
Laminar Flames

39

DISTRIBUTION OF RADICALS IN LAMINAR FLAMES^a

By G. MILLAN AND I. DA RIVA

Introduction

One of the fundamental and more difficult problems of the laminar-flame theory involving chain reactions is the computation of the distribution of the radicals in the flame, which is essential in determining the flame properties and structure.

This difficulty is due to the fact that, whereas the distributions of the reactants and final products are determined mainly by the effects of diffusion, making it possible to obtain approximate expressions for them without solving the flame equations, the distributions of the radicals depend basically on the chemical reactions, so that they cannot be obtained without integrating the differential equations of the flame.

A similar problem presents itself in the homogeneous reactor studied by the classical chemical kinetics, where the difficulty again lies in the calculation of the concentration of the intermediate species which propagate the chains. For such cases, Bodenstein¹ proposed a method conventionally called "steady-state assumption" and proved that it can be applied in those cases where the reaction rates of the radicals are very great by comparison with the rates of the principal species. The method based on the assumption that the concentrations of the radicals are those corresponding to the equilibrium conditions

obtained when their reaction rates are equated to zero. The problem has been studied recently by Benson,² for a set of typical reactions, in a homogeneous and isothermal reactor.

In 1952, von Kármán and Penner³ proposed the extension of the "steady-state assumption" to the theory of flames and applied it with success to the ozone decomposition flame, which had been numerically computed by Hirschfelder and his collaborators⁴ without applying this assumption. The comparison of the results showed a complete coincidence between the oxygen-atom distributions obtained by the two methods, except over a very narrow interval of temperatures at the hot boundary of the flame. Subsequently the method was applied to the study of a certain number of cases, such as the hydrazine decomposition flame,⁵ the hydrogen-bromine flame,⁶ and so forth, proving that, while the steady-state assumption appears to be fully justified for some radicals, it is not for others, although, in all of these cases it gives values for the propagation velocity of the flame which approach the actual ones, within limits of error which can be tolerated in the present state of development of the theory.

The discrepancies between the distributions of the radicals given by the steady-state assumption and those computed by numerical integrations, observed in some of the aforementioned cases, have been attributed to two different causes. One is the lack of time available during passage of the gases through the flame, for the radicals to reach the concentrations corresponding to the steady-state values; another is the influence of the diffusion of the radicals from the

^a This investigation was performed at the Combustion Laboratory of the National Institute of Aeronautical Technique, Madrid, Spain. It was partially sponsored by the Air Research and Development Command, United States Air Force, through Contracts No. AF 61(514)-997 and AF 61(052)-221.

points of maximum concentration toward both sides.

Recently, Giddings and Hirschfelder⁷ have studied the applicability of the assumption for several typical flames, comparing results obtained in this way with those obtained by numerical integration, and they have proposed a criterion for the applicability of the steady-state assumption. According to these authors, for the assumption to be applicable, the relation between a "relaxation time" for the radicals (which, essentially, is the time required to reach the steady state) and a "characteristic time" for the reaction of the principal species must be sufficiently small. Giddings and Hirschfelder justify this idea by means of purely physical considerations, without a mathematical demonstration, such as would be expected in a well-defined problem of this type, in which the criterion should naturally be based on the properties of the differential system of the flame equations, and be expressed in terms of the values of its parameters. On the other hand, the proposed criterion is clearly incomplete, since it ignores completely the influence of diffusion which, as already stated, can be of importance. In fact, Giddings' and Hirschfelder's criterion is just as valid for a pure thermal flame as for a flame in which these effects are taken into account.

In the study which follows⁸ it is shown that it is possible to deduce a completely general criterion for the applicability of the steady-state assumption, based on purely mathematical considerations, which also clearly shows the reason of such approximation and permits the development of a procedure of successive approximations from the solution corresponding to the steady-state assumption.

It is shown that the steady-state assumption implies a first-order approximation to the exact solution of the flame equations, when developed in a power series of a well-defined dimensionless parameter, in which both the reaction rate and the radical-diffusions effects are combined. Therefore, the value of this parameter which, from the physical point of view is identified as the first Damköhler parameter for those radicals present in the flame, conditions the applicability of the steady-state assumption.

By illustration, the theory is applied first to a mathematical model which preserves the fundamental properties of the flame and offers an easy way of comparing the exact solutions with

the successive approximations obtained when the proposed method is employed.

Finally, the theory is applied to several typical cases. Normally in these applications the first two perturbations were sufficient to evaluate the accuracy of the assumption.

FLAME EQUATIONS

The general equations of the flame in the form given, for example, by von Kármán,¹⁰ are the following:

Equation for the conservation of total mass:

$$\rho v = m = \text{const.} \quad (1)$$

Continuity equation for the species i :

$$m \frac{d\epsilon_i}{dx} = w_i, \quad i = 1, 2, \dots, n. \quad (2)$$

The mass rate w_i of production of the species i , is the sum of those corresponding to the individual reactions in which the species i participates:

$$w_i = \sum_{j=1}^r w_{ij} \quad (3)$$

each one of which is, in turn, of the form

$$w_{ij} = M_i (\nu_{ij}'' - \nu_{ij}') B_j \left(\frac{p}{RT_f} \right)^{n_j} \cdot \theta^{\alpha_j - n_j} \exp - \frac{\theta_{aj}}{\theta} \prod_{s=1}^n X_s^{\nu_{sj}'} \quad (4)$$

where

$$\theta = \frac{T}{T_f} \quad (5)$$

is the reduced temperature of the mixture and

$$\theta_{aj} = \frac{E_{aj}}{RT_f} \quad (6)$$

is the reduced activation temperature of the reaction j .

Energy equation:

$$\frac{\lambda}{mC_p} \frac{d\theta}{dx} = \theta - 1 + \sum_{j=1}^n q_j (\epsilon_j - \epsilon_{jf}) \quad (7)$$

where

$$q_j = \frac{h_j^0}{C_p T_f}. \quad (8)$$

Diffusion equations:

$$\frac{dX_i}{dx} = \frac{mRT_f}{p} \theta \sum_{j=1}^n \frac{1}{D_{ij}} \left(X_i \frac{\epsilon_j}{M_j} - X_j \frac{\epsilon_i}{M_i} \right) \quad i = 1, 2, \dots, n. \quad (9)$$

Hirschfelder and Curtiss¹¹ give the following approximate expression for the diffusion velocity of any species whose concentration is very small with respect to that of the mixture, as usually occurs with the radicals:

$$v_{di} = - \frac{1}{\sum_{j \neq i} \frac{X_j}{D_{ij}}} \frac{1}{X_i} \frac{dX_i}{dx}.$$

It can easily be proved that in such cases Equation (9) can be replaced by the following expression for the corresponding species:

$$\frac{dX_i}{dx} = \frac{mRT_f}{pMD_i} \theta \left(X_i - \frac{M}{M_i} \epsilon_i \right), \quad (9a)$$

where D_i is a coefficient of diffusion of the radical through the mixture, defined by the expression

$$\frac{1}{D_i} = \sum_{j \neq i} \frac{X_j}{D_{ij}}. \quad (10)$$

In the following, Equation (9a) will be used when considering the diffusion of the radicals.

