Life Assessment of Energetic Materials using Advanced Kinetic Elaboration of HFC Signals

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ABSTRACT

High energetic materials can slowly decompose during storage or transport particularly at elevated temperatures which may result in reduced performance and correct functionality. Even very low decomposition progress of the exothermic reaction resulting in minor heat release can significantly change the properties of the propellants leading to shortening of the service life-time. The reaction progress influencing already the behaviour of the samples can be in the range of ca. 1-2% of the total decomposition degree. There are the literature reports showing that the amount of the evolved heat during decomposition as low as ca. 40 J/g can alter the material properties [1]. Monitoring such a minor heat release requires very sensitive techniques as Heat Flow Calorimetry (HFC).

The prediction of the shelf life of energetic materials requires the precise determination of the kinetics of their decomposition. Due to the fact that energetic materials decompose with the evolution of heat, the thermoanalytical methods such as Heat Flow Calorimetry (HFC) are often used for the monitoring the reaction rate and the evaluation of the kinetic parameters of these reactions [2]. In the present paper we describe the precise, advanced method of the evaluation of the kinetic parameters from HFC signals. Proposed method was applied for the kinetic evaluation of the decomposition process of two spherical double base and one EI® propellants type, all for small calibre used in defence applications. The kinetic parameters were determined from the experiments carried out between 50-100°C. The very good description of the low temperature data by the kinetic parameters determined at higher temperatures indicates the constancy of the decomposition mechanism between 50 and 100°C. The experimental data collected during more than 7 years by means of HFC (at 50°C) were well simulated by the kinetic parameters derived from the high temperature HFC signals. Such a possibility enables e.g. the precise prediction of the shelf life of the energetic materials at any temperature mode in the range of 50-10°C, at different climatic categories proposed by STANAG 2895 [3] and, more generally, the precise simulation of the reaction at any temperature profile close to the ambient temperature.

1. INTRODUCTION

HFC is a very sensitive technique allowing detection of the heat generation in µW range. Such a high sensitivity makes possible the investigation of the early stages of the decomposition i.e. the reaction progress α ranging from 0 to e.g. 0.05. However, the drawback of this technique consists in long measuring time (up to month's scale) allowing therefore, even at relatively high temperature range of 70-100°C, the investigations in reasonable time frame of few percent of the total reaction progress only. Moreover, one cannot exclude the change of the mechanism between the real storage temperature and temperatures of the investigations. This problem has been already mentioned in STANAG 4582 [1] where it was assumed that the activation energy *E* of the decomposition changes above 60°C from 80 to 120 kJ/mol. However, the simplified STANAG procedure does not take into consideration the other values of *E* and, often occurring, the change of the *E* during the reaction course.

The rate of the processes influencing property changes of the high energetic materials during storage depends namely on: (i) the external factors as geometry, storage temperature, thermal insulation and (ii) the intrinsic properties of the materials such as e.g. kinetic parameters of the decomposition processes, their specific heat, thermal conductivity. The temperature dependence of the decomposition rate applied in the test procedures for the prediction of safe storage and service life of high energetic materials is conventionally used in the form of the Arrhenius equation. Three kinetic parameters namely: the activation energy *E*, pre-exponential factor in Arrhenius equation *A* and the function of the reaction progress $f(\alpha)$ dependent on the decomposition mechanism are required for the prediction of the thermal stability of the materials under the temperature conditions different than those experimentally investigated. In the commonly applied computational procedures before the computation of the *E* and *A* values the function $f(\alpha)$ is very often arbitrarily chosen assuming e.g. the first or zero-th order of the reaction. Such an assumption influences arbitrarily the determination of the kinetic parameters and significantly lowers the accuracy of the simulation of the thermal stability.

