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# Correctness of determination of energetic materials high temperature decomposition kinetics

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**Abstract.** The kinetic parameters of high temperature decomposition kinetics are widely used in evaluating the characteristics of thermal explosion, ignition and combustion of energetic materials. At present, the true and correct data on the high temperature kinetics of energetic materials condensed phase reactions are unknown and probably will remain unattainable in the nearest future. This is because of enormous technical difficulties to obtain such information and the absence of proper theoretical approaches for treatment of non-isothermal data. Evidently, with highly exothermic reactions it is impossible to conduct experiments at elevated temperatures using approaches of a low heating rate or isothermal ones. The improvement of characteristics of existing devices for thermal analysis is impeded by both technical complications and difficulties of performing experiments with ultrathin specimens of energetic material to ensure the conditions of uniform heat-up of the bulk of the substance. Based on the results of numerical simulation it is shown in this paper that the approach suggested 50 years ago by A.G. Merzhanov of using ignition delay data for deriving high temperature kinetics was not theoretically justified and can provide only very approximate values for such kinetics. The paper concludes on the today's relevance of the tasks on elaboration of mathematically justified techniques for determining kinetic parameters of global exothermic condensed-phase reaction, which will be based on the experiments on EMs ignition.

## 1. Introduction

The knowledge of kinetic parameters of energetic materials (EMs) high temperature decomposition is necessary for evaluating the characteristics of their thermal explosion, ignition and combustion. It can be stated that at present the correct data on the EM condensed phase high temperature reaction kinetics are not available and probably will remain unattainable in the nearest future. This is because of great technical difficulties one faces in efforts to obtain such the data. The reasons are high temperatures in the reaction zone and extremely high heating rates under ignition and combustion wave propagation conditions. For example, with the burning rate of 1 cm/s the heating rate in subsurface layer of EMs may reach  $10^5$  K/s and higher but in conventional methods of DTA and DSC it does not exceed 1 K/s. It clearly shows that the processes of diffusion and convection in this layer are strongly retarded in the course of ignition and combustion and kinetic parameters determined by existing methods of thermal analysis could not be used directly for description of the EM ignition and combustion behavior. Nevertheless, till now the calculation of the EMs ignition and combustion parameters is performed on the basis of kinetic data determined by classical thermal analysis methods at relatively low heating rates. Consequently, rather good agreement between calculation results and experimental data on the combustion behavior, reported in several works, is the result of using numerous fitting coefficients,



which allow getting already known results. This underlines necessity of developing proper methods to determine correct information about high temperature EM decomposition kinetics.

Existing problems of obtaining such information were described in detailed reviews prepared by international team of experts in thermal analysis and calorimetry [1, 2]. It was stressed that “hazardous materials”, including energetic materials, can generate heat at very fast rates exceeding the rate of heat transfer in available devices. This leads to accumulation of heat and self-heating of the sample accompanied by creation of a temperature gradient inside the sample. That may become a source of serious error in kinetic data [3-6]. The recommendations are focused mainly on selecting the proper sample mass and heating rate (as low as possible). Unfortunately, it does not allow obtaining needed information about high temperature decomposition kinetics.

The possible solution of the above problem was proposed more than 50 years ago by A. G. Merzhanov [7] who suggested using the data on the EMs ignition delay for deriving required values of kinetic parameters. The essence of this approach was very simple and seemed rather reasonable. Indeed, at ignition process the heating rate usually reaches  $10^2$  K/s and even more that provides better correspondence to conditions in the combustion wave. The approach is based on use of ignition criterion which states that at the ignition instant the heat loss rate from the reaction zone becomes equal to the heat release rate due to exothermic reactions in the reaction zone. It can be mentioned that a qualitative formulation of the ignition criterion was first proposed many years ago by famous Dutch scientist van't Hoff [8].

Unfortunately, justification of using ignition criterion for deriving the kinetics data was not made by neither Merzhanov or by numerous researchers over the world during next 50 years. The important issue is that experimentally the Merzhanov approach could not be justified in principle because at present the true high temperature kinetics of EMs is not available. Therefore it can be suggested to conduct virtual experiments using mathematical model of the EM transient combustion to obtain data on ignition delays. Below this approach is analyzed on the basis of mathematical simulation along with proposals on further development of appropriate investigations.

