An Asymptotic Analysis of Radiant and Hypergolic Heterogeneous Ignition of Solid Propellants

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I. INTRODUCTION

Bradley and Williams (1970) formulated a model for the radiant ignition of a solid propellant which reacts at its surface with a gaseous oxidizer. A schematic representation of their model is given in Figure 1; it represents an extension of a model of Williams (1966), modified so as to include the effects of in-depth absorption of the radiation and to account for the possibility of having different initial temperatures of the solid propellant and gaseous oxidizer. Waldman and Summerfield (1969) had already shown that the numerical solutions obtained by Williams, for the hypergolic ignition problem (no radiant flux), could be used for the analysis of heterogeneous ignition of solid propellants under shock tube conditions, resulting in different initial temperatures for the solid and gas phases. Waldman (1970) obtained more accurate numerical solutions and some approximate analytical solutions to the hypergolic ignition problem.

In their formulation Bradley and Williams neglected other homogeneous reactions, as well as the surface regression during the ignition transient. As a consequence of these and other reasonable assumptions, the non-linearity of the mathematical problem was limited to the boundary conditions where it was introduced by the Arrhenius reaction at the interface. As a result, they were able, by means of Laplace transform techniques, to reduce the problem to a single non-linear integral equation. They presented numerical solutions of this equation for the limiting case of infinite absorption coefficient. Their numerical results show that, for the large activation energies involved in realistic overall reactions, a well defined ignition event occurred, with a precipitous rise in temperature (thermal runaway) at a certain ignition time. For sufficiently large radiant fluxes, thermal runaway was preceded by an inert heating stage.

In this paper we present an asymptotic analysis, for large activation energies, of the ignition model proposed by Bradley and Williams. We retain in our analysis the effects of in-depth absorption for a constant radiant flux, without cut-off of this radiant flux; on the other hand for moderately exothermic reactions, with large activation energies, the cut-off time can not be appreciably shorter than the time of thermal runaway if ignition is to occur.

The asymptotic analysis results in fairly simple analytical expressions for the ignition time. When comparison with existing numerical results is possible, the asymptotic analysis is found to yield very accurate predictions of the ignition time.

In Section II, after quoting the integral equation obtained by Bradley and Williams for their model, we shall show that this equation is also obtained for a simpler problem. Thus, it is the governing equation for the calculation of the surface temperature of a semi-infinite solid undergoing a surface decomposition Arrhenius reaction, when subjected to a radiant flux without heat losses to the gas phase. The effects of heat losses and of oxidizer depletion at the surface, can be shown to appear
through a modification of the radiant flux, the transport properties of the propellant, and the overall reaction rate. Also included in Section II is a discussion of the surface temperature history under inert heating conditions, which will give the background information for the analysis of the reacting case, for large radiant fluxes, presented in Section III.

Section IV is devoted to the analysis of hypergolic heterogeneous ignition without a radiant flux, as is the case in shock tube ignition. In Section V we analyze the heterogeneous ignition problem for radiant fluxes small enough that they produce increments in the surface temperature of the order of those produced by the chemical reaction at the initial surface temperature. In this case the surface reaction plays a role in increasing the surface temperature of the order of those produced by the chemical reaction at the surface due to the chemical reaction. The time has been made non-dimensional with the characteristic time \( t_\chi \),

\[ t_\chi = \pi \eta^2 (1 + 1/\gamma) T_0^2 (\Gamma_1 + \Gamma_1)^{-2} \]

where \( \eta \) is the incident radiant flux, and \( \Gamma_1 \) and \( \Gamma_1 \) are the thermal responsivities \( (\rho c_\chi) \) of the gas and solid phases. Notice that the jump temperature \( T_0 \) is given in terms of the initial temperatures by

\[ T_0 = (\Gamma_1 T_{10} + \Gamma_2 T_{20})/(\Gamma_1 + \Gamma_2). \]

The factor \( (1 - \alpha(1 - \theta_j))^{n} \) in the heat source \( G \), accounts for the reduction in oxidizer concentration at the surface due to the chemical reaction. The diffusion parameter

\[ \alpha = \gamma (1 + \Gamma_1) T_0 (\rho D_L)^{1/2} Q \]

involves the gas density, diffusion coefficient \( D \), heat release \( Q \) per unit mass of oxidizer, and initial oxidizer mass fraction \( Y_0 \).

