

SPONTANEOUS IGNITIONS IN DUST LAYERS: COMPARISON OF EXPERIMENTAL AND CALCULATED VALUES

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A laboratory study has been made of ignitions in thin layers; the test material used was sodium dithionite. Ignition temperatures were measured for layers of 5 to 40 mm depth and for mixtures containing up to 75% inert. Thermochemical and kinetic parameters were measured independently to permit comparison with theory and computations were made using the experimentally established kinetic law. Comparisons with theory show the importance of allowing for variation of heat transfer parameter at the cold surface with depth of layer and confirm the use of the theory as a guide to extrapolation of data and to the extinction of ignition upon dilution. However, absolute comparisons of the critical parameter,  $\delta_c$ , were poor.

SPONTANEOUS IGNITION, DUST LAYERS, SELF-HEATING

INTRODUCTION

Many flammable materials will spontaneously ignite if formed into a sufficiently deep layer on a heated surface and one test applied to dusts is the determination of the contact temperature at which a 5 mm deep layer will ignite (see for example Palmer 1973). The practical need for such data lies in the presence in most industrial operations of heated surfaces such as furnaces, motor casings and steam pipes, on which a dust layer could accumulate and, if heated sufficiently, ignite and form the origin of a more major fire or dust explosion. Thus the practical test is a valuable pointer to the potential for hazard. Alongside the practical tests there have been theoretical analyses, both analytical and computational, which aim to identify the controlling parameters of self-ignition and so allow extrapolation from limited measurements and prediction from material properties. Examples of these approaches are the analytical work of Thomas and Bowes, 1961, and the computations of Tyler and Jones, 1981. The analytical approaches, of necessity, must simplify the problem. Thus Thomas and Bowes assumed simple kinetic behaviour for the material, ignoring reactant consumption, and adopted the Frank-Kamenetskii approximation for the temperature dependence. Within these constraints their results predict a sharp boundary between stability and ignition, with a critical ignition parameter,  $\delta_c$ , obtained as a function of the material properties, the temperature of the heated surface, the heat loss characteristics from the upper surface of the layer and, of course, the layer thickness.

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Their analysis indicated that when an ignition developed it started some little way above the heated surface, and that there was a maximum stable temperature that could exist within the layer. In principle, their results could be used to calculate ignition temperatures for different layer depths given a single experimental ignition temperature and the activation energy of the material.

The effects of lifting these limiting assumptions were investigated by Tyler & Jones using computational simulation of a developing ignition within a layer. No approximation of the temperature dependence was required and reactant consumption was allowed, taking the case of first order kinetics. A similar pattern of results emerged, although the value of the critical parameter diverged increasingly from that of Thomas and Bowes as the material's exothermicity was reduced. Much larger internal temperature rises were predicted and the division into ignition/non-ignition became blurred as the exothermicity decreased and reactant consumption became more critical in determining the outcome. In the limit the predicted critical  $\delta$  value was over an order of magnitude larger than that from the analytic model.

In order to evaluate these different models and to see how well critical conditions could be predicted from measurements of material properties well away from critical conditions an experimental study has been made using sodium dithionite as the test material. Measurements included ignition temperatures at several depths as well as kinetic and thermochemical properties of the test material. Further computational calculations were made using a model which matched the actual kinetic behaviour of the test material.

#### Existing models.

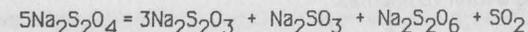
Thomas and Bowes considered a uniform layer of material at temperature  $T_0$  and thickness  $2r$  formed instantaneously on a heated surface of temperature  $T_p$ . This surface temperature was taken as invariant with time. They sought limiting conditions for the formation of a stable temperature profile within the layer, and expressed these as values of the dimensionless parameter,  $\delta c$ , given as functions of the difference between the plate and external temperature and the heat transfer parameter at the upper layer surface, expressed via the Biot number,  $\alpha$ . Some typical results are given in Fig 1. From the definition of  $\delta c$  it is clearly possible to predict critical conditions using this theory and the material properties or to extrapolate from a measured critical temperature at one depth to that at another. The potential importance of removing the approximations made in this approach is indicated by Fig 1 where similar curves from computational results are shown. A further factor,  $B$ , is introduced; this is a measure of the exothermicity of the material. With highly exothermic materials ( $B > 100$ ) there is little difference between the two models but at low exothermicities (e.g.  $B < 25$ ) a large discrepancy is predicted. However an important similarity is the variation of  $\delta c$  with  $\alpha$ ; this is examined quantitatively later in this paper. In both cases the same material properties are required to test the predictions, with the addition for the computational model of the kinetics of the heat release reaction.

