THE OZONE FLAME

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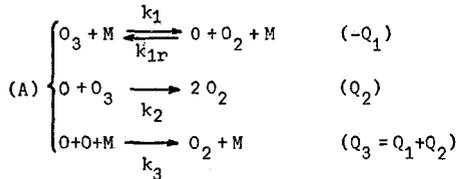
Résumé - La structure de la flamme d'Ozone est analysée dès point de vue des méthodes asymptotiques, ayant compte du fait que les ratios des temps caracteristiques associés aux différentes réactions, variables avec la temperature de la flamme et la concentration initiale d'Ozone, peuvent être très grands ou très petits en comparaison avec l'unité. On trouve pour la flamme une structure à deux zones, dans lesquelles le mécanisme de réaction peut être simplifié.

Abstract - The Ozone flame structure is analyzed from the point of view of asymptotic methods, using the fact that the ratios of the characteristic times associated with the different reactions, which change with the flame temperature and therefore with the initial Ozone concentration, take values very large or very small compared with unity. A two-zone structure is found for the flame, with simplified forms of the reaction mechanism for each of the zones.

I - INTRODUCTION AND FORMULATION

The Ozone decomposition flame has attracted the interest of many of those involved in theoretical studies of flame propagation, because its kinetic scheme is well known and fairly simple. It has been used as a benchmark for numerical computation methods of analyzing the flame structure; see, for example, references /1/ to /5/. As we shall see in these notes, by analyzing the Ozone flame structure from the viewpoint of asymptotic or singular perturbation methods, it is possible to illustrate clearly many of the essential aspects and simplifying techniques of the modelling of the flame propagation processes with multiple kinetics.

The reaction follows a kinetic scheme with three elementary reactions

$$(A) \begin{cases} O_3 + M \underset{k_{1r}}{\overset{k_1}{\rightleftharpoons}} O + O_2 + M & (-Q_1) \\ O + O_3 \xrightarrow{k_2} 2\,O_2 & (Q_2) \\ O+O+M \xrightarrow{k_3} O_2 + M & (Q_3 = Q_1 + Q_2) \end{cases}$$

where $Q_1 = 25.45$ Kcal/mole and $Q_2 = 93.65$ Kcal/mole.

For the rate constants k_1 and k_2 we shall use the following expressions:
$k_1 = B_1 \cdot \exp(-T_a/T)$, $k_2 = B_2 \cdot \exp(-b \cdot T_a/T)$ where, if we use the values given in referen-

ce /1/, the activation temperatures are $T_a = 12000$ °K and $b \cdot T_a = 3000$ °K, so that $b = 1/4$, and the pre-exponential factors, in cm-mole-sec units, are $B_1 = 2.03 \times 10^{15}$ and $B_2 = 2.96 \times 10^{13}$. The same reference gives for k_{1r} and k_3 the values $k_{1r} = 2.64 \times 10^{13} \cdot \exp(300/T)$, $k_3 = 4.12 \times 10^{14} \cdot \exp(767/T)$; the rate constants k_1, k_{1r} and k_3 have been chosen as those associated with O_2 as a third body, because O_2 is the dominant species in the hot side of the flame where those reactions are important. The value of k_1 is eight times larger than the value proposed by Hirschfelder and used by Bledjian /2/. Heimerl & Coffee /5/ use slightly different values for the rate constants, with a value of $b=0.206$.

The dissociation reactions reverse to 2 and 3 are not included because their activation energies are larger than that of the dissociation reaction 1, so that their rates are too small to play a significant role in the flame propagation process.

We shall use, in the following analysis, the fact that the activation energy of the first reaction is large compared with the thermal energy, or equivalently that $T_a/T \gg 1$, and also that the three body reactions are slow, at least at ambient pressures; this will enable us to obtain a simplified description of the Ozone flame structure and of its dependence on the initial mixture temperature and Ozone concentration. The analysis carried out here uses the point of view of asymptotic methods, but many of the resulting simplifying ideas originated in the work of Zeldovich and his school, see references /6/ to /8/. It can be used in the analysis of other simplified multi-step mechanisms, as the two step kinetic mechanism proposed by Westbrook and Dryer for the hydrocarbon/air combustion /9/. See references /8/ to /14/, for examples of other analysis where asymptotic techniques are used to describe flames with multiple kinetic mechanisms.

We shall use Fick's law, when calculating the diffusion fluxes, with constant values for the Lewis numbers L_1 and L_3 of the species O and O_3, and also a constant specific heat c_p for the mixture. We shall consider that $\rho\lambda$, the product of the density and heat conductivity is a constant $(\rho\lambda)_m$. We use, when describing the steady planar flame structure, a reference system that moves with the flame front, with a stretched coordinate x defined in terms of the normal distance $\tilde{x}$ to the front by the relation $\rho d\tilde{x} = \rho_o dx$, where ρ_o is the initial density of the fresh mixture.

If U is the flame velocity with respect to the fresh mixture, the conservation equations become

$$U \frac{dY_1}{dx} - \frac{(\rho\lambda)_m}{\rho_o^2 c_p L_1} \frac{d^2Y_1}{dx^2} = \frac{\rho}{3M_1} \left(k_1 \frac{M_1}{M} Y_3 - k_2 Y_3 Y_1 \right) - \left\{ \frac{\rho^2}{M_1 M} \left(\frac{1}{2} k_{1r} Y_1 Y_2 + 2k_3 Y_1^2 \right) \right\} \tag{1}$$

$$U \frac{dY_3}{dx} - \frac{(\rho\lambda)_m}{\rho_o^2 c_p L_3} \frac{d^2Y_3}{dx^2} = -\frac{\rho}{M_1} \left(k_1 \frac{M_1}{M} Y_3 + k_2 Y_3 Y_1 \right) + \left\{ \frac{3\rho^2}{2M_1 M} k_{1r} Y_1 Y_2 \right\} \tag{2}$$

$$U\frac{dT}{dx} - \frac{(\rho\lambda)_m}{\rho_o^2 c_p}\frac{d^2T}{dx^2} = \frac{p}{3M_1}\left(-\frac{Q_1}{c_pM_1}k_1\frac{M_1}{M}Y_3 + \frac{Q_2}{c_pM_1}k_2Y_3Y_1\right) + \left\{\frac{\rho^2}{M_1M}\left(\frac{Q_1}{2c_pM_1}k_{1r}Y_1Y_2 + \frac{Q_3}{M_1c_p}k_3Y_1^2\right)\right\} \quad (3)$$

for the temperature T and mass fractions Y_1, Y_3 and $Y_2 = (1-Y_1-Y_3)$, of O, O_3 and O_2. We consider that the initial mixture contains only O_2 and O_3 (if another inert species was present its mass fraction would be constant); M, the mean molecular mass, is $M = 2M_1/(1+Y_1-Y_3/3)$, while $2M_1$ is the molecular mass of O_2. The flame velocity U is very small compared with the sound velocity, so that the variation of the pressure across the flame can be neglected, and the pressure considered constant, equal for example to its known upstream value, in the equation of state; then, $\rho = pM/RT$ determines ρ in terms of M, T and p.

