted to the global two-step reaction

$$v_r R \to \mu_i I, \tag{1}$$

$$v_i I \to \mu_p P \tag{2}$$

subject to Arrhenius kinetics. Here, v_r, μ_i, v_i, μ_p are stoichiometric coefficients and R, I, P are reactant, intermediate, and product species, respectively. It is shown that the linearized asymptotic theory is only applicable for the special case $v_r = v_i = 1$, in which event the asymptotic approach to burned equilibrium as $x \to \infty$ is exponential.

Sec. 6 develops the nonlinear asymptotic theory for the general case in which either $v_r > 1$ and/or $v_i > 1$ (they need not be integers if Eqs. (1) and (2) are global approximations to a much more intricate reaction mechanism) and shows that the asymptotic approach to burned equilibrium as $x \to \infty$ is generally algebraic, rather than exponential (cf. Carrier et al. [5]). Both the linear and nonlinear theories predict the same number of unphysical solutions and hence the same number of arbitrary boundary conditions which may be specified in order to guarantee a physical solution for the semi-infinite problem. In particular, the critical, or equilibrium, point of the governing ordinary differential system corresponds to the burned state at infinity and is a saddle point of type 3 (cf. Hale [11]). Thus, the problem is mathematically unstable with respect to the spatial coordinate and although the original differential system governing the reaction mechanism (1), (2) is sixth-order, only three boundary conditions may be arbitrarily applied in order to assure that nonphysical solutions are absent. The existence of unphysical solutions was noted by Hirschfelder et al. [2] in their analysis of the unimolecular flame, but the presence of such solutions in more complicated flames and their impact on the boundary conditions were not pursued.

A complete analytical example is worked out in Sec. 7 to illustrate the above remarks, and the implications for the general N-species computational problem are discussed in Sec. 8. In particular, it is shown quantitatively how the characteristically large disparities in chemical reaction rates produce a problem which is both severely unstable and extremely stiff. For realistic flames involving dozens of chemical species and 50 or more reversible chemical reactions, the numerical problem takes on near-pathological proportions, and thus a critical survey is made of the various numerical techniques which have

actually been applied to this problem. Briefly, the time-dependent methods appear to be the most reliable; consequently, a realistic numerical calculation of an ammonia/oxygen nonadiabatic flame is presented using the spline collocation technique discussed previously by Margolis [12] in connection with the adiabatic problem.

2. Governing equations.   The basic assumptions underlying the model are (i) the flow is one-dimensional; (ii) velocities are sufficiently small for viscous effects, and hence pressure variations, to be neglected; (iii) body forces (e.g., gravity) are negligible; (iv) radiative heat transfer, heat diffusion due to concentration gradients (Dufour effect), and species diffusion due to temperature gradients (Soret effect) are all negligible; and (v) a multicomponent Fick's law governs the diffusion of each species with respect to the mixture of remaining species. These approximations are common in premixed laminar flame studies (cf. Spalding et al. [13]) and are thoroughly discussed by Williams [1]. Consequently, the steady-state governing equations are overall continuity,

$$\frac{d}{dx}(\rho u) = 0, \tag{3}$$

conservation of species,

$$u\frac{dY_k}{dx} = \frac{1}{\rho}\frac{d}{dx}\left(\rho D_k \frac{dY_k}{dx}\right) + \frac{1}{\rho}R_k M_k, \qquad k = 1, \dots, N-1, \tag{4}$$

conservation of energy,

$$u\frac{dT}{dx} = \frac{1}{\rho c_p}\frac{d}{dx}\left(\lambda\frac{dT}{dx}\right) - \sum_{k=1}^{N} R_k M_k h_k + \sum_{k=1}^{N} D_k \frac{c_{p,k}}{c_p}\frac{dY_k}{dx}\frac{dT}{dx}, \tag{5}$$

and an equation of state

$$\rho = \rho(Y_1, Y_2, \dots, Y_n, T; p), \tag{6}$$

which for the case of an ideal gas is

$$\rho = p \bigg/ \left(\sum_{k=1}^{N} \frac{Y_k}{M_k} RT\right). \tag{7}$$

The various symbols appearing in these equations have their usual meanings. In particular, Y_k is the mass fraction of the kth species (molecular weight M_k, specific heat capacity $c_{p,k}$, specific enthalpy h_k), R_k is the rate of production of the kth species (moles/vol-sec) by chemical reactions, and D_k is the binary diffusion coefficient for the kth species with respect to the mixture of remaining species. The various transport coefficients, heat capacities, and rate functions R_k are, in general, specified functions of the mass fractions Y_k and temperature T. However, the definition constraints

$$\sum_{k=1}^{N} Y_k = 1, \qquad \sum_{k=1}^{N} Y_k V_k = 0, \tag{8a,b}$$

where the diffusion velocities V_k are given by

$$Y_k V_k \equiv -D_k \frac{dY_k}{dx}, \tag{9}$$

imply that the N multicomponent diffusion coefficients D_k are not all independent. In particular, Eqs. (8) and (9) imply that

$$D_N \frac{dY_N}{dx} = - \sum_{k=1}^{N-1} D_k \frac{dY_k}{dx}, \tag{10}$$

where

$$Y_N = 1 - \sum_{k=1}^{N-1} Y_k. \tag{11}$$

Furthermore, summing Eqs. (4) from $k = 1$ to $k = N$ and utilizing Eqs. (8) and (9) yields an identity, since conservation of mass implies that $\sum_{k=1}^{N} R_k M_k = 0$. Thus, only the $N - 1$ independent species conservation equations are included in Eqs. (4) and Eq. (10) is only needed in the last term of Eq. (5).

Introducing the Lagrangian coordinate ψ,

$$\psi(x) = \int_0^x \rho(\bar{x}) \, d\bar{x}, \tag{12}$$

and letting m_0 denote the mass flux ρu, which is constant according to Eq. (3) and assumed to be specified, leads to the set of equations

$$m_0 \frac{dY_k}{d\psi} = \frac{d}{d\psi} \left[\rho^2 D_k \frac{dY_k}{d\psi} \right] + \frac{1}{\rho} R_k M_k, \qquad k = 1, \dots, N-1, \tag{13}$$

$$m_0 \frac{dT}{d\psi} = \frac{1}{c_p} \frac{d}{d\psi} \left(\rho \lambda \frac{dT}{d\psi} \right) - \frac{1}{\rho c_p} \sum_{k=1}^{N} R_k M_k h_k + \sum_{k=1}^{N} \frac{c_{p,k}}{c_p} \rho^2 D_k \frac{dY_k}{d\psi} \frac{dT}{d\psi}$$

$$= \frac{1}{c_p} \frac{d}{d\psi} \left(\rho \lambda \frac{dT}{d\psi} \right) - \frac{1}{\rho c_p} \sum_{k=1}^{N-1} R_k M_k (h_k - h_N)$$

$$+ \sum_{k=1}^{N-1} \frac{1}{c_p} (c_{p,k} - c_{p,N}) \rho^2 D_k \frac{dY_k}{d\psi} \frac{dT}{d\psi} \tag{14}$$

where Eq. (10) and the mass conservation relation

$$R_N M_N = - \sum_{k=1}^{N-1} R_k M_k \tag{15}$$

have been used to obtain Eq. (14). (The rate functions themselves are given by the law of mass action,

$$R_k = \sum_{m=1}^{M} (v''_{k,m} - v'_{k,m}) \left[k_m^f(T) \prod_{n=1}^{N} \left(\frac{\rho Y_n}{M_n} \right)^{v'_{n,m}} - k_m^b(T) \prod_{n=1}^{N} \left(\frac{\rho Y_n}{M_n} \right)^{v''_{n,m}} \right],$$

where $v'_{k,m}(v''_{k,m})$ is the stoichiometric coefficient of species k, $k = 1, \dots, N$, appearing as a reactant (product) in the reversible reaction m, $m = 1, \dots, M$. The function $k_m^f(k_m^b)$ is the so-called specific rate constant for the forward (backward) mode of reaction m and is usually given an Arrhenius temperature dependence, as in Eqs. (53), (54) below.)

The coordinate transformation (12) was employed by Spalding [6] in connection with the adiabatic time-dependent equations, thereby eliminating the continuity equation. For the time-dependent nonadiabatic problem, the terms $\partial Y_k/\partial t$ and $\partial T/\partial t$ are appended to the left-hand sides of Eqs. (13) and (14) and $m_0 = m_0(t) = \rho u|_{x=\psi=0}$ is the incoming mass flux (cf. Margolis [12]). For the steady-state problem, the transformation (12) is useful both for comparison with the time-dependent formulation and for analyzing the equations under certain additional approximations, such as constant $\rho^2 D_k$ and $\rho\lambda$ (cf. Bledjian [14]).

Although alternative formulations are possible (cf. Carrier et al. [5]), the boundary conditions on Eqs. (13) and (14) are taken to be an arbitrary specification of temperature and species mass flux fractions at $\psi = x = 0$ (cf. Spalding and Stephenson [7]). That is,

$$T\bigg|_{\psi=0} = T_u, \tag{16}$$

$$\frac{\rho Y_k(u + V_k)}{\rho u}\bigg|_{\psi=0} = Y_k - \frac{\rho^2 D_k}{m_0}\frac{dY_k}{d\psi}\bigg|_{\psi=0} = \varepsilon_k, \qquad k = 1, \ldots, N - 1. \tag{17}$$

As will be shown later, the remaining N boundary conditions on the order-$2N$ system (13), (14) are non-arbitrary compatibility conditions at $\psi = \infty$ needed to assure bounded solutions there.

3. Nondimensionalization. At this point it is useful to nondimensionalize Eqs. (13) and (14). First, a characteristic time $\bar{t}$ is chosen based on a "significant" chemical time scale. There are in general a number of time scales due to the fact that there is wide variation among the characteristic rates at which different chemical reactions occur, but it is often possible to distinguish a particular reaction or a small group of reactions which essentially determines the rate at which fuel is converted into product species. For example, the relevant rate-controlling reaction in an ozone decomposition flame (cf. Margolis [12]) is the decay of O_3 into $O_2 + O$. The combination of O_3 and O to form $2O_2$ occurs on a much faster time scale, and the much slower recombination of $O + O$ to form O_2 is relatively unimportant in determining the global structure of the flame, as are all the reverse reactions. The proper characteristic length $\bar{l}$ is then a diffusion length scale based on $\bar{t}$. (Alternatively, if $\bar{l}$ is known from experimental observations, then $\bar{t}$ would be a diffusion time scale based on $\bar{l}$.) Hence, nondimensional quantities are introduced in the following manner:

$$t^* \equiv t/\bar{t}; \qquad \rho^* \equiv \rho/\bar{\rho}; \qquad T^* \equiv T/\bar{T};$$

$$\lambda^* \equiv \lambda/\bar{\lambda}; \qquad D_k^* \equiv D_k/\bar{D}_k; \qquad M_k^* \equiv M_k/\bar{M}_k;$$

$$c_{p,k}^* \equiv c_{p,k}/\bar{c}_{p,k}; \qquad c_p^* \equiv c_p/\bar{c}_p, \quad \text{where} \quad \bar{c}_p \equiv \sum_{k=1}^{N} \bar{Y}_k \bar{c}_{p,k}; \tag{18}$$

$$x^* \equiv x/\bar{l}, \quad \text{where} \quad \bar{l} \equiv (\bar{\lambda}\bar{t}/\bar{\rho}\bar{c}_p)^{1/2}; \qquad \psi^* \equiv \psi/\bar{\rho}\bar{l};$$

$$m_0^* \equiv m_0\bar{t}/\bar{\rho}\bar{l}; \qquad h_k^* \equiv h_k/\bar{c}_{p,k}\bar{T}; \qquad R_k^* \equiv R_k\bar{M}_k\bar{t}/\bar{\rho},$$

where all quantities with bars are characteristic values.