For a constant radiant flux without cut-off, the inert surface temperature is given by

\[ \theta_j(\tau) = \gamma/(\gamma + 1) \theta J(\tau) \]

and solid propellants. In this paper we use the method and the assumptions. In this paper we use the method and the overall reaction rate. We refer also to the paper by Bradley and Williams (1970) for the basic background information for the analysis of the heterogeneous ignition problem for large radiant fluxes, presented in Section III.

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For a constant radiant flux without cut-off, the inert surface temperature is given by

\[ \theta_j(\tau) = \gamma/(\gamma + 1) \theta J(\tau) \]
where
\[ H(\tau) = \frac{2\sqrt{\tau}}{\pi} - 1 + \exp(v) \text{erfc} \left( \sqrt{v} \right). \] (4)

In the above \( \delta \) is a radiant absorption parameter such that
\[ v = (\gamma + 1)\delta \gamma \] (5)
is the radiant absorption coefficient \( \mu \) made non-dimensional with the characteristic length
\[ 1_c = \left(1 + \frac{T_0}{T_\infty} \right) \lambda_\infty T_0 / \dot{q} \]
That is \( v = \mu_{1_c} \). The factor \( \lambda_\infty \) in \( 1_c \) is the heat conductivity of the solid.

We could obtain the inert surface temperature after cut-off of the radiant flux in terms of the function \( \theta_I \) given by equation (3) as
\[ \theta_I(\tau) = \theta_I(\tau - \tau_{\text{off}}), \]
where \( \tau_{\text{off}} \) is the cut-off time.

Figure 2 represents the inert surface temperature as a function of time, before cut-off (solid line) and after cut-off (dashed line), for different values of the cut-off time.

We write here, for future reference, the following asymptotic and ordinary expansions for \( H(\tau) \)
For \( v \gg 1 \)
\[ H(\tau) = 2v/\pi^{1/2} - 1 + (\pi v)^{-1/2} - 2(v^{3/2} + \cdots) \]
and for \( v \ll 1 \)
\[ H(\tau) = v - (\sqrt{v} - 1)^3/2 + v^{3/2} + \cdots \] (6)

If during most of the ignition period
\[ v = \delta \tau / \pi \gg 1, \]
then \( H(\tau) \approx 2(\pi v/\tau)^{1/2} \), and \( \theta_I \approx 2\sqrt{\pi \tau / \tau (\gamma + 1)} \); a result that corresponds to surface absorption of the radiation.

If during the ignition period \( v \ll 1 \), then
\[ H(\tau) \approx v \]
and \( \theta_I \approx \gamma \delta \tau / \pi (\gamma + 1) \); a result obtained when heat conduction effects are neglected in the calculation of the solid propellant heating by the radiant flux.

If equation (1) is written in term of the new non-dimensional time \( v = \delta \tau / \tau = \tau \mu^3 \lambda_\infty / \rho_\infty c_\infty \), or
\[ v = \sqrt{\pi \tau / \pi (\gamma + 1)^3} \]
and of the increment in surface temperature due to the surface reaction, \( \psi(\tau) \),
\[ \psi = \theta(\tau) - \theta_I(\tau) \] (9)
we obtain the integral equation
\[ \phi(v) = \frac{1}{\sqrt{\pi}} \times \int_0^\infty (1 - z\psi) \exp \left\{ \beta(\phi + \theta_I)/(1 + \phi + \theta_I) \right\} d\lambda, \]
where
\[ \beta = v^{-1} H(\lambda) \] (10)
It may be noted that the integral equation (10) is also satisfied by the surface value \( \phi(0, v) \) of the solution \( \phi(u, v) \), for \( u \geq 0 \) and \( v \geq 0 \), of the heat conduction equation
\[ \phi_u - \phi_{uu} = 0 \] (12)
with the initial and boundary conditions,
\[ \phi(u, 0) = \phi(\infty, v) = 0 \] (13)
and
\[ \phi_u(0, v) = -(\gamma v^{-1}(1 - x\phi)^n \exp \{\beta(\phi + \theta_I)/(1 + \phi + \theta_I) \} \]
(14)
where \( \theta_I \) is the surface value (at \( u = 0 \)) of the solution, for \( u \geq 0 \) and \( v \geq 0 \), of the heat conduction equation,
\[ \theta_I - \theta_{Iu} = v^{-1} \exp (-u) \] (15)

