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SELF HEATING IN CONSOLIDATED Al/Cu_2O THERMITES

Gary D. Miller, Jonathan H. Mohler, and Michael D. Kelly

ABSTRACT

The ignition theory of Frank-Kamenetskii, which follows from a solution of the steady-state heat flow equation for an isotropic chemical heat source, predicts that a measurable temperature difference will be established between the center and wall of a sample that is near its ignition point. We have measured this temperature difference in a cylindrical Al/Cu_2O thermite part under conditions approximating a steady-state. The results of the measurements lead to a calculation of the activation energy and a pseudo-zero order preexponential factor for the thermite reaction rate constant.

DISCLAIMER

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INTRODUCTION

The Frank Kamenetskii theory of thermal ignition [1] provides a model through which the ignition temperature of an explosive or pyrotechnic material can be calculated. An interesting prediction of the model is that just below the ignition point a measurable temperature difference will be established between the center and wall of the sample because of the self-heating phenomenon. Essentially, the model predicts that for a slowly heated sample, thermal ignition will occur when a temperature is reached at which the rate of heat production from chemical exoergicity exceeds the rate of heat loss caused by thermal conduction. The basic assumptions of the model are: (1) the combustion or decomposition reaction occurs at all temperatures but is imperceptibly slow below the ignition temperature, (2) the reaction does not occur through a chain mechanism, and (3) the Arrhenius Equation is a valid description of the reaction rate constant. The physical properties required for an ignition temperature prediction are the reaction exoergicity, Q, the thermal conductivity, λ, the sample geometry and size, the activation energy, E, and the preexponential factor of the reaction rate constant, A. If it is assumed that ignition occurs before significant reaction has taken place, the concentration dependence of the reaction rate is also included in A.

Frank-Kamenetskii's theory has been described in detail elsewhere [1]. Briefly, it begins with the general heat flow equation for an isotropic chemical heat source,

$$c\rho\frac{\partial T}{\partial t} - \lambda\nabla^2 T = QAe^{-E/RT} \tag{1}$$

where: c = the mean specific heat
ρ = the density
T = the temperature
t = time
R = the gas constant
∇^2 = the Laplacian operator

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Restriction to slow heating rates, the use of the Todes approximation [2]:

$$\frac{E}{RT} \simeq \frac{E}{RT_W}\left(1 - \frac{T - T_W}{T_W}\right), \tag{2}$$

and the introduction of two dimensionless quantities:

$$\theta = \frac{E}{RT_W{}^2}(T-T_W), \tag{3}$$

and z=x/r lead to the temperature distribution (solution of Eq. 1) for a cylindrical sample having a length much greater than its radius:

$$\theta = \ln(8/\delta) - 2\ln(e^{-b}z^2 + e^b), \tag{4}$$

where T_W is the temperature at the curved wall of the cylinder, θ is a reduced temperature, z is the reduced spatial coordinate, x is the real spatial coordinate, r is the cylinder radius, and δ is the dimensionless criticality parameter defined as:

$$\delta = \frac{QEAr^2e^{-E/RT_W}}{\lambda RT_W{}^2} . \tag{5}$$

Finally, b is an integration constant given by $b = \cosh^{-1}\sqrt{2/\delta}$. The point of thermal ignition for a long cylinder under slow heating has been found by both numerical [3] and analytical [1] procedures to occur when $\delta = \delta_{cr} = 2.00$, at which point $T_W = T_O$, the wall ignition temperature. Substitution of $\delta = 2.00$, $z = 0$, and $T = T_C$, the center temperature at ignition, into Eq. 4 gives the center-wall temperature difference at ignition, $\Delta T_m = T_C - T_O$, as:

$$\Delta T_m = 1.38\ RT_O{}^2/E . \tag{6}$$

Although the usual application of ignition theory is to use Eq. 5 and a knowledge of thermal conductivity, thermochemical properties, and kinetic parameters to predict the ignition temperature for a sample of known size and geometry, the process has been inverted here to find the kinetic parameters, E and A, in a system for which classical kinetic methods would be difficult. By measuring simultaneously the center and wall temperatures at ignition, the activation energy, E, can be found directly from Eq. 6. Once E is found, the preexponential factor, A, can be found from Eq. 5 and previously determined values for Q and λ.