Introducing these definitions into Eqs. (13) and (14) yields the nondimensional equations

$$m_0^* \frac{dY_k}{d\psi^*} = Le_k^{-1} \frac{d}{d\psi^*}\left(\rho^{*2}D_k^* \frac{dY_k}{d\psi^*}\right) + \frac{1}{\rho^*} R_k^* M_k^*, \qquad k = 1, \ldots, N-1, \tag{19}$$

$$m_0^* \frac{dT^*}{d\psi^*} = \frac{1}{c_p^*} \frac{d}{d\psi^*}\left(\rho^* \lambda^* \frac{dT^*}{d\psi^*}\right) - \frac{1}{\rho^* c_p^*} \sum_{k=1}^{N-1} R_k^* M_k^* (h_k^* - h_N^*)$$

$$+ \sum_{k=1}^{N-1} Le_k^{-1} \frac{1}{c_p^*} (c_{p,k}^* - c_{p,N}^*) \rho^{*2} D_k^* \frac{dY_k}{d\psi^*} \frac{dT^*}{d\psi^*}, \tag{20}$$

where

$$Le_k = \frac{\bar{\lambda}}{\bar{\rho} \bar{D}_k \bar{c}_p} \tag{21}$$

is the Lewis number for the kth species. In what follows, the asterisks will be omitted, but all variables are now understood to be dimensionless. Finally, it is assumed that $\rho\lambda$, $c_{p,k}$, and $\rho^2 D_k$ are all constants (cf. [14]) and that $c_{p,k} = c_p$ for all k, but the value of $\rho^2 D_k$ is allowed to be k-dependent. Under these approximations, Eqs. (19) and (20) become

$$m_0 \frac{dY_k}{d\psi} = Le_k^{-1} \frac{d^2 Y_k}{d\psi^2} + \rho^{-1} R_k M_k, \qquad k = 1, \ldots, N-1, \tag{22}$$

$$m_0 \frac{dT}{d\psi} = \frac{d^2 T}{d\psi^2} - \rho^{-1} \sum_{k=1}^{N-1} R_k M_k (h_k^0 - h_N^0), \tag{23}$$

where h_k^0 is the standard specific heat of formation for species k at temperature T^0.

4. A conservation law. Eqs. (22) and (23) may be written as an equivalent first-order system. The result is

$$dY_k/d\psi = W_k, \qquad k = 1, \ldots, N-1, \tag{24}$$

$$dW_k/d\psi = m_0 Le_k W_k - \rho^{-1} Le_k M_k R_k, \qquad k = 1, \ldots, N-1, \tag{25}$$

$$dT/d\psi = S, \tag{26}$$

$$dS/d\psi = m_0 S + \rho^{-1} \sum_{k=1}^{N-1} R_k M_k (h_k^0 - h_N^0). \tag{27}$$

Eqs. (24)–(27), which constitute a differential system of order $2N$, may be reduced to a system of order $2N - 1$ as follows. Multiplying Eq. (25) by $(h_k^0 - h_N^0)Le_k^{-1}$, summing the resulting equations from $k = 1$ to $k = N - 1$, and adding the result to Eq. (27) gives

$$\frac{dS}{d\psi} + \sum_{k=1}^{N-1} \left[Le_k^{-1}(h_k^0 - h_N^0)\frac{dW_k}{d\psi} - m_0(h_k^0 - h_N^0)W_k\right] - m_0 S = 0. \tag{28}$$

Utilizing Eqs. (24) and (26) thus yields the conservation law

$$\frac{d}{d\psi}\left\{\frac{dT}{d\psi} + \sum_{k=1}^{N-1} \left[Le_k^{-1}(h_k^0 - h_N^0)\frac{dY_k}{d\psi} - m_0(h_k^0 - h_N^0)Y_k\right] - m_0 T\right\} = 0, \tag{29}$$

or

$$\frac{dT}{d\psi} + \sum_{k=1}^{N-1} \left[Le_k^{-1}(h_k^0 - h_N^0)\frac{dY_k}{d\psi} - m_0(h_k^0 - h_N^0)Y_k \right] - m_0 T = \text{const.} \tag{30}$$

Assuming chemical equilibrium in the burned region at $\psi = \infty$, one has that

$$R_k\Big|_{\psi=\infty} = S\Big|_{\psi=\infty} = W_k\Big|_{\psi=\infty} = 0, \qquad k = 1, \ldots, N-1. \tag{31}$$

This, of course, implies that

$$T\Big|_{\psi=\infty} = T_b, \qquad Y_k\Big|_{\psi=\infty} = Y_{k,b}, \qquad k = 1, \ldots, N-1, \tag{32}$$

but it is emphasized that T_b and the $Y_{k,b}$ are still unspecified at this point. Thus, using Eqs. (31) and (32), Eq. (30) may be evaluated at $\psi = \infty$ to give

$$\text{const} = -m_0 \sum_{k=1}^{N-1} (h_k^0 - h_N^0)Y_{k,b} - m_0 T_b. \tag{33}$$

Consequently, Eq. (30) becomes

$$\frac{dT}{d\psi} = -\sum_{k=1}^{N-1} \left[Le_k^{-1}(h_k^0 - h_N^0)\frac{dY_k}{d\psi} - m_0(h_k^0 - h_N^0)(Y_k - Y_{k,b}) \right] + m_0(T - T_b) \tag{34}$$

which now replaces Eqs. (26) and (27).

5. Linear asymptotic analysis. At $\psi = \infty$, the right-hand sides of Eqs. (24), (25), and (34) vanish and thus the burned state is a critical, or equilibrium, point of this differential system. Consequently, the asymptotic behavior of the solution as $\psi \to \infty$ may often be obtained by linearizing these equations about the burned state (cf. Hirschfelder et al. [2]). The procedure is straightforward and the result is

$$d\tilde{Y}_k/d\psi = W_k, \qquad k = 1, \ldots, N-1, \tag{35}$$

$$dW_k/d\psi = m_0 Le_k W_k - \rho_b^{-1} Le_k M_k$$
$$\cdot \left(R_{k,b} + \sum_{i=1}^{N-1} R_{k,b}^{(Y_i)}\tilde{Y}_i + R_{k,b}^{(T)}\tilde{T} + \text{h.o.t.} \right), \qquad k = 1, \ldots, N-1, \tag{36}$$

$$d\tilde{T}/d\psi = \sum_{k=1}^{N-1} \left[m_0(h_k^0 - h_N^0)\tilde{Y}_k - Le_k^{-1}(h_k^0 - h_N^0)\frac{d\tilde{Y}_k}{d\psi} \right] + m_0 \tilde{T}, \tag{37}$$

where ρ_b is the burned density,

$$\tilde{Y}_k \equiv Y_k - Y_{k,b}; \qquad \tilde{T} \equiv T - T_b, \tag{38a,b}$$

$$R_{k,b} \equiv R_k(Y_1 = Y_{1,b}, \ldots, Y_{N-1} = Y_{N-1,b}, T = T_b) = 0, \tag{39}$$

$$R_{k,b}^{(Y_i)} \equiv \frac{\partial R_k}{\partial Y_i}(Y_1 = Y_{1,b}, \ldots, Y_{N-1} = Y_{N-1,b}, T = T_b), \tag{40}$$

$$R_{k,b}^{(T)} \equiv \frac{\partial R_k}{\partial T}(Y_1 = Y_{1,b}, \ldots, Y_{N-1} = Y_{N-1,b}, T = T_b), \tag{41}$$

and "h.o.t." denotes "higher-order terms." The linearized system may now be written in the vector form

$$d\vec{Z}/d\psi = \mathbf{A}\vec{Z} + \text{h.o.t.}, \tag{42}$$

where

$$\vec{Z} = (\tilde{Y}_1, \ldots, \tilde{Y}_{N-1}, W_1, \ldots, W_{N-1}, \tilde{T})^t. \tag{43}$$

Introducing the definition

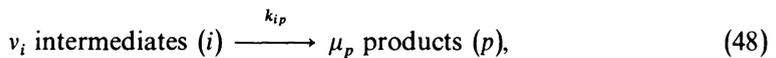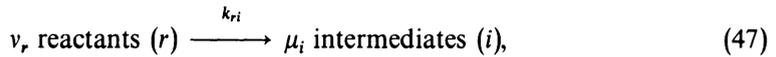$$\tilde{h}_k^0 \equiv h_k^0 - h_N^0, \qquad k = 1, \ldots, N-1, \tag{44}$$

the matrix $\mathbf{A}$ is

$$\mathbf{A} = \begin{bmatrix} 0 & 0\ldots\ldots 0 & 1 & 0 & \ldots\ldots & 0 & 0 \\ 0 & 0\ldots\ldots 0 & 0 & 1 & \ldots\ldots & 0 & 0 \\ \vdots & \vdots \quad \vdots & \vdots & \vdots & & \vdots & \vdots \\ 0 & 0\ldots\ldots 0 & 0 & 0 & \ldots\ldots & 1 & 0 \\ -\rho_b^{-1}Le_1 M_1 R_{1,b}^{(Y_1)} & \cdots -\rho_b^{-1}Le_1 M_1 R_{1,b}^{(Y_{N-1})} & m_0 Le_1 & 0 & \ldots\ldots & 0 & -\rho_b^{-1}Le_1 M_1 R_{1,b}^{(T)} \\ -\rho_b^{-1}Le_2 M_2 R_{2,b}^{(Y_1)} & \cdots -\rho_b^{-1}Le_2 M_2 R_{2,b}^{(Y_N)} & 0 & m_0 Le_2 & \ldots\ldots & 0 & -\rho_b^{-1}Le_2 M_2 R_{2,b}^{(T)} \\ \vdots & \vdots \quad \vdots & \vdots & \vdots & & \vdots & \vdots \\ -\rho_b^{-1}Le_{N-1} M_{N-1} R_{N-1,b}^{(Y_1)} & \cdots -\rho_b^{-1}Le_{N-1} M_{N-1} R_{N-1,b}^{(Y_{N-1})} & 0 & 0 & \ldots\ldots & m_0 Le_{N-1} & -\rho_b^{-1}Le_{N-1} M_{N-1} R_{N-1,b}^{(T)} \\ m_0 \tilde{h}_1^0 & \ldots\ldots m_0 \tilde{h}_{N-1}^0 & -\tilde{h}_1^0 Le_1^{-1} & \cdots & \ldots\ldots & \tilde{h}_{N-1}^0 Le_{N-1}^{-1} & m_0 \end{bmatrix}$$

$$\tag{45}$$

Dropping the higher-order terms, the solution to Eq. (42) is, formally,

$$\vec{Z} = \exp(\mathbf{A}\psi)\vec{C}, \tag{46}$$

where $\vec{C}$ is an arbitrary constant vector. However, the practical evaluation of the matrix $\exp(\mathbf{A}\psi)$ requires a knowledge of the eigenvalues and corresponding generalized eigenvectors of $\mathbf{A}$ and thus it is necessary to be more specific about $\mathbf{A}$ in order to obtain tractable results.

The analysis will now be specialized to deal with a specific problem, namely the general two-step chemical reaction

$$v_r \text{ reactants } (r) \xrightarrow{\;k_{ri}\;} \mu_i \text{ intermediates } (i), \tag{47}$$

$$v_i \text{ intermediates } (i) \xrightarrow{\;k_{ip}\;} \mu_p \text{ products } (p), \tag{48}$$

where v_r, μ_i, v_i, and μ_p are stoichiometric coefficients and k_{ri}, k_{ip} are the rate constants. The subscripts r, i, and p refer to the species (reactants, intermediates, products) and the double subscripts ri and ip refer to the reaction steps (reactants → intermediates, intermediates → products). This problem is a generalization of both the classical unimolecular decomposition flame and the $A \to B \to C$ adiabatic flame of Berman and Riazantsev [15], since it permits an analytical investigation of the effects of the reaction orders (i.e., the values of v_r and v_i) on the asymptotic structure of the flame. The two-step decomposition flame is also the simplest flame problem which possesses multiple time scales (due to the two reactions occurring at disparate rates). Consequently, the corresponding flame equations are "stiff" (see Sec. 8) and thus this problem is also of computational interest.

From a physical point of view, the mechanism (47) and (48) is only rigorously valid when r, i, and p each refer to a single species. However, such a model is also useful for gaining insight into the types of solutions which arise in more complicated flames. In such a context, simplistic reaction schemes such as (47) and (48) may be interpreted as global reactions, in which case the stoichiometric coefficients need not be integers [1] and the molecular weights M_r, M_i, M_p are characteristic values for the groups of species which essentially behave as reactants, intermediates, and products, respectively. For example, the decomposition of acetaldehyde (CH_3CHO) into the products CH_4 and CO takes place via at least several simple reactions,

$$CH_3CHO \rightarrow CH_3 + CHO, \quad CH_3 + CH_3CHO \rightarrow CH_4 + CH_3CO,$$

$$CH_3CO \rightarrow CO + CH_3, \text{ etc.,}$$
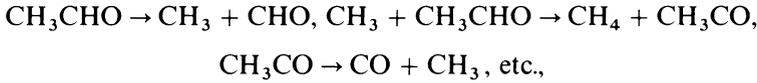
and the overall reaction order of the decomposition is usually taken to be 3/2. For hydrocarbons burning in oxygen, Kanury [16] notes that the overall order of the single step global reaction generally lies between 1.7 and 2.2. The more general two-step mechanism (47) and (48) allows for the specification of two overall reaction orders v_r and v_i.

