Gas Phase Ignition Theory for Homogeneous Propellants under Shock Tube Conditions

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Theoretical characteristics of the ignition phenomenon, wherein a homogeneous propellant is exposed to stagnant gas after a shock reflection, derived by a combination of numerical and approximate techniques, are discussed. The one-dimensional model considered variable gas density, simultaneous diffusion and chemical reaction, self-determining (feedback) conditions at the solid-gas interface, and various solid and gas phase compositions. The descriptive equations were integrable over the whole time to achieve steady combustion of the solid, giving a complete spectrum of ignition results. In particular, approaching the steady state, a predictable, inverse square dependence on external oxidizer mole fraction was found for the ignition delay. This was true with large external oxidizer mole fractions, even with feedback operative, and resulted n a twin reaction zone structure which disappeared at low oxidizer mole fractions. This effect was found for a wide range of gas phase stoichiometry and solid composition. Further data are presented for a wide range of pyrolysis rates of the solid.

Nomenclature

A = (QR/c_pnbE), dimensionless heat release parameter
B = pre-exponential factor of pyrolysis law of solid, g/cm^2 sec
b = ($\rho_g{}^3ZD/m_o{}^2$), dimensionless mass flux parameter
C_f,C_{ox} = gas phase concentrations of fuel and oxidizer, respectively; g/cm^3, $\dot{C}_i = \partial C_i/\partial t$
C = a constant, Eqs. (23) and (25)
c_p = specific heat of gas phase, 0.3 cal/g°K
$\mathfrak{D}$ = local mass diffusivity, cm^2/sec
D = ($\rho^2\mathfrak{D}/\rho_g{}^2$) = constant, effective mass diffusivity, cm^2/sec
E = activation energy of gas phase reaction, kcal/mole
E_p = activation energy of pyrolysis, kcal/mole
h_v = heat of pyrolysis, kcal/g
$L^*(\theta)$ = any particular ignition criterion
m = total mass flux issuing from the solid-gas interface, g/cm^{2}sec by pyrolysis
m_o = pyrolysis mass flux at 400°K surface temperature, a reference value
n = molar stoichiometric ratio of gas phase reaction
Q = heat of combustion in gas phase, kcal/g
R = universal gas constant, 1.986 cal/mole°K
t = time, sec
t^* = ignition delay, sec
T,T_o = local, initial, gas phase temperature
T_s,T_{so} = local, initial, solid phase temperature
x = distance, cm
$y_f,y_{\text{ox}}{}'$ = respectively, mole fractions of fuel, oxidizer gaseous species produced by the solid
$y_{\text{ox}}{}'',y_{\text{ox}}$ = gas phase supplied, and total oxidizer mole fractions in the gas phase ($y_{\text{ox}} = y_{\text{ox}}{}' + y_{\text{ox}}{}''$)
$y_{\text{ox}}{}^\infty$ = initial mole fraction of oxidizer in gas phase
Z = pre-exponential factor of gas phase chemical reaction, cm^3/g sec
α = m_f/m = ratio of fuel mass flux to total mass flux
α_s = thermal diffusivity of solid phase, cm^2/sec
β = (Rh_v/c_pE) = dimensionless heat of pyrolysis and $\beta = Anb^2\alpha(1-\alpha)$ [Eq. (24)]
δ = reaction zone thickness in gas phase, cm
ϵ = ($\Delta\theta_{\max}/\theta_{\max}$)($\tau/\Delta\tau$) = ignition criterion
$\eta_f,\eta_{\text{ox}},\eta_{\text{ox}}{}^*$ = nby_f, by_{ox}, and $by_{\text{ox}}{}^\infty$, respectively, dimensionless reactant mole fractions
θ = RT/E = dimensionless gas phase temperature
θ_s = RT_s/E_p = dimensionless solid phase temperature
κ = gas phase thermal diffusivity, cm^2 sec
Λ = (λ_sE_p/ρ_gDc_pE) = dimensionless thermal conductivity ratio
λ_s,λ_g = thermal conductivities of solid and gas phases, respectively, cal/cm sec°K
μ = (ρ_g/ρ_s) = ratio of initial gas phase, to solid, density
ξ = (m_o/ρ_gD)ψ = dimensionless length coordinate in gas phase
ξ_s = ($m_o/\rho_gD\Sigma^{1/2}$)x = dimensionless length coordinate in solid phase
ρ,ρ_g,ρ_s = local gas phase, initial gas phase, and solid phase, densities, g/cm^3
Σ = (α_s/D) = ratio of solid to gas phase thermal diffusivities
τ = ($m_o{}^2/\rho_g{}^2D$)t = dimensionless time
τ^* = dimensionless ignition delay for some particular ignition criterion
ψ = $\int_o^x [\rho(x,t)/\rho_g]dx$, Howarth length dimension, cm
ω = (m/m_o) = ratio of actual to reference pyrolysis mass fluxes

Subscripts

NSS = refers to "near steady state"
ST = refers to "short time"

Arbitrary constants

C_1,C_2,m_1,m_2 = constants, see Eqs. (18) and (19)

I. Introduction

THE ignition of solid propellants, under conditions where the propellant sample is exposed to controlled conditions of gas phase temperature, pressure and composition behind a reflected shock wave has undergone intensive experimental investigation.[1] The propellant samples were mounted in the end wall of the shock tube. The well-known results

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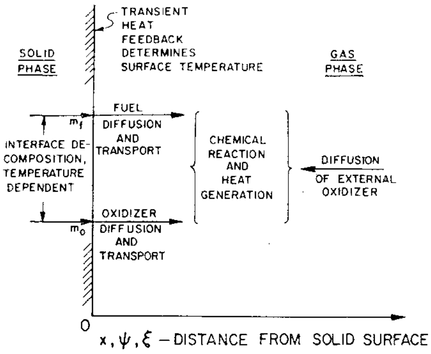

Fig. 1 Schematic of physical model.

indicate that for all other conditions constant, the ignition delay is very sensitive to the quantity of oxidizer initially present in the gas phase. Several theoretical attempts to explain this sensitivity have been made, based upon the premise that ignition occurred primarily because of reaction of propellant pyrolysis products in the gas phase. These attempts had varying degrees of sophistication, and assumed only the fuel binder pyrolized, producing a reactable mixture (in the gas phase adjacent to the solid) by diffusion into a stagnant gas containing an oxidizer. Some satisfactory success was obtained by these analyses when the fuel pyrolysis rate was allowed to depend upon the surface temperature of the fuel through an Arrhenius relationship. This temperature, in turn, depended on the heat feedback from the gas phase.[2] In summary, it was shown in Ref. 2 that ignition of even hard-to-pyrolize fuels was predicted in times commensurate with those observed experimentally, and that the dependence of the ignition delay on the initial gas phase oxidizer concentration could be as large as found in experiments. However, these results were of limited value in so far as real propellants are concerned, since no ignition was possible for pure fuels in inert atmospheres, where real propellants are routinely ignited.