\[ \text{FIG. 2. Surface temperature history. The solid lines correspond to two values of } \gamma \text{ which result in thermal runaway at } \gamma_r = 0.5 \text{ and } \gamma_r = 2. \text{ The dashed lines correspond to inert heating with cut-off of the radiation at } v = 10^{-4}, 1, 10 \text{ and } \infty. \]
with the initial and boundary conditions
\[ \theta_1(u, 0) = \theta_1(\infty, v) = \theta_1(0, v) = 0 \]  
(16)
The variable \( u \) appearing in this formulation is a non-dimensional distance to the solid surface. It can be shown to be equal to the stream function
\[ \int_0^u \rho_c \, dx \]  
in the solid made non-dimensional by dividing by the solid density \( \rho_c \), multiplied by the characteristic absorption length \( \mu^{-1} \).

The system of equations (12) to (16) results from trying to determine the temperature distribution within a semi-infinite solid, subject to radiant heat flux, without heat losses to the gas phase, and undergoing an Arrhenius reaction at the surface which results in a surface heat release given by equation (14). However, it is clear that the solution may be used with slight modification for a more general problem. Thus, it is equivalent to finding the solution of the integral equation (10) where \( \theta_l \) is given by equation (11), the problem considered by Bradley and Williams (1970).

In this paper we shall look for the asymptotic solution of equations (1) or (10) for large values of the non-dimensional activation energy \( \beta \). We shall consider the parameters \( n \) and \( \gamma \) to be of order unity (for \( x \gg 1 \) a well defined ignition event will not exist), and we shall cover the whole range of values of \( \gamma \), from zero to infinity.

An approximate classification of the ignition regimes, which we shall analyze in this paper, results from the initial value, \( 1/\sqrt{\gamma} (\gamma + 1) \), of the reaction heat source \( G_c \).

If \( \gamma \gg 1 \), \( G_c \) will be initially very small compared with 1, and it will remain so, if \( \beta \gg 1 \), until the surface temperature reaches a value close to the value \( \theta_i \), for which
\[ \{1/\sqrt{\gamma} (\gamma + 1)\} \exp \{\beta \theta_i/1 + \theta_i\} = 1 \]  
(17)
We may then expect that an inert stage, with surface temperatures lower than \( \theta_i \), will precede a reaction stage. The ignition process in this case will be analyzed in Section III.

If \( \gamma \ll 1 \) the radiant heat flux may be neglected compared with the reaction heat release, during the whole ignition transient. This case corresponds to hypergolic ignition which will be analyzed in Section IV.

If \( \gamma \) is of order 1, the reaction heat release and the radiant heat flux will give comparable contributions to the surface temperature rise during the whole ignition period. The analysis of the ignition process for these moderately small values of the radiant flux will be left for Section V.

III. IGNITION FOR LARGE RADIANT FLUXES

We shall begin by analyzing the ignition process for values of \( \gamma \) so large that the effects of the chemical reaction may be neglected at the initial surface temperature. Only when this temperature reaches a value close to the value \( \theta_i \), given by equation (17), for which \( G_c \) will be of order 1, will the chemical reaction begin to have an influence on the temperature field.

A small increment in temperature \( \theta - \theta_i \approx (1 + \theta_i)^2/\beta \), below or above \( \theta_i \), will be sufficient to make the reaction heat release \( G_r \) very small or very large compared with 1. The time involved in this small temperature rise, characteristic time for reaction stage, will therefore be very short compared with the time required, under inert heating conditions, for the surface temperature to increase up to the value \( \theta_i \). As a consequence, a first approximation \( \tau_c \) for the ignition time will result, when equation (17) is taken into account, from the equation
\[ \theta_i = \theta_1(\tau_c) \]  
(18)
which becomes, for a constant large value \( \gamma \) of the radiant flux,
\[ \theta_i \delta = H(\delta^2 \tau_c/\pi) \]  
(19)
This relation simplifies to \( \theta_i = 2 \sqrt{\tau_c/\pi} \) if \( \theta_i \delta \) is large compared with 1; for small values of \( \theta_i \delta \) it simplifies to \( \theta_i = 2 \delta \tau_c/\pi \). These two cases correspond to large and small values, respectively, of the absorption coefficient \( \delta \) when \( \theta_i \) is of order 1.