## 2. Checking the applicability of Merzhanov's approach

### 2.1. Essence of the approach

In accordance with the above mentioned, the ignition instant is characterized by the equality of chemical reactions heat release rate  $q_{ch}$  and heat loss from the reaction zone  $q_{th}$ . To simplify analytical calculations it was suggested to characterize the heat loss by the value of heat flux  $q_s$  impinging the exposed surface of EM. In [7] it was expressed as

$$q_{ch} = q_{th} \quad (1)$$

For the sake of simplicity below we discuss the case of one-dimensional surface heating (specifically by radiation) by a constant heat flux  $q_s$  to illustrate an approach for determining the kinetic parameters of exothermic condensed-phase reaction. Further we assume that the chemical heat release occurs in a narrow reaction zone  $x_{ch}$  within the EM subsurface layer. When neglecting the temperature distribution across the reaction zone, the surface temperature  $T_s$  in the first approximation can be taken equal to ignition temperature  $T_{ig}$ . As a result, for zero order reaction (small conversion degree)  $q_{ch}$  can be represented in the form

$$q_{ch} = Q\rho x_{ch} k_0 \exp\left(-\frac{E}{RT_s}\right)$$

To determine  $x_{ch}$  we use the following approximate expressions

$$x_{ch} = \frac{\Delta T_{ch}}{\left(\frac{\partial T}{\partial x}\right)_{x=0}}; \Delta T_{ch} = \frac{RT_s^2}{E}; \left(\frac{\partial T}{\partial x}\right)_{x=0} = \frac{q_s}{\lambda}$$

Here  $E$  is the reaction activation energy and  $\lambda$  is the EM thermal conductivity. Important issue is that the value of surface temperature during heating of reacting EM could not be calculated analytically and correctly measured experimentally. Therefore, Merzhanov suggested using the value of surface temperature corresponding to so called inert heating, which is easily calculated analytically. In this case, to make correlation with numerical calculations for reacting EM it is necessary to introduce the fitting coefficient  $\Psi$  in approximate Eq.1:  $\Psi q_{ch} = q_s$ . The value of this coefficient depends on chosen ignition model and magnitudes of energy of activation and heating rate.

After simple derivations one can obtain expression (2) correlating the heat flux with the parameters of global exothermic reaction:

$$q_s^2 = \Psi \lambda Q \rho k_0 \left( \frac{RT_s^2}{E} \right) \exp\left( -\frac{E}{RT_s} \right) \quad (2)$$

In original works of A.G. Merzhanov [7, 9, 10], the fitting coefficient equaled  $\Psi = 17.64$ . That value was obtained for the case of selecting the ignition temperature as the inflection point at the EM (solid nitrocellulose) surface temperature vs time curve. More detailed calculations of coefficient  $\Psi$  depending on the heating rates and activation energy of exothermic reaction in condensed phase were made first by Bradley [11]. All these results corresponded to the case of heating by a constant heat flux. Later, there were presented [12] calculation results on the values of  $\Psi$  when using different heat transfer modes. Note that all listed works had deal with simplest chemical mechanism of EM reacting considering elementary models of single-stage chemical transformations in condensed phase.

The logarithm transformation of Eq.2 with coefficient  $\Psi = 1$  produces the expression (3) allowing determination of kinetic parameters on the basis of ignition delay data, which are used to calculate “inert” surface temperature.

$$\ln \frac{T_s}{q} = \frac{1}{2} \ln \frac{E}{\lambda Q \rho k_0 R} + \frac{E}{2R} \cdot \frac{1}{T_s} \quad (3)$$

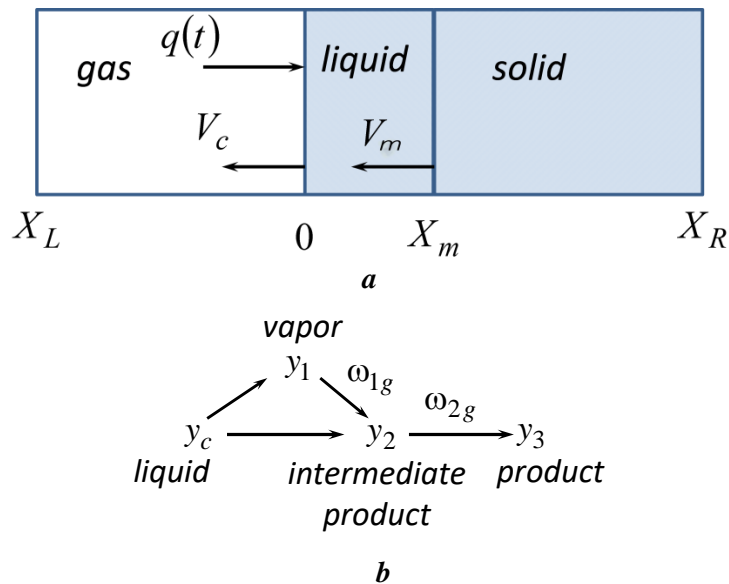
Indeed, when plotting the experimental data in coordinates  $\ln(T_s/q); (1/T_s)$ , the inclination of the line gives the value of  $E/2R$ , whereas the section on the vertical axis corresponds to the value of complex  $0.5 \ln(E/\lambda Q \rho k_0 R)$ . Further, taking the known magnitudes of  $\lambda$  and  $R$  and determined  $E$  value one may calculate the product of  $Qk_0$ . The inert temperature on the exposed EM specimen surface is calculated via analytical formula

