

Escuela Ingenieros Aeronáuticos, Madrid, Spain

The Internal Structure of Hydrogen-Air Diffusion Flames¹

By

Ignacio Da-Riva

With 9 Figures

*(Received May 4, 1966)***Abstract**

The Internal Structure of Hydrogen-Air Diffusion Flames. The purpose of this paper is to study finite rate chemistry effects in diffusion controlled hydrogen-air flames under conditions appearing in some cases in a supersonic combustor. Since for large reaction rates the flame is close to chemical equilibrium, the reaction takes place in a very thin region, so that a "singular perturbation treatment" of the problem seems appropriate. It has been shown previously that, within the inner or reaction zone, convection effects may be neglected, the temperature is constant across the flame, and the mass fraction distributions are given by ordinary differential equations, where the only independent variable involved is the coordinate normal to the flame surface. The solution of the outer problem, which is a pure mixing problem with the additional condition that fuel and oxidizer do not coexist in any zone, provides the following information: the flame position, rates of fuel consumption, temperature, concentrations of species, fluid velocity outside of the flame, and the boundary conditions required to solve the "inner problem." The main contribution of this paper consists in the introduction of a fairly complicated chemical kinetic scheme representing hydrogen-oxygen reaction. The nonlinear equations expressing the conservation of chemical species are approximately integrated by means of an integral method. It has been found that, in the case considered of a near-equilibrium diffusion flame, the role played by the dissociation-recombination reactions is purely marginal, and that some of the second order "shuffling" reactions are close to equilibrium. The method shown here may be applied to compute the distance from the injector corresponding to a given separation from equilibrium, say ten to twenty per cent. For the cases where this length is a small fraction of the combustion zone length, the equilibrium treatment describes properly the flame behavior.

Résumé

La structure interne d'une flamme de diffusion hydrogène-air. Par cette étude nous prétendons examiner les effets de vitesse de réaction chimique finie en flammes de diffusion d'hydrogène-air, dans les conditions semblables à celles qui se présentent dans certains cas,

¹ This research, done at INTA, Madrid, Spain, has been sponsored by the Office of Scientific Research under Grant No. AF EOAR 65-69 through the European Office of Aerospace Research (OAR), United States Air Force.

dans les chambres de combustion supersonique. Etant donné que pour les grandes vitesses de réaction, la flamme est proche de l'équilibre chimique et la zone de réaction est très mince, il semble approprié d'utiliser une méthode de perturbations singulières pour résoudre ce problème. Il a été précédemment démontré que dans la zone de réaction, on peut négliger les effets de convection, la température est constante dans chaque section de la flamme, et les distributions des espèces chimiques sont données par des équations différentielles, par lesquelles la coordonnée normale à la surface de la flamme est l'unique variable indépendante. La solution du problème extérieur, qui est un problème de mélange ajouté à ce que combustible et oxydant ne coexistent nulle part, donne l'information suivante: position de la flamme, consommation de combustible, température, concentration d'espèces et vitesse du fluide à l'extérieur de la flamme, et les conditions de contour nécessaires pour résoudre le "problème intérieur". Ce qu'apporte principalement cette étude est l'introduction d'une loi de cinétique-chimique assez compliquée, et représentative de la réaction hydrogène-oxygène. Les équations non-linéaires, qui expriment la conservation des espèces chimiques, s'intègrent approximativement par une méthode intégrale. On constate que, dans le cas considéré de flamme de diffusion proche de l'équilibre, le rôle des réactions de dissociation-recombinaison est peu important et que quelques réactions de second ordre sont très proches de l'équilibre. La méthode exposée permet de calculer la distance existante jusqu'à l'injecteur correspondant à un certain degré d'écart d'équilibre (de 10 à 20%). Dans les cas où cette longueur serait petite comparée à la longueur de la zone de combustion, l'hypothèse d'équilibre décrirait proprement la conduite de la flamme.

Резюме

Внутренняя структура пламени диффузии водорода — воздуха. В этой работе сделана попытка изучения эффектов скорости конечной химической реакции в пламени диффузии водорода-воздуха в аналогичных условиях, которые часто встречаются в некоторых сверхзвуковых камерах сгорания. Ввиду того, что при больших скоростях реакции пламя находится близко к состоянию равновесия и, что область реакции очень тонка, кажется целесообразным использование метода perturbаций для решения этой задачи. Ранее было доказано, что внутри зоны реакции можно пренебречь эффектами конвекции, считать в каждой секции пламени температуру постоянной, и распределение массовых фракций данным

в форме обыкновенных дифференциальных уравнений, в которых в качестве независимой переменной взята только координата нормальная к поверхности пламени. Решение внешней задачи, представляющей собой задачу смеси с дополнительным условием, что горючее и окислитель не могут сосуществовать вместе, дает нам следующие данные: положение пламени, расход горючего, температуру, концентрацию продуктов, скорость газа в наружной части пламени и пограничные условия, необходимые для решения «внутренней задачи». Главный вклад этой работы заключается в введении довольно сложной, новой химически-кинетической схемы, представляющей реакцию водорода с кислородом. Неоднородные уравнения, выражающие превращения химических продуктов, приближенно интегрируются с помощью интегрального метода. Доказывается, что в случае рассмотренной пламени, близкого к состоянию равновесия, роль реакции разложения-восстановления мало важна, и что некоторые реакции второго порядка также очень близки состоянию равновесия. Предложенный метод позволяет рассчитывать расстояние до инжектора, соответствующее некоторой неуравновешенности (от десяти до двадцати процентов). В тех случаях, когда это расстояние очень мало по сравнению с длиной зоны горения, гипотеза равновесия приближенно описывает поведение пламени.

1. Introduction

In order to make a realistic appraisal of the performance of a diffusion controlled supersonic combustor for a *Screamjet*, we need a previous knowledge of the internal structure of diffusion flames.

When flying at high Mach numbers in the atmosphere, within the range proposed for vehicles operating with this type of engine, the static temperature and pressure in the combustor may be sufficiently large as to make chemical time small compared to the characteristic mechanical time. In that case, the reaction is diffusion controlled throughout the combustion chamber, except near the injector exit (if a coflowing jet of fuel is introduced in the oxidizer stream) where, owing to the large concentration gradients and low temperatures involved, the diffusion time is smaller than the chemical time.

Since for large reaction rates the flame is close to chemical equilibrium, the reaction takes place in a very thin region. The subject of the present paper is the study of this inner region when hydrogen and air are the fuel and oxidizer respectively.

A solution of the problem, obtained by assuming infinitely fast reaction rates, has been known long ago: the "thin flame" or BURKE-SCHUMANN equilibrium solution [1]. This solution is not uniformly valid because concentration and temperature derivatives normal to the flame surface are discontinuous at the flame. These discontinuities, which are due to the fact that, in the limiting process, the reaction region shrinks to a sheet, indicate that transport terms play a dominant role in the combustion zone of the large, although finite, reaction rate case.

The infinitely fast reaction solution, may be viewed as the "outer solution" of our problem, useful to calculate the flame position, fuel consumption per unit flame area, and to provide the outer boundary conditions for the "inner problem."

From the solution of this "inner problem" we get a criterion for the existence of an infinitely thin flame. Such a thin flame seems to be desirable from the combustion efficiency point of view.