The Frank-Kamenetskii theory has most frequently been applied to explosion of an unstable gas [4] or gas mixture, and as a result is usually known as thermal explosion theory. There is nothing in the mathematical treatment, however, which requires explosion. The theory only deals with processes at temperatures below the point at which heat production begins to exceed heat loss. At this point, the temperature increase becomes very rapid; in turn, heat production becomes more rapid because of the exponential temperature dependence of chemical rate constants. The increasingly faster heat evolution boosts the system temperature still faster and the reaction is said to "run away with itself." The occurrence of an explosion depends solely upon whether the chemical reaction has gaseous products. Attempts have been made at choosing systems for study which do not explode after the ignition point to minimize damage to experimental apparatus. Collister and Pritchard, [5] for example, have studied thermal ignition for the slightly exoergic ($Q = 27.3$ kcal mol^{-1}) isomerization of methyl isocyanide.

The consolidated thermites of this study are particularly well suited to thermal ignition experiments for several reasons. First, the reaction:

$$3\,Cu_2O_{(s)} + 2\,Al_{(s)} \longrightarrow Al_2O_{3(s)} + 6Cu_{(s)} + 573 \text{ cal g}^{-1} \quad (7)$$

has no gaseous products to result in explosion. In addition, because the thermite mixture is consolidated to 90% of its theoretical maximum density by a hot pressing process, there is little air present to cause a large pressure increase during burning. Third, the Todes approximation used in the derivation of Eq. 4 is much better in the ignition temperature range of normal size Al/Cu_2O thermite parts (~500 °C) than at ignition temperatures of most organic explosives (~250 °C). Finally, the requirements of the ignition model, that the medium be isotropic and have a definite simple geometry, are easily satisfied for consolidated thermite parts.

EXPERIMENTAL

Stoichiometric proportions of finely divided Al and Cu_2O were hot pressed into four cylindrical pellets of density, 4.71 g/cm^3. The four cylinders were aligned end to end as shown in Figure 1; the resultant cylinder had a total length of 10.19 cm and a diameter of 2.870 cm. The cylinder was inserted into a graphite sample holder (also shown in Figure 1) and end caps were screwed in place to fix the position of the thermite. Stainless-steel sheathed chromel-alumel thermocouples were inserted, to a depth of half the cylinder's length, into predrilled holes in the graphite holder and thermite sample at the cylinder wall and center. The assembled sample holder and thermocouples are shown in Figure 2. A tube furnace was placed outside the sample holder. The heating rate of the furnace was controlled by a Focal-11 program running on a PDP 11/10 computer. The computer is coupled to the thermocouples and to a relay in the furnace power line through a Digital Equipment Corporation laboratory peripheral system (LPS). Temperatures acquired by the program were compared to a linear temperature-time equation and the furnace was then turned on or off, as required, at a frequency of 1 Hz. The heating rate at the sample wall was 10°C/min from ambient temperature to 300°C, 5°C/min from 300 to 400°C and 2°C/min above 400°C. The deviation of the wall temperature from the program temperature was a maximum of ±1.5°C at temperatures above 400°C.