$$T_s = T_0 + \frac{2q}{\sqrt{\pi \lambda c \rho}} \sqrt{t_{ig}}$$

The approach described has been used for many years by experimenters and recommended in several articles and manuscripts (see, e.g. [13,14]). Below an attempt is made to evaluate the consistency of Merzhanov’s approach via using results of the EM ignition mathematical simulation.

## 2.2. Mathematical simulation of EM ignition by a constant heat flux

Let us consider an EM with a global exothermic condensed-phase reaction, which is melting and evaporating under heating and produces vapor and decomposition semi-products. The physical model is presented in Fig.1a [15]. It describes propagation of heat in melted solid EM where the reaction, by assumption, proceeds only in a liquid phase with the activation energy  $E_l$ . The density, specific heat and thermal conductivity of solid and liquid phases are assumed to be equal. It is also assumed that the condensed phase reactions produce intermediate products  $y_2$  and vapor produces the same ones. Later these semi-products react with formation of (final) product  $y_3$  (Fig 1b).



**Figure 1.** Diagrams of calculation domain (a) and reaction scheme (b).

The governing equations are written in the coordinates attached to the moving reacting surface.

a) solid phase ( $x_m \leq x \leq x_R$ ) (4)

$$C_c \rho_c \left( \frac{\partial T_c}{\partial t} - V_c \frac{\partial T_c}{\partial x} \right) = \lambda_c \frac{\partial^2 T_c}{\partial x^2} + q(0, t) \alpha_c \exp(-\alpha_c x)$$

Initial and boundary conditions

$$T_c(x, 0) = T_0, \quad T_c(x_m, t) = T_m, \quad \left( \frac{\partial T_c}{\partial x} \right)_{x=x_R} = 0, \quad V_m = \frac{dx_m}{dt},$$

b) liquid phase ( $0 \leq x \leq x_m$ ) (5)

$$C_c \rho_c \left( \frac{\partial T_c}{\partial t} - V_c \frac{\partial T_c}{\partial x} \right) = \lambda_c \frac{\partial^2 T_c}{\partial x^2} + \Phi_l + q(0, t) \alpha_c \exp(-\alpha_c x) \tag{6}$$

$$\rho_c \left( \frac{\partial y_c}{\partial t} - V_c \frac{\partial y_c}{\partial x} \right) = -\omega_l$$

$q(0, t) = q_0 \sum_{j=1}^N \delta_{gj} \exp \left( -\alpha_{gj} \int_{x_L}^0 \rho y_1 dx \right)$  is the radiant flux impinging the burning surface with due

account for its absorption in the gas phase. In Eqs. (4-6)  $\alpha_c$  [1/m] is the condensed phase radiation absorption coefficient;  $\delta_{gj}$  and  $\alpha_{gj}$  [m<sup>2</sup>/kg] are the coefficients describing radiation absorption at chosen wavelengths in the gas phase.

$$\Phi_l = Q_l \omega_l, \quad \omega_l = A \rho_c y_c \exp(-E_l / RT_c),$$

At the melting front

$$y_c(x_m, t) = 1, \quad T_c(x, 0) = T_0, \quad T_c(x_m, t) = T_m, \quad -\lambda \left( \frac{\partial T_c}{\partial x} \right)_{x=x_m+0} + L_m (V_m + V_c) \rho_c = -\lambda \left( \frac{\partial T}{\partial x} \right)_{x_m-0}$$

The gas phase consists of two reacting components, vapor and combustible gas with equal temperatures, and final combustion products.