To obtain, for large values of \( \beta \), a more accurate relation between the ignition time and the radiant flux \( \gamma \), we pose our problem as to find the asymptotic solution of equation (1) and the value of \( \gamma \) which results in thermal runaway occurring at a given value \( \tau_c \) of \( \tau \).

Let \( \theta_c \) be the surface temperature under inert heating conditions at time \( \tau_c \), and let \( \theta'_c \) be the time derivative of \( \theta'_c(\tau) \) at \( \tau = \tau_c \). That is
\[ \theta_c = \theta_1(\tau_c) \quad \text{and} \quad \theta'_c = \theta'_1(\tau_c) \]  
(20)
If we assume
\[ \beta_1 = \beta(1 + \theta_i)^2 \]  
(21)
to be large compared with 1, we may anticipate that
during the reaction stage, ending in thermal runaway, both \( \phi = \theta - \theta_i \) and \( \theta_\tau - \theta_c \) are small, of order \( 1/\beta_1 \). Thus, when solving equation (1) for large values of \( \beta_1 \), we may in first approximation

(a) Linearize the Arrhenius exponent around \( \theta = \theta_\sigma \), following the Frank-Kamanetzky procedure.

(b) Approximate \( \phi_z - \theta_c \) by \( \theta_c'(\tau - \tau_c) \).

(c) Neglect the oxidizer consumption, if we assume that \( \alpha \gamma / \Sigma \ll 1 \).

With these approximations equation (1) becomes

\[
\phi = \frac{1}{\sqrt{\pi}} \int_0^\infty \frac{\exp \left\{ \beta \theta_\sigma (1 + \theta_\sigma) \right\}}{\sqrt{\pi} (\gamma + 1)} \times \exp \left\{ \beta_1 \phi + \beta \phi_\sigma (\lambda - \tau_c) \right\} \frac{d\lambda}{\sqrt{\tau - \lambda}}
\]

(22)

We shall write this equation in terms of the variables

\[
\psi = \beta_1 \phi, \quad z = \beta_1 \phi_{\sigma}(\tau - \tau_c) + \ln p
\]

(23)

where \( p \), which will turn out to be of order unity for large values of \( \beta_1 \), is given by,

\[
p = \frac{\beta}{\sqrt{\pi} \theta_\sigma} \frac{\exp \left\{ \beta \theta_\sigma (1 + \theta_\sigma) \right\}}{\sqrt{\pi} (1 + \theta_\sigma)(1 + \gamma)}
\]

(24)

Then we obtain the following integral equation for \( \psi \),

\[
\psi(z) = \frac{1}{\sqrt{\pi}} \int_{-\infty}^z \frac{\exp \left\{ \psi(z_1) + z_1 \right\}}{\sqrt{z - z_1}} dz_1
\]

(25)

if we replace the lower limit of integration, which should be written as \( -\beta_1 \phi_\sigma + \ln p \), by its limiting form, \(-\infty\), for large values of \( \beta_1 \).

This equation was obtained and integrated numerically by Linan and Williams (1970), in connection with their analysis of condensed phase ignition of a reactive solid. The numerical results show that \( \psi(z) \) grows very rapidly toward infinity, when \( z \) approaches the value \(-0.431\), what is indicative of a thermal runaway. The infinite in \( \psi(z) \) results from the approximations (a) and (c).

If we take into account the definition, equations (23) and (24), of the new time variable \( z \), and the fact that \( \tau = \tau_c \), is the ignition time, we obtain the following relation

\[
\psi(z) = \frac{1}{\sqrt{\pi}} \int_{-\infty}^z \frac{\exp \left\{ \psi(z_1) + z_1 \right\}}{\sqrt{z - z_1}} dz_1 = 1
\]

(26)

because \( \ln p = -0.431 \). This relation, equation (26), is to be used, together with equations (20), for an analytical prediction of the ignition time, more accurate than the one resulting from equation (17).

