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THE EFFECT OF REACTANT CONSUMPTION ON THE INDUCTION PERIOD
AND CRITICAL CONDITION FOR A THERMAL EXPLOSION

by

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Summary

An approximate theoretical analysis is given of a thermal explosion or ignition. The treatment leads to analytic expressions for the effect of reactant consumption on the critical explosion parameter and the induction period for a theoretical model where spacial variation of temperature is neglected, i. e. where it is treated in terms of an effective transfer coefficient. The results are found to agree satisfactorily in a certain range with the more detailed analyses leading to graphical solutions by Rice, Allen and Campbell and Todes and Melentiev. The effect of reactant consumption on the critical value of the explosion parameter is shown to be about twice that calculated by Frank-Kamenetskii. In particular it is shown that for a heat of reaction of 100 cal/gm and an activation energy of about 25,000 cal/mole - values typical for the self heating and ignition of fibre insulating boards - there is a significant effect of reactant consumption on the induction period if the explosion or ignition parameter is less than about twice the critical value calculated assuming no reactant loss.

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Notation

We have the following notation

θ = dimensionless temperature equal to $\frac{E}{RT_0^2}(T - T_0)$

x = distance co-ordinate

r = half width of slab, radius of cylinder or sphere

t = time

a = thermal diffusivity of the solid = $K/\rho c$

τ = dimensionless time equal to $\frac{a t}{r^2}$

ρ = density of solid

c = the specific heat

K = the thermal conductivity of the reacting material.

f = the frequency factor

δ = the dimensionless rate of heat evolution

$$\frac{Q \cdot \rho \cdot W_0^{n-1} \cdot f \cdot E \cdot \tau^2 \cdot e^{-E/RT_0}}{K \cdot R \cdot T_0^2}$$

n = order of reaction

B = the dimensionless adiabatic temperature rise = $\frac{E}{RT_0^2} \frac{Q}{c}$

E = activation energy

R = universal gas constant

Q = heat of reaction per unit mass of substance

$m^{(0)}$ = mass consumption of reactant per unit volume per sec.

k = 0, 1 or 2 for the slab, cylinder and sphere respectively.

The suffix c denotes critical conditions

A = effective transfer coefficient

W = concentration of reactant by volume

W_0 = initial concentration

T = absolute temperature

T_0 = initial temperature and the ambient temperature

X = modified dimensionless time

Y = modified dimensionless temperature

p = a mean value of $1 + 0.72 \theta + \theta^2$

$N = 1.39 \left(\frac{B}{np}\right)^{2/3} \Delta$

A_i and B_i = Airy functions

τ_r = dimensionless time as defined by Todes and Melentiev

μ = a parameter defined by Todes and Melentiev

ψ a constant mean value of $\frac{d\theta}{d\tau}$

$$\gamma = - \frac{A_i(-N)}{B_i(-N)}$$

$$\lambda = \frac{w}{w_0}$$

$$\Delta = 1 - \delta_c/\delta$$

1. Introduction

Rice Allen and Campbell (1) and Todes and Melentiev (2)(3) have given theoretical analyses of thermal explosions in which the loss of reactant during the induction of the explosion was taken into account. Solutions such as these and those by electronic computers give results in an exact numerical form but it is also desirable to obtain where possible a more general and simpler solution with fewer independent parameters, even at the expense of some exactness. Frank Kamenetskii (4), with this object in mind, made an analysis which led to a simple formula showing the effect of the heat and order of reaction on the critical parameter of explosion. In this paper it is shown that Frank Kamenetskii's results underestimate the effect by a factor of about 2.

In gaseous explosions reactant loss is very small because the heats of reaction are high, but in the application of thermal explosion theory to the self heating and ignition of wood and similar materials with low heats of reaction, the effect of reactant loss is not negligible and must be considered in any theoretical analysis or interpretation of experimental data. Such an application of theoretical results to experimental data will be considered elsewhere.

In this paper the equations of thermal explosion for the near critical conditions are reduced by means of certain approximations to a non-linear differential equation, the solution of which can be obtained in terms of tabulated Airy functions. In particular, an equation similar to that obtained by Frank Kamenetskii, but with a different numerical constant, is obtained relating the critical explosion parameter to the heat of reaction, and an equation giving an upper limit to the induction period is obtained from a single relation between two groups of parameters. A method is given for evaluating the induction period generally. The results obtained by this analysis compare satisfactorily with the detailed calculations of Rice Allen and Campbell.

In this paper we shall use the word explosion to include the self ignition of self heating materials.

