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DETERMINING THE TEMPERATURE TO INITIATE THE EXPLOSION OF A PROPELLANT

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Gun propellants are per definition instable substances. During their lifetime a slow decomposition process is going-on. During this decomposition process the heat that is generated accelerates the process, which could result to an unsafe situation, or an unexpected explosion of the material.

The temperature to initiate the explosion of a propellant is of importance for the storage conditions of such a substance. The method used so far to evaluate this temperature is based on an extrapolation of the Kissinger equation at zero heating rate. A new proposal is the use of the invariant kinetic parameters (IKP) method to determine the iso-kinetic temperature and extrapolating it to zero heating rate as an alternative method. The results are discussed for some examples.

Keywords: *autoignition temperature, decomposition, iso-kinetic temperature, propellant*

Introduction

The propellants are materials which are thermodynamically unstable. Storing them rises always the question of highest temperature to be allowed to meet [1]. The propellants decompose at ambient temperatures. The rate of decomposition increases exponentially with temperature and the products of decomposition are usually dissipated to the surroundings. Above certain temperatures, the dissipation process cannot take over all the produced energy and the explosive begins to self-heat. The lowest temperature at which self-heating occurs is those of initiating the explosion of a propellant.

A method to determine the temperature to initiate the explosion of a propellant has been proposed earlier [2]. The method makes use of experimental data acquired at several heating rates and applies, subsequently, Kissinger method [3], which is extrapolated at zero heating rate.

The present work proposes the use of the invariant kinetic parameters for calculating the iso-kinetic temperature and extrapolates it at zero heating rate. This process avoids, thus, the need of taking the logarithm of zero, as required by the use of Kissinger method.

Experimental

Four propellants, A, B, C and D, respectively, were used for our experiments. Their composition is based on a variable mixture of nitro-cellulose and nitroglycerine. The thermal analysis (TG) was carried out in a Mettler TGA/SDTA 851^e 1600 LF/MT5 at heating rates of 0.5, 1, 2 and 5 K min^{-1}. A 50 mL min^{-1} flow of nitrogen was used to remove the evolved gases and the experiments were carried for temperature ranging from 25 to 300°C.

Results and discussion

The TG curves for one of the energetic materials are shown in Fig. 1. Since the gas products are removed by the continuous nitrogen flow, we may assume that the reaction obeys a first order decomposition rate equation, based on a simple bond breaking [4].

The earlier work of Harris [2] suggests the use of Kissinger method to calculate the values of the activation energy, E, and pre-exponential factor, A, respec-

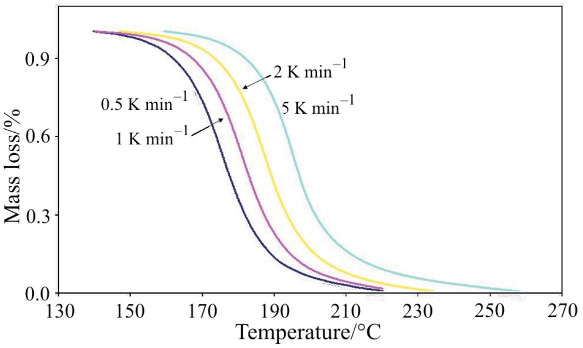

Fig. 1 TG curves of the propellant A

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tively. Then considering that for heating rate tending to zero the ratio $E\beta/RT^2$ equals 0.1, one calculates the value of peak temperature corresponding to it from the equation [2]:

$$T = \frac{E/R}{\ln A - \ln 0.1} \tag{1}$$

This temperature is stated to be the autoignition one.

There are many errors which may affect this calculation, from the accuracy of the E and A value obtained via Kissinger method to the arbitrary value of 0.1 towards which is considered that the ratio $E\beta/RT^2$ tends when heating rate, β, becomes zero.

Our approach is based on the concept of invariant kinetic parameters (IKP) and it is, thus, fundamentally different from those of Harris.

Like in all the kinetic studies we shall start from the empirical relationship of the reaction rate for overall process after substituting time with temperature [5]:

$$\mathrm{d}\alpha/\mathrm{d}T = A/\beta f(\alpha)\exp(-E/\mathrm{R}\mathrm{T}) \tag{2}$$

where α is the conversion degree, T is the temperature, $f(\alpha)$ is the kinetic function, $\beta=\mathrm{d}T/\mathrm{d}t$ is the heating rate, and A and E are the pre-exponential factor and the activation energy, respectively, or the kinetic parameters of the process.

The experimental data, as acquired by thermal analysis equipment, is a collection of pairs (α_i, T_i), recorded under a heating programme, β. For various heating programmes, β_j, these collections are $(\alpha_i, T_i)_j$, and, out of these, the kinetic parameters are calculated.

The total experimental data we obtain from a non-isothermal experiment can be, then, summed up as:

$$\ln\left[\left(\frac{\mathrm{d}\alpha_i/\mathrm{d}T_i}{f_n(\alpha_i)}\right)_j \beta_j\right] = -\frac{E_n/R}{(T_i)_j} + \ln A_n \tag{3}$$

For the data acquired at each heating rate the plot of left side member *vs.* $1/T_i$ supplies the value of parameters E and A, respectively, from the slope and intercept of the plot. As it appears from Eq. (3), their values are affected by the choice made for the analytical form of the kinetic function, f. One can write this by including an index, n, to the kinetic function: f_n, and, accordingly, to E and A: E_n and A_n, showing their dependence on the form of the kinetic function. Also their values are inter-related, or, in other words, once the value of parameter E is obtained, those of parameter A results subsequently. This fact leads to the so-called mathematical compensation effect (MCE), to be distinguished from the real one (RCE) which might appear due to the change of the reaction environment, etc. [6, 7].