Due to the fact that both steps are irreversible, it must be true that

$$Y_{r,b} = Y_{i,b} = 0; \qquad Y_{p,b} = 1, \tag{49a}$$

since otherwise all the reaction rates would not be zero at $\psi = \infty$ and hence equilibrium could not prevail there. (Note that the mixture of reacting species is implicitly restricted to be stoichiometric.) For general reversible reactions, the burned values of the mass fractions are problem-dependent and are thus not known *a priori*. In fact, integrating Eq. (22) from $\psi = 0$ to $\psi = \infty$ yields

$$Y_{k,b} = \varepsilon_k + \int_0^\infty \rho^{-1} R_k M_k \, d\psi. \tag{49b}$$

Assuming that an Arrhenius law governs each reaction step, the reaction rates R_r, R_i have the functional form

$$R_r = -v_r k_{ri} \rho^{v_r} M_r^{-v_r} Y_r^{v_r} g_{ri}(T), \tag{50}$$

$$R_i = -v_i k_{ip} \rho^{v_i} M_i^{-v_i} Y_i^{v_i} g_{ip}(T) + \mu_i k_{ri} \rho^{v_r} M_r^{-v_r} Y_r^{v_r} g_{ri}(T)$$

$$= -v_i k_{ip} \rho^{v_i} M_i^{-v_i} Y_i^{v_i} g_{ip}(T) - \frac{\mu_i}{v_r} R_r. \tag{51}$$

(From Eq. (15), $R_p = -M_p^{-1}(R_r M_r + R_i M_i)$). Note that since mass is conserved in Eqs. (47), (48),

$$v_r M_r = \mu_i M_i \quad \text{and} \quad v_i M_i = \mu_p M_p. \tag{52}$$

The precise functional form of $g_{ri}(T)$ and $g_{ip}(T)$ is unimportant for the asymptotic analysis of both this and the next sections, but they usually are taken to be

$$g_{ri}(T) = T^{s_{ri}} \exp(-E_{ri}/RT), \tag{53}$$

$$g_{ip}(T) = T^{s_{ip}} \exp(-E_{ip}/RT), \tag{54}$$

where E_{ri}, E_{ip} denote the activation energies of the two reaction steps and $T^{s_{ri}}$, $T^{s_{ip}}$ are pre-exponential factors (R is the gas constant).

In general, the stoichiometric coefficients v_r and v_i will be assumed greater than or equal to unity. However, as pointed out earlier, they need not be integers unless (47) and (48) each denote a simple reaction involving a single reactant species being converted to a single product species. Due to the appearance of the factors $Y_r^{v_r}$, $Y_i^{v_i}$ in the expressions for R_r and R_i above, it turns out that the asymptotic solution as $\psi \to \infty$ to Eqs. (35)–(37) is fundamentally different for each of the four cases (i) $v_r = v_i = 1$; (ii) $v_r > 1$, $v_i = 1$; (iii) $v_r = 1$, $v_i > 1$; and (iv) $v_r > 1$, $v_i > 1$. In particular, the linearized approach described above is only valid for the case $v_r = v_i = 1$. The other categories, which are of interest due to the fact that they correspond to higher-order reaction mechanisms as discussed above, require a nonlinear theory which is developed in the next section. Accordingly, the remainder of this section is concerned only with case (i).

(i) $v_r = v_i = 1$. For this case, one has that

$$R_{r,b}^{(T)} = R_{i,b}^{(T)} = R_{r,b}^{(Y_i)} = 0, \tag{55}$$

$$R_{r,b}^{(Y_r)} = -k_{ri}\rho_b M_r^{-1}g_{ri}(T_b), \tag{56}$$

$$R_{i,b}^{(Y_r)} = \mu_i k_{ri}\rho_b M_r^{-1}g_{ri}(T_b) = k_{ri}\rho_b M_i^{-1}g_{ri}(T_b), \tag{57}$$

$$R_{i,b}^{(Y_i)} = -k_{ip}\rho_b M_i^{-1}g_{ip}(T_b). \tag{58}$$

Introducing the definitions

$$\gamma_{r,b} \equiv k_{ri}g_{ri}(T_b) > 0, \tag{59}$$

$$\gamma_{i,b} \equiv k_{ip}g_{ip}(T_b) > 0, \tag{60}$$

the matrix $\mathbf{A}$ for this problem is

$$\mathbf{A} = \begin{bmatrix} 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ Le_r\gamma_{r,b} & 0 & m_0 Le_r & 0 & 0 \\ -Le_i\gamma_{r,b} & Le_i\gamma_{i,b} & 0 & m_0 Le_i & 0 \\ m_0\tilde{h}_r^0 & m_0\tilde{h}_i^0 & -\tilde{h}_r^0 Le_r^{-1} & -\tilde{h}_i^0 Le_i^{-1} & m_0 \end{bmatrix}. \tag{61}$$

The characteristic equation for $\mathbf{A}$ is

$$(m_0 - \Lambda)(\Lambda^2 - m_0 Le_r\Lambda - \gamma_{r,b} Le_r)(\Lambda^2 - m_0 Le_i\Lambda - \gamma_{i,b} Le_i) = 0 \tag{62}$$

and thus the eigenvalues of $\mathbf{A}$ are

$$\Lambda_1 = m_0, \tag{63}$$

$$\Lambda_{2,3} = \tfrac{1}{2}m_0 Le_r \pm [(\tfrac{1}{2}m_0 Le_r)^2 + \gamma_{r,b} Le_r]^{1/2}, \tag{64}$$

$$\Lambda_{4,5} = \tfrac{1}{2}m_0 Le_i \pm [(\tfrac{1}{2}m_0 Le_i)^2 + \gamma_{i,b} Le_i]^{1/2}. \tag{65}$$

The corresponding eigenvectors, assuming a complete set of eigenvectors (which is the case unless both $Le_r = Le_i$ and $\gamma_{r,b} = \gamma_{i,b}$), are

$$\hat{e}_1 = [0, 0, 0, 0, 1]^t, \tag{66}$$

$$\hat{e}_{2,3} = [1, -d_{2,3}^{-1}Le_i\gamma_{r,b}, \Lambda_{2,3}, -d_{2,3}^{-1}Le_i\gamma_{r,b}\Lambda_{2,3}, (\Lambda_3 - m_0)^{-1}$$
$$\times \{\tilde{h}_r^0(m_0 - Le_r^{-1}\Lambda_{2,3}) - \tilde{h}_i^0\gamma_{r,b}d_{2,3}^{-1}(Le_i m_0 - \Lambda_{2,3})\}]^t, \tag{67}$$

$$\hat{e}_{4,5} = [0, 1, 0, \Lambda_{4,5}, \tilde{h}_i^0(\Lambda_{4,5} - m_0)^{-1}(m_0 - Le_i^{-1}\Lambda_{4,5})]^t, \tag{68}$$

where

$$d_{2,3} = (Le_r - Le_i)m_0 \Lambda_{2,3} + (\gamma_{r,b} Le_r - \gamma_{i,b} Le_i). \tag{69}$$

Hence, the general asymptotic solution as $\psi \to \infty$ is

$$\begin{bmatrix} Y_r \\ Y_i \\ T \end{bmatrix} \sim \begin{bmatrix} 0 \\ 0 \\ T_b \end{bmatrix} + \sum_{i=1}^{5} C_i \begin{bmatrix} e_{i1} \\ e_{i2} \\ e_{i5} \end{bmatrix} \exp(\Lambda_i \psi), \tag{70}$$

where e_{ij} is the jth component of the ith eigenvector $\hat{e}_i$. Since the three eigenvalues Λ_1, Λ_2, and Λ_4 are strictly positive (and the remaining two eigenvalues Λ_3 and Λ_5 are strictly negative), the structure of the equilibrium, or critical, point in (Y_r, Y_i, W_r, W_i, T) phase space is that of a saddle point of type 3 (cf. Hale [11]). Furthermore, the saddle-point structure is preserved under small perturbations (i.e., the truncated nonlinear terms) of the linearized system (42), and thus it must be required that $C_1 = C_2 = C_4 = 0$ in order to have a bounded solution at $\psi = \infty$. Hence, the only physical asymptotic solution is

$$\begin{bmatrix} Y_r \\ Y_i \\ T \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ T_b \end{bmatrix} + C_3 \begin{bmatrix} e_{31} \\ e_{32} \\ e_{35} \end{bmatrix} \exp(\Lambda_3 \psi) + C_5 \begin{bmatrix} e_{51} \\ e_{52} \\ e_{55} \end{bmatrix} \exp(\Lambda_5 \psi). \tag{71}$$

There are thus three free parameters T_b, C_3, and C_5 which are in principle determined by the three boundary conditions (16) and (17), where $k = r, i$. Thus, although the original ordinary system was of order 6, the arbitrary specification of any more than three conditions at $\psi = 0$ is an overspecification of the semi-infinite problem.

The special case $Le_r = Le_i$, $\gamma_{r,b} = \gamma_{i,b}$, which implies that $\Lambda_2 = \Lambda_4$, $\Lambda_3 = \Lambda_5$, requires the construction of generalized eigenvectors corresponding to each of the double eigenvalues Λ_2, Λ_3. Now the asymptotic solution corresponding to (70) is

$$[Y_r, Y_i, W_r, W_i, \tilde{T}]^t \sim \sum_{i=1}^{3} C_i \hat{e}_i \exp(\Lambda_i \psi) + \sum_{i=2}^{3} C_{i+2}[\hat{g}_i + (\mathbf{A} - \Lambda_i \mathbf{I})\hat{g}_i \psi] \exp(\Lambda_i \psi) \tag{72}$$

where $\hat{e}_1, \hat{e}_2, \hat{e}_3$ are the ordinary eigenvectors corresponding to $\Lambda_1, \Lambda_2, \Lambda_3$ and $\hat{g}_2, \hat{g}_3$ are the generalized eigenvectors of rank 2 corresponding to the eigenvalues Λ_2, Λ_3. As before, three of the five eigensolutions are unphysical and thus the equilibrium point is still a saddle point of type 3. Hence, the above remarks concerning the boundary conditions at $\psi = 0$ apply to this special case also.

6. Nonlinear asymptotic analysis. For the cases where $v_r > 1$ and/or $v_i > 1$ the linearized theory is not applicable. First of all, the rate functions R_r, R_i are not even analytic (unless v_r, v_i are integers) at the equilibrium point. Consequently, the Taylor expansions in Eq. (36) which lead to the linearized system (42) are not valid. For the special cases where v_r and/or v_i are integers greater than unity, dropping the nonlinear terms is equivalent to replacing $\gamma_{r,b}$ and/or $\gamma_{i,b}$ with zeros. As a result, the "good" eigenvalues Λ_3 and/or Λ_5 become zero (see Eqs. (64), (65)), which from Eq. (71) simply says that the asymptotic solutions are $Y_r \sim 0$ and/or $Y_i \sim 0$ (there always exists a complete set of ordinary eigenvectors for these cases, so the linearized solution is described by Eq. (71)). Consequently, no nontrivial information is obtained on the asymptotic

behavior and the structure of the equilibrium point under nonlinear perturbations is unknown.

For the purposes of this section, it will be convenient to analyze the second order equations for Y_r, Y_i directly. Consequently, from Eqs. (22), (34), (50), and (51), the governing system is

$$m_0 \frac{dY_r}{d\psi} = Le_r^{-1} \frac{d^2 Y_r}{d\psi^2} - v_r k_{ri} \rho^{v_r - 1} M_r^{-(v_r - 1)} Y_r^{v_r} g_{ri}(T), \tag{73}$$

$$m_0 \frac{dY_i}{d\psi} = Le_i^{-1} \frac{d^2 Y_i}{d\psi^2} - v_i k_{ip} \rho^{v_i - 1} M_i^{-(v_i - 1)} Y_i^{v_i} g_{ip}(T)$$

$$+ \mu_i k_{ri} \rho^{v_r - 1} M_r^{-v_r} M_i Y_r^{v_r} g_{ri}(T), \tag{74}$$

$$\frac{d\tilde{T}}{d\psi} = -Le_r^{-1} \tilde{h}_r^0 \frac{dY_r}{d\psi} - Le_i^{-1} \tilde{h}_i^0 \frac{dY_i}{d\psi} + m_0 \tilde{h}_r^0 Y_r + m_0 \tilde{h}_i^0 Y_i + m_0 \tilde{T}. \tag{75}$$

To obtain the asymptotic solution as $\psi \to \infty$, the analytical factors in the rate expressions may be expanded about the burned state. Thus,

$$\rho^{v_r - 1} g_{ri}(T) = \rho_b^{v_r - 1} g_{ri}(T_b) + O(Y_r, Y_i, \tilde{T}), \tag{76}$$

$$\rho^{v_i - 1} g_{ip}(T) = \rho_p^{v_i - 1} g_{ip}(T_b) + O(Y_r, Y_i, \tilde{T}). \tag{77}$$

Then, using the fact that $\mu_i M_i = v_r M_r$ (Eq. (52)) and defining

$$\gamma_{r, b} \equiv v_r \rho_b^{v_r - 1} M_r^{-(v_r - 1)} k_{ri} g_{ri}(T_b), \tag{78}$$

$$\gamma_{i, b} \equiv v_i \rho_b^{v_i - 1} M_i^{-(v_i - 1)} k_{ip} g_{ip}(T_b) \tag{79}$$

(these reduce to the previous definitions when $v_r = v_i = 1$), Eqs. (73) and (74) become, to lowest order,

$$m_0 \frac{dY_r}{d\psi} = Le_r^{-1} \frac{d^2 Y_r}{d\psi^2} - \gamma_{r, b} Y_r^{v_r}, \tag{80}$$

$$m_0 \frac{dY_i}{d\psi} = Le_i^{-1} \frac{d^2 Y_i}{d\psi^2} - \gamma_{i, b} Y_i^{v_i} + \gamma_{r, b} Y_r^{v_r}. \tag{81}$$

Eq. (75) is unchanged, and thus Eqs. (80), (81), and (75) may be solved successively to obtain the leading asymptotic behavior for the three remaining cases.