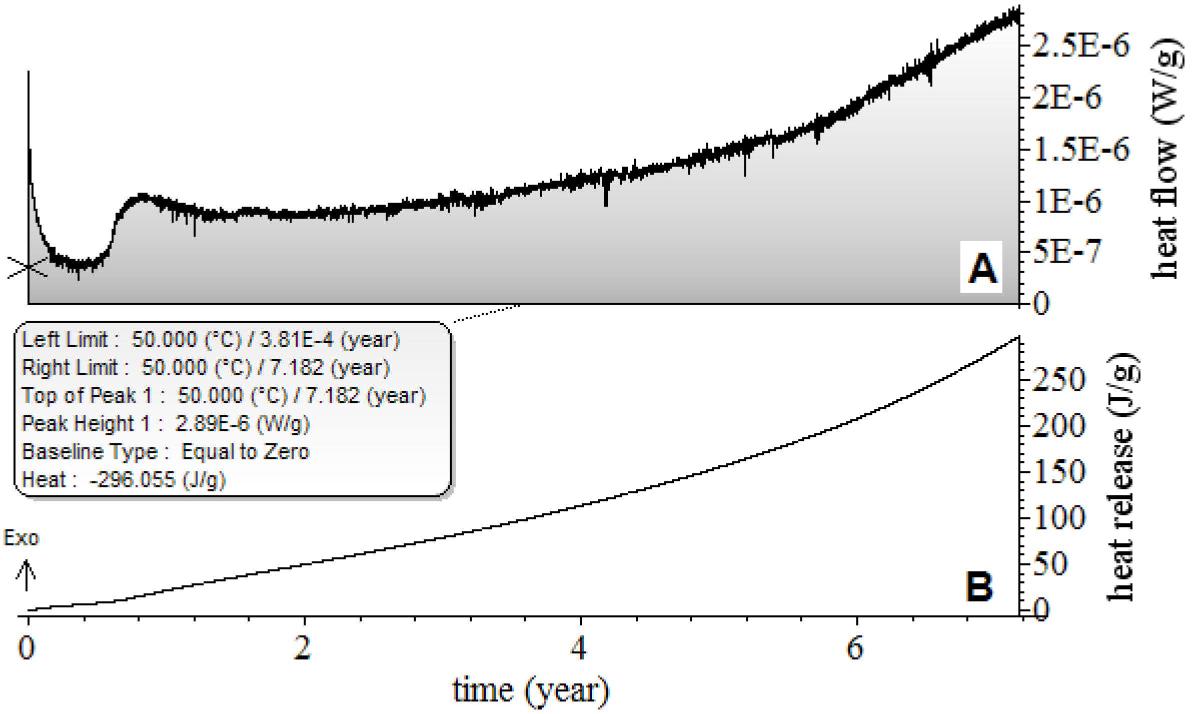
The another assumption concerning the constancy of the kinetic parameters during the course of the decomposition process, especially in the case of so complicated, multistage process as decomposition of energetic materials, can in certain cases handicap the correct prediction of the thermal stability. The evaluation of the kinetics of the propellants decomposition by DSC clearly indicated [4,5] the significant change of the kinetic parameters *E* and *A* and therefore the change of the mechanism during the decomposition course. These changes have to be also clearly determined at low values of the reaction progress between 0- 5% of the total decomposition i.e. in the range being very important for the prediction of the service life time. In order to gain better knowledge on kinetic description of the early stage of the decomposition the kinetic parameters may therefore be calculated from the heat flow calorimetry (HFC) experimental data collected for very low decomposition range. The aim of the presented paper was the calculation of the kinetic parameters obtained by advanced kinetic evaluation (differential isoconversional analysis) of HFC data. An additional task was the illustration how the method of the determination of kinetic parameters can be applied to determine the prediction of the thermal stability of the propellants at any temperature profile.

2. EXPERIMENTAL

The presented study contains the results of the evaluation of the kinetics of the decomposition of 3 propellants: two spherical double base propellants (denoted hereafter A and B), and one EI® propellant type, all for small calibre used in defence applications. The low-temperature isothermal microcalorimetric investigations were done with Thermal Activity Monitor (TAM), TA Instruments (formerly Thermometric AB), in the range of 50-100°C. The kinetic parameters were calculated using AKTS Thermokinetics software [6].

3. APPLICATION OF HEAT FLOW CALORIMETRY (HFC)

The use of HFC enables the monitoring early stage of the decomposition process from e.g. $\alpha = 0$ to $\alpha = 0.05$ (where α depicts the reaction progress varying from 0 to 1). To apply the heat flow signals monitored by HFC for the kinetic analysis it is necessary to convert them into α-time dependences. As the baseline is here well defined, the integration of heat flow signal is fortunately not influenced by the course of the baseline. Accurate baselines are especially important at the beginning of the reaction, when the heat flow is very low what results in weak HFC signals. The α range between 0-0.05 of the total decomposition is therefore very important for the prediction of the service life time because small deviations of the baseline at the beginning of the signal lead to the uncertainty in the determination of the reaction progress. The HFC measurement carried out during more than 7 years at 50°C for the propellant A is presented in Fig.1.



Left Limit : 50.000 (°C) / 3.81E-4 (year)
Right Limit : 50.000 (°C) / 7.182 (year)
Top of Peak 1 : 50.000 (°C) / 7.182 (year)
Peak Height 1 : 2.89E-6 (W/g)
Baseline Type : Equal to Zero
Heat : -296.055 (J/g)

Fig. 1 (A) heat flow and (B) cumulated heat release vs time of the spherical double base propellant A measured at 50°C during more than 7 years.

4. DETERMINATION OF THE KINETIC PARAMETERS

Isoconversional methods

These methods of the determination of the kinetic parameters are based on so called isoconversional principle saying that the reaction rate at constant reaction progress α is only a function of temperature. They allow determination of the activation energy (or dependence E on α) without assuming the explicit form of $f(\alpha)$. The kinetic parameters are not assumed to be constant during the course of the reaction. All isoconversional methods are based on the determination of temperatures corresponding to certain, arbitrarily chosen values of the reaction progress α recorded in the experiments carried out at e.g. different heating rates β or at different temperatures.

There are three main modifications of the isoconversional method:

- differential (Friedman) [7]
- integral (Flynn-Ozawa- Wall) [8-9]
- advanced integral based on non-linear procedure (Vyazovkin) [10]

One has to mention also the method based on the isoconversional principle namely ASTM E698 analysis [11].

Differential method of Friedman

Based on the Arrhenius equation, Friedman proposed to apply to the commonly used expression in solid state kinetics, the logarithm of the conversion rate $d\alpha/dt$ as a function of the reciprocal temperature at any conversion α:

$$\frac{d\alpha}{dt} = A\, exp\left(-\frac{E}{RT(t)}\right) f(\alpha) \tag{1}$$

$$\ln\left(\frac{d\alpha}{dt_\alpha}\right) = \ln\{A_\alpha f(\alpha)\} - \frac{E_\alpha}{R}\frac{1}{T_\alpha} \tag{2}$$

where T, t, A, E and R are the temperature, time, pre-exponential factor, activation energy and gas constant, respectively.

