

TECHNIQUE FOR MEASURING HEAT QUANTITY AND HEAT RELEASE KINETICS IN A CONDENSED PHASE

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A technique is described for measuring the heat release in a condensed phase. The substance studied, coated on a metal plate, is heated nearly instantaneously by electric current to the required temperature and is then maintained at a constant level in the course of the experiment. In the experiment we measure the amount of heat released (or absorbed) in the course of the chemical reaction and also the rate of heat release (or heat absorption).

Some data for pyroxylin are presented.

Measurements of heat release at temperatures above two hundred degrees encounter severe difficulties associated with the high rate of the chemical processes, on the one hand, and with the small values of the thermal conductivity and thermal diffusivity of the powders, on the other. The latter poses a fundamental temperature limit, above which it is impossible to obtain information on the kinetics of the chemical process, even having inertialess equipment, first because of the impossibility of heating a finite mass of matter sufficiently rapidly (i.e., avoiding chemical change in so doing) and, second because of the impossibility of transmitting the heat released to the metering element.

In the present paper we describe an impulsive technique for measuring the heat release rate and the overall amount of heat in the condensed phase of powders and explosives at high temperatures. The test material is applied in a very thin layer on the inner sides of two titanium plates which are folded together. This packet is heated impulsively by electric current to the required temperature. During this time the test material does not experience any marked chemical transformation. Thereafter the constant current I is passed through the packet to compensate for heat losses into the surrounding medium. The material begins to react, releasing (or absorbing) the heat, causing a rise (fall) of the temperature, which is measured by the change of the packet resistance. Because of the small thickness of the material layer, the temperature in the material is equal to the substrate temperature through the test time. The heat release (absorption) rate is calculated from the packet temperature change resulting from the chemical transformation. The temperature change (useful signal t) is determined by heating the packet twice: with the material (basic heating) and then without the material (control heating).

For the selected plate dimensions (thickness $d = 40 \mu$, length $L = 30$ cm) the heat losses at the ends do not exceed a fraction of a percent of the magnitude of the heat losses from the side surface. Therefore the heat balance equation for the packet has the form

$$(1 + \varphi) \frac{dT}{d\tau} = \frac{I^2 \Pi (1 + \beta T_0)}{c} - \frac{\alpha F - \beta \Pi I^2}{c} (T - T_0) + \frac{q}{c} \quad (1)$$

with the initial condition $T = T_1$ for $\tau = 0$.

Here T is the packet temperature; T_1 is the temperature reached as a result of impulsive heating; T_0 is the ambient temperature; τ is the time measured from the moment of termination of the impulsive heating; I is the current; α is the heat transfer coefficient; ω is the rate of heat release by chemical reactions; φ is the ratio of the specific heat of the test material to the specific heat of the packet; Π is the packet electric resistance at 0°C ; β is the packet temperature resistance coefficient; F is the side surface area; and c is the heat capacity of the packet.

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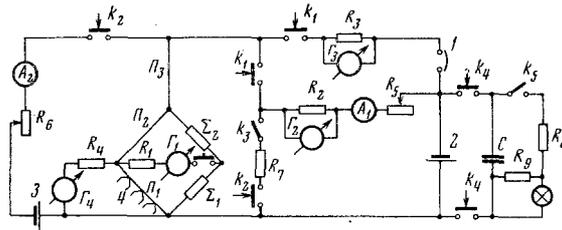


Fig. 1

For the control experiment (when $q = 0$ and $\varphi = 0$) the solution has the form

$$T_2 - T_0 = (T_* - T_0) + D e^{-k\tau} \quad (2)$$

$$k = \frac{\alpha F - \beta \Pi I^2}{c}, \quad T_* - T_0 = \frac{\Pi I^2 (1 + \beta T_0)}{\alpha F - \beta \Pi I^2}, \quad D = T_1 - T_* \quad (3)$$

We see from the solution (2) that the packet temperature in the course of time approaches the stationary value T_* with the time constant $1/k$. The differential equation describing the time variation of the useful signal t will be the difference of equations (1) for the basic and control heatings.

$$\frac{dt}{d\tau} + \frac{k}{1 + \varphi} t = \frac{q}{c(1 + \varphi)} - \frac{\varphi}{1 + \varphi} \frac{dT_2}{d\tau} \quad \text{for } \tau = 0, t = -t_0 \quad (4)$$

The experimental heat release rate q_1 is found from the simplified equation (4), in which we set $\varphi = 0$

$$\frac{dt}{d\tau} + kt = \frac{q_1}{c} \quad (5)$$

Analysis of the errors which arise in this case showed the following: a) the condition $D = t_0$ should be satisfied to reduce the experimental error; b) under the assumption that condition a) is satisfied, the relative error in the heat release rate and heat content for the majority of the practically important cases does not exceed $0.5 \varphi_0$, except for the initial period. The exception is eliminated if the initial heat capacity of the test material is taken into account in calculating q_1 and Q_1 for the times $\tau \leq (0.5-1) \tau_1$, where τ_1 is the reaction time.

