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THERMAL ANALYSIS AND KINETICS OF THE $TiH_x/KClO_4$ SYSTEM

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ABSTRACT

A combined experimental and theoretical study of the system $TiH_x/KClO_4$ has been undertaken to investigate the thermodynamic and kinetic aspects of initiation of the $TiH_x/KClO_4$ pyrotechnic system and to obtain parameters of interest in mathematical modeling of the initiation and propagation from a hot bridgewire source. Experimental results along with kinetic computations are of interest in understanding the chemical processes involved and in determining the stability of the pyrotechnic system. Initial computation from a number of experimental reaction exotherms obtained by use of a differential scanning calorimeter yielded a reasonably consistent set of kinetic parameters over a range of heating rates.

1. INTRODUCTION

An interest in the initiation characteristics and long term stability of the pyrotechnic materials $TiH_x/KClO_4$ led to a thermoanalytical study of these materials. Thermoanalysis data were obtained by use of both a Perkin-Elmer DSC-2 differential scanning calorimeter and a Mettler TA-1 thermobalance. This discussion will be confined to the results of work with the differential scanning calorimeter (DSC) because the thermal output is directly calorimetric. Typical exotherms obtained in the initiation temperature region for the pyrotechnic blend containing titanium subhydride and potassium perchlorate are shown in Figures 1 and 2.

A kinetic analysis of the thermal data established a basis for predicting the behavior of these pyrotechnic blends at other temperatures such as would be experienced during rapid initiation or at somewhat lower temperatures where a slow, prolonged reaction would be evidence of a compatibility problem. The kinetic analysis consisted of fitting DSC data to a series of Arrhenius equations, each associated with an apparent separate process.

2. EXPERIMENTAL

The experimental procedure involved heating small samples of pyrotechnic blends at constant heating rates through the temperature range of interest. Only features of the DSC curves in the vicinity of the reaction exotherm were treated in this study. No significant features were observed between the phase change in $KClO_4$

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at 573 K and the reaction exotherm at approximately 750 K. The sample weight was limited to approximately 100-150 μg to minimize temperature gradients through the sample. The powder samples were spread thinly over the sample pan surface, again to minimize temperature gradients and thermal resistance. The samples were contained in sealed platinum pans with pressed-on lids. Considerable quantities of gas were released during the reaction exotherm; these gases had to be contained to minimize thermal losses as ΔPV work. Samples larger than about 140-150 μg tended to vent, with corresponding large thermal losses.

Because the differential scanning calorimeter operates on the principle of maintaining a constant heating rate by electrical heating with compensation for sample exothermic or endothermic changes, the sample temperature was maintained very close to the programmed temperature. In addition, a relatively large thermal mass or heat sink was available to supply or dissipate heat during large thermal effects. During the measuring cycle the sample pan was maintained at the same temperature as in the reference pan. Differences in electrical energy required to maintain identical temperatures in both pans were converted directly to heat flow, i.e., dq/dt in units of mcal sec^{-1}. Output (heat flow as a function of time) was converted to punched cards for data reduction. The temperature was calculated from the initial temperature and heating rate.

Several techniques were used in an attempt to obtain kinetic parameters for these pyrotechnic reactions. Initially, isothermal annealing work was done to obtain constants for the Arrhenius equation. Very large deviations were observed in the energy obtained after isothermal annealing. Little useful information was obtained from the poor isothermal annealing data when an attempt was made to obtain the constants for an Arrhenius equation. It was then decided to attempt a direct fit of the data by a chisquare minimization technique. This work assumes an exponential rate dependence on temperature and a power dependence of rate on concentration of reactive material present. It is further assumed that the heat evolved in the reaction can be used as a measure of the completeness of reaction.

3. DISCUSSION

The output of the differential scanning calorimeter after appropriate adjustment of baseline was used directly as the rate of reaction. The rate of heat production was assumed to be directly proportional to the reaction rate and the quantity of heat released at a given time was assumed proportional to the extent of the reaction.