Although the work presented has been undertaken to investigate the behavior of a supersonic combustor, some of the results will become relevant to other problems of technical interest, namely: transpiration cooling and hybrid combustion.

Hydrogen is very effective to protect a surface exposed to convective heat flux [2, 3, 4]. The effectiveness is due to the large heat absorption capability per unit mass of hydrogen. However, when hydrogen-oxygen combustion occurs in the boundary layer, the mass flow required to maintain a prescribed surface temperature raises.

Concerning hybrid combustion, it seems interesting to study the kinetic effects of reaction intermediates (in particular, oxygen atoms) reaching the wall, since evidence exists [5] that these atoms are very active in attacking the surface, hence, we must know the structure of the homogeneous reaction zone, to calculate the amount of the atoms going to the surface.

The internal structure of laminar diffusion flames, supported by a one step, second order chemical reaction of the Arrhenius type, has been analyzed previously [6].

We will present in this paper the fundamental ideas of the method used in [6]. However, specific emphasis is placed on its application to the study of the hydrogen-oxygen or hydrogen-air flames.

The study presented here, allows us to calculate, to the first order, the distribution of species across the flame for a quite general set of outer solutions. But we must calculate higher order terms to account for flames not too close to equilibrium. This computation requires additional analysis not presented here.

The paper is organized as follows. Firstly we present a small account of the method used in [6]. Then we consider the hydrogen-oxygen chemical kinetics. The distributions of species are computed, by using an integral method, for given outer conditions. Finally we consider the matching of the inner solution with a general set of outer solutions.

2. Structure of Laminar Diffusion Flames

Let us begin by writing the governing equations of a reacting gas mixture. Since we assume that the Reynolds number is large, we use the laminar boundary layer equations to study the mixing layer, up to order $Re^{-1/2}$. For the details of the arguments and basic assumptions leading to these equations see [7, 8].

When using a boundary layer coordinate system, Fig. 1, these equations take the following non-dimensional form:

$$\text{Continuity for the mixture} \\ \frac{\partial}{\partial x} (\rho u r^k) + \frac{\partial}{\partial y} (\rho v r^k) = 0 \quad (1)$$

$k = 0$ for two-dimensional flow and $k = 1$ for axially symmetrical flow.

Conservation of reactants and intermediate species

$$u \frac{\partial Y_i}{\partial x} + v \frac{\partial Y_i}{\partial y} = \frac{1}{Re \varrho} \frac{\partial}{\partial y} \left(\frac{\mu}{Sc} \frac{\partial Y_i}{\partial y} \right) + \frac{w_i}{d \varrho} \quad (2)$$

where

$Re = VL \varrho_0 / \mu_0$ is the Reynolds number

$Sc = \mu / \varrho D$ is the Schmidt number

$d^{-1} = LU/V$ is the first Damköhler parameter

V, L, ϱ_0, μ_0 are characteristics magnitudes, and U a characteristic reaction frequency. The remaining variables are non-dimensional.

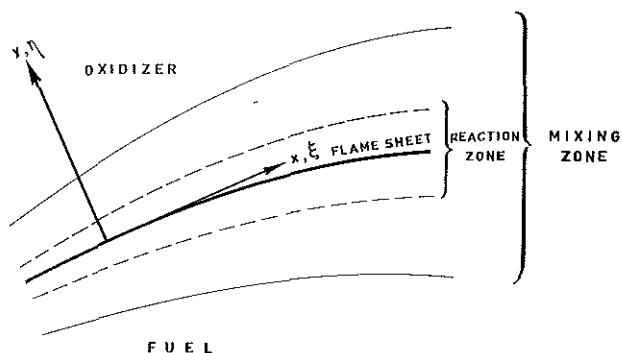


Fig. 1. Coordinate system of the boundary layer type

The concentration of products is obtained by using the expression

$$\Sigma Y_i = 1 - Y_N$$

where Y_N is the concentration of inert species.

Momentum

$$u \frac{\partial u}{\partial x} + v \frac{\partial u}{\partial y} = -\frac{1}{\varrho} \frac{d p_e}{d x} + \frac{1}{Re \varrho} \frac{\partial}{\partial y} \left(\mu \frac{\partial u}{\partial y} \right) \quad (3)$$

Energy

$$u \frac{\partial h_s}{\partial x} + v \frac{\partial h_s}{\partial y} = \frac{1}{Re \varrho} \frac{\partial}{\partial y} \left(\frac{\mu}{Pr} \frac{\partial h_s}{\partial y} \right) + \frac{1}{Re \varrho} \frac{\partial}{\partial y} \left[\mu \left(1 - \frac{1}{Pr} \right) \frac{\partial}{\partial y} \frac{u^2}{2} \right] + \frac{1}{Re \varrho} \frac{\partial}{\partial y} \left[\frac{\mu}{Sc} \left(1 - \frac{1}{Le} \right) \Sigma h_i \frac{\partial Y_i}{\partial y} \right] \quad (4)$$

where

$h_s = \Sigma h_i Y_i + \frac{u^2}{2}$ is the total specific enthalpy,

$h_i = h_i^0 + \int c_{pi} dT$ is the chemical enthalpy of species i ,

$Pr = \mu c_p / \lambda$ is the Prandtl number on the basis of a mean c_p and

$Le = Pr / Sc$ is the Lewis number.

State of gases

$$M p_e - \varrho T \quad (5)$$

where M is a nondimensional mean molecular mass.

According to the usual boundary layer approximation, the mixing layer thickness δ_m is of order $L/Re^{1/2}$. v and y are of the same order, while $x, u, \varrho, p_e, Y_i, h_s$ and T are of order unity.

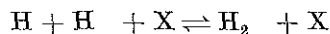
In the limiting case of infinite reaction rate, the solution presents the following peculiarities:

(a) The thickness of the reaction zone is zero.

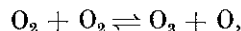
(b) Concentrations of intermediate species are zero everywhere, while the concentration of oxidizer is zero at the fuel side of the flame and concentration of fuel is zero at the oxidizer side.

(c) The first derivatives of the principal species and temperature normal to the flame are discontinuous there.

Paragraph (b) deserves more careful analysis when dissociation-recombination reactions, such as



or chain initiation reactions, like



play an important role in the zone considered, since these reactions do not reach equilibrium under conditions stated in (b). In our case we may assume these reactions to be frozen in the diffusion flame zone, although some of them control the ignition process near the injector exit. This assumption will be discussed later.

The above mentioned peculiarities suggest us that in the case of very large although finite values of d^{-1} , the following properties hold in the reaction zone.

(a) The thickness δ_c of the zone is very small. y/δ_c is of order unity.

It must be pointed out that, although the Reynolds number is usually fairly large, we assume $\delta_c/\delta_m \ll 1$, so that in problems such as diffusive combustion in a boundary layer or a free mixing layer, the reaction zone thickness is smaller than the boundary layer, or mixing layer, thickness. This happens to be true in cases of technical interest [9].

(b) The concentrations of reactants and intermediate species are of order δ_c/δ_m , but the mass fraction of products Y_p and inert species Y_m are of order unity.

(c) The diffusion terms will balance the chemical production terms.

Since for a second order chemical kinetics, the reaction terms are of order $d^{-1}(\delta_c/\delta_m)^2$ and the diffusion terms of order δ_m/δ_c , we conclude that the nonequilibrium zone thickness δ_c must be of order $d^{1/3} \delta_m$.