2. Theory

2.1. The basic equations

We write the reaction equation as

$$m''' = -\rho \frac{dw}{dt} = \rho f e^{-E/RT} w^n \quad (1)$$

where $w = w_0$ at $t = 0$

We employ the quadratic approximation to the Arrhenius law as given by Gray and Harper (5)

$$\text{i.e. } e^{-E/RT} \doteq e^{-E/RT_0} (1 + 0.72\theta + \theta^2) \quad (2)$$

so that from the definitions of λ , δ & B

equation (1) becomes

$$\frac{d\lambda}{d\tau} = -\frac{\delta}{B} \lambda^n (1 + 0.72\theta + \theta^2) \quad (3)$$

The equation of heat conservation for a symmetrically heated material is

$$K \left(\frac{\partial^2 \theta}{\partial x^2} + \frac{k}{x} \frac{d\theta}{dx} \right) = \rho c \frac{d\theta}{d\tau} - \frac{Q}{w_0} m''' \quad (4)$$

where $T = T_0$ at $t = 0$.

We approximate the left hand side of this equation by $-K.A.(T-T_0)/r^2$ where A may be regarded as an effective transfer coefficient. It can be shown (6) that this is satisfactory for the steady state and that A can be evaluated in terms of k and the real surface transfer coefficient. Because the spatial temperature distribution will not be greatly different in form in the transient state, i.e. it can be approximated by a sine distribution, the same approximation is assumed applicable in the transient state. The thermal equation then reduces to

$$\frac{d\theta}{d\tau} = \delta \lambda^n (1 + 0.72\theta + \theta^2) - A.\theta \quad (5)$$

Apart from the inclusion of λ and the use of the quadratic instead of the exponential approximation, this is similar to the form originally discussed by Semenov (7). Rice, Allen and Campbell made no approximation

to the Arrhenius law.

In the reaction equation (3) we shall conventionally neglect the effect of temperature variation on the rate constant and we assume a mean value p for $1 + 0.72\theta + \theta^2$. Approximate upper and lower limits can be ascribed to p . We then obtain

$$\lambda^n = \left(1 + (n-1)p \cdot \delta \cdot \tau / B\right)^{-\frac{n}{n-1}} \quad (6)$$

or $\lambda = e^{\frac{-p \cdot \delta \cdot \tau}{B}}$ for $n = 1$

To obtain an asymptotic solution for large values of B , we may further approximate and write

$$\lambda^n = 1 - \frac{n p \cdot \delta \cdot \tau}{B} \quad (7)$$

on the assumption that $1 - \lambda^n \ll 1$

Equation (7) can be inserted into equation (5) which we now proceed to solve for the asymptotic case of large but finite B/n .

2.2. Solution of equation

We introduce certain parameters and variables defined by the following equations:

$$(a) \quad \theta = 1 + \sqrt{2.72A} \frac{Y}{N^{1/2}} \quad (8)$$

Y is a modified temperature variable.

$$(b) \quad \frac{n p \cdot \delta \cdot \tau}{B} = \Delta \left(1 + \frac{X}{N}\right) \quad (9)$$

X is a modified time variable.

$$(c) \quad \frac{2.72 \delta}{A} = (1 - \Delta)^{-1} \quad (10)$$

For no loss of reactant, i.e. for n equal to zero, the critical value of δ is

$$\delta_c = \frac{A}{2.72} \quad (11)$$

which is the critical value given by Semenov's theory (7).

In equation (10) Δ is a measure of the excess of δ over the critical value for no reactant loss.

(d) Lastly we introduce a parameter

$$N = \frac{2.72^{1/3} B^{2/3} \Delta}{(np)^{2/3}} \quad (12)$$

Introducing these into equations (5) and (7) gives

$$\frac{dY}{dX} = Y^2 - X - Y^2 \Delta (1 + X/N) - YX \sqrt{2.72 \Delta / N} \quad (13)$$

$$\text{i.e. } \frac{dY}{dX} = Y^2 - X - Y^2 (X + N) \frac{(np)^{2/3}}{2.72^{1/3} B^{2/3}} - XY \left(\frac{2.72 np}{B} \right)^{1/3} \quad (14)$$

which is independent of Δ

The initial condition is

$$Y = - \sqrt{\frac{N}{2.72 \Delta}} = - \left(\frac{B}{2.72 np} \right)^{1/3}$$

when $X = -N$.

Because the quadratic approximation underestimates the actual temperature function in the Arrhenius term when $\theta > 2$ we shall, like Rice, Allen and Campbell, consider θ equal to 2 as the end of the induction. Thus, if X_i is the value of X at the end of the induction, i.e. onset of explosion or ignition

$$Y = + \sqrt{\frac{N}{2.72 \Delta}} = \left(\frac{B}{2.72 np} \right)^{1/3}$$

when $X = X_i$

the suffix, i , denoting the end of the induction.