The energy equation makes it possible to eliminate the variable x of the system (2) through (9), which is then transformed as follows:

$$\frac{d\epsilon_i}{d\theta} \frac{\lambda}{m^2 C_p} \frac{w_i}{\theta - 1 + \sum_{j=1}^n q_j (\epsilon_j - \epsilon_{jf})} \quad (11)$$

$$i = 1, 2, \dots, n$$

$$\frac{dX_i}{d\theta} = \frac{\lambda RT_f}{p C_p} \theta \frac{\sum_{j=1}^n \frac{1}{D_{ij}} \left(X_i \frac{\epsilon_j}{M_j} - X_j \frac{\epsilon_i}{M_i} \right)}{\theta - 1 + \sum_{j=1}^n q_j (\epsilon_j - \epsilon_{jf})}. \quad (12)$$

For the diffusion of the radicals, Equation (12) should be replaced, according to Equation (9a), by the following:

$$\frac{dX_i}{d\theta} = \frac{\lambda RT_f}{p M C_p D_i} \frac{\left(X_i - \frac{M}{M_i} \epsilon_i \right)}{\left(\theta - 1 \right) + \sum_{j=1}^n q_j (\epsilon_j - \epsilon_{jf})}. \quad (12a)$$

The solution sought from the system formed by Equations (11) and (12) must be such that the values of ϵ_i and X_i pass from the values ϵ_{i0} and X_{i0} corresponding to the composition of the mixture in the cold boundary of the flame (which corresponds to value θ_0 of the temperature), to the values ϵ_{if} and X_{if} corresponding to the chemical equilibrium for the combustion products in the hot boundary (where $\theta = 1$).

Compatibility of this set of boundary conditions with the remark made in the work cited in reference 10 for the problem of the cold boundary, determines the eigenvalue m , that is, the propagation velocity of the flame:

$$S \equiv v_0 = \frac{m}{\rho_0}. \quad (13)$$

Aside from the fundamental difficulty due to lack of knowledge of the kinetics of flame reactions, the nature of system in Equations (11) and (12) is such that its integration in an explicit form is impossible, even in the simplest cases corresponding to flames with over-all reaction rates, thus making it necessary to seek methods both numerical and analytical, which lead to approximate solutions of the system, combined with reasonable assumptions for some of the properties of the flame.

As an illustration, a description of some of the most important analytical methods, including a comparison of the approximations obtained for typical cases, are to be found in the work cited in references 12 and 13.

THE STEADY-STATE ASSUMPTION

Mathematically it can be expressed as follows: if w_i is the reaction rate of radical i , the condition of pseudo-equilibrium corresponding to the steady-state assumption for it, is:

$$w_i = 0. \quad (14)$$

Because w_i depends on the temperature θ of the mixture and on the molar fractions X_j of different chemical species, including the X_i of the radical, Equation (14) gives a relation between these magnitudes which enables X_i to be expressed as a function of the rest. In particular, if the steady-state assumption is applicable to all the intermediate species of the mixture, as many independent conditions¹⁴ exist as there are radicals, and all their molar fractions can be expressed as functions of the main reactants and products and of the temperature. Because, as we

have said, the concentrations of the main species can be expressed as a function of the temperature, by means of the diffusion equations, the concentrations of the radicals can also be expressed, finally, as functions of θ , which represents a fundamental simplification of the problem.

CRITERION FOR THE APPLICABILITY OF THE STEADY-STATE ASSUMPTION

In order to deduce the criterion, it will be advantageous to consider first the case in which only one radical exists in the flame. The corresponding reaction equation will be written in the following form:

$$\frac{d\epsilon}{d\theta} = \frac{\lambda}{m^2 C_p} \frac{w}{\theta - 1 + \sum_{j=1}^n q_j (\epsilon_j - \epsilon_{jf})}. \quad (15)$$

In Equation (15), w is a known function of the temperature θ and of the molar fraction X of the radical, since it is supposed that the molar fraction of all the other species can be expressed, as already stated, as functions of θ , by means of the corresponding equations of diffusion. Therefore,

$$w = w(\theta, X). \quad (16)$$

As for the denominator of the right-hand side of Equation (15), we will suppose also that $q_j (\epsilon_j - \epsilon_{jf})$ is a known function of the temperature, because approximate methods exist for expressing it in this form, *e.g.*, the method of Sendagorta.^{13b} Then the denominator of Equation (15) is a known function of θ , which we shall now designate with the notation $f(\theta)$:

$$\theta - 1 + \sum q_j (\epsilon_j - \epsilon_{jf}) \equiv f(\theta) \quad (17)$$

and this equation can be written in the form:

$$\frac{d\epsilon}{d\theta} = \frac{\lambda}{m^2 C_p} \frac{w(\theta, X)}{f(\theta)}. \quad (18)$$

As for the diffusion equation of the radical, since its concentration is always very small, Equation (12a) can be applied. Assuming for simplicity that $M = M_i$, (12a) can be written as follows:

$$\frac{dX}{d\theta} = L \frac{X - \epsilon}{f(\theta)}, \quad (19)$$

where L is the Lewis-Semenov number for the

^b If we did not make this supposition, the deduction would become somewhat complicated, but the conclusions remain integrally valid.

diffusion of the radical in the mixture:

$$L = \frac{\lambda}{\rho D_i C_p}. \quad (20)$$

In order to simplify computations, it will be assumed that L is a constant, as well as the value of $\lambda/m^2 C_p$ in Equation (18).

The problem now reduces to the integration of the system formed by the two Equations (18) and (19) with the two unknowns ϵ and X . For this it is convenient to eliminate ϵ from the system, thus obtaining:

$$\begin{aligned} f^2(\theta) \frac{d^2 X}{d\theta^2} + f(\theta)[f'(\theta) - L] \frac{dX}{d\theta} \\ = -L \frac{\lambda}{m^2 C_p} w(\theta, X). \end{aligned} \quad (21)$$

The criterion sought should result, therefore, from the properties of this differential equation and from the values of its parameters.

