Journal of Thermal Analysis and Calorimetry, Vol. 60 (2000) 581–594

A DIFFERENTIAL METHOD WHICH USES LOCAL HEATING RATES TO EVALUATE NON-ISOTHERMAL KINETIC PARAMETERS

E. Urbanovici[1], *C. Popescu*[1] *and E. Segal*[2]*

[1]LACECA Research Centre, Str. Siret Nr. 95, 78308 Bucharest
[2]Department of Physical Chemistry, Faculty of Chemistry, University of Bucharest
Bd. Elisabeta 4-12, Bucharest, Romania

(Received January 20, 1999; in revised form August 18, 1999)

Abstract

A differential method is proposed which uses local heating rates to evaluate non-isothermal kinetic parameters. The method allows to study the influence of the deviation of the true heating rate with respect to the programmed one on the values of the kinetic parameters. For application, the kinetic parameters of the following solid-gas decomposition reaction were evaluated: $[Ni(NH_3)_6]Br_{2(s)} \rightarrow [Ni(NH_3)_2]Br_{2(s)} + 4NH_{3(g)}$. The results obtained revealed significant differences between the values of the non-isothermal kinetic parameters obtained by using local heating rates and those obtained by using the programmed heating rate. It was also demonstrated that the kinetic equation which makes use of the local heating rates permits a better description of the experimental (α, t) data than the kinetic equation which uses the programmed constant heating rate.

Keywords: differential method, evaluation of kinetic parameters, local heating rate, non-isothermal kinetics

Introduction

In conventional investigations of non-isothermal kinetics with a linear heating rate, the change in the programmed temperature (T) with time (t) is given by [1, 2]

$$T = T_o + \beta t \tag{1}$$

where T_o is the initial temperature and β is the programmed constant heating rate. Due to the thermal effects which occur in the investigated sample, its temperature differs from the programmed one, as expressed by a modified form of Eq. (1) [3–5]:

$$T = T_o + \beta t + s(t) \tag{2}$$

---

[*] Author to whom all correspondence should be addressed.

1418–2874/2000/ $ 5.00
© 2000 Akadémiai Kiadó, Budapest
Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

where the supplementary term, $s(t)$, accounts for the deviation from linearity of the programmed temperature. The analytical form of the function $s(t)$ is not known; it may be approximated by a polynominal of 4th degree, selected so as to fit a certain number of experimentally determined points (t, T). The experimental data allow the expression of t as a function of T:

$$t=\varphi(T) \tag{3}$$

where $\varphi(T)$ is the appropriate function determined by interpolation.

By taking the derivatives of Eqs (2) and (3) with respect to t, the true heating rate, β^*, [3–5] in the investigated sample can be expressed either as a function of time:

$$\mathrm{d}T/\mathrm{d}t\equiv\beta^*(t)=\beta+s'(t) \tag{4}$$

or as a function of temperature:

$$\mathrm{d}T/\mathrm{d}t\equiv\beta^*(T)=1/\varphi'(T) \tag{5}$$

In order to derive the non-isothermal kinetic equations based on relationships (1) and (2), we shall start from the general rate equation [1, 2]:

$$\mathrm{d}\alpha/\mathrm{d}t=Af(\alpha)\exp[-E/RT] \tag{6}$$

which describes the dependence of the reaction rate, $\mathrm{d}\alpha/\mathrm{d}t$, on the temperature and the degree of conversion (α). In the above equation, A is the pre-exponential factor, E is the activation energy, and $f(\alpha)$ is the differential conversion function, which characterizes the reaction mechanism.

On inserting Eq. (2) into Eq. (6), we obtain

$$\mathrm{d}\alpha/\mathrm{d}t=\mathrm{A}f(\alpha)\exp[-E/R(T_0+bt+s(t))] \tag{7}$$

By replacing the variable t by the variable T, and taking into account Eq. (4), we can rewrite Eq. (7)

$$\mathrm{d}\alpha/\mathrm{d}T=(A/\beta^*)f(\alpha)\exp[-E/RT] \tag{8}$$

Through variable separation and integration, Eq. (8) leads to the well-known integral equation

$$g(\alpha)\equiv\int_0^\alpha \mathrm{d}\alpha/f(\alpha)=A\int_0^T 1/\beta^*\exp[-E/RT]\mathrm{d}T \tag{9}$$

where $g(\alpha)$ is the integral conversion function.

Relationships (7), (8) and (9) represent, in fact, the 'corrected' non-isothermal kinetic equations, as they take into account the deviation of the true heating rate from the programmed one. It is easy to see that, for $s(t)=0$, which represents the 'ideal' case, β^* is equal to β over the whole experiment and we obtain the equations of non-isothermal kinetics widely used to evaluate non-isothermal kinetic parameters [3–5].

The complication due to the variable heating rate, $\beta^*(T)$, raised by the integral equation (9), can be overcome by integrating it over small ranges of variables. In such a way, we obtain [3–6]

$$\int_{\alpha_i}^{\alpha_k} \mathrm{d}\alpha / f(\alpha) = (A/\beta_{ik}) \int_{T_i}^{T_k} \exp[-E/RT]\mathrm{d}T \tag{10}$$

where β_{ik} is the local heating rate in the range $\alpha \in [\alpha_i, \ \alpha_k] \leftrightarrow [\alpha_i, \ \alpha_k]$. An iterative method to evaluate non-isothermal kinetic parameters, based on Eq. (10), has been proposed previously [4–6].