If we assume the Arrhenius equation, then the output of the calorimeter, dq/dt in mcal mg^{-1} sec^{-1}, can be represented by

$$(d_q/dt)_i = A\,(Q_i)^n e^{-\varepsilon/RT_i} \qquad (1)$$

where subscript i represents the i^{th} data point, $(dq/dt)_i$, at temperature T_i. The quantity Q_i can be obtained by a numerical integration over dq/dt from a temperature where (dq/dt) is essentially 0 to the i^{th} data point. The equation defining Q_i, the fractional heat remaining at time t_i and temperature T_i, is:

$$Q_i = 1 - \frac{\int_0^{t_i} dq/dt \cdot dt}{\int_0^{\infty} dq/dt \cdot dt}, \qquad (2)$$

where $t_i = T_i/(dT/dt)$

The denominator in Equation 2 is the integral over the total exotherm and represents complete reaction.

If we assume that the total exotherm represents a single process we can use a chisquare minimization technique to fit the data to the above Equation 1. This can be and has been done. However, the exotherms appear to represent more than one process as indicated by the several peaks observed in the exotherms of Figures 1 and 2. In Figure 1 a major maximum appears at about 885 K with subsidiary maxima at about 835 K and 810 K. In Figure 2 the major maximum is at about 940 K with at least one subsidiary maximum at about 860 K. If these subsidiary peaks are assumed to be produced by separate processes it would be desirable to fit each process separately.

A technique has been developed to separate the peaks by first fitting the higher temperature region of the high temperature peak where there appears to be little interference from lower temperature processes. Equations 1 through 3 are assumed to hold for each single process with appropriate constants for Equation 1. Special procedures, however, are required to obtain the function Q_i since a simple integration from T_0 to T_i will not yield the proper value of Q_i.

Equation 2 yields the following

$$Q_i = \frac{\int_0^{\infty} dq/dt \cdot dt - \int_0^{t_i} dq/dt \cdot dt}{\int_0^{\infty} dq/dt \cdot dt} \qquad (3)$$

and

$$Q_i = \frac{\int_{t_i}^{\infty} dq/dt \cdot dt}{\int_0^{\infty} dq/dt \cdot dt} \qquad (4)$$

If we then let

$$\Lambda = A/(\int_0^{\infty} dq/dt \cdot dt)^n \qquad (5)$$

and

$$\Omega_i = \int_{t_i}^{\infty} dq/dt \cdot dt \qquad (6)$$

then Equation 1 becomes

$$(dq/dt)_i = \Lambda(\Omega_i)^n e^{-\varepsilon/RT_i} \qquad (7)$$

Equation 7 allows us to fit a peak from an arbitrary T_i to the high temperature cutoff where no more reactive material remains.

An iterative procedure is required to obtain the values for the Ω_i function for each T_i from Λ, n, ε and the computed value of $(dq/dt)_i$.

One such procedure used here follows:

let $\quad D_i = \text{computed } (dq/dt)_i \qquad (8)$

$$\delta = 0.5\ (t_{i+1} - t_i) \qquad (9)$$

$$F = D_i - D_{i+1} \cong (dq/dt)_i - (dq/dt)_{i+1} \qquad (10)$$

$$E_i = \Lambda e^{-\varepsilon/RT_i} \qquad (11)$$

then $\mathrm{DIF} = E_i[\Omega_{i+1} + \delta(2D_i+F)]^n - F - D_{i+1}$

$$\mathrm{DIF} = E_i[\Omega_{i+1} + \delta(2D_i+F)]^n - F - D_{i+1} \qquad (12)$$

$$F = F + \mathrm{DIF} \qquad (13)$$

$$D_i = D_{i+1} + F \qquad (14)$$

$$\Omega_i = \Omega_{i+1} + \delta(2D_i + F). \qquad (15)$$

The values of D_i and Ω_i become the new estimates for the chisquare fitting procedure.

4. RESULTS

These techniques have been applied to a limited number of differential scanning calorimeter data runs. Reasonably consistent sets of parameters have been obtained for A, n and ε over a fairly wide range of heating rates. The values obtained for the Arrhenius equation constants are shown in Table 1. The heating rates cover a range of 40 K min^{-1} to 320 K min^{-1}. The fastest heating rate available on the calorimeter is 320 K min^{-1}. Slower heating rates have been run, but to date no fits have been attempted at the slower heating rates.

A typical plot of the fitted data is shown in Figure 3 for data obtained at 40 K min^{-1}. The solid curve is the raw data after baseline adjustment. The dotted line is the computed dq/dt from the Arrhenius constants. The dashed lines are the Q functions corresponding to the fitted curve. This fit was obtained for the temperature region 850 K to 895 K. A fit of data obtained at 160 K/min is shown in Figure 4. The residual fit for this data is shown in Figure 5 and the second residual in Figure 6.