From the in vacuo experiments for the packet of titanium plates of thickness 40μ it was found that the equalization rate $k = (7.5 \pm 0.5) \cdot 10^{-2} \text{ sec}^{-1}$. With increase of the pressure from 0.05 to 1 mm Hg, the variation of k does not exceed the limits indicated above. The value of the useful signal corresponding to times greater than $5.3/k$ after termination of any marked chemical transformations is taken as the position of the zero line.

Uniform heating through the thickness during the time of the impulsive stage is achieved by the use of sufficiently thin layers. The time for temperature equalization through the layer thickness is found from the formula [1]

$$\tau_* \approx \frac{\delta^2}{\mu_1^2 a} \approx \frac{\delta^2}{10a}$$

Here $\mu_1 = \pi$ is the first eigenvalue of the first boundary problem for the one-dimensional case, a is the thermal diffusivity, δ is the layer thickness. In application to colloidal powders ($a \approx 10^{-3} \text{ cm}^2/\text{sec}$ [2]) for the thicknesses 10 and 1μ respectively, $\tau_* \approx 10^{-4} \text{ sec}$ and $\tau_* = 10^{-6} \text{ sec}$. For the titanium plates ($a \approx 6.4 \cdot 10^{-2} \text{ cm}^2/\text{sec}$ [3, 4]) of thickness 40μ $\tau_* \approx 2.5 \cdot 10^{-5} \text{ sec}$.

Overheating of the material in the course of thermal decomposition is eliminated by the use of thin layers, as a result of which the critical thermal explosion temperature is raised considerably. Specifically, for pyroxylin of thickness 10 and 1μ the critical temperature equals respectively 310 and 390°C (for $E = 48,500 \text{ cal/mol}$, $Q \cdot z = 4.23 \cdot 10^{21} \text{ cal/g} \cdot \text{sec}$ [5], $\gamma = 1.3 \text{ g/cm}^3$), and the superheat of the outer surface of the film relative to the substrate for $T = 300^\circ \text{C}$ is found to be 2.9 and $5.4 \cdot 10^{-2}^\circ \text{C}$, respectively.

It was found that at a distance 11 cm from the center of a packet 30 cm long the temperature decrease does not exceed 4°C for $T_* = 300^\circ \text{C}$, $T_0 = 25^\circ \text{C}$. This working segment length is recommended for use.

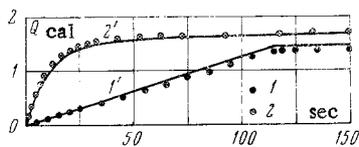


Fig. 2

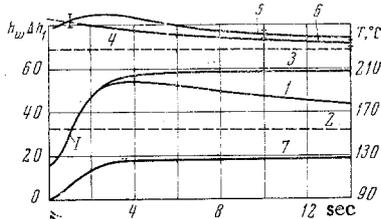


Fig. 3

A schematic of the electrical circuit is shown in Fig. 1. The measurement of the useful signal t is made on the basis of the resistance of the packet Π_1 (on the plates of which the test material is applied prior to the basic heating) with the aid of a bridge circuit consisting of the two identical packets Π_1 and Π_2 and the two identical resistors Σ_1 and Σ_2 . The controllable impulsive heating is accomplished with the aid of the fusible copper wires 1 [6], which burn out when the switch K_1 is closed. The electrical circuit is supplied from the bank of starter batteries 2 of at least 100 A·h capacity with total voltage 282-324 V. Connection of the bank of electrometric type "EF" capacitors C in parallel with the batteries makes it possible to reduce the heating time. The temperature changes discretely when changing from one wire diameter to another. Intermediate values of the temperature are realized by controlled preheating of the calorimetric packets by electric current from the storage battery 3 through the regulating rheostat R_6 .

After the wire fuses there flows through the bridge the metering current, established prior to the experiment with the aid of galvanometer R_5 with the switches K_2 and K_3 closed (the resistance R_7 is approximately equal to the resistance of the bridge cell together with Π_3 at the operating temperature). In the course of the experiment the metering current is recorded by the galvanometer Σ_2 .

