Journal of Thermal Analysis and Calorimetry, Vol. 79 (2005) 703–708

SINGLE-STEP KINETICS APPROXIMATION EMPLOYING NON-ARRHENIUS TEMPERATURE FUNCTIONS

P. Šimon[*]

Department of Physical Chemistry, Faculty of Chemical and Food Technology, Slovak University of Technology, Radlinského 9,
812 37 Bratislava, Slovak Republic

Solid-state reactions ordinarily demonstrate a tangled interplay of various chemical and physical processes. The single-step kinetics approximation resides in substituting a generally complex set of kinetic equations by the sole single-step kinetics equation. It enables to describe the kinetic hypersurface in a simple way irrespective of the complexity of the overall process. The kinetic hypersurface is the dependence of conversion on temperature and time. The functions describing the temperature and conversion components of the hypersurface should be separable. For a complex process, the adjustable parameters in the temperature function have no mechanistic significance so that there is no reason to be confined to the Arrhenius relationship. Two groups of isoconversional methods based on non-Arrhenius temperature functions are presented and the corresponding formulas for isothermal, integral, differential and incremental isoconversional methods are derived. As an example of the method using the explicit expression of the conversion function, the first-order kinetics is treated. Comparing with the methods based on the Arrhenius relationship, the greatest advantage of the methods presented here is that the problems with calculating the temperature integral are eliminated since the corresponding integrals can be expressed in a closed form.

Keywords: *condensed phase, isoconversional methods, modelling, non-isothermal kinetics*

Introduction

Processes in condensed phase are extensively studied by thermoanalytical methods. Mechanisms of these processes are very often unknown or too complicated to be characterised by a simple kinetic model. They tend to occur in multiple steps that have different rates. To describe their kinetics, the methods based on a single-step approximation are often used.

In the previous paper [1], fundamentals of the isoconversional methods based on the Arrhenius expression of the temperature function have been summarised. The physical meaning of the activation parameters has been analysed and it was concluded that the parameters are apparent quantities without a mechanistic interpretation. Two other functions were suggested to express the temperature function. In this paper, the single-step kinetics approximation is defined and two groups of methods based on the two non-Arrhenius functions are presented.

Theoretical

Single-step kinetics approximation

Rate of the processes in condensed state is generally a function of temperature and conversion:

$$\mathrm{d}\alpha/\mathrm{d}t=\Phi(T,\alpha) \tag{1}$$

The single-step approximation employs the assumption that the function Φ in Eq. (1) can be expressed as a product of two separable functions independent of each other, the first one, $k(T)$, depending solely on temperature T and the other one, $f(\alpha)$, depending solely on the conversion of the process, α:

$$\Phi(T,\alpha)=k(T)f(\alpha) \tag{2}$$

Combining Eqs (1) and (2), the rate of the complex multi-step condensed-state process can be formally described by a single-step general rate equation [1]

$$\mathrm{d}\alpha/\mathrm{d}t=k(T)f(\alpha) \tag{3}$$

The temperature function $k(T)$ is mostly considered to be the rate constant and the conversion function $f(\alpha)$ is considered to reflect the mechanism of the process. Equation (3) resembles a single step kinetics equation, even though it is a representation of the kinetics of a complex condensed-phase process. The single-step kinetics approximation thus resides in substituting a generally complex set of kinetic equations by the sole single-step kinetics equation. Equation (3) represents a mathematical formulation of the single-step kinetics approximation.

Except a few exceptions, the temperature function is exclusively expressed by the Arrhenius equation

---

[*] peter.simon@stuba.sk

1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

$$k(T)=A\exp[-E/RT] \tag{4}$$

where A and E are considered the preexponential factor and the activation energy, respectively, T is the absolute temperature and R stands for the gas constant. The isoconversional methods based on Eq. (4) have been reviewed in [1].

Non-Arrhenius temperature functions

Various functions suggested to express the temperature dependence of the rate constant on temperature are summarised in [2, 3]. Of those functions, the following two ones were suggested to be highly suitable to be used as temperature functions [1]:

$$k(T)=AT^{\mathrm{m}} \tag{5}$$

$$k(T)=A\mathrm{e}^{\mathrm{DT}} \tag{6}$$

where A, m and D are adjustable parameters. Both functions given by Eqs (5) and (6) were sporadically employed for the treatment of thermoanalytical kinetic data [3]. During the last decade, Eq. (5) was used several times in interpreting the kinetics of solid-state decomposition [4–6]. When using Eqs (5) and (6), the formulas describing the kinetics are nicely simple. It is thus surprising that the methods based on Eqs (5) and (6) did not find a more extensive application. To my opinion, the two kinetic functions deserve much more attention. The formulas for the kinetic methods based on Eqs (5) and (6) are thus further derived.