The flame separates two regions of uniform temperature and concentration, so that the production terms in the right hand side of Eqs. (1-3) must be zero upstream of the flame, at $x \to -\infty$, and downstream at $x \to \infty$. If we assume that, due to its large activation energy, the first forward reaction is frozen upstream; the condition of chemical equilibrium[*] then implies that the rate of the reverse of the first reaction as well as the rates of the second and third reactions must be zero, because we have not considered the effects of the corresponding reverse reactions. This condition is insured if

$$x \to -\infty: \quad T = T_o, \quad Y_1 = 0, \quad Y_3 = Y_{3o} \quad (4)$$

where T_o and Y_{3o} are known.

Downstream the flow will be considered to be at equilibrium, so that

$$x \to \infty: \quad T = T_e, \quad Y_3 = Y_1 = 0 \quad (5)$$

with T_e to be determined.

We can derive, taking into account the upstream conditions (4), the following conservation equation

$$T - T_o + \frac{Q_1+Q_2}{2c_pM_1}Y_1 + \frac{Q_2-Q_1}{6c_pM_1}(Y_3-Y_{3o}) = \frac{(\rho\lambda)_m}{\rho_o^2 c_p U}\frac{d}{dx}\left(T + \frac{Q_1+Q_2}{2c_pM_1L_1}Y_1 + \frac{Q_2-Q_1}{6c_pM_1L_3}Y_3\right) \quad (6)$$

that is free from the chemical production terms.

We can use Eq. (6) together with the downstream conditions (5) to calculate the final equilibrium temperature

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(*) A system, with a reaction mechanism such as (A), is in chemical equilibrium when the total production rates associated with each of the elementary reactions are identically zero; i.e. when there is detailed balance for each of the reactions between the reaction rates in the forward and reverse directions.

$$T_e = T_o + (Q_2 - Q_1)Y_{3o}/6c_p M_1 \ .$$ (7)

Notice also that if the initial mixture contains only O_2 and O_3, the final equilibrium value of M is $M_e = 2M_1$.

It is important to stress the point that the possibility for the kinetic scheme (A) of leading to travelling wave solutions of the conservation equations, in the form of premixed flames, is associated with the fact that the nondimensional activation energy, T_a/T, of the first forward reaction is large. If $T_a/T_o \gg 1$, the ratio $B_1 \cdot \exp(-T_a/T_o) \ / \ B_1 \cdot \exp(-T_a/T_e)$ of the reaction "constants" at the initial temperature T_o and at the final temperature T_e is very small compared with 1. Then we can consider the first forward reaction as chemically frozen in the bounded upstream region, because the time taken for the flame to move across that region is short compared with the characteristic reaction time at $T = T_o$.

Because the activation energies of the other reactions are not large, these reactions must be in equilibrium upstream, so that the Oxygen atom concentration must be zero there, in order to have zero values for the reaction rates of those reactions.

II - STRUCTURE OF THE PRIMARY FLAME

The flame structure depends very much on the relative values of the reaction constants or, equivalently, of the reaction rates, at the equilibrium temperature T_e. The reaction constants in units of that of the second reaction are

$$k_1/k_2, \quad 1, \quad \rho k_{1r}/Mk_2 \quad \text{and} \quad \rho k_3/Mk_2$$

that represent also the inverse of the ratios of the respective characteristic reaction times.

The last two ratios are very small compared with unity for pressures of the order 10 atmospheres or lower. As a consequence, the flame structure will include a main upstream zone or primary flame that controlls the flame propagation process, followed by a very thick downstream convective-reactive zone; see a sketch of the flame structure in Figure 1. In the primary flame the recombination reactions do not play a role; in the trailing convective-reactive zone all the reactions must be taken into account, but the steady state approximation can be used to calculate the small Ozone concentration in this zone. For sufficiently high flame temperatures, or lower pressures, the reverse reactions to 2 and 3 should be taken into account in the convective-reactive zone, although they may be neglected in the primary flame. This two-zone structure originates from looking for the asymptotic solution of the system of Eqs. (1-5) for small values of the ratios $\rho k_{1r}/Mk_2$ and $\rho k_3/Mk_2$; the resulting problem is of the singular perturbation type. This is so because if these ratios are replaced by zero in Eqs. (1-3) then we obtain the equations that describe the prima-
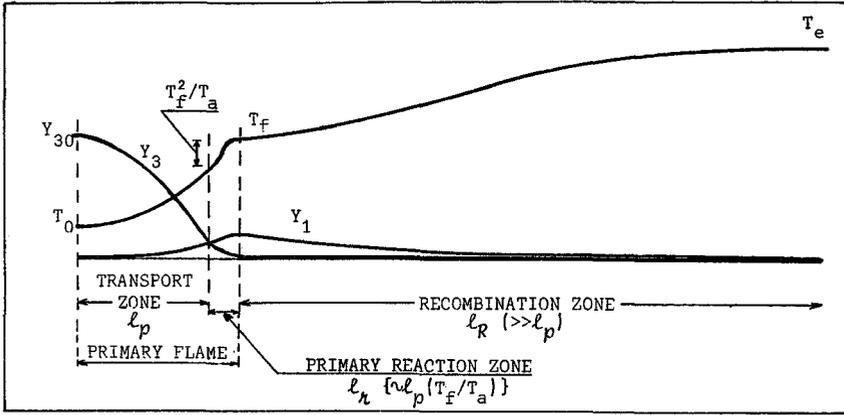
Fig. 1 - Temperature and concentration distributions in the Ozone flame.

ry flame structure in first approximation; however, the solutions of the simplified equations cannot satisfy the boundary conditions (5), and, after the primary flame, a second long recombination zone is required, where the effects of the reverse reactions 1 and 3 will slowly change the concentration and temperature to their final values given by (5).