Upon comparing the calculated exotherm curves in Figures 3 through 6 with the the experimental, it appears that the Arrhenius constants derived by this fitting technique can be used to predict initiation processes occurring at somewhat faster heating rates where the major exotherm occurs at a higher temperature. This, of course, assumes the data are a reasonable measure of the rate of the reaction of interest. Over the range of heating rates studied the activation energy, ε, does not vary greatly, indicating that this assumption is reasonable.

5. FUTURE PLANS

Extending the work to much lower heating rates should give an indication of the reliability of the data. There are techniques available which can be used to estimate the effect of thermal resistance. Large thermal resistance would indicate lower temperature than actually exists. Corrections have been made using the phase change in $KClO_4$ as an indication of actual temperature. It is possible to use the shape of the endotherm occurring during a phase change to obtain an indication of the extent of thermal resistance and thus obtain an additional temperature correction. This correction has not been incorporated into this work, but will be included in future work.

Using the Arrhenius parameters obtained by this technique without applying additional temperature corrections to the raw data should yield lower reaction rates at lower temperatures than would be obtained with additional temperature corrections. Any temperature corrections would indicate a higher observed temperature than indicated by the raw data. The corrections would then yield a less rapid rate of increase of dq/dt and a subsequent lowering of the computed activation energy, ε. To date, the extent of this correction and the effect on activation energy have not been determined. This correction will be applied in future work.

Improvements in the fitting technique are possible, but it is not anticipated that radical changes in the computed parameters will result. An improved chisquare search routine would improve the precision of the fitting process for any data set, but would not be expected to make large changes in the parameters. A second obvious improvement would be to extend the technique to fit data over several peaks. This appears to be possible in principle. A slight change in the iterative procedure for computing Ω_i in Equations 10 through 15 will allow an independent computation of Ω_i for each peak. In principle a more consistent set of Arrhenius parameters would be obtained over the full temperature range of the data. In practice, however, obtaining a convergence in the fitting process may be quite difficult, or indeed, impossible.

Future work will involve primarily improving the techniques for temperature corrections and secondarily improving the fitting procedure. An improved chisquare minimization search program will be developed and applied to a general fit of the DSC data over the complete reaction exotherm temperature range.

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John W. Reed is a senior research chemist with Monsanto Research Corporation, Mound Facility, where he has been employed for ten years. His chief responsibilities presently are physical properties of pyrotechnic materials and thermochemical properties and reaction processes involving pyrotechnic blends. Mr. Reed received a bachelors degree from Franklin and Marshall College in 1951 and has been involved with physical properties, thermodynamics and thermochemistry of energetic materials since that time while employed at Battelle Memorial Institute, at Callery Chemical Co., and with his present employer. Chief fields of interest have been rocket propellants, storage of energy in defects of crystal lattices and, presently, pyrotechnic materials.

Carl L. Fread has been employed by Monsanto Research Corporation for eleven years. During his term of employment Mr. Fread served as a health surveyor for four years and as a technician for seven years. As a technician, he worked in solid waste recovery, operated a thermal diffusion column system, and served as a research technician in thermoanalysis. Mr. Fread attended Miami University for three years and is presently enrolled at Wright State University.