Let us suppose, for example, that chain breaking is of the first order. Then, once the molar fractions of the principal species are expressed as functions of the temperature, w will be of the form:

$$w = a(\theta) - b(\theta)X \quad (22)$$

and Equation (21) will take the form:

$$\begin{aligned} D(X) = -L \frac{\lambda}{m^2 C_p} b(\theta)[a(\theta) - X]; \\ \alpha(\theta) = \frac{a(\theta)}{b(\theta)}, \end{aligned} \quad (23)$$

where, for brevity, the left-hand side of Equation (21) has been designated by means of the notation $D(X)$.

$$D(X) \equiv f^2(\theta) \frac{d^2 X}{d\theta^2} + f(\theta)[f'(\theta) - L] \frac{dX}{d\theta}.$$

Finally, let k be a measure of the order of magnitude of $b(\theta)$, in such a way that the relation

$$\beta(\theta) = \frac{b(\theta)}{k} \quad (24)$$

is nondimensional and of the order of magnitude of unity.^c Then (23) takes the form:

^c Often, $b(\theta)$ is constant, but if it is not, its maximum value, for example, can be adopted for k .

$$D(X) = -\Omega\beta(\theta)[\alpha(\theta) - X] \quad (25)$$

where

$$\Omega \equiv L \frac{\lambda k}{m^2 C_p} \quad (26)$$

is a dimensionless parameter, the value of which will determine the applicability of the steady-state assumption.

In fact, the steady-state assumption is expressed, by virtue of Equation (14), by the condition:

$$w(\theta, X) \simeq 0, \quad (27)$$

that is to say, by:

$$\alpha(\theta) - X \simeq 0. \quad (28)$$

Comparison of this condition with the differential Equation (25), shows that the necessary and sufficient condition for it to hold, is the following:

$$\frac{D(X)}{\Omega\beta(\theta)} \ll X, \quad (29)$$

which will occur if the parameter Ω is sufficiently large.

PHYSICAL INTERPRETATION OF Ω

The parameter Ω can be written in the form

$$\Omega = L \frac{1/v}{\rho/k}, \quad (30)$$

where

$$1 = \frac{\lambda}{mC_p}$$

is a characteristic length of the thickness of the flame. Therefore,

$$\frac{1}{v} = t_r. \quad (31)$$

Likewise,

$$\frac{\rho}{k} = t_{ch} \quad (32)$$

is a measure of the "chemical time" of the radical.

Therefore, Ω can be expressed in the form:

$$\Omega = L \frac{t_r}{t_{ch}}; \quad (33)$$

and the criterion is reduced to the condition that

the residence time be much greater than the chemical time of the radical.

Therefore, the parameter of the criterion is proportional to the reciprocal of the first Damköhler parameter D_{a1} for the radical in the flame,¹⁴ which is given by the expression:

$$D_{a1} \equiv \frac{t_{ch}}{t_r} = \frac{L}{\Omega}. \quad (34)$$

Even when the deduction has been performed for the particular form of $w(\theta, X)$ given by Equation (22), all conclusions and in particular the value of Ω are completely general. For example, if the chain is one of second-order breaking then Equation (22) must be replaced by the following:

$$w = a(\theta) - b(\theta)X^2, \quad (35)$$

which in no way changes the ultimate development of the calculations.

COMPARISON WITH THE CRITERION OF GIDDINGS AND HIRSCHFELDER

The relation between Ω and the parameter of Giddings and Hirschfelder Ω_H , appears when we consider that t_{ch} is essentially the time that they propose, while m^2 , which appears in Ω , is proportional to the time of reaction of the principal species in the flame. In effect, if one considers the over-all reaction rate w_g of the main species, a simple dimensional analysis shows that m must be of the form:

$$m \sim \sqrt{\frac{\lambda w_g}{C_p}} \quad (36)$$

so that Ω is:

$$\Omega \sim \frac{k}{w_g} = \Omega_H. \quad (37)$$

However, Ω has the advantage of being a well-defined magnitude for the calculation of each practical case, which includes, also, the effects of diffusion.

RECURRENCE METHOD

From the observation that the distribution of radicals corresponding to the steady-state assumption constitutes a good approximation for large values of the parameter Ω , it seems logical to apply the method of Poincaré to the solution of Equation (25), by expressing it as a

power series of $1/\Omega$, in the form:

$$X = \sum_{j=0}^{\infty} \frac{1}{\Omega^j} X_j(\theta) \tag{38}$$

where $X_j(\theta)$ are functions of θ to be determined by means of Equation (25), the expressions of which are obtained immediately in the usual way. The result is:

$$X_0(\theta) = \alpha(\theta)$$

$$X_j(\theta) = \frac{f^2(\theta)}{\beta(\theta)} \frac{d^2 X_{j-1}(\theta)}{d\theta^2} + \frac{f(\theta)}{\beta(\theta)} \left[\frac{df(\theta)}{d\theta} - L \right] \frac{dX_{j-1}(\theta)}{d\theta} \tag{39}$$

Therefore, in this development, the first approximation, $X_0 = \alpha$, of X is that corresponding to the distribution given by the steady-state assumption, and the successive approximations can be obtained from this, by means of the recurrence law (39), thus obtaining:

$$X^{(n)} = X^{(n-1)} + \frac{1}{\Omega^n} X_n \tag{40}$$

In the practical application of this method, the

fact that $f(\theta)$ is always zero in the hot limit $\theta = 1$ of the flame, plays an important role, favoring the rapid convergence of the successive approximations in the proximity of this boundary, whose region influences more decisively the characteristics of the flame.

On the contrary, the function $\beta(\theta)$, which takes on very small values in the proximity of the cold zone when the activation energy of the chain-breaking reaction is appreciable, slows up considerably the convergence of the solution (40) in the said region, where the knowledge of the exact distribution of the radicals is of very little interest.

Such behavior is not surprising, because the steady-state assumption is only valid in the zone where the product $\Omega\beta(\theta)$ is very large with respect to unity and this ceases to be the case in the zone where $\beta(\theta)$ is very small.

INFLUENCE OF DIFFUSION

To show the influence of the diffusion of the radicals on the validity of the steady-state assumption, Equation (25) must be written

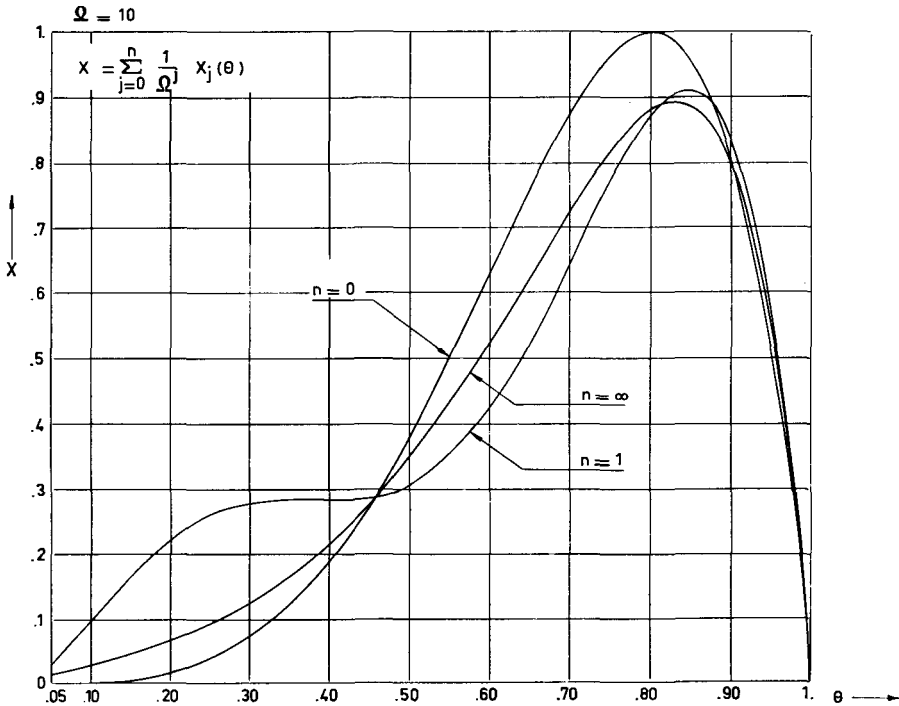


FIG. 1

in the form:

$$X = \alpha(\theta) - \frac{f(\theta)}{\Omega_1 \beta(\theta)} \frac{dX}{d\theta} + \frac{1}{\Omega \beta(\theta)} \left[f^2(\theta) \frac{d^2 X}{d\theta^2} + f(\theta) f'(\theta) \frac{dX}{d\theta} \right] \quad (41)$$

where Ω_1 is the value of Ω corresponding to a Lewis-Semenov number equal to unity.

$$\Omega_1 = \frac{\lambda k}{m^2 C_p}$$

Equation (43) shows that the distribution of the radicals is a sum of the $\alpha(\theta)$ corresponding to the steady-state assumption and of two cor-

rection terms. The first is independent of diffusion and measures the deviation produced by purely chemical effects, due to the fact that the total process must occur within the "residence time"; the second, on the contrary, measures the influence of diffusion and is directly proportional to D . In practical cases, the deviation originated by diffusion is frequently of the same order of magnitude, or even greater than that corresponding to the chemical effects.

Although the diffusions of the principal species influence the values of $\alpha(\theta)$ and $f(\theta)$ as well as that of Ω through the value of m , this last is the dominant effect, so that the diffusion of the main species is favorable, because it increases the residence time in the flame.

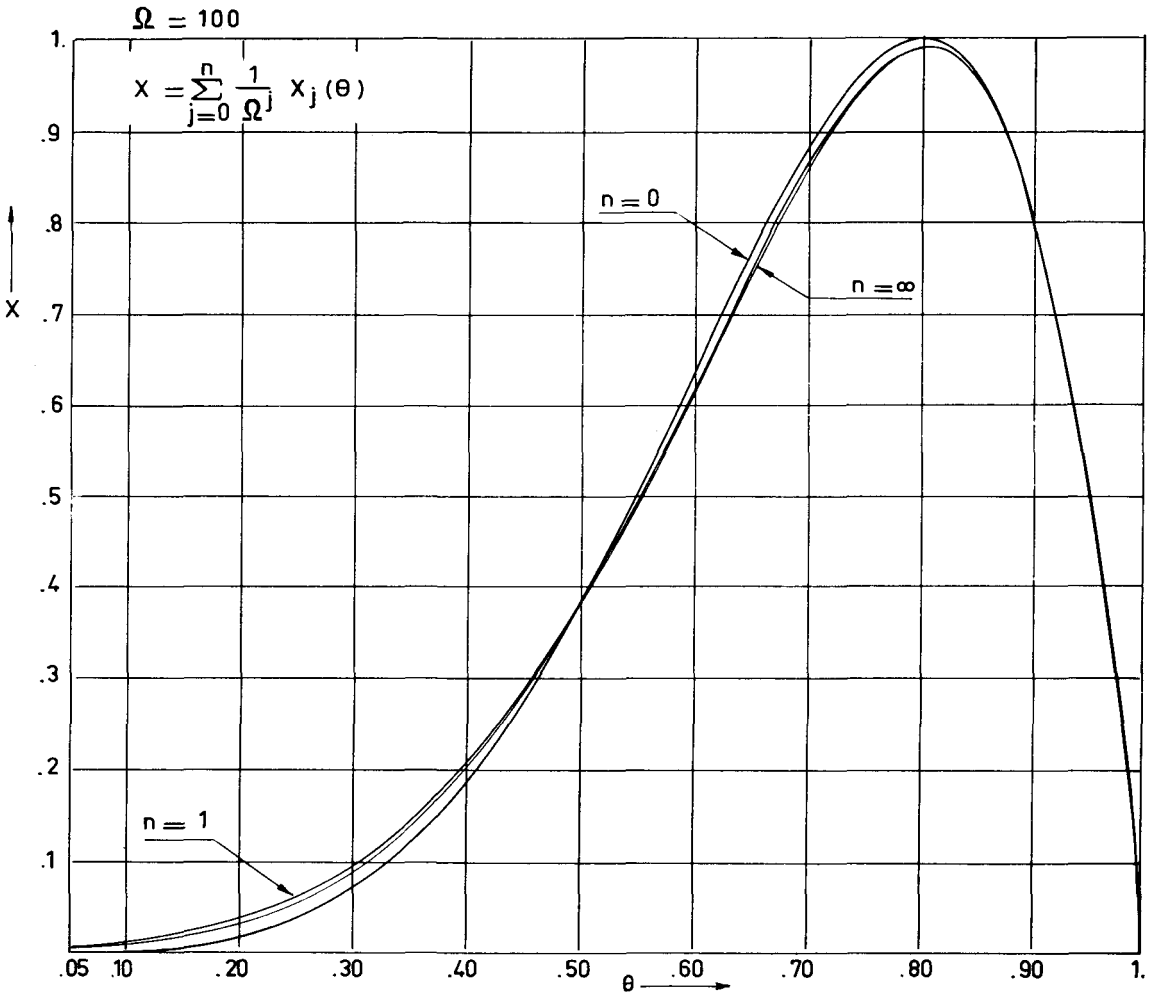


FIG. 2

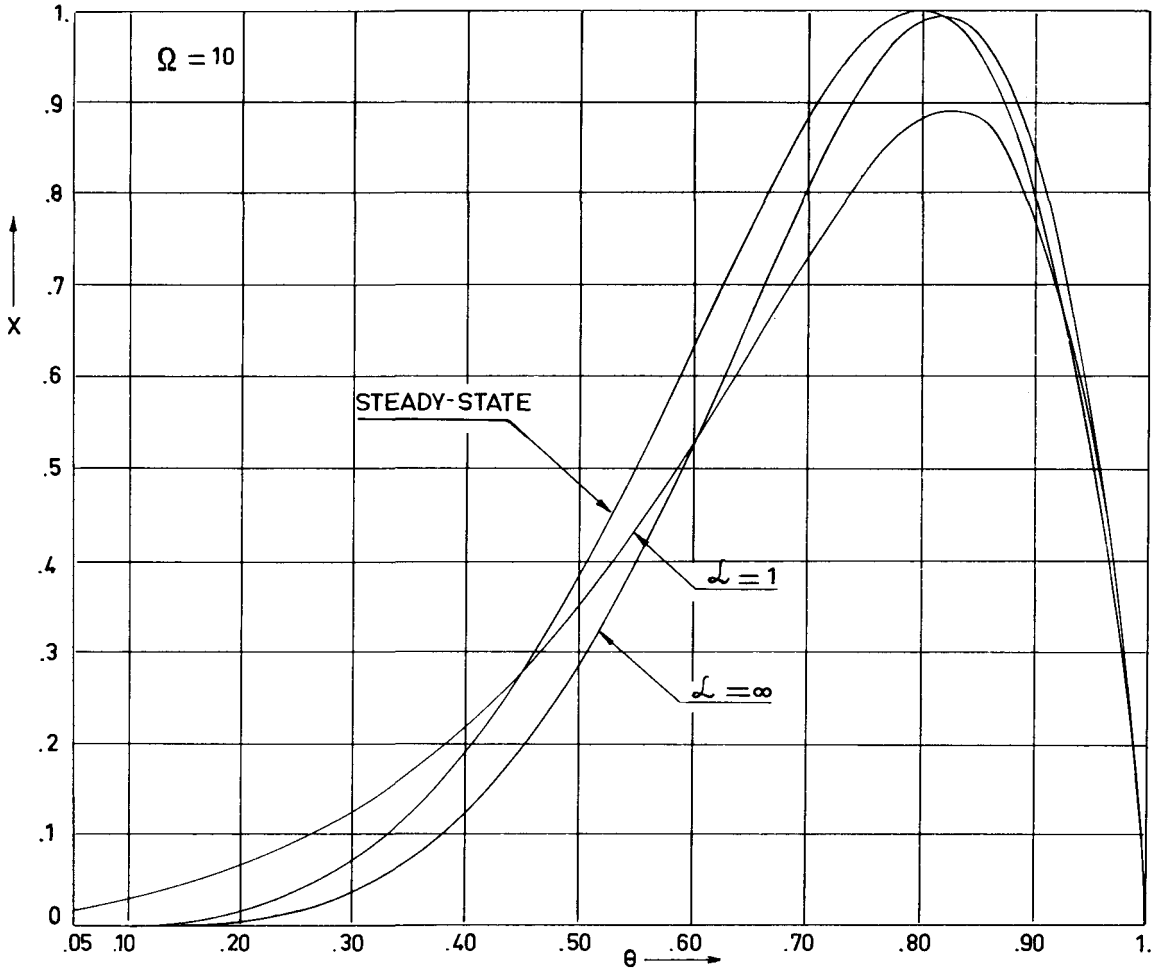


FIG. 3

MATHEMATICAL MODEL

By proper choice of $\alpha(\theta)$, $f(\theta)$ and $\beta(\theta)$ in Equation (25), it is possible to obtain a simplified equation which, keeping all the characteristics of the flame, makes it possible to obtain an explicit solution of it which allows an easy comparison between the exact and approximate solutions.

For this purpose, the following expression is adopted for $\alpha(\theta)$:

$$\alpha(\theta) \equiv \frac{(n + 1)^{n+1}}{m^n} (1 - \theta) \theta^n \quad (42)$$