Isothermal isoconversional method

For isothermal conditions, the rate constant is a constant. After separation of variables, Eq. (3) can be rearranged into the form:

$$\int_0^{\alpha}\frac{\mathrm{d}\alpha}{f(\alpha)}=k\int_0^{t_\alpha}\mathrm{d}t \tag{7}$$

where t_α is the time at which the conversion α is reached. If we denote the primitive function of the integral at the left side of Eq. (7) as F, one can get:

$$F(\alpha)-F(0)=kt_\alpha \rightarrow t_\alpha=\frac{F(\alpha)-F(0)}{k} \tag{8}$$

If the temperature function $k(T)$ is expressed by Eq. (5) or Eq. (6), one can get the expressions for the time t_α:

$$t_\alpha=\frac{1}{A_\alpha T^{\mathrm{m}}} \tag{9}$$

$$t_\alpha=\frac{1}{A_\alpha \mathrm{e}^{\mathrm{DT}}} \tag{10}$$

In both cases, the parameter A_α is given as:

$$A_\alpha=\frac{A}{F(\alpha)-F(0)} \tag{11}$$

The subscript α at A_α and t_α designates the values related to the fixed value of conversion. Hence, the parameters A_α and m (or A_α and D) can be obtained from a series of isothermal measurements, even by the direct treatment using Eqs (9) or (10), respectively, or from their linearized logarithmic transformations.

Isoconversional methods at linear heating

Integral methods

For non-isothermal conditions, combinations of Eqs (3) and (5), or Eqs (3) and (6) give:

$$\int_0^{\alpha}\frac{\mathrm{d}\alpha}{f(\alpha)}=A\int_0^{t_\alpha}T^{\mathrm{m}}\mathrm{d}t \tag{12}$$

$$\int_0^{\alpha}\frac{\mathrm{d}\alpha}{f(\alpha)}=A\int_0^{t_\alpha}\mathrm{e}^{\mathrm{DT}}\mathrm{d}t \tag{13}$$

Taking into account Eqs (11), (12) and (13) can be rewritten as:

$$1=A_\alpha\int_0^{t_\alpha}T^{\mathrm{m}}\mathrm{d}t \tag{14}$$

$$1=A_\alpha\int_0^{t_\alpha}\mathrm{e}^{\mathrm{DT}}\mathrm{d}t \tag{15}$$

The parameter A_α is defined by Eq. (11). Equations (14) or (15) should hold for any temperature regime and enable to calculate the time at which the fixed conversion α is reached. For the linear heating program, the furnace temperature can be expressed as

$$T=T_0+\beta t \tag{16}$$

where T_0 is the starting temperature of the measurement and β stands for the heating rate. From Eqs (14) and (16), or from Eqs (15) and (16) can thus be obtained:

$$\beta=A_\alpha\int_0^{T_\alpha}T^{\mathrm{m}}\mathrm{d}T \tag{17}$$

$$\beta=A_\alpha\int_0^{\mathrm{T}_\alpha}\mathrm{e}^{\mathrm{DT}}\mathrm{d}T \tag{18}$$

where T_α is the temperature at which the fixed conversion α is reached. The lower integration limit in Eqs (17) and (18) is set T_0=0 K since no process occurs in the sample at the starting temperature of the experiment.

The temperature integral at the right side of Eqs (17) and (18) can be expressed in a closed form. After integration one can get:

$$\beta = A_\alpha \frac{T_\alpha^{m+1}}{m+1} \tag{19}$$

$$\beta = \frac{A_\alpha}{D}(e^{DT_\alpha} - 1) \tag{20}$$

Differential method

For the linear temperature program, from combination of Eqs (3) and (5), or Eqs (3) and (6) one can obtain

$$\left(\frac{d\alpha}{dt}\right)_\alpha = \left(\beta\frac{d\alpha}{dT}\right)_\alpha = [Af(\alpha)]T_\alpha^m = A_\alpha T_\alpha^m \tag{21}$$

$$\left(\frac{d\alpha}{dt}\right)_\alpha = \left(\beta\frac{d\alpha}{dT}\right)_\alpha = [Af(\alpha)]e^{DT_\alpha} = A_\alpha e^{DT_\alpha} \tag{22}$$

The subscript α at the reaction rate indicates the rate at the fixed conversion α. In Eqs (21) and (22), the parameter A_α is defined as the product $Af(\alpha)$. From Eqs (21) and (22) it follows that the dependences of $\ln(\beta d\alpha/dT)_\alpha=f(\ln T_\alpha)$ or $\ln(\beta d\alpha/dT)_\alpha=f(T_\alpha)$ should be linear.

