The Theory of Steady, One-dimensional, Laminar Flame Propagation for One-step Chemical Reactions[*,1]

By

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(With 2 Figures)

Abstract — Zusammenfassung — Résumé

The Theory of Steady, One-dimensional, Laminar Flame Propagation for One-step Chemical Reactions. The present status of the theory of one-dimensional, steady, laminar flame propagation for one-step chemical reactions is reviewed with particular emphasis on methods of solution and on the physical processes that dominate observable results.

Die Theorie der stationären eindimensionalen und laminaren Flammenausbreitung für einstufige chemische Reaktionen. Es wird ein Überblick über den gegenwärtigen Stand der Theorie der eindimensionalen stationären und laminaren Flammenausbreitung einer einstufigen chemischen Reaktion gegeben. Teilweise werden Lösungsmethoden besprochen, sowie physikalische Prozesse, die leichter der Beobachtung zugänglich sind.

La théorie unidimensionnelle de la propagation des flammes en régime permanent laminaire pour des réactions chimiques simples. Une revue de l'état actuel de la théorie unidimensionnelle de la propagation des flammes en régime permanent et laminaire pour des réactions chimiques simples.

I. Introduction

Combustion processes occur in all of the currently available propulsion engines utilized in space exploration. They are likely to play an important role also for a good many years to come. Perhaps the most fundamental combustion problem that requires for successful analytical description (in VON KÁRMÁN's terminology) the "marriage of chemistry and fluid mechanics" is one-dimensional, steady, laminar flame propagation.

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The problem of determining the propagation velocity of a nearly constant pressure combustion wave was first studied by MALLARD and LE CHATELIER [1], who considered the rate of heat liberation by chemical reactions to be of secondary importance. Using simplified models of the wave, TAFFANEL [2] and, independently at a later date, DANIELL [3] were the first investigators to demonstrate the important result that the burning velocity is proportional to the square root of the reaction rate and to the square root of the ratio of an effective thermal conductivity to a specific heat at constant pressure. Further development of the theory has been pursued vigorously in recent years both in the U.S.S.R. and in the West. VON KÁRMÁN's significant contributions to this field will be evident from the following critical summary description of relevant analytical procedures.

The essential features of the mathematical problem of predicting the propagation speed of a steady, one-dimensional, laminar deflagration wave may be well illustrated by examining the unimolecular process $R \to P$. The necessary modifications required in the presence of chain reactions will be discussed in Section III where a criterion for the validity of the steady-state approximation of VON KÁRMÁN and PENNER for reaction intermediates is mentioned. Recent investigations of flames with heat loss that lead to predictions of flammability limits will not be considered in the present survey.

The basic set of conservation equations [4] for steady, adiabatic, one-dimensional laminar flame propagation may be written in simple form if the following approximations are introduced: velocity gradients are sufficiently small to justify neglect of viscous terms, radiative heat transfer is unimportant, the pressure p is practically constant, the kinetic energy of the fluid mixture is negligibly small compared with the internal energy, thermal and pressure diffusion may be neglected, the ideal gas law is applicable, and all of the chemical species may be assumed to have constant average specific heats equal to $\bar{c}_p$.

A convenient expression for the equation of energy conservation in a fluid mixture containing N separate species is the following [4]:

$$\frac{\lambda}{m\,\bar{c}_p}\,\frac{dT}{dx} = (T - T_f) + \sum_{i=1}^{N} (\varepsilon_i - \varepsilon_{i,f})\,(h_i^0/\bar{c}_p). \tag{1}$$

Here λ represents the thermal conductivity of the fluid mixture, m is the constant mass flow rate per unit area and is an eigenvalue for a given system (see below), x identifies the position coordinate, T is the local temperature and T_f denotes the adiabatic flame temperature (attained at $x = \infty$), $\varepsilon_i = Y_i\,[1 + (V_i/v)]$ is the mass flux fraction carried by species i if Y_i denotes the mass fraction of species i whose diffusion velocity is V_i in a fluid mixture moving with the mass-weighted average velocity $v = m/\varrho$ ($\varrho =$ density of the fluid mixture), $\varepsilon_{i,f}$ is the value of ε_i when $T = T_f$, and h_i^0 equals the standard specific enthalpy of formation of species i. The species conservation equation has the form

$$m\,\frac{d\varepsilon_i}{dx} = w_i, \quad i = 1, 2, \ldots, N, \tag{2}$$

if w_i represents the mass rate of production of species i per unit volume by chemical reactions. The overall conservation of mass equation is accounted for by the statement

$$m = \varrho\,v = \text{constant.} \tag{3}$$

The integrated momentum equation has been replaced by the statement

$$p = \text{constant} \tag{4}$$

which is approximately valid for laminar flames.

The general equation for concentration diffusion in a multicomponent gas mixture has the form [4—6]

$$\frac{dX_i}{dx} = \frac{m R^0 T}{p} \sum_{j=1}^{N} \frac{1}{D_{ij}} \left(X_i \frac{\varepsilon_j}{W_j} - X_j \frac{\varepsilon_i}{W_i} \right), \quad i = 1, 2, \ldots, N, \tag{5}$$

where X_i is the mole fraction of species i, R^0 is the molar gas constant, D_{ij} is the binary diffusion coefficient for species i and j, W_i and W_j denote the molecular weights of species i and j, respectively.

For a complex chemical reaction involving p' distinct chemical reaction steps, the chemical source function w_i is given by the expression [4, 5]

$$w_i = W_i \sum_{r=1}^{p'} (\nu_{i,r}'' - \nu_{i,r}') k_r \prod_{j=1}^{N} (c_i)^{\nu_{i,r}'} \tag{6}$$

where the rth process corresponds to the chemical change

$$\sum_{i=1}^{N} \nu_{i,r}' M_i \rightarrow \sum_{i=1}^{N} \nu_{i,r}'' M_i, \quad (r = 1, 2, \ldots, p'),$$

i.e., $\nu_{i,r}'$ and $\nu_{i,r}''$ denote, respectively, the stoichiometric coefficients for the reactant M_i and for the reaction product M_i, k_r is the specific reaction rate constant for the rth reaction step, and c_i identifies the molar concentration of species i. We shall assume that k_r has the following functional form:

$$k_r = B_r T^{a_r} \left[\exp \left(\frac{-E_r}{R^0 T} \right) \right] \tag{7}$$

where B_r, a_r, and E_r are empirically determined constants.

