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THE SURFACE HEATING OF A REACTIVE SOLID

by

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SUMMARY

Merzhanov and Averson[1] have recently reviewed thermal ignition theory and, in particular, the various approximate theories for calculating the time at which thermal instability leads to large rises in temperature when the surface of a self-heating material is subjected to a constant thermal flux. Subsequently, Bradley[2] showed that his computer calculations corresponded in effect to a mean between two simple conventional results, and Linan and Williams[3] have derived the same relation. This was of a form different from previous ones, viz:

$$\sigma \propto \theta_o^{1/4}$$

where σ is a dimensionless flux

and θ_o is a dimensionless temperature rise dependent on σ and the time, which is thereby found as a function of σ.

This paper shows how a simple approximation to the conduction loss term in the basic differential equation can lead analytically to this result, agreeing within 1 per cent with Linan and William's result obtained by a different theoretical development.

The approximation described has already been used to obtain an analytic criticality condition for simple hot spots[4] and the main interest of this paper is the application to surface ignition.

KEY WORDS: Self-heating, surface, ignition

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1. INTRODUCTION

A material capable of self-heating may behave in various ways according to how it is heated. If a small part of a large volume of such material is itself heated to a much higher temperature than its immediate surroundings, it may not be able to lose heat by conduction fast enough to prevent its temperature rising significantly to produce ignition. A small volume of material, self-heating in this way, can be described as a thermal 'hot spot.

If a large mass of self-heating material is held in sufficiently cool inert surroundings but is not initially hot itself, the material may reach a steady temperature above its surrounding. A runaway temperature rise in sufficiently hot surroundings is variously described as a thermal explosion, or spontaneous ignition.

If the material is heated more quickly, ignition can occur at the surface and the interior of the material plays no part in the heating; its only role is that of a heat sink.

These three kinds of behaviour have been reviewed in detail elsewhere[1,5,6] and this paper is concerned primarily with one particular feature of the theory, namely, the extension of a simple approximate method developed by Thomas[4] for a hot spot to a certain class of surface ignition problems. Like many of the other approximate methods reviewed by Merzhanov and Averson[1] the method is satisfactory for the continuous heating of a surface by a constant flux, but fails for continuous heating with the surface maintained at a constant temperature. For the constant flux condition the method readily yields results for the critical condition which are in almost exact agreement with a formula proposed by Bradley[2] to represent his computer calculations and which was later derived by an approximate analysis by Linan and Williams[3]. Bradley considered a pulse of finite duration and Linan and Williams a continuous flux. This latter treatment requires one detailed numerical integration: what follows is an approximate but entirely analytic and simple derivation of virtually the same result.

The interest in this paper is mainly in the demonstration of the wider scope of the method of approximation rather than any new physical and chemical insight.

2. THEORY: APPROXIMATION AND 'INERT EQUIVALENT'

We consider a semi-infinite volume of material of constant and uniform properties for which the differential heat balance is written as[1,5]

$$\frac{\partial \theta}{\partial \tau} = \frac{\partial^2 \theta}{\partial z^2} + e^{\theta} \quad \text{......... (1)}$$

where $$\theta = \frac{E}{RT_1^2}(T - T_1)$$

$$\tau = \frac{Q f E}{\rho c R T_1^2} e^{-E/RT_1} t$$

$$z = \left(\frac{Q f E e^{-E/RT_1}}{K R T_1^2} \right)^{1/2} x$$

where T is absolute temperature

T_1 is a reference temperature to be defined and evaluated below

E is activation energy

R is universal gas constant

Q is heat of reaction

f is frequency factor

ρ is density

c is specific heat

K is thermal conductivity

t is time

and x is distance from the heated surface.

We shall consider first a boundary condition

$$-K(\partial T/\partial x) = q \quad \text{at } x = 0$$

so that $$-\frac{\partial \theta}{\partial z} = \sigma \quad \text{......... (2)}$$

where $$\sigma = q\left[E/(K Q f R T_1^2 e^{-E/RT_1})\right]^{1/2}$$

The initial condition is

$$T = T_0 < T_1 \qquad \text{...... (3)}$$

i.e.

$$\theta = -\theta_0 \text{ at } t = 0$$

where for convenience θ_0 is defined as a positive quantity

i.e.

$$\theta_0 = \frac{E}{RT_1^2}(T_1 - T_0)$$

is the dimensionless temperature excess over the ambient temperature of the datum temperature defining ignition.

It must be remembered that T_1 is as yet unspecified and we now <u>define</u> it by

$$T_1 - T_0 = \frac{2q}{\sqrt{\pi}\,K}\sqrt{Kt_{ig}/\rho c}$$

or

$$\theta_0 = \frac{2\sigma}{\sqrt{\pi}}\sqrt{\tau_{ign}} \qquad \text{...... (4)}$$

where τ_{ign} is the value of τ at ignition.

The imposition of some ignition criterion, say $\theta \to \infty$, $\frac{\partial \theta}{\partial z} = 0$ etc gives a solution of the form

$$\sigma = \sigma(\theta_0)$$

so obtaining T_1 and τ_{ign}.

