

USING ORDINARY DIFFERENTIAL EQUATIONS SYSTEM TO SOLVE ISOCONVERSIONAL PROBLEMS IN NON-ISOTHERMAL KINETIC ANALYSIS

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The mathematical evaluation of the activation energy, E , of non-isothermal degradation reactions is usually made using the Ozawa/Flynn–Wall isoconversion principle and involves the numerical resolution of a set of integrals without closed form solution, which are solved by polynomial approximation or by numeric integration. In the present work, the isoconversion principle, originally described and maintained until now as an algebraic problem, was written as a set of ordinary differential equations (ODEs). The individual ODEs obtained are integrated by numeric methods and are used to estimate the activation energy of simulated examples. A least square error (LSE) objective function using the introduced ODEs was written to deal with multiple heating rate CaCO_3 thermal decomposition TG experiments.

Keywords: activation energy calculation, non-isothermal methods, temperature integrals

Introduction

The kinetic analysis of chemical degradation reactions involves the use of mathematical models with several parameters. The determination of the degradation activation energy parameter has a central role in these models. In the 60's the isoconversion principle presented by Ozawa [1] and Flynn–Wall [2] introduced the application of non-isothermal methods for the activation energy evaluation of reactions induced by different heating rates. These original and subsequent works were all based on the resolution of temperature integrals which arises during the application of the isoconversional principle, some of them using polynomial approximations [3–5] and others based on numeric solutions of temperature integrals [6–8].

Non-isothermal methods and isoconversion principle

In spite of some controversial objections [9, 10], the chemical kinetics of reactions have been usually modeled by differential equations of the form:

$$d\alpha/dt = k[T(t)]f(\alpha) \quad (1)$$

where α – conversion degree of reaction or equivalent, t – time, T – temperature, $k[T(t)]$ – function of time dependent temperature and $f(\alpha)$ – function of conversion degree α .

Using the method of separation of variables, this model can be written:

$$\int_{\alpha_0}^{\alpha_1} d\alpha / f(\alpha) = \int_{t_i}^{t_f} k[T(t)] dt \quad (2)$$

Non-isothermal conversion processes can be carried out under different heating rates β_k , and a linear relationship between time and temperature can be established by:

$$T_k = T_{ki} + \beta_k(t_k - t_{ki}) \quad (3)$$

where t_{ki} – initial heating time in 'k' process, t_k – heating time in 'k' process, β_k – heating rate of 'k' process, T_{ki} – initial temperature in 'k' process and T_k – temperature in 'k' process.

The derivation of Eq. (3) in t_k and its substitution in Eq. (2) gives:

$$\int_{\alpha_0}^{\alpha_1} d\alpha / f(\alpha) = 1 / \beta_k \int_{T_i}^{T_f} k(T_k) dT_k \quad (4)$$

The isoconversion principle assures that processes conducted under different heating rates for the same isoconversion boundaries can be represented as an equality of the form [1, 2]:

$$\int_{\alpha_0}^{\alpha_1} d\alpha / f(\alpha) = 1 / \beta_1 \int_{T_{i1}}^{T_{f1}} k(T_1) dT_1 = 1 / \beta_2 \int_{T_{i2}}^{T_{f2}} k(T_2) dT_2 = \dots = 1 / \beta_n \int_{T_{in}}^{T_{fn}} k(T_n) dT_n \quad (5)$$

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The first term of this equality can not be evaluated, because $f(\alpha)$ can not be determined a priori. The numeric solution of Equality (5) involves the substitution of the integrals of $k(T)$ by linear approximations and the subsequent minimization of errors according to the least square error (LSE) method [1, 2, 11]. As an example of implementation for non-isothermal processes, Ozawa [12] used the approximating function

$$-2.315-0.4567E/(RT)$$

instead of

$$\log \left\{ (R/E) \int_0^{T_r} \exp[-E/(RT)] dT \right\}$$

More recently, Vyazovkin [6, 13] proposed a new approach to evaluate of activation energy minimizing the function:

$$\Phi(E_\alpha) = \sum_{i=1}^n \sum_{j=1}^n J[E_\alpha, T_i(t_\alpha)] / J[E_\alpha, T_j(t_\alpha)] \quad (6)$$

where i, j – experimental runs, E_α – activation energy (parameter to be calculated), t – time and

$$J[E_\alpha, T_i(t_\alpha)] = \int_{T_i}^{T_r} \exp\{-E_\alpha/[RT(t)]\} dt.$$

The function defined in Eq. (6) is shown to be independent of $f(\alpha)$ [13].