Following conventional procedures for the solution of one-dimensional combustion problems [4, 5, 7—19], we replace the distance as independent variable by the normalized dimensionless temperature

$$\tau = (T - T_0)/(T_f - T_0), \tag{8}$$

where the subscript 0 is used to identify conditions at the upstream boundary $(x = -\infty)$. This objective may be accomplished by dividing Eqs. (2) and (5) by Eq. (1). In this manner we find the following set of $2N$ basic equations:

$$\frac{d\varepsilon_i}{d\tau} = \frac{\lambda}{m^2 \bar{c}_p} \frac{w_i}{(\tau - 1) + \sum\limits_{j=1}^{N} (\varepsilon_j - \varepsilon_{j,f}) h_j^0 / [\bar{c}_p (T_f - T_0)]}, \quad i = 1, \ldots, N, \tag{9}$$

$$\frac{dX_i}{d\tau} = \frac{\lambda R^0 T}{\bar{c}_p p} \frac{\sum\limits_{j=1}^{N} (1/D_{ij}) [X_i (\varepsilon_j/W_j) - X_j (\varepsilon_i/W_i)]}{(\tau - 1) + \sum\limits_{j=1}^{N} (\varepsilon_j - \varepsilon_{j,f}) h_j^0 / [\bar{c}_p (T_f - T_0)]}, \quad i = 1, \ldots, N. \tag{10}$$

We have, in general, a problem involving $2N$ equations and $2N$ dependent variables (N flux fractions ε_i and N mole fractions X_i). At constant pressure, the quantities w_i, ϱ, etc., are known functions of the $2N+1$ quantities ε_i, X_i, and τ. A solution of the $2N$ first-order differential equations for the $2N$ unknowns and a specified set of boundary conditions (e.g., $Y_i = \varepsilon_i$ at $\tau = 0$ and at $\tau = 1$ where the ε_i at $\tau = 0$ are specified for a given chemical system and the ε_i at $\tau = 1$ are determined by the equilibrium conditions $w_i = 0$) exists, in general, only for a particular mass flow rate m if $w_i = 0$ for $0 \leq \tau \leq \tau_i$ and w_i is given by Eqs. (6) and (7) for $\tau > \tau_i$. Here τ_i is a dimensionless ignition temperature (see Section II B) and the characteristic value of m determines the eigenvalue $v_0 = m/\varrho_0$ for the laminar flame propagation velocity.

II. The Unimolecular Decomposition Flame with Lewis Number Unity

A. Formulation of the Problem

For the unimolecular process $R \to P$ with the subscripts 1 and 2 identifying the properties of species R and P, $W_1 = W_2 \equiv W$, $X_i = Y_i$, $Y_1 = (1 - Y_2)$, and $\varepsilon_1 = (1 - \varepsilon_2)$. The equation of state is evidently

$$\varrho T = pW/R^0 = \text{constant} = \varrho_f T_f, \tag{11}$$

and Eqs. (6) and (7) lead to the result

$$w_1 = -w_2 = -\varrho B_1 T^{a_1} (1 - Y_2) \exp(-E_1/R^0 T). \tag{12}$$

If the standard heat of reaction is defined as $q = h_1^0 - h_2^0$, then Eq. (1) becomes

$$\frac{\lambda}{m \overline{c}_p} \frac{d\tau}{dx} = \tau - 1 - \frac{(\varepsilon_2 - \varepsilon_{2,f}) q}{\overline{c}_p (T_f - T_0)}. \tag{13}$$

At the cold boundary ($x = -\infty$, $\tau = 0$, $d\tau/dx = 0$) Eq. (13) reduces to the familiar expression for the adiabatic flame temperature

$$T_f = T_0 + (\varepsilon_{2,f} - \varepsilon_{2,0}) q/\overline{c}_p. \tag{14}$$

Since we have assumed that the reaction $R \to P$ goes to completion as $x \to \infty$, $\varepsilon_{2,f} = 1$ and $\varepsilon_{1,f} = 0$. Using Eq. (14), the normalized flux fraction

$$\varepsilon \equiv (\varepsilon_2 - \varepsilon_{2,0})/(\varepsilon_{2,f} - \varepsilon_{2,0}) = (\varepsilon_2 - \varepsilon_{2,0})/(1 - \varepsilon_{2,0}), \tag{15}$$

and the dimensionless distance

$$\xi \equiv \int_0^x (m \overline{c}_p/\lambda) \, dx, \tag{16}$$

it may be seen that Eq. (13) becomes

$$d\tau/d\xi = \tau - \varepsilon. \tag{17}$$

For the present two-component mixture, Eq. (5) reduces to

$$\frac{\varrho D_{12}}{m} \frac{dY_2}{dx} = Y_2 - \varepsilon_2. \tag{18}$$

The fact that $dY_2/dx = 0$ at $x = \pm\infty$ implies that $Y_{2,0} = \varepsilon_{2,0}$ and $Y_{2,f} = \varepsilon_{2,f} (=1)$. It is now convenient to define a normalized mass fraction as

$$Y \equiv (Y_2 - Y_{2,0})/(Y_{2,f} - Y_{2,0}). \tag{19}$$

Hence Eq. (18) becomes

$$(1/Le)\, dY/d\xi = Y - \varepsilon, \tag{20}$$

where use has been made of Eq. (16) and the LEWIS Number has been defined as

$$Le = \lambda/(\varrho\, D_{12}\, \overline{c}_p). \tag{21}$$

Substituting Eqs. (12), (15), (16) and (19) into Eq. (2) yields

$$\frac{d\varepsilon}{d\xi} = \left[\frac{\lambda\varrho\, B_1\, T^{a_1}}{m^2\, \overline{c}_p}\right](1 - Y)\exp\left(-E_1/R^0\, T\right). \tag{22}$$

In order that the quantity in the square brackets in Eq. (22) may be treated as a constant, it will be assumed that the temperature dependence of λ is given by

$$\lambda\, T^{a_1 - 1} = \text{constant};$$

two gas models for which this relation is valid have $a_1 = 0$, $\lambda \sim T$ and $a_1 = 1/2$, $\lambda \sim \sqrt{T}$. Eqs. (17), (20), and (22) constitute a dimensionless set of governing differential equations for the present simple case.

From Eqs. (17) and (20) it can be seen that the reasonable approximation $Le = 1$ enables us to solve for Y in terms of τ. The difference of Eqs. (17) and (20) is

$$\frac{d\tau}{d\xi} - \frac{1}{Le}\frac{dY}{d\xi} = \tau - Y.$$

For $Le = 1$, this expression has the general solution

$$(\tau - Y) = A\, e^{\xi},$$

where A is an arbitrary constant. Since $\tau - Y$ must remain bounded as $x \to \infty$, the only acceptable value of A is $A = 0$, implying

$$Y = \tau, \tag{23}$$

which also satisfies the correct boundary conditions at $x = \pm\infty$ [compare Eqs. (8) and (19)].

The distance variable ξ may now be eliminated by dividing Eq. (22) by Eq. (17). Thus, using Eqs. (8) and (23),

$$\frac{d\varepsilon}{d\tau} = \frac{\Lambda(1 - \tau)\exp\left[-\beta(1 - \tau)/(\gamma + \tau)\right]}{\tau - \varepsilon} \equiv \frac{\Lambda\,\omega}{\tau - \varepsilon}. \tag{24}$$

Here $\omega = \omega(\tau)$ is a dimensionless reaction rate; the dimensionless activation energy is

$$\beta \equiv E_1/(R^0\, T_f); \tag{25}$$

a dimensionless measure of the initial temperature is

$$\gamma \equiv T_0/(T_f - T_0); \tag{26}$$

the dimensionless (constant) burning rate eigenvalue is defined by the expression

$$\Lambda \equiv \frac{\lambda\varrho\, B_1\, T^{a_1}}{m^2\, \overline{c}_p}\, e^{-\beta}. \tag{27}$$

The two-point boundary conditions for Eq. (24) are $\varepsilon = 0$ at $\tau = 0$ and $\varepsilon = 1$ at $\tau = 1$ [see Eqs. (8) and (15)]. Since Eq. (24) is a first-order equation with two boundary conditions, it is expected that solutions will exist only for particular values of the eigenvalue Λ. After solving Eq. (24) for $\varepsilon(\tau)$ and Λ, the profiles in the physical coordinate are obtained by integrating Eq. (17), viz.,

$$\xi = \int_{\tau_1}^{\tau} d\tau/(\tau - \varepsilon),$$

where τ_1 is the value of τ at $x = 0$.