As $f(\alpha)$ is a constant in the last term of at any fixed α, the logarithm of the conversion rate $d\alpha/dt$ over $1/T_\alpha$ shows a straight line with the slope $m = E_\alpha/R$ and the intercept on Y-axis equal to $ln\{A_\alpha f(\alpha)\}$.

So, having determined E_α and $\{A_\alpha f(\alpha)\}$ we can predict the reaction rate or reaction progress using the following expression:

$$\frac{d\alpha}{dt_\alpha} = \{A_\alpha\ f(\alpha)\} exp\left(-\frac{E_\alpha}{RT(t_\alpha)}\right) \tag{3}$$

Integral Ozawa-Flynn-Wall method

This method is also based on the use of several dependences α-T measured at different heating rates. Starting from the commonly applied equation (1) for the constant heating rate β and taking $dT/dt = \beta =$ constant and $T(t)=T_o+\beta t$ after integration we obtain:

$$g(\alpha) = \int_{\alpha=0}^{\alpha} \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta}\int_{To}^{T(\alpha)} exp\left(-\frac{E}{RT(t)}\right) dt \tag{4}$$

If T_o lies below the temperature at which the reaction rate is noticeable, then one can set the lower limit of integration to $T_o = 0$, so that the following equation in the logarithm form is obtained after integration:

$$ln(g(\alpha)) = ln(\frac{A\,E}{R}) - \ln(\beta) + \ln(p(z)) \tag{5}$$

with :

$$p(z) = \frac{\exp(-z)}{z} - \int_{-\infty}^{z} \frac{\exp(-z)}{z} dz \quad \text{and} \quad z = \frac{E}{RT} \tag{6}$$

By using the approximation given by Doyle [12]
$ln\, p(z) = -5.3305 - 1.052 \cdot z$
one obtains:

$$\ln(\beta) = ln(\frac{A\,E}{R}) - ln(g(\alpha)) - 5.3305 - 1.052\frac{E}{RT} \tag{7}$$

With data collected in series of measurements performed with the different heating rates β at a fixed degree of conversion α, it ensues from the above equation that the dependence $ln(\beta)$ versus $1/T$ will be linear with a slope $m = - 1.052 \text{-} E/R$.

Advanced integral method of Vyazovkin

According to this method, for a set of n experiments carried out at different arbitrary heating programs $T_i(t)$, the E_α is determined as the value that minimizes the function

$$\phi(E_a) = \sum_{i=1}^{n} \sum_{j \neq 1}^{n} \frac{J[E_a, T_i(t_\alpha)]}{J[E_a, T_j(t_\alpha)]} \tag{8}$$

where J denotes the integral

$$J[E_a, T_i(t_\alpha)] = \int_{t_{\alpha-\Delta\alpha}}^{t_\alpha} \exp\left[\frac{-E_a}{R\,T_i(t)}\right] dt \tag{9}$$

The systematic error is eliminated by carrying out the integral in this last equation over small time intervals. Generally, α varies from $\Delta\alpha$ to $1\text{-}\Delta\alpha$ with a step $\Delta\alpha$ which is usually taken to be 0.02.

ASTM method E698

The analysis according to ASTM E698 is based on the assumption that the maximum (e.g. on the DSC or DTG curves) of a single step reaction is reached at the same conversion degree independent on the heating rate. Although this assumption is only partly right, the resulting errors are sometimes low [11]. In this method, the logarithm of the heating rate is plotted over the reciprocal temperature of the maximum. The slope of the yielded straight line is proportional to the activation energy, as in the Ozawa-Flynn-Wall method.

Comparison of the isoconversional methods

A detailed analysis of the differential and integral isoconversional methods for the determination of the activation energy has been reported by Budrugeac [13]. The convergence of the activation energy values obtained by means of a differential method like Friedman [7] with those obtained by integral methods with integration over small ranges of reaction progress α comes from the fundamentals of the differential and integral calculus. In other words, it can be mathematically demonstrated that the use of isoconversional integral methods can yield systematic errors when determining the activation energies. These errors depend directly on the size of the small ranges of reaction progress $\Delta\alpha$ over which the integration is performed. These errors can be avoided by using infinitesimal ranges of reaction progress $\Delta\alpha$. As a result, isoconversional integral methods turn back to the differential isoconversional methods formerly proposed by Friedman.

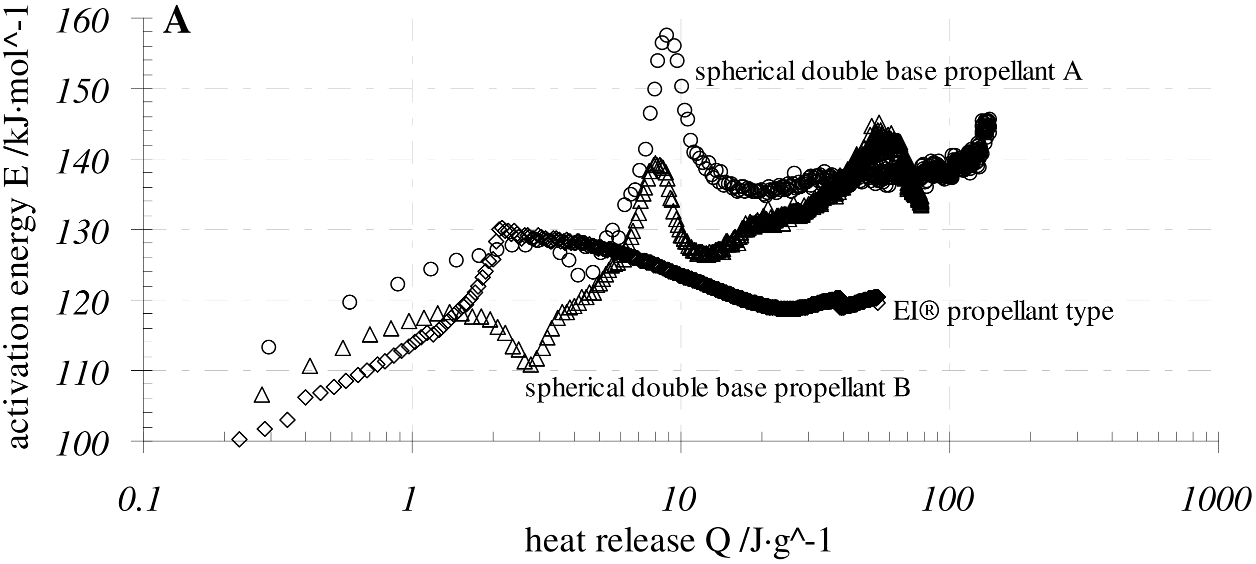
In the current study the kinetic parameters have been calculated by the differential isoconversional method of Friedman using the isothermal data obtained by means of HFC.