Table 1

Heating Rate (K/min)	Peak Temperature (K)	A $(\text{cal}\cdot g^{-1}\cdot \text{sec}^{-1})$	Λ	η	ε $(\text{Kcal}\cdot \text{mole}^{-1}\cdot K^{-1})$	Range of Fit (K)
320	965	1.19×10^{21}	7.57×10^{18}	0.663	83.7	925-980
		3.91×10^{20}	2.38×10^{18}	0.666	81.3	920-980
		1.18×10^{20}	7.57×10^{18}	0.664	83.7	925-980
	890	1.03×10^{22}	2.11×10^{19}	0.946	84.5	865-945
160	930	9.34×10^{21}	3.30×10^{19}	0.782	85.3	915-950
		9.80×10^{21}	3.34×10^{19}	0.785	85.3	920-950
		1.11×10^{22}	3.45×10^{19}	0.795	85.7	925-950
		9.34×10^{21}	3.30×10^{19}	0.782	85.3	915-950
	865	1.53×10^{21}	8.19×10^{18}	0.867	79.0	845-900
		1.49×10^{21}	8.28×10^{18}	0.863	79.0	850-910
	830	7.23×10^{20}	3.18×10^{19}	0.773	77.4	820-850
		6.81×10^{20}	3.21×10^{19}	0.755	77.0	815-845
80	885	2.30×10^{20}	5.48×10^{18}	0.623	76.7	850-900
		5.38×10^{20}	5.07×10^{18}	0.726	79.4	865-900
		5.36×10^{20}	4.66×10^{19}	0.735	77.4	835-900
		6.08×10^{20}	4.80×10^{19}	0.749	77.8	855-900
	830	9.06×10^{20}	2.81×10^{19}	0.770	77.0	820-855
	800	1.22×10^{21}	2.81×10^{19}	0.546	73.8	785-815
40	885	6.32×10^{20}	2.62×10^{19}	0.581	79.3	850-895
		5.54×10^{21}	1.95×10^{21}	0.615	87.0	855-895
	835	4.10×10^{20}	1.13×10^{19}	0.372	74.2	827-845
	810	1.49×10^{20}	2.33×10^{19}	0.603	73.8	785-825
		1.48×10^{20}	2.32×10^{19}	0.602	73.8	781-825
(810 & 835 combined)		1.30×10^{20}	9.10×10^{18}	0.717	74.4	785-845

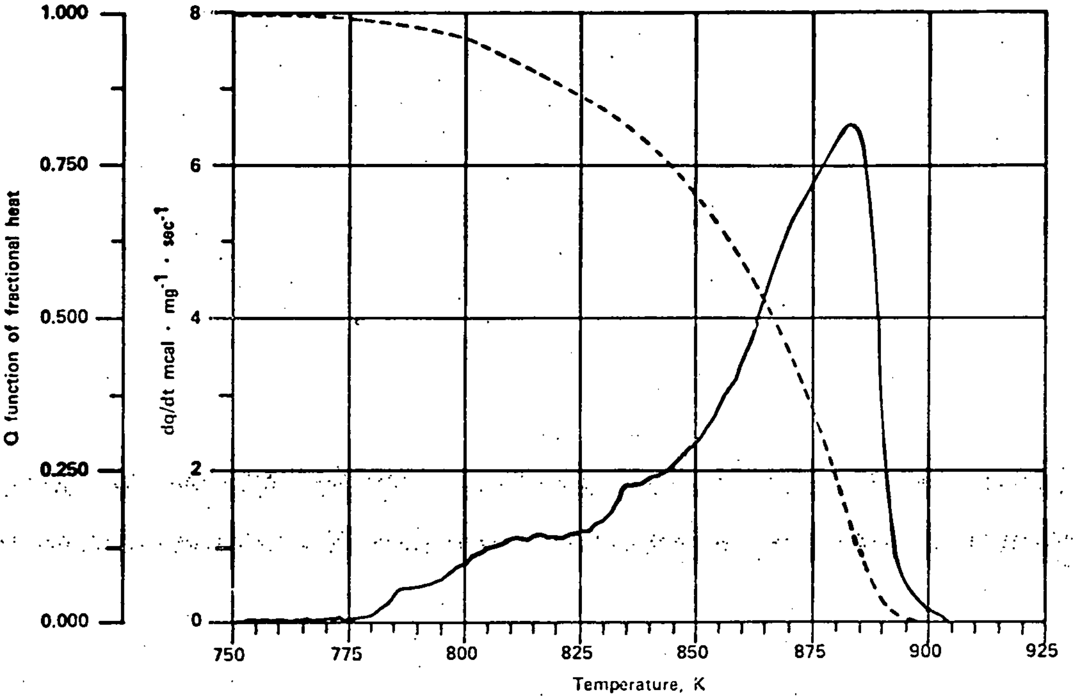

FIGURE 1 - Differential scanning calorimeter reaction exotherm obtained from $TiH_x/KClO_4$ pyrotechnic blend at a heating rate of 40 K•min^{-1}. The dashed line is the fractional heat remaining to drive the reaction process at temperature T.

