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APPLICATION OF THE THEORY OF THERMAL EXPLOSION TO THE SELF-HEATING AND IGNITION OF ORGANIC MATERIALS

by

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SUMMARY

The theory of thermal explosion, first expressed in quantitative forms by Semenov and Frank-Kamenetskii has been extensively developed in recent years and provides a model for self-heating and explosion in certain gas reactions, explosives, propellants and unstable chemical substances.

The present paper outlines the application of the simple 'stationary state' form of the model to the self-heating and ignition, by oxidation, of organic materials. Application in this area is often near the borderline of validity of the theoretical model but nevertheless is of great practical value in treating problems of self-heating and ignition of organic materials in storage and transport.

The applications considered include the ignition of cellulosic materials, activated carbon, and mixtures of vegetable oils and sawdust intended to simulate commodities such as oilseed meals, oiled textiles and fishmeal.

The paper is principally concerned with experimental results and their interpretation with the aid of the model. Theoretical results needed will be stated without derivation but can be amplified in discussion as necessary.

KEY WORDS: Thermal explosion, self-heating

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INTRODUCTION

The theory of thermal explosion, first expressed in quantitative form by Semenov[1] and Frank-Kamenetskii[2] (with different assumptions governing the temperature distribution) has been developed extensively in recent years and provides a model for self-heating and explosion in certain gas reactions, explosives, propellants and unstable chemical substances.

Following a brief account of the, now, well-known basic ideas and the principal results of Frank-Kamenetskii's 'steady state' model, this paper indicates the usefulness of this simple model when applied to the self-heating and ignition of organic materials. These materials are typified by wood products, activated carbon, and mixtures of wood sawdust and vegetable oil intended to simulate commodities such as oilseed meals, oiled textiles and fishmeal.

In the relatively dry state, self-heating in these materials is due to atmospheric oxidation and it is with this aspect that the paper is principally concerned. Finally, however, some consideration is given to the way in which microbiological heating (which, as is well-known, plays an important part in the initial self-heating of moist material), might be fitted into the framework of the thermal ignition model. This is necessarily tentative but it is offered in the hope that it will, at the least, contribute towards linking the two topics of this symposium, microbiological heating and chemical heating.

SIMPLE MODEL

The basic idea of thermal explosion is illustrated in the well-known diagram of Fig.1. A body of material (e.g. a sphere, shaded in Fig.1) at a temperature T generates heat at a rate which increases in a non-linear manner with temperature, as curve A. Heat is lost to the surroundings, which are at temperature T_A, at a rate proportional to $T - T_A$; represented by parallel lines B (for constant heat transfer coefficient). At a relatively low initial temperature, T_A' say, the temperature in the body can increase until the total rate of heat generation is equalled by the total rate of heat loss, corresponding to the lower intersection of A and B, and a steady state is reached. The upper intersection of A and B represents an unstable steady state and is normally inaccessible. At a higher initial temperature, T_A''' say, the rate of heat generation always exceeds the rate of heat loss and the temperature of the body may rise to high values associated with active explosion or combustion.

The 'critical' condition for explosion is associated with tangency of the heat generation and heat loss curves, here for an initial temperature T_A''. Inasmuch as the rate of heat generation per unit volume and the rate of heat loss per unit area of surface depend on temperature only (not on dimensions), equating the total rate of heat generation and the total rate of heat loss, and also the gradients of A and B, at the point of tangency will provide two equations defining a unique critical temperature increase at criticality and a unique critical ambient temperature for a given surface to volume ratio, i.e. for a body of given shape and size.

By considering all possible intersections of lines B with curve A, it is possible to construct Fig.2 showing the steady state temperature increase, ΔT, as a function of the ~~initial~~ ambient temperature T_A. The lower branch of this curve up to the critical value of T_A represents the stable states and the upper branch the unstable states. This curve will be needed later below.

Frank-Kamenetskii's original mathematical analysis[3] of thermal explosion in a solid exposed to a uniform ambient temperature was based on the steady-state heat conduction equation for a solid in which heat is generated at a rate which depends on temperature in accordance with the Arrhenius equation but which is independant of time. This yielded the condition for thermal explosion as

$$\delta > \delta_c$$

where δ_c is the maximum value, for which steady states can exist, of a dimensionless parameter δ defined as

$$\delta = \frac{E}{R{T_A}^2} \cdot \frac{\rho r^2}{K} \cdot QAe^{-\frac{E}{RT_A}} \qquad (1)$$

where A = pre-exponential factor of Arrhenius equation
E = activation energy in Arrhenius equation
K = thermal conductivity of the solid
Q = heat of reaction per unit mass
R = universal gas constant
r = characteristic length (radius of sphere or infinite cylinder, semi-thickness of infinite slab)
T_A = ambient temperature, K
ρ = density of solid.