Recently, an investigation of the gas phase ignition characteristics of a homogeneous propellant, which decomposes into both fuel and oxidizing components, has been presented,[3] thus allowing ignition in an inert, external gas phase. This work assumed fixed conditions of temperature, and mass decomposition rate, at the surface of the homogeneous propellant exposed to the hot, stagnant gas phase conditions behind a suitably reflected shock wave. The results indicated some rather surprising trends. The ignition delay, defined as the time to attain some critical "flame" temperature, was found to have only a weak dependence upon the quantity of oxidizer present in the gas phase, for a wide range of investigated conditions of propellant decomposition rate and composition, and external gas phase properties. On the other hand, it was also found that the dependence of the ignition delay on the quantity of oxidizer initially in the gas phase was as strong, or stronger than, that found experimentally if an ignition criterion based upon the time to reach "almost steady" burning was used. The calculated real ignition delays using this criterion were acceptably rational as well.

These results raised the obvious question of whether similar behavior would also be found if the decomposition rate of the solid were allowed to suit itself to the surface temperature caused by heat feedback from the gas phase to the initially cold solid. The results obtained using such a quite realistic model are the subject of the present paper.

II. Model

Assumptions

In formulating the model the following assumptions were made. 1) The diffusion of heat and mass is one-dimensional. 2) The mass decomposition rate of the solid surface depends on the surface temperature through an Arrhenius rate expression of the form $m = \rho_s B \exp(-E_p/RT_s)$. 3) The gas phase is assumed to be stagnant, initially, at a constant temperature and pressure such as that produced by a suitable shock wave reflected from the solid (propellant) surface. 4) The specific heats and thermal conductivities of the solid and gas phase are constant and equal. 5) The gas phase chemical reactions are second order, and obey an Arrhenius law such that $(\partial y_f/\partial t)|_{\text{chem}} = (1/n)(\partial y_{\text{ox}}/\partial t)|_{\text{chem}} = -\rho Z y_f y_{\text{ox}} e^{-E/RT}$ with a constant molar stoichiometry of the form $F + n(Ox) \rightarrow (n+1)P$. 6) $\rho^2\kappa = \rho^2\mathfrak{D} = \text{const.}$ 7) Lewis number is unity. 8) ρZ is a constant. 9) Both the external gas phase oxidizer and the oxidizer produced by decomposition of the solid phase have the same physical and chemical properties.

Assumption 9 allows the conservation equations of the two oxidizer species in the gas phase to be added together, producing a diffusion equation for all oxidizing species. This is possible because the boundary conditions for these species are compatible. A sketch of the model is shown in Fig. 1.

After using the Howarth transformation

$$\psi = \int_o^x (\rho/\rho_g)dx$$

to transform the spatial dimension in the gas phase to a constant density form in ψ space, and noting that $D = (\rho^2\mathfrak{D}/\rho_g^2) = \text{const}$, the diffusion equations for species and energy take on the forms to be described below.

Equations

Let Γ be a diffusing quantity, and define the operator $K(\Gamma)$ as

$$K(\Gamma) = (\partial\Gamma/\partial t) + (m/\rho_g)(\partial\Gamma/\partial\psi) - D(\partial^2\Gamma/\partial\psi^2) \quad (1)$$

Then the species and energy equations are thus

Fuel:

$$K(y_f) = -\rho Z y_f y_{\text{ox}} \exp(-E/RT) \quad (2)$$

Oxidizer:

$$K(y_{\text{ox}}) = -n\rho Z y_f y_{\text{ox}} \exp(-E/RT) \quad (3)$$

Energy: (Gas Phase)

$$K(T) = (\rho Q Z/c_p) y_f y_{\text{ox}} \exp(-E/RT) \quad (4)$$

Energy: (Solid Phase)

$$(\partial T_s/\partial t) + (m/\rho_s)(\partial T_s/\partial x) = \alpha_s(\partial^2 T_s/\partial x^2); \quad x < 0 \quad (5)$$

and have the following constraints:

$$y_f(\psi,0) = 0, \text{ and } my_f(0,t) - \rho_g D(\partial y_f/\partial\psi)_{0,t} = \alpha m$$

$$y_f(\infty,\tau) = 0$$

$$y_{\text{ox}}(\psi,0) = y_{\text{ox}}{}^{\infty}, \text{ and } my_{\text{ox}}(0,t) - \rho_g D(\partial y_{\text{ox}}/\partial\psi)_{0,t} = (1-\alpha)$$

$$y_{\text{ox}}(\infty,\tau) = y_{\text{ox}}{}^{\infty}$$

$$T(\psi,0) = T_o, \text{ and } m = \rho_s B \exp|-E_p/RT_s(0,t)|, \ T(\infty,\tau) = T_0$$

$$T_s(x,0) = T_{so}, \text{ and } T_s(0,t) = T(0,t), \ T_s(-\infty,\tau) = T_{so}$$

$$\lambda_s(\partial T_s/\partial x)_{0,t} - mh_v = \rho_g D c_p(\partial T/\partial\psi)_{0,t} \quad (6)$$

The preceding equations were nondimensionalized by the following set of parameters:

$$m_o = \rho_s B \exp(-E_p/400R)$$

$$m = \rho_s B \exp|-E_p/RT(0,t)|$$

$$\omega = m/m_o$$

$$\Sigma = \alpha_s/D$$

$$\theta = RT/E$$

$$\theta_s = RT_s/E_p$$

$$\eta_f = nby_f$$

$$\eta_{\text{ox}} = by_{\text{ox}}$$

$$\Lambda = (\lambda_s E_p/\rho_g D c_p E) \qquad \xi = (m_o/\rho_g D)\psi$$

$$b = \rho_g{}^3 ZD/m_o{}^2 \qquad \tau = (m_o{}^2/\rho_g{}^2 D)t$$

$$A = QR/(nc_p Eb) \qquad \xi_s = (m_o/\rho_g D\Sigma^{1/2})x$$

$$\beta = (Rh_v/c_p E)$$

$$\mu = \rho_g/\rho_s$$

Equations (1–5) then take the following nondimensional form where the operator H is defined as $H = (\partial/\partial\tau) + \omega(\partial/\partial\xi) - (\partial^2/\partial\xi^2)$

$$H(\eta_{\text{ox}}) = H(\eta_f) = -\eta_f\eta_{\text{ox}}e^{-1/\theta} \tag{7,8}$$

$$H(\theta) = A\eta_f\eta_{\text{ox}}e^{-1/\theta} \tag{9}$$

$$(\partial\theta_s/\partial\tau) + (\mu\omega/\Sigma^{1/2})(\partial\theta_s/\partial\xi_s) = (\partial^2\theta_s/\partial\xi_s{}^2) \tag{10}$$

