

KINETIC PARAMETERS FROM SELF-HEATING MEASUREMENTS ON EXOTHERMIC SOLID-STATE REACTIONS

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ABSTRACT

A method, based on the autoignition criterion, has been developed that exploits the self-heating phenomenon to determine the activation energy, E , and pseudo-zero order pre-exponential factor, A , for highly exothermic solid state reactions. Simultaneous measurement of center and wall temperatures of a cylindrical solid during programmed heating to the ignition point leads to direct calculation of the kinetic parameters. The method has been applied to the thermite reaction $3 \text{Cu}_2\text{O} + 2 \text{Al} \rightarrow 6 \text{Cu} + \text{Al}_2\text{O}_3 + 2406 \text{J g}^{-1}$. Values of $E = 658 \text{ kJ mole}^{-1}$ and $\log A = 41.1$ (A in $\text{mol m}^{-3}, \text{sec}^{-1}$) were found for the reaction

INTRODUCTION

Extraction of kinetic parameters from programmed heating experiments such as differential thermal analysis (DTA), differential scanning calorimetry (DSC), and thermogravimetry (TG) is a topic that is currently under intense investigation by researchers in the fields of thermal analysis and non-isothermal kinetics. This fact is witnessed to most effectively by the plethora of analytical methods being proposed in the current literature for extraction of the parameters. E , the activation energy; A , the pre-exponential factor; and n , the reaction order. In addition to the more classical methods that have been in use for a decade or so [1], many new methods have been presented in just the past few years [2]. All these methods based on DTA, DSC, and TG are most reliable for reactions or processes that are not too exothermic. If a reaction is more than moderately exothermic there are two problems encountered in extracting reliable kinetic parameters from programmed heating experiments. First, the self-heating phenomenon causes a temperature distribution through the sample which decreases in uniformity with increasing reaction exothermicity. Second, for highly exothermic reactions, a sample cannot be heated slowly enough to avoid thermal explosion. Both effects have been thoroughly investigated and described by Merzhanov et al [3]. Their calculations show that for the thermal decomposition of pyroxy-

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line (exothermicity, $Q = 4707 \text{ J g}^{-1}$), the surface-to-center temperature difference in the sample can be greater than 30°C . The magnitude and sign of this temperature difference are highly dependent on the heating rate.

Clearly a method for extraction of kinetic parameters from programmed heating of highly exothermic materials is needed. Our purpose here is to present such a method. This method exploits the self-heating phenomenon and the center-to-surface temperature difference associated with it. The analytical foundation for this method has been described by Frank-Kamenetskii [4]. Briefly, it begins with the heat flow equation for long cylinder geometry, which was chosen both for experimental convenience and mathematical simplicity. If the cylinder's length, L , is much greater than its radius, r , ($L/r > 6$ is sufficient) we have, to a very good approximation, a one-dimensional problem, the heat equation for which is

$$c\rho \frac{\partial T}{\partial t} - \lambda \left(\frac{\partial^2 T}{\partial x^2} + \frac{1}{x} \frac{\partial T}{\partial x} \right) = QA \exp(-E/RT) \quad (1)$$

where T is the absolute temperature, c is the heat capacity, ρ is the density, λ is the thermal conductivity, t is time, x is the spatial coordinate, Q is the exoergicity, and R is the gas constant. We also wish to introduce the dimensionless variables, $\theta = E(T - T_w)/RT_w^2$ and $z = x/r$ in which T_w is the wall temperature of the sample. If one limits application to very low heating rates the first term in eqn. (1) can be dropped and one is left with a steady-state equation. Use of the Tode's approximation

$$\frac{E}{RT} \simeq \frac{E}{RT_w} \left(1 - \frac{T - T_w}{T_w} \right) \quad (2)$$

allows the analytical solution under steady-state conditions to be found as

$$\theta = \ln(8/\delta) - 2 \ln(e^{-b}z^2 + e^b) \quad (3)$$

in which δ is the criticality parameter and is defined as

$$\delta = \frac{QEAr^2 \exp(-E/RT_w)}{\lambda RT_w^2} \quad (4)$$

and b is an integration constant given by $b = \cosh^{-1} \sqrt{2/\delta}$. The heat flow equation for a long cylinder cannot be solved for $\delta > 2.00$. Any combination of parameters leading to $\delta > \delta_{cr} = 2.00$ will result in a situation which corresponds physically to thermal explosion. Substitution of $\delta_{cr} = 2.00$, $z = 0$, and $T = T_c$, the center temperature, into eqn. (3) shows that the maximum temperature difference, $\Delta T_m = T_c - T_w$, just prior to explosion is given by

$$\Delta T_m = 1.38 RT_0^2/E \quad (5)$$

where T_0 is the wall temperature at the critical point.