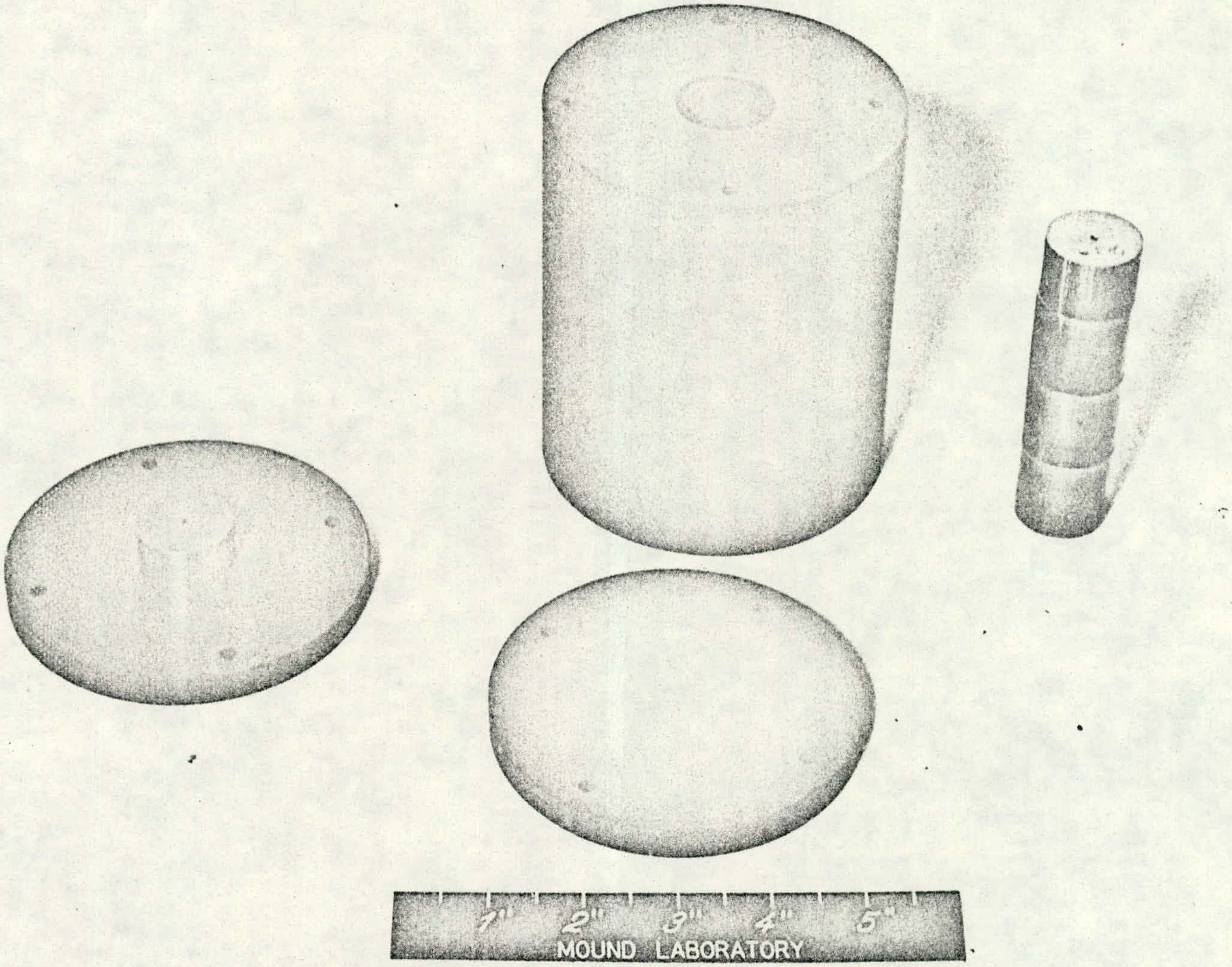

FIGURE 1 - The disassembled sample cylinders stacked end-to-end are shown with the graphite sample holder and end caps.