The initial and boundary conditions for Eqs. (7–10) have the nondimensional forms given below;

$$\eta_f(\xi,0) = 0, \quad \eta_f(0,\tau) - (\omega^{-1})(\partial\eta_f/\partial\xi)_{0,\tau} = nb\alpha$$

$$\eta_{\text{ox}}(\xi,0) = \eta_{\text{ox}}{}^{\infty}, \quad \eta_{\text{ox}}(0,\tau) - (\omega^{-1})(\partial\eta_{\text{ox}}/\partial\xi)_{0,\tau} = (1-\alpha)b$$

$$\theta(\xi,0) = \theta_o, \quad \theta_s(0,\tau) = \theta(0,\tau)$$

$$\theta_s(\xi_s,0) = \theta_{so}, \quad (\Lambda/\Sigma^{1/2})[\partial\theta_s/\partial\xi_s]_{0,\tau} + \beta\omega = [\partial\theta/\partial\xi]_{0,\tau}$$

and

$$\eta_f(\infty,\tau) = 0, \ \eta_{\text{ox}}(\infty,\tau) = \eta_{\text{ox}}{}^{\infty}$$

$$\theta(\infty,\tau) = \theta_o, \ \theta_s(-\infty,\tau) = \theta_{so}$$

Defining the nondimensional space variable in the solid phase in this fashion allows immediate calculation of the correct value of θ_s when the equations are integrated numerically by a forward difference method. In addition it has been found[2] that the effect of various endothermic values of the heat of pyrolysis of the solid phase, h_v, has very little effect on the resulting ignition behavior. Consequently $h_v = 120$ was selected for all calculations in the present work. A rather wide range of solid fuel type binders have thermal conductivity values which are approximately equal to the gas phase thermal conductivity. Since Λ is effectively equal to the ratio (λ_s/λ_g), a value of $\Lambda = 1$ was also assumed in the calculations. E_p and E were assumed in the calculation.

Equations (7–10), with the boundary conditions of Eq. (11), were integrated numerically using an IBM 360/75 digital computer. During the course of the investigations, a number of different numerical methods were employed, as described in Refs. 3 and 4. Recently it was found that an "explicit-implicit" method of integration[5] is the fastest and most accurate method. Computational times for a typical set of data were reduced to about 5 min when a "weak" ignition criterion was used, and 1 hr or less when a criterion satisfied near the achievement of steady state was used. These times are shorter by up to a factor of five than those obtained with integration techniques previously used. Discussion of the ignition criteria is included in the next section.

III. Ignition Criteria

As has been strongly indicated in the past, the choice of ignition criterion largely determines the character of the ignition process, both in experiment[6] and theory.[2,3,7] In the present study results are reported in terms of two basic ignition criteria, $L^*(\theta)$. The first of these is what is termed a "short time" criterion, which corresponds to the first time a maximum gas phase temperature of $1.5\theta_o$ is achieved anywhere in the gas phase—or $L^*(\theta) = 1.5\theta_o$. This criterion was used to allow comparison of results reported herein to those of previous papers.[2–4] In the present work, this criterion corresponds to the physical situation of the occurrence of significant heat release in the gas phase but with negligible consumption of oxidizer species. It is not proposed to give the criterion $L^*(\theta) = 1.5\theta_o$ any significance other than that of being convenient in a theoretical sense, for in fact the second criterion discussed below may have more significance in relating theoretical and experimental results.

Table 1 Values of the physical parameters used in the numerical calculations

$E_p/R = 6000°\text{K}$	$\theta_o = 0.3$
$E/R = 6000°\text{K}$	$\theta_{s,o} = 0.05$
$Q/c_p = 40{,}000°\text{K}$	
$\rho Z = 5 \times 10^5/\text{sec}$	

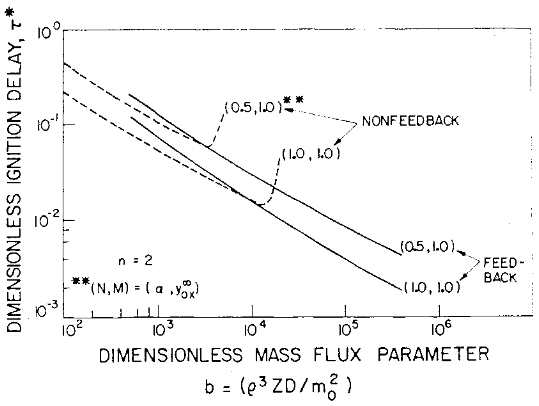

Fig. 2 The effect of feedback on ignition as the mass flux parameter is varied.

The second criterion will be termed the "near steady-state" criterion and is descriptive of the ignition process at times greater than those at which $L^*(\theta) = 1.5\theta_o$ (the "short time" criterion) are achieved. The physical situation is that of a flame structure which is still transient, but approaching steady conditions in terms of specie and temperature distributions in the gas phase. The temperature of the solid-gas interface is constant, and in the transient part of the gas phase flame structure (to be described in detail in a later section), the rate of chemical heat generation is almost equal to the local heat loss. Operationally, for numerical computations, the "near steady-state" criterion was related to the rate of change of the maximum gas phase temperature in the system, wherever it might be in spatial location. The most convenient operational criterion was $L^*(\theta) = \epsilon = (\Delta\theta_{\max}/\Delta\tau)(\tau/\theta_{\max}) = 0.01$ or any other selected, arbitrary constant.

IV. Numerical Results

A representative range of results of this investigation of ignition when feedback is operative is included in the paper.

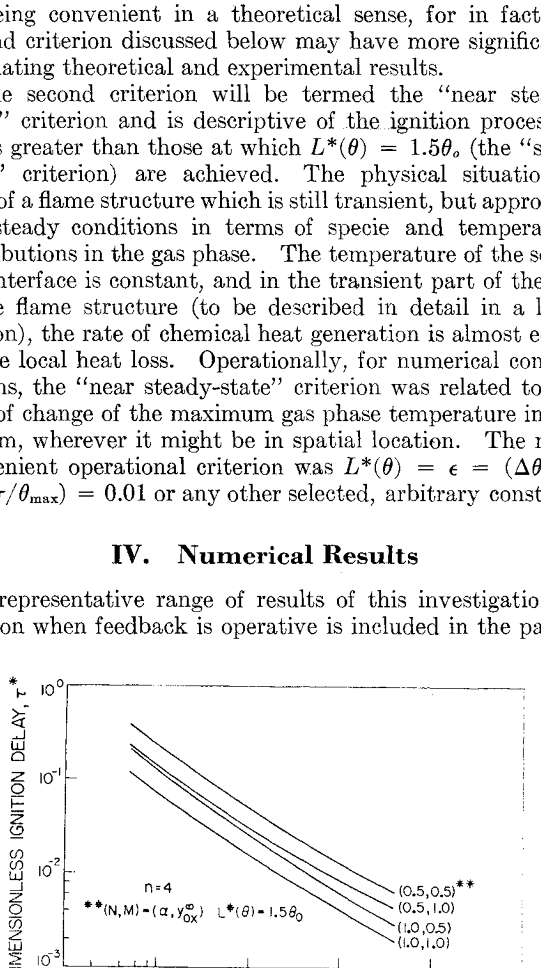

Fig. 3 Variation of dimensionless ignition delay with dimensionless mass flux for various propellant and ambient gas phase compositions.