which is a good approximation of the expression

$$\alpha(\theta) \equiv A(1 - \theta)e^{-\theta_a(1-\theta)/\theta} \quad (43)$$

corresponding to a first-order reaction for the production of the radical.

For $f(\theta)$ the following simple expression

$$f(\theta) \equiv 1 - \theta \quad (44)$$

is taken, because the only condition of interest for this function is that it must be zero in the hot boundary ($\theta = 1$), and it permits integration of Equation (25).

Finally, it will be assumed that $\beta(\theta)$ is constant and equal to unity, which corresponds to a zero-activation energy for the destruction of the radical, and that the Lewis-Semenov number for it is equal to one.

With all of these assumptions, Equation (25) is reduced to the following:

$$(1 - \theta)^2 \frac{d^2 X}{d\theta^2} - 2(1 - \theta) \frac{dX}{d\theta} = -\Omega \left[\frac{(n + 1)^{n+1}}{n^n} (1 - \theta)\theta^n - X \right] \quad (45)$$

whose solution is

$$X = c(1 - \theta)^{(\sqrt{1+4\Omega}-1)/2} + (1 - \theta) \sum_0^n a_j \theta^j \quad (46)$$

where a_j are numerical coefficients, depending on n and Ω , and the value of the constant c is determined by the condition at the cold

boundary:

$$\theta = \theta_0 \quad X = X(0). \quad (47)$$

Figures 1 and 2 compare the exact and the approximate results for $\Omega = 10$ and $\Omega = 100$. It is observed that for $\Omega = 100$, the approximation of the steady-state assumption is excellent. For $\Omega = 10$, although it is not so good, can be considered acceptable and improves considerably, particularly in the zone of greater interest, when the second approximation is taken into account.

Figure 3 shows the influence of radical diffusion for $\Omega = 10$. It is observed that it is considerable, and consists, mainly, in a reduction of the maximum concentration.