## RESULTS

### Material properties

Sodium dithionite,  $\text{Na}_2\text{S}_2\text{O}_4$ , was chosen as the test material as it is known to exhibit self-heating properties and there had been some previous studies of its thermochemistry. Also the heat release reaction does not require oxygen and the main products are solids - thus it was anticipated that reaction would occur without significant changes in the bed depth. The material used was supplied by BDH Chemicals and was sieved before use to 60-80 mesh size. The kinetics were investigated using differential scanning calorimetry (DSC) in both scanning and isothermal modes and by isothermal decomposition, following the reaction by the pressure rise in a closed volume due to the product gas released. In both cases the measurement was done using samples of a few mg in each experiment. In the event the analysis by gas production was more precise and formed the basis of the final derived kinetic law. However, comparison with the less detailed isothermal DSC results confirmed that the gas release and heat release processes were directly parallel.

Early experiments showed the kinetics were complex, with a rapid, virtually immediate, reaction of between 10 and 20% of the total followed by an S-shaped decomposition curve, i.e. acceleratory kinetics leading to maximum rate followed by a gradual decay. Figure 2(a) shows a typical pressure trace. The early fast reaction was eliminated by pre-treatment of the material at 120 °C for 20 minutes; a reaction curve for pretreated material is shown as Fig 2(b). Chemical analysis of this pretreated material using the volumetric method of Kilroy (1980) showed that the test material was  $81 \pm 4\%$  dithionite by weight, compared to  $91 \pm 6\%$  for untreated material. The remainder was predominantly sodium sulphate and sodium sulphite, expected impurities from the manufacture of the dithionite. The decomposition reaction was not examined in detail since it was sufficient to determine the kinetics of the heat release reaction. Tests showed that the gas released was predominantly (>90%)  $\text{SO}_2$  and that after an ignition there was no detectable dithionite left in the reaction products. From previous work (Cleghorn and Davis, 1970) and from the amount of sulphur dioxide produced the most likely reaction is to give sodium thiosulphate as the major solid product with some sodium sulphite and sodium dithionate:



As it was not possible to fit the experimental data to any of the commonly used acceleratory rate equations (see Henderson, 1986) a simple polynomial relationship was used. The kinetic data, obtained in the range 164 to 195 °C, could be reduced to fit a common curve of fraction reacted vs reduced time (= elapsed time/reaction time to 50% reaction). These data were fitted to the following quartic expression for reaction rate in terms of the fraction of unreacted material ( $1 \geq \mu \geq 0$ )

$$-d\mu/dt = k(a\mu + b\mu^2 + c\mu^3 + d\mu^4)$$

where  $k/s^{-1} = (2.7 \pm 1.0) \times 10^{16} \exp(-170 \pm 9 \text{ kJ mol}^{-1}/RT)$ , i.e.  $k$  is expressed as a normal Arrhenius constant, and where  $a=2.7936$ ,  $b=-5.3895$ ,  $c=5.7513$  and  $d=-2.9184$ . These kinetic data were later used in a computational program to predict critical conditions.

The required material properties were reaction exothermicity, heat capacity and thermal diffusivity. The reaction enthalpy has been reported variously between -43 and -93 kJ mol<sup>-1</sup> (see Henderson, 1986). In view of the large range a value was obtained for our

material using a Perkin-Elmer DSC 1B differential scanning calorimeter. The instrument was calibrated using pure indium and then the reaction enthalpy measured using eight samples of 4 to 10 mg; the average value for the pretreated sodium dithionite used here was -78.5±6 kJ mol<sup>-1</sup> (360±30 J g<sup>-1</sup> for pretreated material).

The heat capacity of the material, C, was measured for us by Dr P.Laye, University of Leeds, using a Perkin-Elmer DSC2 instrument calibrated with a sapphire sample. Over the temperature range 29 to 133 °C, in which no thermal reactions of sodium dithionite occur, the average heat capacity was found to be 1.076 J K<sup>-1</sup> g<sup>-1</sup>.