We shall now describe the structure of the primary flame using the conservation equations (1-3), leaving out the terms in curly brackets that are associated with the recombination reactions. The simplified equations must be solved with the upstream boundary conditions (4). However, the downstream conditions (5) must be replaced by the conditions

$$x \to \infty: \quad T = T_f, \quad Y_3 = 0, \quad Y_1 = Y_{1f} \tag{5'}$$

reflecting the equilibrium condition for the simplified kinetic mechanism

$$(B) \begin{cases} O_3 + M \longrightarrow O + O_2 + M & (-Q_1) \\ O_3 + O \longrightarrow 2\,O_2 & (Q_2) \end{cases}$$
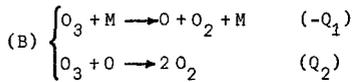
Notice that the equilibrium concentration of O may be different from zero for this mechanism, so that Y_{1f} must be determined as part of the solution. The primary flame temperature T_f will then be lower than T_e; it is given, according to Eq. (6) by the relation

$$T_f = T_e - (Q_1 + Q_2) Y_{1f} / 2 c_p M_1 \tag{8}$$

in terms of Y_{1f}.

We shall then determine the primary flame structure by solving Eqs. (1)-(3), with $k_{1r} = k_3 = 0$, and the boundary conditions (4) and (5'), and in the process we shall

calculate U, T_f and Y_{1f}, which are eigenvalues of the problem. Afterwards we shall analyse the structure of the thick downstream convective-reactive zone, where Y_1 decreases from Y_{1f} to 0 and T increases from T_f to T_e.

When solving the problem of analysing the primary flame, we shall consider that $T_a/T_f \gg 1$, and also that $bT_a/T_f \gg 1$; when these inequalities hold, the primary flame has also a two-zone structure; the reactions are confined to a thin zone, where convective effects can be neglected in first approximation, following a thicker transport zone. Although the inequality $bT_a/T_f \gg 1$ is not strictly satisfied the results are at least qualitatively correct, and in many cases of interest, when the flame temperature is not too high, they will also be quantitatively correct (we shall also include in this case the asymptotic results corresponding to the assumption $bT_a/T_f \sim 1$).

The primary flame structure also depends very much on the value of the ratio, R, defined by

$$R = B_1 \cdot \exp(-T_a/T_e) \; / \; B_2 \cdot \exp(-bT_a/T_e) \quad , \tag{9}$$

of the reaction rates of the first and second reactions, at the final equilibrium temperature T_e, which is given by (7) in terms of the initial mass fraction of Ozone. The equilibrium temperature, and thus R, is lowered by drecreasing T_o or by diluting, with O_2 or any other inert species, the Ozone in the initial mixture; $T_e - T_o$ is proportional to Y_{3o}, so that $T_e = 2700$ °K when $T_o = 298$ °K and $Y_{3o} = 1$.

Notice that $B_1/B_2 \sim 10^2$ so that the value of R ranges from values very small compared with unity, at small equilibrium temperatures, to values moderately large compared with unity when T_e is high. R, for example, grows from 0.01 to 2.5 when T_e increases from 1000 °K to 2700 °K.

The quasi-steady state approximation for atomic Oxygen

For very small values of R, the second reaction consumes 0 as soon as it is produced by the first reaction; then Y_1 takes values, $Y_1 \ll 1$, given by the steady state approximation for 0

$$Y_1 = (M_1/M)(B_1/B_2) \cdot \exp\{(b-1)T_a/T\} \tag{10}$$

obtained from Eq. (1), with $k_{1r} = k_3 = 0$, by neglecting the transport terms; these are very small compared with the production term that is balancing the consumption term. Notice that the value of Y_1 at the maximum temperature T_e is of the order R, and that it decreases sharply with T. It should be noticed that the validity of the steady state approximation for Y_1 for small R, that leads to Eq. (10), holds also for values of $bT_a/T_f \sim 1$.

When this value (10) of $Y_1 \ll 1$ is used together with Eq. (3), with $k_{1r} = k_3 = 0$, and Eq. (6) we obtain the equations

$$U \frac{dT}{dx} - \frac{(\rho\lambda)_m}{\rho_o^2 c_p} \frac{d^2 T}{dx^2} = \frac{\rho}{M_1} \frac{(Q_2 - Q_1)}{3 c_p M_1} \frac{M_1}{M} B_1 e^{-T_a/T} \tag{11}$$

$$U\{T - T_o + \frac{Q_2 - Q_1}{6 c_p M_1} (Y_3 - Y_{3o})\} = \frac{(\rho\lambda)_m}{\rho_o^2 c_p} \frac{d}{dx} \left\{ \frac{Q_2 - Q_1}{6 c_p M_1 L_3} Y_3 + T \right\} \tag{12}$$

to be solved with the boundary conditions

$$x \to -\infty: \quad T = T_o, \quad Y_3 = Y_{3o} \tag{13}$$

$$x \to \infty: \quad T = T_e, \quad Y_3 = 0 \tag{14}$$

that corresponds to an Arrhenius reaction of stoichiometry

$$2 O_3 \longrightarrow 3 O_2 \qquad (Q_2 - Q_1) \tag{15}$$

with the rate of the slower reaction 1, and a global heat release per mole $(Q_2 - Q_1)$, which includes the effects of both reactions.

The solution to this problem can be obtained by means of asymptotic techniques, for large values of the ratio T_a/T_e, following Zeldovich and Frank-Kamenetskii /6/. The analysis leads to the following expression for U

$$U = 2 \sqrt{\frac{(\rho\lambda)_m}{\rho_o^2 c_p} \frac{\rho_e}{M_e} L_3 B_1} \frac{T_e^2}{T_a (T_e - T_o)} \cdot \exp(-T_a/2 T_e) . \tag{16}$$

Notice that in the limit $R \to 0$, the mass fraction Y_{1f} of O, just downstream of the trigger flame, is $Y_{1f} = R/2$, negligible, and thus $T_f = T_e$, and the downstream recombination zone does not play a significant role.