B. The Cold Boundary Difficulty [7], [8], [9]

Multiplying Eq. (24) by $[1 - (\varepsilon/\tau)]$ and passing to the limit $\tau \to 0$ where $\varepsilon \to 0$ and $\varepsilon/\tau \to d\varepsilon/d\tau$, we obtain a quadratic equation for $(d\varepsilon/d\tau)_0$, the solution of which is

$$(d\varepsilon/d\tau)_0 = \left[1 \pm \sqrt{1 - 4\Lambda \lim_{\tau \to 0} (\omega/\tau)} \right] \Big/ 2.$$

Since ω remains finite as $\tau \to 0$, the right-hand side of this equation is complex for $\Lambda > 0$, implying that Eq. (24) does not possess solutions with acceptable
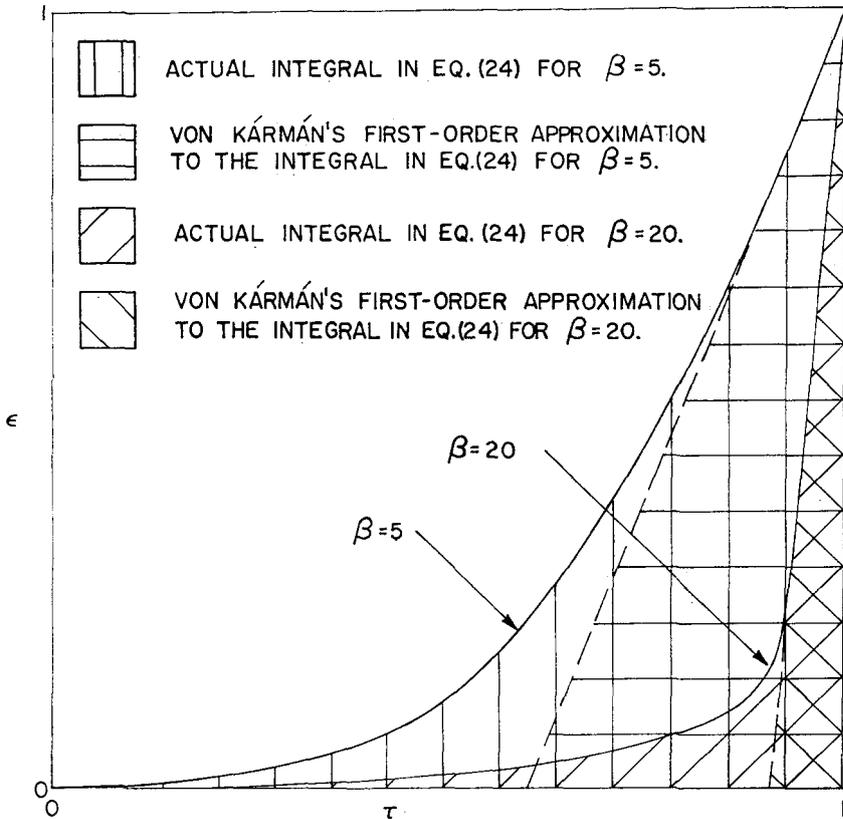

Fig. 1. Schematic representation of the solution $\varepsilon(\tau)$ of Eq. (24) for large and small dimensionless activation energies β, illustrating the error in VON KÁRMÁN's first-order approximation for the burning rate eigenvalue Λ

(real) $d\varepsilon/d\tau$ at $\tau = 0$ for acceptable values of Λ. The cold-boundary problem may also be exemplified by utilizing the result that solutions starting from the hot boundary show that ε approaches zero much more rapidly than τ as the cold boundary is approached (see Fig. 1). In the vicinity of the cold boundary

it is therefore reasonable to neglect ε in comparison to τ in the denominator of Eq. (24), whence Eq. (24) becomes

$$\Lambda = \int_0^{\varepsilon'} d\varepsilon \Big/ \int_0^{\tau'} (\omega/\tau)\, d\tau\,,$$

where ε' is the value of ε at $\tau = \tau'$ and τ' is close to zero. The fact that the integral in the denominator of this equation diverges at $\tau = 0$ implies that Λ vanishes and both m and v_0 are infinite.

The cold-boundary difficulty is a consequence of the fact that the mathematical model does not represent the physical situation precisely: the combustible mixture has not been prepared for the infinitely long time required for it to flow from $x = -\infty$ to $x = 0$ at finite speed. The reaction rate ω becomes so small as $\tau \to 0$ that, for all practical purposes, $\lim_{\tau \to 0} (\omega/\tau)$ should not be infinite.

In order to avoid the "cold boundary difficulty", VON KÁRMÁN and MILLÁN [8] replaced the reduced temperature $\tau = 0$ by $\tau = \tau_i$ (where $0 < \tau_i < 1$) at $\varepsilon = 0$. Introduction of this artifice is equivalent to the physical concept of an ignition temperature T_i below which the chemical reaction rate vanishes [compare Eqs. (6), (7) and (22)]. An alternative procedure for determining a finite, non-zero value for Λ involves the assumption that the flame holder serves as a weak heat sink [9] that removes $[\lambda\,(dT/dx)]_i = m\,\overline{c}_p\,(T_f - T_o)\,(d\tau/d\xi)_i$ cal/cm²-sec. Since $\varepsilon = 0$ at the flame holder if there is no reaction upstream, Eq. (17) implies $(d\tau/d\xi)_i = \tau_i$, whence it follows that the heat sink concept is mathematically equivalent to the ignition-temperature concept at the cold boundary.

It is easily shown that Λ assumes a pseudo-stationary value as τ_i (or the heat loss to the flame holder) is allowed to vary between reasonable limits. This conclusion depends directly on the exponential form of the reaction rate function: for β appreciably greater than unity, the eigenvalue Λ is determined by the behavior of the differential equation in the vicinity of the hot boundary where ε and τ are close to unity. This fact allows the determination of approximate estimates for Λ by a great number of simplified methods. We shall now outline representative mathematical techniques that are known to yield a fair approximation to the eigenvalue Λ.