For a boundary condition which assumes that the surface temperature of the solid remains equal to that of the surroundings, the critical value of δ is a constant depending only on the geometrical shape of the body, subject to the essential, but easily satisfied condition that $E/RT_A \gg 1$. More generally[4], δ is a function of $\alpha = hr/K$ where h is a coefficient for heat transfer by radiation and convection between the surface of the body and the surroundings.

In Frank-Kamenetskii's formulation, the temperature rise in the body is defined, in dimensionless form, as

$$\theta = \frac{E}{RT_A^2}(T - T_A) , \tag{2}$$

the central value, θ_o where $T = T_o$, being the maximum in problems of interest in this paper.

When, as in all real systems, the rate of the reaction generating heat decreases with time, there are no steady states but θ_o shows maxima with respect to time which increase as δ is increased. The rapidity, and the maximum value, of this increase is determined by the value of the adiabatic temperature increase defined, in dimensionless form, as

$$B = \frac{E}{RT_A^2} \cdot \frac{Q}{c} \tag{3}$$

(where c = specific heat). As B becomes large, the maximum value of θ_o may increase from small to large values as δ increases over a small range, i.e. the system will tend to show 'critical' explosion behaviour. Recent numerical analysis by Tyler and Wesley[5] suggests that, for practical purposes, critical explosion behaviour will begin to appear when B exceeds 14, certainly as B approaches 25

Provided B is large enough for the system to exhibit critical behaviour, Frank-Kamenetskii's 'steady state' model may be used with, where necessary (see further below), a corrected value for δ. For a reaction of order n, the correction is given by[6,7]

$$\delta_c\,(B) = \delta_c\,(\infty)\left[1 - 2.52\,(n/B)^{\frac{2}{3}}\right]^{-1} \qquad (4)$$

APPLICATION TO SIMPLE SYSTEMS

With appropriate values for δ_c, equation (1) can be rearranged[8,9] to give a linear relationship for experimental determinations of the critical ambient temperatures for ignition (T_A) of bodies of material of different shapes (δ_c) and sizes (r), thus:-

$$\ln\left(\delta_c\,T_A^2/r^2\right) = -\frac{E}{RT_A} + \text{constant} \qquad (5)$$

Figure 3 shows the results obtained by Mitchell[10] for ignition of blocks of wood fibre-insulating board (mainly cubes) plotted in accordance with this relationship[8]. δ_c has been taken as 2.52 for cubes and corrected for estimated values of α. A few results for slabs are also included, for which $\delta_c = 0.88$.

With the exception of the highest point (for a cube of 3.2 mm side), all the experimental points, which cover a size range of 6.4 mm to 560 mm and a temperature range of 250°C to 109°C (the ignition temperature for the largest size) obey the linear relationship well. The slope of the line is $-E/R$ and yields a value for the apparent activation energy of 104 kJ/mole (25,000 cal/mole).

Provided, of course, that the apparent activation energy remains constant, the above relationship provides a means of extrapolation to larger sizes and lower temperatures. The determination of the minimum ambient temperature, to the nearest 2-3°C, for ignition of, say, cubes in small sizes is experimentally simple and, in the author's experience, this approach has proved to be of considerable practical value.

A recent example, to be published in detail elsewhere[11], concerns self-heating and ignition in chemically activated carbon. A few years ago, a series of fires occurred in this material during carriage on board ship through tropical atlantic waters in quantities of 4-14 tons. The fires appeared to have been due to self-ignition and it was necessary to re-examine the procedure for the safe carriage of this material.

Predictions based on experimental determinations of critical ambient temperatures for cubes of the fully weathered carbon, in sizes ranging from 25.4-610 mm, indicated that for the quantities carried, stacked in piles varying in shape between cubes and rectangular parallelepipeds with sides in the ratio 1 : 2 : 3, critical ambient temperatures for ignition would be within the range 31-42°C. An estimate based on a survey[12] of temperatures in ships' holds, suggested that mean ambient temperatures to which the carbon (which was stowed above the waterline), could have been exposed in transit were likely to have been within the range 29-38°C for major parts of the voyages. This range is consistent with the predicted range for ignition. Times to ignition were considerably less than predicted[11].

It was shown that the hazard could not be appreciably reduced by, for example, increasing the weathering period at ordinary temperatures; the counter-measure finally adopted was to pack the carbon in polythene bags to prevent oxygen access.

Values of the parameter B for the low temperature oxidation responsible for self-heating in examples of the above kind tend to be somewhat low. Thus, a value of 13 has been estimated for wood-fibre insulating board[8], although comparison with the calculations of Tyler and Wesley[5] suggest that this figure is an underestimate. At this level, the corrected value of δ_c for $n = 1$ (equation 4) may be up to twice the value when $B = \infty$ (equivalent to effectively zero order reaction) and, over a temperature range of 170°C, may vary by about 40 per cent. This does not, however, materially affect predictions of the above kind based on the simple model which neglects reactant consumption[8].