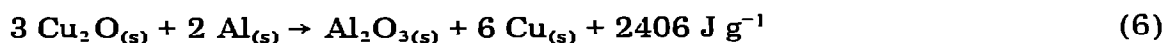
It should be recognized that the term thermal explosion is used loosely in the above discussion. What is really meant is a chemical reaction that has a continually increasing velocity due to conditions having reached the point at which thermal energy is being produced by the reaction faster than heat conduction is carrying it away. Whether or not an explosion as we normally

think of it actually occurs is mainly dependent upon whether a gas is produced in the reaction. The reaction of interest in this study, for example, is essentially gasless and a very rapid burn is all that is observed when critical conditions are exceeded.

From eqn. (5) it can be seen that simultaneous measurement of the center and wall temperatures of a sample heated at an infinitesimally slow rate yields the quantity E . By referring to the computer calculation of Merzhanov et al. [3] it is clear that at heating rates of $\leq 2^\circ\text{C min}^{-1}$ the observed temperature difference is very close to the steady-state value. To account for the perturbation due to the finite heating rates used we have plotted the values obtained for E as a function of the heating rate and extrapolated to infinitesimally slow heating. The same procedure was used to determine A which is calculated from eqn. (4) once E has been found. We wish to emphasize at this point that A , as formulated above, is a pseudo-zero order pre-exponential factor. Equation (1) is valid only over the initial part of the reaction because of the use of a constant value, A , to represent the product of a true pre-exponential factor and a factor giving the composition dependence of the reaction.

EXPERIMENTAL

The chemical reaction chosen for this study is the thermitic reaction



This reaction seems to be especially amenable to the method because it produces very little gas (only interstitial air and some copper vapor) that could result in explosion and consequent damage to laboratory apparatus. The sample mixture was prepared by mixing stoichiometric quantities of aluminum powder (Reynolds XD28) and Cerac "Pure" Cu_2O powder. For product application reasons and in order to remove as much interstitial air as possible, the mixture was hot pressed in a graphite die for 1 h at 480°C and $4.79 \times 10^5 \text{ N m}^{-2}$ pressure. These conditions yielded a compacted sample of high tensile and shear strength having a density of $88 \pm 1\%$ of the theoretical maximum value of 5.29 g cm^{-3} . The consolidated cylindrical sample of dimensions $r = 1.435 \text{ cm}$ and $L = 10.19 \text{ cm}$ was inserted into a graphite sample holder (shown in Fig. 1), and end caps were screwed in place in order to fix the position of the sample. Stainless-steel-sheathed chromel-alumel thermocouples were inserted into predrilled holes in the graphite holder and thermite sample at the cylinder wall and center, to a depth of half the length of the cylinder. The assembled sample holder and thermocouples are shown in Fig. 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 Digital Equipment Corporation 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 turned on and off, as required, at

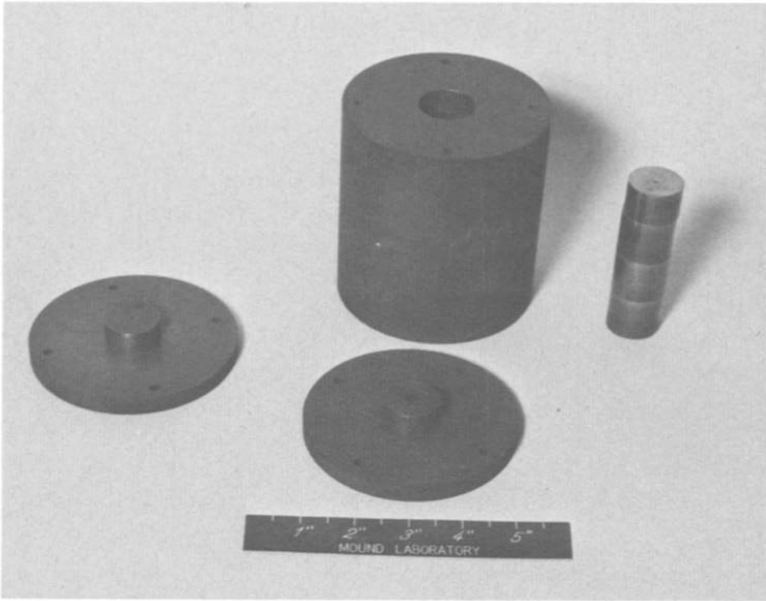


Fig. 1 The thermite sample (right), sample holder (top center) and end caps (foreground) are shown here.