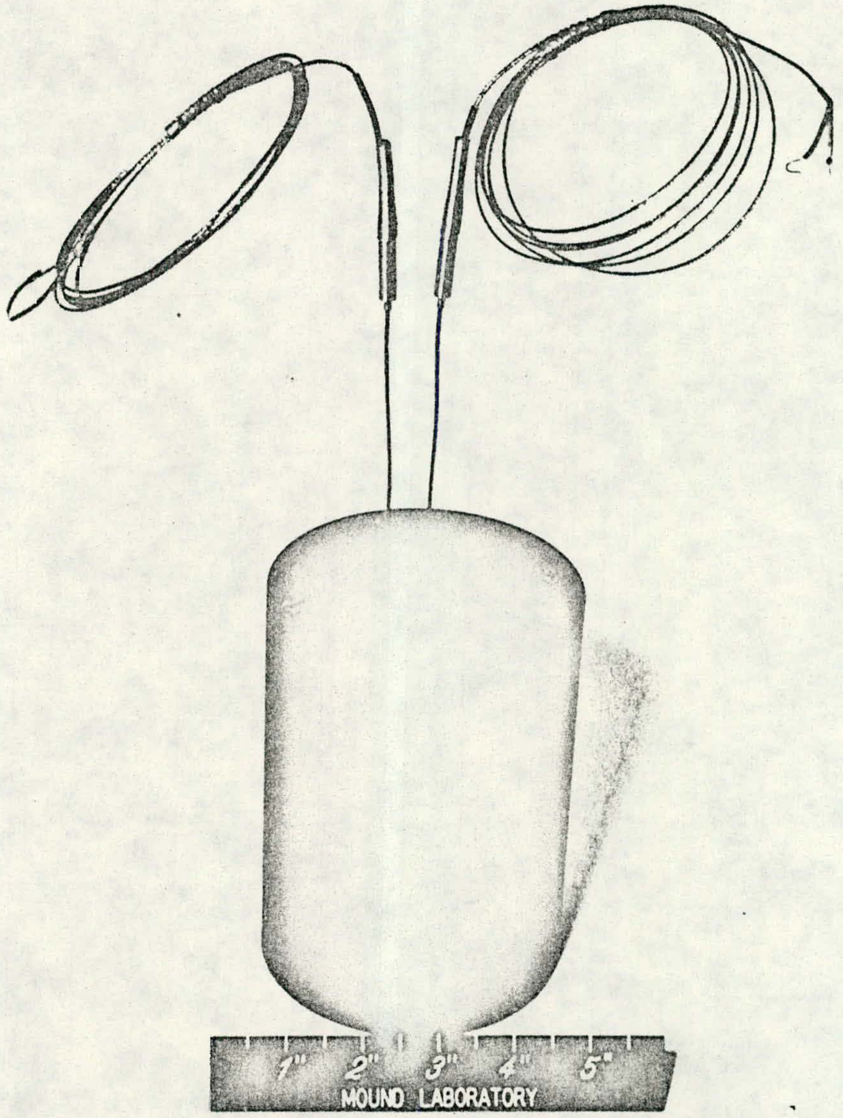

FIGURE 2 - The assembled sample holder is shown with thermocouples in-place.

RESULTS

The temperature versus time data of the experiment were read out in digital form on the computer terminal every two seconds. Samples of these data are reproduced in Figure 3. Inspection of the figure shows that significant self heating begins to occur at a wall temperature of about 470°C. The ignition point was identified by a sharp jump of the center temperature off the scale of the A/D converter in the LPS (maximum digital number corresponded to 1038°C). The wall temperature rose to only 719°C at this point, evidently because of the large heat capacity of the graphite sample holder. Inspection of the sample after burning revealed that combustion was complete. Most of the molten thermite reaction products had drained out of the sample holder through a 6.35 mm diam hole in the lower end cap.

The wall ignition temperature observed for the thermite part described above was 511.5 ± 0.5°C. At that point, the center temperature was 522.5 ± 0.5°C. From these data and Eq. 6, an activation energy of 642 ± 58 kJ/mol for the reaction of Eq. 7 was obtained.

In order to calculate the preexponential factor, A, additional measurements are required. The thermal conductivity was previously determined in our laboratory by the comparative method [6] with a Dynatech Corporation model TCFCM thermal conductivity instrument. The result obtained was $\lambda = 6.0 \pm 0.4$ W/m·K at 500°C for Al/Cu_2O thermite consolidated to $\rho = 4.71$ g/cm^3. The heat of reaction, Q, was determined by bomb calorimetry to be 1080 ± 20 kJ/mol. The value of the pseudo-zero order preexponential factor calculated from these values and Eq. 5 is $\log A = 42.4 \pm 3.9$ when A is in $mol \cdot m^{-3} \cdot s^{-1}$. A summary of all relevant measurements, results, and the uncertainty in each is given in Table 1.