It may also be shown that for self-heating by oxidation of materials with porosities and thermal conductivities similar to those of wood sawdust or fibre-insulating board[13], the critical condition for ignition is not greatly affected by the finite rate of diffusion of oxygen into the material, although the temperature increase following ignition eventually does become limited by diffusion[13,14].

An alternative approach to practical applications is to measure rates of heat evolution at different temperatures and use the results to calculate critical conditions for ignition directly from equation (1). This procedure has been followed in effect by Walker and his associates (e.g. Refs 15-18) for organic materials (wool and brewer's grains) and by van Geel[19] and Gross and [20] of the model and, in addition to requiring a knowledge of the chemical and physical constants (individually or as a group[15]) it is desirable to use a fully corrected value for δ_c. This approach can also be unduly sensitive to complexities in the self-heating reactions, some of which will now be outlined.

APPLICATION TO COMPLEX SYSTEMS

In the context of this paper, wood sawdust and activated carbon have been described as simple systems in the sense that their ignition behaviour was consistent with the simple steady-state thermal explosion model, and sub-critical temperature maxima (not reported in detail above) were reasonably normal. Wood-fibre insulating board, however, showed high sub-critical temperature maxima (up to about 10 times the expected values) which could be interpreted as being due to a short-lived exothermic reaction which, it could be argued[8,21], did not seriously affect the application of the simple model for purposes of extrapolating critical ignition data; this material could therefore also be regarded as simple.

However, as indicated in the introduction, there is an important class of materials of vegetable or animal origin in which self-heating to ignition depends strongly on the presence of a limited quantity of readily oxidisable oil on a combustible base material.

The self-heating and ignition behaviour of such materials is illustrated in Fig.4 which compares temperature/time curves for 51-mm cubes of wood sawdust alone and wood sawdust containing a proportion of olive oil. The sub-critical temperature increase observed for the sawdust alone at an ambient temperature of 185°C is in reasonable agreement with the expected sub-critical maximum of about 27°C (i.e. for a single zero order reaction). The maximum sub-critical temperature increase for the oiled sawdust, which ignites at an ambient temperature 45°C lower, is about 4 times the value expected for a simple system. However, the value of B corresponding to the amount of oil present may be estimated[22] to be in the range 7-9, and ignition followed an increase of ambient temperature of 5°C corresponding to an increase in δ of about 30% for a simple system. Comparison, by inspection, with Tyler & Wesley's calculations (their Fig.1) shows that this observed 'sharpness' of the ignition, and the sub-critical temperature increase, are incompatible with the level of B and, hence, with ignition due to the oil alone; ignition must therefore be a cooperative effect involving heat generation by the sawdust as well.

Experience indicated moreover that the use of the simple model for extrapolating small-scale ignition data for materials of this kind could seriously overestimate the risk of ignition at ordinary ambient temperatures. It therefore seemed desirable to devise a more elaborate model for systems of this type, the simplest possible consisting of two components generating heat independantly with one component, the minor one, exhaustible and the other, the major component, effectively inexhaustible.

The physical picture which emerged from the approximate analysis of this more complex model[21] may be illustrated in terms of Fig.2 which may be regarded as representing all possible steady states for self-heating of the major component alone. At a given temperature below the critical value indicated for ignition, the temperature increase due to self-heating will lie on the lower branch of this curve. Heat generation by a second, exhaustible, component could temporarily increase the temperature above this level but, if the maximum fell short of the upper branch of the curve, the system would finally settle to the value on the lower branch as the second component became exhausted. If, on the other hand, the second component could increase the temperature above the upper branch, the system would ignite. The approximate analysis suggested in fact that criticality would correspond to the upper branch being reached just as the minor component became exhausted and, in terms of the value of δ_1 for ignition of the major component alone, denoted by ${}_1\delta_c$, yielded the following relationship between the value of $\delta_1/{}_1\delta_c$ critical for ignition of the two-component system and the critical temperature increase (upper branch):-

$$(\delta_1/{}_1\delta_c)_c = \theta\, e^{(1-\theta)} \qquad (6)$$

Figure 5 shows a comparison between this relationship (continuous curve) and experimental observations of the critical temperature increase and values of $(\delta_1/{}_1\delta_c)_c$ for cubes of wood sawdust of different sizes treated with olive oil in amounts varying between 0 and 35 per cent. The critical temperature increases were taken as the mean values between the maximum sub-critical values and the corresponding upward inflexions in the super-critical self-heating curves (see Fig.4) and were inserted into equation (2) to calculate θ (the appropriate value for E, E_1, being that for the major coponent[21], i.e. the sawdust). Values of $(\delta_1/{}_1\delta_c)_c$ were calculated as follows:

$$(\delta_1/{}_1\delta_c)_c = \left(\frac{T_A'}{T_A}\right)^2 e^{-\frac{E_1}{R}\left(\frac{1}{T_A} - \frac{1}{T_A'}\right)} \qquad (7)$$

where T_A is the critical ambient temperature for ignition of a given sized cube of a mixture and T'_A the value for the sawdust alone corrected, by a small amount, for the presence of the oil as an inert diluent[21]. The points at $(\delta_1/{}_1\delta_c)_c = 1$ are those for sawdust alone.