5. RESULTS AND DISCUSSION

5.1 KINETIC ANALYSIS OF HFC DATA

The heat flow signals were recorded by HFC in isothermal runs at 50, 60, 70, 80, 89°C for two spherical double base propellants A and B and at 60, 70, 80, 90 and 100°C for the EI® samples. The dependence of the heat flow and heat cumulated on the time enabled the calculations of the reaction rate and the reaction progress. The reaction progress considered for the calculations of the kinetic parameters was calculated by relating the cumulative heat after certain time of the decomposition to the maximum heat release of the reaction measured by HFC in isothermal runs.

The data presented in Table 1 were applied for the calculation of the E_α and $\{A_\alpha f(\alpha)\}$ kinetic parameters by isoconversional method of Friedman (see Eqs. 2 and 3). The dependence of the activation energy on the cumulative heat release is presented in Figure 2A. Clearly visible is that the activation energy and the pre-exponential factor are not constant during the reaction course and change as a function of the cumulative heat release.



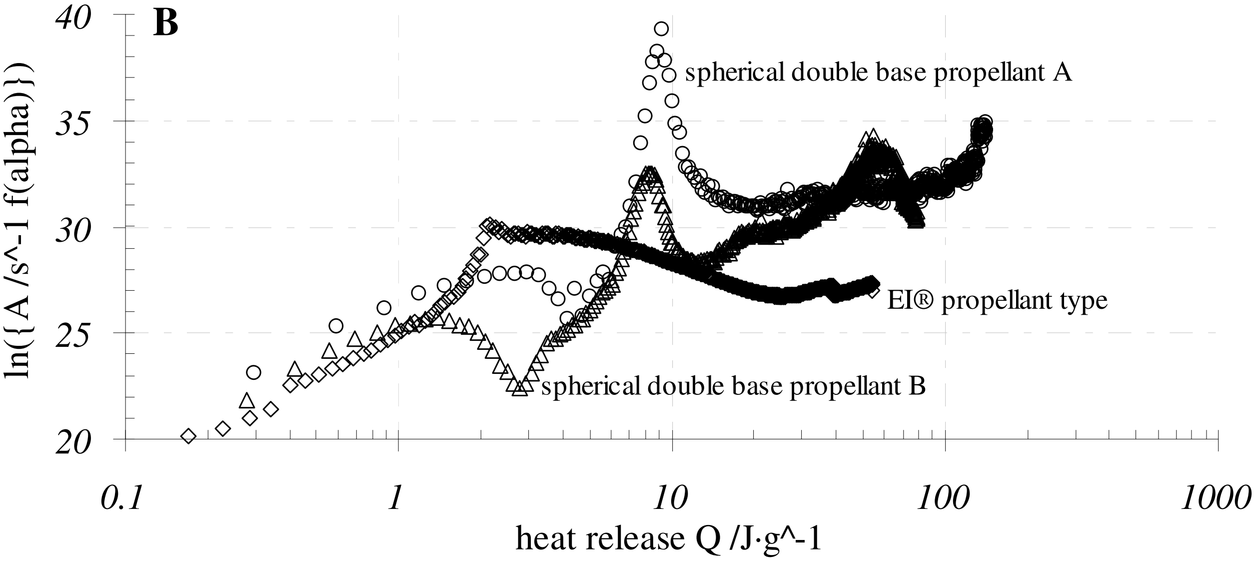


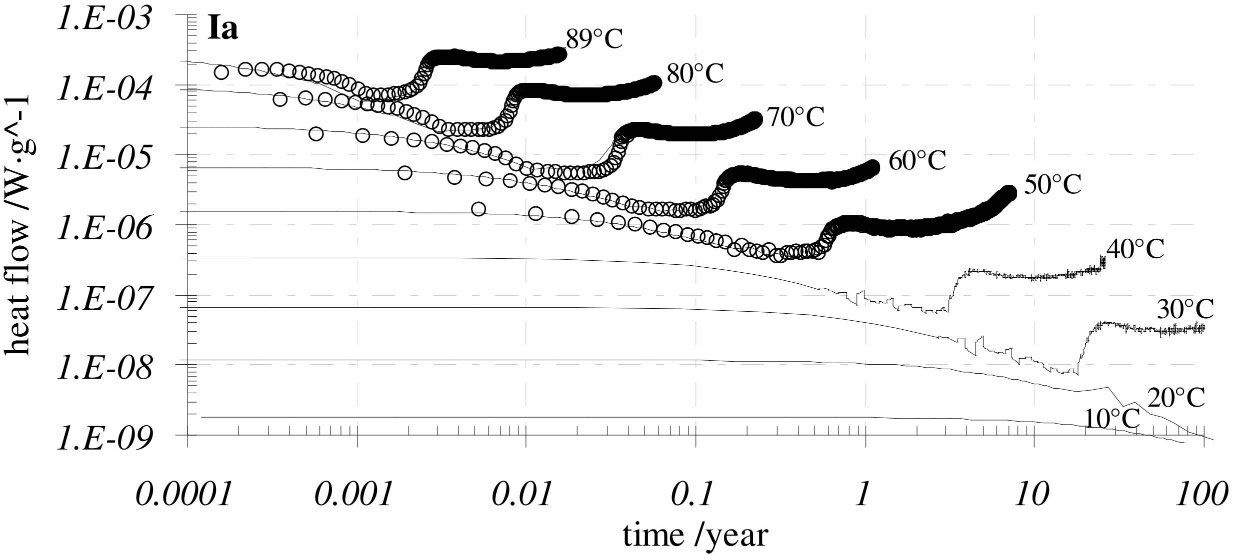
Fig. 2. (A) Activation energy *E* (kJ/mol) and (B) pre-exponential factor expressed as $\{A_\alpha f(\alpha)\}$ for the propellants calculated from HFC signals by the Friedman analysis.

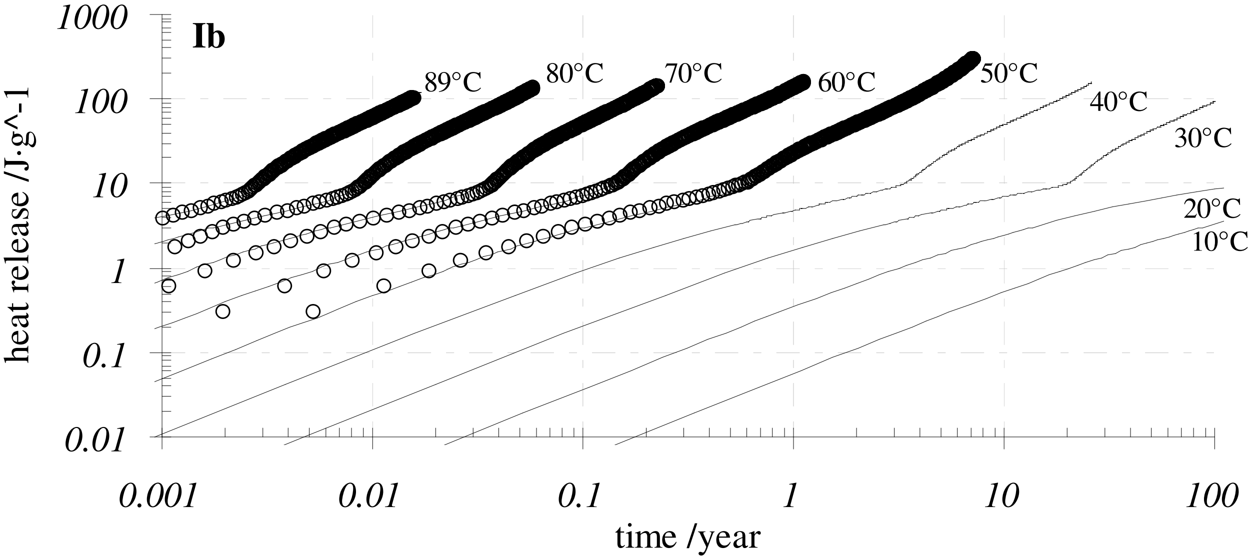
Table 1. The cumulative heat of the reaction as a function of time and temperature

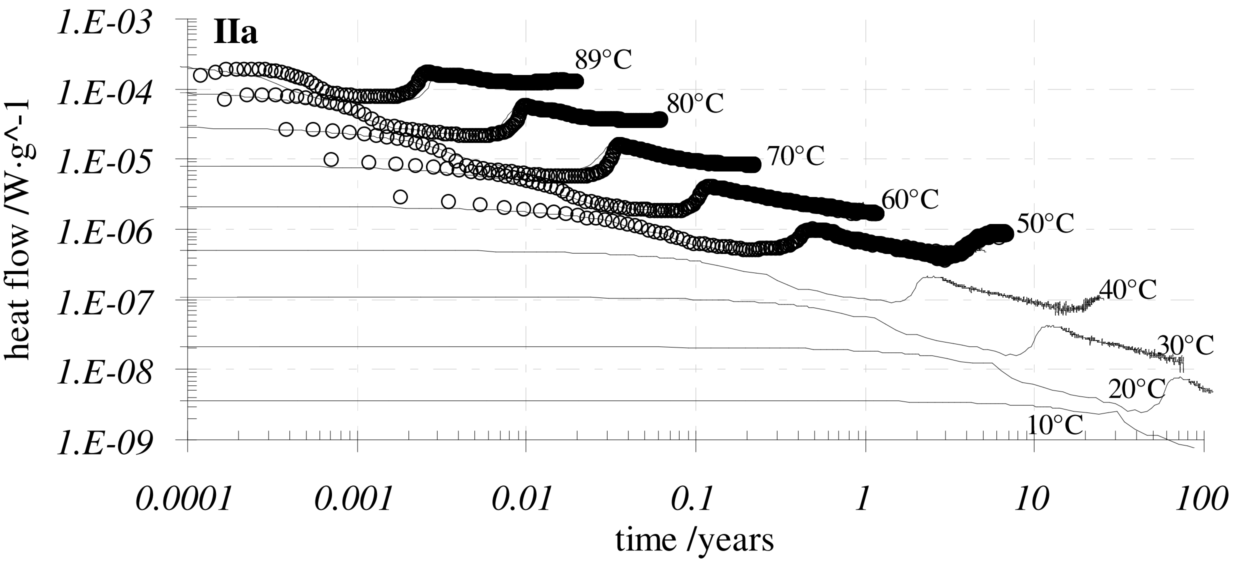
Propellant	T (°C)	t (days)	Heat release Q (J/g)
Spherical double base A	50	2621.48	296.055
Spherical double base A	60	408.16	155.593
Spherical double base A	70	82.79	141.998
Spherical double base A	80	21.18	132.315
Spherical double base A	89	13.14	102.77
Spherical double base B	50	2491.34	138.712
Spherical double base B	60	432.29	83.168
Spherical double base B	70	81.47	65.124
Spherical double base B	80	22.73	72.798
Spherical double base B	89	7.32	78.891
EI® type propellant	60	122.99	54.121
EI® type propellant	70	34.8	54.204
EI® type propellant	80	10.6	57.008
EI® type propellant	90	3.43	55.015
EI® type propellant	100	1.18	55.927