The equations for the gas phase ( $x_L \leq x \leq 0$ ) are as follows:

c) gas phase ( $x_L \leq x \leq 0$ )

$$C_p \rho \left( \frac{\partial T}{\partial t} - \left( V - V_c - \sum_{i=1}^3 \frac{C_{pi}}{C_p} D_i \frac{\partial y_i}{\partial x} \right) \frac{\partial T}{\partial x} \right) = \frac{\partial}{\partial x} \left( \lambda \frac{\partial T}{\partial x} \right) + \Phi_1 + \Phi_2 +$$

$$+ q_0 \rho y_1 \sum_{j=1}^N \delta_{gj} \alpha_{gj} \exp \left( -\alpha_{gj} \int_{x_L}^x \rho y_1 dx \right) \quad (7)$$

$$\rho \left( \frac{\partial y_1}{\partial t} + (V - V_c) \frac{\partial y_1}{\partial x} \right) = \frac{\partial}{\partial x} \left( \rho D_1 \frac{\partial y_1}{\partial x} \right) - \omega_1 \quad (8)$$

$$\rho \left( \frac{\partial y_2}{\partial t} + (V - V_c) \frac{\partial y_2}{\partial x} \right) = \frac{\partial}{\partial x} \left( \rho D_2 \frac{\partial y_2}{\partial x} \right) - \omega_2 + \omega_1 \quad (9)$$

$$\frac{\partial \rho}{\partial t} - V_c \frac{\partial \rho}{\partial x} + \frac{\partial (\rho V)}{\partial x} = 0 \quad (10)$$

$$p = R \rho T / M \quad (11)$$

$$\frac{1}{M} = \left( \frac{y_1}{M_1} + \frac{y_2}{M_2} + \frac{y_3}{M_3} \right), \quad \Phi_1 = Q_1 \omega_1, \quad \Phi_2 = Q_2 \omega_2$$

$$\omega_1 = A_1 (\rho y_1)^{N_1} \exp(-E_1/RT), \quad \omega_2 = A_2 (\rho y_2)^{N_2} \exp(-E_2/RT),$$

Initial and boundary conditions

$$T(x, 0) = T_0, \quad y_1(x, 0) = y_2(x, 0) = 0, \quad \frac{\partial T}{\partial x} = \frac{\partial y_1}{\partial x} = \frac{\partial y_2}{\partial x} = 0 \quad \text{at } x = x_L$$

$$y_1 + y_2 + y_3 = 1, \quad D_1 \frac{\partial y_1}{\partial x} + D_2 \frac{\partial y_2}{\partial x} + D_3 \frac{\partial y_3}{\partial x} = 0 \quad (12)$$

It is assumed that there is a functional binding between the surface temperature  $T_s$  and vapor concentration in the gas phase in the form of the Clapeyron-Clausius equation. This allows determining the non-stationary rate of solid propellant combustion on the basis of equations (13)–(16).

$$\lambda \left( \frac{\partial T}{\partial x} \right)_{x=-0} = \lambda_c \left( \frac{\partial T_c}{\partial x} \right)_{x=+0} + q(t) - y_c \rho_c V_c L \quad (13)$$

$$-\rho(V - V_c) y_1 + D_1 \rho \frac{\partial y_1}{\partial x} = \rho_c V_c y_c \quad (14)$$

$$-\rho(V - V_c) y_2 + D_2 \rho \frac{\partial y_2}{\partial x} = \rho_c V_c (1 - y_c) \quad (15)$$

$$-\rho(V - V_c) = -\rho_c V_c, \quad y_1 = \frac{M_1}{M} \exp \left[ -\frac{LM_1}{R} \left( \frac{1}{T_s} - \frac{1}{T_b} \right) \right] \quad (16)$$

In Eqs (4) – (16),  $V_c$  and  $V_m$  are the rates of burning and melting front motion,  $T$  is the temperature,  $T_b$  is the boiling temperature,  $M$  is the molecular mass,  $\rho$  is the density of the gas and condensed phase,  $\lambda$  is the thermal conductivity,  $D$  is the diffusion coefficient,  $L_m$  is the melting heat and  $L$  is the