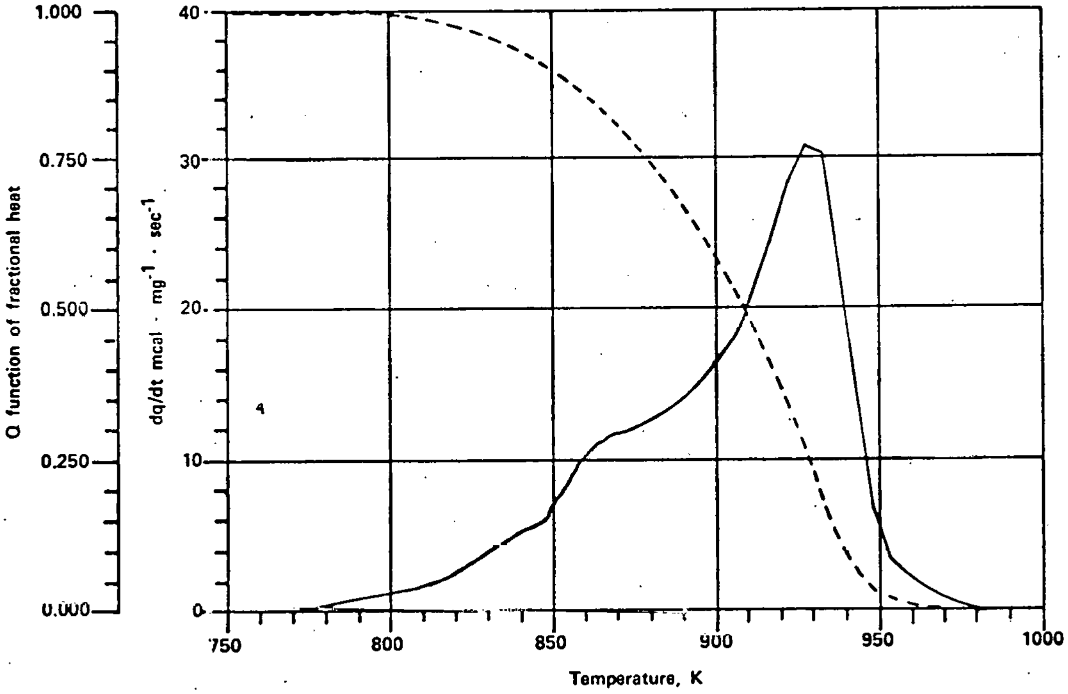

FIGURE 2 - Differential scanning calorimeter reaction exotherm obtained from $TiH_x/KClO_4$ pyrotechnic blend at a heating rate of 160 K•min^{-1} along with fractional heat remaining to drive the reaction process.

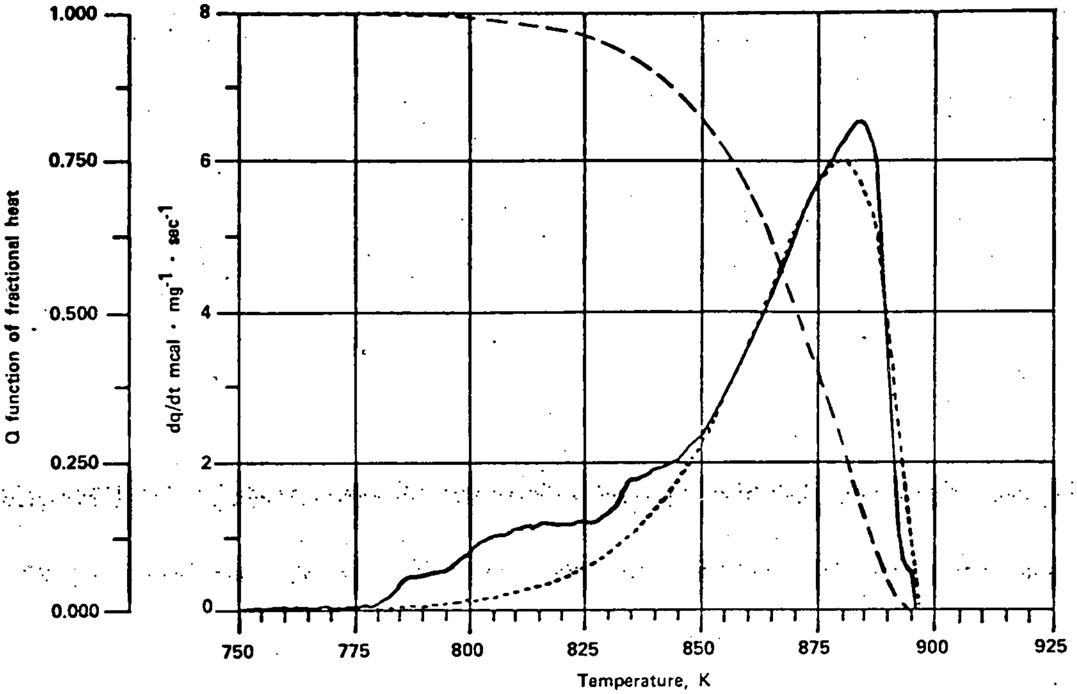

FIGURE 3 - Exotherm obtained from $TiH_x/KClO_4$ pyrotechnic blend along with the exotherm computed from the Arrhenius constants. Heating rate of 40 K·min^{-1} was used. The Arrhenius constants were obtained by fitting the 855 K peak over the region 855 to 895 K.