The thermal diffusivity of the material was found from the heating up curve for a layer of cold material placed onto a thermostatted hot plate. The material used was residue from ignition experiments - this was necessary as a high temperature was needed to give adequate data for analysis and sodium dithionite would have reacted at the temperatures used. It was assumed that the value for sodium dithionite would not be greatly different from that of its reaction products. The layer was 20 mm deep and temperature-time curves were obtained at 1, 5 and 11 mm above the plate. The approach to the final equilibrium temperature can be expressed (Carslaw & Jaeger, 1959) as a complex series function involving position, time and thermal diffusivity. By trial and error fitting of this theoretical expression to the observed data obtained from the 5 and 11 mm thermocouples the thermal diffusivity was determined as  $(1.25±0.05)×10^{-3}$  cm<sup>2</sup> s<sup>-1</sup>. This was an average value over the temperature range 30 to 220 °C. Since C was known the thermal conductivity could also be obtained.

#### Measurement of ignition temperatures

The layers were formed on a thermostatically controlled, 25cm diameter by 5 cm thick aluminium hotplate. The temperature of the plate was constant to within ±0.2 °C over the area used and the time variation at any point was no more than this. When a 20 mm deep layer was formed on the plate the surface temperature was depressed by no more than 2 °C, recovering within 10 minutes.

Layers were formed within a cylindrical retaining ring, usually of an asbestos-cement material, and normally of 75 mm diameter. The ring heights were between 5 and 40 mm. Experiments were initiated with a ring in place on the hot plate and then a layer was formed by pouring in a slight excess of reactant and quickly levelling the surface. In addition to the temperature of the hotplate, measured by a thermocouple placed just beneath the surface, other thermocouples were placed within the reaction material, usually centrally, at several heights above the hot plate and with a further thermocouple placed in the air just above the layer surface. All thermocouples were made from 0.2 mm diameter platinum to platinum/13% rhodium wire. The output from each of up to 8 thermocouples was sampled at 20 s intervals and recorded digitally, after amplification of the signal, using a Commodore PET 32K microcomputer. After internal conversion to °C the data were output either as a hard-copy or graphically. The data handling system

could resolve differences to 0.1 °C. Use of multiple thermocouples allowed certain determination of whether an ignition had occurred, indicated where the greatest self-heating was in non-ignitions and also, from final equilibrium temperature distributions, allowed heat transfer coefficients from the surface to be determined.

#### Experimental ignition temperatures

Early experiments showed that ignition temperatures could be measured to within ±1 °C or better, that the nature of the ring material did not affect the ignition temperature and that ignitions started at or very near to the centre of the layer but at depths which depended on the mixture composition. An important concern was whether heat losses

from the edges of the ring could affect the ignition temperature. This was resolved for the 20 mm deep by 75 mm diameter ring by allowing an equilibrium temperature profile to be established just below the ignition temperature and then taking temperature measurements across a diameter at a height of 5.0±0.5 mm above the plate. The measured temperatures were constant to ±1 °C in the central 90% of the diameter but fell off at the edge. When a downward air flow was provided over the layer (see below) the temperature drop at the edge was larger and affected the outer 10 mm of each radius. From these observations it was concluded that results typical of a semi-infinite layer were being obtained for layers of ≤20 mm depth but this might not apply to appreciably deeper layers (e.g. 40 mm).

It was shown, not unexpectedly, that ignition temperatures were considerably affected by the air flow pattern over the layer, for example ignition temperatures were altered by 5 to 10 °C on changing from an uncontrolled flow (natural convection due to the surrounding uncovered hot plate), to a controlled downward air flow. In view of this virtually all experimental measurements were made using a downward air flow within a glass cylinder which fitted around the former with a 1 mm gap all round. After trials the downward air flow was set at 35 dm<sup>3</sup> min<sup>-1</sup>, at which value it was not forceful enough to disturb the layer, and gave an air temperature above the layer of 35 °C; without this flow the background air temperature was 60 °C and the ignition temperature of a 20 mm layer was 168 °C compared to 175 °C with the air flow on.

Figure 3 shows temperature/time traces for events just bracketting an ignition limit. Interesting features are that in the non-ignition there was no measureable temperature rise within the layer above the plate temperature; that the greatest rise (compared to the final equilibrium temperature at each level) was for the 5 mm thermocouple and that the time to maximum increased slightly with increasing height above the plate. In the ignition event, at a plate temperature 2 °C higher, the ignition appears to start very close to the plate and for all four thermocouples the plate temperature is exceeded. With material being hotter than the plate this lower surface acts as a heat sink and so the highest temperature observed is not near to the plate but well within the layer, in this instance at the 11 mm thermocouple. However, the greatest rise from the time of the ignition being detected by the thermocouple is for the 16 mm thermocouple, the rise being a "step" of almost 300 °C.