Using the usual technics to write the first order inner and outer equations in the method of "matched asymptotic expansions" [10], we have the following equations:

(a) *Inner zone.* We introduce magnified inner concentrations of reactants and intermediate species $J_i = Y_i(\xi, \eta)/d^{1/3}$, where $\xi = x, \eta = y/d^{1/3} \delta_m$.

Continuity for the mixture

$$\frac{\partial}{\partial \eta} (\rho v) = 0 \quad (6)$$

Conservation of reactants and intermediate species

$$\frac{1}{Re \rho} \frac{\partial}{\partial \eta} \left(\frac{\mu}{Sc} \frac{\partial J_i}{\partial \eta} \right) = - \frac{w_i}{\rho} \quad (7)$$

Momentum

$$\frac{\partial}{\partial \eta} \left(\mu \frac{\partial u}{\partial \eta} \right) = 0 \quad (8)$$

Energy

$$\frac{\partial}{\partial \eta} \left[\frac{\mu}{Pr} \left(Y_p \frac{\partial h_p}{\partial \eta} + Le h_p \frac{\partial Y_p}{\partial \eta} + Pr \frac{\partial u^2/2}{\partial \eta} \right) \right] = 0 \quad (9)$$

State of gases given by Eq. (5)

(b) *Outer zone.* Eqs. (1), (3), (4) and (5) are valid throughout, while Eqs. (2) are transformed to the following

$$w_i = 0 \quad (10)$$

(c) *Matching conditions.* The solution of the outer problem, i.e., mixing with chemical equilibrium, gives us the position and characteristics of the "flame sheet." These characteristics are the "outer" boundary conditions of the inner zone.

The matching conditions are: at either side of the flame, $\rho = \rho(\xi)$, $u = u(\xi)$, $v = v(\xi)$, $T = T(\xi)$, $Y_p = Y_p(\xi)$, $Y_R = 0$, where subscript R means radical. In addition, at the fuel side of the flame, $Y_o = 0$, $dY_F/d\eta = A_F(\xi)$, where O and F mean respectively oxidizer and fuel; at the oxidizer side $Y_F = 0$, $dY_o/d\eta = A_o(\xi)$.

From Eqs. (6), (8) and (9) with the above mentioned boundary conditions, we deduce the following expressions which are valid, up to order $d^{1/2} \delta_m$, in the inner zone

$$\rho v = \rho(\xi) v(\xi) \quad (6a)$$

$$u = u(\xi). \quad (8a)$$

Finally, since to the first order $Y_p = Y_p(\xi)$, we deduce that

$$T = T(\xi). \quad (9a)$$

The distributions of species are given by Eqs. (7), which are ordinary differential equations. In addition since the temperature is close to the adiabatic flame temperature and constant across the flame, the problem of computing the reaction rate is greatly simplified.

It may be shown that the present treatment is valid, to the first order, in the turbulent case when using mean values of the appropriate magnitudes, and turbulent transport coefficients.

3. Hydrogen-Oxygen Chemical Kinetics

Due to its high calorific value, its high capacity for cooling, its thermal stability, and its high reaction rate, hydrogen is the most promising fuel for a hypersonic engine. The characteristics of such common liquid fuels as kerosene are also of interest in the

range of Mach numbers from 4 to 25, but the specific impulses attained with kerosene in this range of Mach numbers, are, at most, 40% of the corresponding values for hydrogen.

On the other hand, the mechanism of the hydrogen combustion reaction has been studied in great detail, since the experimental study of this reaction has given significant contributions to the theory of chain branching reactions. Moreover, it has been shown that the main features of the mechanism of this reaction are also characteristic of more general gas combustion reactions.

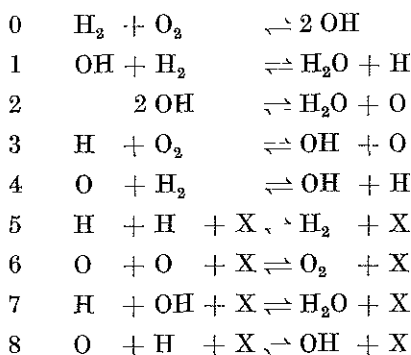
In spite of these facts, considerable uncertainty exists as to the individual reaction steps and reaction rates involved. This uncertainty is due to the following facts:

(a) The experiments do not establish the pertinent individual steps, rather they verify the overall consistency of the scheme assumed.

(b) The ranges of pressure and temperatures used in the experiments are limited, and not necessarily the most appropriate for a practical supersonic combustor.

(c) No reliable information exists on the values of the reaction rates in turbulent flows.

The following individual steps and reaction rates are widely used in supersonic hydrogen-air combustion evaluation studies [11]:



Writing the rate constants of the forward (K_j) and reverse reactions (K_{-j}) in the form

$$K_j = k_j e^{-E_j/RT},$$

we condense the pertinent values in Table 1 (see next page).

The temperatures are in °K. The rate constants are given in $(\text{mole/cc})^{-1} \text{sec}^{-1}$ for second order reactions, and in $(\text{mole/cc})^{-2} \text{sec}^{-1}$ for third order reactions.

The symbol X denotes any third body. All third bodies are assumed to be equally effective, but in order to get conservative results, maximum effectiveness has been assumed in order to select the pertinent rate constant. The role of reactions 0 and 5 to 8 is purely marginal in the diffusion flame zone, since H_2 and O_2 do not coexist in appreciable amounts within the flame, and the concentrations of radicals are very small, as we shall show later. However, it seems interesting to point out that these reactions control the ignition zone.

Table 1

<i>j</i>	<i>k</i> , <i>k</i> _{-<i>j</i>}	<i>E</i> _{<i>j</i>} , <i>E</i> _{-<i>j</i>} cal/mole °K
0	10 ¹⁴ 2 × 10 ¹³	7 × 10 ⁴ 6 × 10 ³
1	3 × 10 ¹⁴ 1.2 × 10 ¹⁵	6 × 10 ³ 2 × 10 ⁴
2	3 × 10 ¹⁴ 3 × 10 ¹⁵	6 × 10 ³ 2.5 × 10 ⁴
3	3 × 10 ¹⁴ 2.7 × 10 ¹³	1.8 × 10 ¹ 3.3 × 10 ⁴
4	3 × 10 ¹⁴ 1.3 × 10 ¹⁴	8 × 10 ³ 6 × 10 ³
5	10 ¹⁶ 2.3 × 10 ¹⁷ (1000/ <i>T</i>) ^½	0 1.1 × 10 ⁵
6	10 ¹⁵ 10 ¹⁸ (1000/ <i>T</i>) ^½	0 1.3 × 10 ⁵
7	10 ¹⁷ 3 × 10 ²² <i>T</i> ⁻¹	0 1.1 × 10 ⁵
8	10 ¹⁶ 10 ¹⁷ (1000/ <i>T</i>) ^½	0 1.1 × 10 ⁵

4. Hydrogen-Air Diffusion Flame

The above mentioned kinetic scheme will be used to study the internal structure of the Hydrogen-Air Diffusion Flames. Nitrogen is treated as an inert diluent. This assumption seems to be valid for temperatures below roughly 2500° K:

The species being produced or destroyed are:

Specie 1	H ₂ O
2	H ₂
3	O ₂
4	HO
5	H
6	O

Within the reaction zone, assuming constant values of μ ρ^n and Schmidt number, the conservation equations for the principal species and radicals become:

$$\frac{d^2}{dy_1^2} \frac{Y_i}{m_i} = F_i; \quad (i = 1, 2, 3) \tag{11}$$

$$\frac{d^2}{dy_1^2} \left(\frac{Y_1}{m_1} + \frac{Y_4}{m_4} \right) = F_4 \tag{12}$$

$$\frac{d^2}{dy_1^2} \left(\frac{Y_4}{m_4} + \frac{Y_5}{m_5} \right) + = -2 (F_1 + F_2) \tag{13}$$

$$\frac{d^2}{dy_1^2} \left(\frac{Y_1}{m_1} + \frac{Y_6}{m_6} \right) = - (F_1 + 2 F_3) \tag{14}$$

where

$$y_1 = \int_0^y \left(\frac{\rho(x, y)}{\rho(x, 0)} \right)^n dy,$$

m_i is the molecular weight of species i . and the F_i are known functions of pressure, temperature and concentrations. The boundary conditions are:

Fuel side $y = -\infty$

$$\begin{aligned} \frac{d}{dy_1} Y_2 &= -\frac{d}{dy_1} (Y_1 + Y_N) = -A; \\ -\frac{d}{dy_1} Y_i &= 0; \quad (i = 3, 4, 5, 6) \end{aligned} \tag{15}$$

Oxidizer side $y = +\infty$

$$\begin{aligned} \frac{d}{dy_1} Y_3 &= -\frac{d}{dy_1} (Y_1 + Y_N) = 8A; \\ -\frac{d}{dy_1} Y_i &= 0; \quad (i = 2, 4, 5, 6) \end{aligned} \tag{16}$$

A is known from the solution of the outer problem.

4.1 Distribution of Principal Species and Radicals

Eqs. (11) to (14), with boundary conditions (15) and (16), will be approximately solved by using an integral method.

Let us consider, for instance, the equation corresponding to depletion of hydrogen molecules.

If we introduce a straining parameter $\delta_2(x)$ such that $\eta_2 = y_1/\delta_2$ is of order unity throughout the reaction zone, the following approximate equations holds:

$$-\frac{d^2}{d\eta_2^2} \frac{Y_2}{m_2} = \delta_2^2 F_2(\eta_0) e^{-(\eta_2 - \eta_0)^2} \tag{17}$$

η_0 is the point where the depletion term of molecular hydrogen reaches its maximum.

The boundary conditions are:

$$\begin{aligned} \text{Fuel side} \quad |\eta_2| \gg 1 \quad Y_2 &= -A \delta_2 \eta_2 \tag{18} \\ \text{Oxidizer side} \quad \eta_2 \gg 1 \quad Y_2 &= 0 \end{aligned}$$

Integrating twice (17) with conditions (18) we deduce the following relations

$$\begin{aligned} \eta_0 &= 0 \\ A &= 2 \delta_2 \pi^{1/2} F_2(0) \end{aligned} \tag{19}$$

$$\frac{Y_2}{m_2} = \frac{A}{4} \delta_2 \left[\frac{1}{\pi^{1/2}} e^{-\eta_2^2} - \eta_2 (1 - \text{erf } \eta_2) \right]$$

where

$$\text{erf } \eta_2 = \frac{2}{\pi^{1/2}} \int_0^{\eta_2} e^{-x^2} dx$$

Following a similar way, we get

$$A = 4 \delta_3 \pi^{1/2} F_3(0)$$

$$\frac{Y_3}{m_3} = \frac{A}{8} \delta_3 \left[\frac{1}{\pi^{1/2}} e^{-\eta_3^2} + \eta_3 (1 + \text{erf } \eta_3) \right] \tag{20}$$

$$A = -2 \delta_1 \pi^{1/2} F_1(0)$$

$$\frac{1 - Y_N - Y_1}{m_1} = \frac{A}{4} \delta_1 \left(\frac{1}{\pi^{1/2}} e^{-\eta_1^2} + \eta_1 \text{erf } \eta_1 + \frac{7}{9} \eta_1 \right) \tag{21}$$

In particular, for $\eta_1 = 0$

$$1 - Y_N - Y_1 = Y_{1f} - Y_1$$

where f means equilibrium conditions at the flame sheet.

$$A = -2 \delta_4 \pi^{1/2} F_4(0)$$

$$1 - \frac{Y_N - Y_1}{m_1} - \frac{Y_4}{m_4} =$$

$$= \frac{A}{4} \delta_4 \left(\frac{1}{\pi^{1/2}} e^{-\eta^2} + \eta_4 \operatorname{erf} \eta_4 + \frac{7}{9} \eta_4 \right) \quad (22)$$

Finally Eqs. (13) and (14) will be expressed in closed form as follows:

$$\frac{Y_4}{m_1} - \frac{Y_5}{m_5} = \frac{A}{2} \left[\delta_1 \left(\eta_1 \operatorname{erf} \eta_1 + \frac{1}{\pi^{1/2}} e^{-\eta_1^2} \right) - \delta_2 \left(\eta_2 \operatorname{erf} \eta_2 + \frac{1}{\pi^{1/2}} e^{-\eta_2^2} \right) \right] \quad (23)$$

$$\frac{Y_4}{m_1} + \frac{Y_6}{m_6} = \frac{A}{4} \left[\delta_1 \left(\eta_1 \operatorname{erf} \eta_1 + \frac{1}{\pi^{1/2}} e^{-\eta_1^2} \right) - \delta_3 \left(\eta_3 \operatorname{erf} \eta_3 + \frac{1}{\pi^{1/2}} e^{-\eta_3^2} \right) \right] \quad (24)$$

The equation expressing the conservation of nitrogen is automatically satisfied.

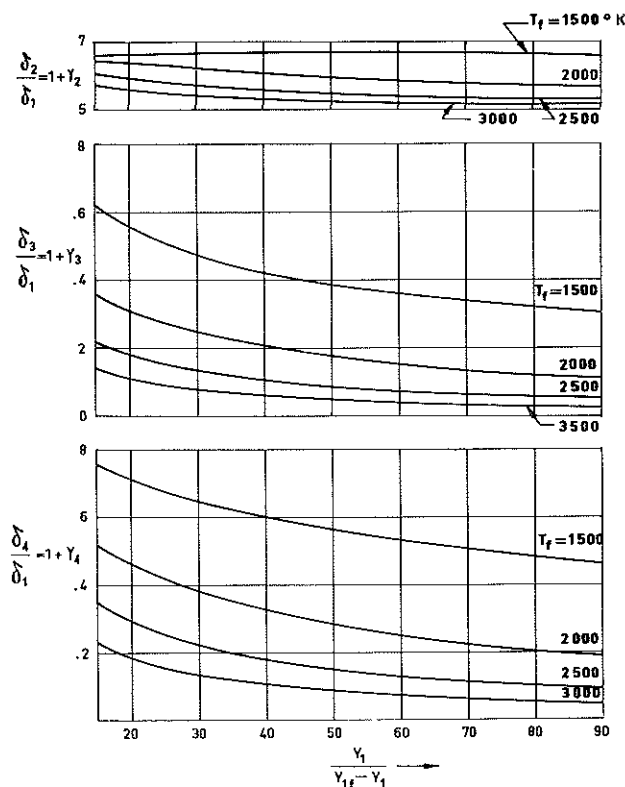


Fig. 2. Parameters, given the thickness of the different non-equilibrium zones

4.2 The Straining Parameters

In order to calculate the parameters δ_i , we write the $F_i(0)$, by means of the Law of Mass Action, as functions of pressure, temperature, and the concentration of species, for $\eta_i = 0$, given by Eqs. (19) to (24).