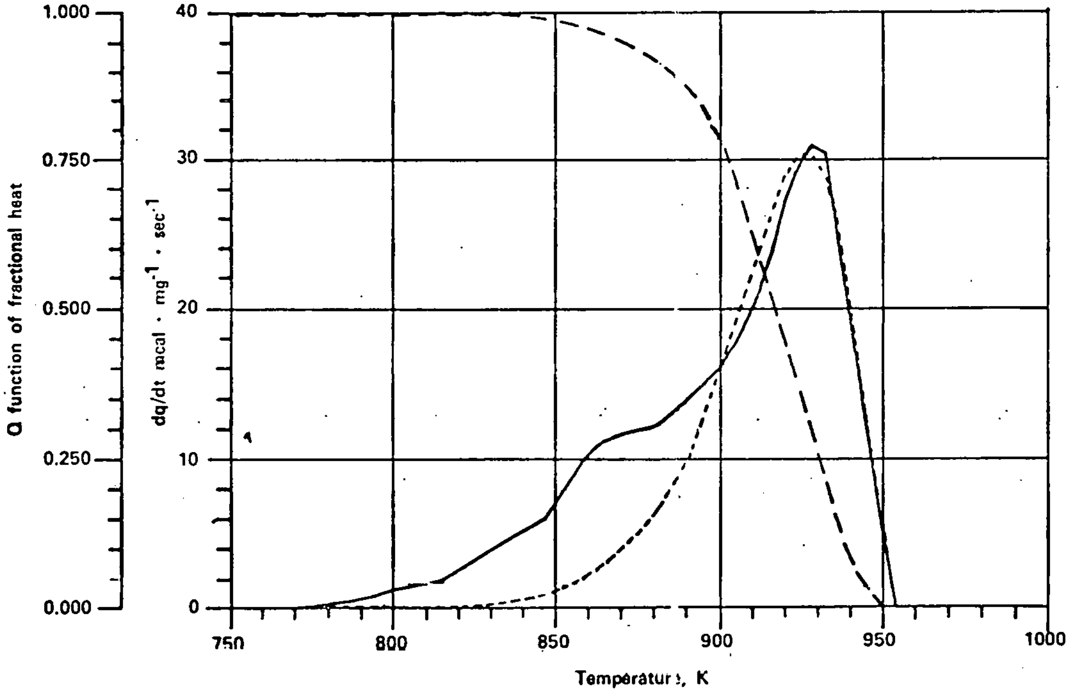

FIGURE 4 - Exotherm obtained from $TiH_x/KClO_4$ pyrotechnic blend at a heating rate of 160 K·min^{-1}. Dotted line is the computed exotherm computed from the Arrhenius constants. The Arrhenius constants were obtained by fitting data from the 930 K peak over a temperature range of 915 - 950 K.