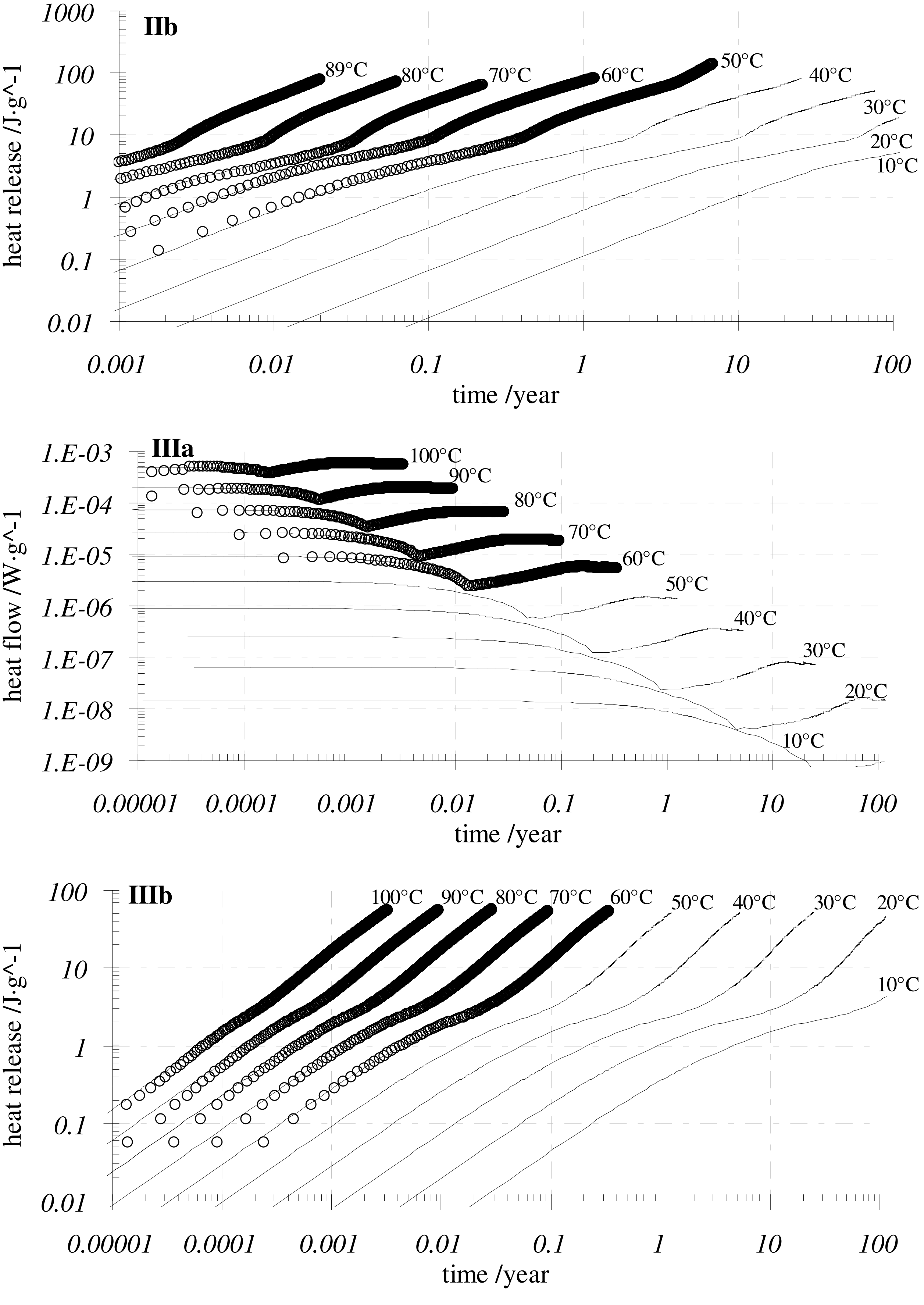
5.2 PREDICTION OF THE HEAT FLOW AND HEAT RELEASE UNDER ISOTHERMAL CONDITIONS

The comparison of the experimental data (symbols) with the simulated course of the reactions (lines) using the kinetic parameters derived by Friedman method is depicted in Fig.3. Presented relationships indicate that application of the isoconversional approach enables the proper simulation of the change of the reaction course during at the early stage of the decomposition. The very good description of the high and low temperature data by the same kinetic parameters indicates that independent of the temperature they stay constant at the same reaction progress and can be used for the simulation of the reactions occurring in wide temperature range.