In order to be consistent with the asymptotic analysis, the constant values $(\rho\lambda)_m$ of $\rho\lambda$ should be calculated at the equilibrium state. Then $(\rho\lambda)_m = (\rho\lambda)_e$ represents a good approximation for the heat conductivity in this limiting regime.

The distinguished "complex" flame regime

When at higher flame temperature R becomes of the order of T_e/T_a the mass fraction of Oxygen atoms in the reaction zone grows to values of the order T_e/T_a, and the steady state approximation for O can no longer be used when describing the structure of the reaction zone. In addition, if we notice that, according to Eq. (8), T_f turns out to be very sensitively dependent on Y_{1f}, we can expect values of T_f well below the value T_e; T_f drops from T_e to T_o when the ratio Y_{1f}/Y_{3o} increases from 0 to the small value $\mu/3 = (Q_2 - Q_1)/3(Q_2 + Q_1) = 0.191$.

We shall describe the flame structure in the distinguished regime corresponding to these higher values of R such that $R T_a/T_e$ is of order unity. We shall use asymptotic techniques based on the assumption that both T_a/T_f and $b T_a/T_f$ are large compared with unity; with these assumptions, both reactions 1 and 2 are limited to a commom

thin zone on the hot side of the flame. The main effect of the assumption $bT_a/T_f \gg 1$, that it is not strictly valid for the Ozone scheme, is to freeze the second reaction, artificially, in the transport zone; however, the results will be quantitatively correct in a wide range of values of RT_a/T_f, not large compared with unity, for which the second reaction is fast enough to consume the Oxigen atoms before reaching the transport zone. It is more convenient, when analysing the reaction zone structure in this distinguished regime, to consider that T_f is given as a data, while Y_{3o} and U will be determined as functions of T_f.

For large values of $T_a/T_f \gg 1$ and $bT_a/T_f \gg 1$ we find a thick transport zone where the chemical reactions are frozen (or if $bT_a/T_f \sim 1$, the mass fraction Y_1 is zero and the first reaction is frozen). The conservation Eqs. (1-3) can then be integrated in the transport zone to give for $x < 0$, up to terms of order ε, the following expressions for the temperature and concentrations

$$Y_1 = \varepsilon a_1 \cdot \exp(XL_1) \tag{17a}$$

$$Y_3 = Y_{3o}\{1 - \exp(XL_3)\} \tag{17b}$$

$$T = T_o + (T_f - T_o)(1 + \varepsilon a_2) \cdot \exp(X) \tag{17c}$$

where $X = xU\rho_o^2 c_p/(\rho\lambda)_m$, and $\varepsilon = T_f/T_a \ll 1$. The origin of the coordinate system is chosen so that the value of Y_3, as given by the outer expansion (17), vanishes at $x = X = 0$. The values of a_1 and a_2, of order unity, are to be determined by the matching conditions with the expansions, that we shall give below, for the inner reaction zone; $a_1\varepsilon$ represents the mass fraction of 0 just upstream of the thin reaction zone, and $(T_f - T_o)a_2\varepsilon$ is the apparent jump in temperature at this thin zone.

Downstream of the reaction zone, for $X > 0$, we have a uniform state of chemical equilibrium,

$$Y_3 = Y_1 - Y_{1f} = T - T_f = 0 , \tag{18}$$

consistent with the simplified kinetic scheme associated with $k_{1r} = k_3 = 0$.

In the thin reaction zone the values of Y_1, Y_3 and T are given, in first approximation for small ε, by Eqs. (18). The first order deviations from these values are of order ε (also the order of the thickness of the reaction zone in the variable X). These deviations from equilibrium are given in first approximation by the following equations corresponding to a diffusive-reactive balance:

$$-\frac{(\rho\lambda)_m}{\rho_o^2 c_p} \frac{d^2 T}{dx^2} = -\frac{Q_1}{3c_p M_1} \frac{\rho_f}{M_1} k_{1f} \frac{M_1}{M_f} Y_3 e^\psi + \frac{Q_2}{3c_p M_1} \frac{\rho_f}{M_1} k_{2f} Y_1 Y_3 e^{b\psi} \tag{19}$$

$$-\frac{(\rho\lambda)_m}{\rho_o^2 c_p L_3} \frac{d^2 Y_3}{dx^2} = -\frac{\rho_f}{M_1}\left\{ k_{1f} \frac{M_1}{M_f} Y_3 e^\psi + k_{2f} Y_1 Y_3 e^{b\psi} \right\} \tag{20}$$

and

$$\frac{Q_1+Q_2}{2c_p M_1 L_1} (Y_1-Y_{1f}) + \frac{Q_2-Q_1}{6c_p M_1 L_3} Y_3 + T - T_f = 0 \ , \tag{21}$$

where $k_{1f} = B_1 \cdot \exp(-T_a/T_f)$, $k_{2f} = B_2 \cdot \exp(-bT_a/T_f)$ and

$$\psi = (T-T_f)T_a/T_f^2 \tag{22}$$

is the Frank-Kamenetskii variable appropriate for the temperature variations across the reaction zone. M_f and ρ_f are the values of M and ρ just downstream of the reaction zone; M_f and ρ_f are given, very accurately, by M_2 and the value obtained from the equation of state with $Y_1 = 0$ and $T = T_f$. We must also write $(\rho\lambda)_m = (\rho\lambda)_f$, in order to be consistent with the asymptotic analysis. The small changes of T from T_f in the thin reaction zone allowed us to linearize the Arrhenius exponents around T_f. The convective terms do not appear in Eqs. (19-21) because they are of order ε relative to the diffusive terms, a consequence of the small thickness of the reaction zone. The downstream boundary conditions (18) have been used to obtain (20) from Eq. (6), simplified in the thin reaction by neglecting the convective terms in the left hand side of the equation.