C. Von Kármán's Zero-Order Approximation [5], [8], [10]

Multiplying Eq. (24) by $(1 - \varepsilon) - (1 - \tau)$ and integrating from 0 to 1 yields

$$\Lambda I = 1/2 - \int_0^1 (1 - \tau)\, d\varepsilon\,, \tag{28}$$

where

$$I \equiv \int_0^1 \omega\, d\tau = \int_0^1 (1 - \tau) \exp\left[-\beta\left(\frac{1 - \tau}{\gamma + \tau}\right)\right] d\tau \tag{29}$$

and the identity $\int_0^1 (1 - \varepsilon)\, d\varepsilon = 1/2$ has been used. Since the integral I, which

depends upon β and γ, may be evaluated in terms of exponential integrals [5], Eq. (28) will determine Λ if a reasonable approximation for $\tau\,(\varepsilon)$ is substituted into the integral on the right-hand side of the equation.

In von Kármán's zero-order approximation, $(1 - \tau)$ is set equal to zero in the integral of Eq. (28), which is seen to provide an upper bound for Λ. This simplification[1] is equivalent to neglecting $(1 - \tau)$ in comparison with $(1 - \varepsilon)$ and is justified if the thermal enthalpy $[m\bar{c}_p\,(T_f - T_o)\,(1 - \tau)]$ leaving the gas volume between the planes τ and $\tau = 1$ is much smaller than the chemical energy entering this gas volume $[mq\,(\varepsilon_{2,f} - \varepsilon_{2,0})\,(1 - \varepsilon) = m\bar{c}_p\,(T_f - T_0)\,(1 - \varepsilon)]$. Applicability of the specified inequality has been illustrated by von Kármán and Penner [5]. In this approximation the eigenvalue Λ becomes

$$1/\sqrt{\Lambda} = \sqrt{2\,I}. \tag{30}$$

D. The Zeldovich-Frank-Kamenetski Equation

The result given in Eq. (30) becomes identical with the classical formula obtained by Zeldovich and Frank-Kamenetski [11] if I is evaluated by the use of a semi-convergent series of which only the first term is retained. Transforming from the variable τ to $z \equiv \beta\,(1 - \tau)/(\gamma + \tau)$ in Eq. (29), we find

$$I = \left(\frac{1 + \gamma}{\beta}\right)^2 \int_0^{\beta/\gamma} \frac{z\,e^{-z}}{[1 + (z/\beta)]^3}\,dz.$$

The activation energy and heat of reaction are usually sufficiently large that a negligible error in the evaluation of the preceding integral is produced by extending the upper limit to infinity $(\gamma/\beta \approx 0)$. The factor $[1 + (z/\beta)]^{-3}$ in the integrand of the resulting expression for I may be expanded in powers of z/β in order to obtain an asymptotic expression for I that is useful for large values of β. Keeping only the first term in the expansion gives

$$I \approx \left(\frac{1 + \gamma}{\beta}\right)^2 \int_0^\infty z\,e^{-z}\,dz + O\left(\frac{1}{\beta^3}\right) = \left(\frac{1 + \gamma}{\beta}\right)^2 + O\left(\frac{1}{\beta^3}\right).$$

Introduction of this result into Eq. (30) yields the Zeldovich-Frank-Kamenetski equation

$$1/\sqrt{\Lambda} \approx \sqrt{2}\,(1 + \gamma)/\beta. \tag{31}$$

E. Von Kármán's First-Order Approximation [5], [8], [10]

The approximation $(1 - \tau) = 0$ in Eq. (28) may be improved upon by setting $(1 - \tau)$ equal to a linear function of $(1 - \varepsilon)$ with slope equal to that of the actual curve at $\tau = 1$. It may be seen from Fig. 1 that this approximation should be valid to somewhat smaller values of β than von Kármán's zero-order approximation. Letting

$$1 - \tau = c\,(1 - \varepsilon), \tag{32}$$

the constant c may be determined by requiring that $d\tau/d\varepsilon = c$ at the hot boundary. Evaluating Eq. (24) at the hot boundary yields

$$\frac{1}{c} = \Lambda \lim_{\tau \to 1} \left\{ \frac{(1 - \tau)\exp\left[-\beta\left(\dfrac{1 - \tau}{\gamma + \tau}\right)\right]}{(1 - \varepsilon)\left[1 - \left(\dfrac{1 - \tau}{1 - \varepsilon}\right)\right]} \right\} = \Lambda\left(\frac{c}{1 - c}\right)$$

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[1] With this approximation, the "cold boundary difficulty" disappears altogether from Eq. (24).

whence

$$c = (-1 + \sqrt{1 + 4\varLambda})/(2\varLambda).\tag{33}$$

Substituting Eq. (32) into the integrand in Eq. (28) and evaluating the integral then gives

$$\varLambda I = \frac{1}{2} - \left(\frac{1}{4\varLambda}\right)(-1 + \sqrt{1 + 4\varLambda}),\tag{34}$$

which may be solved for the square root term and then squared, showing that

$$\varLambda^2 (4 I^2 \varLambda^2 - 4 I \varLambda - 2 I + 1) = 0.\tag{35}$$

Since $\varLambda \neq 0$, the solution to this equation is

$$\varLambda = (1 - \sqrt{2 I})/2 I,\tag{36}$$

where the negative square root has been chosen to agree with Eq. (34). Therefore the result of von Kármán's first approximation is

$$1/\sqrt{\varLambda} = \sqrt{2 I/(1 - \sqrt{2 I})}.\tag{37}$$

F. Other Approximate Methods of Solution

The second-order approximation in the iterative scheme proposed by von Kármán involves numerical integrations, which have been completed for some cases. Boys and Corner [12] using a linear approximation in a somewhat different manner than von Kármán, obtain an analytical expression for the burning rate which is improved upon by a subsequent (numerical) iteration. Adams [13] proposed a method, yielding analytical results, which involves a power-law approximation for $\tau(\varepsilon)$ instead of the linear relation. Wilde [14] modified Adams's result empirically in order to obtain closer agreement with exact numerical solutions. A new power approximation, similar to von Kármán's first approximation and yielding a cubic equation for $\varLambda$, has also been developed[1]. Friedman and Burke [15] set $\gamma = 0$ in Eq. (24) in order to remedy the cold-boundary difficulty but still found it necessary to solve the equation numerically.

In Fig. 2 we have reproduced a plot that is similar to a curve given by von Kármán [10] in which the parameter $\varLambda^{-1/2}/\varLambda_{\text{exact}}^{-1/2}$ is shown as a function of β for most of the approximation procedures described above; here $\varLambda_{\text{exact}}^{1/2}$ was obtained by an exact numerical (machine) computation and corresponds to the plateau value observed for the dimensionless ignition temperature $\tau_i (0 < \tau_i < 1)$. Reference to Fig. 2 shows, for example, that the zero-order approximation of von Kármán is comparable in accuracy with the second iteration of Boys and Corner; of the two approximation procedures which require a numerical integration, von Kármán's second approximation is much more accurate than the Boys-Corner iteration method. Depending on the value of β, the most accurate analytical results are von Kármán's first approximation, the new power approximation, and Wilde's empirical result. Von Kármán's first approximation agrees with the exact result within 5 % for $\beta \gtrsim 10$. The accuracy of these analytical approximation methods illustrates that a numerical integration of Eq. (24) is seldom justified.

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[1] Unpublished work of Th. von Kármán, S. S. Penner, and F. A. Williams.