From the nature of the definition of σ in terms of the Arrhenius term one can see that T_1 is relatively insensitive to differences in σ. That is, significant theoretical differences in estimates of σ may be tolerated in practice because they may not imply much error in the estimate of T_1. We now proceed to obtaining an approximate solution to equation (1)-(4).

Because of the boundary condition, (equation (2)) it follows that, unless the temperature has a minimum (and a maximum) internally, the maximum temperature is at the surface. The former requires two positions where $\partial^2\theta/\partial z^2$ is zero but without any formal discussion of this possibility we shall consider only the possibility of the highest temperature being on the surface.

We now make the approximation that has been made by Thomas[4] for hot spots.

$$\frac{\partial^2 \theta}{\partial z^2} \doteqdot \frac{\partial^2 \psi}{\partial z^2} \qquad \text{...... (5A)}$$

where ψ satisfies

$$\frac{\partial^2 \psi}{\partial z^2} = \frac{\partial \psi}{\partial \tau} \qquad \text{...... (5B)}$$

and ψ is $-\vartheta_0$ at $t = 0$

so that
$$\frac{\partial \psi}{\partial \tau} = \frac{\partial \theta}{\partial \tau} - e^{\theta} \qquad \text{...... (6)}$$

ψ is a temperature rise in an inert solid and we seek a boundary condition analagous to equation (2) which is consistent with this formulation. We are in effect regarding the conduction loss from the reacting material, not anything else, as unaffected by the reactivity, and it must be remembered that ψ is not the temperature in the same equivalent inert material heated in the same way.

Equation (1) can be differentiated

$$\frac{\partial^2 \psi}{\partial z \partial \tau} = \frac{\partial^2 \psi}{\partial \tau \partial z} = \frac{\partial}{\partial \tau}\left(\frac{\partial \theta}{\partial z}\right) - e^{\theta}\left(\frac{\partial \theta}{\partial z}\right) \qquad \text{...... (7)}$$

From equations (7) and (2) it follows that

$$\frac{\partial^2 \psi}{\partial \tau \partial z} = \sigma e^{\theta}$$

i.e.

$$-\left.\frac{\partial \psi}{\partial z}\right)_0 = \sigma\left(1 - \int_0^{\tau} e^{\theta} d\lambda\right) \qquad \text{...... (8)}$$

Appendix 1 deals with a flux varying as τ^n $(n > 0)$.

Equation (6) has the solution[4]

$$e^{\theta} = \frac{e^{\psi - \vartheta_0}}{1 - \int_0^{\tau} e^{\psi} d\lambda} \qquad \text{...... (9)}$$

Hence
$$-\left.\frac{\partial \psi}{\partial z}\right)_0 = \sigma(1 + \psi - \theta - \vartheta_0) \qquad \text{...... (10)}$$

and
$$\int_0^{\tau} e^{\theta} d\lambda = -\log_e\left(1 - \int_0^{\tau} e^{\psi - \vartheta_0} d\lambda\right) \qquad \text{...... (11)}$$

The equation for $d\psi/dz$ is linear in terms of ψ, θ and θ_0 and some development in terms of the Laplace transform is possible, but we shall not pursue this here.

It may be pointed out here that the equations above, given equation (1), are all exact if ψ is defined by $\int_0^\tau \frac{\partial^2\theta}{\partial z^2}\, d\tau$.

without involving the constraint that ψ is a solution for an inert solid. We shall discuss some mathematical aspects of the approximation in Appendix 2.

From equation (10) we see that an infinite temperature on the surface means that $-\partial\psi/\partial z$, beginning as σ could fall to zero and become negative. Heat is then abstracted from the 'inert equivalent' and ψ could become negative.

For an inert solid it follows from Carslaw and Jaeger[7] that, if ψ satisfies equation (5B)

$$\psi = -\frac{1}{\sqrt{\pi}}\int_0^\tau \left(\left(\frac{d\psi}{\partial z}\right)_0 \Big/ \sqrt{\tau-\lambda}\right) d\lambda$$

so that from equation (8)

$$\psi_{0,\tau} = \frac{\sigma}{\sqrt{\pi}}\int_0^\tau \frac{\left(1-\int_0^\lambda e^{\theta}\, d\lambda\right) d\lambda}{\sqrt{\tau-\lambda}}$$

$$= \frac{2\sigma\sqrt{\tau}}{\sqrt{\pi}} - \frac{2\sigma}{\sqrt{\pi}}\int_0^\tau \sqrt{\tau-\lambda}\; e^{\theta}\, d\lambda \quad \ldots\ldots (12)$$

$$= \frac{2\sigma\sqrt{\tau}}{\sqrt{\pi}} - \frac{\sigma}{\sqrt{\pi}}\int_0^\tau \frac{1}{\sqrt{\tau-\lambda}} \log_e \frac{1}{\int_\lambda^{\tau_1} e^{\psi-\theta_0}\, d\lambda}\, . d\lambda \quad (13)$$