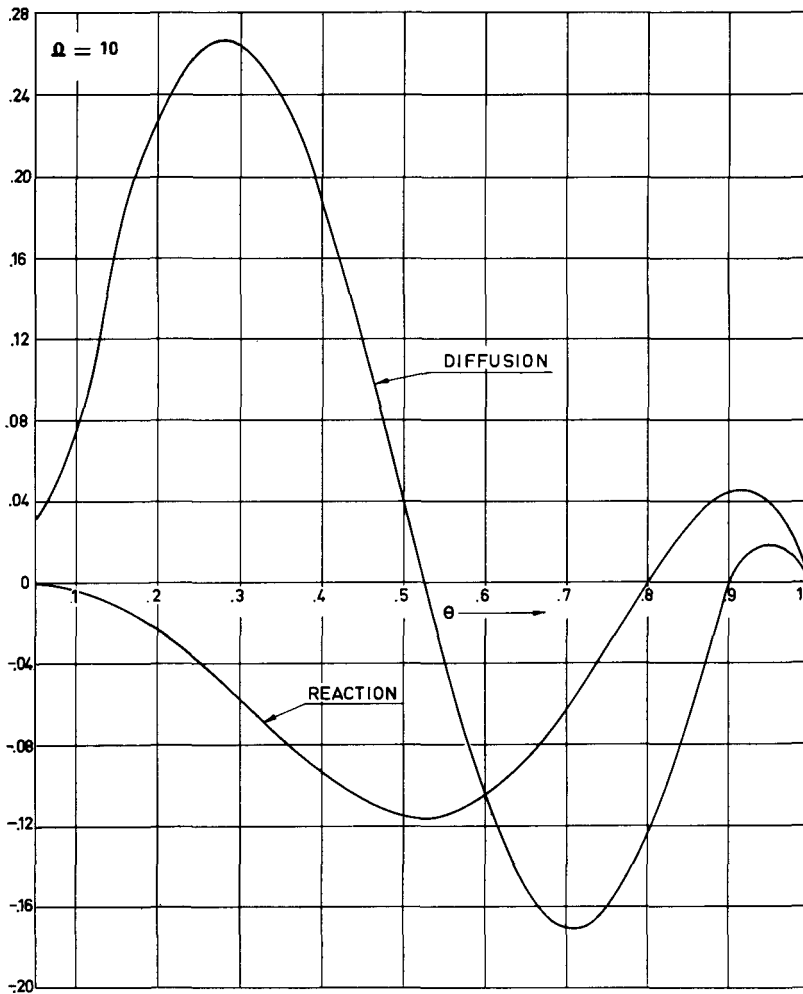


FIG. 4

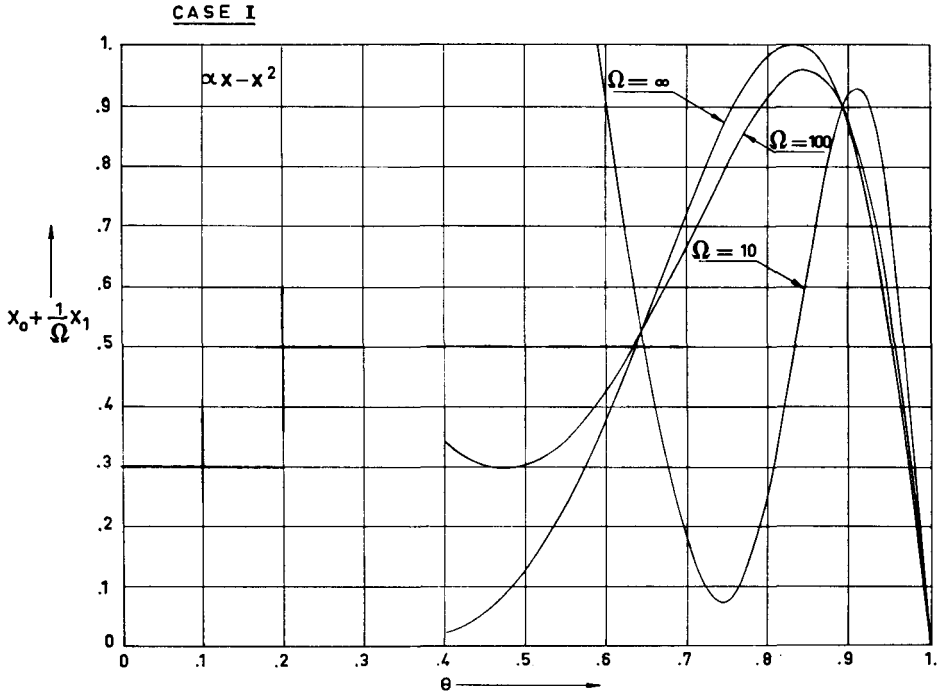


FIG. 5

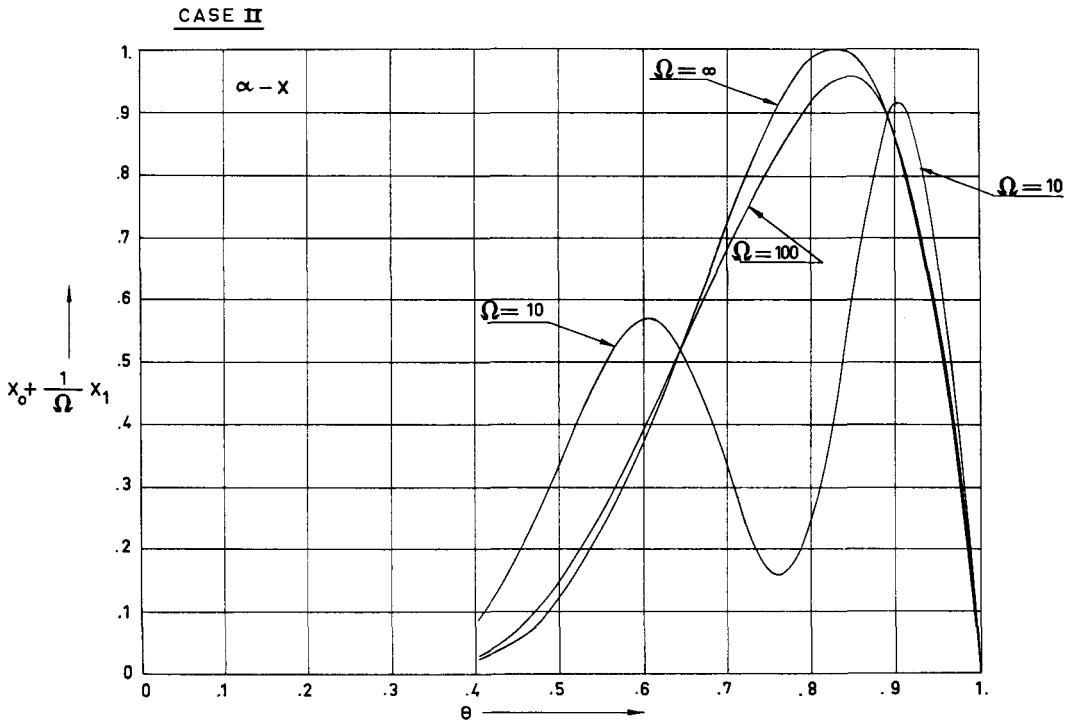


FIG. 6

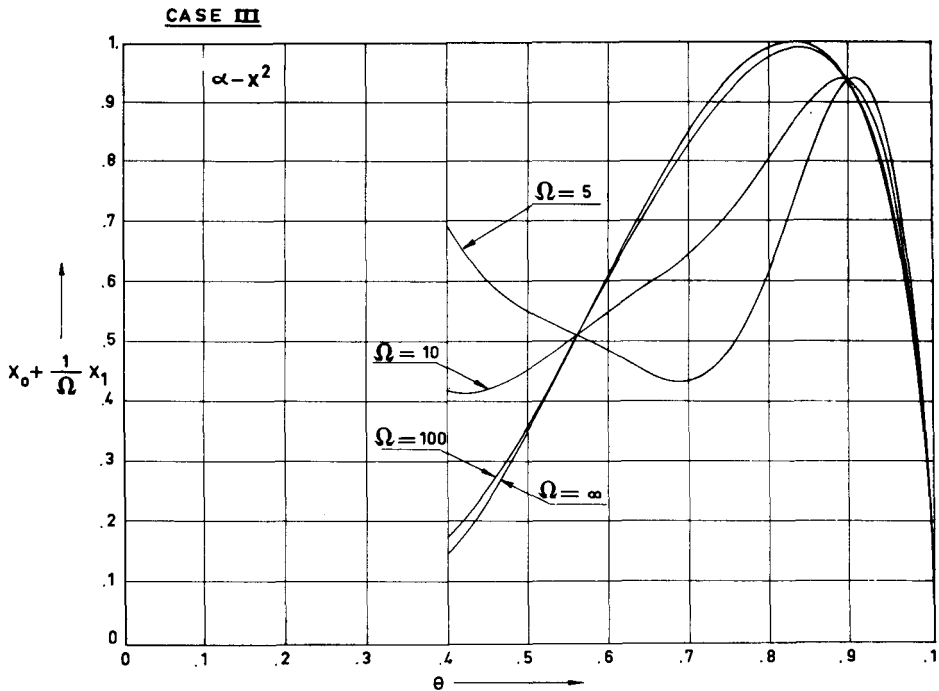


FIG. 7

Finally, Figure 4 shows the deviations of the steady-state distribution for $\Omega = 10$ due to the separate effects of diffusion and chemical reaction.