Description of the proposed method

Transforming isoconversion equality into ordinary differential equation system

In all the models based on the isoconversional principle, the main challenge is to work with the unknown function $f(\alpha)$ that appears in the first term of Equality (5). The proposed and innovative way to circumvent this difficulty is simply to ignore the first term of the Equality (5) based on the fact that equalities are mathematically equivalence relations and then all the terms are equal between themselves. Then, Equality (5) can be written in its differential form as:

$$\begin{aligned} [k(T_1)/\beta_1]dT_1 &= [k(T_2)/\beta_2]dT_2 = \\ [k(T_3)/\beta_3]dT_3 &= \dots = [k(T_n)/\beta_n]dT_n \end{aligned} \quad (7)$$

Combining two by two the terms of Equality (7), a set of differential equations can be written:

$$dT_2/dT_1 = (\beta_2/\beta_1)[k(T_1)/k(T_2)] \quad (8)$$

$$dT_3/dT_1 = (\beta_3/\beta_1)[k(T_1)/k(T_3)] \quad (9)$$

$$dT_3/dT_2 = (\beta_3/\beta_2)[k(T_2)/k(T_3)] \quad (10)$$

$$dT_n/dT_r = (\beta_n/\beta_r)[k(T_r)/k(T_n)] \quad (11)$$

Each one of the dT_k/dT_r differential equations in this set can be integrated in the independent variable, and can be stated in the generic form:

$$\int_{T_{ki}^E}^{T_{kf}^C} dT_k = \int_{T_{ri}^E}^{T_{rf}^E} (\beta_k / \beta_r) [k(T_r) / k(T_k)] dT_r \quad (12)$$

or

$$T_{kf}^C = T_{ki}^E + \int_{T_{ri}^E}^{T_{rf}^E} (\beta_k / \beta_r) [k(T_r) / k(T_k)] dT_r \quad (13)$$

where T_{ri}^E and T_{rf}^E are initial and final experimental temperatures obtained from thermogravimetric data of a ‘r’ reference process, and T_{ki}^E is the initial experimental temperature of a ‘k’ process. In function of these initial conditions, and supposing an initial value for E_c , the right side of Eq. (13) can be numerically evaluated, generating a calculated final temperature T_{kf}^C for the ‘k’ process. The desired value of E_c is the one that promotes convergence between the calculated T_{kf}^C and the experimental ‘k’ process temperature, T_{kf}^E , and can be obtained by iterations. In this way, E_c can be calculated for each pair of processes at constant heating rates β_k and β_r .

Equations (8)–(11) represent the theoretical solutions for Equality (7). They are free from modeling errors being affected only by numerical integration errors. In the usual range of temperatures used in thermogravimetry, far from absolute zero, numeric methods such as Runge–Kutta usually yield accurate results.

By inspection of equality (7) and Eqs (8)–(11) it can be concluded that the proposed model is independent of $f(\alpha)$ and other adjusting parameters such as frequency factor, being a free model in the same way but different from Vyazovkin’s proposal.

The first advantage of this methodology is that any $k(T)$ model can be applied with this new procedure. As an example, all the $k(T)$ models presented in Flynn [14] were transformed into the corresponding differential equation form as predicted by Eq. (12), and presented in Table 1. According to the $k(T)$ model selected, a differential equation system can be written in the form of the Eqs (8) to (11) as presented in Table 1.

Adapting the proposed method to the minimum least square error algorithm

Differential equations solutions are sensible to initial conditions and consequently to measurement errors in TG experiments. The proposed method, from now named JUJ method may be improved if it could be written as a least square error algorithm by the use of the objective function [11]:

$$S = \sum_{r=1}^m \left[\sum_{k=2}^n (T_{k,r}^c(E) - T_{k,r}^e)^2 \right] \quad (14)$$

Table 1 Differential equations corresponding to the main kinetic models summarized by Flynn [14]