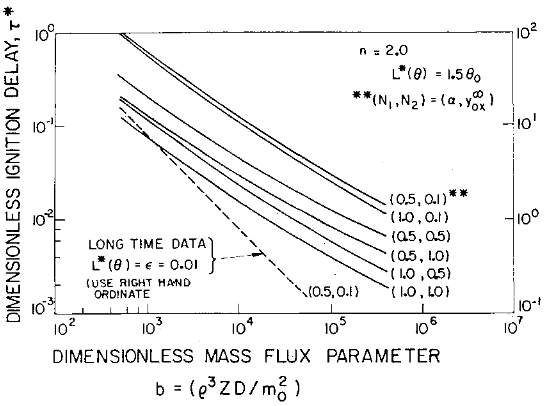

Fig. 4 Variation of dimensionless ignition delay with dimensionless mass flux for various propellant and ambient gas phase compositions.

They illustrate the dependence of the ignition delay, both dimensionless and dimensional, upon ignition criterion, decompositional rate of the solid (including several different solid phase compositions), and oxidizer content of the external gas phase. The parameter values used in all computations are listed in Table 1.

Figure 2 contains nonfeedback results to facilitate comparison with the present work; it illustrates that no errors in principal ignition characteristics are found if feedback is neglected—providing the mass flux is sufficiently large—for propellants such as are considered here, or for pure fuels.

For the most part the ($\tau^* - b$) curves, Figs. 2–4, are obtained using the "short time" ignition criterion $L^*(\theta) = 1.5\theta_o$. These results are reported to allow comparison of the present work to results reported in previous papers.[2–4] Figure 4 and Fig. 7 of Ref. 3 also indicate that in an inert external atmosphere, the dependence of τ^* on b approaches $\tau^* \sim b^{-1/2}$, a result that is predicted by the asymptotic analysis discussed in Sec. V.

The complete system of equations of this model are completely interactive, with interface conditions on temperature and mass decomposition rate that adjust in time as energy is fed back to the interface. Continued integration in the time domain until unchanging (steady-state) conditions are established in both the solid and gas phases was thus possible. Some very interesting behavior was observed as the system approached steady state, particularly when a significant amount of oxidizer was present in the external gas phase. Our previous studies,[3] with fixed conditions of temperature and mass flux, also achieved a steady-state condition, and indicated a basic change in ignition characteristics as this condition was approached. However, it was not clear that similar results would indeed be found if feedback were considered. In fact, essentially the same behavior when feedback is included has been found and can be reported in detail.

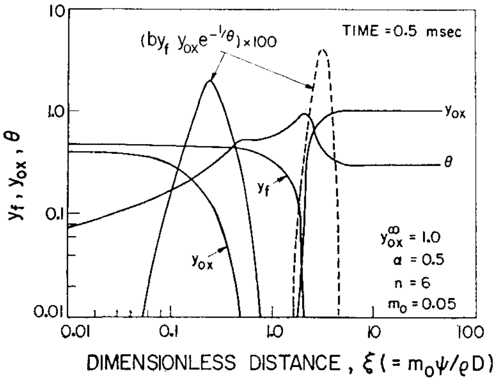

Fig. 6 Gas phase distributions of y_f, y_{ox}, and θ.

For a wide range of compositions of the mass flux supplied by decomposition of the solid phase, for a neutral atmosphere or one containing an oxidizer, and for a wide range of stoichiometry of the gas phase chemical reaction ($2 < n < 6$), steady-state conditions of burning were achieved, starting from the initial and boundary conditions describing the system. The steady state, while requiring an order of magnitude greater time than the short time ignition criterion $L^*(\theta) = 1.5\theta_o$, was still achieved rapidly, in times on the order of ten msec, even in a neutral gas phase. Consequently, an ignition criterion based on the behavior of the system as it approached steady state gave ignition delays commensurate with those observed in shock tube ignition experiments. The behavior of the model in this time domain is termed "near steady-state" behavior, and the operation ignition criterion used was $L^*(\theta) = \epsilon$ as discussed in the previous section.

Figure 4 indicates that application of the near steady state criterion with $\epsilon = 0.01$ causes the result $\tau_{NSS}^* \sim b^{-1}$ to be obtained, rather than the short time result $\tau_{ST} \sim b^{-2/3}$. $\tau_{NSS}^* \sim b^{-1}$ is predicted by the near steady-state asymptotic analysis presented in Sec. V.

A second result of integration into the near steady-state domain, and the most interesting in so far as ignition characteristics are concerned, is the formation of a twin flame zone structure in the gas phase, when conditions permit. The secondary reaction zone is formed by a reaction between the fuel vapor which is unconsumed in the primary reaction zone, and any oxidizer which is present in the external gas phase. The fuel vapor is available because the reaction stoichiometry consumes more oxidizer than fuel, since according to the law of mass action $(\dot{C}_f) = -(\dot{C}_{ox})/n$. Consequently, a secondary reaction can exist providing the fraction of fuel mass flux supplied by decomposition of the solid, α, is sufficiently large. An approximate criterion for the existence of a secondary reaction zone, when oxidizer exists in the

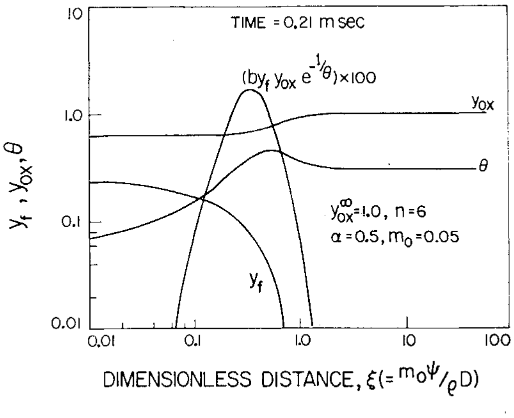

Fig. 5 Gas phase distributions of y_f, y_{ox}, and θ.

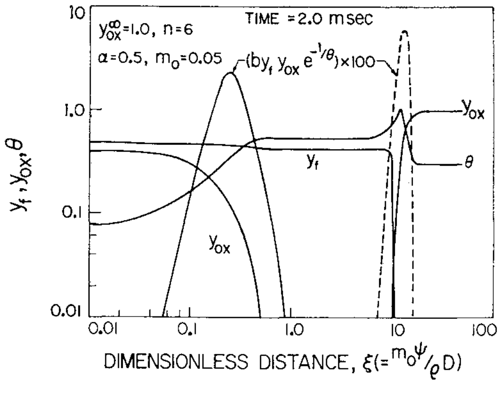

Fig. 7 Gas phase distributions of y_f, y_{ox}, and θ.

gas phase (showing how large α must be) is thus $m_f/m = \alpha/(1-\alpha) > 1/n$, or $\alpha > (1+n)^{-1}$. Since most solid propellants burn with a fuel rich flame, and stoichiometric ratios are generally greater than two, the presence of a secondary reaction zone can usually be expected. It was found for all α and n values used in these investigations.