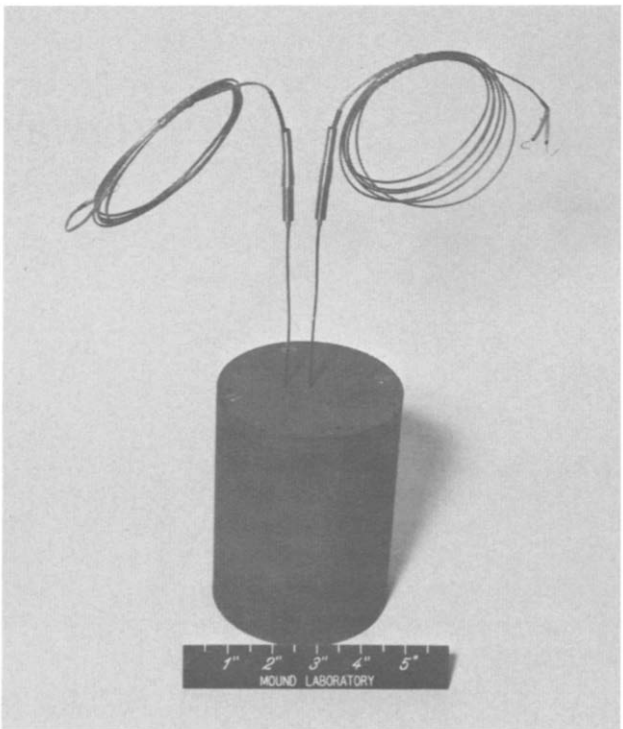


Fig 2. The assembled sample and holder are shown here with thermocouples in place

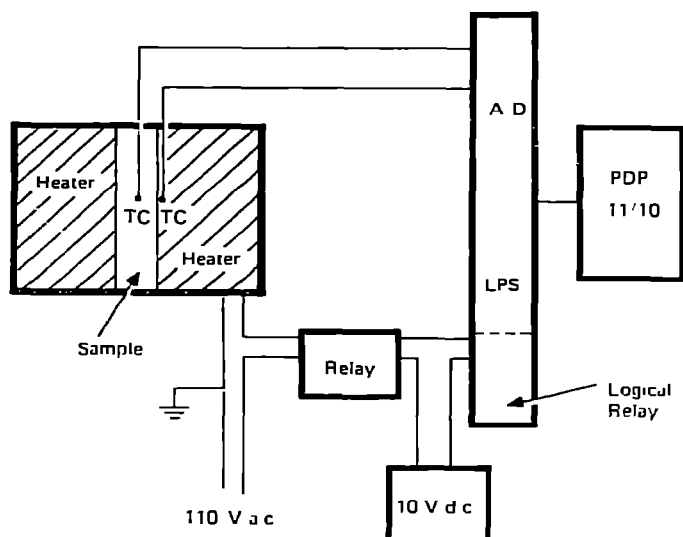


Fig. 3. The block diagram shows schematically how the PDP-11/10 computer working through the LPS interface both acquires the data and controls the heating rate

a frequency of 1 Hz. Time proportional temperature control was attempted, but adherence of the sample temperature to the program temperature, which was $\pm 1.5^\circ\text{C}$ at temperatures above 400°C , showed no improvement over simple on-off control. The heating rates used were $10^\circ\text{C min}^{-1}$ up to 300°C , 5°C min^{-1} from 300 to 450°C , and whatever heating rate (always $\leq 2^\circ\text{C min}^{-1}$) was desired above 450°C . Figure 3 shows a block diagram of the heater, sample holder, thermocouples, and the computer-LPS used for temperature acquisition and control.

RESULTS

The temperature as a function of time data of the experiment were read out in digital form on the computer terminal every 2 sec. Samples of these data (from trial 0 of Table 1) are reproduced in Fig. 4. Inspection of the

TABLE 1
Kinetic determinations on Al/Cu₂O thermite

Trial No	0	3	4
Sample density (% tmd) *	88.6 ± 1	87.7 ± 1	86.5 ± 1
Heating rate ($^\circ\text{C min}^{-1}$)	2.0 ± 0.5	1.5 ± 0.5	0.84 ± 0.20
Wall ignition temp. ($^\circ\text{C}$)	511.5 ± 0.5	524.8 ± 0.5	537.2 ± 0.5
Center ignition temp. ($^\circ\text{C}$)	522.5 ± 0.5	538.6 ± 0.5	548.8 ± 0.5
Maximum temp. difference ($^\circ\text{C}$)	11.0 ± 1	13.8 ± 1	11.6 ± 1
Activation energy (kJ mole ⁻¹)	642 ± 58	529 ± 40	667 ± 60
Pre-exponential factor (mol m ⁻³ sec ⁻¹)	$10^{42.4 \pm 3.9}$	$10^{34.4 \pm 3.1}$	$10^{42.7 \pm 3.9}$