Differential equations	Model
$dT_j/dT_k=(\beta_j/\beta_k)\exp[E(T_k-T_j)]$	Berthelot, Hood
$dT_j/dT_k=(\beta_j/\beta_k)(T_k/T_j)^B$	Harecourt, Esson
$dT_j/dT_k=(\beta_j/\beta_k)\exp[-(E/R)(1/T_k-1/T_j)]$	Arrhenius
$dT_j/dT_k=(\beta_j/\beta_k)(T_k/T_j)^B\exp[-(E/R)(1/T_k-1/T_j)]$	Kooij
$dT_j/dT_k=(\beta_j/\beta_k)\exp[E'(T_k-T_j)]\exp[-(E/R)(1/T_k-1/T_j)]$	Van't Hoff
$dT_j/dT_k=(\beta_j/\beta_k)(T_k/T_j)^B\exp[E(T_k-T_j)]$	by analogy
$dT_j/dT_k=(\beta_j/\beta_k)(T_k/T_j)^B\exp[E'(T_k-T_j)]\exp[-(E/R)(1/T_k-1/T_j)]$	Van't Hoff
$dT_j/dT_k=(\beta_j/\beta_k)\exp[-a[1/(T_k+b)-1/(T_j+b)]]$	VFT or WLF

where l corresponds to the integration interval and k to the heating rate. The notation c and e indicate the calculated temperature from ODEs integration, and experimental temperature data, respectively. The parameter E is selected so as to minimize the sum S for each integration interval considered.

Results and discussion

Simulated examples using the proposed JJJ method and Ozawa method

Design of simulated experiments for different A , E , $f(\alpha)$ and β

The model $d\alpha/dT=A/\beta\exp[-E/(RT)]f(\alpha)$ was integrated for different values of the parameters A , β and E and for different reaction mechanisms $f(\alpha)$. Two levels of A (10^6 and 10^{11} s $^{-1}$), three levels of β (5, 10 and 20 K min $^{-1}$), two levels of E (80 and 160 kJ mol $^{-1}$), and two functions for $f(\alpha)$ (α^1 and α^3) were used to compose a factorial design of experiments. The differential equations were integrated for each set of parameters and selected function using Matlab software. The values of A and

E were presented by Yeremin [15], as current kinetic data. The values of α as a function of T obtained from the simulation were established. Each set of α values was normalized. For $\alpha=0.9$, 0.8 and 0.5 (values of isoconversion of 10, 20 and 50%, respectively), the temperatures T_{90} , T_{80} and T_{50} were obtained. Temperatures T_{90} , T_{80} and T_{50} were considered using Ozawa method, implemented using Excell software. For each C_2^3 combination between these temperatures and for each pair of (β_k, β_l) , Eq. (12) was integrated by iteration in a 4th order Runge–Kutta implementation for the JJJ proposed method using Fortran software.

The E parameter considered in the simulation and the calculated values of E_c obtained using Ozawa and JJJ methods are presented in Tables 3 to 8, where each set of initial conditions are represented by four digits labels. The first digit label corresponds to the parameter A (0,1), the second corresponds to heating rate β (0,1,2), the third corresponds to the activation energy E (0,1), and the fourth corresponds to the reaction mechanism $f(\alpha)$ (0,1). For example, the set identified with the label number 1201 is associated with the simulation using the parameters: $A=10^{11}$ s $^{-1}$, $\beta=20$ K min $^{-1}$, $E=80$ kJ mol $^{-1}$ and $f(\alpha)=\alpha^3$. Table 2 lists the labels and their respective simulation parameters.

Table 2 Labels and parameters of simulation

Label	A/s^{-1}	$\beta/K \text{ min}^{-1}$	$E/kJ \text{ mol}^{-1}$	$f(\alpha)$	Label	A/s^{-1}	$\beta/K \text{ min}^{-1}$	$E/kJ \text{ mol}^{-1}$	$f(\alpha)$
0000	10^6	5	80	α^1	1000	10^{11}	5	80	α^1
0001	10^6	5	80	α^3	1001	10^{11}	5	80	α^3
0010	10^6	5	160	α^1	1010	10^{11}	5	160	α^1
0011	10^6	5	160	α^3	1011	10^{11}	5	160	α^3
0100	10^6	10	80	α^1	1100	10^{11}	10	80	α^1
0101	10^6	10	80	α^3	1101	10^{11}	10	80	α^3
0110	10^6	10	160	α^1	1110	10^{11}	10	160	α^1
0111	10^6	10	160	α^3	1111	10^{11}	10	160	α^3
0200	10^6	20	80	α^1	1200	10^{11}	20	80	α^1
0201	10^6	20	80	α^3	1201	10^{11}	20	80	α^3
0210	10^6	20	160	α^1	1210	10^{11}	20	160	α^1
0211	10^6	20	160	α^3	1211	10^{11}	20	160	α^3