(ii) $v_r > 1$, $v_i = 1$. Considering Eq. (80) first and motivated in part by the algebraic approach to equilibrium for nonunity reaction orders obtained in various other physical contexts [5, 17, 18], an asymptotic solution for Y_r is sought in the form

$$Y_r \sim \alpha \psi^{-\beta}[1 + f(\psi)], \tag{82}$$

where $f(\psi) \to 0$ as $\psi \to \infty$ and $\beta > 0$. Substituting Eq. (82) into Eq. (80), the nonlinear term becomes

$$-\gamma_{r, b} Y_r^{v_r} = -\gamma_{r, b} \alpha^{v_r} \psi^{-\beta v_r}[1 + f(\psi)]^{v_r}$$

$$\approx -\gamma_{r, b} \alpha^{v_r} \psi^{-\beta v_r}[1 + v_r f + O(f^2)], \tag{83}$$

and the linear terms behave as

$$m_0 \frac{dY_r}{d\psi} - Le_r^{-1} \frac{d^2 Y_r}{d\psi^2} = -m_0 \alpha \beta \psi^{-\beta-1} + o(\psi^{-\beta-1}) \tag{84}$$

Hence, equating the largest terms gives

$$-\beta - 1 = -\beta v_r \Rightarrow \beta = \frac{1}{v_r - 1}, \tag{85}$$

$$-\gamma_{r,b} \alpha^{v_r} = -m_0 \alpha \beta \Rightarrow \alpha = (m_0 \beta / \gamma_{r,b})^{1/(v_r - 1)}. \tag{86}$$

The remaining terms yield, after multiplying through by the factor $Le_r \psi^\beta$, an equation for f:

$$\frac{d^2 f}{d\psi^2} - \left(m_0 Le_r + \frac{2\beta}{\psi} \right) \frac{df}{d\psi} + \left[-\frac{m_0 Le_r}{\psi} + \frac{\beta(\beta+1)}{\psi^2} \right] f = \frac{-\beta(\beta+1)}{\psi^2}, \tag{87}$$

where the nonlinear $O(f^2)$ terms have been neglected in Eq. (83). Note that $\psi = \infty$ is an irregular singular point of Eq. (87).

The homogeneous solution f_h of Eq. (87) may be obtained as follows. Introducing

$$p(\psi) = -m_0 Le_r - (2\beta/\psi), \tag{88}$$

the transformation

$$f_h = \exp\left(-\frac{1}{2} \int^\psi p(\bar\psi) \, d\bar\psi \right) v$$

$$= \exp(\tfrac{1}{2} m_0 Le_r \psi) \psi^\beta v \tag{89}$$

results in the homogeneous equation

$$\frac{d^2 v}{d\psi^2} + \left[-\frac{1}{4} m_0^2 Le_r^2 - \frac{(\beta+1)m_0 Le_r}{\psi} \right] v = 0. \tag{90}$$

This is in a standard form [19] and has the formal asymptotic solution

$$v \sim \exp[S(\psi)], \tag{91}$$

where

$$S(\psi) = S_0 \psi + S_1 \ln \psi + S_2 \psi^{-1} + S_3 \psi^{-2} + \cdots. \tag{92}$$

Substituting Eq. (91) into Eq. (90) and equating like-order terms yields

$$S_0 = \pm \tfrac{1}{2} m_0 Le_r, \tag{93}$$

$$S_1 = \pm (\beta + 1), \tag{94}$$

$$S_2 = \mp \frac{1}{m_0 Le_r} \left| \frac{(\beta+2)(\beta+1)}{\beta(\beta+1)} \right|, \tag{95}$$

$$\vdots$$

Hence the two homogeneous solutions to Eq. (87) are

$$f_h^{(1)} \sim \exp(m_0 Le_r \psi)\psi^{2\beta+1}\left[1 - \frac{(\beta+1)(\beta+2)}{m_0 Le_r}\psi^{-1} + \cdots\right], \tag{96}$$

$$f_h^{(2)} \sim \psi^{-1}\left[1 + \frac{\beta(\beta+1)}{m_0 Le_r}\psi^{-1} + \cdots\right]. \tag{97}$$

The first solution increases without bound and thus must be discarded in order to be consistent with the assumptions on $f(\psi)$. Also, one should only retain the first term of Eq. (97) since f^2 was assumed negligible relative to f in deriving Eq. (87). Hence,

$$f_h \sim C_r \psi^{-1}, \tag{98}$$

where C_r is an arbitrary constant.

A particular solution f_p of Eq. (87) may be obtained in the form

$$f_p \sim a_1 \psi^{-1} \ln \psi + a_2 \psi^{-2} \ln \psi + \cdots + b_1 \psi^{-1} + b_2 \psi^{-2} + \cdots. \tag{99}$$

Substituting this form into Eq. (87) and equating like-order terms gives

$$a_1 = -\beta(\beta+1), \qquad a_2 = \frac{\beta(\beta+1)^2(\beta+2)}{m_0 Le_r}, \ldots \tag{100}$$

$$b_1 = 0, \qquad b_2 = \frac{\beta(\beta+1)(\beta^2+\beta-1)}{m_0 Le_r}, \ldots \tag{101}$$

and thus to $O(f^2)$,

$$f_p \sim -\beta(\beta+1)\psi^{-1} \ln \psi. \tag{102}$$

(Actually the value of b_1 was arbitrary since the homogeneous solution (98) is $O(\psi^{-1})$). Hence, from Eqs. (82), (85), (86), (98), and (102), the asymptotic solution to Eq. (80) as $\psi \to \infty$ is

$$Y_r \sim \left[\frac{m_0}{\gamma_{r,b}(v_r-1)}\right]^{1/(v_r-1)}\psi^{-1/(v_r-1)}\left[1 - \frac{v_r}{(v_r-1)^2}\psi^{-1}\ln\psi + C_r\psi^{-1} + \cdots\right], \tag{103}$$

Substituting Eq. (103) into Eq. (81) gives the equation for Y_i for this case:

$$Le_i^{-1}\frac{d^2 Y_i}{d\psi^2} - m_0 \frac{dY_i}{d\psi} - \gamma_{i,b}Y_i$$

$$= -\gamma_{r,b}\left[\frac{m_0}{\gamma_{r,b}(v_r-1)}\right]^{v_r/(v_r-1)}\psi^{-v_r/(v_r-1)}\left[1 - \frac{v_r}{(v_r-1)^2}\psi^{-1}\ln\psi + C_r\psi^{-1}\cdots\right]^{v_r}$$

$$\approx -\gamma_{r,b}^{-\beta}(m_0\beta)^{\beta+1}\psi^{-\beta-1}[1 - (\beta+1)^2\psi^{-1}\ln\psi + v_r C_r\psi^{-1} + \cdots], \tag{104}$$

where the relation $v_r/v_r - 1 = \beta v_r = \beta + 1$ has been used to simplify some of the terms. The homogeneous equation is linear and its solutions are

$$Y_{i_h}^{(1)} \propto \exp(\Lambda_4 \psi), \tag{105}$$

$$Y_{i_h}^{(2)} \propto \exp(\Lambda_5 \psi), \tag{106}$$

where $\Lambda_4 > 0$ and $\Lambda_5 < 0$ were defined in Eq. (65). Clearly the first solution must be discarded and hence the homogeneous solution is

$$Y_{i_h} \sim C_i \exp(\Lambda_5 \psi). \tag{107}$$

The particular solution Y_{i_p} to Eq. (104) may be obtained in the form

$$Y_{i_p} \sim \delta \psi^{-\varepsilon}[1 + g(\psi)], \tag{108}$$

where $\delta > 0$ and $g(\psi) \to 0$ as $\psi \to \infty$. Substituting Eq. (108) into Eq. (104) and matching largest terms gives

$$\varepsilon = \beta + 1 = \frac{v_r}{v_r - 1}, \tag{109}$$

$$\delta = \frac{\gamma_{r,b}^{-\beta}}{\gamma_{i,b}} (m_0 \beta)^{\beta + 1}, \tag{110}$$

and the equation for $g(\psi)$:

$$\frac{d^2 g}{d\psi^2} - \left(m_0 Le_i - \frac{2\varepsilon}{\psi}\right)\frac{dg}{d\psi} + \left[-\gamma_{i,b} Le_i + \frac{\varepsilon m_0 Le_i}{\psi} + \frac{\varepsilon(\varepsilon + 1)}{\psi^2}\right] g$$

$$= -\frac{m_0 Le_i}{\psi} - \frac{\varepsilon(\varepsilon + 1)}{\psi^2} - \gamma_{r,b}^{-\beta}(m_0 \beta)^{\beta + 1} v_r C_r \psi^{-1}$$

$$+ \gamma_{r,b}^{-\beta}(m_0 \beta)^{\beta + 1}(\beta + 1)^2 \psi^{-1} \ln \psi + \cdots. \tag{111}$$

The homogeneous solution to Eq. (111) is readily obtained in the same manner as that employed to solve Eq. (87). In this case, however, the series (92) terminates, and results in the solutions (105), (106). The particular solution g_p is obtained in the form (99), where now

$$a_1 = (\beta + 1)^2, \qquad a_2 = \frac{\varepsilon m_0}{\gamma_{i,b}}(\beta + 1)^2, \ldots, \tag{112}$$

$$b_1 = \frac{m_0}{\gamma_{i,b}} + v_r C_r, \ldots. \tag{113}$$

Thus,

$$Y_{i_p} \sim \frac{\gamma_{r,b}^{-\beta}}{\gamma_{i,b}} (m_0 \beta)^{\beta + 1} \psi^{-\beta - 1}\left[1 + (\beta + 1)^2 \psi^{-1} \ln \psi + \left(\frac{m_0}{\gamma_{i,b}} + v_r C_r\right)\psi^{-1} + \cdots\right] \tag{114}$$

and hence,

$$Y_i \sim C_i \exp(\Lambda_5 \psi) + \frac{\gamma_{r,b}}{\gamma_{i,b}}\left[\frac{m_0}{\gamma_{r,b}(v_r - 1)}\right]^{v_r/(v_r - 1)} \psi^{-v_r/(v_r - 1)}$$

$$\times \left[1 + (\beta + 1)^2 \psi^{-1} \ln \psi + \left(\frac{m_0}{\gamma_{i,b}} + v_r C_r\right)\psi^{-1} + \cdots\right] \tag{115}$$

Note that the asymptotic decay of Y_i is clearly dominated by Y_{i_p}, which simply indicates that for this case the asymptotic behavior of Y_i is controlled by Y_r. Physically, the species (i), once present, disappears exponentially as $\psi \to \infty$ through the reaction (48), but its

rate of production due to the decay of species (r) through reaction (47) only dies off algebraically.