where τ_1 is defined by

$$\int_0^{\tau_1} e^{\psi-\theta_0}\, d\lambda = 1$$

3. CRITERION OF IGNITION

Clearly on this model infinite temperatures result when

$$\int_0^{\tau_1} e^{\psi-\theta_0}\, d\lambda = 1 \qquad \ldots\ldots (14)$$

and this defines the value of τ_{ign} ($= \tau_1$) required. From equations (8) and (11) this condition is equivalent to

$$\frac{\partial \psi}{\partial z} \to \infty$$

However, we so far only have an integral equation for defining ψ. A first approximation is

$$\psi(u) = \frac{2\sigma\sqrt{u}}{\sqrt{\pi}}$$

with θ_0 defined by $\dfrac{2\sigma\sqrt{\tau_{ig}}}{\sqrt{\pi}}$

and for large $\theta_0 \gg 1$ equation (14) results in

$$1 = \frac{\pi}{2\sigma^2}\left(\frac{2\sigma\sqrt{\tau_{ig}}}{\sqrt{\pi}} - 1\right)$$

i.e.

$$\sigma = \sqrt{\frac{\pi}{2}}\sqrt{\theta_0 - 1} \qquad \ldots\ldots (15)$$

which from the discussion by Merzhanov and Averson[1] appears to be too high, presumably because we have used an estimate for ψ.

Now equation (12) with θ_0 equal to $\dfrac{2\sigma\sqrt{\lambda}}{\sqrt{\pi}}$ also gives an upper limit to ψ. Clearly as θ rises to infinity ψ must fall rapidly. Extracting heat from a surface at infinite rates leads to infinitely high rates of fall of surface temperatures, though a priori we cannot distinguish between the behaviour of Fig.1 and Fig.2.

To obtain the behaviour following Fig.1 we would need a discontinuity in $\partial\psi/\partial z$ but $\partial^2\psi/\partial z^2$ is continuous so without formality we presume that ψ falls to zero before τ_{ig} is reached. Hence an alternative method of estimating τ_{ig} is to take $\psi = 0$ as our criterion. This is a better approximation than $\partial\psi/\partial z = 0$ which is reached earlier (see below).

With $\theta_0 + \theta = \frac{2\sigma\sqrt{\lambda}}{\sqrt{\pi}}$ in equation (12)

and τ_{ig} defined by $\theta_0 = \frac{2\sigma\sqrt{\tau_{ig}}}{\sqrt{\pi}}$

i.e. we solve

$$0 = \frac{2\sigma\sqrt{\tau_{ig}}}{\sqrt{\pi}} - \frac{2\sigma}{\sqrt{\pi}} \int_0^{\tau_{ig}} e^{-\theta_0} e^{\frac{2\sigma\sqrt{\lambda}}{\sqrt{\pi}}} \sqrt{\tau_{ig} - \lambda}\, d\lambda$$

Since the peak of the integrand on the r.h.s. occurs when $\lambda \to \tau_{ig}$ we put

$$\sqrt{\lambda} = \sqrt{\tau_{ig}} \left(1 - \frac{\tau_{ig} - \lambda}{2\,\tau_{ig}}\right) \qquad \ldots\ldots\ (16)$$

in the index of the exponential term and obtain

$$\frac{2\sigma\sqrt{\tau_{ig}}}{\sqrt{\pi}} = \frac{2\sigma}{\sqrt{\pi}} \frac{(\pi\tau_{ig})^{3/4}\sqrt{\pi}}{2\sigma^{3/2}}$$

$$\sigma = \left(\frac{\pi}{2}\right)^{3/4} \theta_0^{1/4} \qquad \ldots\ldots\ (17)$$

This is the result being sought. We shall refer below to this value of σ as σ_T.

4. COMPARISON WITH OTHER RESULTS

It is possible to write, from equation (6)

$$\psi = \theta + \theta_0 - \int_0^{\tau} e^{\theta} d\lambda$$

but putting $\theta + \theta_0 = \frac{2\sigma\sqrt{\lambda}}{\sqrt{\pi}}$ as an approximation on the right hand side leads (for $\psi \to 0$) to $\sigma \sim \sqrt{\pi/2}$. It is $\partial\theta/\partial z$ which is specified so equation (8) is preferable.

The condition $\left(\partial\theta/\partial z\right)_0 = 0$ is similar to that used by some other writers[1,8,9]. In the notation of Merzhanov and Averson[1] it is $\hat{\delta} = 0$. Used with equations (9) and (10) it gives

$$\int_0^{\tau_{ig}} e^{\psi - \theta_0} d\lambda = 1 - 1/e$$

as the criterion for infinite temperature rise.

With the approximation of equation (14) this gives

$$\sigma = \left(\frac{\pi}{2}\theta_0 \frac{e}{e-1}\right)^{1/2}$$

which is a relatively high value of σ for typical values of θ_0.