Taking these into account and omitting the index i, Eq. (3) can be, simply, rewritten as:

$$Y_{j,n} = E_{j,n}X_j + \ln A_{j,n} \tag{4}$$

Equation (4) points out that by using the experimental data $(\mathrm{d}\alpha/\mathrm{d}T, T)$, and various kinetic functions $f_n(\alpha)$, for each heating rate β_j one may plot a straight line whose slope equals E_j and whose intercept equals to $\ln A_j$. The group of all these straight lines forms, as shown by several other authors [6, 8], a pencil of lines in the plane (X, Y). The crossing point (or better saying crossing region) has coordinates that are invariant for all the straight lines plotted in that plane. These are called the invariant values of the kinetic parameters E and A, as they are not depending on the choice of the kinetic function any longer.

As Eq. (4) suggests, one may also use the plot of the experimental points in the plane $(E, \ln A)$. The plot of the values of $\ln A_{j,n}$ *vs.* $E_{j,n}$, the values being calculated for several kinetic function, $f_n(\alpha)$, and the same heating rate, equals $1/RT_{ik}$ which gives the iso-kinetic temperature, T_{ik} for that heating rate. The plot of these iso-kinetic temperatures *vs.* the heating rates for which has been calculated gives a straight line, whose intercept is the iso-kinetic temperature at zero heating rate, T_{ik}^0. This temperature we consider to be more appropriate to the autoignition temperature.

An example of such calculation is given for the propellant A. For heating rate equals 0.5 K min^{-1}, out of the primary data α and T (Fig. 1) and by choosing the analytical form of the kinetic function from the Table 1, we calculated the left-hand member in Eq. (3).

For each analytical form of the kinetic function, the plot of left-hand member of Eq. (3) *vs.* $1/T$ leads to a straight line, whose slope and intercept gives the values of E and $\ln A$, corresponding to that kinetic function. The plot of all the values of $\ln A$ *vs.* those of E, calculated for all the kinetic functions, leads also to a

Table 1 Kinetic functions used for our calculations

Reaction model	$f(\alpha)$
power law	$(n+1)\alpha^{n/(n+1)}$ $n=1, 2, 3$
first order (Mampel), F1	$1-\alpha$
n^{th} order	$(1-\alpha)^n$ $n=1/2, 2/3, 1, 2$
Avrami–Erofeev (1D, 2D, 3D)	$(n+1)(1-\alpha)[-\ln(1-\alpha)]^{n/(n+1)}$ $n=1, 2, 3$
1D diffusion	$1/\alpha$
2D diffusion (Jander)	$\frac{1}{-\ln(1-\alpha)}$
3D diffusion	$\frac{3/2(1-\alpha)^{2/3}}{1-(1-\alpha)^{1/3}}$
Ginstling–Brounshtein (4D diffusion)	$\frac{3/2(1-\alpha)^{1/3}}{1-(1-\alpha)^{1/3}}$
Prout–Tompkins	$\alpha(1-\alpha)$

Table 2 The values of the iso-kinetic temperature calculated at four different heating rates for propellant A. The value extrapolated at zero heating rate is also listed, together with the value calculated according to Harris method [2]

Heating rate/K min^{-1}	Iso-kinetic temperature/°C	Autoignition temperature (this method)/°C	Autoignition temperautre (Harris method)/°C
0.5	154.867		
1	157.052		
2	164.252		
5	174.853		
0	153.371	153.371	178.57

Table 3 The results of the autoignition temperatures calculated according to our method and according to Harris method for four propellants. The results are rounded to the first digit

Propellant	Autoignition temperature (this method)/°C	Autoignition temperautre (Harris method)/°C
A	153.4	178.6
B	154.6	177.0
C	149.9	178.3
D	149.4	177.7

straight line, whose slope allows calculating the value of the iso-kinetic temperature, T_{ik}, corresponding to heating rate 0.5 K min^{-1}. The calculations are resumed for data acquired at the other heating rates (of 1, 2 and 5 K min^{-1}). The obtained iso-kinetic temperatures are, further, plotted *vs*. the corresponding heating rates and the intercept of the straight line is evaluated as being the autoignition temperature and listed in Table 2. In the same Table 2 we have given the value calculated according to the Harris method.

The same methodology has been applied for the other three propellants. All the results are collected in Table 3.

The differences between the values obtained by two methods are readily explainable by the approximations included in Harris method. As a matter of fact, by changing the value of 0.1 into 0.01, the autoignition temperatures drop by some 15 degrees. This only exhibits the arbitrary of the assumption.

Conclusions

We have proposed a method to calculate the autoignition temperature of a propellant based on the invariant kinetic approach. The method involves no approximations and allows calculating the values independent of the kinetic model assumed for the reaction. A comparison of the results obtained by the proposed method and by the alternative method of Harris exhibit differences that may be attributed to the approximations included in the other method.

References

1 G. Herder, F. P. Weterings and W. P. C. de Klerk, J. Therm. Anal. Cal., 72 (2003) 921.
2 J. Harris, Thermochim. Acta, 14 (1976) 183.
3 H. E. Kissinger, Anal. Chem., 29 (1959) 1702.
4 W. P. C. de Klerk, C. Popescu and A. E. D. M. van der Heijden, J. Therm. Anal. Cal., 72 (2003) 955.
5 C. Popescu and E. Segal, Int. J. Chem. Kin., 30 (1998) 313.
6 J. Pysiak and B. Sabalski, J. Thermal Anal., 17 (1979) 287.
7 H. Tanaka and N. Koga, J. Thermal Anal., 34 (1988) 685.
8 A. I. Lesnikovich and S. V. Lavchik, J. Thermal Anal., 27 (1983) 89.