Turning attention to Eq. (75), the homogeneous solution is the same as that obtained for the linear theory of Sec. 5, namely

$$\tilde{T}_h \propto \exp(\Lambda_1 \psi) = \exp(m_0 \psi) \tag{116}$$

As before, this solution must be discarded since $\Lambda_1 > 0$. The particular solution to Eq. (75), after substituting in Eqs. (103) and (115), is obtained in the form

$$\tilde{T} \sim \psi^{-\beta}[a_0 + a_1 \psi^{-1} \ln \psi + a_2 \psi^{-1} + \cdots], \tag{117}$$

where

$$a_0 = -\tilde{h}_r^0 (m_0 \beta / \gamma_{r,b})^\beta, \tag{118}$$

$$a_1 = \beta(\beta + 1)\tilde{h}_r^0 (m_0 \beta / \gamma_{r,b})^\beta, \tag{119}$$

$$a_2 = \tilde{h}_i^0 (\gamma_{r,b}/\gamma_{i,b})(m_0 \beta / \gamma_{r,b})^{\beta+1} + \tilde{h}_r^0 (m_0 \beta / \gamma_{r,b})^\beta \left[-C_r + \frac{\beta}{m_0}(1 - Le_r^{-1}) \right], \tag{120}$$

and thus

$$T - T_b \sim - \left[\frac{m_0}{\gamma_{r,b}(\nu_r - 1)} \right]^{1/(\nu_r - 1)} \tilde{h}_r^0 \psi^{-1/(\nu_r - 1)} \left[1 - \frac{\nu_r}{(\nu_r - 1)^2} \tilde{h}_r^0 \psi^{-1} \right.$$
$$\left. - \left\{ \frac{m_0}{\gamma_{i,b}(\nu_r - 1)} \frac{\tilde{h}_i^0}{\tilde{h}_r^0} - C_r + \frac{1 - Le_r^{-1}}{m_0(\nu_r - 1)} \right\} \psi^{-1} \ln \psi + \cdots \right]. \tag{121}$$

As one would expect, the asymptotic decay of $\tilde{T} = T - T_b$ is dominated by Y_r through (47), unless $\tilde{h}_r = 0$.

In summary, therefore, the asymptotic solution for the case $\nu_r > 1$, $\nu_i = 1$ is given to lowest order by

$$Y_r \sim \left[\frac{m_0}{\gamma_{r,b}(\nu_r - 1)} \right]^{1/(\nu_r - 1)} \psi^{-1/(\nu_r - 1)}, \tag{122}$$

$$Y_i \sim \frac{\gamma_{r,b}}{\gamma_{i,b}} \left[\frac{m_0}{\gamma_{r,b}(\nu_r - 1)} \right]^{\nu_r/(\nu_r - 1)} \psi^{-\nu_r/(\nu_r - 1)}, \tag{123}$$

$$T - T_b \sim \left[\frac{m_0}{\gamma_{r,b}(\nu_r - 1)} \right]^{\nu_r/(\nu_r - 1)} \tilde{h}_r^0 \psi^{-1/(\nu_r - 1)}, \tag{124}$$

From the discussion of this section, it is clear that the presence of only three unspecified parameters C_r, C_i, and T_b permit the same conclusions as to the proper specification of the boundary conditions as was obtained for the linearized theory in Sec. 5. As before, the other three solutions were discarded on physical grounds. (Technically speaking, it has only been shown that there exists only one solution for Y_r of the form (82) that approaches zero as $\psi \to \infty$. However, for $Y_r \ll O(1)$, the nonlinear term in Eq. (80) may be neglected as in the linear theory to obtain the exponentially growing solution.) Although C_r and C_i do not appear explicitly in the lowest order terms, the boundary conditions (16), (17) all enter into the determination of T_b, which in turn determines $\gamma_{r,b}$ and $\gamma_{i,b}$, which do appear in Eqs. (122)–(124). Finally, it is seen that all variables now

decay algebraically (rather than exponentially). In the limit $v_r \to 1^+$, they decay faster than any algebraic power of ψ^{-1}, which is consistent with the exponential decay obtained for the case $v_r = v_i = 1$.

(iii) $v_r = 1$, $v_i > 1$. For this case, Eq. (80) for Y_r is linear and its solutions are

$$Y_r^{(1)} \propto \exp(\Lambda_2 \psi), \tag{125}$$

$$Y_r^{(2)} \propto \exp(\Lambda_3 \psi), \tag{126}$$

where $\Lambda_2 > 0$ and $\Lambda_3 < 0$ are defined by Eq. (64). Discarding (125) on physical grounds, the asymptotic solution is

$$Y_r \sim C_r \exp(\Lambda_3 \psi). \tag{127}$$

The asymptotic solution to Eq. (81) may be obtained as before by postulating an algebraically decaying solution of the form (82). Since the inhomogeneous term $\gamma_{r,b} Y_r^{v_r}$ decays exponentially and thus does not appear in the asymptotic development, the resulting solution procedure is identical to that used to solve Eq. (80) for the case (ii) in which v_r was greater than unity. Consequently, the solution to Eq. (81) is Eq. (103) with the subscript "i" substituted for "r":

$$Y_i \sim \left[\frac{m_0}{\gamma_{i,b}(v_i - 1)} \right]^{1/(v_i - 1)} \psi^{-1/(v_i - 1)} \left[1 - \frac{v_i}{(v_i - 1)^2} \psi^{-1} \ln \psi + C_i \psi^{-1} + \cdots \right]. \tag{128}$$

Finally, the asymptotic solution to Eq. (75) is

$$T - T_b \sim -\left[\frac{m_0}{\gamma_{i,b}(v_i - 1)} \right]^{1/(v_i - 1)} \psi^{-1/(v_i - 1)} [1 + a_1 \psi^{-1} \ln \psi + a_2 \psi^{-1} + \cdots] \tag{129}$$

where

$$a_1 = -\tilde{h}_i^0 \frac{v_i}{(v_i - 1)^2}, \qquad a_2 = \frac{Le_i^{-1} \tilde{h}_i^0 - 1}{m_0(v_i - 1)} + \tilde{h}_i^0 C_i. \tag{130}$$

Since Y_r decays exponentially, the asymptotic decay of $T - T_b$ is completely determined by the algebraic decay of Y_i.

(iv) $v_r > 1$, $v_i > 1$. For this last case, Eq. (80) is the same as in Case (ii) and thus its asymptotic solution is Eq. (103):

$$Y_r \sim \left[\frac{m_0}{\gamma_{r,b}(v_r - 1)} \right]^{1/(v_r - 1)} \psi^{-1/(v_r - 1)} \left[1 - \frac{v_r}{(v_r - 1)^2} \psi^{-1} \ln \psi + C_r \psi^{-1} + \cdots \right]. \tag{131}$$

To solve Eq. (81), the approximation

$$Y_r^{v_r} \approx \left[\frac{m_0}{\gamma_{r,b}(v_r - 1)} \right]^{v_r/(v_r - 1)} \psi^{-v_r/(v_r - 1)} \left[1 - \frac{v_r^2}{(v_r - 1)^2} \psi^{-1} \ln \psi + v_r C_r \psi^{-1} + \cdots \right] \tag{132}$$

is used and a solution for Y_i is sought in the form (108):

$$Y_i \sim \delta \psi^{-\varepsilon} [1 + g(\psi)], \tag{133}$$

where $g(\psi) \to 0$ as $\psi \to \infty$. Thus,

$$Y_i^{v_i} \approx \delta^{v_i} \psi^{-\varepsilon v_i} [1 + v_i g(\psi) + \cdots]. \tag{134}$$

Substituting Eqs. (132)–(134) into Eq. (81) and matching the largest algebraic terms gives

$$\varepsilon = \frac{v_r/v_i}{v_r - 1}, \qquad v_i \le v_r, \tag{135}$$

$$\varepsilon = \frac{1}{v_i - 1}, \qquad v_i \ge v_r, \tag{136}$$

$$\delta = \frac{\gamma_{r,b}}{\gamma_{i,b}} \left[\frac{m_0}{\gamma_{r,b}(v_r - 1)} \right]^{(v_r/v_i)/(v_r - 1)}, \qquad v_i < v_r, \tag{137}$$

$$\delta = \left[\frac{m_0}{\gamma_{i,b}(v_i - 1)} \right]^{1/(v_i - 1)}, \qquad v_i > v_r, \tag{138}$$

$$\delta^v - \frac{m_0 \varepsilon}{\gamma_{i,b}} \delta = \frac{\gamma_{r,b}}{\gamma_{i,b}} \left[\frac{m_0}{\gamma_{r,b}(v - 1)} \right]^{v/(v - 1)}, \qquad v_i = v_r \equiv v. \tag{139}$$

The remaining terms yield the following equations for $g(\psi)$:

$$\frac{d^2g}{d\psi^2} - \left(m_0 Le_i + \frac{2\varepsilon}{\psi} \right) \frac{dg}{d\psi} + \left[\frac{\varepsilon m_0 Le_i}{\psi} + \frac{\varepsilon(\varepsilon + 1)}{\psi^2} - Le_i \gamma_{i,b} \delta^{v_i - 1} \psi^{-v_r(v_i - 1)/v_i(v_r - 1)} \right] g$$

$$= \frac{\varepsilon m_0 Le_i}{\psi} - \frac{\varepsilon(\varepsilon + 1)}{\psi^2} - Le_i \gamma_{i,b} \left[\frac{m_0}{\gamma_{r,b}(v_r - 1)} \right]^{v_r(1 - 1/v_i)/(v_r - 1)}$$

$$- Le_i \gamma_{i,b} \left[\frac{m_0}{\gamma_{r,b}(v_r - 1)} \right]^{v_r/v_r - 1(1 - (1/v_i))}$$

$$\times \left\{ \psi^{(-2v_r v_i + v_r + v_i)/v_i(v_r - 1)} \left[-\frac{v_r^2}{(v_r - 1)^2} \ln \psi + v_r C_r \right] \right\}, \qquad v_i < v_r, \tag{140}$$

$$\frac{d^2g}{d\psi^2} - \left(m_0 Le_i + \frac{2\varepsilon}{\psi} \right) \frac{dg}{d\psi} + \left[\frac{\varepsilon m_0 Le_i}{\psi} + \frac{\varepsilon(\varepsilon + 1)}{\psi^2} - Le_i \gamma_{i,b} \delta^{v_i - 1} \psi^{-1} \right] g$$

$$= -\frac{\varepsilon(\varepsilon + 1)}{\psi^2} - \frac{Le_i \gamma_{r,b}}{\delta} \left[\frac{m_0}{\gamma_{r,b}(v_r - 1)} \right]^{v_r/(v_r - 1)}$$

$$\times \left\{ \psi^{-v_r/(v_r - 1) + 1/(v_i - 1)} - \frac{v_r^2}{(v_r - 1)^2} \psi^{(1 - 2v_r)/(v_r - 1) + 1/(v_i - 1)} \ln \psi \right.$$

$$\left. + v_r C_r \psi^{(1 - 2v_r)/(v_r - 1) + 1/(v_i - 1)} \right\}, \qquad v_i > v_r, \tag{141}$$

$$\frac{d^2g}{d\psi^2} - \left(m_0 Le_i + \frac{2\varepsilon}{\psi} \right) \frac{dg}{d\psi} + \left[\frac{\varepsilon m_0 Le_i}{\psi} + \frac{\varepsilon(\varepsilon + 1)}{\psi^2} - Le_i \gamma_{i,b} \delta^{v - 1} \psi^{-1} \right] g$$

$$= -\frac{\varepsilon(\varepsilon + 1)}{\psi^2} - \frac{Le_i \gamma_{r,b}}{\delta} \left[\frac{m_0}{\gamma_{r,b}(v - 1)} \right]^{v/(v - 1)} \psi^{-2} \left[-\frac{v^2}{(v - 1)^2} \ln \psi + v C_r \right],$$

$$v_i = v_r \equiv v. \tag{142}$$

For simplicity, only Eq. (142) is considered further. The left-hand side of Eq. (142) has the same form as the homogeneous part of Eq. (87). Hence, discarding the growing

solution, one finds the homogeneous solution to Eq. (142) to be

$$g_h \sim \psi^{-(\gamma_{r,b}/m_0\delta)[m_0/\gamma_{r,b}(v-1)]^{v/(v-1)}}\left[1 - \frac{\gamma_{i,b}}{m_0^2 Le_i}\delta^{v-1}\left(1 - \frac{\gamma_{i,b}}{m_0}\delta^{v-1}\right)\psi^{-1} + \cdots\right] \quad (143)$$

where δ is obtained from (139), which has a single positive root which is greater than $[m_0/\gamma_{i,b}(v-1)]^{1/(v-1)}$. The particular solution of Eq. (142) is

$$g_p \sim -\frac{v^2}{(v-1)^2}\psi^{-1}\ln\psi + \psi^{-2}$$

$$\times \left\{vC_r + \left[\frac{m_0}{\gamma_{r,b}(v-1)}\right]^{-v/(v-1)}\frac{\delta v}{(v-1)^2\gamma_{r,b}}(m_0 v + Le_i^{-1}) + \cdots\right\}. \quad (144)$$

Thus, for $v_i = v_r \equiv v$,

$$Y_i \sim \delta\psi^{-1/(v-1)}[1 + g_h(\psi) + g_p(\psi) + \cdots]. \quad (145)$$

Finally, the asymptotic behavior of $T - T_b$ is found to be

$$T - T_b \sim -\tilde{h}_r\left[\frac{m_0}{\gamma_{r,b}(v_r-1)}\right]^{1/(v_r-1)}\psi^{-1/(v_r-1)}, \qquad v_i < v_r, \quad (146)$$

$$T - T_b \sim -\tilde{h}_i\delta\psi^{-1/(v_i-1)}, \qquad v_i > v_r, \quad (147)$$

$$T - T_b \sim -\left\{\tilde{h}_r\left[\frac{m_0}{\gamma_{r,b}(v-1)}\right]^{1/(v-1)} + \tilde{h}_i\delta\right\}\psi^{-1/(v-1)}, \qquad v_i = v_r \equiv v, \quad (148)$$

where δ is given by Eqs. (137)–(139).