The condition $\frac{\partial\psi}{\partial\tau} = 0$ is also of interest. This gives a higher value of σ i.e. a lower ignition temperature

$$\sigma = \left(\frac{3}{2}\right)^{1/2}\left(\frac{\pi}{2}\right)^{3/4}\theta_0^{1/4} = 1{\cdot}23\,\sigma_T$$

For $\theta_0 = 20$, σ_T = 2.96, which compares favourably with the values reviewed by Merzhanov and Averson[1].

We have followed the conventions and, in the main, the details of the notation of Merzhanov and Averson and their procedures for dealing with the limiting case of $RT_0/E = 0$.

Bradley and Linan and Williams also deal with the case of high E so that their results like those of Merzhanov and Averson do not involve T_0 as an <u>absolute</u> temperature - only as part of a temperature difference. However, many of the variables used by Bradley, and Linan and Williams, include T_0 as an absolute temperature (the results depend on combinations not involving T_0). Table I shows some comparable notation.

<u>Table 1</u>

Comparison of notation

Terms as used by Bradley & Linan and Williams	Equivalent in the notation of this paper
A	KT_0Qf/q^2
θ_0	T_1/T_0
τ	$\frac{q^2 k t}{(KT_0)^2}$
E'/θ	E/RT
ξ or $\frac{qx}{kT_0}$	$z\sqrt{\frac{q^2 T_1^2 R}{KT_0^2 EQf} e^{E_1/RT_1}}$ or $z\sigma\frac{RT_1^2}{ET_0}$

Bradley's solution σ_B may be written in the notation of this paper as

$$\sigma_B = \left(\frac{\pi}{2}\right)^{1/4} \theta_0^{1/4} = \sqrt{\frac{2}{\pi}}\,\sigma_T$$

and for $\theta_0 = 20$ this gives

$$\sigma_B = 2.37$$

Linan and Williams obtained the same result as Bradley except for a coefficient 0.65 which was obtained by numerical integration. They formulated the problem for continuous heating, not a pulse as did Bradley.

In this notation their result is

$$T_{ig} = 0.65\,\frac{\pi}{2\sqrt{2}}\,\theta_0^{3/2}$$

Hence

$$\sigma_{L+W} = \frac{\sigma_B}{\sqrt{0.65}} \sim \sigma_T$$

Thus the results of Linan and Williams and of this paper agree even when using a sensitive measure of σ rather than the actual ignition temperature.

These results all compare favourably with other estimates of σ (see Merzhanov and Averson[1]) but add little or nothing to accuracy and perhaps nothing to the physical picture except there is a different dependence of σ on θ_0 from all other results except those of Bradley, and Linan and Williams. Another method giving $\sigma = \left(\frac{\pi}{2}\theta_0\right)^{1/4}$ is described in Appendix 3.

The difficulties for an approximate treatment of the indefinite exposure to constant temperature are discussed by Merzhanov and Averson whose own work shows that the dependence of τ_{ig} on θ_0 for a continuous source is somewhat weaker than θ_0^2. The essential difficulty is that the position of the ignition is not known a priori and it cannot take place on the surface if this is defined as at constant temperature.

5. DISCUSSION AND CONCLUSION

The method is subject to the same limitations as several other approximate methods and the continuous constant surface temperature boundary condition cannot be dealt with. The approximation of the transient heat loss in a reacting material to that in an inert material with a modified boundary condition gives, by a simple development, results agreeing with more detailed theories and in particular it agrees with the form of the critical parameter obtained empirically by Bradley and with theoretical support by Linan and Williams for the constant surface flux condition.

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APPENDIX 1

A varying surface flux

Equation (7) has the solution

$$-\left(\frac{\partial \psi}{\partial z}\right)_0 = \sigma(\tau) - \int_0^{\tau} q(\lambda)\, e^{\theta(\lambda)}\, d\lambda$$

where now σ varies with $q(\tau)$

Let
$$Y(\tau) = \frac{1}{\sqrt{\pi}} \int_0^{\tau} \frac{\sigma(\lambda)\, d\lambda}{\sqrt{\tau - \lambda}}$$

Hence our required solution

$$\psi = 0 = Y_{ig} - \frac{2}{\sqrt{\pi}} \int_0^{\tau_{ig}} e^{-Y(\tau_{ig})}\, e^{Y(\lambda)}\, \sigma(\lambda) \sqrt{\tau_{ig} - \lambda}\, d\lambda$$

Therefore, since the important part of the integral arises when $\lambda \to \tau_{ig}$

$$Y(\tau_{ig}) = \frac{2}{\sqrt{\pi}} \int_0^{\tau_{ig}} e^{-(\tau_{ig} - \lambda)\left(\frac{dY}{d\tau}\right)_{\tau_{ig}}}\, \sigma(\lambda) \sqrt{\tau_{ig} - \lambda}\, d\lambda$$

and
$$\psi(\tau_{ig}) = \sigma(\tau_{ig}) \Big/ \left(\frac{dY}{d\tau}\right)_{\tau_{ig}}^{3/2} \qquad \left(\frac{dY}{d\tau} > 0\right)$$