In the general case the bridge is unbalanced. The difference of the Π_1 and Π_2 packet resistances is calculated from the formula

$$\Pi_1 - \Pi_2 = \Delta = [2(r_1 + R_1) + \Sigma] \frac{R_5 S_2 h_1}{r_1 S_1 h_2} \quad (6)$$

which is derived from the known formula [7] for the current in a bridge diagonal for the conditions $\Pi \ll \Sigma$ and $\Sigma_1 = \Sigma_2 = \Sigma$, which are satisfied with good accuracy. Here r_1 , S_1 , h_1 are the internal resistance, sensitivity, and "spot" deflection of the i -th galvanometer on the oscillograph paper, respectively. The useful signal t is proportional to the difference of the quantities Δ of the basic and control experiments. The coefficient of proportionality is $1/\beta\Pi$.

When conducting the in-vacuo experiments there was connected in series with the bridge cell the packet Π_3 (similar to packets Π_1 and Π_2), on which a coating of material equal to the coating of packet Π_1 was applied prior to the control heating. The use of this packet makes it possible to maintain the same heat transfer conditions in the control and basic experiments.

The pressure variation was monitored by a special vacuum meter of the resistance type with sensitive element made from 5- μ -diam. tungsten wire. Titanium was selected as the material for the calorimetric plates because of its low thermal conductivity and high electric resistivity [3, 4].

The packet temperature is measured from the resistance of packet Π_1 (galvanometer Γ_4) and by the indications of four or five manganin-constantan strip thermocouples 4, bonded perpendicular to the length of the packet on the layer of material using a high-temperature polymer (poly-[2,2-bis(4'-methoxy-3'-ethynyl-phenyl)-propane]) (A. S. Zanina, I. L. Kotlyarevskii, N. M. Gusenkova, I. E. Sokolov, and E. N. Cherepov, USSR Patent No. 180197, dated 29 Mar 1965).

The thermocouples were fabricated by electrowelding from 20- μ -diam. wire and then rolled to a thickness of 5-6 μ . The temperature measurement error was 2-3%.

All the signals were recorded on an H-105 12-channel rotating-mirror oscillograph [8]. The method was checked in experiments measuring the Joule heat related in a heater bonded in place of the test material on the inner side of the packet of plates. The heater was a 6- μ -thick constantan strip obtained by rolling from 20- μ diam. wire. The strip was arranged in a zigzag pattern covering the entire width. The complex pressure pattern was obtained with the aid of pyroxylin films applied to the packet Π_3 prior to the basic and control heating cycles.

Figure 2 shows results of measurements when passing constant current (point 1) and time-varying current (points 2) through the heater. Comparison of these points with the Joule heat released in the heater (curves 1' and 2') made it possible to evaluate the errors in the measurements of the heat content and the heat release rate. Analysis of results of a large number of experiments showed that these errors do not exceed 5-7 and 10-15%, respectively.

Experiments were made with pyroxylin. Pyroxylin film about one micron thick and weighing 12.2 mg was obtained by withdrawing the calorimetric plates at a constant rate from a solution of pyroxylin in acetone with subsequent drying in a dry atmosphere above P_2O_5 . The excess pyroxylin was wiped off using cotton moistened in acetone. The residual solvent (about 2% by weight) was removed from the film prior to the experiment by heating the plate and film at 160° C in a vacuum for one minute. Figure 3 shows results of one of these tests, conducted at a temperature of 250-260° C and pressure $0.05 < p < 0.5$ mm Hg. Here 1 is the useful signal in mm deflection of the spot of the first galvanometer; 2 is the position of the reference line; 3 is the useful signal in mm after reduction using equation (5) (the scale factor $M = 3.0$ cal/g·mm); 4 is the limiting value which curve 3 approaches; 5 is the average temperature T during the basic heating cycle; 6 is the average temperature during the control heating cycle; and 7 is the pressure variation during the basic cycle heating from the tungsten vacuum meter recording in mm deflection on the oscillogram.

The magnitude of the thermal effect obtained in this experiment is about 160 cal/g. This is approximately 1.5-2 times the value presented in [9]. The heat release rate for a decomposition depth $\eta = 0.25$ (point 1 in Fig. 3) is about 70 cal/g·sec. The temperature at that moment was 254° C. For comparison we note that the heat release rate at 250° C obtained using the ignition method is equal to 30 and 80 cal/g·sec [5].

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