In summary, the asymptotic analysis of this section has thus shown that as $\psi \to \infty$, the number of growing solutions (three) for the nonlinear cases (ii)–(iv) is the same as for the linear case (i). Consequently, as with the case in which $v_r = v_i = 1$, only three arbitrary boundary conditions may be applied at the burner and the three remaining degrees of freedom in the original sixth-order system (22), (23) must be used to filter out the asymptotically growing solutions. The major effect of the higher reaction orders is on the manner in which the solutions approach equilibrium as $\psi \to \infty$. In particular, the asymptotic behavior of Y_r, Y_i, and T is a v_r-, v_i-dependent algebraic decay for all cases in which v_r and v_i are not both equal to unity, except when $v_r = 1$ and $v_i > 1$, in which case Y_r still approaches equilibrium in an exponential fashion. As discussed in Sec. 5, all variables decay exponentially when $v_r = v_i = 1$.

7. Example. As an analytical example, the asymptotic results will be used to solve a complete flame problem governed by the two-step reaction (47), (48) with $v_r = v_i = 1$. Instead of the exponential dependence on temperature for $g_{ri}(T)$ and $g_{ip}(T)$ exhibited in Eqs. (53) and (54), the cruder approximations

$$g_{ri}(T) = G_{ri} = \text{const}, \qquad T > T_{ri},$$

$$g_{ri}(T) = 0, \qquad T < T_{ri}, \quad (149)$$

$$g_{ip}(T) = G_{ip} = \text{const}, \qquad T > T_{ip},$$

$$g_{ip}(T) = 0, \qquad T < T_{ip} \quad (150)$$

are used. For simplicity, it is assumed that the two "ignition" temperatures T_{ri} and T_{ip} are equal; that is,

$$T_{ri} = T_{ip} \equiv T_0. \tag{151}$$

From the analysis of the preceding sections one can expect to apply only three nontrivial boundary conditions at $\psi = 0$. These are taken to be (16) and (17), which in nondimensional form are

$$\left. T \right|_{\psi = 0} = T_u, \tag{152}$$

$$\left. Y_r - (m_0 Le_r)^{-1} \frac{dY_r}{d\psi} \right|_{\psi = 0} = \varepsilon_r \geq 0, \tag{153}$$

$$\left. Y_i - (m_0 Le_i)^{-1} \frac{dY_i}{d\psi} \right|_{\psi = 0} = \varepsilon_i \geq 0. \tag{154}$$

According to the previous results the three remaining boundary conditions *must* be taken as

$$\left. Y_r \right|_{\psi = \infty} = 0, \tag{155}$$

$$\left. Y_i \right|_{\psi = \infty} = 0, \tag{156}$$

$$\left. \frac{dT}{d\psi} \right|_{\psi = \infty} = 0 \tag{157}$$

in order to give physically meaningful solutions at $\psi = \infty$. (For the more general case of reversible reactions, one would replace Eqs. (155) and (156) with the less stringent requirements $dY_r/d\psi|_{\psi = \infty} = dY_i/d\psi|_{\psi = \infty} = 0$). As will be illustrated below, the imposition of any additional boundary information (e.g., a specified value for $T|_{\psi = \infty}$ in place of $dT/d\psi|_{\psi = \infty} = 0$) overspecifies the semi-infinite problem.

Due to Eqs. (149) and (150), this nonlinear problem naturally separates into two linear problems, one on $0 \leq \psi < \psi_0$, the other on $\psi_0 < \psi < \infty$, where ψ_0 is determined from the condition that $T(\psi_0) = T_0 > T_u$. Since the reaction rates are zero in $0 \leq \psi < \psi_0$, the governing equations in this region are

$$dY_r/d\psi = (m_0 Le_r)^{-1}(d^2 Y_r/d\psi^2), \tag{158}$$

$$dY_i/d\psi = (m_0 Le_i)^{-1}(d^2 Y_i/d\psi^2), \tag{159}$$

$$dT/d\psi = m_0^{-1}(d^2 T/d\psi^2). \tag{160}$$

Imposing the boundary conditions (152)–(154), their solution is

$$Y_r = \varepsilon_r + C_r \exp(m_0 Le_r \psi), \qquad 0 \leq \psi < \psi_0, \tag{161}$$

$$Y_i = \varepsilon_i + C_i \exp(m_0 Le_i \psi), \qquad 0 \leq \psi < \psi_0, \tag{162}$$

$$T = T_u + C_t[\exp(m_0 \psi) - 1], \qquad 0 \leq \psi < \psi_0, \tag{163}$$

where C_r, C_i, and C_t are constants of integration. Note that the flux fractions $Y_r - (m_0 Le_r)^{-1}(dY_r/d\psi)$, $Y_i - (m_0 Le_i)^{-1}(dY_i/d\psi)$ are conserved quantities in $0 \le \psi < \psi_0$, as can be seen from a single integration of Eqs. (158) and (159).

For $\psi > \psi_0$, the physically acceptable solution, which must satisfy Eqs. (155)–(157), is given by the asymptotic solution (71) (unless both $Le_r = Le_i$ and $\gamma_{r,b} = \gamma_{i,b}$, in which case (72) must be used). There are thus seven unknowns which must be determined: C_r, C_i, C_t, ψ_0, T_b, C_3, and C_5. There are, however, seven continuity restrictions which must be satisfied at ψ_0, namely

$$Y_r(\psi_0^-) = Y_r(\psi_0^+), \tag{164}$$

$$Y_i(\psi_0^-) = Y_i(\psi_0^+), \tag{165}$$

$$T(\psi_0^-) = T_0, \tag{166}$$

$$T(\psi_0^+) = T_0, \tag{167}$$

$$\left.\frac{dT}{d\psi}\right|_{\psi_0^-} = \left.\frac{dT}{d\psi}\right|_{\psi_0^+}, \tag{168}$$

$$Y_r - (m_0 Le_r)^{-1}\left.\frac{dY_r}{d\psi}\right|_{\psi_0^+} = Y_r - (m_0 Le_r)^{-1}\left.\frac{dY_r}{d\psi}\right|_{\psi_0^-} = \varepsilon_r, \tag{169}$$

$$Y_i - (m_0 Le_i)^{-1}\left.\frac{dY_i}{d\psi}\right|_{\psi_0^-} = Y_i - (m_0 Le_i)^{-1}\left.\frac{dY_i}{d\psi}\right|_{\psi_0^-} = \varepsilon_i. \tag{170}$$

These conditions are implied by the fact that the rate of chemical reaction at ψ_0^+ is finite. As a result, Eqs. (164)–(170) imply that

$$\psi_0 = \frac{-1}{m_0} \ln[1 - d^{-1}m_0(T_0 - T_u)], \tag{171}$$

$$C_3 = \frac{\varepsilon_r}{1 - \Lambda_3(m_0 Le_r)^{-1}} \exp(-\Lambda_3 \psi_0), \tag{172}$$

$$C_5 = \left(1 - \frac{\Lambda_5}{m_0 Le_i}\right)^{-1}\left[\varepsilon_i - \varepsilon_r e_{32}\frac{1 - (m_0 Le_i)^{-1}\Lambda_3}{1 - (m_0 Le_r)^{-1}\Lambda_3}\right]\exp(-\Lambda_5 \psi_0), \tag{173}$$

$$T_b = T_0 - C_3 e_{35} \exp(\Lambda_3 \psi_0) - C_5 e_{55} \exp(\Lambda_5 \psi_0), \tag{174}$$

$$C_r = \varepsilon_r\left(\frac{\Lambda_3}{m_0 Le_r - \Lambda_3}\right)\exp(-m_0 Le_r \psi_0), \tag{175}$$

$$C_i = (m_0 Le_i - \Lambda_5)^{-1}\left[\varepsilon_i\Lambda_5 - \varepsilon_r Le_r e_{32}\left(\frac{\Lambda_5 - \Lambda_3}{m_0 Le_r - \Lambda_3}\right)\right]\exp(-m_0 Le_i \psi_0), \tag{176}$$

$$C_t = \frac{T_0 - T_u}{\exp(m_0 \psi_0) - 1}, \tag{177}$$

where

$$d = \frac{\Lambda_3 e_{35} \varepsilon_r}{1 - \Lambda_3(m_0 Le_r)^{-1}} + \frac{\Lambda_5 e_{55}\{\varepsilon_i[1 - \Lambda_3(m_0 Le_r)^{-1}] - \varepsilon_r e_{32}[1 - \Lambda_3(m_0 Le_i)^{-1}]\}}{[1 - \Lambda_5(m_0 Le_i)^{-1}][1 - \Lambda_3(m_0 Le_r)^{-1}]} \tag{178}$$

and e_{32}, e_{35}, e_{55}, Λ_3, Λ_5 were defined in Sec. 3. Note that $\psi_0 \to \infty$ as $T_0 - T_u \to d/m_0$, indicating that there is a maximum ignition temperature T_0 which will yield a flame. Alternatively, $\psi_0 \to \infty$ as $m_0 \to d/(T_0 - T_u)$, which is of course the adiabatic limit for the mass flux m_0. (The adiabatic flame speed is thus $d/\rho_u(T_0 - T_u)$, where ρ_u is the density at $\psi = 0$).

As a numerical example, let $m_0 = 1.0$, $Le_r = 0.5$, $Le_i = 1.0$, $\gamma_{r,b} = 1$, $\gamma_{i,b} = 2$, $\tilde{h}_r^0 = 1$, $\tilde{h}_i^0 = 2$, $\varepsilon_r = 1.0$, $\varepsilon_i = 0$, $T_u = 1.0$, $T_0 = 1.1$. Then Eqs. (171), (174) give $\psi_0 = 1.386$ and the burned temperature $T_b = 59/30$. The complete solution is then

$$Y_r = 1 - \tfrac{1}{2} \exp[\tfrac{1}{2}(\psi - \psi_0)], \qquad 0 \le \psi < \psi_0, \tag{179}$$

$$Y_r = \tfrac{1}{2} \exp[-\tfrac{1}{2}(\psi - \psi_0)], \qquad \psi > \psi_0, \tag{180}$$

$$Y_i = \tfrac{1}{10} \exp(\psi - \psi_0), \qquad 0 \le \psi < \psi_0, \tag{181}$$

$$Y_i = \tfrac{2}{5} \exp[-\tfrac{1}{2}(\psi - \psi_0)] - \tfrac{3}{10} \exp[-(\psi - \psi_0)], \qquad \psi > \psi_0, \tag{182}$$

$$Y_p = \tfrac{1}{2} \exp[\tfrac{1}{2}(\psi - \psi_0)] - \tfrac{1}{10} \exp(\psi - \psi_0), \qquad 0 \le \psi < \psi_0, \tag{183}$$

$$Y_p = 1 + \tfrac{3}{10} \exp[-(\psi - \psi_0)] - \tfrac{9}{10} \exp[-\tfrac{1}{2}(\psi - \psi_0)], \qquad \psi > \psi_0, \tag{184}$$

$$T = \tfrac{29}{30} + \tfrac{1}{30} \exp(\psi), \qquad 0 \le \psi < \psi_0, \tag{185}$$

$$T = T_b - \tfrac{22}{15} \exp[-\tfrac{1}{2}(\psi - \psi_0)] + \tfrac{3}{5} \exp[-(\psi - \psi_0)], \qquad \psi > \psi_0, \tag{186}$$

and is plotted in Fig. 2. Note that although the incoming fluxes of the intermediate and product species were specified to be zero, back diffusion has resulted in nonzero concentrations of these variables at $\psi = 0$.