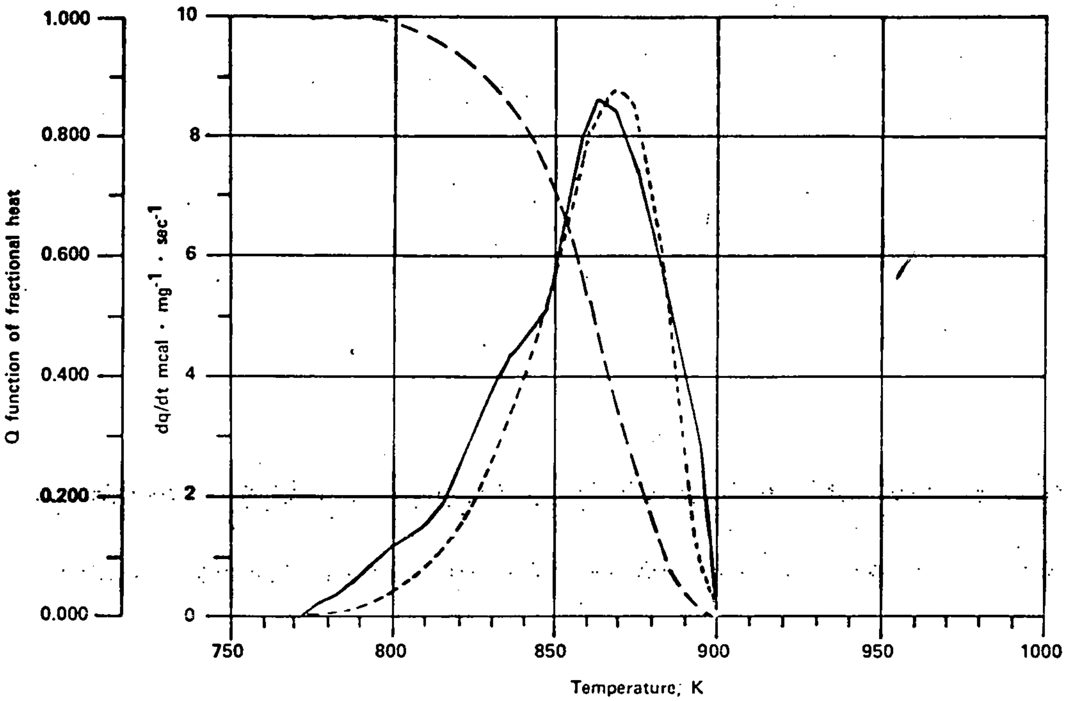

FIGURE 5 - The partial fit of residuals from fitting the 930 K peak of the exotherm obtained at a heating rate of 160 K·min^{-1}. Dotted line is the computed exotherm.

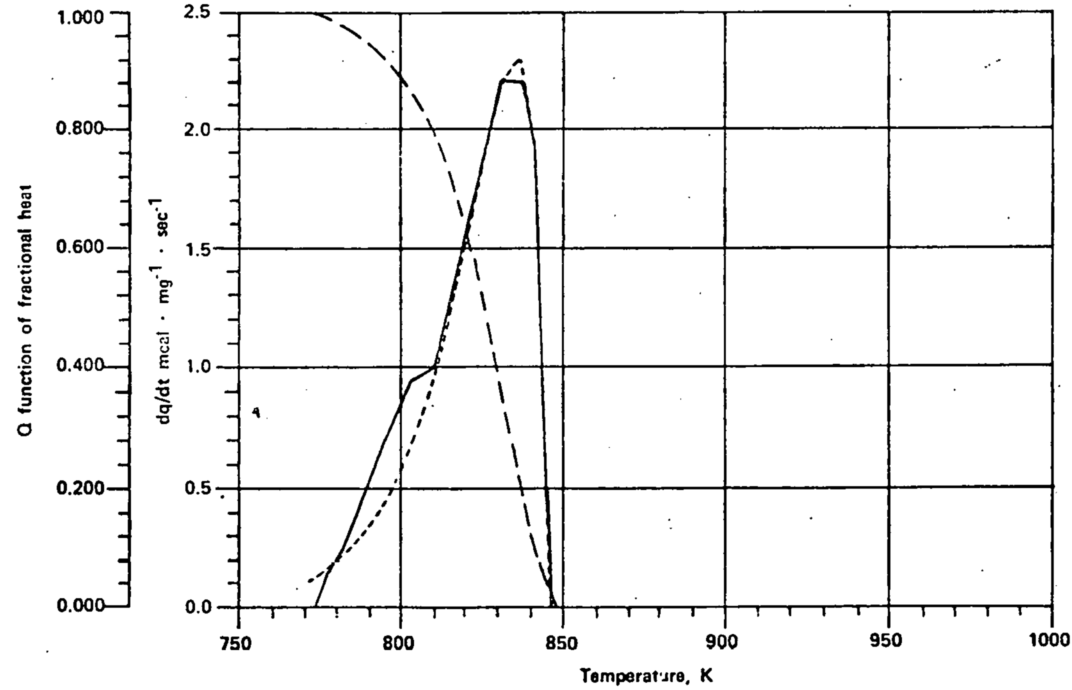

FIGURE 6 - The partial fit of residues from fitting the 870 K peak of the exotherm obtained at a heating rate of 160 K·min^{-1}. Dotted line is the computed exotherm.