INFLUENCE OF THE FORM OF THE REACTION EQUATION OF THE RADICAL

To determine how the applicability of the steady-state assumption affects the reaction equation of the radical, the corresponding solutions to three cases which differ only in such an equation have been calculated,¹⁵ with the use of the same differential Equation (20) but with the following models of the reaction rate $w(\theta, x)$ of the radical, which correspond to typical models of chain reactions:

$$\text{Case I} \quad w = \alpha(\theta)X - X^2 \quad (48)$$

$$\text{Case II} \quad w = \alpha(\theta) - X \quad (49)$$

$$\text{Case III} \quad w = \alpha(\theta) - X^2. \quad (50)$$

The solutions are shown in Figures 5, 6 and 7, respectively, in which it can be proved that for equal values of Ω , the greater approximation corresponds to Case III and the lesser to I, even

TABLE 1

Flame ^a	Reaction Rate of the Radical	Value of Ω	Applicability of the Steady-State Assumption
Hydrazine ^{5, 16, 17}	$\alpha - X^2$	0.793 L	No
Hydrogen ⁷	$\alpha X - X^2$	4.500 L	Yes
Ozone ⁴	$\alpha - X$	1.800 L	Yes
Hydrogen-bromine ^{6, 18, 19}	H: $\alpha - X$ Br: $\alpha - X^2$	54.500 L 45 L	Yes No

^a Previous studies from which the kinetic schemes and values of the physical/chemical constants have been taken.

though the difference between this and the second is really very small.

Applications

The method described has been applied to the study of various flames previously considered by different authors, following different procedures.

Table 1 contains the data relative to each of these flames and the values of Ω corresponding to the different radicals which justify the known results referring to the validity or not of the steady-state assumption.

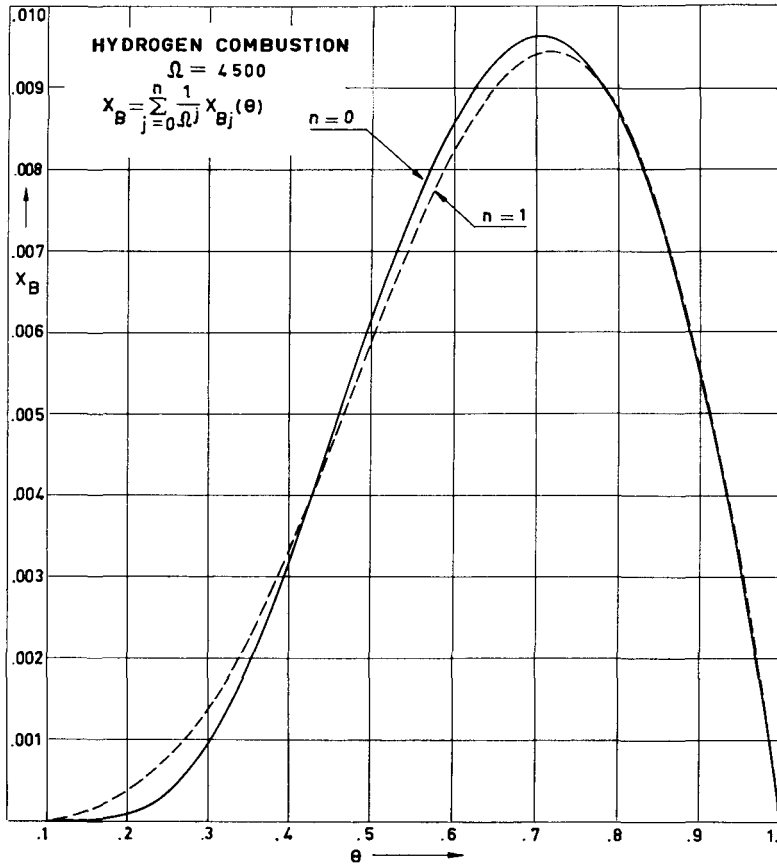


FIG. 8

As an illustration, Figures 8 and 9 give the distribution of radicals corresponding to the steady-state assumption and to the successive approximations that are obtained by application of the proposed method, in two different cases. In the case of the hydrazine-decomposition flame, the method is not valid because it does not converge. The exact solution has been obtained by numerically integrating the flame equations.

Nomenclature

- | | | | |
|----------|---|------------|--|
| B | frequency factor in the specific reaction rate | M | mean molar mass |
| C_p | specific heat at constant pressure | M_i | molar mass of species i |
| D_i | diffusion coefficient of a radical in the mixture | m | mass flow per unit surface parallel to the flame |
| D_{ij} | binary diffusion coefficient | p | pressure |
| E_a | activation energy | q | specific reaction heat |
| h | specific enthalpy | R | constant of gases |
| k | reaction-rate constant | S | propagation velocity of the flame |
| L | Lewis-Semenov number | T | absolute temperature |
| l | characteristic length of the flame | t_{ch} | chemical time |
| | | t_r | residence time |
| | | v | velocity of the mixture |
| | | v_d | diffusion velocity |
| | | w | reaction rate |
| | | w_g | over-all reaction rate of main species |
| | | X | mole fraction |
| | | x | spatial coordinate |
| | | ϵ | flux fraction |
| | | θ | reduced temperature = T/T_f |
| | | θ_a | reduced activation temperature |
| | | Δ | dimensionless parameter of the flame equations |
| | | λ | thermal conductivity coefficient |