Table 3 Activation energy, E_c , calculated between T_{90} and T_{80} using JJJ method

Label		$E/\text{kJ mol}^{-1}$	$E_c/\text{kJ mol}^{-1}$
0000	0100	80	80.046
0000	0200	80	80.017
0001	0101	80	79.988
0001	0201	80	79.997
0010	0110	160	159.978
0010	0210	160	159.990
0011	0111	160	159.986
0011	0210	160	159.987

Simulated results for $A=10^6 \text{ s}^{-1}$

Table 4 Activation energy, E_c calculated between T_{90} and T_{50} using JJJ method

Label		$E/\text{kJ mol}^{-1}$	$E_c/\text{kJ mol}^{-1}$
0000	0100	80	79.979
0000	0200	80	79.992
0001	0101	80	80.009
0001	0201	80	80.006
0010	0110	160	159.995
0010	0210	160	159.993
0011	0111	160	159.986
0011	0210	160	159.998

Simulated results for $A=10^6 \text{ s}^{-1}$

For the frequency factor $A=10^6 \text{ s}^{-1}$ both JJJ and Ozawa methods reproduced adequately theoretical values of E , regardless of the function $f(\alpha)$ and the activation energy used.

The E_c values calculated by the proposed JJJ method are more accurate than those obtained using the Ozawa method. The observed difference between E and E_c calculated by JJJ method is less than 0.06% against about 5% deviation achieved when the Ozawa method is applied.

As observed in Table 6, for the frequency factor $A=10^{11} \text{ s}^{-1}$, the proposed JJJ method of calculating activation energy for the simulated condition using $E=80 \text{ kJ mol}^{-1}$ and isoconversion temperatures between T_{90} and T_{80} resulted in a simulated mass loss of 45% and the temperature interval analyzed was less than 0.02 K,

Table 5 Activation energy, E_c calculated using Ozawa method

Label	$E/\text{kJ mol}^{-1}$	$E_c/\text{kJ mol}^{-1}$				
		T_{90}	T_{80}	T_{50}		
0000	0100	0200	80	83.51	83.52	83.74
0001	0101	0201	80	83.51	83.54	83.99
0010	0110	0210	160	165.70	166.20	166.90
0011	0111	0211	160	165.80	166.30	167.40

Simulated results for $A=10^6 \text{ s}^{-1}$

Table 6 Activation energy, E_c calculated between T_{90} and T_{80} using JJJ method

Label		$E/\text{kJ mol}^{-1}$	$E_c/\text{kJ mol}^{-1}$
1000	1100	80	0.585
1000	1200	80	0.00073
1001	1101	80	0.000
1001	1201	80	338.818
1010	1110	160	160.035
1010	1210	160	160.016
1011	1111	160	159.993
1011	1210	160	160.041

Simulated results for $A=10^{11} \text{ s}^{-1}$

Table 7 Activation energy, E_c calculated between T_{90} and T_{50} using JJJ method

Label		$E/\text{kJ mol}^{-1}$	$E_c/\text{kJ mol}^{-1}$
1000	1100	80	143.261
1000	1200	80	108.709
1001	1101	80	74.464
1001	1201	80	83.221
1010	1110	160	159.942
1010	1210	160	159.972
1011	1111	160	159.996
1011	1210	160	160.010

Simulated results for $A=10^{11} \text{ s}^{-1}$

an unfeasible experimental condition, due to round-off errors during integration. Evaluating the JJJ method in an extended temperature interval, between T_{90} and T_{50} , better results were obtained as shown in Table 7. In this case the temperature interval analyzed was around 0.05 K showing that the error encountered in the first in-

Table 8 Activation energy calculated using Ozawa method

Label	$E/\text{kJ mol}^{-1}$	$E_c/\text{kJ mol}^{-1}$				
		T_{90}	T_{80}	T_{50}		
1000	1100	1200	80	$3.553 \cdot 10^7$	$1.674 \cdot 10^7$	$5.473 \cdot 10^6$
1001	1101	1201	80	$3.165 \cdot 10^7$	$1.331 \cdot 10^7$	$2.578 \cdot 10^6$
1010	1110	1210	160	161.300	161.500	161.800
1011	1111	1211	160	161.400	161.600	162.100

Simulated results for $A=10^{11} \text{ s}^{-1}$

Table 9 Calculated activation energies, in kJ mol^{-1} , using the proposed JJJ method applied to Ginstein Brounshtein heterogeneous reaction mechanism function for each heating rate (β_k, β_l) pair as a function of isoconversion temperatures