We shall first find the asymptotic solution for large values of B , that is, we neglect the last two terms in equation (13) and (14) and solve

$$\frac{dY}{dX} = Y^2 - X \quad (15i)$$

with $Y = -\infty$ when $X = -N$

and $Y = +\infty$ when $X = X_i$

We substitute $Y = -\frac{1}{u} \frac{du}{dX}$ to obtain

$$\frac{d^2 u}{dX^2} = -X u \quad (15ii)$$

which is the standard form of Airy's equation to which the solution is

$$u = c_1 A_i(x) + c_2 B_i(x)$$

where c_1 and c_2 are constants and A_i and B_i are the two independent Airy functions, which have been tabulated (8). The solution for Y is thus

$$Y = - \frac{A_i'(x) + \gamma B_i'(x)}{A_i(x) + \gamma B_i(x)} \quad (16)$$

where the dash denotes differentiation and γ is c_2/c_1 and is obtained from the initial condition.

i.e.
$$\gamma = - \frac{A_i(-N)}{B_i(-N)} \quad (17)$$

The equation for Y is sketched in Fig. (1). The curve $Y^2 = X$ defines the locus of all points where $\frac{dY}{dx}$ is zero and the two branches of

$$X = Y^2 - \frac{1}{2Y}$$

the locus of points of inflexion.

Typical $Y(X)$ curves are shown in Fig. 1. The value of Y for the point P is $2^{1/3} \approx 1.26$ so that the value of θ corresponding to this point is $1 + 1.76 \left(\frac{\mu P}{B}\right)^{1/3}$. Apart from heating conditions near the critical state the value of θ at the inflexion is between 1 and $1 + 1.76 \left(\frac{\mu P}{B}\right)^{1/3}$ i.e. θ is near unity for large values of B .

3. The critical condition

As will be seen from Fig. (1), the critical value of N is that which makes Y infinite at an infinite value of X ;

$$\text{i.e. } A_i(\infty) = \frac{A_i(-N_c)}{B_i(-N_c)} \cdot B_i(\infty)$$

From tables of the Airy functions N_c is found to be 2.338.

We must now obtain a value for P .

We have

$$P = \frac{1}{\tau} \int_0^\theta (1 + 0.72\theta + \theta^2) d\tau$$

and since over a large range of Y , θ is close to unity, we get $p \approx 2.72$ approximately as an upper limit. This corresponds approximately to the assumption by Rice, Allen and Campbell of a mean rate constant determined by the temperature at the inflexion. θ increases less rapidly than in proportion to τ so a minimum estimate can be obtained from

$$= p = \int_0^1 (1 + 0.72\theta + \theta^2) d\theta = 1.69.$$

The choice of a best estimate for p without a more sophisticated mathematical treatment is somewhat arbitrary and the mean value of 2.2 is taken for the purposes of this paper.

From the definition of N we then obtain the equation defining the effect of reactant consumption on the critical parameter

$$d_c(B) = d_c(\infty) \left(1 - 2.85 \left(\frac{\mu}{B}\right)^{2/3}\right)^{-1} \quad (18)$$

which for large values of B becomes

$$d_c(B) = d_c(\infty) \left(1 + 2.85 \left(\frac{\mu}{B}\right)^{2/3}\right)$$

which is similar in form to the result given by Frank Kamenetskii (4) only that 2.85 replaces 1.39. We can evaluate

$$B^{2/3} \left[\frac{d_c(B) - d_c(\infty)}{d_c(B)} \right]$$

from the detailed calculation by

Rice, Allen and Campbell. The value of this quantity over the range of their calculation $22 < B < 880$ varies between 2.45 and 3.00 but in view of the approximations made in both treatments, little significance can be attached to this variation and the two results may be regarded as being in good agreement.

4. The explosive or ignition state

4.1. Limiting values of Δ

We now consider the induction time for explosion or ignition.

The equation

$$A_i(X_i) + \delta B_i(X_i) = 0 \quad (19)$$

defines values of X_i for values of N greater than N_0 and we obtain the relation shown graphically in Fig. (2).

From equations (9) and (12) we have

$$\tau_i = \frac{0.61}{\delta} (X_i + N) \sqrt{N/\Delta} \quad (20i)$$

$$= \frac{1}{\delta} \left(\frac{B}{n}\right)^{1/3} \frac{(X_i + N)}{(2.72 p)^{1/3}} \quad (20ii)$$

which with $p = 2.2$ is

$$\tau_i = \frac{0.55}{\delta} \left(\frac{B}{n}\right)^{1/3} (X_i + N) \quad (20iii)$$

The ordinate $X_i + N$ may thus be directly related to the induction period T_i .

Equation (19) refers to a zero value of Δ ; this gives an upper limit to the value of the induction period. A lower limit is given by the adiabatic case Δ equal to 1 and neglecting reactant loss, (thereby slightly reducing the value of $(X_i + N)$). We have from equation (5) with $A = 0$ and $\lambda = 1$

$$\tau_i \delta = 0.89$$

where the end of the induction has been taken at $\theta = 2$.

In the notation used here this becomes

$$(X_i + N) \sqrt{N} = 1.47 \quad (21)$$

Alternatively putting Δ equal to 1 in equation (13) gives

$$\frac{N dY}{Y^2 + aNY + N} = -X dX$$

where $a = \sqrt{\frac{2.72}{N}}$

Integrating this between the limits $-\frac{1}{a} \leftarrow Y \leftarrow \frac{1}{a}$ and $-N \leftarrow X \leftarrow X_i$ gives after some rearrangement

$$N^2 - X_i^2 = 2.93\sqrt{N} \quad (22)$$

Equation (22) has also been plotted in Fig. (2). For large N this tends to the result given by equation (21).