The conservation Eqs. (19-20) must be integrated with the downstream boundary conditions

$$x \to \infty: \quad T \to T_f, \quad Y_3 \to 0 \ . \tag{23}$$

The upstream boundary conditions are obtained from the matching conditions with the solution for the upstream transport zone. In the intermediate matching region the reaction terms in Eqs. (19-20) are negligible, so that the temperature and concentration gradients are constant. The Oxygen atoms reach the transport zone by diffusion from the reaction zone, where their mass fraction is of order ε; thus the upstream gradient of Y_1 is of order ε relative to its typical reaction zone values and, therefore, it appears as zero in first approximation. Hence one of the upstream boundary condition for Eqs. (19) and (20) is $dY_1/dx = 0$. The other upstream boundary condition requires only that Y_3 be a linear function of x or, because of the choice of the origin of x, that Y_3 is proportional to x. That is we require that

$$x \to -\infty: \quad \frac{dY_1}{dx} = 0 \quad \text{and} \quad \frac{(\rho\lambda)_m}{\rho_o c_p L_3} \frac{dY_3}{dx} = -g \tag{24}$$

where g is the burning rate of Ozone per unit flame surface. We can use Eqs. (21) and (24) to calculate the heat flux q from the reaction zone to the upstream transport zone; we thus obtain

$$q = \frac{(\rho\lambda)_m}{\rho_o} \frac{dT}{dx} = \frac{Q_2-Q_1}{6M_1} g \ . \tag{24'}$$

Notice that, as it has been indicated before, these boundary conditions are a conse-
quence of the upstream freezing of the chemical reactions, due to the linearized
form of the exponents of the Arrhenius factors. In the limiting case $b = 0$ the freez-
ing disappears and the boundary condition $dY_1/dx = 0$ at $x \to -\infty$ must be replaced by
$Y_1 = 0$ at $x \to -\infty$.

We can write the conservation equations (19-21) and their boundary conditions in a
universal form in terms of the variable ψ, the scaled concentrations

$$Y = Y_3/Y_{3c}, \quad Z = (3L_3/\mu L_1)Y_1/Y_{3c} \tag{25}$$

and the independent, stretched, variable

$$\xi = x/x_c . \tag{26}$$

Here Y_{3c}, defined by

$$Y_{3c} = \varepsilon \frac{6c_p M_1 L_3 T_f}{Q_2 - Q_1} = \varepsilon \frac{L_3 Y_{3o} T_f}{T_e - T_o} \tag{27}$$

is the characteristic value, of order $\varepsilon = T_f/T_a$, of the mass fractions of O and O_3 in
the reaction zone. The scale x_c for the reaction zone thickness, also of order ε re-
lative to the scale of the transport zone, is defined by

$$x_c = \sqrt{\frac{(\rho\lambda)_m M_f}{\rho_o^2 c_p L_3 \rho_f k_{1f}}} . \tag{28}$$

The following system of equations is obtained for the description of the reaction
zone structure

$$\frac{d^2 Y}{d\xi^2} = Y e^\psi + K Y Z e^{b\psi} \tag{29}$$

$$\frac{d^2 \psi}{d\xi^2} = \frac{1-\mu}{\mu} Y e^\psi - \frac{1+\mu}{\mu} K Y Z e^{b\psi} \tag{30}$$

$$\psi + Y + Z - Z_f = 0 \tag{31}$$

to be solved with the boundary conditions

$$\xi \to \infty: \quad \psi = Y = 0 \tag{32}$$

$$\xi \to -\infty: \quad Y + m\xi = Z - Z_{-\infty} = 0 \tag{33}$$

where Z_f, $Z_{-\infty}$ and m, defined by

$$m = \frac{g}{Y_{3c}} \sqrt{\frac{c_p M_f L_3}{(\rho\lambda)_m \rho_f k_{1f}}} , \tag{34}$$

are eigenvalues of the problem, to be calculated as functions of the parameters μ
and K given by

$$\mu = \frac{Q_2 - Q_1}{Q_2 + Q_1}, \qquad K = \frac{k_{2f}}{k_{1f}} \frac{2 L_1 c_p M_f T_f^2}{(Q_2 + Q_1) T_a} . \tag{35}$$

The parameter μ is fixed, $\mu = 0.573$, while the parameter K measures the relative values of the reaction rates of the two reactions at the temperature T_f. K varies with the flame temperature, taking values of order unity in the distinguished regime that we are now analysing, for which $R T_a / T_f \sim 1$.

For the numerical solution of the problem (29-33) we can use a shooting method beginning on the hot side of the flame, $\xi \to \infty$, which is a critical point of Eqs. (29-30) than are translational invariant with respect to ξ. These equations take, for $\xi \gg 1$, the simplified form obtained by replacing the Arrhenius factors by 1, and Z by Z_f. Then, Y is given in that region by

$$Y = e^A \cdot \exp(-\sqrt{1 + K Z_f} \; \xi) \; ,$$

with an unknown translational constant A that can be removed from the numerical process by a trivial change in ξ; ψ is given by

$$\psi / Y = \left(\frac{1-\mu}{\mu} - \frac{1+\mu}{\mu} K Z_f \right) / (1 + K Z_f) .$$

Now Z_f must be chosen so that the upstream slopes of ψ and $-Y$ are identical, and A so that $(Y + m\xi)_{-\infty} = 0$.

The matching conditions with the distributions of temperature and concentration in the upstream zone, given by Eqs. (17), can be used to calculate the flame velocity U, and the values of a_1 and a_2. For example, by matching the slopes of Y_3, upstream of the thin reaction zone, we obtain

$$g = \rho_o Y_{30} U \tag{36}$$

and therefore

$$U = \frac{T_f}{T_a} \frac{T_f}{(T_e - T_o)} \sqrt{\frac{(\rho \lambda)_m \rho_f L_3 B_1}{\rho_o^2 c_p M_f}} \cdot \exp(-T_a / 2 T_f) \cdot m(K) . \tag{37}$$

By matching the values of Y_1, just upstream of the thin reaction zone, we obtain for this value the relation

$$\varepsilon a_1 = \frac{2 c_p M_1 L_1 T_f^2}{(Q_1 + Q_2) T_a} \cdot Z_{-\infty}(K) . \tag{38}$$

The downstream value Y_{1f} of Y_1 is given by

$$Y_{1f} = \frac{2 c_p M_1 L_1 T_f^2}{(Q_1 + Q_2) T_a} \cdot Z_f(K) . \tag{39}$$

The value of a_2 that characterizes the apparent jump in temperature is given by

$$a_2 = (Z_f - Z_{-\infty}) T_f / (T_f - T_o) . \tag{40}$$

We should notice that K depends on T_f according to the relation

$$K = \frac{B_2}{B_1} \frac{2L_1 c_p M_f T_f^2}{(Q_1 + Q_2) T_a} \cdot \exp\{(1-b) T_a / T_f\} \tag{41}$$

where T_f is still unknown. To calculate T_f we must use Eq. (41), together with Eq. (39) and the relation

$$T_f = T_o + \frac{Q_2 - Q_1}{6 c_p M_1} Y_{3o} - \frac{L_1 T_f^2}{T_a} Z_f(K) \tag{42}$$

obtained from Eqs. (7-8) and (39).