The essential result in Fig.5 is that, although the experimental points lie consistently somewhat above the theoretical curve, they closely follow the expected trend and demonstrate that the approximate theoretical model has some physical reality.

A more detailed account is to be published elsewhere[22] together with a test of the two-component model for predicting ignition in absolute terms. Meanwhile the above simple physical picture indicates a possible quantitative approach to the role of microbiological heating in the self-ignition of moist organic materials, as follows.

MICROBIOLOGICAL HEATING

Rothbaum's investigation[23] of the self-heating of moist hay in an adiabatic calorimeter has shown that the occurrence of self-heating to ignition is most likely to occur with moisture contents restricted to the range in equilibrium with relative humidities of 95-97 per cent, i.e. about 63-92 per cent moisture. At lower humidites, the moisture content becomes too low for vigorous bacterial activity and, at higher values, heat losses associated with moisture vapour transport become too high. Further heating beyond the upper temperature limit for microbiological activity, about 70°C (sic), was found to be dependant on a 'wet' oxidation process which was eventually followed by oxidation of the dry hay as moisture dried out. The rate of heat production during the 'wet' oxidation, at temperatures too high for microbiological activity, was about two orders of magnitude greater than for dry hay and was not dependant on previous microbiological activity.

This last result suggests that the principal role of the microbiological activity may be to provide an impetus to self-ignition simply by raising the temperature to a supercritical value in a stack which is otherwise sub-critical with respect to chemical oxidation alone- thus behaving as the minor component in the two-component model outlined above.

This picture may be pursued quantitatively in terms of estimates of critical size for ignition in a haystack, based on Rothbaum's data, at an ambient temperature of, say, 15°C.

Hay in equilibrium with an initial relative humidity of 96.5 per cent at 30°C (moisture content 71 per cent), was found[23] to have a rate of heat generation of 3.3×10^{-4} cal $s^{-1}g^{-1}$ at a temperature of 85°C. Adopting Rothbaum's suggested value of 20,000 cal/mole for the activation energy, the rate of heat generation at 15°C may be calculated as 3.7×10^{-7} cal $s^{-1}g^{-1}$.

The thermal conductivity was estimated as 6×10^{-4} cal cm^{-1} s^{-1} $^{o}C^{-1}$. Assuming a density of 0.3 g/cm^3 and taking $\delta_c = 2.6$ for a cube[24], it may be calculated from equation (1) that, in terms of the above wet oxidation alone, the critical size (2 r) for self-ignition of the sterile haystack at the ambient temperature of 15°C will be about 7 m.

If microbiological heating can raise the temperature of the stack to 70°C, i.e. 55°C above ambient we have, from the definition of θ (equation(2)), $\theta = 6.5$. Using the experimental, dotted, curve in Fig.5 as the best guide to criticality, it then follows that, in the presence of both microbiological and wet oxidation, criticality will correspond to $\delta_1/_1\delta_c$ 0.1 with respect to the wet oxidation alone, i.e. the microbiological activity will reduce the critical size to $7\sqrt{0.1} = 2.2$ m, or by about one-third.

Little significance can be attached to the absolute values of the critical sizes estimated above - although they do not appear to be unreasonable. They will be very dependant on the value assumed for the activation energy. Moreover, they will be subject to modification by effects associated with the eventual loss of the large amount of moisture present; effects which, at present, cannot readily be evaluated.