* % tmd = Percent of theoretical maximum density

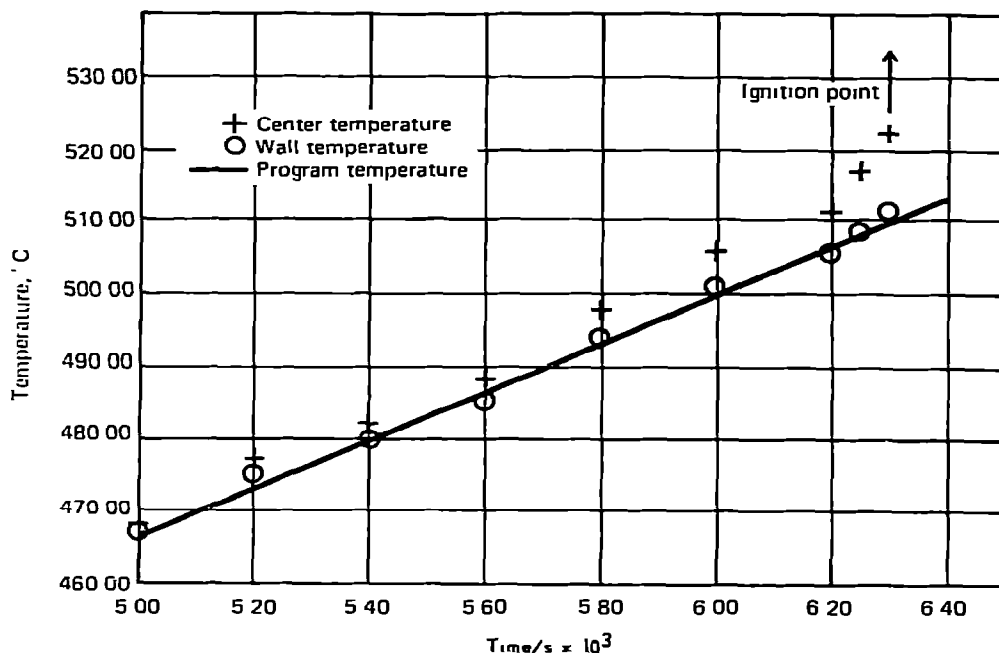


Fig. 4. Temperatures acquired by the FOCAL-11 program operating through the LPS are shown above for Trial 0. Only sample data points are shown for clarity because temperatures were acquired at a frequency of 0.5 Hz.

figure shows that significant self-heating begins 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 for this run rose to only 719°C at ignition, evidently due to the large heat capacity of the graphite sample holder. Two additional experiments were performed.

Physical quantities other than the temperature difference at ignition are required for the calculation of A . The thermal conductivity, $\lambda = 6.0 \pm 0.4 \text{ W m}^{-1} \text{ K}^{-1}$, was determined by the comparative method [5] and the heat of reaction, $Q = 1080 \pm 20 \text{ kJ mole}^{-1}$, was determined by bomb calorimetry.

Recall that the mathematical foundation for this method requires infinitesimally slow sample heating. The activation energies of Table 1 are apparent values at their respective heating rates. To get the true value of E a linear least squares analysis of the E as a function of heating rate data was performed and a value at the intercept, $E = 658 \text{ kJ mole}^{-1}$, was obtained. The same analysis was performed for $\log A$ and a value at the intercept, $\log A = 41.1$ (A in $\text{mole m}^{-3} \text{ s}^{-1}$), was found. It is not clear that either E or $\log A$ should be linear in the heating rate. Because of the low number of data points and their scatter there is no information to suggest a better form, however. A theoretical investigation of what this form should be is one of the first steps to be undertaken in the continued development of this method. The uncertainties in E and $\log A$, estimated purely on the basis of the scatter of the data to be about $\pm 25\%$, are quite high. It is hoped that a future collection of additional data points will lower this uncertainty considerably.

DISCUSSION

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. Further, a large value of the pseudo-zero order pre-exponential factor is consistent with the fast burn rate observed after initiation. The pre-exponential factor measured must contain a density and particle size dependence. Additional experiments are required, however, to isolate these factors.

We know of no other measurements of the kinetic parameters for the Al/Cu₂O thermite reaction with which to compare our results. Such comparisons would, in any case, be difficult, for it should be noted that our results are specific to the aluminum and Cu₂O powder sizes and the density of the sample used here. The lack of other data on the kinetics of the Al/Cu₂O thermite reaction derives from three major causes. First, solid state reactions are difficult to study 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 maintain isothermal conditions, as is done in most classical kinetic experiments. We believe, therefore, that the method described above is the best method for determination of the rate constant for the reaction of consolidated thermite. In addition, we expect the method to find applications to other systems.

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