By using the scheme considered in § 3, we get, after some manipulations, the following equations:

$$1 + \frac{1}{1 + \gamma_4} - \frac{1}{1 + \gamma_2} - \frac{1}{2(1 + \gamma_3)} = 0 \quad (25)$$

$$\gamma_4(1 + \gamma_2) + L_1(\gamma_4 - 2\gamma_2) - \frac{K_2}{K_1} [\gamma_4^2 - L_2(\gamma_4 - \gamma_3)] = -\frac{K_3}{K_1} L_3 \quad (26)$$

$$\gamma_4(1 + \gamma_2) + L_1(\gamma_4 - 2\gamma_2) - \frac{K_4}{K_1} \left[(\gamma_4 - \gamma_3)(1 + \gamma_2) + \frac{K_{-1}}{K_4} \gamma_4(\gamma_4 - 2\gamma_2) \right] =$$

$$= -\frac{1}{1 + \gamma_2} \frac{K_3}{K_1} L_3 \quad (27)$$

$$(\gamma_4 - 2\gamma_2)(1 + \gamma_3)^2 = L_3 \quad (28)$$

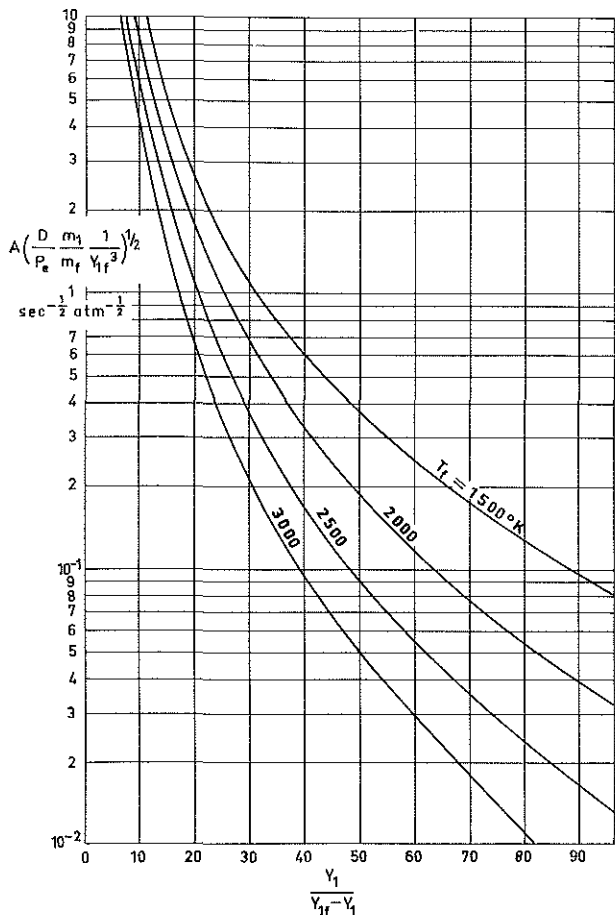


Fig. 3. Matching of the inner and outer solutions. This figure is valid for any concentration of inert species and for either laminar or turbulent flow

In Eq. (28), the third reverse reaction has been neglected. In these equations

$$1 + \gamma_i = \delta_i / \delta_1$$

$$L_i = \frac{Y_1}{Y_{1f} - Y_1} \frac{K_{-i}}{K_i}; \quad (i = 1, 2)$$

$$L_3 = \frac{81}{2\pi} \frac{1}{(Y_{1f} - Y_1)^3} A^2 D \frac{m_1}{\rho K_3}$$

The solution of Eqs. (25) to (28) is a routine but tedious affair. Fortunately, as a consequence of the physical origin of the problem, we have some idea on the behavior of the different terms of equations, so that we solve the foregoing system by using an

iterative method. The zero order iteration is equivalent to the assumption that reactions 1 and 2 do not depart from equilibrium, i.e.:

$$1 + \frac{1}{1 + \gamma_{40}} - \frac{1}{1 + \gamma_{20}} - \frac{1}{2(1 + \gamma_{30})} = 0$$

$$\gamma_{40}(1 + \gamma_{20}) + L_1(\gamma_{40} - 2\gamma_{20}) = 0$$

$$\gamma_{40}^2 - L_2(\gamma_{40} - \gamma_{30}) = 0$$

Only the zero and first order iterations have been considered in our case.

$$\log_{10} K_i \frac{m_i^2}{m_j m_i} \frac{Y_j Y_i}{Y_{1f}^2}$$

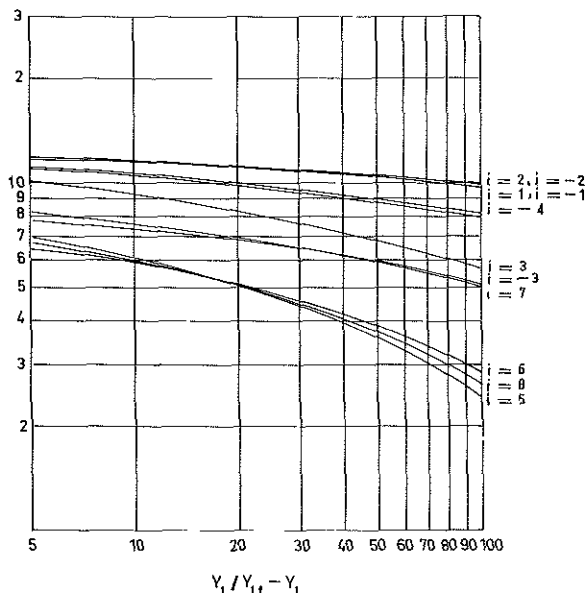


Fig. 4. Reaction rates in the study of the structure of the diffusion hydrogen-air flame, $p_e = 1$ atm, $T_b = 2500$ °K

The straining parameters δ_i/δ_1 have been plotted in Fig. 2, versus the degree of departure from equilibrium, measured by the ratio $Y_1/Y_{1f} - Y_1$.

Eq. (28) gives L_3 , as a function of Y_1/Y_{1f} and flame temperature. From this relation we draw Fig. 3, which connects the inner and outer solutions, in the following way:

(a) The solution of the outer problem provides the values of m_f (mean molecular weight at the flame sheet point), Y_{1f} , T_f , p_e , and A .

(b) By using Fig. 3, we calculate $Y_1/Y_{1f} - Y_1$, and from Fig. 2 the parameters δ_i/δ_1 .

(c) Finally, Eq. (21) particularized at $\eta_1 = 0$ gives us the value of δ_1 .

Some of the reaction rates involved in the study of the inner structure of the hydrogen-air flame, have been represented in Fig. 4, where the rates of some dissociation-recombination reactions are also included. From this figure we deduce that the later reactions do not play a significant role in the zone considered, as it has been assumed throughout this study. On the other hand, the fact that reactions 1 and 2 do not depart substantially from equilibrium, as seen in this figure, may be used to arrive at a simpler description of the chemical kinetics involved.