G. Iterative Procedures

A number of iterative methods for solving Eq. (24) for Λ has been proposed; those of VON KÁRMÁN and of BOYS and CORNER have been mentioned previously. An elegant procedure is due to KLEIN [16] and will now be described briefly.
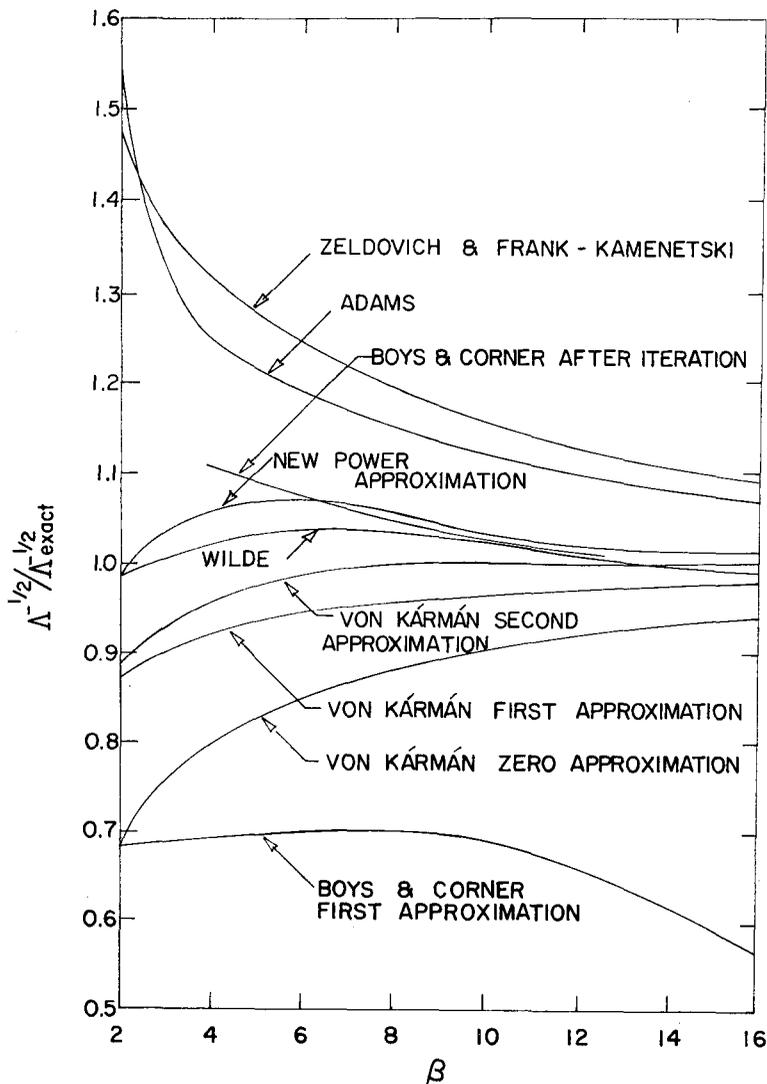

Fig. 2. Comparison of some approximate methods for computing the burning rate eigenvalue Λ

The most thorough iterative approach is that of NACHBAR and JOHNSON [17, 18] which is discussed in Section II L.

Differentiating Eq. (17) and using Eq. (24) we find that

$$d^2\tau/d\xi^2 - d\tau/d\xi = -\Lambda\omega. \tag{38}$$

Utilizing the ignition temperature concept (or the equivalent heat-sink procedure), the cold boundary condition becomes $\tau = \tau_i > 0$ at $\xi = 0$ where the previously

unspecified origin of the ξ coordinate has now been chosen to be the ignition plane. Since no reaction is assumed to occur upstream of the ignition plane, $\varepsilon = 0$ for $-\infty \leq \xi \leq 0$ and Eq. (17) shows $d\tau/d\xi = \tau = \tau_i$ at $\xi = 0$. Also $\tau = 1$ and $d\tau/d\xi = 0$ at $\xi = \infty$. By letting τ become the independent variable and defining $g = d\tau/d\xi$ as the dependent variable, it is seen that Eq. (38) reduces to

$$g - g \, dg/d\tau = \Lambda \omega,$$ (39)

with the hot boundary condition $g = 0$ at $\tau = 1$ and the cold boundary condition $g = \tau_i$ at $\tau = \tau_i$.

KLEIN [16] starts from Eq. (39) which he integrates from τ to $\tau = 1$ with the result

$$g^2/2 = \Lambda \int_\tau^1 \omega \, d\tau - \int_\tau^1 g \, d\tau$$ (40)

or

$$\Lambda \left(\int_{\tau_i}^1 \omega \, d\tau \right) = \tau_i^2/2 + \int_{\tau_i}^1 g \, d\tau]$$ (41)

when evaluated at $\tau = \tau_i$[1]. An iterative method is now used by assuming a reasonable zeroth approximation for $g(\tau)$, computing Λ from Eq. (41), finding a new approximation for $g(\tau)$ from Eq. (40), and repeating this process until convergence is obtained. The n'th approximation is given by

$$g_{[n]}^2/2 = \Lambda_{[n-1]} \int_\tau^1 \omega \, d\tau - \int_\tau^1 g_{[n-1]} \, d\tau$$ (42)

whence

$$\Lambda_{[n]} = \left[\tau_i^2/2 + \int_{\tau_i}^1 g_{[n]} \, d\tau \right] \bigg/ \int_{\tau_i}^1 \omega \, d\tau.$$ (43)

Since numerical integrations are generally required in the first and higher iterations, direct numerical solution of Eq. (24) may be simpler to perform than the evaluation of $\Lambda_{[n]}$ for large n.

H. Rosen's Variational Method [19]

ROSEN has presented an analysis showing that, if the eigenvalue Λ is unique and the first variation of a certain functional of τ vanishes, then Eq. (24) must be satisfied and the numerical value of the functional must be equal to Λ. In order to obtain approximations for Λ, it is therefore possible to use the RAYLEIGH-RITZ procedure of choosing trial functions τ with adjustable parameters which are determined by the requirement that the functional assumes a stationary value. The essential features of ROSEN's analysis will now be outlined.

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[1] Actually, KLEIN's procedure was developed only for rate functions which approach zero rapidly as $\tau \to 0$, in which case the cold boundary difficulty is absent, and the original boundary conditions may be used. Thus, in place of Eq. (41), KLEIN has $\Lambda I = \int_0^1 g \, d\tau$, where I is defined in Eq. (29).

Transforming from the independent variable ξ to

$$\eta = e^\xi \tag{44}$$

in Eq. (38), it is found that

$$d^2 \tau / d \eta^2 = - \Lambda \omega / \eta^2. \tag{45}$$

Since $\eta = 1$ at $\xi = 0$, the boundary conditions for Eq. (45) are $\tau = \tau_i > 0$ at $\eta = 1$ and $\tau = 1$ at $\eta = \infty$. Although these boundary conditions are used in the present discussion, Rosen actually employed the original boundary conditions $\tau = 0$ at $\eta = 0$ ($\xi = -\infty$) and $\tau = 1$ at $\eta = \infty$. He developed other ways of remedying the cold boundary difficulty for solution of the flame equations in the special case when the variational method is employed[1].