Thus if

$$\sigma = A\tau^{n} \qquad n \geqslant 0$$

$$Y(\tau_{ig}) = \frac{2A}{\sqrt{\pi}} \int^{\tau_{ig}} \frac{\lambda^{n}}{\sqrt{\tau_{ig} - \lambda}}\, d\lambda$$

$$= \frac{\Gamma(n+1)}{\Gamma(n+3/2)}\, \tau_{ig}^{\,n+1/2}$$

and hence $$\sigma = \gamma^{1/4}\left[\frac{\Gamma(n+3/2)}{\Gamma(n+1)}\right]^{3/2}\frac{1}{(n+1/2)^{1/2}}$$

When $n=0$, $\sigma/\gamma^{1/4} = \left(\frac{\pi}{2}\right)^{3/4}$ as obtained previously,

When $n \to \infty$ $\sigma/\gamma^{1/4} = 1$

It is this similarity in the forms rather than the difference between the constants $(\pi/2)^{3/4}$ and unity that is significant.

APPENDIX 2

We shall here examine some aspects of the approximation.
The 'Hot Spot' problem includes the surface heating case if $\left(\frac{\partial\theta}{dz}\right)_0 = 0$

Firstly, we define an approximation appropriate for the 'hot spot' and write

$$\psi = \theta_0 + \int_0^\tau \frac{d^2\theta}{dz^2}\, d\tau$$

Then, exactly

$$\theta = \psi - \theta_0 - \ln\left(1 - \int_0^\tau e^{\psi-\theta_0}\, d\lambda\right)$$

$$\frac{d\theta}{dz} = \frac{\partial\psi}{\partial z} + \frac{\int_0^\tau e^{\psi-\theta_0}\frac{d\psi}{dz}\, d\lambda}{1 - \int_0^\tau e^{\psi-\theta_0}\, d\lambda}$$

$$= \frac{\partial\psi}{\partial z} + \int_0^\tau e^{\theta}\frac{d\theta}{dz}\, d\lambda.$$

and

$$\frac{\partial^2\theta}{dz^2} = \frac{\partial^2\psi}{\partial z^2} + \frac{\int_0^\tau e^{\psi-\theta_0}\left\{\frac{\partial^2\psi}{\partial z^2} + \left(\frac{\partial\psi}{\partial z}\right)^2\right\}d\lambda}{1 - \int_0^\tau e^{\psi-\theta_0}\, d\lambda}$$

$$+ \left(\frac{\int e^{\psi-\theta_0}\frac{d\psi}{dz}\, d\lambda}{1 - \int_0^\tau e^{\psi-\theta_0}\, d\lambda}\right)^2$$

It folows from the above that $\frac{\partial\psi}{\partial z}=0$ where $\frac{\partial\theta}{\partial z}$ has a continuous zero i.e. at the axis of symmetry.
Hence at the axis of symmetry but not near boundary except where ψ is low,

$$\frac{\partial\psi}{\partial\tau}=\frac{\partial^2\theta}{\partial z^2}=\frac{\partial^2\psi}{\partial z^2}+\frac{\int_0^{\tau} e^{\psi-\theta_0}\left\{\int_0^{\lambda}\frac{\partial^4\theta}{\partial z^4}\,du\right\}d\lambda}{1-\int_0^{\tau} e^{\psi-\theta_0}\,d\lambda}$$

Since $\psi \ll \theta_0$ and since $-\partial^4\theta/\partial z^4$ initially increases from zero with time, we have for short times at the centre

$$-\frac{\partial^2\psi}{\partial z^2}<-\frac{\partial^2\theta}{\partial z^2}<-\frac{\partial^2\psi}{\partial z^2}+\frac{\tau^2}{2}\left\{\frac{-\frac{\partial^4\theta}{\partial z^4}}{1-\tau}\right\}.$$

Hence the approximation of $\frac{\partial^2\theta}{\partial z^2}$ to $\frac{\partial^2\psi}{\partial z^2}$ is reasonable for short times.
On the otherhand instead of under-estimating the conduction losses we can over-estimate them and put

$$\frac{\partial\psi}{\partial\tau}<\frac{\partial^2\theta}{\partial z^2}=\frac{\partial^2\psi}{\partial z^2}+\left(1-\int_0^{\tau} e^{\psi-\theta_0}d\lambda\right)^{-1}\frac{\partial^2\psi}{\partial z^2}\int_0^{\tau} e^{\psi-\theta_0}\,d\lambda$$

or

$$\frac{\partial\psi}{\partial\tau}<\frac{\partial^2\theta}{\partial z^2}<\frac{\partial^2\psi}{\partial z^2}\frac{1}{(1-\tau)}$$