4.3 Distribution of Species Across the Flame

A typical distribution of concentrations across the flame, computed by means of Eqs. (19) to (24), is plotted in Fig. 5. Y_N has been assumed to be constant through the reaction zone, but in a practical case, this function is obtained from the outer solution.

Figs. 6 to 8 compare the theoretical distribution of principal species with experimental values taken from [9, 12].

In order to evaluate the approximation attained by using the integral method presented in §4.1, excluding the influence of outer conditions, the following procedure has been used to plot this figure.

(a) The concentrations are referred to the expression $(Y_{1f} - Y_{1\max})/m_1$.

The Y_{1f} have been estimated from experimental data by the, rather crude, procedure of tracing tangents to the curve representing water concentration.

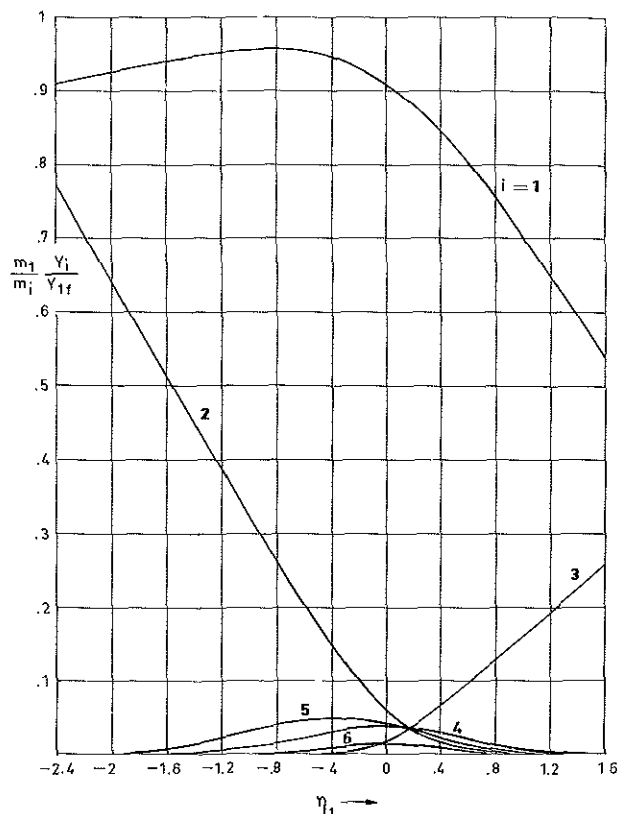


Fig. 5. Typical distribution of concentrations across the flame, $p_e = 1$ atm, $T = 2000$ °K, $Y_1/Y_{1f} - Y_1 = 20$

(b) These data have been represented *vs.* a dimensionless variable $\bar{\eta} = a\eta_1 + b$, where a and b are deduced by adjusting the scale of the appropriate theoretical curve until the best fit with the behavior of the water data is obtained.

(c) No correction has been introduced to take into account the variation of nitrogen across the flame.

4.4 Matching with the Outer Solution

Let us assume that the outer mixing problem admits a treatment within the boundary layer approximation. No loss of generality is implied in this

assumption since there is a wide variety of problems, such as those connected with jets, wakes and mixing of semiinfinite streams, for which such an approximation is appropriate.

It may be shown that, in our case, the outer problem is a mixing one for a "reduced concentration" $Y = Y_2 - Y_3/8$, with the additional conditions that $Y_2 = 0$ in the oxidizer side of the flame, and $Y_3 = 0$ in the fuel side.

Limiting ourselves to the case of isobaric turbulent mixing, with turbulent Prandtl and Lewis numbers of unity, we have:

$$\frac{Y - Y_0}{Y_F - Y_0} = \frac{Y_N - Y_{N0}}{Y_{NF} - Y_{N0}} = \frac{u - u_0}{u_F - u_0} = \frac{h_s - h_{s0}}{h_{sF} - h_{s0}} = f(\zeta) \tag{29}$$

In these equations subscripts 0 and F mean conditions at the oxidizer and fuel edges of the mixing layer respectively, Y_N represents concentration of inert diluent, and ζ is a similarity variable.

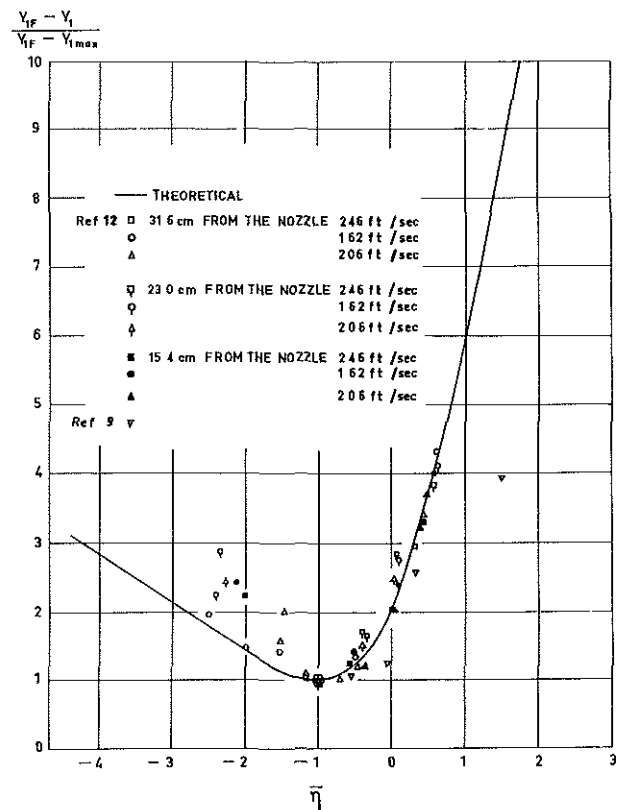


Fig. 6. Distribution of water across the flame

The problem is solved once $f(\zeta)$ and a function defining the spreading rate of the mixing zone are given.

At the "flame sheet" (subscript f); $Y = 0$ and $Y_{NF} = 1 - Y_{1f}$, so that Eqs. (29) become:

$$\frac{Y_0}{Y_0 - Y_F} = f(\zeta_f) \tag{30}$$

$$Y_{1f} = 1 - Y_{N0} - (Y_{NF} - Y_{N0}) \frac{Y_0}{Y_0 - Y_F} \tag{30a}$$

$$\frac{u_f - u_0}{u_F - u_0} = \frac{h_{s,f} - h_{s0}}{h_{s,F} - h_{s0}} = f(\zeta_f) \tag{30b}$$

We get from Eq. (30) the position of the "flame sheet", and from Eq. (30a) the value of Y_{1f} and the mean molecular mass m_f , since

$$\frac{1}{m_f} = \frac{Y_{1f}}{m_1} + \frac{1 - Y_{1f}}{m_N} \tag{31}$$

The slope A of Y_2 at the "flame sheet" is given by

$$A = (Y_F - Y_0) \left(\frac{df}{d\zeta} \right)_{\zeta = \zeta_f} \frac{\partial \zeta}{\partial y} \tag{32}$$