We now have obtained upper and lower limits for the induction period in terms of a parameter N. We now develop approximate equations for intermediate values of Δ and the results of these are compared below with some results of more detailed calculations by other authors.

4.2. Intermediate values of Δ

For large values of N, equations (17) and (19) tend to

$$X_i + N = \frac{\pi}{\sqrt{N}} \quad (23)$$

which is similar to the result for the adiabatic case except π replaces 1.47. The fact that $(X_i + N)\sqrt{N}$ approaches a constant value, expresses the fact that at large values of B the product $\tau_i \delta$ becomes independent of B. We thus write:

$$X_i + N = \frac{\Omega}{\sqrt{N}} \quad N \rightarrow \infty \quad (24)$$

where Ω depends on Δ and lies between 1.47 and π . Since X varies between $-N$ and $-N + \frac{\Omega}{\sqrt{N}}$ - a range which decreases as N increases - we may as a first approximation treat X as constant in equation (13). This is equivalent to treating λ as constant on the right hand side of equation (5). Thus, in that equation we put X equal to its mean value

$$X = -N + \frac{\Omega}{2\sqrt{N}}$$

and solve the equation to obtain a better approximation. Equation (13), therefore, becomes

$$\frac{dY}{dX} = Y^2 \left(1 - \frac{\Omega \Delta}{2N^{3/2}} \right) + N - \frac{\Omega}{2\sqrt{N}} + Y \sqrt{\frac{2.72\Delta}{N} \left(N - \frac{\Omega}{2\sqrt{N}} \right)} \quad (25)$$

This may be solved by the substitution

$$Y = -\frac{1}{u} \cdot \frac{1}{\left(1 - \frac{\Omega}{2N^{3/2}} \right)} \frac{du}{dX}$$

and we eventually obtain

$$Y = -\frac{aN_0}{2} - \sqrt{M^2 - \frac{a^2N_0^2}{4}} \cot \left\{ \phi + X \sqrt{M^2 - \frac{a^2N_0^2}{4}} \right\} \quad (26)$$

where

$$a = \sqrt{\frac{2.72}{N}}$$

$$N_0 = N - \frac{\Omega}{2\sqrt{N}}$$

$$M = N_0 \left(1 - \frac{\Omega \Delta}{2N^{3/2}} \right)$$

and an integration constant ϕ

Inserting the initial and final conditions eventually gives

$$\tan \left\{ (X_i + N) \sqrt{M - \frac{a^2 N_0^2}{4}} \right\} = - \frac{2a \sqrt{M - \frac{a^2 N_0^2}{4}}}{1 - Ma^2} \quad (27)$$

When $N \rightarrow \infty$, $M \rightarrow N_0 \rightarrow N$ and $\frac{a^2 N_0^2}{4} \rightarrow 0.68 \Delta N$

Hence from equation (27) and equation (24)

$$\tan \left(\Omega \sqrt{1 - 0.68 \Delta} \right) = - \frac{2 \sqrt{2.72 \Delta} (\sqrt{1 - 0.68 \Delta})}{1 - 2.72 \Delta} \quad (28)$$

For small values of Δ we have the approximation

$$\Omega \approx \pi (1 - 1.05 \sqrt{\Delta}) \quad (29)$$

From the definition of Ω in equation (24) and equation (20)

it follows

$$\tau_i \delta = 0.61 \frac{\Omega}{\sqrt{\Delta}} \quad (30)$$

Eliminating Ω between equations (28) and (30) gives the asymptotic solution for large N for any value of Δ . That is, it gives the solution to the case of infinite B/n and is equivalent to that given by Gray and Harper.

Equation (27) is an approximate solution for any value of N or Δ . In the case of zero Δ , it reduces to

$$X_i + N = \frac{\pi}{\sqrt{N - \frac{\pi}{2\sqrt{N}}}} \quad (31)$$

This equation which is essentially derived from equation (5) with λ equal to a constant is shown in Fig. (2). It agrees well with the "exact" solution for $N > 4$. It gives an incorrect critical value because near the critical state the temperature time behaviour is more closely governed by the maximum value of X rather than the mean. Thus, had we adopted

$$X + N = \frac{\pi}{\sqrt{N}}$$

as an approximation in the differential equation we would have obtained

$$X_i + N \doteq \frac{\pi}{\sqrt{N - \frac{\pi}{\sqrt{N}}}}$$

This gives too high a value for $X_i + N$ except of course at infinite N , but the critical value $\pi^{2/3}$ i.e. 2.15 is in good agreement with the value 2.34 already obtained. Equation (27) is also plotted in Fig. (2) for Δ equal to $\frac{1}{2}$. This gives values of $X_i + N$ slightly higher than equation (22) which was derived from equation (13), while for Δ zero equation (27) in the simplified form of equation (31) gives values which are slightly lower than those obtained from (19), also derived from equation (13). It is ~~not~~ reasonable to expect, therefore, that for intermediate values of Δ equation (27) is as good or better an approximation than at the extreme values of Δ .