So we consider

$$(1-\tau)\frac{\partial\psi}{\partial\tau}=\frac{\partial^2\psi}{\partial z^2}$$

or

$$\frac{\partial\psi}{\partial\tau'}=\frac{\partial^2\psi}{\partial z^2}\qquad \text{where } \tau'=\operatorname{Log}\frac{1}{1-\tau}$$

and provided the initial boundary condition remains the same for τ' as for τ we can define a ψ_N such that .

$$\psi_N\left(\frac{\tau}{\Delta}\right) = \psi\left(\frac{\tau'}{\Delta}\right) = \psi\left(\frac{\log\frac{1}{1-\tau}}{\Delta}\right)$$

where $$\Delta = \frac{Q f E e^{-E/RT_1} r^2}{K R T_1^2}$$

The sufficient condition for ignition (4) is

$$\tau = e^{\vartheta_0 - \psi}$$

$$\frac{\tau}{\Delta}\frac{d(\psi\Delta)}{d\tau} = 1$$

i.e. $$\frac{1-e^{-\tau'}}{e^{-\tau'}}\psi'\left(\frac{\tau'}{\Delta}\right) = \Delta \quad \text{and} \quad 1 - e^{-\tau'} = e^{\vartheta_0 - \psi}$$

This gives no result (i.e. $\frac{\partial\vartheta}{\partial\tau}$ is always same sign).

Hence this approximation has raised the heat loss so much that all results with it are subcritical.

In surface heating $\partial^2\vartheta/\partial z^2$ is positive so we over-estimate heat loss (under-estimate heat gain) by our approximation and we shall therefore make estimates of the ignition time which are too long and our estimate of ϑ_0 will similarily be too large. For a given q we under-estimate σ by the approximation.

APPENDIX 3

On the Linan - Williams treatment: an integral method

Linan and Williams employ a method of expanding various terms as a series in $(T_1/T_0)\sqrt{RT_0/E}$ which they treat as small to obtain asymptotic solutions for large E and they derive the form of the solution which in our notation is

$$\sigma \propto \theta_0^{1/4}$$

A constant in the expression is evaluated by numerical integration.

As explained above, the conventional Frank-Kamenetskii approximation to the Arrhenius law gives an equation which is appropriate for $RT_0/E \to 0$ This equation does not, however, then appear to permit expansion in a series of powers of $(T_1/T_0)\sqrt{RT_0/E}$

Linan and Williams point out that the equation they derive for computation can be written in integral form and it is on these lines that we proceed here.

It is possible to write down by the methods of Carslaw and Jaeger the expression

$$\theta_{z,\tau} = \frac{1}{\sqrt{\pi}}\int_0^\tau -\left(\frac{\partial\vartheta}{\partial z}\right)_0 \frac{e^{-z^2/4(\tau-\lambda)}}{\sqrt{\tau-\lambda}}\,d\lambda \;+$$

$$+\frac{1}{2\sqrt{\pi}}\int_0^\tau d\lambda\int_0^\infty dz'\, q'''(z',\lambda)\left\{\frac{e^{-\frac{(z-z')^2}{4(\tau-\lambda)}}+e^{-\frac{(z+z')^2}{4(\tau-\lambda)}}}{\sqrt{\tau-\lambda}}\right\}$$

This gives θ in terms of the surface gradient $\left(\frac{d\vartheta}{dz}\right)_0$ and the volumetric heat generation rate q''' so that here we write

$$q''' = e^{\theta}$$

$$-\left.\frac{\partial\vartheta}{\partial z}\right)_0 = \sigma$$

Hence $$\Theta_{z=0} = \frac{2\sigma\sqrt{\tau}}{\sqrt{\pi}} + \frac{1}{\sqrt{\pi}}\int_0^\tau d\lambda \int_0^\infty dz' \, \frac{e^{\theta(z') - z'^2/4(\tau-\lambda)}}{\sqrt{\tau-\lambda}} \, \delta$$

Now here we can follow Linan and Williams and use the inert solution Θ_i as a basis for Θ but on the right hand side we need the solution as a function of z'

We employ

$$\theta = \Theta_{z=0} + \left(\frac{\partial\theta}{\partial z'}\right)_0 z' + \left(\frac{\partial^2\theta}{\partial z'^2}\right)\frac{z'^2}{2}$$

i.e.

$$\theta = \Theta_i + \phi + \left(\frac{\partial\theta}{\partial z'}\right)_0 z' + \left(\frac{\partial\theta}{\partial\tau} - e^{\theta}\right)\frac{z'^2}{2}$$

where ϕ is the excess of the surface temperature over that for an inert solid

This is in effect the series used by Linan and Williams (they linearize $\left(\frac{\partial\theta}{\partial\tau}\right)$ in the last term.

Now because e^{θ} is used in the form $e^{\theta(\lambda)}$ and we have a term in $z'^2/4(\tau-\lambda)$ we can neglect $\frac{\partial\theta}{\partial\tau}\frac{z^2}{2}$ which is $\frac{\sigma z'^2}{2\sqrt{\pi}\lambda}$ by comparison with $\frac{z'^2}{4(\tau-\lambda)}$ when $\tau-\lambda \ll \lambda$.