The effect on the ignition temperature of varying the layer depth is shown in Table 1. In all cases the layer diameter was 75 mm; the Biot numbers recorded are those determined experimentally using the equilibrium temperatures eventually reached in a non-ignition event to estimate the surface temperature of the layer. The Biot number was calculated as  $\alpha = 0.5(T_p - T_s)/(T_s - T_o)$

Table 1  
Variation of ignition temperature with layer depth

Layer depth/mm	Ignition temperature/°C	Biot number
5	191.5	0.42
10	183.0	1.2
20	175.0	2.5
40	168.5	4.3

#### Ignitions in diluted reactant mixtures

To study the effect of reaction exothermicity on ignition temperatures and ignition characteristics a series of experiments was carried out using sodium dithionite diluted with an inert additive. The inert used was reaction product from previous ignitions. This was of similar size to the reactant, was known to be devoid of dithionite, and was likely to have similar thermal properties. The inert was thoroughly mixed with reactant and experiments were carried out in layers of 20 mm depth by 75 mm diameter, using mixtures containing up to 75% w/w inert. The downward airflow was not used in these experiments

Figures 4 and 5 illustrate the progressive changes resulting from dilution. The maximum temperature achieved above the plate temperature, Fig.4, falls rapidly after the inert reaches 65% and the variation of the maximum exotherm with plate temperature becomes more gradual at this level. Clearly ignition characteristics are lost at about this level of dilution. Table 2 lists the ignition temperatures for diluted dithionite mixtures.

Table 2  
Variation of ignition temperature with % inert, 20 mm layer

% inert (by weight)	Ignition temperature/°C
0	168
50	178
60	187
63	200
66	not observable
75	not observable

Another pointer to the impending loss of ignition characteristics can be seen in the rapid rise in the ignition temperature with further dilution above 50% inert.

#### Computational results

To make direct comparison between experimental and computed results possible it was necessary to make further computations for the particular acceleratory kinetics found for dithionite. To do this the program used by Tyler & Jones, 1981, was modified (we are grateful to Dr D.R.Jones for carrying out the necessary alterations) to cope with the experimental kinetic law described above. The program was then used as in the earlier study of first order kinetics; full details are given by Henderson, 1986. When reactant consumption is allowed it is necessary to determine the ignition characteristic,  $\alpha_c$ , at particular value of the reactant exothermicity, expressed via B. Results for B=25 and B=50, bracketing the value expected for sodium dithionite, are shown in Figure 6. Comparison with Figure 1 shows that the predicted values are considerably greater than those for first order kinetics, although the general trend is retained. Another aspect pursued in this analysis was to determine the value of B at which ignition was predicted to disappear. This proved to be a difficult task as computational instabilities developed as run times lengthened at the low B values involved. Predicted ignition was found at B=12.5,  $\theta_o = -10$  and  $\alpha_c = 2.5$  at  $\alpha_c = 105$ . Changing  $\theta_o$  to -12.5 gave a probable ignition at  $\alpha_c = 470$ , illustrating the rapid change in critical conditions around this point. It was concluded that the best prediction was for loss of ignition characteristics at about B=12.5.

#### DISCUSSION

Possible comparisons between the experimental and theoretical results include (i) *relative tests*, such as the effects of changes in the Biot number or the layer depth or the reactant exothermicity, and (ii) *absolute tests*, as when observed and predicted values of  $\alpha_c$  are compared. The former type of test is of importance when limited results are extrapolated or ignition measurements for one shape, say a layer, are used to predict ignition conditions for another shape, such as a cube. The second type of test indicates the potential that theory has for predicting ignition conditions based only upon independent measurements of material properties. Both types of test are considered below.

Test 1: variation of Biot number. When the controlled airflow system was introduced the ignition temperature for the 20 mm layer was increased from 168 to 175 °C; the measured values of the Biot number were 1.5 and 2.3 respectively. However, there was a concurrent change in the background temperature above the layer from 60 to 35 °C and hence the value of  $\theta_o$  was altered as well. Examination of the definition of  $\alpha_c$  shows that the ratio of the values at two temperatures is

$$\alpha_{c,1}/\alpha_{c,2} = \exp(-E/RT_1)/\exp(-E/RT_2) \times (T_2/T_1)^2$$

Using the experimental value  $E = 170$  kJ/mol gives the experimental ratio for  $\alpha_{c,175}/\alpha_{c,168} = 2.0$ . A predicted ratio can be estimated from the results of Thomas and Bowes for zero order kinetics, effectively assuming that reactant consumption effects will not be appreciably different in these two closely related experiments, allowing for the effects of changes in  $\alpha$  and  $\theta_o$ . Also the values computed for the quartic kinetics interpolated for B=35 are given.