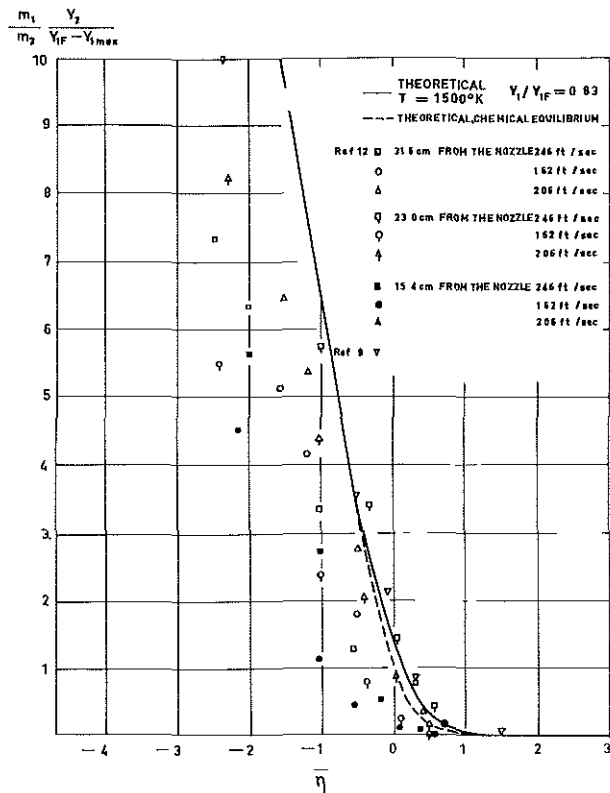


Fig. 7. Distribution of hydrogen across the flame

It only remains to calculate the turbulent diffusion coefficient D . According to PRANDTL, this coefficient could be defined by means of the expression:

$$D = kb(u_{max} - u_{min}) \tag{33}$$

where u_{max} and u_{min} are the maximum and minimum velocities in the section, K is a dimensionless proportionality factor, and b is the thickness of the concentration mixing zone.

Eq. (33) is no longer useful when dealing with the mixing of two streams having different densities, so that it has been suggested [11] to substitute this equation by

$$\rho D = kb[(\rho u)_{max} - (\rho u)_{min}], \tag{33a}$$

however, the problem is not completely solved in this way, since experimental evidence indicates that the mixing rate does not go to zero when the stream momentum difference is zero.

In order to substantiate our approach, let us consider the isobaric mixing of two co-flowing streams of hydrogen and air respectively.

For the initial region of the jet, we have:

$$\begin{aligned}
 Y_0 &= -0.0290 \\
 Y_F &= 1 \\
 Y_{N_0} &= 0.768 \\
 Y_{NF} &= 0
 \end{aligned}$$

$$D = k b u_0 \frac{m_0}{m_f} \frac{T_f}{T_0} \left(1 - \frac{\rho_F u_F}{\rho_0 u_0} \right)$$

where

$$\frac{m_0}{m_f} = 1.17$$

The curves plotted in Fig. 9 were calculated from those of Fig. 3. While the last figure is valid for dealing with any hydrogen-oxygen diffusive combustion problem, within the range of validity of the present theory; Fig. 9 will be used exclusively in the hydrogen-air case. This figure shows the thickness b of the mixing zone *vs.* the parameter $(Y_{1f} - Y_1) h_1 / c_p T_f$, where h_1 is the hydrogen enthalpy corresponding to $T = T_f$, and c_p has been computed on the basis of the values Y_{1f} and Y_{Nf} . This parameter represents the relative departure from equilibrium temperature provided the thermal influence of the remaining species is negligible.

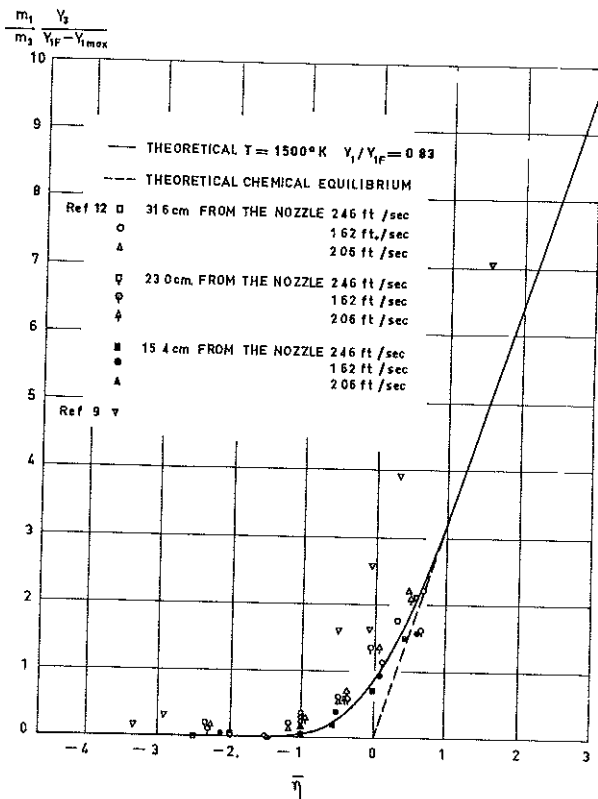


Fig. 8. Distribution of oxygen across the flame

The "flame sheet" position is given by

$$f(\zeta_f) = \frac{0.0290}{1.0290} = 0.0282$$

Since, as it has been shown in [13], the incompressible velocity profile is unusually insensitive to compressibility effects, we will assume that $f(\zeta)$ is given by the Schlichting formula

$$f(\zeta) = (1 - \zeta^{3/2})^2$$

where

$$\zeta = \frac{y}{b} - \frac{y_F}{b}$$

for the initial and transition regions of the jet.

From these equations we deduce:

$$\begin{aligned}
 \zeta_f &= 0.885 \\
 Y_{Nf} &= 0.746 \\
 Y_{1f} &= 0.254 \\
 \frac{1}{m_f} &= 0.0407 \\
 \frac{m_1}{m_f Y_{1f}^3} &= 44.9 \\
 A &= -\frac{0.487}{b}
 \end{aligned}$$

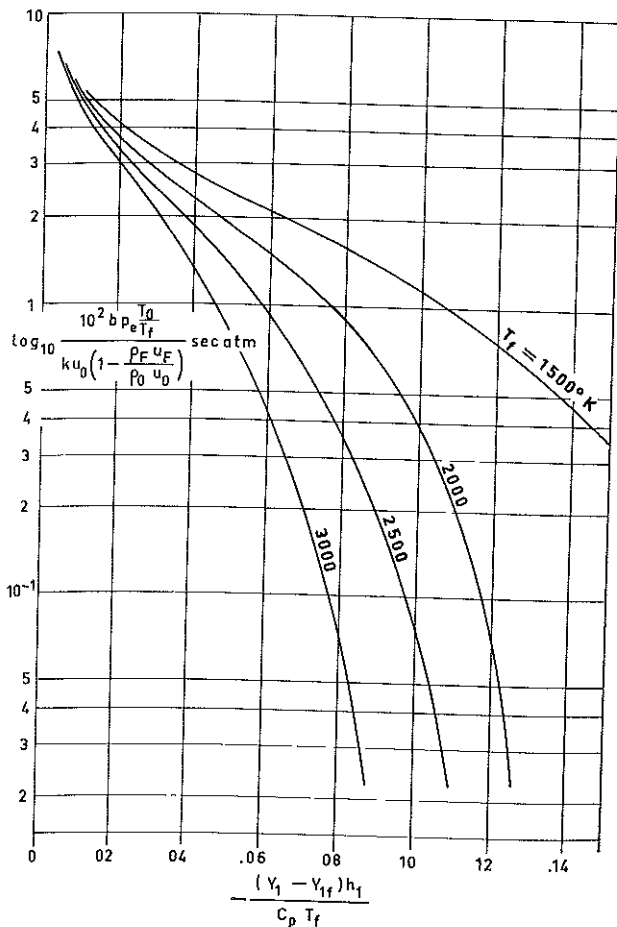


Fig. 9. Matching of the inner and outer solutions. This figure is valid for the hydrogen-air case, assuming turbulent shear flow and turbulent transport coefficients given by Eq. (33a)