It should be noticed that the mode of heating the solid propellant enters into equation (26) only through the values \( \theta_c = \theta_i(\tau_c) \) and \( \theta_c' = \theta_i'(\tau_c) \).

For a constant radiant flux, \( \theta_i(\tau) \) is given by equation (3) in terms of \( \tau \); and, therefore, we obtain,

\[
\theta_c = \left\{ \frac{\gamma}{(\gamma + 1)} \delta \right\} H(\delta^2 \tau_c / \pi)
\]

(27a)

\[
\theta_c' = \left\{ \frac{\gamma}{(\gamma + 1)} \delta \right\} H(\delta^2 \tau_c / \pi)
\]

(27b)

where \( H(\delta) \) is the derivative of \( H(\delta) \) with respect to \( \delta \). When equations (27) are substituted into equation (26), a relation (which is explicit if the factor \( \gamma / (\gamma + 1) \) is left out of equation (27) when \( \gamma \) is large) is obtained for the radiant flux \( \psi \) in terms of the ignition time \( \tau_c \), the absorption coefficient \( \delta \) and the activation energy \( \beta \).

Figure 3 shows the resulting values of \( \tau \) in terms of \( \psi \), for three typical values of \( \beta \) and several values of \( \delta \). For \( \delta = 10^2 \), the resulting values of \( \gamma \) do not differ significantly from those corresponding to \( \delta \rightarrow \infty \), or surface absorption of the radiation.
In this case, if \( y \) is large,
\[
\theta_\epsilon = 2\sqrt{\tau_\epsilon / \pi} \quad \text{and} \quad \theta'_\epsilon = 1 / \pi \sqrt{\tau_\epsilon}
\] (28)

When the analytical prediction of the ignition time, given by equations (26) and (28) for \( \delta \to \infty \), is compared with the numerical results of Bradley and Williams (1971) no difference is found in Figure 3, for \( y > 10 \) because of thickness of the lines. An excellent agreement is also found with the numerical predictions by Baer and Ryan (1965), for the heterogeneous ignition of solid propellants subject to a radiant flux with surface absorption.

For small values of \( \delta \), and large values of \( y \), the following relations
\[
\theta_\epsilon = \delta \tau_\epsilon / \pi \quad \text{and} \quad \theta'_\epsilon = \delta / \pi
\] (29)
can be used, together with equation (26), for the prediction of the ignition time.

For the validity of this asymptotic analysis the following inequalities should hold
\[
\theta_\epsilon \beta \gg 1, \quad \beta \theta_\epsilon^2 \gg 1 \quad \text{and} \quad \beta \alpha \theta_\epsilon^2 \gg 1 \] (30)

The first inequality is obtained from the requirement that \( \beta \theta_\epsilon^2 \gg 1 \), so that we may be able to replace by \(-\infty\) the lower limit, \( \ln \rho - \beta \theta_\epsilon \tau_\epsilon \), of integration in equation (25). In Section V we shall analyze those cases for which \( \beta \theta_\epsilon \) is of order 1.

The second inequality allows us to linearize the Arrhenius exponent, and the third enables us to neglect the oxidizer consumption. We may expect relative errors of order \( \theta_\epsilon^2 \beta \) and \( \alpha \theta_\epsilon^2 \beta \) in the calculation of the radiant flux \( y \) in terms of the ignition time. Thus, it is not difficult to show that the factor \( \{1 - \alpha n(1 + \theta_\epsilon)^2 / \beta \} \) should be introduced in the left hand member of equation (26), to account for the effects of oxidizer consumption for small values of \( \alpha n(1 + \theta_\epsilon)^2 / \beta \). If the two last inequalities in equation (30) do not hold the ignition event is not well defined.

The perturbation procedure described by Liñán and Williams (1971) could be used to obtain higher order terms in an asymptotic expansion for large values of \( \beta \) of the problem posed in this Section. It is clear that the present analysis fails when, at times \( \tau \) very close to \( \tau_\epsilon \), \( \beta \) becomes large, of order \( \beta_1 \), so that the approximations (a) and (c) are no longer justified. The surface temperature \( \theta \) will grow very rapidly to the equilibrium value \( \theta_\epsilon + 1 / \alpha \), which at \( \tau = \tau_\epsilon \) has the value \( \theta_\epsilon + 1 / \alpha \).