We may note that the condition for the employment of equation (7) for a first order reaction is that to a 5 per cent approximation

$$\frac{P.O.T.}{B} < \frac{1}{4}$$

i.e. $X + N < 0.2 B^{2/3}$

Provided B is in excess of 30 this condition may be regarded as being satisfied for $N > 3.4$ and for lower values of N when B is larger. We can for convenience in cases where Δ is small, use equation (27) in the form of a correction to the solution for Δ equal zero, by developing a series for $X_i + N$ in ascending powers of $\Delta^{1/2}$.

This gives

$$(X_i + N)_\Delta = (X_i + N)_{\Delta=0} \left\{ 1 - 1.05 \sqrt{\Delta} \left(1 - \frac{\pi(1.05\sqrt{\Delta})}{2N^{1/2}} \right) + 0.34 \Delta \dots \right\} \quad (32)$$

5. Comparison with more detailed calculation

5.1. Calculations of Todes and Melentiev

Todes and Melentiev (2) have published various graphs of temperature against time for four values of B . Two of these are for low values of B which do not give a sharp ignition or explosion.

Of the two others one can be used for obtaining the induction time over a small range of values of δ near to the critical state which is a sensitive test of this calculation method. This is Fig. (7) p1605 of reference (2). The parameter δ does not appear explicitly but the ratio δ/δ_c equals μ_c/μ in their notation. Denoting the time variable used by Todes and Melentiev as τ_r we have

$$\tau_r \cdot \mu = e \cdot \delta \cdot T \quad (33)$$

The graphs are for the condition $n = 1$ and $B = 300$ so that with $p = 2.2$

$$\Delta_c = \frac{2.34}{0.83 \cdot 300^{2/3}} = 0.063$$

Therefore the critical μ given by Todes and Melentiev, 0.693×10^{-10} corresponds to a μ_c for no loss of reactant of $\frac{0.693 \times 10^{-10}}{0.937}$ i.e. 0.740×10^{-10} . From μ and μ_c we calculate Δ as $1 - \mu/\mu_c$ and hence N . From Fig. (2) we find $X_i + N$ for zero Δ , apply the correction given by equation (32) and use equations (33) or (22) to evaluate τ_r .

The calculations are given in Table (1) for the region near the critical condition.

Table 1. Comparison with some calculations by Todes and Melentiev

μ	Δ	N	$(X_i + N)_0$ from Fig.(2)	$(X_i + N)$	$\tau_r \times 10^{-10}$ calculated (Thomas)	$\tau_r \times 10^{-10}$ calculated (T & M)
0.65×10^{-10}	0.121	4.5	1.61	1.03	15.9	16.5
0.68×10^{-10}	0.088	3.05	2.25	1.80	26.5	23
0.69×10^{-10}	0.0725	2.53	2.93	2.46	35.5	33

The induction times given by the two methods of calculation are in good agreement.

5.2. Calculations of Rice, Allen and Campbell

The results of the calculations by Rice, Allen and Campbell are given graphically for a range of conditions and we have accordingly evaluated a number of results by both methods in the range just above the critical. Certain values of the parameters f and θ used by Rice, Allen and Campbell were taken and Δ was then found from

$$f = \delta_c/\delta = 1 - \Delta$$

The parameter I used by Rice, Allen and Campbell is in the notation of this paper, $I = p \cdot \delta \cdot T$, and $\theta = 1/2B$.

We have $1 + \frac{X_1}{N} = \frac{I}{B\Delta}$

so that from the definition of N, with $p = 2.2$

$$(X_1 + N) = \frac{0.83I}{B^3}$$

This equation was used to obtain an estimate of $X_1 + N$ from the values of I given by Rice, Allen and Campbell. The calculations are summarised in Table 2.

Table 2.

Comparison with some calculations by Rice, Allen and Campbell

17608	B	$-\log_{10} f$	Δ	N	$(X_1+N)_0$ from Fig.2.	$(X_1+N)_A$ by equation(32)	$(X_1 + N)$ from Rice, Allen & Campbell
30	29.4	0.175	0.33	2.59	2.83	1.71	1.67
30	29.4	0.20	0.364	2.86	2.44	1.44	1.51
10	88	0.075	0.158	2.58	2.85	2.15	2.05
10	88	0.100	0.204	3.27	2.94	1.47	1.50
10	88	0.175	0.33	5.4	1.41	0.81	1.04
5	176	0.045	0.098	2.57	2.87	2.36	2.25
5	176	0.05	0.108	2.79	2.51	1.96	1.88
5	176	0.10	0.204	5.21	1.44	0.94	1.04
4	220	0.05	0.103	3.07	2.24	1.73	1.71
4	220	0.10	0.188	5.52	1.40	0.92	0.94

Again the agreement is quite satisfactory in view of the approximations made in both treatments.