8. Conclusions and computational implications. The purpose of this last section is to suggest generalizations of the results obtained for the global two-step reaction (47), (48) to more complicated flames and to indicate the computational implications of these
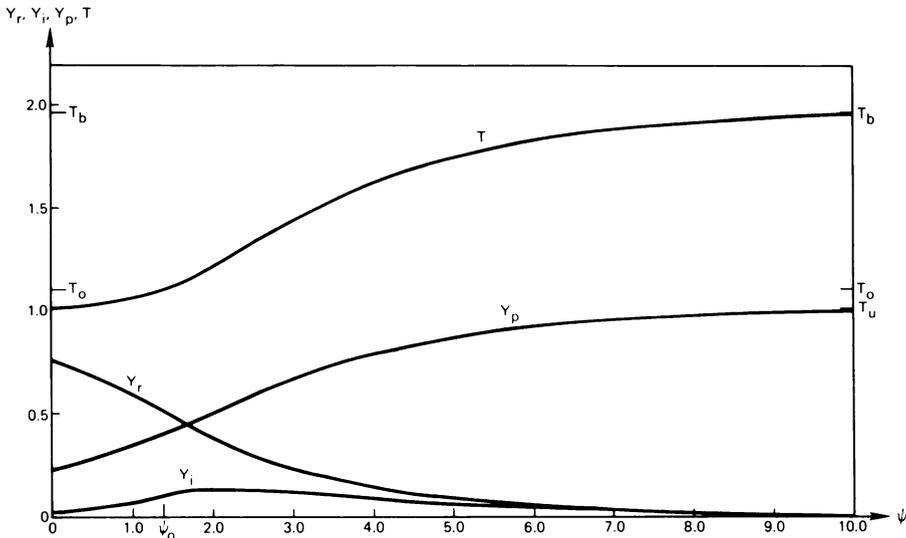

FIG. 2. Profiles of temperature and species mass fractions for the analytical example in Sec. 7.

results. In particular, the present analysis is able to help explain a number of the pitfalls and successes associated with various numerical treatments of the problem. Consequently, a brief review of some of the major computational techniques used in attempting to solve the general N-species problem will be presented and re-examined in light of the results obtained in this paper. This is a worthwhile endeavor because although computational techniques for steady two point boundary value problems are mathematically well-developed (cf. Keller [20]), a careful reading of the combustion literature reveals only a very marginal measure of success in applying those methods to realistic flame problems.

The analysis presented above for a simple flame involving three species, the results of which were summarized at the end of Sec. 6, appears to be sufficiently nonrestrictive to suggest similar results for more complicated flames subject to realistic reaction mechanisms. Hence, it is reasonable to conjecture that Eqs. (19) and (20), which are equivalent to a system of order $2N$ involving N species, admit N asymptotically growing solutions as $\psi \to \infty$. Consequently, the N-species flame can only be supplied with N arbitrary boundary conditions (e.g., the burner temperature T_u and the $N - 1$ independent incoming flux fractions ε_k, $k = 1, \ldots, N - 1$, are usually regarded as known quantities). The remaining N degrees of freedom must be utilized to filter out the growing asymptotic solutions by imposing zero derivative conditions on the temperature T and the $N - 1$ independent mass fractions Y_k, $k = 1, \ldots, N - 1$, at $\psi = \infty$.

In order to start a numerical integration of Eqs. (19), (20) (or Eqs. (24)-(27)) from $\psi = 0$, $2N$ starting conditions are required, N more than can be arbitrarily specified. In normal circumstances, a classical shooting procedure would appear to be indicated. However, due to the mathematical instability of these equations, it is extremely difficult using standard initial-value techniques to carry the integration through the flame to start the iterative correction process for the N "guessed" boundary conditions at $\psi = 0$.

This stability difficulty has been known qualitatively for some time and is usually mentioned in the present context in conjunction with the problem of stiffness, or "overstability" [2]. Basically, (mathematical) instability is due to the presence of locally positive eigenvalues of the linearized equations (i.e., growing solutions), whereas stiffness is due to the presence of negative eigenvalues of disparate magnitudes (i.e., solutions which decay at widely differing rates). The latter phenomenon is caused in the present context by the fact that the various chemical reactions occur at rates which can differ from one another by half a dozen orders of magnitude or more. For example, the two nondimensional reaction rates $\gamma_{r,b}$, $\gamma_{i,b}$ defined in Eqs. (59), (60) were both taken to be $O(1)$ in the analytical calculation presented in Sec. 7. As a result, the "bad" (i.e., positive) eigenvalues Λ_1, Λ_2, Λ_4 as well as the "good" (i.e., negative) eigenvalues Λ_3, Λ_5 all turned out to be $O(1)$. This problem, though unstable, was therefore not stiff since Λ_3 and Λ_5 were of the same magnitude. However, a more typical case might have $\gamma_{r,b} \sim O(1)$ and $\gamma_{i,b} \sim O(10^6)$; that is, reaction (48) takes place much faster than the rate controlling reaction (47). Now (see Eqs. (63)-(65)) the "bad" eigenvalues are $\Lambda_1 \sim O(1)$, $\Lambda_2 \sim O(1)$, $\Lambda_4 \sim O(1000)$ and the "good" eigenvalues are $\Lambda_3 \sim O(1)$, $\Lambda_5 \sim O(1000)$. Not only is this problem stiff (due to the difference in magnitude between Λ_3 and Λ_5), but the stiffness has caused the instability to become much more severe (due to the large magnitude of Λ_4). For larger problems involving dozens of chemical species and 50 or more chemical reactions, one can expect to encounter a near-pathological solution behavior due to the increased number of growing solutions and the greater stiffness which would be likely to result from the presence of additional chemical time scales.

In light of the existence of stiff codes [21] which have been highly successful in integrating large systems of very stiff ode's which are not unstable (such as those arising in chemical kinetics), it would appear that stiffness alone does not cause any insurmountable difficulties. However, the above argument shows that when instability is also present, stiffness can have a very significant effect on the severity of the instability. Although some success in other contexts has been obtained in integrating unstable differential systems of low ($\lesssim 5$) order using parallel (multiple) shooting techniques [20], as well as a combination of quasilinearization and reorthonormalization [22], this success has yet to be duplicated for the highly stiff flame problem. Wilde [9] apparently calculated several adiabatic flames (O_3/O_2, H_2/Br_2, H_2/O_2) by a variant of the latter technique, but found the time-dependent approach (to be discussed shortly) to be more reliable in terms of convergence to the desired solution (one must iterate on the solutions obtained by quasilinearization). For more complicated flames, it should be expected that this conclusion would be even stronger.

One remedy of sorts which has yielded some positive results, at least for the strictly adiabatic flame, is to start the integration at the "hot boundary" (i.e., at $\psi = \psi_L \approx$ "∞") and integrate backwards through the flame [8, 10]. The instability, though still present (since the "bad" eigenvalues become the "good" eigenvalues and vice versa), apparently has a less severe effect on the numerical integration. This can be qualitatively understood by noting that one may pursue a local asymptotic analysis in the unburned region (for the adiabatic problem) in a manner similar to that performed in the burned region at $\psi = +\infty$. The major difference is that now all the quantities in the matrix A [Eq. (45)] are evaluated at the unburned state, where most reaction rates are extremely small due to the low temperature (some recombination reaction rates would still be large). Thus, although one still expects both "good" and "bad" eigenvalues, most will be $\lesssim O(1)$ regardless of how stiff the problem is and thus the stability difficulties are apparently reduced (though not eliminated). Dixon-Lewis [10], in calculating a fuel-rich $H_2/O_2/N_2$ adiabatic flame (8 species), appears to have been the most successful of numerous investigators who have tried the backwards integration technique, although he requires a preliminary time-dependent computation to predict the adiabatic flame speed. This procedure is in principle extendable to the nonadiabatic problem, but the fact that neither the burned temperature T_b nor the burned mass fractions $Y_{k,b}$ are known (see Eq. (49b)) in the nonadiabatic case would probably make it difficult to establish a sufficiently good starting guess for the solution at $\psi =$ "∞". Also, in light of the present analysis, it does not appear likely that a classical shooting method which does not employ some type of reorthonormalization or parallel shooting would be very reliable in a general computational setting.

Finally, it should be noted that Kendall and Kelly [23] have recently been successful in discretizing the spatial coordinate of the steady-state equations and utilizing an iterative method to solve the resulting system of nonlinear algebraic equations. However, Wilde [9] also tried this approach and again concluded that the transient technique was more reliable in terms of convergence.

An alternative approach, which has led to a much greater degree of success, is to model the flame as a time-dependent initial-boundary value problem, which leads to Eqs. (22) and (23) with $\partial Y_k/\partial t$ and $\partial T/\partial t$ appended to their respective left-hand sides. This technique was introduced by Spalding [6] for the purely adiabatic case and by Spalding and Stephenson [7] for the general nonadiabatic problem. Briefly, both spatial and time coordinates are discretized and the solution is then advanced in time by a
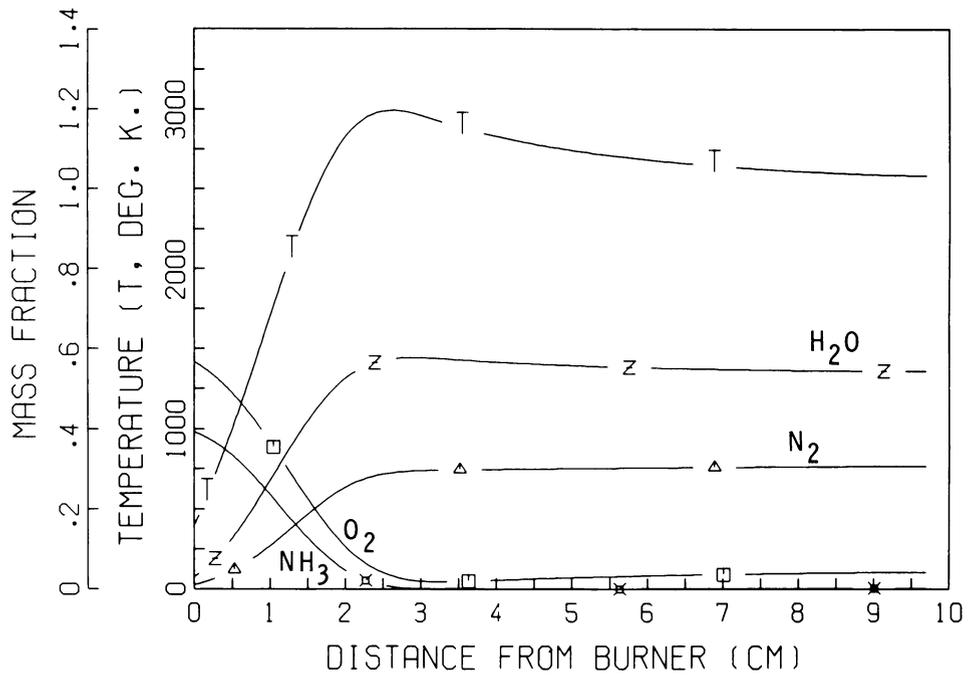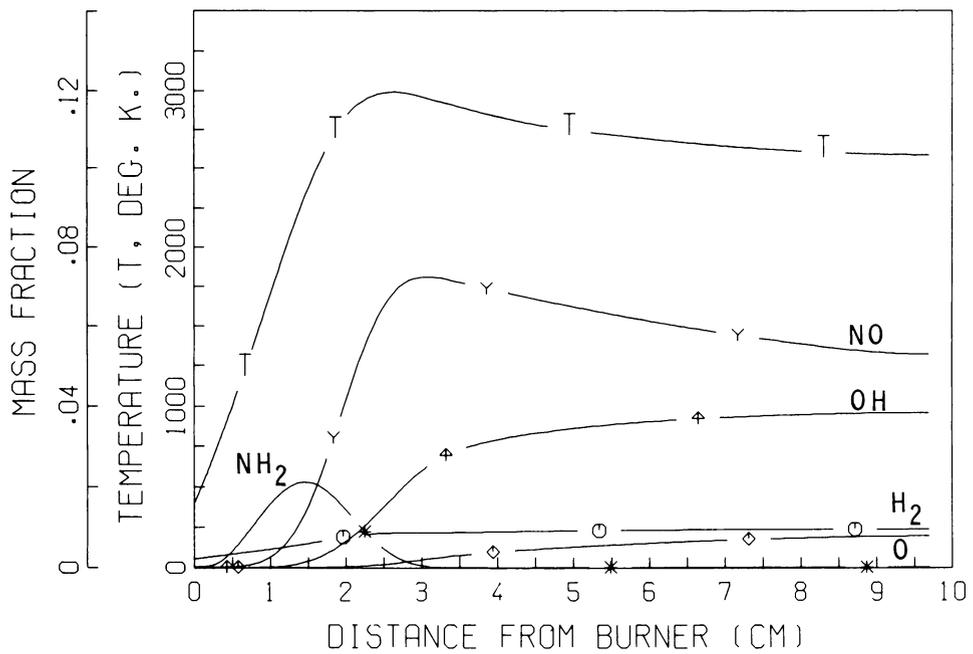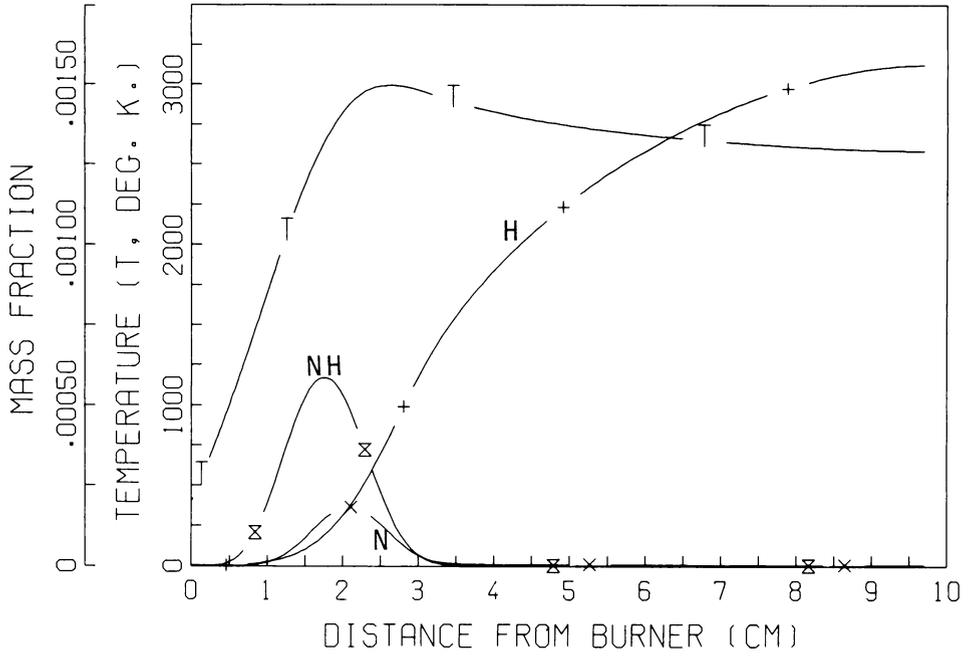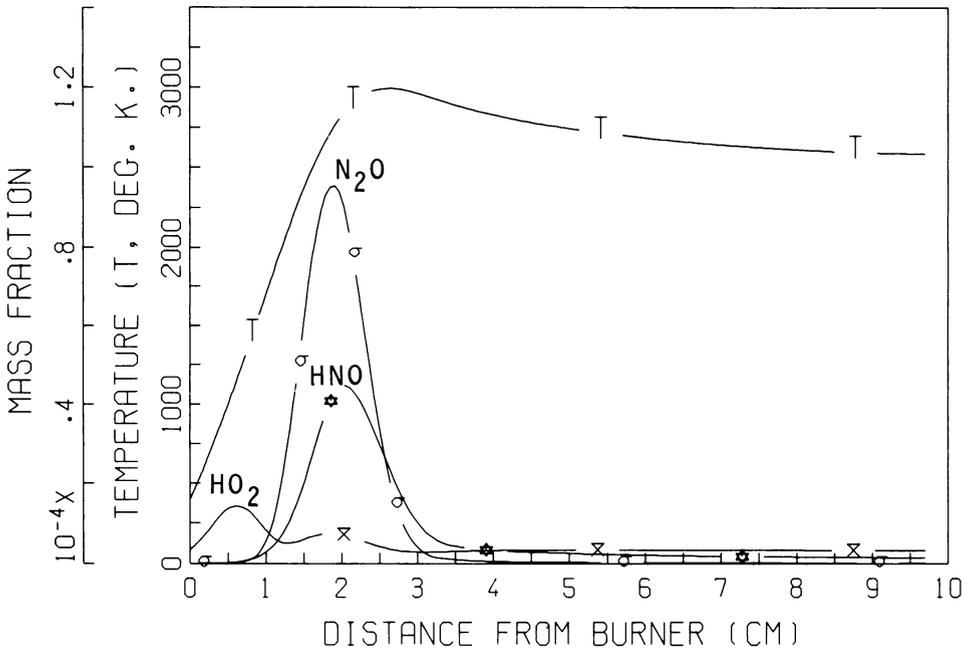
Figure 3a