A pictorial representation of the development of the secondary reaction zone in the gas phase is shown in Figs. 5–7. The relatively extreme stoichiometry of $\alpha = 0.5$ and $n = 6$ was used in order to illustrate the structure more graphically. Figure 5 illustrates the conditions existing just at the time at which the weak ignition criterion of $L^*(\theta) = 1.5\theta_0$ is satisfied; the theoretical real time is 0.21 msec. Notice the relatively little consumption of oxidizer. Figure 6 shows the changes which have occurred by the time 0.5 msec have elapsed. Most notable are: 1) the surface temperature has risen sharply to almost its steady-state value, 2) the fuel vapor has penetrated through the primary reaction zone, 3) a secondary reaction is already well established; it has a greater magnitude than the primary zone and has caused further increase in gas phase temperature, and 4) between the two reaction zones the oxidizer mole fraction has diminished to zero, effectively. By the time 2.0 msec have elapsed (Fig. 7), the twin reaction zone structure is sharply emphasized, with the secondary (outer) zone almost three times greater in magnitude than the primary zone. The thicknesses of the two zones are actually the reverse of the way they appear, though the logarithmic distance scale makes the secondary zone appear thinner. The solid-gas interface conditions of y_f, y_{ox}, and θ_s are almost the same as in Fig. 6 and are already virtually steady-state conditions. Between the two reaction zones, heat and mass diffusion are quite unimportant, with convection being the most important transfer mechanism, since the fuel and temperature gradients are effectively zero. On the other hand, convection is clearly negligible compared to diffusion within the secondary reaction zone, as indicated by the steepness of the gradients of fuel and oxidizer. These conditions continue as the steady state is approached, which takes approximately 6 msec for the parameter values quoted in the figures. Near the steady state, one is tempted to call the outer flame zone structure a Burke-Schumann type diffusion flame because of its thinness compared to its distance from the solid surface. However, the secondary zone is much thicker than the primary zone, since it is a diffusion flame, whereas the primary is essentially a premixed flame in the present model.

The strength of the secondary reaction zone, and its importance during the ignition process at long times, depends on the amount of oxidizer initially present in the gas phase. For large amounts of external oxidizer, a strong secondary reaction zone forms, and dominates the near steady-state shape of the temperature profile. As y_{ox}^∞ is decreased, this zone diminishes in size and effect, until for some sufficiently small value of y_{ox}^∞ its effect on the long time ignition delay disappears sharply. As y_{ox}^∞ is further reduced, the secondary zone continues to diminish in magnitude, disappearing, of course, when $y_{ox}^\infty = 0$.

Consider the surface temperature to have rapidly reached a steady value; then the amount of fuel and oxidizer supplied by the surface, and their concentrations at the surface, are fixed. [They are almost α and $(1-\alpha)$, respectively, except for a minor amount of combustion products.] The fraction of fuel consumed on the primary reaction zone is thus $\alpha' = (1+n)^{-1}$. The remaining fuel mole fraction available for secondary reaction is therefore $\alpha_f \cong \alpha(1-\alpha') = \alpha n(1+n)^{-1}$. [If $\alpha = 0.5$, then $\alpha_f = 0.50\frac{6}{7} = 0.43$, as it is approximately, according to Fig. 6.] The wall concentrations of fuel and oxidizer effectively control the magnitude of the primary reaction zone, and are approximately 0.48 and 0.4 for the case at hand. The product of the fuel concentration remaining after the primary reaction, α_f, and the oxidizer concentration in the gas phase, y_{ox}^∞, control the magnitude of the secondary reaction zone. Therefore the secondary reaction zone will cause a greater gas phase temperature to exist than that produced by the primary zone if, approximately $(\alpha_f y_{ox}^\infty) > (y_{f,\text{wall}})(y_{ox,\text{wall}})$. Thus, for the case illustrated in Figs. 5–7, the effect of the secondary zone will be large if $y_{ox}^\infty > (y_{f,\text{wall}})\,[(y_{ox,\text{wall}})/(\alpha n/(1+n)] = (0.48 \times 0.4)/(0.5\frac{6}{7}) = 0.46$ as is found, approximately in our numerical results. In essence, to a coarser degree of approximation, the secondary reaction is stronger than the primary reaction zone and the near steady-state ignition delay will strongly depend on y_{ox}^∞ if $y_{ox}^\infty > (1-\alpha)(1+n)/n$.

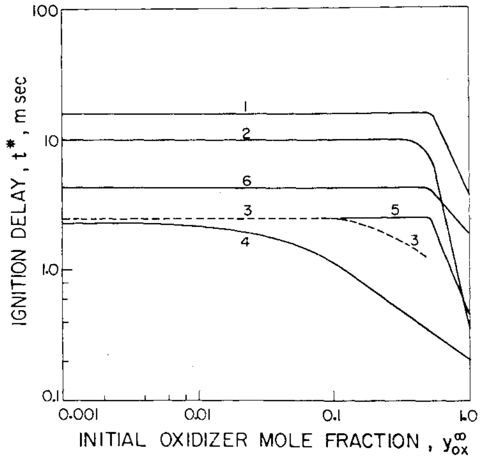

Fig. 8 Effect of choice of ignition criterion upon ignition delay, the numbers of the curves are keyed to the ignition criteria used: 1) close to steady state; $\epsilon = (\Delta\theta_{\max}/\Delta\tau)(\tau/\theta_{\max}) \leq 0.01$; 2) absolute maximum reaction rate; 3) y_{ox} in the field first becoming zero; 4) $L^*(\theta) = 1.5\ \theta$; 5) $\Delta\theta_{\max}/\Delta t < 0.016\ \text{msec}^{-1}$; 6) $\Delta\theta_{\max}/\Delta t < 0.005\ \text{msec}^{-1}$.

Table 2 Description of curves in Fig. 9

Curve no.	m_o	n	$L^*(\theta)$
1	0.05	6	$\epsilon = 0.01$
2	0.05 0.005	4	$\epsilon = 0.01$
3	0.05	4	$1.5\theta_o$
4	0.005	4	$1.5\theta_o$
Pure fuel ($\alpha = 1$)	0.05	6	$\epsilon = 0.01$

All other parameter values are given in Table 1

The apparent ignition characteristics exhibited by the model in "near steady-state" time domain depend upon the criterion selected to define ignition, as should be expected. Several criteria other than $L^*(\theta) = \epsilon$ are possible, for example: the time required for a zero oxidizer concentration in the gas phase to occur, the time required to achieve an absolute maximum reaction rate in the gas phase, or the time required for the rate of change of the maximum gas phase temperature to decrease to some specified value. The result of these choices is illustrated in Fig. 8, showing the variety of ignition delay variation with y_{ox}^∞ that can be obtained. Because of the difference in rates of approach of the maximum gas temperature to its steady-state value between cases where $y_{ox} = O(1.0)$, illustrated by curves 5 and 6 of Fig. 8, the most satisfactory criterion is that used to plot curve 1, in which ignition is said to have occurred when $\epsilon = (\Delta\theta_{\max}/\theta_{\max})(\tau/\Delta\tau) \leq 0.01$. This criterion tends to compensate for the comparatively small values of $(\Delta\theta/\Delta\tau)$ when y_{ox} approaches 0.1.