The functional Λ_R may be defined as

$$\Lambda_R = \int\limits_1^\infty \frac{1}{2} (d \tau / d \eta)^2 \, d \eta \Big/ \int\limits_1^\infty V \, d \eta \tag{46}$$

where

$$V \equiv \int\limits_{\tau_i}^\tau \omega \, d \tau / \eta^2. \tag{47}$$

Since $\omega \geqslant 0$ and ω is bounded, V is non-negative and bounded in the range of integration in Eq. (46), whence it follows that Λ_R is a finite positive number. For a variation of $\tau(\eta)$ to a neighbouring member of the class of functions $\tau(\eta)$ satisfying the given boundary conditions, the variation in Λ_R is

$$\delta \Lambda_R = \frac{\int\limits_1^\infty V d\eta \int\limits_1^\infty \dot{\tau} \, \delta \dot{\tau} \, d\eta - \int\limits_1^\infty \frac{1}{2} (\dot{\tau})^2 d\eta \int\limits_1^\infty \delta V \, d\eta}{\left(\int\limits_1^\infty V d\eta \right)^2}$$

$$= \left(\int\limits_1^\infty V d\eta \right)^{-1} \left\{ \dot{\tau} \delta \tau \Big|_1^\infty - \int\limits_1^\infty \ddot{\tau} \, \delta \tau \, d\eta - \Lambda_R \int\limits_1^\infty \frac{\omega}{\eta^2} \, \delta \tau \, d\eta \right\}$$

$$= -\int\limits_1^\infty \left(\ddot{\tau} + \frac{\Lambda_R \omega}{\eta^2} \right) \delta \tau \, d\eta \Big/ \int\limits_1^\infty V \, d\eta, \tag{48}$$

where a dot indicates differentiation with respect to η. Since $\delta \tau$ is arbitrary, this equation implies that

$$\delta \Lambda_R = 0 \tag{49}$$

if, and only if, Eq. (45) is satisfied and

$$\Lambda_R = \Lambda \tag{50}$$

is a unique eigenvalue.

Rosen states without proof that the stationary value $\Lambda_R = \Lambda$ is a minimum. If this is indeed the case, then the correct function $\tau(\eta)$ is that particular

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[1] If τ_i is replaced by zero and the lower limit $\eta = 1$ is replaced by $\eta = 0$ in Eqs. (46) and (47), then the usual cold-boundary difficulty becomes apparent because the integral in the denominator of Eq. (46) diverges at $\eta = 0$ unless $\omega(\tau)$ goes to zero sufficiently rapidly as $\tau \to 0$.

function for which Λ_R assumes its smallest possible value and Eq. (50) may then be used to find the correct mass burning velocity m. In this case, the RAYLEIGH-RITZ method [20] may be employed to obtain successively better estimates for $\tau(\eta)$ and Λ. This straightforward procedure does not appear to have been carried out beyond the first rough approximation given in [19].

I. Spalding's "Centroid Rule" [21]

A procedure belonging in a different category from those considered above is the "centroid rule" developed by SPALDING. This author showed empirically that, for

$$\omega = \text{constant} \, (1 - \tau)^m \tau^n ,$$

the eigenvalue Λ is given by the expression

$$\Lambda I = \frac{1}{2} - 0.6604 \, (1 - \tau_c) - 0.4283 \, (1 - \tau_c)^2 \tag{51}$$

where the "centroid of the reaction rate" is defined as

$$\tau_c \equiv \int_0^1 \omega \tau \, d\tau \Big/ \int_0^1 \omega \, d\tau \tag{52}$$

and I is given by Eq. (29). An estimate for the burning rate may then be obtained rapidly by plotting ω as a function of τ, determining the centroid τ_c, and using Eq. (51) for the computation of Λ. Although the results of SPALDING's procedure agree well with those derived from more accurate calculations, a small discrepancy exists between the values of Λ obtained from the "centroid rule" and from an exact numerical integration for ω determined by an ARRHENIUS-type rate function.

For some rate functions which go to zero rapidly as $\tau \to 0$, ROSEN [19] has presented a theoretical confirmation of SPALDING's "centroid rule". When $\omega \to 0$ as $\tau \to 0$, the boundary condition $\tau = 0$ at $\eta = 0$ may be used for Eq. (45) and in Eqs. (46) and (47) the lower limits of the integrals may be taken as $\eta = 0$ and $\tau = 0$ (instead of $\eta = 1$ and $\tau = \tau_i$). Assuming that

$$\tau = \begin{cases} \eta/(1 + \alpha\eta), & 0 \le \eta \le 1/(1 - \alpha), \\ 1, & \eta > 1/(1 - \alpha), \end{cases}$$

where the shape parameter α is to be varied in order to determine the extremum for Λ_R, it is found by the variational procedure discussed in the preceding Section II H [i.e., by evaluating $\Lambda_R(\alpha)$, solving the equation $d\Lambda_R/d\alpha = 0$ for α, and substituting the result into the expression for $\Lambda_R(\alpha)$] that

$$\alpha = 1 + \hat{q} - (1 - \hat{q} + \hat{q}^2)^{1/2}$$

and

$$\Lambda = \Lambda_R = \left\{ \frac{1}{6} + \frac{1}{3} [(1 - \hat{q} + \hat{q}^2)^{1/2} - \hat{q}] \right\} \Big/ I \tag{53}$$

where I is defined in Eq. (29) and

$$\hat{q} \equiv \int_1^\infty \left(\int_0^{1/x} \omega \, d\tau \right) dx \Big/ \int_0^1 \omega \, d\tau. [1] \tag{54}$$

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[1] The fact that $\hat{q} = \infty$, yielding $\Lambda = 0$ in Eq. (53), for ARRHENIUS rate functions illustrates the inapplicability of this procedure when ω does not approach zero as $\tau \to 0$.

While Eq. (53), in general, need not be equivalent to the "centroid rule", for two of the rate functions considered by SPALDING [20], i.e.[1],

$$\omega_1 = \text{constant} \, (1 - \tau)\tau^n$$

and

$$\omega_2 = \text{constant} \, (1 - \tau)^2 \, \tau^n,$$

Eqs. (52) and (54) show that

$$\hat{q}_1 = 2/n = 2 \, (1 - \tau_c)/(3 \, \tau_c - 1)$$

and

$$\hat{q}_2 = 3/n = 3 \, (1 - \tau_c)/(4 \, \tau_c - 1),$$

respectively, whence a MACLAURIN expansion of Eq. (53) yields

$$I \Lambda_1 = \frac{1}{2} - \frac{1}{2} \, (1 - \tau_c) - \frac{13}{24} \, (1 - \tau_c)^2 + O \, [(1 - \tau_c)^3], \tag{55}$$

and

$$I \Lambda_2 = \frac{1}{2} - \frac{1}{2} \, (1 - \tau_c) - \frac{11}{24} \, (1 - \tau_c)^2 + O \, [(1 - \tau_c)^3], \tag{56}$$

respectively. Eqs. (55) and (56) agree with Eq. (51) within 1% for $(1 - \tau_c)^3 < 0.005$, corresponding to the range of values of τ_c that is of interest in practically important problems. Although the preceding development implies that Eq. (53) is more accurate than Eqs. (55) and (56), it is actually impossible to determine whether Eq. (51) or Eq. (53) will be more accurate in any given case because of the rough approximation for $\tau \, (\eta)$ used in obtaining Eq. (53). In practice it is usually easier to employ the "centroid rule" than to use Eq. (53).