Incremental method

Since the differential method employs instantaneous rate values, it is very sensitive to experimental noise and tends to be numerically unstable [7, 8]. Using incremental methods can obviate this trouble. For the linear heating program, if Eqs (17) and (18) are integrated within the conversion increment α_1–α_2, one can arrive at:

$$\beta = \frac{A}{[F(\alpha_2) - F(\alpha_1)](m+1)}(T_2^{m+1} - T_1^{m+1}) = \frac{A_\alpha}{m+1}(T_2^{m+1} - T_1^{m+1}) \tag{23}$$

$$\beta = \frac{A}{D[F(\alpha_2) - F(\alpha_1)]}(e^{DT_2} - e^{DT_1}) = \frac{A_\alpha}{D}(e^{DT_2} - e^{DT_1}) \tag{24}$$

The conversions α_1 and α_2 are kept constant for various heating rates. In this case, the definition of the parameter A_α is obvious from Eqs (23) and (24). Due to the integration, the influence of experimental noise is eliminated to a great extent. For an infinitely small increment, Eq. (23) degenerates into Eqs (21) and (24) into Eq. (22). If it is set $\alpha_1=0$ at $T_1=0$, Eq. (23) degenerates into Eqs (17) and (24) into Eq. (18).

Methods with explicit expression of the conversion function

As it is obvious from Eq. (11), in the isoconversional methods, the value of the conversion function at the fixed conversion α is implicitly involved in the parameter A_α. However, the conversion function can be set in Eq. (3) explicitly.

For the isothermal process, Eq. (8) gives:

$$F(\alpha)-F(0)=kt \tag{25}$$

For the linear heating, combinations of Eqs (11) and (19) or Eqs (11) and (20) lead to the relationships:

$$F(\alpha) - F(0) = \frac{A}{\beta}\frac{T^{m+1}}{m+1} \tag{26}$$

$$F(\alpha) - F(0) = \frac{A}{\beta D}(e^{DT} - 1) \tag{27}$$

Equation (26) was derived by Dollimore *et al*. [4]. As it has been defined above, $F(\alpha)$ is the primitive function of $1/f(\alpha)$. Various conversion functions are reviewed, e.g., in [4]. For example, if the conversion function is expressed as a first-order kinetics function, then $F(\alpha)$–$F(0)$ is equal to $-\ln(1-\alpha)$. In this case, for the isothermal kinetics one can get from Eq. (25):

$$\alpha=1-e^{-kt} \tag{28}$$

For the linear heating, from Eq. (26) or Eq. (27) one can obtain for the first-order kinetics:

$$\alpha = 1 - \exp\left[-\frac{A}{\beta}\frac{T^{m+1}}{m+1}\right] \tag{29}$$

$$\alpha = 1 - \exp\left[-\frac{A}{\beta D}(e^{DT} - 1)\right] \tag{30}$$

In Eqs (28)–(30), the subscript 'α' is omitted since the evaluation of kinetic parameters is carried out for arbitrary values of conversion. The conversion can be expressed in an analogical way for other conversion functions.

Discussion

Main advantage of the methods

Two groups of isoconversional methods based on non-Arrhenius temperature functions are presented. The first group is based on Eq. (5) and the corresponding formulas for isothermal, integral, differential and incremental isoconversional methods are given by Eqs (9), (19), (21) and (23). The other group, based on Eq. (6), is represented by Eqs (10), (20), (22) and (24). Comparing with the methods presented in [1], the greatest advantage of the methods presented here is that the problems with calculating the temperature integral are eliminated since the corresponding integrals can be expressed in a closed form. Consequently, no special programs are needed for the calculation of adjustable parameters; any commercially available program package suitable for the treatment of experimental results can be employed (for example, the program ORIGIN).