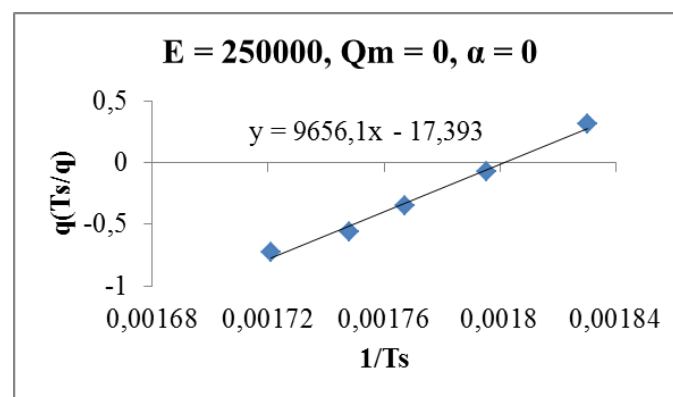
evaporation latent heat. Index  $c$  corresponds to solid,  $l$ -liquid,  $m$ -melting; 1 corresponds to vapor, 2 – intermediate gas product, 3 – final gas product.

The equations (4)–(16) were used for simulation of some model EM ignition by a constant radiant flux with the parameters of exothermic condensed phase reaction being varied. The magnitudes of gas phase reactions parameters were intentionally fitted to ensure a weak effect on the ignition behavior. In calculations, the ignition instant  $t_{ig}$  corresponded to attaining the 50% level of stationary burning rate under irradiation. The values of thermophysical and initial kinetic parameters, used for the numerical modeling the model EM ignition by radiant flux, are shown in table 1.

**Table 1.** Parameters of model EM.

Parameter	Dimensionality	Magnitude
Density, $\rho$	kg/m <sup>3</sup>	1720
Condensed phase reaction heat, $Q$	kJ/kg	1700
Thermal conductivity coefficient, $\lambda$	kW/(m·K)	2.3·10 <sup>-4</sup>
Specific heat capacity, $c$	kJ/(kg·K)	1.256
Melting temperature, $T_m$	K	480
Melting heat, $L_m$	kJ/kg	0
Boiling temperature, $T_b$	K	575
Evaporation heat, $L$	kJ/kg	1000
Pre-exponential factor in Arrhenius equation, $k_0$	s <sup>-1</sup>	1019

In calculations, the radiant flux  $q_o$  magnitude varied in the range of 400-1200 kJ/m<sup>2</sup> and activation energy  $E_l$  varied in the range of 200-300 kJ/mole. Figure 2 shows an example of treating the virtual ignition data of the opaque model EM ( $\alpha_c = 0$  by default corresponds to an opaque body) with an exothermic reaction activation energy in the condensed phase of 250 kJ/mole.

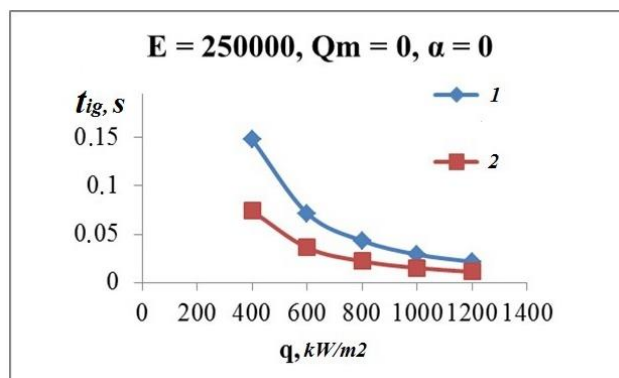


**Figure 2.** Representation of virtual ignition data for the model EM. X=1/TS; Y= ln(Ts/q).

In accordance with Fig. 2 the magnitude of “virtual” exothermic reaction activation energy in the condensed phase equals 160 484 J/mole, whereas  $Qk_0=6.25 \cdot 10^{20}$  kJ/kg·s. Consequently, the correlation coefficient  $\Psi$  in equation (2) with initial value of  $Qk_0=1.7 \cdot 10^{22}$  kJ/kg·s turns out to be 272. It is also seen that derived value of activation energy of exothermic reaction in the condensed phase is essentially lower of its input value (160.5 kJ/mole versus 250 kJ/mole).

When using ignition condition in the form of Eq. (2) one can calculate the ignition delays depending on the heat flux values. An example of such calculations along with the results of numerical modeling is presented in Fig. 3. It is seen that there exists a qualitative similarity between the two

curves but analytically calculated ignition delays are ca. 50% lower than those determined numerically.



**Figure 3.** Ignition delay vs heat flux dependencies calculated by the two methods (1– numerical calculations, blue symbols; 2 - analytical calculations via Eq. (2), red symbols).