J. The Johnson and Nachbar Method of Upper and Lower Bounds [17]

The method of JOHNSON and NACHBAR constitutes the most accurate technique for the solution of simple laminar flame problems since it permits the rigorous determination of upper and lower bounds for the eigenvalues. This procedure, which was originally developed for the deflagration of a solid propellant, may be applied to the case of a gaseous laminar flame without modification. It has recently been extended to include an iterative method (see Section II L) for narrowing the discrepancy between the bounds [18].

JOHNSON and NACHBAR [17] use Eq. (39) with the boundary conditions $g = \tau_i$ at $\tau = \tau_i \, (0 < \tau_i < 1)$ and $g = 0$ at $\tau = 1$. They state without proof [17] that there exists a unique solution $g \, (\tau)$ and a unique positive eigenvalue Λ.

Dividing Eq. (39) by g and integrating from $\tau = \tau_i$ to τ yields

$$g = \tau - \Lambda \int\limits_{\tau_i}^{\tau} (\omega/g) \, d\tau. \tag{57}$$

By substituting Eq. (57) into the integral on the right-hand side of Eq. (41) it is found that

$$\Lambda \int\limits_{\tau_i}^{1} \omega \, d\tau = \frac{1}{2} - \Lambda \int\limits_{\tau_i}^{1} \int\limits_{\tau_i}^{\tau} [\omega \, (\tau')/g \, (\tau')] \, d\tau' \, d\tau,$$

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[1] The close relationship (almost everywhere within 2%) between these functional forms for $\omega \, (\tau)$ and the ARRHENIUS expression has been demonstrated by ROSEN [22] for typical values of $n \, (n \sim 11)$.

which becomes

$$2 \Lambda \int_{\tau_i}^{1} \omega \left[1 + \left(\frac{1-\tau}{g} \right) \right] d\tau = 1 \tag{58}$$

when the double integral is reduced to a single integral through integration by parts. Eq. (58) may be used to determine an upper bound for Λ (see below).

Eq. (39) may also be written in the form

$$d(g^2)/d\tau = 2(g^2)/g - 2\Lambda\omega, \tag{59}$$

which resembles a linear equation for g^2 for which a solution may be effected by means of an integrating factor. NACHBAR noted that multiplication of Eq. (59) by $\exp\left[-2\int_{\tau_i}^{\tau}(1/g)\,d\tau \right]$ leads to the result

$$\frac{d}{d\tau}\left\{ g^2 \exp\left[-2\int_{\tau_i}^{\tau}\left(\frac{1}{g}\right)d\tau \right] \right\} = -2\Lambda\omega \exp\left[-2\int_{\tau_i}^{\tau}\left(\frac{1}{g}\right)d\tau \right], \tag{60}$$

as may be verified by expanding the derivative on the left-hand side of Eq. (60) by parts. Integrating Eq. (60) from $\tau = \tau_i$ to $\tau = 1$ and utilizing the boundary conditions on g yields

$$2 \Lambda \left(\frac{1}{\tau_i^2} \right) \int_{\tau_i}^{1} \omega \exp\left[-2\int_{\tau_i}^{\tau}\left(\frac{1}{g}\right)d\tau \right] d\tau = 1 \tag{61}$$

after division by τ_i^2. Eq. (61) may be used to determine a lower bound for Λ (see below).

Since ω, $(1-\tau)$, and g are all non-negative, it is apparent that substitution of an upper bound for $g(\tau)$ in Eq. (58) will lead to a lower bound for the integral and the resulting value of Λ is therefore an upper bound. On the other hand, substituting this same upper bound for $g(\tau)$ into Eq. (61) yields a lower bound for Λ because the inner integral is a lower bound; hence the exponential and therefore the outer integral are upper bounds. Eqs. (58) and (61) can therefore be used to provide limits between which the eigenvalue must lie.

Since $\Lambda \int_{\tau_i}^{\tau} (\omega/g)\, d\tau \geqslant 0$, it follows from Eq. (57) that

$$g \leqslant \tau. \tag{62}$$

Hence τ may be used for the upper bound of g in Eqs. (58) and (61). Eq. (58) then implies that

$$\Lambda \leqslant \left[2\int_{\tau_i}^{1} (\omega/\tau)\,d\tau \right]^{-1} \tag{63}$$

and Eq. (61) shows that

$$\Lambda \geqslant \left[2\int_{\tau_i}^{1} (\omega/\tau^2)\,d\tau \right]^{-1} \tag{64}$$

after the inner integration over τ is performed. Eqs. (63) and (64) constitute explicit rigorous bounds for the burning rate eigenvalue Λ.

K. Comparison of the Method of Johnson and Nachbar with Other Procedures

It is of interest to compare the preceding bounds with various approximate formulae. Since $\tau \leq 1$, it is apparent that

$$\int\limits_{\tau_i}^{1} (\omega/\tau)\, d\tau \geqslant \int\limits_{\tau_i}^{1} \omega\, d\tau \approx I, \qquad (65)$$

where I is defined in Eq. (29) and it is assumed that τ_i is nearly zero. Hence it follows from Eq. (63) that

$$\varLambda \lesssim 1/(2\,I). \qquad (66)$$

Comparison of Eq. (66) with Eq. (30) shows that von Kármán's zeroth approximation yields an upper bound for $\varLambda$, a result which is also apparent from Eq. (28) or from Fig. 2. Eq. (65) further implies that the bound in Eq. (63) is closer to the correct value of $\varLambda$ than is von Kármán's zeroth approximation.

Expanding the identity $(1\text{-}\tau)^2/\tau \geq 0$ yields $1/\tau \geq 2\text{-}\tau$, from which it follows that

$$\int\limits_{\tau_i}^{1} (\omega/\tau)\, d\tau \geqslant 2\int\limits_{\tau_i}^{1} \omega\, d\tau - \int\limits_{\tau_i}^{1} \tau\omega\, d\tau \approx I\,(2-\tau_c) \qquad (67)$$

where use has been made of Eqs. (29) and (52). From Eqs. (67) and (63) it may now be seen that

$$I\,\varLambda \lesssim \frac{1}{2\,(2-\tau_c)} = \frac{1}{2} - \frac{1}{2}\,(1-\tau_c) + \frac{1}{2}\,(1-\tau_c)^2 + O\,[(1-\tau_c)^3] \qquad (68)$$

where the denominator has been expanded in powers of $(1\text{-}\tau_c)$ in order to obtain the last equality. Comparison of Eqs. (51) and (68) shows that Spalding's "centroid rule" lies very near but below the upper bound given in Eq. (68) for practical values of τ_c. It has been noted by Nachbar and Spalding that the mean value of the upper and lower bounds given by Eqs. (63) and (64) is in close agreement with the results obtained from Spalding's "centroid rule" for many rate functions.