Table 3  
Predicted values of  $\delta c$ 

T <sub>ig</sub> /°C	T <sub>p</sub> /°C	$\infty$	$\theta_0$	$\delta c(T\&B)$	$\delta c(\text{quartic}, B=35)$
168	60	1.5	-11.4	11	39
175	35	2.5	-14.3	21.5	97

The ratio of the  $\delta c$  values are 1.95 for the zero order case and 2.5 for the computations using quartic kinetics. The agreement with the experimental value (2.0) is satisfactory, showing that the effects on  $\delta c$  due to changes in  $\infty$  and  $\theta_0$ , as first predicted by Thomas and Bowes, are observed in experimental measurements and have effects on ignition temperatures far in excess of the experimental uncertainties.

Test 2: variation of ignition temperature with layer depth. When a simpler thermal ignition problem is analysed it is possible (see Bowes, 1984) to relate ignition temperature values at different sizes by plotting  $\ln(\delta c T_{ig}^2/r^2)$  vs  $1/T_{ig}$  and expect a linear plot of slope  $-E/R$ . This supposes that  $\delta c$  does not vary with the test dimension,  $r$ . In the present case, as illustrated above,  $\delta c$  varies considerably with quite small changes in conditions, certainly for the wide range of conditions covered in Table 1. Thus it is necessary to determine how  $\delta c$  is affected by the change of Biot number and  $\theta_0$ . To do so requires a value of  $E$  to calculate  $\theta_0$  and normally iteration would be required. In the present case, however, we have preferred to use the value of 170 kJ/mol from the kinetic studies. Table 4 gives the computed  $\delta c$  values for both the zero order case and for dithionite kinetics.

Table 4  
Computed values of  $\delta c$  for the experimental condition used

Depth/mm	T <sub>ig</sub> /°C	$\infty$	$\theta_0$	$\delta c$ , zero order	$\delta c$ , quartic B=50	ratio of $\delta c$ values
5	191.5	0.42	-14.8	6.7	18.5	2.76
10	183.0	1.2	-14.6	15.9	47.6	2.99
20	175.0	2.5	-14.3	21.8	59.6	2.73
40	168.5	4.3	-14.0	24.6	69.1	2.81

This table illustrates a number of important features. Firstly it reinforces the change in  $\delta c$  over a quite small experimental range, there being an almost fourfold change. Hence the common approach of taking  $\delta c$  to be constant would be quite wrong.

Secondly the table shows a feature noticed also for the first order computations, namely that for the ratio of  $\delta c(\text{zero order})/\delta c(\text{other order})$  is practically constant over a wide range of  $\infty$  and  $\theta_0$ . This was checked using all the available first order and acceleratory kinetic values. The most satisfactory statement of the findings is that the ratio is constant to  $\pm 20\%$  or less at a given  $\theta_0$  over the range of  $\infty$  from 0.5 to infinity and the ratio changes only slowly with  $\theta_0$ . The practical implication of this is that the zero order values can be used to interpret experimental results since, whilst the changes in  $\infty$  may be considerable, the changes in  $\theta_0$  are small. This conclusion is important since the zero order results are obtained by an approximate analytical method which is much less time consuming than the computations needed for more realistic kinetics.

Figure 7 shows the usual form of the plot for ignition temperatures using both constant  $\delta c$  and  $\delta c$  as computed for acceleratory kinetics. In the former case, a good straight line results but the activation energy derived from it is 314 kJ mol<sup>-1</sup>, far in excess of the value from the isothermal studies. Using the varying  $\delta c$  does not result in such a good line. A possible reason for this is that the ignition temperature for the 40 mm layer may be too high, due to edge effects. However, the activation energy based on the 5-20 mm points is 176 kJ mol<sup>-1</sup> in excellent agreement with the isothermal value; including the 40 mm point gives 220 kJ mol<sup>-1</sup>. We conclude again that it is essential to allow for the variation of  $\infty$  and, to a lesser extent in this application, of  $\theta_0$  when applying theory to experimental measurements on thin layers.