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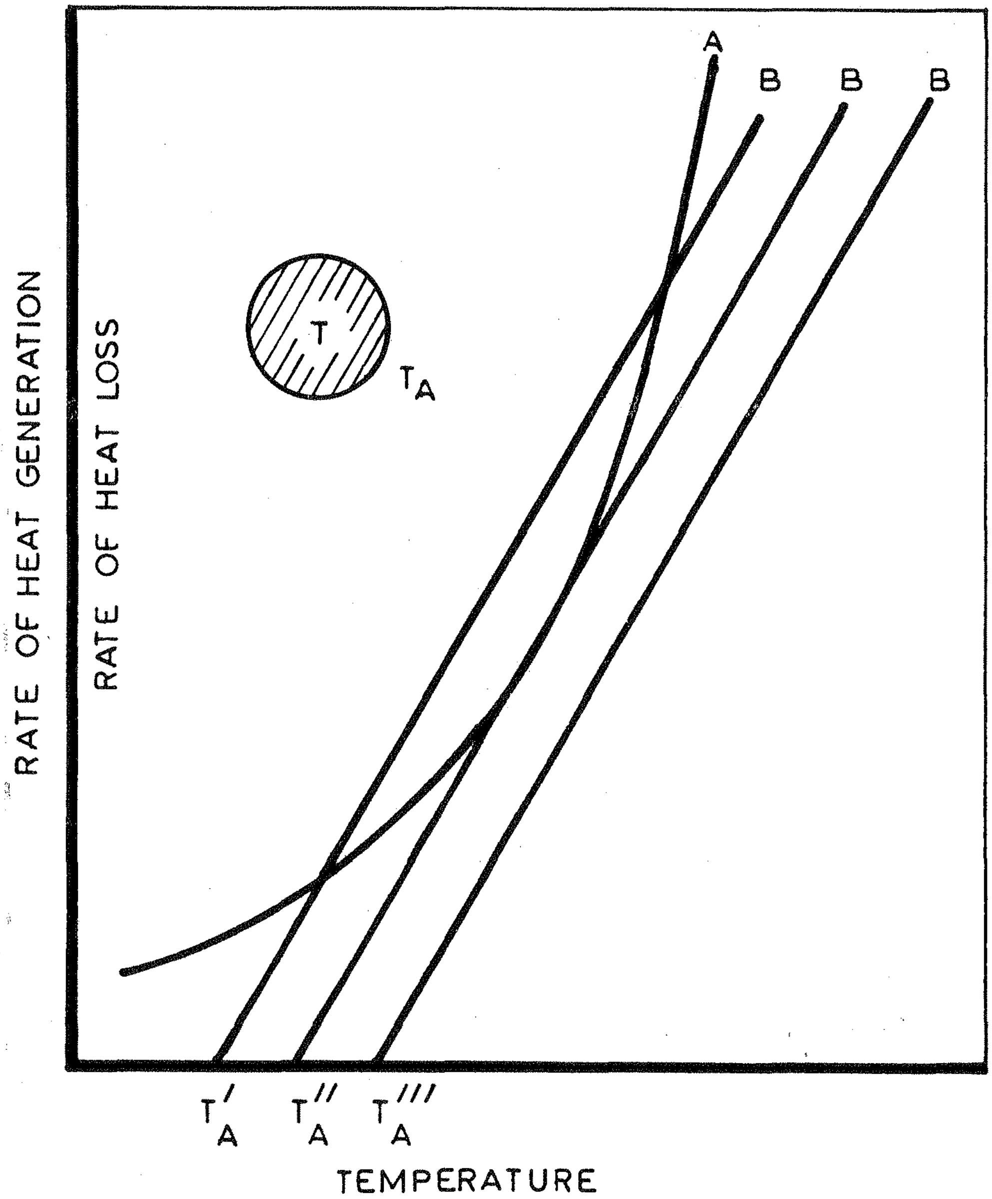