Ia
heat flow /W·g^-1
1.E-03
1.E-04
1.E-05
1.E-06
1.E-07
1.E-08
1.E-09
89°C
80°C
70°C
60°C
50°C
40°C
30°C
20°C
10°C
0.0001
0.001
0.01
0.1
1
10
100
time /year


Ib
heat release /J·g^-1
1000
100
10
1
0.1
0.01
89°C
80°C
70°C
60°C
50°C
40°C
30°C
20°C
10°C
0.001
0.01
0.1
1
10
100
time /year


IIa
heat flow /W·g^-1
1.E-03
1.E-04
1.E-05
1.E-06
1.E-07
1.E-08
1.E-09
89°C
80°C
70°C
60°C
50°C
40°C
30°C
20°C
10°C
0.0001
0.001
0.01
0.1
1
10
100
time /years



Figs. 3. Cumulative heat (a) and heat flow (b) for spherical double base propellants A(I), B (II) and EI® type propellant (III). Experimental and simulation temperatures are marked on curves.

6. APPLICATION OF HFC DATA FOR THE PREDICTION OF THE REACTION PROGRESS UNDER TEMPERATURE MODE CORRESPONDING TO REAL ATMOSPHERIC TEMPERATURE CHANGES

The important goal for investigating kinetics of thermal decompositions of propellants is the need to determine the thermal stability, i.e. the temperature range over which the substance does not decompose at an appreciable rate. During their production, storage or final usage the propellants often undergo temperature fluctuations. Due to the fact that the reaction rate varies exponentially with the temperature it is important that predictive tools enable the simulation of the reaction progress in the real conditions, as a small temperature jump can induce a significant increasing of reaction rate. Since the HFC data are very precise at the early stage of the decomposition process, the reaction rate can, therefore, be predicted very precisely for any temperature profile, such as stepwise variations, oscillatory conditions, temperature shock, or real atmospheric temperature profiles. To illustrate the importance of the influence of the temperature fluctuations on the reaction course, the simulations of the reaction progress (expressed by the cumulative heat release) were carried out for:

- the average daily minimal and maximal temperatures recorded for each day of the year in Beijing,
- the high temperature climatic category A2 according to the STANAG 2895 [3]. This document describes the principal climatic factors which constitute the distinctive climatic environments found throughout the world,
- the storage temperature profile corresponding to various temperature scenarios and cycles as presented in Table 2 and Figure 4.

Table 2. Simulated storage T-profile during ten years (A) and during two cycles (B)

A

T (°C)	Number of days	Cumulative number of hours
15	365	8760
10	365	17520
T-Cycle No 1	200	22320
10	150	25920
15	60	27360
5	50	28560
T-Cycle No 2	365	37320
15	100	39720
20	365	48480
25	100	50880
15	1000	74880
20	530	87600

B

t (hours)	T-Cycle No 1 (°C)	T-Cycle No 2 (°C)
1	27	28
2	25	26
3	25	27
4	26	27
5	25	26
6	26	25
7	28	28
8	30	32
9	35	36
10	32	41
11	35	45
12	41	49
13	49	55
14	50	53
15	52	57
16	51	55
17	51	52
18	48	50
19	45	47
20	43	42
21	42	35
22	40	30
23	35	28
24	30	29

The precise prediction of the influence of the temperatures on the decomposition of the propellants can be determined based on the knowledge of the short (hours) and long (days, weeks or even years) variations of the storage or transit temperatures. Table 2 contains an example of the variations of the storage temperatures during ten years including the various temperature scenarios and cycles. Another case, illustrating the time dependences of the diurnal minimal and maximal meteorological and storage and transit temperatures, is presented in Figure 5. Applying the advanced kinetic software it is possible to calculate the reaction progress using the kinetic parameters determined from HFC data and taking into account the complicated dependence of the real storage temperature changes on time depicted in Figure 4. The results of these simulations for the spherical double base propellant A are presented in Figure 5 as a curve (i). Additionally, Fig.5 contains the simulations for the diurnal storage/transit and meteorological temperature profiles according to STANAG 2895 (ii) and average daily minimal and maximal temperatures recorded in Beijing (iii).