For the explicit expression of conversion functions, the application of temperature functions in the forms given by Eqs (5) and (6) also leads to the analytical expression of conversion on time or temperature (Eqs (28)–(30)).

Obtaining and use of the adjustable parameters

The tendency still persists in thermoanalytical community to treat experimental results employing linearized functional dependences. This approach cannot be considered correct since any transformation of experimental data leads to a deformation of the distribution of errors, heteroskedasticity and a shift in the position of minima of the sum of squares between experimental and calculated values. Thus, the methods using the objective functions with transformed experimental data have to lead principally to biased estimates of adjustable parameters comparing to the values using directly the source experimental data [1]. Mainly in the case if one has an ambition to make quantitative predictions, the parameters obtained directly from the treatment of experimental data using Eqs (9), (19), (21) and (23), or Eqs (10), (20), (22) and (24), should be used for modelling the process. The linearized dependences are suitable to be used just for the illustration of validity of a given formula or for obtaining the starting parameters for the non-linear least squares method.

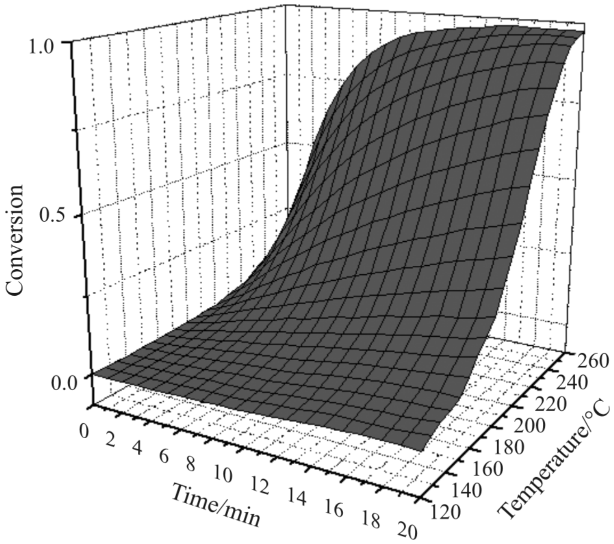

Fig. 1 Kinetic hypersurface calculated using Eq. (28), where the temperature function is expressed by Eq. (5). The parameters are: $A=10^{-55}$, $m=20$

The parameters obtained do not have any mechanistic significance. Knowing their values, one can model the kinetics of the process without a deeper insight into its mechanism [1].

Relationships between the adjustable parameters

The dependence of conversion on time and temperature can be understood as a kinetic hypersurface of the system under study (Fig. 1). Equation (1) describes the hypersurface in a general way whereas Eq. (3) represents a simplified way to make the mathematical description of the kinetic hypersurface feasible. The parameters in temperature and conversion functions are adjusted to reach the closest agreement between the experimental and calculated values of times or temperatures. As it has been noted above, for the isoconversional methods the conversion function is implicitly involved in the adjustable parameter A_α.

As for the temperature functions, the adjustable parameters are A and E for Eq. (4), A and m for Eq. (5) or A and D for Eq. (6). Since the functions describe the same kinetic hypersurface, the parameters have to be interrelated. The relationships among E, m and D can be simply obtained from a temperature derivative of the logarithmic form of Eqs (4)–(6):

$$E=mRT \tag{31}$$

$$E=RT^2D \tag{32}$$

The parameter A has not the same value in Eqs (4)–(6). The kinetic hypersurface should be the same when using any of the temperature functions (4)–(6). Taking into account Eqs (31) and (32), it can be simply derived:

$$A_4=A_5(\mathrm{e}T)^{\mathrm{m}} \tag{33}$$

$$\mathrm{A}_4=A_6\mathrm{e}^{2\mathrm{DT}} \tag{34}$$

where A_4, A_5 and A_6 are the A-parameters appearing in Eqs (4), (5) and (6), respectively. The temperature appearing in Eqs (31)–(34) is an averaged temperature over the measurement region since the parameters in Eqs (4)–(6) are considered constant.

As Eqs (31)–(34) show, the values of adjustable parameters in Eqs (4), (5) and (6) can be mutually recalculated. Thus it can be expected that the values of adjustable parameters m and D from isothermal, integral, differential and incremental isoconversional methods will differ for the same reasons as summarised in [1].