FIG.1 HEAT BALANCE

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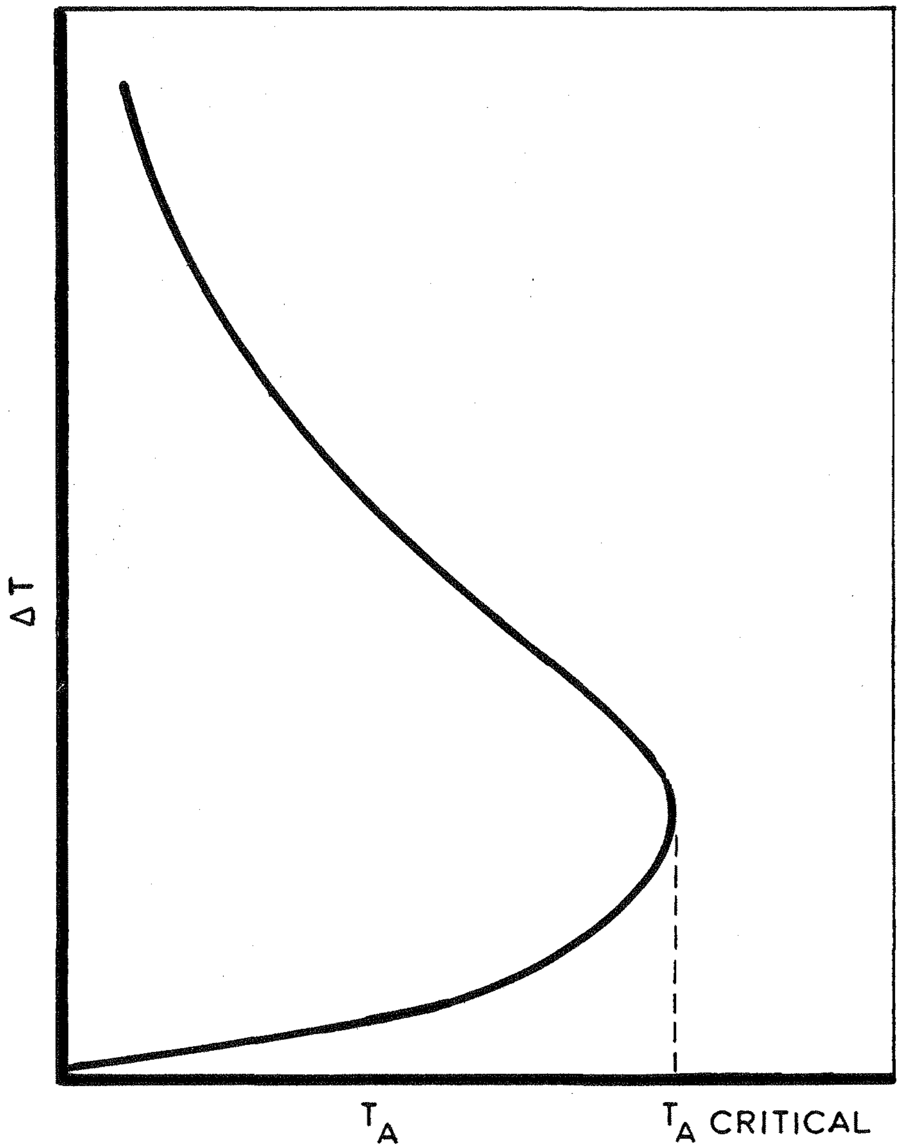
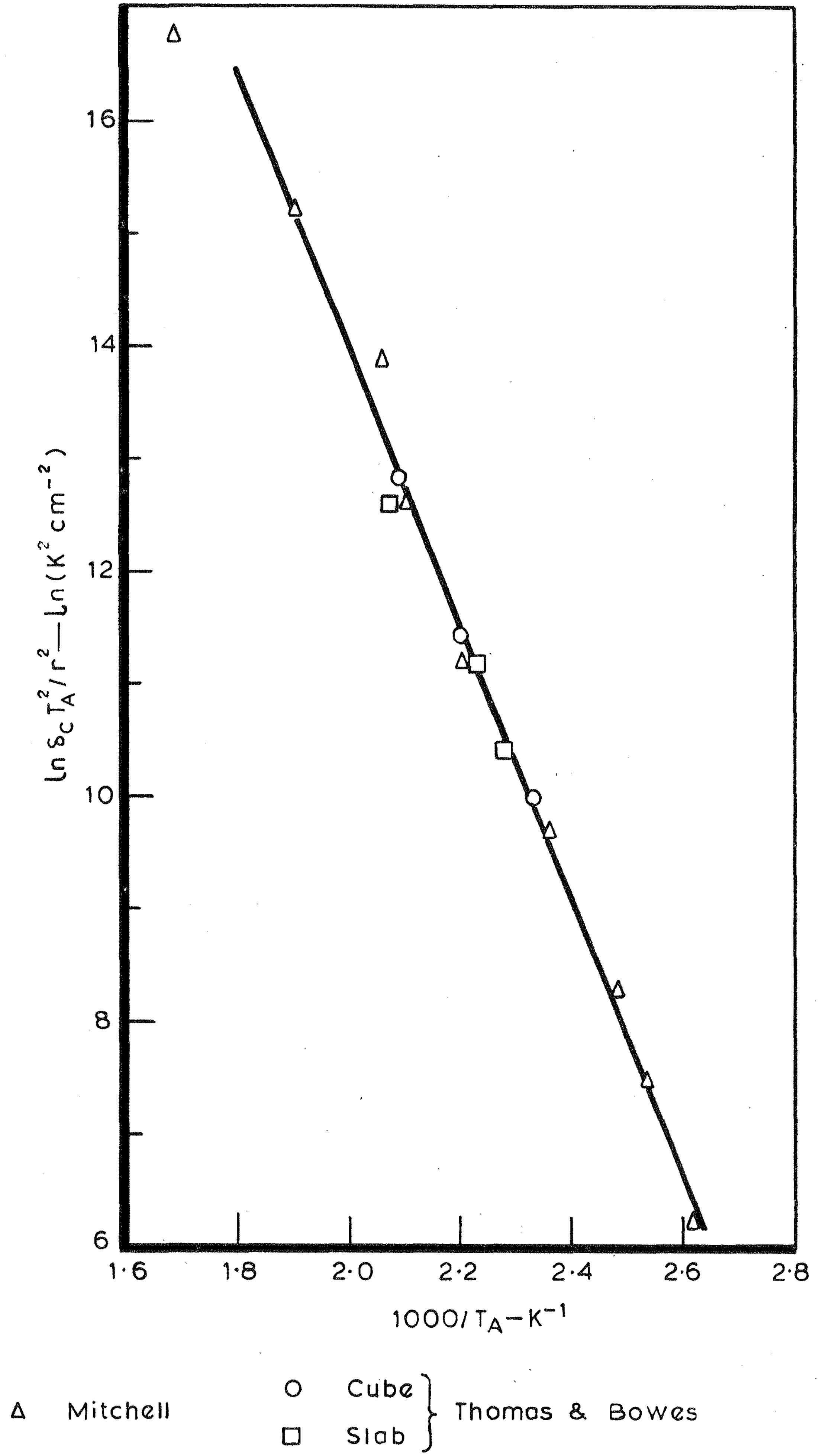