The relations (41) and (42) enable us to calculate T_f, together with Z_f and K. Then U can be determined by means of the relation (37), and the upstream value of Y_1 by means of the relation (38). Notice that the effective activation temperature of the flame propagation, defined by $2T_f^2 \, dU/UdT_f$ is not constant in this complex flame regime.

The solution of the problem of Eqs. (29-33) has been obtained numerically, with $\mu = 0.573$, for the values $b = 0.25$, associated with the kinetic data of Cramarossa and Dixon-Lewis /1/, for $b = 0.206$, corresponding to the kinetic data used by Heimerl & Coffee /5/, and for the limiting case $b = 0$. The results are shown in Figs. 2 and 3, showing m, Z_f, and $Z_{-\infty}$ as functions of K.

When trying to obtain the solution of Eqs. (29-33) for large values of K, it is more convenient to replace Eq. (30) by the conservation equation

$$-\mu \frac{d^2 Z}{d\xi^2} = Y e^{\psi} - K Y Z e^{b\psi} . \tag{30'}$$

Then, we can see that for $K \gg 1$ it is justified to use the steady state approximation for Z, so that (30') simplifies to

$$Z = K^{-1} \cdot \exp\{(1-b)\psi\} \tag{43}$$

obtained by neglecting the diffusive term in (30'), of order $1/K$. Eq. (29) takes the form

$$\frac{d^2 Y}{d\xi^2} = 2Y e^{-Y} \tag{44}$$

That can be easily solved with the conditions (32) and (33). Thus, for $K \gg 1$ we have in first approximation (the second terms in the expansions are given in figures 2 and 3)

$$m = 2, \quad Z_f = 1/K \quad \text{and} \quad Z_{-\infty} = 0 \tag{45}$$

$$m=2+\frac{1}{K}\left[1-\frac{1-(1-b)\mu}{(2-b)^2}\right] \text{ for } K\gg1$$

b=0

b=0.206

b=0.25
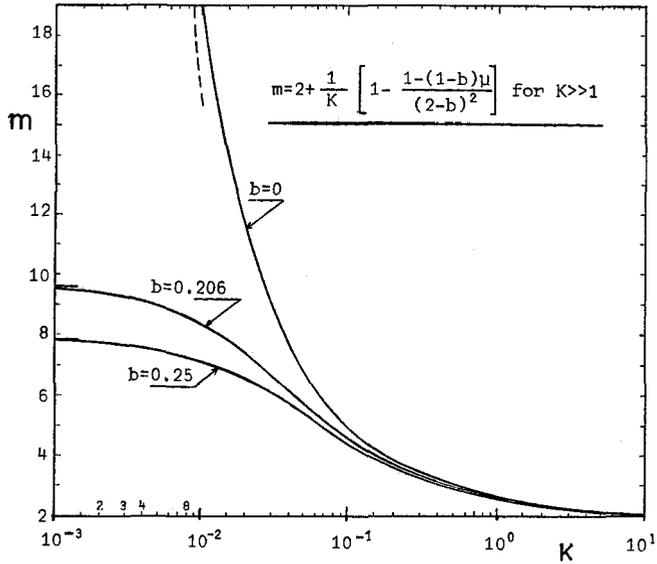
Fig. 2 - The nondimensional burning rate in terms of K or, rougly, the ratio of characteristic times of the first and second reactions at the primary flame temperature.
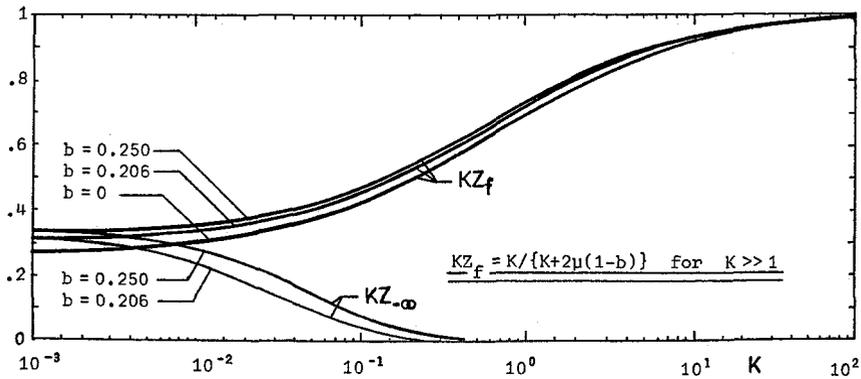

b = 0.250

b = 0.206

b = 0

KZ_f

b = 0.250

b = 0.206

$$\frac{KZ_f = K/\{K+2\mu(1-b)\}}{} \text{ for } K\gg1$$

$KZ_{-\infty}$

Fig. 3 - The nondimensional concentration of atomic Oxygen just upstream, $Z_{-\infty}$, and downstream, Z_f, of the primary flame in terms of K.

recovering the results obtained in the beginning of the section for $RT_a/T_f \ll 1$. Notice that for $K \to \infty$, $T_f \to T_e$ and $1/K \sim RT_a/T_e$; thus the validity of the steady state approximation for O is conditioned to the inequality $K \gg 1$, or $RT_a/T_e \ll 1$.