Justification of applying the non-Arrhenius temperature functions

As discussed above, Eq. (1) represents a general description of the kinetic hypersurface, i.e., of the dependence of conversion on time and temperature

(Fig. 1). The step from Eq. (1) to Eq. (3) implicitly involves the assumption that the differential equation (1) is by separable. Regarding the isoconversional methods, it is generally recognised that they lead to the dependence of adjustable parameters in the temperature function on conversion. As it has been shown in [1], dependence of activation energy on conversion leads to the inseparability of the kinetic equation. One can easily verify that the same would take place if the parameter m or D in Eq. (5) or in Eq. (6) depends on conversion. This is the inherent contradiction of the isoconversional methods since the separation of variables expressed by Eq. (2) is the principal assumption.

Variable values of adjustable parameters indicate that the mathematical description of the kinetic hypersurface is not satisfactory. Since the temperature function is not a rate constant but it is a function describing the temperature component of the kinetic hypersurface, there is no reason to be confined to the Arrhenius relationship. A temperature function leading to constant adjustable parameters is desirable and it would be advantageous if the chosen function would lead to simple mathematical formulas. Equations (5) and (6) lead to simple formulas; however, the constancy of the adjustable parameters should be tested for particular kinetic data. Another temperature function leading to simple mathematical formulas could be a combination of Eqs (5) and (6) in the form:

$$k(T)=AT^{\mathrm{m}}\mathrm{e}^{\mathrm{DT}} \tag{35}$$

where m is a natural number.

The a priori postulate of validity of the chosen temperature function in Eq. (3) predetermines complexity of subsequent mathematical description of the kinetic hypersurface. It is very curious that the thermoanalytical community inclines to the Arrhenius equation, which is, from the point of view of mathematical treatment, one of the most awkward relationships. It is a matter of course that nowadays, when the performance of computers is almost unlimited, it is no problem to employ any function. However, in the last century the situation could have been much simpler and the treatment of non-isothermal kinetics could have been much more straightforward if one of the functions given by Eqs (5), (6) or (35) had been employed. The numerous papers dealing with calculating the temperature integral, published in the second half of the last century, would be needless.

Limitations and application of the single-step kinetics approximation

Solid-state reactions ordinarily demonstrate a tangled interplay of various chemical and physical processes such as solid-state decomposition, reaction of gases with solids, phase transitions, diffusion, adsorption, desorption, etc. [9]. The single-step kinetics approximation, represented by Eq. (3), is an attempt to describe the kinetic hypersurface in a simple way irrespective of the complexity of the overall process. The correct mathematical description of the kinetic hypersurface (Fig. 1) should recover the values of the rates of the process under study.

As early as in 1969, Flynn wrote that the experimental rate may be expressed, for purposes of curve-fitting, as a product of separable functions of conversion and temperature plus conversion-temperature cross term [10]:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=k(T)f(\alpha)g(\alpha,T) \tag{36}$$

Function $g(\alpha,T)$ is the cross term. In general, the cross term in Eq. (36) is disregarded and it is put $g(\alpha,T)=1$ so leading to Eq. (3). I feel inevitable to emphasize again that the functions $k(T)$ and $f(\alpha)$ should be separable, i.e., the function $k(T)$ should not depend on conversion. In general, the function $k(T)$ is not the rate constant and $f(\alpha)$ does not reflect the mechanism of the process, they just represent the temperature and conversion components of the kinetic hypersurface. The parameters A and E in Eq. (3) are called the pre-exponential factor and activation energy just because of the force of habit; as discussed in [1], they are adjustable parameters in the temperature function, having generally no physical meaning. The physical meaning of the parameters A and E in Eq. (4) as the preexponential factor and activation energy is connected exclusively with the formation of activated complex in an elementary reaction step, which is not the case in the complex condensed-phase processes. In order to avoid misunderstanding in terminology, it would be advisable to introduce the adjustable parameter B as [1]:

$$B=E/R \tag{37}$$

The imperative condition of the separability of both temperature and conversion functions indicates that the deductions drawn from the concept of variable activation energy ([9] and the references cited therein) should be judged very critically and carefully. As it has been noted above, variable values of adjustable parameters E, m or D in Eqs (4), (5) or (6) indicate that the mathematical description of the kinetic hypersurface is not satisfactory. For the acceptable description it is necessary to find a couple of separable functions. If the couple of separable functions cannot be found, to my opinion it indicates that the single-step kinetics approximation is too crude and a more sophisticated approach should be chosen. The functions with variable adjustable parameters enable just a crude, mathematically incorrect description of the kinetic hypersurface. As a result, inconsistency in 'activation parameters' obtained from isothermal and non-isothermal methods occurs [1, 10]. The concept of variable activation energy achieved some success [9]. However, due to the mathematical incorrectness, modelling of the process using variable adjustable parameters should be carried out only within the temperature region where the measurements have been carried out. It is very likely that the temperature function with constant adjustable parameters would enable a trustworthy extrapolation of the kinetic hypersurface outside the measurement region.