FIG. 2 STEADY STATES



$\ln \delta_c T_A^2/r^2 — \ln(K^2 cm^{-2})$
16
14
12
10
8
6
1·6
1·8
2·0
2·2
2·4
2·6
2·8
$1000/T_A — K^{-1}$
Δ Mitchell
○ Cube
□ Slab
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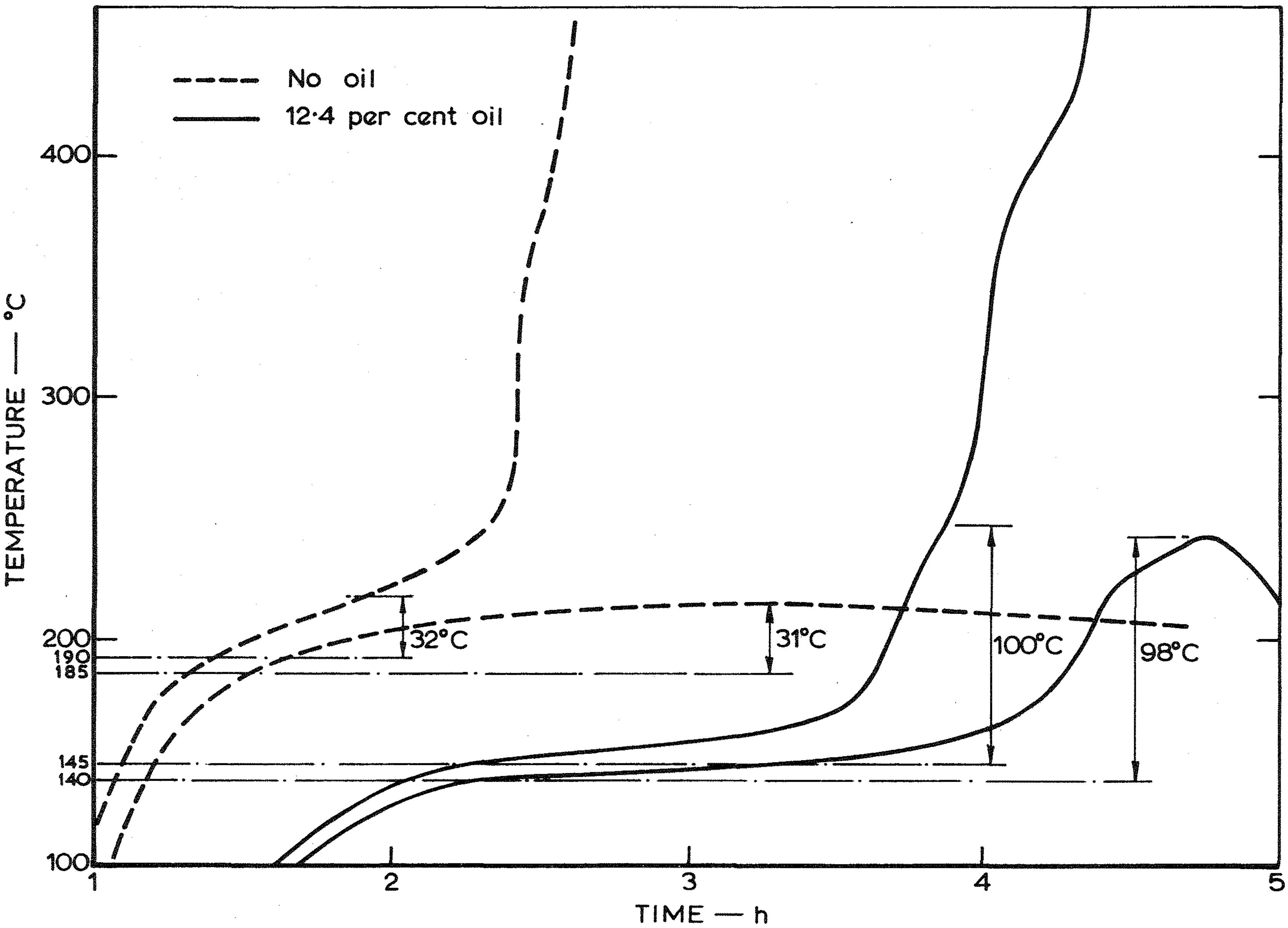
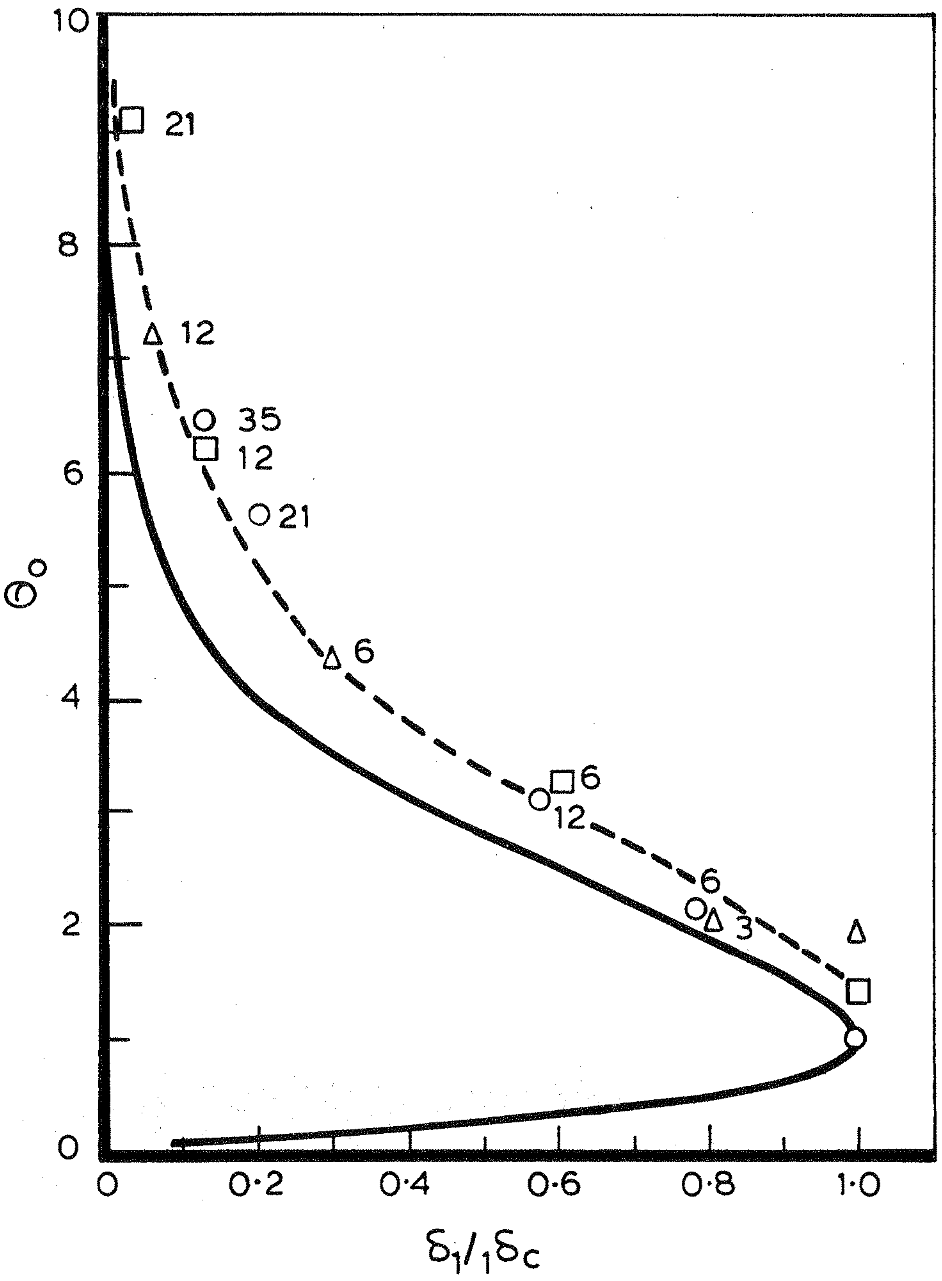


FIG. 4 SELF-HEATING AND IGNITION OF SAWDUST CUBES



CUBE SIZE: ○ – 25·4mm, □ – 51mm, Δ – 76mm

Numbers indicate oil content per cent by weight

FIG.5 CRITICAL TEMPERATURE RISE FOR OILED SAWDUST CUBES

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