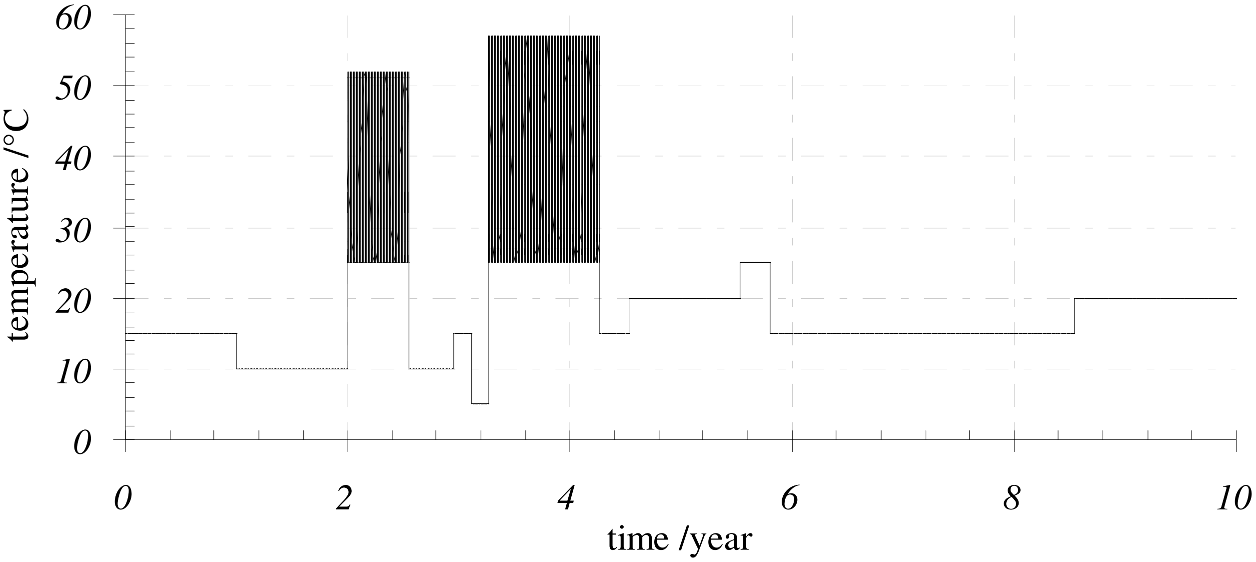


Fig. 4. Storage temperature profile during ten years corresponding to T-t dependences displayed in Table 2.

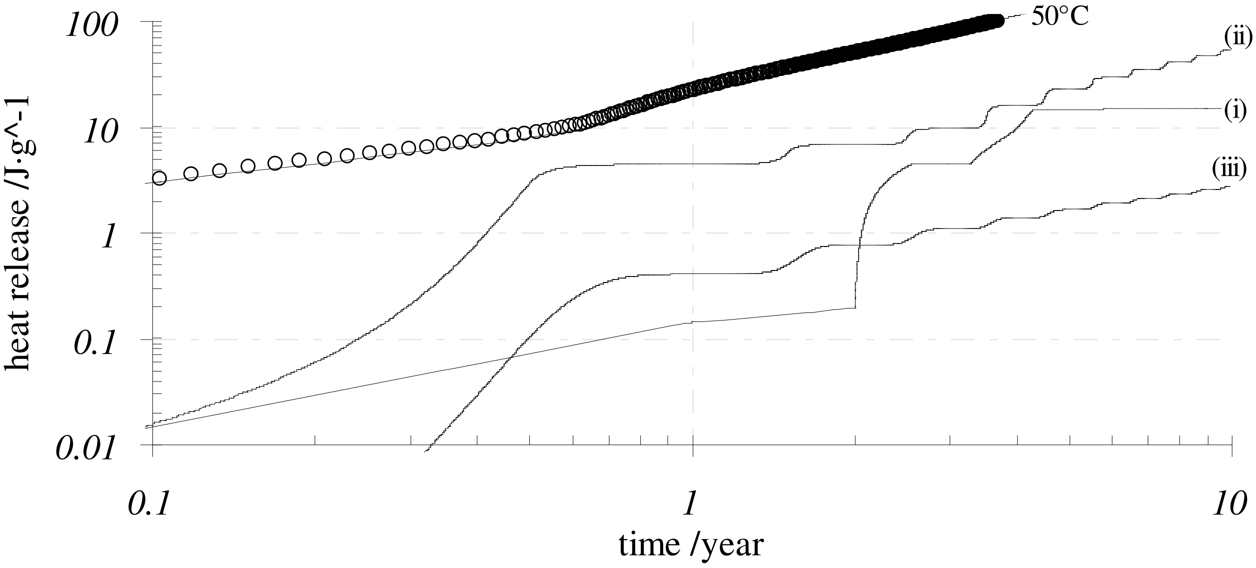


Fig.5. Prediction of the reaction progress of the spherical double base propellant A expressed as the cumulative heat release for the temperature profile depicted in Tab.2 and Fig.4 (i), for the diurnal storage/transit temperature for climatic category A2 according to the STANAG 2895 (ii) and for the meteorological temperature profiles of Beijing (iii). For comparison the simulation and HFC data at 50°C are presented in the figure.

By implementing the temperature variations, occurring during shorter and longer time periods, into advanced kinetic description gathered from the HFC data it was possible to uncover the differences of the reaction progress for the same propellant in different climatic categories. Results presented in Figure 5 indicate the very significant dependence of the thermal stability of the investigated propellants on the storage conditions. This important issue could be traced only due to the high precision of the HFC data and the unique ability of the isoconversional analysis approach which enables to describe very precisely the early stage of the complicated decomposition process. This, in turn, indicates that the prediction of the reaction progress, when using simplified kinetic models (e.g. first- or zero-th reaction order) and average mean temperature values, may be of little value.

7. CONCLUSION

The precise prediction of the thermal stability of energetic materials requires:

- (i) the exact determination of the reaction progress at the early beginning of the decomposition process in the range of the reaction progress α between 0 and ca. 0.05. This task can be fulfilled by applying HFC measurements due to the high sensitivity of this technique which enables even at low temperatures the determination of the reaction rate and the reaction progress at the early stages of the decomposition process,

- (ii) the application of the advanced methods for the determination of the kinetic parameters applied later in the computations of the thermal stability of the energetic materials,

- (iii) the necessity of introducing into calculations the real temperature profiles under which the investigated compounds will be stored.

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