6. Non explosive conditions

For $N < N_0$ there is no inflexion and θ rises to a maximum value of order unity and then falls. The position of this maximum is obtained for $\Delta = 0$ by differentiating equation (15) and putting $\frac{d\theta}{dx}$ zero. The solution is given in Fig. (2) in terms of the modified time $X_1 + N$ for the special case of zero Δ .

7. The induction period at the critical condition

Rice, Allen and Campbell pointed out that in theory very large induction periods can be obtained near the critical condition when the heat of reaction is large, but in practice it is not possible to achieve these (1). The mathematical analysis given by Rice, Allen and Campbell and that given here are hardly valid for this case, because of the approximation of a rate constant which does not vary with temperature. However, for the sake of generality we shall obtain, by means of different approximation, a theoretical result for this situation which it is interesting to compare with a numerical theoretical result obtained by Todes and Melentiev (2). We note that the critical state is characterised by an almost linear rise in temperature over a relatively long time. We shall revert to the exponential approximation to the Arrhenius law for mathematical convenience and write equation (5) in the form

$$\lambda'' = \left\{ \frac{d\theta}{dt} + A\theta \right\} \frac{e^{-\theta}}{\delta} \quad (34)$$

This is differentiated treating $\frac{d\theta}{dt}$ as a constant ψ . The elimination of λ and $\frac{d\lambda}{dt}$ by means of equation (3) then gives, for a first order reaction

$$A\psi + (\psi + A\theta)\psi = -\frac{\delta}{B} e^{\theta} (\psi + A\theta) \quad (35)$$

At the critical condition δ is approximately A/e and we solve equation (35) which is quadratic in ψ to give

$$\frac{2\psi}{A} = -\left(\theta - 1 - \frac{e^{\theta-1}}{B}\right) + \sqrt{\left(\theta - 1 - \frac{e^{\theta-1}}{B}\right)^2 + \frac{4\theta e^{\theta-1}}{B}} \quad (36)$$

In the case of large values of B , a minimum value of $\frac{\psi}{A}$ occurs at a value of θ_m , where $\theta_m - 1 \gg \frac{(e^{\theta_m-1})}{B}$

so that equation (36) can be simplified to

$$\frac{\psi}{A} \doteq \frac{\theta e^{\theta-1}}{B} \quad (37)$$

and ψ is a minimum when

$$\theta_m^2 - 1 - \theta_m = 0 \quad (38)$$

$$\text{i.e. } \theta_m = 1.62 \quad (39)$$

Hence from equation (37)

$$\frac{\psi_{min}}{A} = \frac{4.87}{B} \quad (40)$$

Approximately, the induction period is given by

$$\tau_i = \frac{\theta_m}{\psi_{min}}$$

which from equations (25) and (27) gives

$$\tau_i = \frac{0.12B}{\delta} \quad (41)$$

Todes and Melentiev give some graphical results in Fig. (f) p.1606 of reference (2) in terms of variables τ_T , the suffix denoting Todes' time variable and a cooling parameter μ . In terms of these, equation (41) becomes

$$\tau_T = \frac{e \cdot \delta \cdot \tau}{\mu} = \frac{0.33B}{\mu} \quad (42)$$

The graph in this figure is for B equal to 216 and it gives the critical value of μ as 6.84×10^{-9} so that we calculate from equation (42) the critical induction period as

$$\tau_T = \frac{0.33 \times 216 \times 10^9}{6.84} = 1.1 \times 10^{10}$$

which agrees very closely (less than 5 per cent) with the result obtained by Todes and Melentiev.

The solutions to equation (36) have been calculated for a range of values of B, $5 < B < \infty$ and these show that $\frac{\tau \cdot \delta}{B}$ is within $\pm 5\%$ of the result derived for large B.

However, the calculations of Todes and Melentiev for B equal to 9 show that at this low value of B, there is no marked distinction between ignition and non-ignition and the identification of an induction period is somewhat arbitrary and the result obtained from equations (41) and (42) only gives the order of magnitude of the time to reach a temperature corresponding to θ unity.

8. Discussion and conclusions

The analysis in this paper of the thermal explosion equations gives general results in terms of tabulated functions. Comparison with more detailed analyses which make fewer approximations but which do not lead to general solutions shows this treatment to be satisfactory for large but finite values of B. In particular, the general formula for the effect of reactant loss on the critical explosion parameter is satisfactory for values of the dimensionless adiabatic temperature rise of the reaction, at least as low as about 20. Induction periods have been obtained in terms of the roots of an equation of tabulated functions and a simple correction which gives results agreeing with more detailed numerical calculations.