Figure 8 demonstrates the marked change in dependence of t^* on y_{ox}^∞ when integrations are carried out into the long time domain, compared to the weak criterion $L^*(\theta) = 1.5\theta_o$. Figure

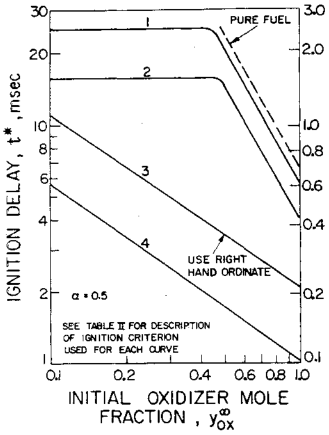

Fig. 9 Effect of initial oxidizer mole fraction on the ignition delay predicted by the feedback model using different ignition criteria.

9 contains similar results for other stoichiometries and pyrolysis rates; see Table 2 for descriptions of the curves.

The steepness of the long time dependence of the ignition delay on y_{ox}^{∞}, even in the present feedback model, is very interesting. (It was found in the nonfeedback case,[3] but it was not known whether it would carry over to the feedback case as well.) These results unequivocally demonstrate that a purely gas phase, propellant ignition process can exhibit an ignition delay which depends upon the inverse square of the oxidizer mole fraction in the gas phase, as has been experimentally observed in shock tube ignition experiments on pure fuels and composite and nitrate ester propellants.[1,8] In the next section it is demonstrated that this behavior is a predictable property of a gas phase ignition process for solid materials under "end wall" shock tube type conditions.

V. Results of Asymptotic Analyses

The complete set of equations describing the model, Eqs. (7)-(11) is so complex as to be intractable for a general analytical solution in any form. However, it is possible to analyze certain interesting situations which are limiting, or asymptotic, in some sense. This is done by deciding upon a consistent set of physical conditions and determining how these conditions modify the complete equations. The characteristic nature of the solution to the modified equations is then established, by merely redefining the independent variables appropriately.

Convective transport terms in the complete equations cause some difficulty when asymptotic analyses are attempted. Fortunately, there exist two special cases in which this difficulty can be removed. The first of these occurs when mass flux is constant. Applying a Galilean transformation of the form $\xi = \bar{\xi} + \omega\tau$ removes the convective term.

Alternatively, one can assert that the convective term is negligible compared to other terms in the equation in a purely order-of-magnitude sense, and summarily ignore it. The validity of this assertion has been demonstrated previously.[1] Therefore, for one reason or another, the general equations for specie and energy diffusion can be written in the form

Specie

$$(\partial N_i/\partial\tau) = (\partial^2 N_i/\partial\xi^2) - N_i N_j e^{-1/\theta} \tag{11}$$

Energy

$$(\partial\theta/\partial\tau) = (\partial^2\theta/\partial\xi^2) + A N_i N_j e^{-1/\theta} \tag{12}$$

for the purposes of asymptotic analysis. The boundary conditions on the specie equations thus have the general form

$$(\partial N_i/\partial\xi)|_{\xi=0} = -\omega_i(\theta) \tag{13}$$

if feedback cases are included. The boundary conditions for the energy equation remain unchanged by virtue of the assumption of constant and equal specific heats for the solid and gas phases. Note that the subsequent analyses neglect any endo/exo-thermicity at the solid/gas interface.

Short Time Asymptotic Analysis

The physical situation is that of significant chemical heat release occurring in the gas phase but a negligible consumption of reactants up to this point. Thus it corresponds to the "short time" domain of the numerical computations. It is a condition that exists in both the feedback model, and the constant mass flux/wall temperature model of Ref. 3. The reason it holds in the feedback model is that upon formation of the solid-gas interface, the surface temperature jumps instantaneously to a specific value, and then starts to increase slowly as reaction generated heat is fed back to the surface. However, if chemical heat generation (reactant consumption) is negligible for some time, this surface temperature stays constant and the feedback model is similar to the constant mass flux model.

Secondly, this condition can be split into two regimes, one when the external gas phase contains appreciable oxidizer, and one of a neutral gas phase. For a gas phase containing significant oxidizer ($y_{ox}^{\infty} > 0.05$ for $\alpha = \frac{1}{2}$) we have $\eta_{0x} = \eta_{ox}^{\infty} = b y_{ox}^{\infty}$ and $\eta_f \sim nb\tau^{1/2}\ \mathrm{ierfc}(\xi/2\tau^{1/2})$. Consequently the energy equation becomes

$$\theta_\tau = \theta_{\xi\xi} + Ab^2 n\, \tau^{1/2} y_{ox}^{\infty}\ \mathrm{ierfc}(\xi/2\,\tau^{1/2}) e^{-1/\theta} \tag{14}$$

Re-definition of τ and ξ according to the transformations

$$\bar{\tau} = \tau(Ab^2 n y_{ox}^{\infty})^{2/3} \text{ and } \bar{\xi} = \xi(Ab^2 n y_{ox}^{\infty})^{1/3}$$

causes the energy equation and its boundary conditions to be independent of the parameter $(Ab^2 n y_{ox}^{\infty})$. Consequently, for any ignition criterion occurring at $\bar{\tau} = \bar{\tau}^*$ we see that $\tau^* \sim (Ab^2 n y_{ox}^{\infty})^{-2/3}$.

Therefore, since $A \sim (1/b)$ we obtain the result $\tau^* \sim b^{-2/3}$ or $t^* \sim m_o^{-2/3}$ and $t^* \sim \tau^* \sim (y_{ox}^{\infty})^{-2/3}$. These results are well known[1,3,7] and are entirely evident in Fig. 7 of Ref. 3, and Figs. 2–4 of the present paper. They are quoted here to demonstrate their validity for the feedback model of propellant ignition, and to demonstrate a portion of the method of analysis. Recently, Waldman[9] has demonstrated the preceding results in a very rigorous fashion.

For the case of a neutral atmosphere, all oxidizer is supplied by the solid itself. Consequently η_f and η_{ox} can be represented by the relations

$$\eta_f \sim nb\alpha\tau^{1/2}\ \mathrm{ierfc}(\xi/2\tau^{1/2}) \tag{15}$$

$$\eta_{ox} \sim b(1-\alpha)\tau^{1/2}\ \mathrm{ierfc}(\xi/2\tau^{1/2}) \tag{16}$$

The energy equation then contains the constant $n\alpha(1-\alpha)b^2A$ which is removable by the transformations $\bar{\tau} = \tau[n\alpha(1-\alpha)b^2A]^{1/2}$, $\bar{\xi} = \xi[n\alpha(1-\alpha)b^2A]^{1/4}$. Then for ignition occurring at $\bar{\tau} = \bar{\tau}^*$, we obtain $\tau^* \sim [n\alpha(1-\alpha)b^2A]^{-1/2}$ or simply $\tau^* \sim b^{-1/2}$. Figure 7, Ref. 3, and Fig. 4 herein indicate that for sufficiently low y_{ox}^{∞}, this condition is approached.