Test 3: Loss of ignition due to reactant dilution. The experimental results show clearly that dilution with inert eventually eliminates the ignition characteristic and, for sodium dithionite, this occurs when the level of inert reaches 66% by weight. Assuming that the inert and reactant have identical thermal properties means that this mixture has a B value of 12; this can be compared with the value given above from the computations for loss of ignition characteristics at about 12.5. The agreement is excellent and provides a valuable indicator of general application.

Thus in the relative tests considered above there is good agreement between the experimental results and theoretical predictions. This allows a strategy for the estimation of ignition temperatures from limited data to be proposed as follows. Firstly the experiments should be done with as deep a layer as possible since the effects of varying Biot number are greatest for thin layers. Secondly values of Biot number should be determined experimentally or be estimated. Then the  $\delta c$  values of Thomas & Bowes can be used to allow the standard plot to be drawn and the best possible predicted values result. If a constant value for  $\delta c$  is assumed, then extrapolation will give a predicted critical layer depth at a given temperature that is greater than the true value, i.e. the error is in an "unsafe" direction. The error will not be large unless one of the points used is for a very thin layer, e.g. 5 mm or less.

The one absolute test which can be applied to our results is to use the ignition temperature in conjunction with the separately measured material properties to calculate a value of  $\delta c$  and to compare this with the computed value. In view of the relative tests carried out already it is only necessary to do this for one layer; the 20 mm layer was used for which the computed  $\delta c$  is 97. Calculating  $\delta c$  (see definition) involves exothermicity, rate at T<sub>p</sub>, depth, activation energy, density, heat capacity and thermal diffusivity. Using our values gives  $\delta c = 11$ , a factor well below the computed value. Whilst there must be considerable experimental error due to the large number of measurements involved, this cannot explain so large a difference and, even after careful re-evaluation of the individual measurements, we are unable to account for this factor. We conclude that it would be unwise to calculate ignition temperatures from basic material properties unless there is at least one experimental ignition temperature available to confirm the predictions. We note that even for the more easily investigated case of thermal ignition of gases there have been few demonstrations of the absolute agreement between observed and theoretical  $\delta c$  values, the best being the study of diethyl peroxide by Fine et al, 1970 where very close agreement resulted.

The system studied here differs from many practical ones where oxygen is required in the heat releasing reaction and so inward diffusion must occur. Our data cannot give any indication of the importance of this process but other workers (see Bowes) have shown that in 50mm layers of sawdust the self-heating starts near the hot plate and then develops smouldering ignition near the outer surface. Whilst this shows that the later stages of development are influenced by oxygen availability, it also demonstrates that the early stages of ignition occur near the hot plate, as expected from the theoretical models. Thus it seems probable that conditions for onset of ignition will not be affected in a major way by the diffusion requirement. Bowes also evaluates theory and experimental results concerning the effects of oxygen diffusion into cubes and again concludes that the consequences on the ignition condition are usually small.

Another feature of practical conditions is that the formation of a layer results in an increase in the surface temperature due to the insulating effect of the layer. Indeed, there may be a constant power source under the layer. Again our data are not directly relevant to this situation but it must be noted that such situations are more severe than those used by us; in consequence lower ignition temperatures will result.

#### CONCLUSIONS

1. Thermal ignition temperatures on a hot plate are significantly affected by the conditions at the upper boundary, as predicted by theory, and this must be taken into account when interpreting or extrapolating results.
2. Theoretical predictions for layers can be used with confidence for relative applications to experimental data.
3. Because of the direct parallel behaviour predicted for different kinetic laws the simple model of Thomas and Bowes can be used to interpret experimental results even when appreciable reactant consumption occurs.
4. Dilution of reactants by inert material results in loss of ignition at a B value of 12, in excellent agreement with the theoretical prediction.

#### ACKNOWLEDGEMENT

This work was supported by the Building Research Establishment through the Fire Research Station, Borehamwood.