Note that numerical calculations were performed in the case of simplest ignition mode (absence of melting or the melting with zero heat effect). The calculations with the finite value of melting heat have shown total invalidity of the ignition criterion expressed in the form of Eq. 2. In this case the correlation coefficient  $\Psi$  turned out to be of the order of magnitude of  $10^8$  with the activation energy determined via processing the virtual ignition delays being twice as low as used in the numerical calculations.

### 3. Concluding remarks

The problem of correct determination of high temperature decomposition kinetics is intensively discussed in the literature [1-6,16]. It has maybe the greatest importance for energetic materials when designing propulsion systems and manufacturing propellants and explosives. As already mentioned this kinetics is unavailable at present time and all calculations of EM high temperature behavior are based on very approximate data. It is worth to underline that more than decade ago the question was raised about shortcomings of thermal methods to provide reliable kinetic information [17]. In particular, it regards solid-state reactions and transformations in which the energy of activation may change depending on extent of conversion. Later on it was formulated that it is necessary to develop new models considering distributed reactivity and temperature dependency of the pre-exponential factor in the Arrhenius equation [16]. Classical recommendations of thermal analysts come to the requirement of using isothermal or low heating rates for obtaining preliminary information about decomposition mechanisms and then to get evidences that these may work under both isothermal and non-isothermal conditions. In the case of EM decomposition the problem of kinetics determination becomes extremely difficult because of ultra-high heating rates. In the most of existing theoretical models of the EMs ignition and combustion the assumption of single-step global exothermic reaction is still used and there is urgent (at least for practical applications) need to determine experimentally high temperature decomposition kinetics. As is shown in this paper the approach proposed more than 50 years ago by Merzhanov does not provide reliable background for using ignition delays to derive values of kinetics parameters. The approach ignores the dependencies of fitting coefficient on the magnitude of heating rate (external heat flux) and values of kinetic parameters. As a result, the derived kinetic parameters give significant errors in evaluating expected magnitudes of ignition delays and burning rates. Therefore there is an urgent task and essential challenge in front of theoreticians working in the EMs chemical physics on developing new models and approaches to appropriately treat non-isothermal data and to determine needed information about the EM high temperature decomposition kinetics.



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### References

- [1] Vyazovkin S, Chrissafis K, Di Lorenzo M L, Koga N, Pijolat M, Roduit B, Sbirrazzuoli N and Suñol J 2014 *Thermochim. Acta* **590** 1–23
- [2] Vyazovkin S, Burnham A K, Criado J M, Pérez-Maqueda L A, Popescu C and Sbirrazzuoli N 2011 *Thermochim. Acta* **520** 1–19
- [3] Várhegyi G. 1983 *Thermochim. Acta* **65** 333–350
- [4] Biader C U, Bucci R and Magri A D 1990 *Thermochim. Acta* **161** 37–49
- [5] Armand J Y and Vergnaud J M 1988 *Thermochim. Acta* **131** 15–27
- [6] Koga N and Tanaka H 1994 *Thermochim. Acta* **240** 141–51
- [7] Merzhanov A G 1967 *Combustion and Flame* **11**(3) 201-211
- [8] van't Hoff J H 1884 *Etudes de dynamics chimique* (Amsterdam: F. Muller und Co.)
- [9] Averson A E, Barzykin V V and Merzhanov A G 1968 *Combustion, Explosion and Shock Waves* **1** 20-32
- [10] Merzhanov A G and Averson A E 1971 *Combustion and Flame* **16** 89-124
- [11] Bradley H H Jr 1970 *Combustion Science and Technology* **2** 11-20
- [12] Lyubchenko I S and Marchenko G N 1987 *Advances in Chemistry* **LVI**(2) 216-240
- [13] Cauty F, Fabignon Y and Eradès C 2010 *Inter. J. of Energetic Materials and Chemical Propulsion* **9**(4) 285-304
- [14] Vilyunov V N and Zarko V E 1989 *Ignition of Solids* (Elsevier Science Publishers. Amsterdam, Oxford, New York, Tokyo)
- [15] Gusachenko L K, Zarko V E and Rychkov A D 1999 *J. Propulsion Power* **15**(6) 816-822
- [16] Skrdla P J 2019 Can We Trust Kinetic Methods of Thermal Analysis? *Analyst*
- [17] Galwey A K 2004 *Thermochim. Acta* **413** 139-183.