In particular, this analysis has shown the importance of a parameter N which has, as was shown by Frank Kamenetskii, a critical value for explosion where there is reactant consumption. Apart from this one can also say from equations (24), (27) and (31), that for induction times to be affected more than 5 per cent by reactant loss the value of N should be such that

$$\frac{\mathcal{R}}{2 N^{3/2}} < \frac{1}{10}$$

$$N > (5\sqrt{\pi})^{2/3}$$

The largest value of \mathcal{R} is π and as \mathcal{R} only varies by a factor of about 2 in the entire range of Δ and $\mathcal{R}^{1/2}$ by about 25 per cent, we take the condition as approximately

$$N > 4.3$$

The range of values of N where reactant consumption affects the behaviour is thus relatively small, $2.4 < N < 4.3$, and this demonstrates the usefulness of this parameter in describing the explosion behaviour.

For a material such as fibreboard, the heat of reaction is of order 100 cal/gm and E about 25,000 cal/gm/mole. B is about 25, so that N is about 7Δ and the role of reactant loss must be considered for heating conditions, where δ is less than $2.5\delta_c$.

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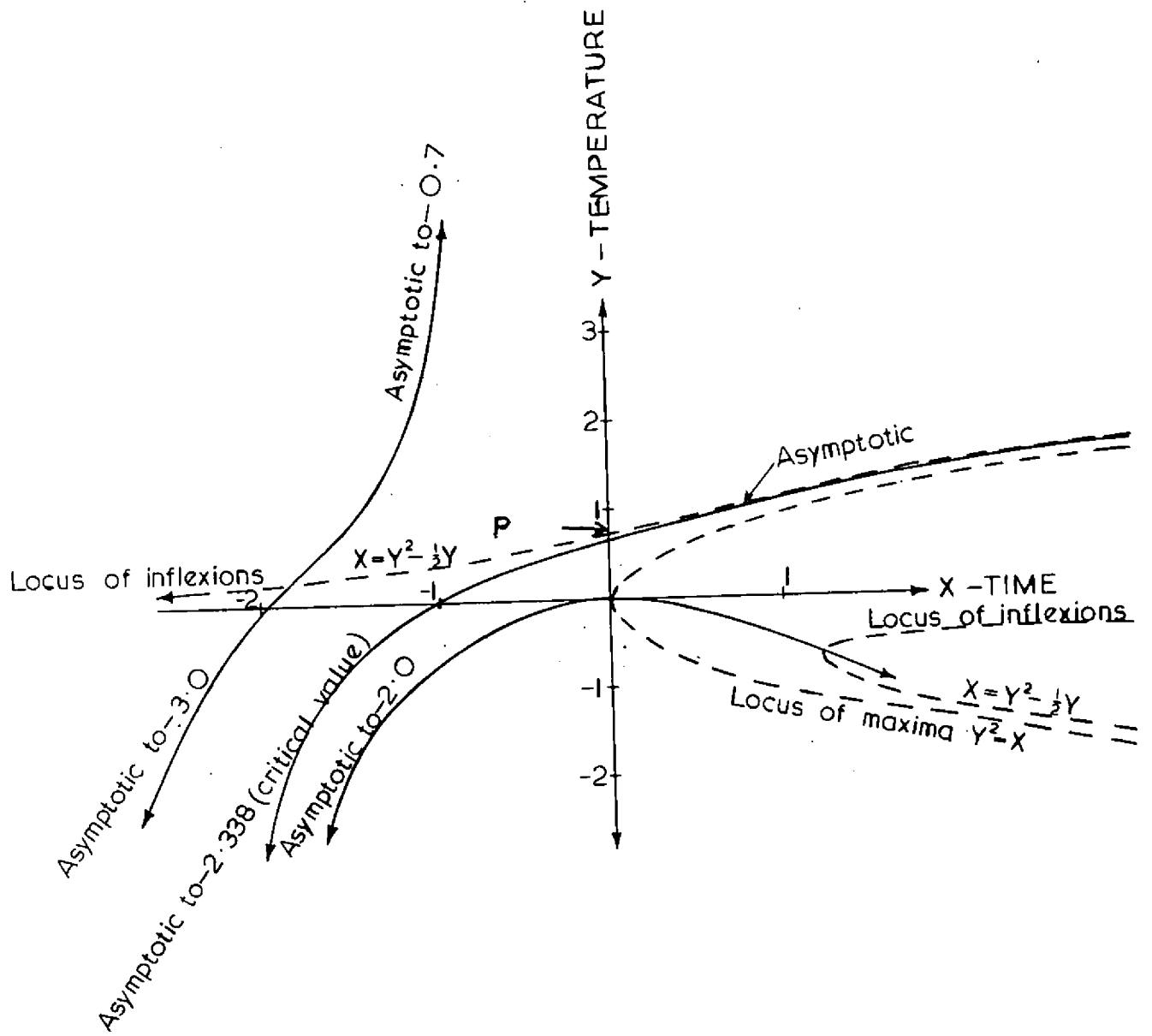
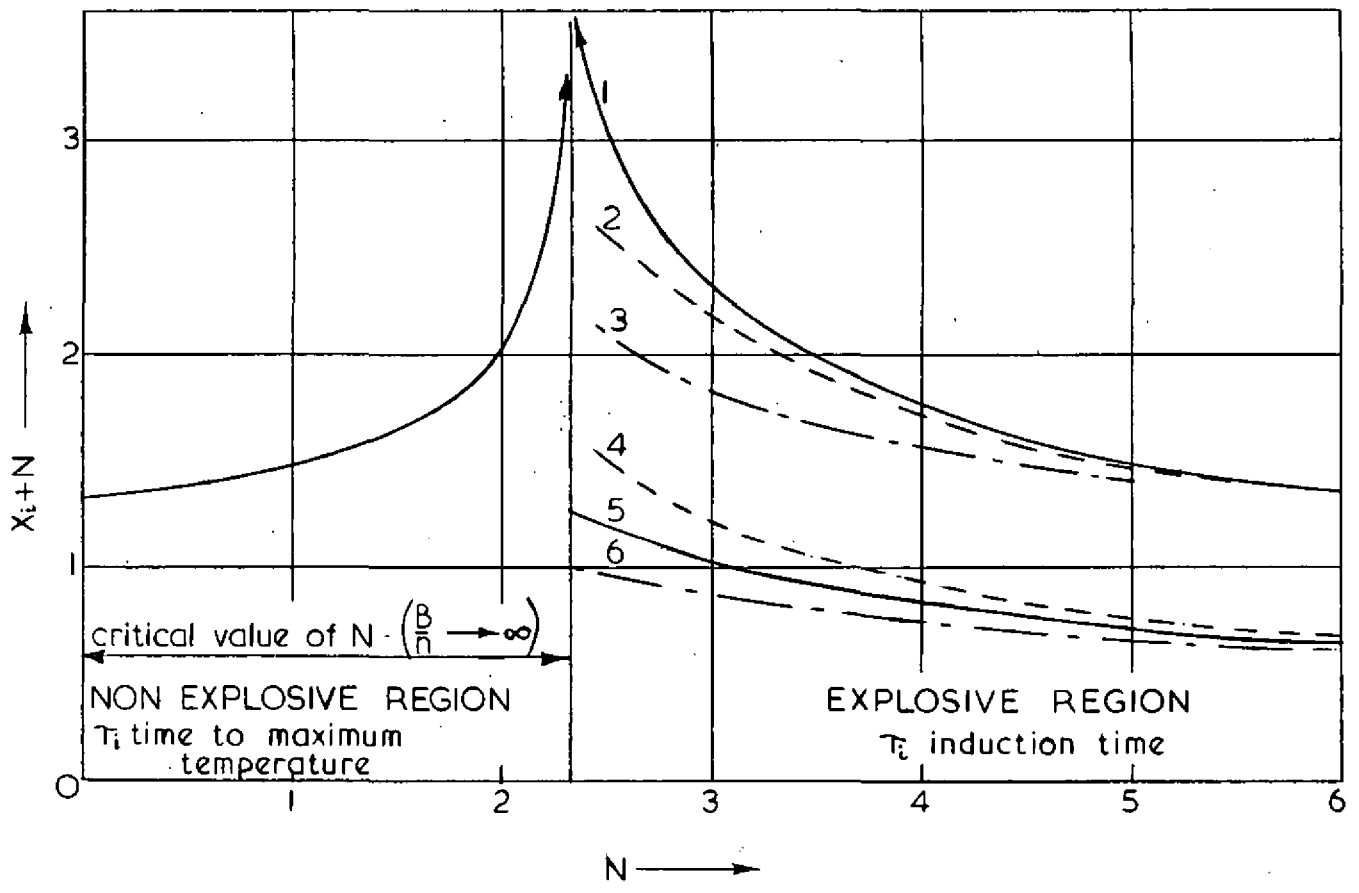


FIG. 1. TYPICAL TEMPERATURE-TIME CURVES FOR NO EXPLOSION AND EXPLOSION ON EACH SIDE OF CRITICAL CONDITION



1	————	from equation 13 with $\Delta = 0$	$A_i(X_i) = \frac{A_i(-N)}{B_i(-N)} B_i(X_i)$
2	-----	equation 27 with $\Delta = 0$	$X_i + N = \frac{\pi}{\sqrt{N - \frac{\pi}{2N}}}$
3	-. - . - .	reactant loss neglected	$X_i + N = \frac{\pi}{\sqrt{N}}$
4	-----	equation 27 with $\Delta = 1$ (adiabatic)	
5	————	from equation 13 with $\Delta = 1$ "	$N^2 - X_i^2 = 2 \cdot 93\sqrt{N}$
6	-. - . - .	reactant loss neglected "	$X_i + N = \frac{1.47}{\sqrt{N}}$

FIG. 2. INDUCTION TIMES AND TIME TO MAXIMUM TEMPERATURE WHERE THERE IS NO IGNITION