#### NOMENCLATURE

A	Arrhenius pre-exponential factor
C	heat capacity
E	activation energy
h	heat transfer coefficient
k	rate constant = $A \exp(-E/RT)$
Q	reaction exothermicity
R	gas constant
r	half thickness of layer
T	temperature (K)
t	time
$\lambda$	thermal conductivity
$\kappa$	thermal diffusivity = $\lambda/\rho C$
$\rho$	density
$\mu$	fraction of material unreacted
$\infty$	Biot number = $hr/\lambda$ [ $=0.5(T_p-T_s)/(T_s-T_0)$ for steady non-reacting conditions]
$\theta$	dimensionless temperature = $E(T-T_p)/RT_p^2$
B	dimensionless exothermicity = $(Q/C\rho)(E/RT_p^2)$
$\delta$	dimensionless reaction parameter = $QEr^2k(at T_p)/\rho\lambda RT_p^2$
Subscripts	
o	ambient
p	plate
s	top surface of layer
c	critical

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Figure 1 Plots of calculated  $\Delta c$  values vs Biot number for zero order kinetics (Thomas & Bowes) and 1st order kinetics (Tyler & Jones). All the 1st order results are for  $\theta_0 = -10$ .

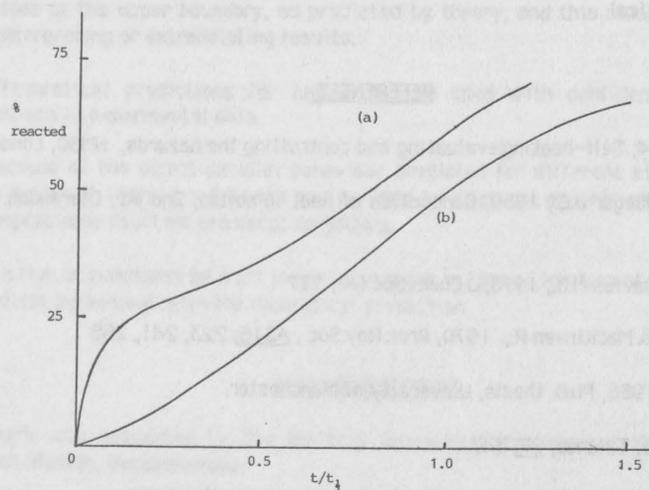
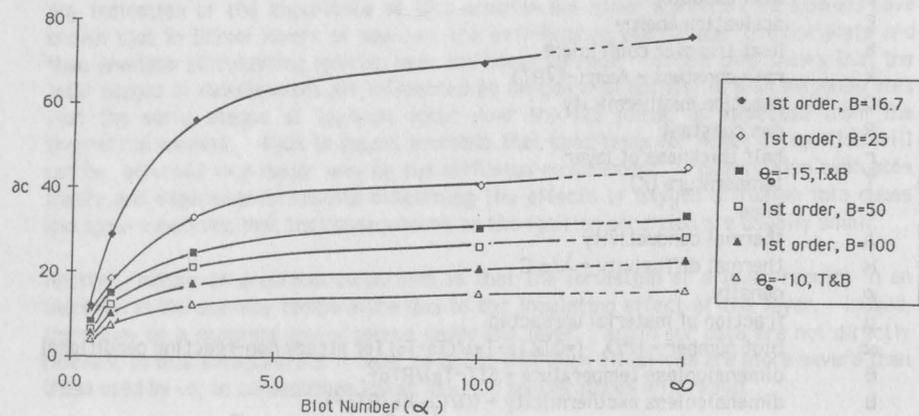


Figure 2. Extent of reaction vs time.  
 (a) Untreated dithionite, 209 °C,  $t_{1/2} = 105$  s  
 (b) Pretreated dithionite, 178 °C,  $t_{1/2} = 35$  min.

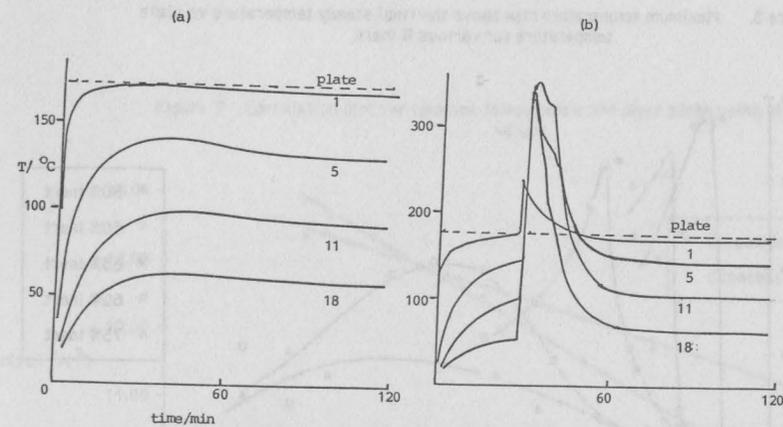


Figure 3. Temperature vs time traces in 20 mm layer. Thermocouple heights above plate are given in mm. (a) Non-ignition at 174 °C; (b) ignition at 176 °C.