$(\beta_k, \beta_l)/\text{K min}^{-1}$	Isoconversion temperatures								
	$T_{95}-T_{90}$	$T_{90}-T_{80}$	$T_{80}-T_{70}$	$T_{75}-T_{60}$	$T_{60}-T_{50}$	$T_{50}-T_{40}$	$T_{40}-T_{30}$	$T_{30}-T_{20}$	$T_{20}-T_{10}$
5, 10	239.230	251.844	252.255	251.935	252.455	250.894	253.339	252.431	252.067
10, 15	252.067	252.209	252.066	252.700	251.227	255.248	250.406	252.362	252.069
5, 15	243.932	251.893	252.067	252.074	251.840	252.327	252.085	252.245	251.936

tegration condition is a numerical problem and can be solved by increasing the analyzed mass loss range. The Ozawa method failed in calculating activation energy values even in the extended T_{90} to T_{50} isoconversion temperatures, as can be seen in Table 8, showing the importance of rounding off errors.

Calculated energy values using the proposed JJJ method presented better agreement with simulated E parameter than Ozawa method results. The elimination of the reaction mechanism and pre-exponential factor, as given in Eqs (8)–(11) does not influence the calculated activation energy.

Simulation applying the proposed JJJ method to Ginstein Brounshtein model for $f(\alpha)$

The three dimensional diffusion Ginstein Brounshtein model $f(\alpha)$ for solid-state reactions $d\alpha/dt = A \exp[-E/(RT(t))] 3/2[(1-\alpha)^{-1/3}-1]$ was integrated for three different heating rates (5, 10 and 15 K min^{-1}) using parameters $A=2.1 \cdot 10^{11} \text{ min}^{-1}$ and $E=251.9 \text{ kJ mol}^{-1}$ as obtained by Perez-Maqueda *et al.* [16], to generate conversion dependent data α into T using Matlab software. The isoconversion temperatures for 95, 90, 80, 70, 60, 50, 40, 30, 20 and 10% of residual mass were used as integration limits (e.g. $T_{95}-T_{90}$) for Eq. (13) and E was renewed iteratively until convergence between the calculated and the experimental temperatures. Table 9 presents the results for E .

Using JJJ method, an average value of $251.378 \text{ kJ mol}^{-1}$ was calculated for E , in good agreement with the simulated value of $251.900 \text{ kJ mol}^{-1}$. The obtained standard deviation was $3.012 \text{ kJ mol}^{-1}$. The fact that no reaction mechanism $f(\alpha)$ was considered in the JJJ method did not interfere in the calculated activation energy values.

Application of the JJJ proposed method using a LSE objective function to calculate E values from experimental non-isothermal thermogravimetric data

CaCO_3 thermal decomposition

About 5 mg of CaCO_3 were transferred to 70 μL aluminium pans and weighed in XS 205 Dual Range Mettler Toledo balance.

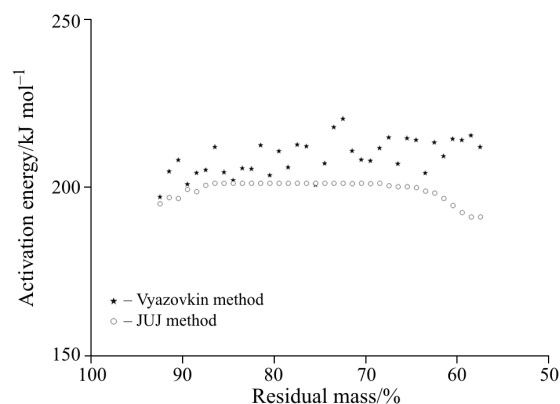


Fig. 1 Activation energy of CaCO_3 thermal degradation data corresponding to the range of 92.5 to 57.5% of residual mass calculated by Vyazovkin and JJJ methods

The thermogravimetric experiments were carried out in TGA/SDTA851^c, Mettler Toledo equipment, with a thermostatic F30-C Julabo bath for temperature control and a TS0800GC1 Mettler Toledo controller for gas purges. The thermal degradations were performed at heating rates of 1, 2 and 3 K min^{-1} under a nitrogen flow rate of 50 mL min^{-1} between room temperature and 1273 K.