Asymptotic Results near Steady-State Conditions

Under conditions where the steady state is approached, several observations can be made about the feedback case under discussion. First of all, conditions at the solid-gas interface are changing only *very* slowly and consequently the surface temperature and concentration of reactants are almost constant. Secondly, between the interface and the flame, reactant transport is primarily convective rather than diffusive, as shown by the very small gradients in Figs. 6 and 7. Conversely, in the intense reaction zone between the fuel vapor and the external gas phase oxidizer, diffusion is the dominant transport mechanism. Thirdly, the development of this reaction zone depends primarily upon chemical heat generation rates compared to the conductive heat loss rate. Finally, one need not consider any oxidizer coming from the solid phase since it is either totally consumed in the primary reaction zone shown in Figs. 5–7 if the solid is a propellant, or is nonexistent if the solid is a pure fuel.

Consider the temperature distribution within a region in the gas phase as sketched in Fig. 10, at $\tau' = 0$, where the thickness of the mass diffusion region is δ, which exists but is undefined for the moment, and τ' measures the time after this region is established. Providing there exists fuel vapor coming from the solid phase, one can consider only the energy equation in describing the ignition process. This equation has the dimensionless form

$$(\partial\theta/\partial\tau) = (\partial^2\theta/\partial\xi^2) + A\eta_f\eta_{\mathrm{ox}}e^{-1/\theta} \tag{17}$$

Let the values of η_f and η_{ox} be represented by the power laws

$$\eta_f = C_1 - m_1\xi^p \tag{18}$$

$$\eta_{\mathrm{ox}} = C_2 + m_2\xi^q \tag{19}$$

The constants can be evaluated by the requirements that at $\xi = 0$, $\eta_{\mathrm{ox}} = 0$, at $\xi = \delta$, $\eta_f = 0$ and $\eta_{\mathrm{ox}} = \eta_{\mathrm{ox}}{}^{\infty}$, and the assumption that on the average, stoichiometry is maintained within the reaction zone, or $\langle\partial\eta_f/\partial\xi\rangle = -\langle\partial\eta_{\mathrm{ox}}/\partial\xi\rangle$. Then the dimensionless fuel and oxidizer concentrations have the form $\eta_f = \eta_{\mathrm{ox}}{}^{\infty}[1 - (\xi/\delta)^p]$, $\eta_{\mathrm{ox}} = \eta_{\mathrm{ox}}{}^{\infty}(\xi/\delta)^q$. Therefore the energy equation becomes

$$(\partial\theta/\partial\tau) = (\partial^2\theta/\partial\xi^2) + A\eta_{\mathrm{ox}}{}^{\infty 2}(\xi/\delta)^q[1 - (\xi/\delta)^p]e^{-1/\theta} \tag{20}$$

Near the steady state, the total rate of heat generation is approximately equal to the rate of heat loss, and is approximately constant. Thus

$$Q_{\mathrm{generation}} = A\eta_{\mathrm{ox}}{}^{\infty 2}\int_0^{\delta}\left(\frac{\xi}{\delta}\right)^q\left[1 - \left(\frac{\xi}{\delta}\right)^p\right]e^{-1/\theta}d\xi \tag{21}$$

or, letting $\phi = \xi/\delta$

$$Q_{\mathrm{generated}} = A\eta_{\mathrm{ox}}{}^{\infty 2}\delta\int_0^1 \phi^q(1 - \phi^p)e^{-1/\theta}\,d\phi \cong$$

$$Q_{\mathrm{lost}} \cong \frac{\mathrm{const}}{\delta} \tag{22}$$

Since the integral in the preceding expression is nearly constant, we obtain $\delta \sim 1/[\eta_{\mathrm{ox}}{}^{\infty}A^{1/2}]$. Consequently, the energy equation takes on the form

$$(\partial\theta/\partial\tau) = (\partial^2\theta/\partial\xi^2) + (C/\delta^2)(\xi/\delta)^q[1 - (\xi/\delta)^p]e^{-1/\theta} \tag{23}$$

subject to the conditions $\theta(0,\tau) = \theta_1$, $\theta(\delta,\tau) = \theta_o$ and $\theta(\xi,0) = f(\xi/\delta)$. This system can be transformed by the definitions $\tau = \bar{\tau}\delta^2$ and $\phi = \xi/\delta$ to completely eliminate the parameter δ from the equation and boundary conditions, such that the solution is of the form $\theta = \theta(\theta_1,\theta_o,C;\ \bar{\tau},\phi)$. For any suitable ignition criterion occurring at $\bar{\tau} = \bar{\tau}^*$, $\tau^* = \bar{\tau}^*\delta^2 \sim (A\eta_{\mathrm{ox}}{}^{\infty 2})^{-1}$.

Consequently, since $\eta_{\mathrm{ox}}{}^{\infty} \sim by_{\mathrm{ox}}{}^{\infty}$ and $A \sim 1/b$, it can be expected that at near steady state, in terms of the real ignition delay $t_{\mathrm{NSS}}{}^* \sim (y_{\mathrm{ox}}{}^{\infty})^{-2}$ and $t_{\mathrm{NSS}}{}^*$ is not a function of m_o. These results are found from the numerical computations also, as illustrated in Fig. 9.

This analysis also applies to the case of ignition of pure fuels, when $y_{\mathrm{ox}}{}^{\infty}$ is sufficiently large, since the effect of any oxidizer supplied by the solid is obliterated by the presence of the primary reaction zone. The numerical computations showed this to be true as is illustrated in Fig. 9 in the $\alpha = 1$ curve.

Furthermore, under conditions of small values of $y_{\mathrm{ox}}{}^{\infty}[y_{\mathrm{ox}}{}^{\infty} < (1 - \alpha)(1 - n)/n]$ where the primary reaction zone is dominant in the feedback propellant ignition case, the ignition delay should also be independent of m_o. This is demonstrated by the following analysis, and was found in the numerical results shown in Fig. 9, curve 2.

For the case of values of $y_{\mathrm{ox}}{}^{\infty} = 0$ the power law expressions for η_f and η_{ox} become $\eta_f = n\alpha b[1 - (\xi/\delta)^p]$, $\eta_{\mathrm{ox}} = b(1 - \alpha)[1 - (\xi/\delta)^p]$ and consequently the energy equation takes the form, with $\beta = Anb^2\alpha(1 - \alpha)$,

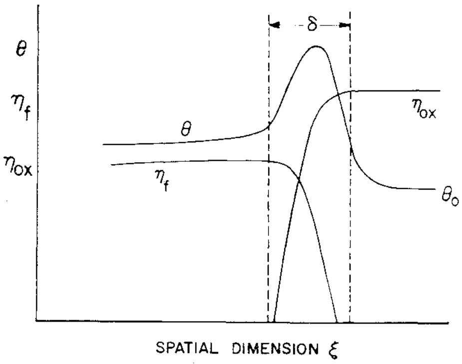

Fig. 10 Sketch of near steady-state spatial distribution of fuel η_f, oxidizer η_f, and temperature θ in secondary reaction zone.