Figure 4. Excess temperature over plate temperature vs % inert in the reactant mixture.

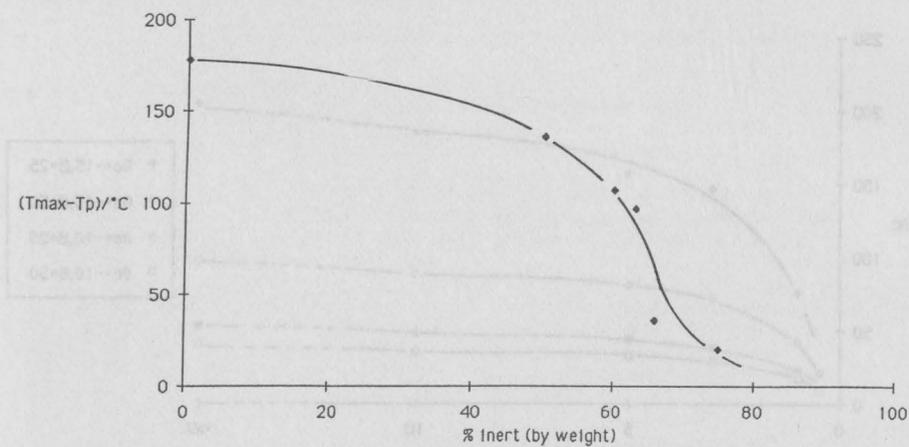


Figure 5. Maximum temperature rise above the final steady temperature vs plate temperature for various % inert.

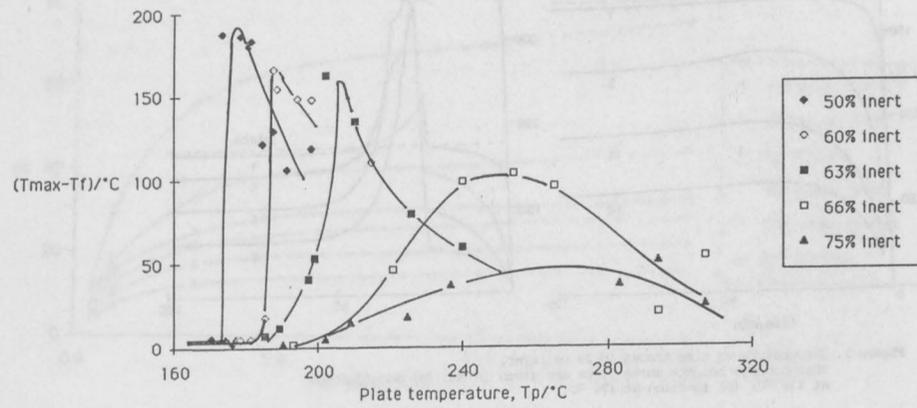


Figure 6.  $\partial c$  vs  $\alpha$  for quartic kinetics

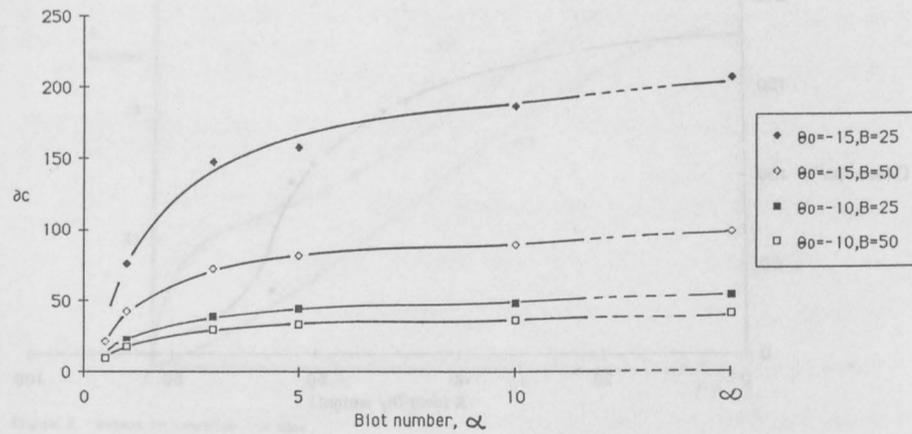


Figure 7. Correlation plot for Ignition temperature and layer depth using alternative  $\partial c$  values