In our problem $\frac{\partial\theta}{\partial z} = -\sigma$ and the integration

$$\int_0^\infty e^{-\theta_0+\phi} \, \frac{e^{\frac{2\sigma\sqrt{\lambda}}{\sqrt{\pi}} - \sigma z' - \frac{z'^2}{4(\tau-\lambda)}}}{\sqrt{\tau-\lambda}} \, dz'$$

becomes

$$e^{-\theta_0} \, e^{\sigma^2(\tau-\lambda)} \operatorname{erfc} \sigma\sqrt{\tau-\lambda} \, \sqrt{\pi} \, \sqrt{\tau-\lambda} \, e^{\phi + \frac{2\sigma\sqrt{\lambda}}{\sqrt{\pi}}}$$

i.e. $$\phi = \int_0^\tau d\lambda \, e^{\sigma^2(\tau-\lambda)} \operatorname{erfc} \sigma\sqrt{\tau-\lambda} \, e^{\phi(\lambda)} \, e^{\frac{2\sigma\sqrt{\lambda}}{\sqrt{\pi}}} \, e^{-\theta_0}$$

where, because ϕ is an increasing function of λ, we are primarily concerned with the region $\lambda \sim \tau$

We have not expanded about the ignition temperature though we have defined $\theta_o + \theta$ in terms of it, but we now consider $\tau - \lambda \ll \tau$. and write

$$\phi(\lambda) = \phi(\tau) - \left(\frac{d\phi}{d\tau}\right)_\tau (\tau - \lambda)$$

Hence we have as an approximation

$$e^{\theta_o - \frac{2\sigma\sqrt{T}}{\sqrt{\pi}}} \phi e^{-\phi} = \int_0^\infty d\xi . e^{\sigma^2 \xi} \operatorname{erfc} \sigma\sqrt{\xi}\, e^{-\xi \left\{ \left(\frac{d\phi}{d\tau}\right)_\tau + \frac{\sigma}{\sqrt{\pi\tau}} \right\}}$$

where $\xi = \tau - \lambda$

which is convergent at large ξ.

The right hand side can be integrated exactly and hence

$$e^{\theta_o} e^{-\frac{2\sigma\sqrt{T}}{\sqrt{\pi}}} \phi e^{-\phi} = \frac{1}{\sigma\left(\frac{d\phi}{d\tau} + \frac{\sigma}{\sqrt{\pi\tau}}\right)^{1/2} + \left(\frac{d\phi}{d\tau} + \frac{\sigma}{\sqrt{\pi\tau}}\right)}$$

$$\phi e^{-\theta} = \frac{1}{\sigma\left(\frac{d\theta}{dt}\right)^{1/2} + \frac{d\theta}{dt}}$$

The denominator of the right hand side may be re-written as

$$\sigma\left(\frac{d\theta}{d\tau}\right)^{1/2} + \frac{d\theta}{d\tau} = \sigma^2 \left[\frac{2}{\sqrt{\pi}} \left(\frac{1}{\theta_o + \theta_i} \frac{d\theta}{d\theta_i} \right)^{1/2} + \frac{2}{\pi(\theta_o + \theta_i)} \frac{d\theta}{d\theta_i} \right]$$

where $\theta_o + \theta_i = \frac{2\sigma\sqrt{T}}{\sqrt{\pi}}$ the 'inert' temperature rise.

The second term $\frac{1}{\theta_o + \theta_i} \frac{d\theta}{d\theta_i}$ can be neglected so long as

$$\frac{d\theta}{d\theta_i} \ll \theta_i + \theta_o$$

that is, until the actual incremental temperature rise in a reactive material $\delta\theta$ is of order $\Theta_0 + \theta_i$ times $\delta\theta_i$ which occurs in an inert material. This clearly is very close to any mathematical definition of runaway temperature rise so we can approximate

$$e^{2\theta_0} e^{-\frac{4\sigma\sqrt{\tau}}{\sqrt{\pi}}} \phi^2 e^{-2\phi} \left\{ \frac{d\phi}{d\tau} + \frac{\sigma}{\sqrt{\pi\tau}} \right\} \doteqdot \frac{1}{\sigma^2}$$

In obtaining an approximation we also neglect $\sigma / \sqrt{\pi\tau}$ and finally obtain

$$\sigma = \left(\frac{\pi}{2} \Theta_0 \right)^{1/4}$$

This is Bradley's result.