Finally, it should be noted that thermoanalytical techniques (TG, DSC, DTA) provide a global, overlapped signal of all processes occurring in the sample. For the same process, the adjustable parameters obtained by various thermoanalytical methods may be different. In DSC, the conversion α is calculated from the heat released/absorbed by the sample. In TG, the conversion is obtained from the sample mass loss. One can imagine that processes exist where the conversion curves determined by the both methods are not identical and, subsequently, the adjustable parameters obtained differ as well. Thus, for modelling the heat released/absorbed by the sample, the parameters obtained from DSC measurements should be used. Analogically, the parameters from TG measurements should be used for modelling the sample mass loss [1].

Conclusions

In this paper, two definitions have been introduced: (*i*) Kinetic hypersurface is the dependence of conversion on temperature and time; (*ii*) Single-step kinetics approximation is a mathematical tool for describing the kinetic hypersurface in a simple way represented by Eq. (3), irrespective of the complexity of the overall process.

Introduction of the both definitions is useful for understanding the physical meaning of Eq. (3). Equation (3) is often called the general kinetic equation which induces an interpretation that $k(T)$ is the rate constant and $f(\alpha)$ reflects the mechanism of the process. In the light of the single-step kinetics approximation, $k(T)$ and $f(\alpha)$ are functions describing the temperature and conversion components of the kinetic hypersurface. For a complex process, the adjustable parameters in the temperature function have no mechanistic significance or physical meaning so that there is no reason to be confined to the Arrhenius relationship.

The functions $k(T)$ and $f(\alpha)$ should be separable. If separable functions cannot be found, it indicates that the single-step kinetics approximation is too crude and a more sophisticated approach should be chosen, such as the one presented in [11] taking into account the detailed mechanism of the process.

Two groups of isoconversional methods based on non-Arrhenius temperature functions are presented and the corresponding formulas for isothermal, integral, differential and incremental isoconversional methods are derived. As an example of the method using the explicit expression of the conversion function, the first-order kinetics is treated, using the relationships given by Eqs (5) and (6) as the temperature functions. Comparing with the methods presented in [1], the greatest advantage of the methods presented here is that the problems with calculating the temperature integral are eliminated since the corresponding integrals can be expressed in a closed form. Knowing the values of adjustable parameters, one can model the kinetics of the process without a deeper insight into its mechanism.

Acknowledgements

The financial support from the Slovak Grant Agency, grant No. 1/0054/03, is greatly acknowledged.

References

1 P. Šimon, J. Therm. Anal. Cal., 76 (2004) 123.
2 K. J. Laidler, J. Chem. Educ., 61 (1984) 494.
3 J. H. Flynn, Thermochim. Acta, 300 (1997) 83.
4 D. Dollimore, P. Tong and K. S. Alexander, Thermochim. Acta, 282/283 (1996) 13.
5 D. Dollimore, S. Lerdkanchanaporn and K. S. Alexander, Thermochim. Acta, 290 (1996) 73.
6 F. Rodante, S. Vecchio, G. Catalani and M. Guidotti, J. Therm. Anal. Cal., 60 (2000) 605.
7 N. Sbirazzuoli, Y. Girault and L. Elégant, Thermochim. Acta, 293 (1997) 25.
8 S. Vyazovkin, J. Comput. Chem., 22 (2001) 178.
9 S. Vyazovkin and C. A. Wight, Revs. Phys. Chem., 17 (1998) 407.
10 J. H. Flynn, in: Thermal Analysis (Proceedings of 2nd ICTA Congress), vol.2, Ed. by R. F. Schwenker Jr. and P. D. Garn, Acad. Press, N. Y., London 1969, p. 1111.
11 A. Korobov, J. Therm. Anal. Cal., 74 (2003) 211.

Received: April 28, 2004
In revised form: August 12, 2004