As an example of the application of this analysis, let us consider the following conditions which seem to be of interest to a hypersonic airbreathing vehicle.

$$p_e = 1 \text{ atm}, \quad T_0 = 800^\circ \text{ K}, \quad M_0 = 3$$

so that:

$$\begin{aligned}
 u/2 &= 345 \text{ cal/g} \quad \text{and} \quad h_{s0} = 461 \text{ cal/g.} \\
 u_F/u_0 &= 0.5, \quad h_{sF} = 500 \text{ cal/g.}
 \end{aligned}$$

From Eqs. (30b) and (34) with $\zeta_f = 0.885$, we get:

$$\begin{aligned} h_{s,f} &= 462 \text{ cal/g,} \\ u_f^2/2 &= 335 \text{ cal/g,} \\ T_f &= 2890^\circ \text{ K.} \end{aligned}$$

If we are interested in obtaining the distance from the injector corresponding to a ten per cent of separation from equilibrium at this temperature, we get from Fig. 9 (with $k = 0.025$, $T_f/T_0 = 3.62$ and $\rho_F u_F/\rho_0 u_0 \ll 1$):

$$b = 1.42 \text{ m}$$

which, according to experimental results concerning supersonic hydrogen-air mixing quoted in [14], corresponds to a distance to the injector of

$$L = 5 \text{ m.}$$

As a comparison, let us calculate the distance travelled during the ignition time τ_i by a hydrogen-air mixture under the following conditions:

$$\begin{aligned} p_e &= 1 \text{ atm, } T_0 = 800^\circ \text{ K,} \\ u &= (u_0 + u_F)/2 = 1270 \text{ m/sec.} \end{aligned}$$

According to [11]

$$p_e \tau_i = 45 \times 10^{-7} e^{10000/T_0} \text{ atm } \mu \text{ sec}$$

so that we obtain

$$L_i = 1.5 \text{ m}$$

In a practical case the ignition distance will be much larger due to the time required for the mixing. This suggests that the zone between the regions of frozen and equilibrium chemistry will be small in most cases of interest.

5. Conclusions

A theoretical analysis of finite chemistry effects in a turbulent diffusion flame of hydrogen and air has been carried out.

It has been assumed that the flame is close to equilibrium conditions and that the outer flow may be appropriately described by using the first order boundary layer approximation. Under such assumptions the theory is valid to the first order in a parameter representing the ratio of a characteristic diffusion time to a chemical time.

No attempt has been done to estimate the range of validity of the theory. The comparison with more elaborate computations seems to be difficult at this stage. This is due to the singular character of the mathematical problem, which renders the solution by machine computation difficult, especially for conditions close to equilibrium. On the other hand the computation of higher order perturbation terms is extremely troublesome. We rely on the hypothesis that the theory is valid up to values of $- \Delta T/T_f - T_0$ below roughly 0.2; this has been shown to be true for the case considered in [6].

The concentration profiles of the principal species obtained from the analysis are compared with available data from low speed hydrogen flames. The agreement is found to be satisfactory.

The model presented does not enable the study of the flame structure near the injector exit where frozen mixing conditions prevail, but this zone may

be studied with sufficient approximation by means of some assumptions similar to those used in computing the ignition delay in premixed flames (no heat release, and concentration of oxidizer and fuel controlled by diffusion). The problem of the transition zone of fast temperature rise, remains yet unsolved.

Acknowledgment

The author is indebted to A. LINAN and J. L. URRUTIA for providing stimulating discussion and helpful suggestions; and to J. M. VALERO who assisted in the numerical analysis with extreme patience.

References

- BURKE, S. P. and SCHUMANN, T. E. W., "Diffusion flames," *Ind. Eng. Chem.* **20**, 998-1004 (1928).
- TEWFIK, O. E., "One-dimensional mass and heat transfer and their coupling," *Int. J. Heat Mass Transfer* **7**, 409-421 (1964).
- KLICH, G. F. and LEYHE, E. W., "Experimental results of cooling a 12.5° semivertex angle cone by ejection of Hydrogen and Helium from its apex at Mach 7," NASA TN-D-2478 (1964).
- ROSNER, D. E., "Transpiration cooling with chemical reactions," Aero Chem. Research Laboratories, Inc. TP-79 (1964).
- ROSNER, D. E., "Comments to paper: Combustion in the turbulent boundary on a vaporizing surface, by GERALD A. MARXMANN," *Tenth International Symposium on Combustion* (The Combustion Institute, Pittsburgh, 1965), p. 1349.
- LINAN, A., "On the structure of laminar diffusion flames," *INTA-AF-EOAR* 63-42 (1963).
- FAY, J. A. and RIDDELL, F. R., "Theory of stagnation point heat transfer in dissociated air," *Recent Advances in Heat and Mass Transfer*, J. P. HARTNETT Ed. (Mc Graw-Hill Book Company, Inc., New York-Toronto-London, 1961), pp. 115-141.
- LEES, L., "Convective heat transfer with mass addition and chemical reactions," *Recent Advances in Heat and Mass Transfer*, J. P. HARTNETT Ed. (Mc Graw-Hill Book Company, Inc., New York-Toronto-London, 1961), pp. 161-207.
- WOOLDRIDGE, C. E. and MUZZY, R. J., "Measurement in a turbulent boundary layer with porous wall injection and combustion," *Tenth International Symposium on Combustion* (The Combustion Institute, Pittsburgh, 1965), pp. 1351-1362.
- VAN DYKE, M., *Perturbation Methods in Fluid Mechanics* (Academic Press, New York and London, 1964), Chap. V, pp. 77-97.
- FERRI, A., LIBBY, P. A., and ZARKAY, V., "Theoretical and experimental investigation of supersonic combustion," *International Council of the Aeronautical Sciences. Third Congress Stockholm, 1962* (Spartan Books Inc., Washington-London, 1964), pp. 1089-1155.
- HAWTHORNE, W. R., WEDDELL, D. S., and HOTTEL, H. C., "Mixing and combustion in turbulent gas jets," *Third Symposium on Combustion and Explosion Phenomena* (The Williams & Wilkins Company, Baltimore, 1949), pp. 267-288.
- HILL, J. A. F. and NICHOLSON, J. E., "Compressibility effects on fluid entrainment by turbulent mixing layers," NASA CR-131 (1964).
- PETERS, C. E., "A model for the free turbulent eddy viscosity," AEDC-TR-65-209 (1965).

Ignacio Da-Riva
Escuela Ingenieros Aeronáuticos
Ciudad Universitaria
Madrid, Spain