DISCUSSION

It is interesting to compare the observed wall ignition temperature of 511.5°C with the reported result of 545°C as measured by differential scanning calorimetry (DSC). [7] The discrepancy is easily explained by the ignition theory through Eq. 5. Though it is not immediately obvious from the form of Eq. 5, we have found through reiterative solutions by the Newton-Raphson procedure that T_O has an inverse dependence on r. We therefore expect the very small sample used in DSC to have a higher ignition temperature than the 2.87 cm diam cylindrical sample of this experiment.

The values obtained for E and A may seem quite high when compared to those of other reactions with which chemists are familiar. One must keep in mind, however, that the thermite reaction is unusual both in its high temperature requirement for thermal ignition and in its speed once ignition has occurred. A high-activation energy is totally consistent with the high temperature required for reaction.

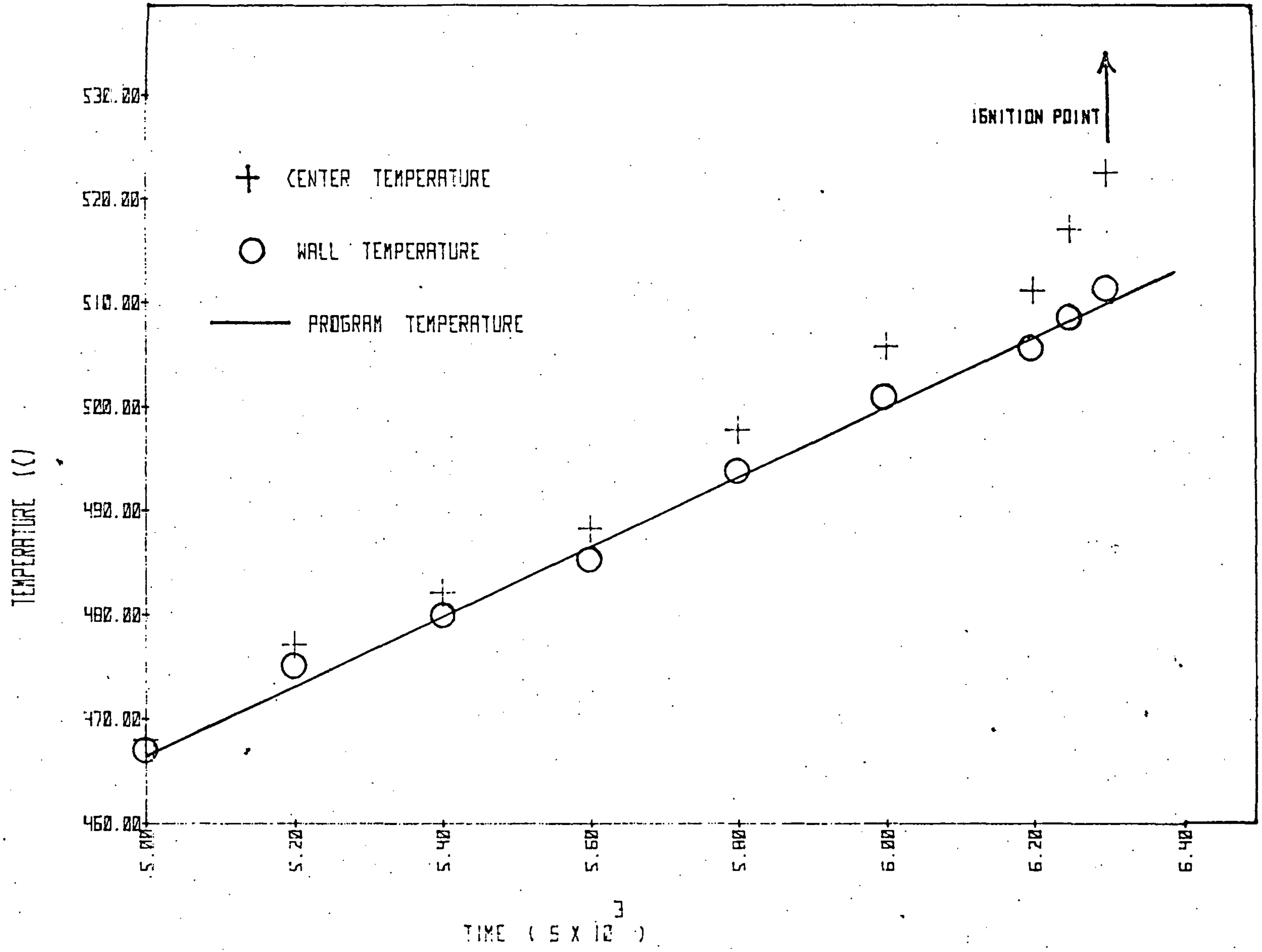

FIGURE 3 - Temperatures acquired by the FOCAL-11 program operating through the LPS are shown here. The upper set of points represents the center temperature, the lower set represents the wall temperature, and the line represents the temperature program. Because a total of over 6000 temperatures were acquired at a print out frequency of 0.5 Hz, only sample points are shown. It is clear that significant self-heating does not occur until the sample is brought within about 40°C of its ignition temperature.

Table 1

SUMMARY OF MEASURED QUANTITIES AND UNCERTAINTIES

Quantity	Value	Uncertainty ($\pm$%)	Method
Q (kJ/mol)	1080	2	Bomb calorimetry
λ (W/m·K)	6.0	7	Comparative
r (cm)	1.435	0.5	-----------
T_o (K)	784.5	0.06	This experiment
T_c (K)	795.5	0.06	This experiment
ΔT_m (C)	11.0	9	This experiment
E (kJ/mol)	642	9	This experiment
log A (mol/m^3·s)	42.4 ± 3.9	-	This experiment
dT/dt (°C/min)[a]	2.0	2	This experiment
ρ (g/cm^3)[a]	4.71	1	This experiment

[a] Quantities not required for determination of E and A.

Furthermore, a large value of the pseudo-zero order preexponential factor is consistent with the fast burn rate observed after initiation. The preexponential factor measured must contain a density and particle size dependence. However, additional experiments will be required to separate these factors out.