There are advantages in writing equations (26) and (27) in terms of the non-dimensional ignition time \( \nu_\epsilon \), and the absorption coefficient \( \nu \). Thus, the following relation is obtained
\[
\gamma = \exp \left( 0.431 \sqrt{\beta / \nu \tilde{H}_\epsilon} (1 + \theta_\epsilon)^{-1} \times \exp \{ \beta \theta_\epsilon / (1 + \theta_\epsilon) \} \right)
\] (31)
giving, explicitly, \( \gamma \) in terms of \( \beta, \nu \) and \( \nu_\epsilon \). Here \( \nu \theta_\epsilon = \tilde{H}_\epsilon = H(v_\epsilon) \) and \( \tilde{H}_\epsilon = H(v_\epsilon) \), where \( H(v) \) is defined by equation (4).

This relation, equation (31), takes a simpler form:
(a) For \( \nu_\epsilon \ll 1 \), when \( \tilde{H}_\epsilon = \nu_\epsilon \) and \( \tilde{H}_\epsilon = 1 \). Then \( \gamma^1 \) is just a function of \( v_\epsilon / \nu \) and \( \beta \) represented in Figure 4 with dashed lines.
(b) For \( \nu_\epsilon \gg 1 \), when \( \tilde{H}_\epsilon = 2 \sqrt{v_\epsilon / \nu} \) and \( \tilde{H}_\epsilon = 1 / \sqrt{v_\epsilon \nu} \). Then \( \gamma \) is just a function of \( v_\epsilon / \nu^2 \) and \( \beta \) represented in Figure 4 with solid lines.

We have represented in Figure 2 two typical surface temperature histories \( \theta(v) = \theta_\epsilon + \psi \beta_1 \) resulting from our analysis.

IV. HYPERGOLICignition

The integral equation (1) reduces for the hypergolic ignition case \( (\gamma = 0) \) to the equation
\[
\theta(\tau) = \int_0^\tau \left( 1 - \alpha \theta \right)^n \exp \left\{ \beta \theta / (1 + \theta) \right\} \sqrt{\tau - \lambda} \, d\lambda
\] (32)
ANALYSIS OF RADIANT AND HYPERGOLIC HETEROGENEOUS IGNITION OF SOLID PROPELLANTS

This equation was integrated numerically, for some representative values of \( x, n, \) and \( \beta, \) by Williams (1966), Bradley and Williams (1970), and Waldman (1970). The numerical results show again that, for large values of \( \beta \) and \( \beta/\alpha, \) thermal runaway occurs at a certain "ignition time" \( \tau_c. \)

To facilitate the asymptotic analysis we write equation (32) in terms of the variables

\[ \Psi = \beta \theta \quad \text{and} \quad \sigma = \tau \beta^2, \quad (33) \]

and then take limit \( \beta \to \infty, \) which results in the equation

\[ \Psi = \frac{1}{\pi} \int_0^\infty \frac{\exp \{ \Psi(\sigma_1) \}}{\sqrt{\sigma - \sigma_1}} d\sigma_1 \quad (34) \]

The numerical solution of this equation shown in Figure 5, indicates that \( \Psi \) becomes infinite at \( \sigma = 0.864. \) The relation,

\[ \tau_c = 0.864 \beta^{-2}, \quad (35) \]

gives the ignition time as a function of \( \beta, \) with relative errors of order \( 1/\beta \) when \( \beta \) is large.

The effects of oxidizer depletion at the surface can be taken into account, for small values of \( \alpha n/\beta, \) by introducing a factor \((1 + 2 \alpha n/\beta)\) in the right hand side of equation (35). We thus obtain

\[ \tau_c = 0.864 \beta^{-2}(1 + 2 \alpha n/\beta). \quad (36) \]

For a simple derivation of this result we may, anticipating that \( \alpha n \theta \ll 1, \) write the factor \((1 - \alpha \theta)^n\) in equation (32) in the approximate form \( \exp (-\alpha n \theta). \) Thus we obtain an apparent change in activation energy from \( \beta \) to \((\beta - \alpha n), \) which explains the delay factor \((1 + 2 \alpha n/\beta)\) in the ignition time.