The software Star^e, SW 7.01 in accordance with Vyazovkin free model theory and LSE Fortran implementation of the proposed JJJ method as given in Eq. (14) were used to calculate the activation energy E of thermal decomposition reaction using experimental data of CaCO_3 . To make a better comparison between the results, E values were calculated at 1 K temperature interval in the range of 92.5 to 57.5% of residual mass data. The calculated values were shown in Fig. 1.

The Vyazovkin method estimates an average activation energy value of $E=209 \text{ kJ mol}^{-1}$ with a variance of 5 kJ mol^{-1} . For the same data, the proposed JJJ method estimate an average activation energy value of $E=199 \text{ kJ mol}^{-1}$ with a variance of 3 kJ mol^{-1} . An excellent agreement between the results obtained from the two considered methods was observed. The activation energy values calculated by JJJ proposed method for CaCO_3 thermal decomposition agree with those presented in current technical literature which lie between 178 kJ mol^{-1} [17] and 205 kJ mol^{-1} [17, 18] due to CO_2 diffusive effects.

Conclusions

This paper presents a new method for the calculation of the activation energy of non-isothermal thermo-analytical experiments based on numerical solution of systems of differential equations derived from the isoconversion principle of Ozawa/Flynn–Wall. The primary innovation consists in using the equivalence relation property of equalities to eliminate the reaction mechanism from the original equality, which allows transforming an algebraic problem into an ordinary differential equation problem. The differential equations obtained demonstrated to be flexible and adapted to absorb others than Arrhenius $k(T)$ models. The obtained solutions were used to create a LSE objective function to solve problems with multiple heating rates. As LSE was employed, the analysis of variance, ANOVA, can be used to select the set of experiments that minimizes variance improving the quality of E values calculated from experimental data. In addition, all the tools of ANOVA can be applied to the JUJ proposed method without restrictions.

Simulated and experimental data were presented comparing the calculated values using the JUJ and other established methods. A good agreement between the results was achieved. The JUJ proposed method is intrinsically model free and can be used as an alternative for actually existent non-isothermal isoconversional calculating methods of activation energies.

Acknowledgements

The authors gratefully acknowledge to Dr. Joseph Henry Flynn, Dr. Eddy Segura Pino, Mr. Po Lam Chang and Dr. Karina Sorrentino Lopes for kindly reading the manuscript and helpful comments.

References

- 1 T. Ozawa, *Bull. Chem. Soc. Jpn.*, 38 (1965) 1881.
- 2 J. H. Flynn and L. A. Wall, *J. Polym. Sci. Part B*, 4 (1966) 323.
- 3 C. D. Doyle, *Quantitative Calculations in Thermogravimetric Analysis*, Marcel Dekker, New York 1966.
- 4 J. Šesták, in: *Wilson and Wilson's Comprehensive Analytical Chemistry*, G. Svehla, Ed., Elsevier, Amsterdam 1984.
- 5 T. Wanjun, *J. Therm. Anal. Cal.*, 74 (2003) 309.
- 6 S. Vyazovkin and C. A. Wight, *Thermochim. Acta*, 341 (1999) 53.
- 7 A. K. Galway and M. E. Brown, *Thermochim. Acta*, 386 (2002) 91.
- 8 A. K. Galway, *Thermochim. Acta*, 397 (2003) 249.
- 9 J. H. Flynn, *Thermochim. Acta*, 203 (1992) 519.
- 10 J. H. Flynn, *J. Thermal Anal.*, 44 (1995) 499.
- 11 E. P. G. Box and N. R. Draper, *Empirical Model-Building and Response Surfaces*, John Wiley & Sons, New York 1987.
- 12 W. W. Wendlandt, *Thermal Analysis*, John Wiley & Sons, New York 1986.
- 13 S. Vyazovkin, *J. Thermal Anal.*, 49 (1997) 1493.
- 14 J. H. Flynn, *Thermochim. Acta*, 300 (1997) 83.
- 15 E. N. Yeregin, *The Foundations of Chemical Kinetics*, Mir Publishers, USSR 1976.
- 16 L. A. Péres-Maqueda, J. M. Criado, F. J. Gotor and J. Málek, *J. Phys. Chem. A*, 106 (2002) 2862.
- 17 A. K. Galway and M. E. Brown, *Thermochim. Acta*, 300 (1997) 107.
- 18 D. Beruto and A. W. Searcy, *J. Chem. Soc., Faraday Trans. I*, 70 (1974) 2145.

Received: February 7, 2006

Accepted: May 10, 2006

OnlineFirst: October 20, 2006

DOI: 10.1007/s10973-006-7527-0