For small values of K, Z becomes large, so that $ZK = \zeta$, as well as ψ and Y, are of order unity. In this case (31) yields, in first approximation,

$$\zeta = \zeta_f. \tag{46}$$

If this constant value of ζ is used in Eqs. (29) and (30), they can now be solved with KZ replaced by the unknown eigenvalue ζ_f, that must be determined, thus providing the nondimensional burning rate m, to insure the existence of the solution. The numerical results give $\zeta_f = 0.334$ and $m = 7.849$ for $b = 0.25$, and $\zeta_f = 0.314$ and $m = 9.603$ for $b = 0.206$, and the limiting values $\zeta_f \simeq (1-\mu)/(1+\mu) = 0.272$ and $m \to 0.153/K$ for $b=0$.

From the results of the numerical analysis we can also calculate, for the limiting case $K \ll 1$, the value of $(\psi+Y)_{-\infty} = (Z_f - Z_{-\infty})K$, that yields a second approximation for the concentration of O just upstream of the reaction zone of the primary flame; we obtain for $(\psi+Y)_{-\infty}$ the values 7.922, 10.217 and 0.272/K for $b = 0.25$, 0.206 and 0, respectively.

It should be noticed, however, that the analysis given here should be modified for very small values of K, when the concentration of Y_1 grows in the reaction zone to values of order ϵ/K. Then the gradient of Y upstream of the reaction zone becomes of order unity if $K \sim \epsilon$. Notice also that due to the small value of b the thickness of the zone where the second reaction takes place becomes very large for small values of K, and then convection effects become important there; this is not the case when K is of order unity or large because then Y is consumed fast enough after being produced, so that in this case it does not diffuse upstream.

The flame structure in the interesting regime $K \sim \epsilon$, or $R \sim 1$, with $b \ll 1$ must include a thin reaction layer for reaction 1 and an extended zone for reaction 2.

III - THE CONVECTIVE-RECOMBINATION ZONE

In the convective-recombination region that trails downstream of the primary zone, the concentration of Ozone is so small, of the order of $\rho k_{1r}/Mk_2 \ll 1$, that we can use the steady state approximation for O_3 when describing the recombination zone, which turns out to be so long that the diffusive effects are negligible there. In this region the O atoms that come out of the primary flame are slowly recombined into O_2, with a heat release that increases the temperature from T_f to T_e.
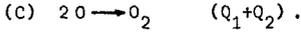
Thus the concentration of O_3 is given by the steady-state approximation

$$Y_3 = (3\rho/2M)k_{1r}Y_1Y_2/(k_1M_1/M + k_2Y_1) \tag{47}$$

obtained by balancing its production by the forward reactions 1 and 2 and its consumption by the reverse reaction 1. Then the evolution of Y_1 is given by

$$U \frac{dY_1}{dx} = - \frac{\rho^2}{M_1 M} \left(\frac{k_{1r} k_2 Y_1^2 Y_2}{k_1 M_1 / M_2 + k_2 Y_1} + 2 k_3 Y_1^2 \right) \tag{48}$$

associated with an overall reaction

(C) $\quad 2 \, O \longrightarrow O_2 \qquad (Q_1 + Q_2)$.

This overall reaction results, on one hand, from reaction 3, represented by the last term in the right hand side of Eq. (48), and also from a combination of reactions 1, 2 and 3 that, in the limit $k_3 \to \infty$, leads to the steady state approximation for O_3. This reaction path is represented by the first term in the right han side of Eq. (48).

If the effect of the reverse reaction 3 is to be included in this region, the term $(\rho/M) k_{3r} Y_2$ should be added to the right hand side of this last equation. Then Y_1 would be given by

$$U \frac{dY_1}{dx} = - \frac{\rho^2}{M_1 M} \left(\frac{k_{1r} k_2 Y_1^2 Y_2}{k_1 M_1 / M + k_2 Y_1} + 2 k_3 Y_1^2 \right) + \frac{\rho}{M} k_{3r} Y_2 \tag{48'}$$

and the final equilibrium concentration Y_{1e} is then different from zero. However the inclusion of the reverse reaction 3 should be accompanied by the inclusion of the reverse reaction 2. These dissociation reactions are only important in the very final region of the recombination zone if T_e is large enough.

In the long convective-recombination region the diffusive terms in the right hand side of Eq. (6) are negligible, so that it simplifies to

$$\frac{Q_2 + Q_1}{2 c_p M_1} Y_1 + \frac{Q_2 - Q_1}{6 c_p M_1} (Y_3 - Y_{3o}) + (T - T_o) = 0 \tag{49}$$

and if we take into account that the steady state approximation gives a value for $Y_3 \ll 1$, then we obtain the relations

$$Y_2 = 1 - Y_1 \tag{50}$$

$$T - T_o \cong \frac{Q_2 - Q_1}{6 c_p M_1} Y_{3o} - \frac{Q_1 + Q_2}{6 c_p M_1} Y_1 \tag{51}$$

giving the molecular Oxygen concentration and the temperature in terms of Y_1. When (50) and (51) are use together with Eq. (48), the equation of state $\rho = pM/RT$, and the initial condition

$$Y_1 = Y_{1f} \quad \text{at} \quad x = 0 \tag{52}$$

we can calculate the evolution of Y_1 in the convective recombination zone by means of a quadrature.

IV - SUMMARY OF THE RESULTS AND CONCLUDING REMARKS

An analysis has been carried out of the structure of the Ozone decomposition flame, which follows the simple reaction mechanism (A). In the analysis we have taken into account the large value of the nondimensional activation energy of the first forward reaction; due to this large value the notion of a premixed flame separating two uniform regions of constant composition and temperature has a physical meaning and, in addition, we can consider this reaction to be frozen in the upstream transport zone of the flame.

The fact that the three-body recombination reactions are very slow at ambient pressures, compared with the two-body reactions, is responsible for the two-zone structure of the flame. The flame propagation process is controlled by a primary flame, where the kinetic scheme can be simplified to (B) by neglecting the three-body reactions. These are only important, after nearly complete consumption of O_3, in a long trailing recombination zone; there heat conduction and diffusion effects can be neglected, and the temperature and concentrations slowly adjust to their final equilibrium values --if the reaction chamber is long enough for these values to be reached. In the recombination zone, it is justified to use the steady state approximation for O_3 and, consequently, the approximate kinetic scheme (C).