$$(\partial\theta/\partial\tau) = (\partial^2\theta/\partial\xi^2) + \beta[1 - (\xi/\delta)^p]^2e^{-1/\theta} \tag{24}$$

Then, near the steady state,

$$Q_{\mathrm{generated}} = \beta\delta\int_0^1 (1 - \phi^p)^2e^{-1/\theta}d\phi \cong \left(\frac{C}{\delta}\right) \cong Q_{\mathrm{lost}} \tag{25}$$

and $\delta \sim (\beta)^{-1/2}$. Consequently the energy equation becomes

$$(\partial\theta/\partial\tau) = (\partial^2\theta/\partial\xi^2) + (C/\delta^2)[1 - (\xi/\delta)^p]^2e^{-1/\theta} \tag{26}$$

and δ can be eliminated by the same transformation as before, namely $\tau = \bar{\tau}\delta^2$ and $\xi = \delta\phi$. For any suitable ignition criterion occurring at $\bar{\tau} = \bar{\tau}^*$, $\tau^* \sim \delta^{-2} \sim b^{-1}$. This behavior was also found from the numerical computations, as previously mentioned in Sec. IV, see the long time $\tau^* - b$ curve shown in Fig. 4. Actually, both the rich and lean cases of $y_{\mathrm{ox}}{}^{\infty}$ show $\tau^* \sim b^{-1}$ and therefore, for all other items constant, one can expect the result shown in Fig. 9, where $t_{\mathrm{NSS}}{}^*$ is not a function of m_o over the entire range of $y_{\mathrm{ox}}{}^{\infty}$ values.

In the preceding analyses, the important assumption was that relating the thickness of the reaction zone to heat loss. This assumption is in contrast to that often made in estimating the thickness of a steady-state diffusion flame. In the former, one obtains $\delta \sim (y_{\mathrm{ox}}{}^{\infty})^{-1}$ whereas the latter (at steady state) gives $\delta \sim (y_{\mathrm{ox}}{}^{\infty})^{-1/2}$. Since the numerical results indicate that $\delta \sim (y_{\mathrm{ox}}{}^{\infty})^{-1}$ is the correct assumption, one must conclude that heat loss affects the kinetics during the development of a steady-state reaction profile rather than diffusion. In effect then, it is concluded that finite reaction rate kinetics play an important role in the time required to establish the steady state.

VI. Summary and Conclusions

The present investigation has revealed properties of a gas phase ignition process for both homogeneous propellants and pure fuels. In addition, it has been possible to evaluate the validity of some simplifying assumptions that have been made in previous studies of this type.

One of the most interesting results is that the completely transient equations, including temperature sensitive decomposition rates of the solid phase (feedback), do indeed allow a steady-state combustion to be achieved. Numerical integration from time = 0+ can thus follow to reveal the entire sequence of events right up to and including the steady state. This point has always been tacitly assumed but has been substantially unproven heretofore. It is found that the feedback mechanism is operative over an extremely wide range of decomposition rates, but does not alter either the short time or near steady-state ignition characteristics.

Interestingly enough, in both the feedback, and the nonfeedback results reported earlier,[3] the short time [weak ignition criterion of $L^*(\theta) = 1.5\theta_o$] ignition characteristics for the propellant-like solids presumed are not similar to the diffusional ignition characteristics of pure fuels.[2] When such weak ignition criteria are assumed, the ignition criterion is quite unimportant in determining the ignition characteristics, much like the results of thermal ignition theory for premixed gases. This is not very surprising, in hindsight, since it was assumed that the decomposition products of the solid were a premixed gas. The question of ignition characteristics of a solid having fuel and oxidant vapors issuing from different sites requires further investigation.

For solids producing fuel and oxidizing decomposition products in nonstoichiometric amounts, a secondary reaction zone, a twin reaction zone flame structure, of a diffusion flame-like nature was found to be established before the steady state was reached. The size and intensity of the zone depended upon the amount of oxidizer present in the external gas phase. The reason for its existence was discussed in the previous section. There is every reason to expect, therefore, that the thin flame structure exists in reality in the "end wall" shock tube experiments.[1] An approximate calculation shows the secondary reaction zone to be about 0.8mm from the surface, which is still rather close in; the primary reaction zone was located at about 0.08mm for an external gas pressure of 25 atm and initial temperature of 1800°K. At higher pressures, these distances decrease considerably.

The presence of the secondary reaction zone markedly altered the dependence of the ignition delay on y_{ox}^{∞} and m_o from that found using the "short time" ignition criterion. As previously shown, near steady state, using the criterion that at "ignition," $\epsilon \leq 0.01$, t_{NSS}^* is not a function of m_o or $(\tau^* \sim b^{-1})$ in contrast with $t_{ST}^* \sim m_o^{-2/3}$. In addition, one obtains the extremely interesting result that $t_{NSS}^* \sim (y_{ox}^{\infty})^{-2}$ contrasted to $t_{ST}^* \sim (y_{ox}^{\infty})^{-2/3}$, for both propellants and pure fuels. Furthermore, for equal values of ϵ, the ignition delay of the pure fuel is greater than that of the propellant.

The preceding results are particularly interesting because they provide an unequivocal theoretical dependence of t^* on y_{ox}^{∞} that is in excellent agreement with the fuel and propellant ignition data derived from the shock tube experiments of McAlevy and Summerfield.[1] (Incidentally, the same ignition behavior was found using shock tube generated, low-speed gas flows as the ignition stimulant.[7] Secondly, McAlevy and Summerfield[1] also observed that under the same shock tube conditions, pure fuels ignited more slowly than composite propellants using the same fuel as a binder. This unexpected result was explained by supposing the presence of "hot spots" on the propellant surface which provided locally higher pyrolysis rates. While this hypothesis may well be valid, the present investigation has shown it need not be invoked to explain the faster ignition of propellants over fuels.

Finally, it may well be that the development of large reaction rates, and shortly thereafter, relatively small values of $(\partial\theta_{max}/\partial t)$ are much more closely related to emission of luminosity in a flame than is the presence of some small temperature rise in the gas phase. Consequently use of the "near steady-state" criterion, concerning the degree of approach to steady-state burning, may be a theoretical criterion more closely related to data obtained using luminosity of the flame than the weaker, "short time" criterion of $L^*(\theta) = 1.5\theta_o$. For example, as mentioned in Ref. 6, increasing the sensitivity of the photocell detection device in shock tube experiments caused a substantial decrease in the observed dependence of t^* on y_{ox}^{∞}.

Therefore, it is fair to conclude that the relatively complete gas phase ignition theory of solid materials under shock tube type conditions, even assuming single step kinetics and equimolar chemistry, is capable of predicting the same type of ignition behavior that has been observed experimentally. Previously, this did not appear to be the case, thereby causing some doubt about the assertion that the rapid ignition of solid propellants was dominated by a gas phase mechanism. The present results indicate this doubt to be unwarranted, and strongly indicate that processes occurring in the gas phase dominate the ignition behavior of pure fuels, and propellants, at least homogeneous propellants.

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