The upper and lower bounds predicted by Eqs. (63) and (64) are usually very close together [17]. Since the integrals in Eqs. (63) and (64) are not difficult to evaluate, these bounds may therefore be used to obtain very accurate approximations to the mass burning rate m with much less labor than is required by iterative procedures or numerical integrations.

L. The Iterative Procedure of Johnson and Nachbar [18]

An iterative technique for obtaining successively narrower upper and lower bounds for the eigenvalue $\varLambda$ and successively lower upper bounds for the function $g(\tau)$ has been developed recently by Johnson and Nachbar [18]. Since they have proven that this procedure converges and that $g(\tau)$ approaches the solution of Eq. (39) monotonically, the oscillating divergence sometimes observed by Klein [16] in his iterative scheme cannot appear here, and the present method constitutes a truly rigorous procedure for obtaining solutions to any desired degree of accuracy.

Integrating Eq. (57) from $\tau = \tau_i$ to τ yields

$$\int_{\tau_i}^{\tau} g\,d\tau = \frac{1}{2}\,(\tau^2 - \tau_i{}^2) - \Lambda \int_{\tau_i}^{\tau}\int_{\tau_i}^{\tau'} \frac{\omega(\tau'')}{g(\tau'')}\,d\tau''\,d\tau'$$

$$= \frac{1}{2}\,(\tau^2 - \tau_i{}^2) - \Lambda \int_{\tau_i}^{\tau}(\tau - \tau')\,\frac{\omega(\tau')}{g(\tau')}\,d\tau'\,, \tag{69}$$

where the last equality is obtained by integrating the last term by parts. Integrating Eq. (39) from $\tau = \tau_i$ to τ gives

$$g^2/2 = \tau_i{}^2/2 - \Lambda \int_{\tau_i}^{\tau}\omega\,d\tau + \int_{\tau_i}^{\tau} g\,d\tau \tag{70}$$

which becomes

$$g^2 = \tau^2 - 2\Lambda \int_{\tau_i}^{\tau}\omega(\tau')\,\{[(\tau - \tau')/g(\tau')] + 1\}\,d\tau' \tag{71}$$

when Eq. (69) is substituted into the last term. Eqs. (61) and (71) provide the basis for an iterative procedure.

An upper bound for $g(\tau)$ is substituted into Eq. (61) in order to obtain a lower bound for Λ. If this value of Λ and the upper bound for $g(\tau)$ are substituted into the right-hand side of Eq. (71), then, since the integral in Eq. (71) will clearly assume a lower bound, the right-hand side of Eq. (71) will assume an upper bound, and hence a new upper bound for $g^2(\tau)$ will be given by Eq. (71). The fact that the resulting new upper bound for $g(\tau)$ is lower than the previous upper bound requires proof by mathematical induction[1].

The n'th approximation for g is finally given by [see Eqs. (71) and (61)]

$$g^2{}_{[n]} = \tau^2 - 2\Lambda_{[n-1]} \int_{\tau_i}^{\tau}\omega(\tau')\,\{[(\tau - \tau')/g_{[n-1]}(\tau')] + 1\}\,d\tau'\,, \tag{72}$$

where

$$\Lambda_{[n-1]} = \left\{\frac{2}{\tau_i{}^2} \int_{\tau_i}^{1}\omega(\tau)\exp\left[-2\int_{\tau_i}^{\tau}\left(\frac{1}{g_{[n-1]}(\tau')}\right)d\tau'\right]d\tau\right\}^{-1}. \tag{73}$$

In accordance with the preceding discussion, as $n \to \infty$ the quantity $g_{[n]}(\tau)$ approaches the correct solution from above and $\Lambda_{[n]}$ approaches the correct eigenvalue from below. From the discussion in Section II J it is seen that for

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[1] It is obvious that if $g = \tau$ is used as the first approximation, then the second approximation obtained from Eq. (71) will be a lower upper bound. The induction proof is then completed by using the assumption that the n'th approximation for g is a lower upper bound than is the $(n-1)$'th approximation to prove that the $(n+1)$'th approximation is a lower upper bound than the n'th approximation. This last proof is obtained quite simply from Eqs. (61) and (71) since the fact that the n'th approximation for g is lower than the $(n-1)$'th approximation immediately shows (in view of Eqs. (61) and (71)) that the right-hand side of Eq. (71) used in obtaining the $(n+1)$'th approximation is smaller than the right-hand side of Eq. (71) used in obtaining the n'th approximation, whence Eq. (71) implies that the $(n+1)$'th approximation is smaller than the n'th approximation.

each $g_{[n]}(\tau)$ a value of Λ may also be computed from Eq. (58) and the resulting sequence of values will approach the correct eigenvalue from above. Thus successively narrower bounds for the burning rate and successively smaller upper bounds for $g = d\tau/d\xi$ are obtained.

Since the first estimates for the bounds of Λ given in Eqs. (63) and (64) are so close together, it appears that only a few iterations will be required in order to obtain very precise results. From Eqs. (72) and (73) it is seen that the integrations which must be performed in carrying out the present techniques are only slightly more complicated than those of other iterative procedures [e.g., Eqs. (42) and (43)]. However, for most practical applications, either Eqs. (63) and (64) or one of the other approximate formulae given in the previous sections will be sufficiently accurate.

III. Distribution of Radicals in Flames
The Extended Steady-State Approximation

The distribution of radicals (atoms and chain carriers) in flames is closely related to the details of the chemical reaction rates in flames. For this reason, it is difficult to obtain reasonable approximations for radical concentrations without complete (numerical) solutions of the flame equations, such as those obtained by KLEIN through an extension of his iterative procedure [16]. Analytical approximations for the radical concentrations in flames were obtained by VON KÁRMÁN and PENNER [5] who first introduced an extended steady-state approximation for the reaction intermediates. They assumed that the net mass rate of production of any radical r is negligibly small, i.e.,

$$w_r \approx 0. \tag{74}$$

The preceding equation may be solved for the mole fraction X_r in terms of the dimensionless temperature τ and the remaining mole fractions $X_i \, (i \neq r)$. If Eq. (74) is valid for all radicals, the mole fractions of the reaction intermediates may be eliminated from the flame equations, and the flame equations may then be solved explicitly to give all of the mole fractions, including the X_r, in terms of τ. This useful steady-state approximation has been well justified for the ozone decomposition flame [5], is of doubtful validity for the hydrazine decomposition flame [23], and yields a rather poor description for the bromine atom concentration in the H_2-Br_2 flame [24].

GIDDINGS and HIRSCHFELDER [25] first proposed an incomplete criterion for determining the applicability of the steady-state approximation. An alternative procedure, involving a demonstration that the steady-state approximation may be used as a first approximation in an iterative scheme for obtaining successively more exact solutions of the flame equations, has been given by MILLÁN and DA RIVA [26]. The critical parameter for applicability of the steady-state approximation has been found to be an appropriate version of DAMKÖHLER's first similarity group [27, 28]. Details of this work have been described elsewhere by the Spanish wing of VON KÁRMÁN's collaborators on combustion theory [26].

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