We have found the following characteristic value for the flame velocity, in the distinguished complex flame regime,

$$U \sim \sqrt{\frac{\lambda_o}{\rho_o c_p} \frac{\rho_e k_{2e}}{M_1}} \left(\frac{T_e}{T_a}\right)^{3/2} .$$

The values of the characteristic thickness ℓ_p of the transport zone of the primary flame, ℓ_h of its reaction zone, and ℓ_R of the recombination zone are

$$\ell_p = \frac{\lambda_o}{\rho_o c_p U}, \quad \ell_h = \ell_p \left(\frac{T_e}{T_a}\right) \quad \text{and} \quad \ell_R = \ell_p \frac{M_1 k_{2e}}{\rho_e k_{3e}} \left(\frac{T_e}{T_a}\right)^{3/2} .$$

The effects of the Oxygen dissociation reaction can be neglected because the reaction is very slow due to its large activation energy; if it plays a role it will only be significant in the tail of the recombination zone, to determine the final equilibrium composition at high equilibrium temperatures. The characteristic times associated with the recombination and dissociation reactions are too large, compared with those of reactions 1 and 2, to play an active role in the structure of the primary flame.

The flame velocity and, more generaly, the dynamics of the Ozone decomposition flame are thus determined by the simplified mechanism (B). For low initial Ozone concentrations, the post primary flame temperature T_f will be low enough to make the rate of the first reaction that produces Oxygen atoms very slow compared to the rate of

the second reaction that consumes O; then the concentration level of O is kept very small, and the transport terms can be neglected in the conservation equation for O compared with the production and consumption terms. This quasi-steady state approxi mation for O was introduced by Von Kármán and Penner /15/, in the analysis of the Ozone flame. Millán and Da Riva /16/, carried out a first systematic study of the validity of the steady state approximation for the computation of the distribution of radicals in flames; it was applied, in particular, to the case of the atomic Oxy gen in the Ozone flame. It turns out that the approximation can not be used, as we have seen before, neither in the long recombination zone, where it can be used to describe the evolution of O_3, nor for higher initial Ozone concentrations, when the rate of the reaction 2 ceases to be very fast compared with that of reaction 1. In this latter case, the atomic Oxygen mass fraction becomes of the order of T_f/T_a, an we must use the analysis of the complex flame regime given in this paper.

It is important to notice that the system of Eqs. (19-24), or equivalently Eqs. (29 33), that determines the reaction zone structure (and simultaneously the Ozone burr ing rate g and associated heat release at the flame q, together with Y_{1f} and Y_{1a}) can be solved, in a general way, for any given value of T_f. Of the two parameters µ and K that appear in the normalized reaction layer problem (29-33), only K, given b (41), varies with T. The dependence, for example, of the burning rate g on T_f is then summarized by Fig. 2 and the definitions (34) and (41).

We can afterwards use the matching conditions with the outer structure to analyse the flame dynamics and, in the process, calculate T_f and the reaction front propaga tion velocity. When the transport zone is assumed to be planar and steady, T_f is given by (42), and U by (37). The resulting values of the flame velocity and tempe- rature are compared in Figure 4 with those calculated numerically by Cramarossa & Dixon-Lewis and by Heimerl & Coffee. The differences between the numerical results c Cramarossa & Dixon-Lewis and those of Heimerl & Coffee are a consequence of the dif- ferences in kinetic data. The asymptotic results for the flame velocity, obtained i this paper for the complex flame regime, correspond only to the first term in an ex pansion for large T_a/T_f. The analysis may be expected to fail for high Ozone concer trations when the mass fraction grows and the reaction zone of the second reaction thickens considerably, so that the convective effects begin to be important in this zone. Rogg and Wichman have recently carried out an asymptotic analysis, to second order for large T_a/T_e, of the Ozone flame, for small values of Y_{3o}.

When the flame dynamics is affected by wrinkling or unsteady or heat loss effects, these first enter as small perturbations in the outher transport zone, and not in the structure of the thin reaction zone. So that the relations $g(T_f)$, $q(T_f)$, $Y_{1a}(T$ and $Y_{1f}(T_f)$ that are obtained from the solution of Eqs. (29-33), hold also in the unsteady wrinkled case. These relations can be used as jump conditions when analyz
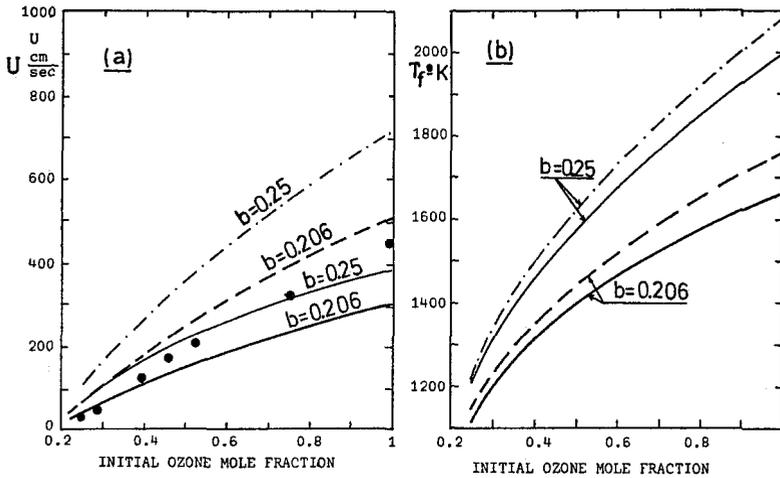
Fig. 4 - Comparison of the asymptotic results, solid lines, for the flame velocity, (a), and temperature, (b), in terms of the initial Ozone concentration with the numerical calculation of references /1/ —·—·—·— , /5/ — — — — and experimental observations of reference /21/ quoted in /1/ ● .

ing the outer problem, for which the reaction zone appears as an infinitely thin surface, where Y_3 and T are continuous but have discontinuous derivatives. The flame temperature is no longer given by Eq. (8); unsteady or wrinkling effects cause changes in T_f of order T_f^2/T_a, leading to changes by a factor of order unity in the flame front propagation velocity. The analysis of flame dynamics or stability carried out in references /17/ to /20/ for Arrhenius kinetics, can be generalized, proceeding as in /9/, to describe the dynamics of the Ozone flame in the complex flame regime, using the jump conditions obtained here.

Acknowledgement

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