Figure 3b

Figure 3c

Figure 3d

FIG. 3. Time-dependent spline calculation of a steady-state NH_3/O_2 nonadiabatic premixed laminar flame ($m_0 = 0.0014$ g/cm²-sec, $p = .02632$ atm., $T_u = 400°$K, $\varepsilon_{NH_3} = 0.41$, $\varepsilon_{O_2} = 0.59$, $\varepsilon_k = 0$, $k \neq NH_3$, O_2).

marching procedure to obtain the steady-state solution. In a slightly more sophisticated variation, Bledjian [14] only discretized the spatial coordinate and then used a method of lines technique to integrate the resulting large ordinary differential system in time. More recently, Margolis [12] has used a combination method of lines and spline collocation technique [24] in which certain piecewise polynomial basis functions (B-splines) were used to approximate the spatial dependence. This has the advantage of yielding a solution which is defined for all ψ, rather than at discrete points, and is especially useful in obtaining the spike-shaped minor species profiles. As an example of this last method, Figs. 3a–d show a nonadiabatic NH_3/O_2 flame (15 species and 45 reversible reactions, as indicated in Table 1) which was calculated using a piecewise cubic B-spline basis. (The reaction rates R_k were calculated from Eq. (15b) and the transformation back to the x-coordinate was made by inverting Eq. (12)). The large differences in magnitudes of the various mass fractions are indicative of the large disparity in chemical reaction rates.

The likely reason for the much greater degree of success of the time-dependent method relative to the shooting approach is that the former is not plagued with the instability difficulty which comes from trying to integrate with respect to the spatial coordinate. That is, the parabolic time-dependent flame equations are apparently asymptotically stable with respect to increasing time under a wide range of realistic parameter values. (There is, however, considerable interest in the phenomenon of flame instability; cf. Markstein [25]. In fact, the author has shown, by use of large activation energy asymptotics applied to a fuel + oxidizer → products flame, that the time-asymptotic solution may undergo a supercritical Hopf bifurcation to a pulsating solution branch

TABLE I. TYPICAL REACTION MECHANISM FOR AN NH_3/O_2 FLAME
Species: O_2, H_2, N_2, H, N, O, OH, HO2, H2O, NO, NH_3, NH_2, NH, HNO, N2O
$X \equiv$ any of the above species

Reaction Mechanism

1. $NH_3 + X \leftrightarrow NH_2 + H + X$	24. $N_2O + NH \leftrightarrow N_2 + HNO$
2. $NH_3 + H \leftrightarrow NH_2 + H_2$	25. $NH_3 + NO \leftrightarrow NH_2 + HNO$
3. $NH_3 + O \leftrightarrow NH_2 + OH$	26. $H + N_2 \leftrightarrow NH + N$
4. $NH_3 + OH \leftrightarrow NH_2 + H_2O$	27. $NH + H + X \leftrightarrow NH_2 + X$
5. $NH_2 + H \leftrightarrow NH + H_2$	28. $NH_2 + NO \leftrightarrow N_2O + H_2$
6. $NH_2 + O \leftrightarrow HNO + H$	29. $NH_2 + NO \leftrightarrow N_2 + H_2O$
7. $NH_2 + O \leftrightarrow NH + OH$	30. $H_2 + O_2 \leftrightarrow 2OH$
8. $NH_2 + OH \leftrightarrow NH + H_2O$	31. $H_2 + OH \leftrightarrow H_2O + H$
9. $NH + H \leftrightarrow N + H_2$	32. $H + O_2 \leftrightarrow OH + O$
10. $NH + O \leftrightarrow NO + H$	33. $O + H_2 \leftrightarrow OH + H$
11. $NH + O \leftrightarrow N + OH$	34. $H + O_2 + X \leftrightarrow HO_2 + X$
12. $NH + OH \leftrightarrow N + H_2O$	35. $OH + HO_2 \leftrightarrow H_2O + O_2$
13. $NH + OH \leftrightarrow NO + H_2$	36. $H + HO_2 \leftrightarrow 2OH$
14. $H + HNO \leftrightarrow NH + OH$	37. $O + HO_2 \leftrightarrow O_2 + OH$
15. $HNO + X \leftrightarrow H + NO + X$	38. $2OH \leftrightarrow O + H_2O$
16. $HNO + H \leftrightarrow H_2 + NO$	39. $H_2 + X \leftrightarrow 2H + X$
17. $HNO + O \leftrightarrow OH + NO$	40. $O_2 + X \leftrightarrow 2O + X$
18. $HNO + OH \leftrightarrow NO + H_2O$	41. $H + OH + X \leftrightarrow H_2O + X$
19. $NH + NO \leftrightarrow N_2O + H$	42. $H + HO_2 \leftrightarrow H_2 + O_2$
20. $N_2O + O \leftrightarrow 2NO$	43. $O + N_2 \leftrightarrow NO + N$
21. $N_2O + O \leftrightarrow N_2 + O_2$	44. $N + O_2 \leftrightarrow NO + O$
22. $N_2O + X \leftrightarrow N_2 + O + X$	45. $OH + N \leftrightarrow NO + H$
23. $N_2O + H \leftrightarrow N_2 + OH$	

when the incoming mass flux m_0 becomes sufficiently small [26].) Hence, the main limitations on the time-dependent calculation are those of computer time and storage. This is due both to stiffness, which is still present because of the multiple time scales in the problem, and the need to solve the flame equations at each grid or collocation point. However, as the present analysis has shown, the stiffness and mathematical instability of the steady-state problem are so severe that the stability attributes of the time-dependent approach will probably always make it extremely useful for either solving the full problem or providing good starting guesses for steady-state methods such as those discussed above.

REFERENCES

[1] F. A. Williams, *Combustion theory* (Addison-Wesley, Palo Alto, 1965), Chapter 5 and Appendix B
[2] J. O. Hirschfelder, C. F. Curtiss, and D. E. Campbell, in *Fourth symposium (International) on combustion* (Williams and Wilkins, Baltimore, 1953), p. 190
[3] W. B. Bush and F. E. Fendell, Combust. Sci. and Tech. **1**, 421 (1970)
[4] J. F. Clarke, Combust. Sci. and Tech. **10**, 189 (1975)
[5] G. F. Carrier, F. E. Fendell, and W. B. Bush, Combust. Sci. and Tech. **18**, 33 (1978)
[6] D. B. Spalding, Phil. Trans. Roy. Soc. London **A249** 1 (1956)
[7] D. B. Spalding and P. L. Stephenson, Proc. Roy. Soc. London **A324**, 315 (1971)
[8] J. O. Hirschfelder, C. F. Curtiss, and D. E. Campbell, J. Phys. Chem. **57**, 403 (1953)
[9] K. A. Wilde, Combust. Flame **18**, 43 (1972)
[10] G. Dixon-Lewis, Proc. Roy. Soc. London **A317**, 235 (1970)
[11] J. K. Hale, *Ordinary differential equations* (Wiley-Interscience, New York, 1969), p. 106
[12] S. B. Margolis, J. Computational Physics **27**, 410 (1978)
[13] D. B. Spalding, P. L. Stephenson, and R. G. Taylor, Combust. Flame **17**, 55 (1971)
[14] L. Biedjian, Combust. Flame **20**, 5 (1973)
[15] V. S. Berman and Iu. S. Riazantsev, J. Appl. Math. and Mech. (PMM) **37**, 995 (1973)
[16] A. M. Kanury, *Introduction to combustion phenomena* (Gordon and Breach, New York, 1975), p. 11
[17] G. F. Carrier, F. E. Fendell, and F. E. Marble, SIAM J. Appl. Math. **28**, 463 (1975)
[18] F. A. Williams, in *Annual review of fluid mechanics*, Vol. **3** (Annual Reviews, Inc., Palo Alto, 1971), p. 171
[19] L. Sirovich, *Techniques of asymptotic analysis* (Springer-Verlag, New York, 1971), p. 285
[20] H. B. Keller, *Numerical solution of two-point boundary-value problems* (SIAM, Philadelphia, 1976)
[21] A. C. Hindmarsh, Lawrence Livermore Laboratory Report UCID-30130 (1976)
[22] M. R. Scott and H. A. Watts, in *Fifth symposium on computers in chemical engineering* (Vysoke Tatry, Czechoslovakia, 1977); also Sandia Laboratories Report SAND77-0091
[23] R. M. Kendall and J. T. Kelly, Aerotherm TR-75-158 (1975)
[24] N. K. Madsen and R. F. Sincovec, ACM Trans. on Math. Software, to appear (1980)
[25] G. H. Markstein, ed., *Non-steady flame propagation* (MacMillan, New York, 1964)
[26] S. B. Margolis, Combust. Sci. Tech., to appear (1980)