The experimental uncertainties reported for E and A compare favorably with typical uncertainties from classical kinetic methods. It should be pointed out, however, that these uncertainties are reflections of only the random error caused by least measure, resolution, and noise limitations of the technique. There may be systematic errors present that cannot be evaluated at this time. The first of these arises from the assumption that a chain mechanism is not involved in the reaction. Although a total lack of mechanistic information makes us unable to rule out a chain, it is felt that there is less liklihood of it with a solid-state reaction, which may be diffusion controlled, than with many of the gas phase reactions to which ignition theory has previously been applied. The second possible systematic error is the finite heating rate used. An improvement in experimental technique would be the determination of ignition temperatures at several slow heating rates, followed by extrapolation to the required condition, $dT/dt = 0$.

We know of no other measurements of the kinetic parameters for the Al/Cu_2O thermite reaction with which to compare our results. Such comparisons would, in any case, be difficult, for it shoud be noted that our results are specific to the Al and Cu_2O powder sizes and the density of the sample used here. The lack of other data on the kinetics of the Al/Cu_2O thermite reaction derives from three major causes. First, solid-state reactions are difficult to follow by the classical kinetic method of following concentration as a function of time. Second, the reaction occurs at an appreciable rate only at high temperatures. Finally, the reaction is so exoergic that it is impossible to carry out isothermally, as is done in most classical kinetic experiments. Therefore, we believe that this method is the best one for determination of the rate constant for the reaction of consolidated thermite. In addition, we expect that the method will be applied to many other pyrotechnic systems in the future.

ACKNOWLEDGEMENTS

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