The differences between the analytical prediction, equation (36), of the ignition time and the numerical predictions of Bradley and Williams (1970) and Waldman (1970) are small, and may be explained in terms of the relative errors, of order \( 1/\beta, \) which may be expected in the first approximation in this asymptotic analysis.

If we were interested in obtaining higher order approximations, we should pose our problem as to find, for given values of \( x \) and \( n \) and large values of \( \beta, \) the solution \( \sigma = \sigma(\Psi, \beta) \) of equation (32) written in terms of \( \sigma \) and \( \Psi. \) We may expect that \( \sigma(\Psi, \beta) \) will be an analytic function of \( 1/\beta \) for small values of \( 1/\beta \) and values of \( \Psi \) small compared with \( \beta/\alpha n. \) Then it could be expanded in powers of \( 1/\beta \) as

\[ \sigma = \sigma_0(\Psi) + \beta^{-1} \sigma_1(\Psi) + \ldots, \]

which when substituted in equation (32) would yield equation (34) for \( \sigma_0(\Psi), \) and a linear integral equation for \( \sigma_1(\Psi). \)

V. IGNITION FOR LOW RADIANT FLUXES

We shall consider now the cases when the radiant flux is so small that its contribution to the rise in surface temperature is of the same order as that of the chemical reaction at the initial surface temperature. Therefore, both will contribute during the ignition period to the surface temperature rise, which ends in a thermal runaway at a time \( \tau_c \) comparable to the hypergolic ignition time.

Only a small temperature rise, of order \( 1/\beta, \) will be necessary, at large values of \( \beta, \) to increase the reaction rate by the large factors which cause the runaway of the reaction. This dictates our choice of the following variables

\[ \Psi = \beta \theta, \quad \sigma = \tau \beta^2(1 + \gamma)^{-2}, \quad (37) \]

for the description of the ignition period. The factor \( \beta \) is introduced so as to make the non-dimensional temperature \( \Psi \) of order unity. The factor \( \beta \) in \( \sigma \) is introduced so as to make the ignition time \( \tau_c \) of order unity. The factor \((1 + \gamma)^{-2}\) is introduced so as to obtain the normalized asymptotic equation, equation (38) below, with a chemical source term free from the radiation parameter \( \gamma. \)

If equation (1) is written in terms of the variables \( \Psi \) and \( \sigma, \) we obtain, in the limit \( \beta \to \infty, \) the following equation for \( \Psi(\sigma), \)

\[ \Psi(\sigma) = \frac{\beta \gamma}{(\gamma + 1)^2} H \int \left[ \frac{\left( (\gamma + 1) \beta \right)^{\sigma_1}}{\beta} \right] \frac{1}{\pi} \int_0^\infty \frac{\exp \left\{ \Psi(\sigma_1) \right\}}{\sqrt{\sigma - \sigma_1}} d\sigma_1 \quad (38) \]
where the first term in the right hand member represents the contribution to the surface temperature rise of the radiant flux; the second term is the contribution of the chemical heat release. For \( \gamma = 0 \), we recover the equation (32) which describes the hypergolic ignition process. We assume that the parameters \( \gamma \) and \( \delta \) grow with \( \beta \) so that in the limit \( \beta \to \infty \) the term \( H \beta \gamma / (\gamma + 1) \delta \) remains of order 1.

Two parameters, \( \gamma \) and \( (\gamma + 1) \delta / \beta \), are involved in equation (38), while five parameters were involved in equation (1).

If \( (\gamma + 1) \delta / \beta \gg 1 \), the argument \( v = \sigma (\gamma + 1) \beta \delta / \beta \pi \) of \( H \) is large during most of the ignition period. Then \( H \approx 2 \sqrt{v} / \pi \), which corresponds to surface absorption of the radiation. The absorption layer is very thin compared with the heat conduction layer during the ignition period. The integral equation (38) reduces in this case to

\[
\Psi = 2 \gamma \sqrt{\sigma / \pi} + \frac{1}{\pi} \int_0^\sigma \frac{\exp \Psi}{\sqrt{\sigma - \sigma_1}} \, d\sigma_1
\]  

(39)

If we want the contributions of the radiant flux and of the chemical heat release to be of the same order, \( \gamma \) must be of order unity. For \( \gamma \ll 1 \) we obtain the hypergolic ignition problem in first approximation. For large values of \( \gamma \), an inert heating stage will precede the reaction stage; the analysis of Section III may be used to predict the ignition time in this case.