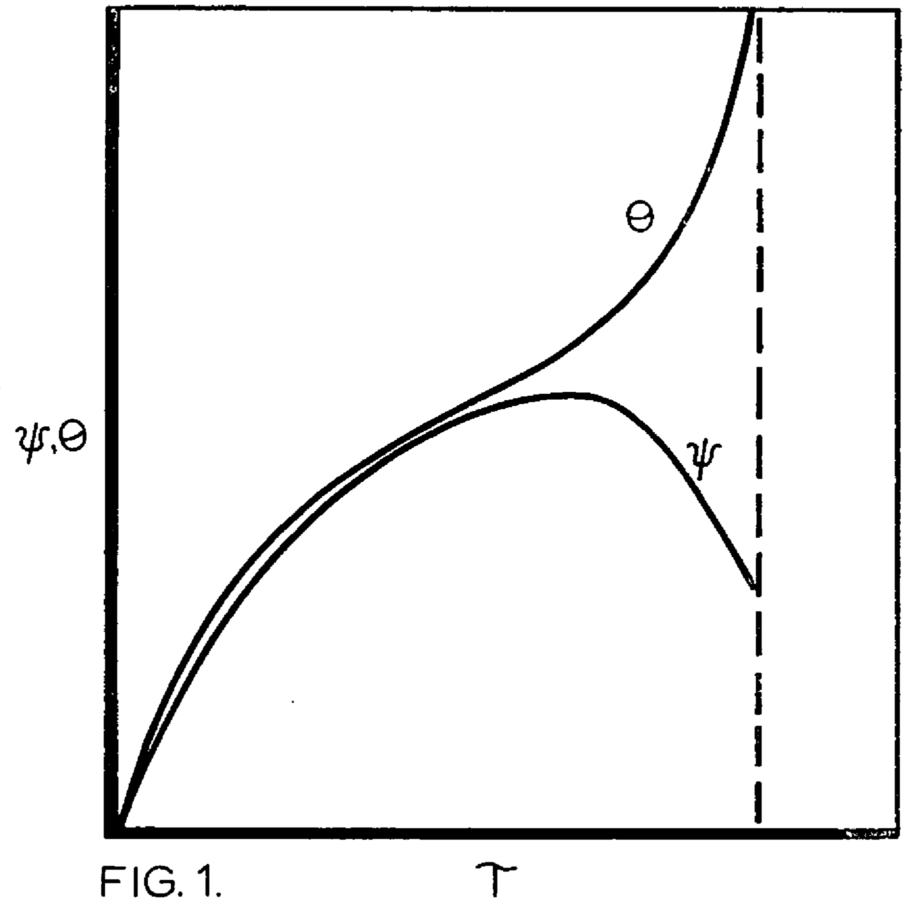

FIG. 1.

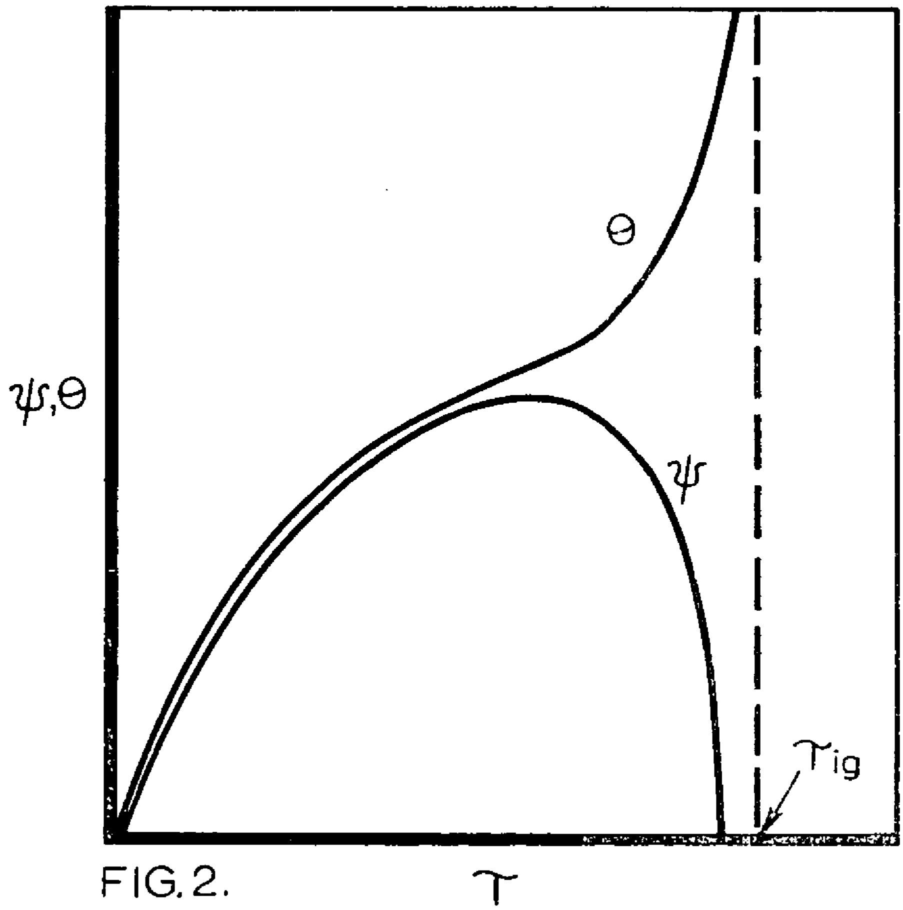

FIG. 2.

Θ AND ψ BEHAVIOUR

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