HYDRAZINE COMBUSTION

$$\Omega = 0.793$$

$$x_B = \sum_{j=0}^n \frac{1}{\Omega} x_{Bj}(\theta)$$

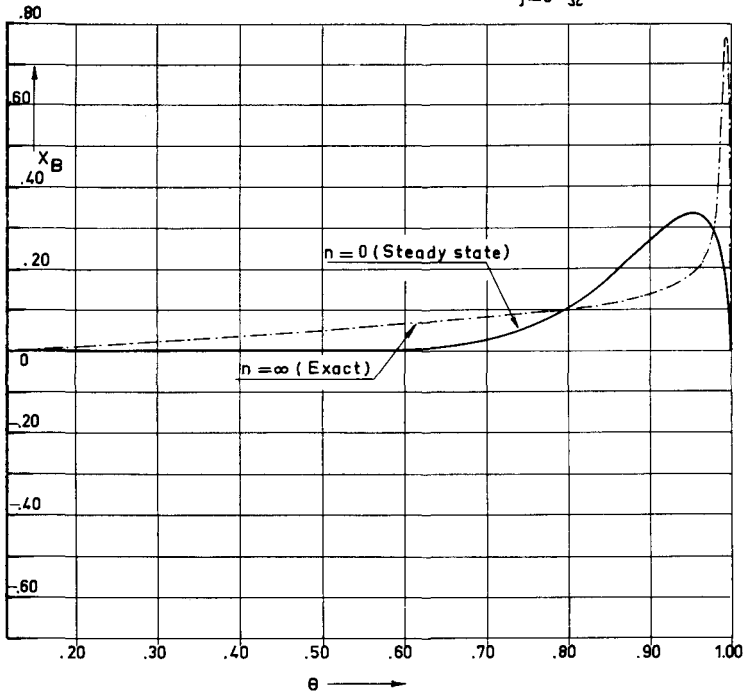


FIG. 9

ν stoichiometric coefficients
 ρ density of the mixture
 Ω dimensionless parameter of the flame equations

SUBSCRIPTS

i, j species
 n order of perturbation
 0 unburned gases
 f products

SUPERSCRIPIT

n recurrence law for calculating the distribution of radicals

REFERENCES

1. BODENSTEIN, M.: *Z. physick Chem.*, **85**, p. 329 (1913).
2. BENSON, S. W.: *J. Chem. Phys.*, **20**, 1605 (1952).
3. VON KÁRMÁN, T., AND PENNER, S. S.: *Selected Combustion Problems*. p. 5. Butterworths Scientific Publications, London, 1954.
4. HIRSCHFELDER, J. O., CURTISS, C. F., AND CAMPBELL, D. E.: Univ. Wisconsin Rep. No. C M-756 1952.
5. MILLÁN, G., AND SANZ, S.: Report Contract No AF-61(514)-734 C. ARDC. 1956.
6. VON KÁRMÁN, T., AND MILLÁN, G.: Tech. Rep. No. 16. Part II Contract No. DA-04-495. Ord 446. 1956.
7. GIDDINGS, J. C., AND HIRSCHFELDER, J. O.: *Sixth Symposium (International) on Combustion*, p. 199. Reinhold Publishing Corporation, New York, 1957.
8. MILLÁN, G., AND DA RIVA, I.: I. N. T. A. Esteban Terradas. Rep (A.F.O.S.R. TN 59-626). [AD 217811] 1959.
9. DA RIVA, I., AND MILLÁN, G.: I. N. T. A Esteban Terradas. Rep (A.F.O.S.R. TN 59-627) [AD 217812] 1959.
10. VON KÁRMÁN, T.: *Sixth Symposium (International) on Combustion*, p. 1. Reinhold Publishing Corporation, New York, 1956.
11. HIRSCHFELDER, J. O., AND CURTISS, C. F.: *Third Symposium (International) on Combustion*, pp. 121-127, The Williams & Wilkins Company, Baltimore, 1949.
12. MILLÁN, G., SENDAGORTA, J. M., AND DA

- RIVA, I.: I. N. T. A. Esteban Terradas, Rep. (A.F.O.S.R. TN 57-663) [AD 13658] 1957.
13. MILLÁN, G., DA RIVA, I.: I.N.T.A. Esteban Terradas. Rep. (A.F.O.S.R. TN 58-823) [AD 202907] 1958.
14. VON KÁRMÁN, T.: Zeitschrift für Flugwissenschaften pp. 3-5, Jan.-Feb. 1956.
15. MILLÁN, G., AND DA RIVA, I.: I.N.T.A. Esteban Terradas. Rep. not yet published.
16. ADAMS, G. K., AND STOCKS, G. W.: *Fourth Symposium (International) on Combustion*, p. 239. The Williams & Wilkins Company, Baltimore, 1953.
17. SPALDING, D. B.: Phil. Trans. Roy. Soc. (London), 1956.
18. CAMPBELL, E., AND HIRSCHFELDER, J. O.: C F 2108, University of Wisconsin 1953
19. GILBERT, M., AND ALTMAN, D.: *Sixth Symposium (International) on Combustion*, pp. 222-236, Reinhold Publishing Corporation, New York, 1957.

40

THE THEORY OF FLAME PROPAGATION IN SYSTEMS INVOLVING BRANCHED CHAIN REACTIONS

By L. A. LOVACHEV

Introduction

The theory of laminar flame propagation in systems involving straight-chain reactions was developed¹⁻⁴ and verified by comparison with experimental results on chlorine-hydrogen flames.^{3, 4}

The first part of this paper is concerned with the theory of flame propagation in chain-branching systems represented by a model reaction with a chain center of a single type. The rates of chain initiation, chain propagation, chain branching, and quadratic-chain termination were taken into account in solving this problem. The problem of flame propagation in a system involving a three-center branched-chain reaction is solved in the second part.⁵ The hydrogen-combustion reaction is taken as a model reaction of this type. A system of equations for heat conductivity and three equations for the diffusion of hydroxyl radicals, hydrogen atoms, and oxygen atoms are also considered in the second part, but without taking into account the quadratic-chain termination.

Theoretical Treatment

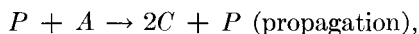
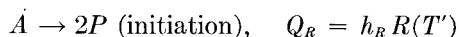
A MODEL ONE-CENTER REACTION

A system of differential equations describing the flame-propagation process for a branched-chain reaction was numerically integrated in the work of Giddings and Hirschfelder.⁶ The branched-chain reaction was represented by a one-center model reaction involving two processes: $2P \rightarrow A$ (quadratic-chain termination) and

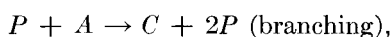
$P + A \rightarrow C + 2P$ (propagation and branching processes).

A general solution for the problem of chain propagation in the case of a one-center model reaction was treated primarily in the 1958 work by the author,⁷ where simple formulae for the determination of burning velocity, taking into account branching and the rate of the quadratic termination of the chain effects, were derived for reactions of the degenerate-branching type. A simple approximate formula consistent with the reaction scheme adopted in the work cited in reference 6 may be obtained,⁷ and the difference in the burning-velocity value calculated by means of this formula and the results obtained by numerical integration⁶ may be determined, as has been done for straight-chain reactions.¹⁻³

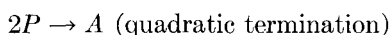
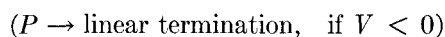
The reaction scheme where A is the initial substance, P is the active center, and C is the reaction product, will be written⁷ as



$$Q_n = hF n = hK(T')n_A n$$



$$Q_V n = h_V V n = h_V K_V(T')n_A n$$



$$Q_W n^2 = h_W W(T')n^2.$$