We have represented in Figure 5 the numerical solution \( \Psi(\sigma) \) of equation (39) for several values of \( \gamma \). The ignition time \( \sigma_c \), for which \( \Psi \) becomes infinite, is represented in Figure 6 in terms of \( \gamma \). Also shown in Figure 6 is the relation,

\[
\sigma_c = (\ln \sqrt{\pi A} - 0.431)/A
\]  

(40)

obtained by means of the asymptotic analysis of section III for large values of \( A \).

For intermediate values, of order unity, of the parameter \( (\gamma + 1) \delta / \beta \), and \( \gamma \) also of order unity, equation (38), with the function \( H(\sigma) \) given in equation (4), should be solved to obtain the ignition time \( \sigma_c \) as a function of \( \gamma \) and \( (\gamma + 1) \delta / \beta \). We have not carried out these numerical calculations, which may be expected to yield values of \( \sigma_c \) of order unity.

Figure 3 shows with thick lines the ignition time, as predicted by means of the asymptotic analysis of this section, for those low values of \( \gamma \) for which the analysis of Section III could not be used.

FIG. 6. Ignition time in terms of \( \gamma \) or \( A \), large or small values of the absorption coefficient respectively, for small radiant fluxes.
VI. CONCLUSIONS AND GENERALIZATIONS

We have carried out in the previous sections an asymptotic analysis for large activation energies for the model of solid propellant ignition with heterogeneous reactions as formulated by Bradley and Williams (1970). This model may be used to describe the ignition of a solid when heated by a radiant flux with in-depth absorption of the radiation, and also for the analysis of hypergolic ignition, and ignition under shock tube conditions.

The ignition process for large radiant fluxes was analyzed in Section III. A short reaction stage, ending in thermal run-away, was shown to follow a longer inert heating stage. Equation (26) was found to relate the ignition time with the characteristics of the surface reaction, entering through \( \beta \) and \( \gamma \), and two data of the inert heating history, \( \theta_c \) and \( \beta_f \). The analysis may be used in connection with other solid propellant geometries and other ways of heating the solid propellant. For a semi-infinite solid heated by a constant radiant flux, an analytical expression, equation (31), was found for \( \gamma \) in terms of the ignition time, \( \nu_s \), and the absorption coefficient, \( \nu \). This relation has been represented in Figure 3 (\( \gamma \) in terms of \( \theta \) and \( \tau_o \)), in Figure 4 for large values of \( \nu_s \) (limit of surface absorption) and also for small values of \( \nu_s \) (limit of small absorption coefficient).

This analytical relation for the ignition time turns out to be a very accurate correlation of the numerical results given by Bradley and Williams (1970) for the case with surface absorption of the radiation. No numerical results, with which to compare our asymptotic analysis are known to the authors for the case with in-depth absorption; however, we have included in this paper an estimate of the errors involved.

It is interesting to note the similarity of the results obtained in Section III and those obtained by Liñán and Williams (1971, 1972) in their analysis of the condensed phase ignition of solid propellants by a radiant energy flux with surface absorption. They found the chemical reaction was important only in a very thin region close to the surface. Therefore, when looking at the solid with other larger characteristic scales, it appears to undergo a surface reaction with the same activation energy as the condensed phase reaction.

A closed form expression was found for the ignition time in the hypergolic ignition case. This expression, equation (36), is an accurate correlation of the existing numerical results of Bradley and Williams (1970) and Waldman (1970).

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Heat evolved in surface reaction per unit mass of oxidizer
Universal gas constant
Temperature
Surface temperature just after contact between gas and solid phases
Mass fraction of oxidizer
Initial mass fraction of oxidizer
Greek letters
Diffusion-heat release parameter
Dimensionless activation energy
External heating parameter
Radiant absorption parameter
Dimensionless surface temperature
Coefficient of thermal conductivity
Radiant absorption coefficient
Dimensionless absorption parameter
Density
Dimensionless time
Density ignition time
Dimensionless surface temperature rise due to the chemical reaction
Gas phase thermal responsivity
Solid phase thermal responsivity
Subscripts
Gas phase
Solid phase
Surface
Initial
Far from the surface.

REFERENCES

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