In the following, Eq. (8) will be used with the aim of deriving a new differential method of evaluating kinetic parameters from non-isothermal experiments.

Presentation of the method

The 'classical' differential methods of evaluating non-isothermal kinetic parameters are based on Eq. (8) for $s(t)=0$ [7–10]. Following the taking of logarithms and rearrangement, this equation becomes

$$\ln[\beta(\mathrm{d}\alpha/\mathrm{d}T)/f(\alpha)] = \ln A - E/RT \tag{11}$$

Thus, for a suitable form of $f(\alpha)$, the plot of $\ln[\beta(\mathrm{d}\alpha/\mathrm{d}T)/f(\alpha)]$ *vs.* $1/T$ gives a straight line whose slope and intercept allow estimation of the values of the activation energy and pre-exponential factor, respectively [7–10]. The most probable mechanism function, $f(\alpha)$, is identified as that which ensures the best linearity of this plot, i.e. it corresponds to the maximum value of the correlation coefficient, r.

It should be emphasized that the graphical procedure presented above furnishes results similar to those obtained by applying the linear least squares method [11–13]. In the present particular case of linear regression, the sum of squares to the residual terms, S_{res}, should be written as [14–18]

$$S_{\mathrm{res}} = \sum_{i-1}^{N} \{\ln[\beta(\mathrm{d}\alpha/\mathrm{d}T)_i / f\alpha_i)] - \ln A + E/RT_i\}^2 \tag{12}$$

where N is the number of experimentally determined data points, $[T_i, \alpha_i, (\mathrm{d}\alpha/\mathrm{d}T)_i]$. The values of the kinetic parameters A and E may be found from the condition of the minimum in S_{res}, which yields to a system of linear equations:

$$\partial S_{\mathrm{res}} / \partial \ln A = \partial S_{\mathrm{res}} / \partial E = 0 \tag{13}$$

The differential method we propose also makes use of the logarithmic form of Eq. (8), but $s(t)$ is kept different from zero:

$$\ln[\beta^*(T)(\mathrm{d}\alpha/\mathrm{d}T)/f(\alpha)] = \ln A - E/RT \tag{14}$$

In order to simplify the mathematical expressions, let us introduce the notations

$$\ln A = a \tag{15}$$

and

$$E/R=b \tag{16}$$

Thus, for a given form of $f(\alpha)$, if we apply the linear least squares method, the sum of squares of the residual terms becomes

$$S_{\text{res}}=\sum_{i-1}^{N}\{\ln[\beta^{*}(T_{i})(\mathrm{d}\alpha/\mathrm{d}T)_{i}/f(\alpha_{i})]-a+b/T_{i}\}^{2} \tag{17}$$

where N is the number of experimental data points involved in the linear regression. The condition of the minimum in S_{res} leads to the system of linear equations

$$\partial S_{\text{res}}/\partial a=\partial S_{\text{res}}/\partial b=0 \tag{18}$$

The values of the parameters a and b are determined by solving the system (18), and the kinetic parameters (A and E) can be evaluated by means of relationships (15) and (16).

The graphical illustration of this method implies a plot of $\ln[\beta^{*}(T_{i})(\mathrm{d}\alpha/\mathrm{d}T)_{i}/f(\alpha_{i})]$ *vs*. $1/T$, which gives a straight line for an appropriate choice of $f(\alpha)$. The slope and intercept of the straight line obtained allow estimation of the values of A and E.

In order to identify the most probable mechanism function, $f(\alpha)$, we make use of two statistical criteria: 1) the correlation coefficient, r, [11–13], and 2) the residual mean squares (S_{xy}^{2}), defined as [11–13]

$$S_{\text{xy}}^{2}=[1/(N-2)]S_{\text{res}} \tag{19}$$

The most probable mechanism function should ensure at the same time the maximum value of the correlation coefficient and the minimum value of S_{xy}^{2}. Use of the residual mean squares together with the correlation coefficient is highly recommended for selection of the most probable mechanism function. Use of the correlation coefficient of the linear regression analysis alone does not seem always well grounded statistically, since the maximum value of the correlation coefficient may differ insignificantly from its lower values [19, 20].

Application and discussion

For application, we have studied the non-isothermal kinetics of the solid-gas decomposition reaction

$$[\mathrm{Ni(NH_3)_6Br_{2(s)}}] \rightarrow [\mathrm{Ni(NH_3)_2Br_{2(s)}}]+4\mathrm{NH_{3(g)}} \tag{I}$$

The decomposition curve was recorded with a programmed heating rate of 10 K min^{-1}. Detailed information concerning the experimental conditions are to be found in [4].

The kinetic parameters were evaluated by employing both the ‘classic’ differential method (the plot based on Eq. (11)) and the proposed one (the plot based on Eq. (14)). In this way, the influence of the deviation of the true heating rate from the programmed one (the effect of function $s(t)$) on the values of the estimated kinetic parameters can be perceived [4].

It should be mentioned that the kinetic parameters of reaction (1) were previously evaluated by the integral method based on Eq. (9) [4]. Thus, we had the opportunity to make a comparison between the values of the kinetic parameters evaluated by using different methods.

The primary experimental data consist of N=39 data points, (t_i, T_i, α_i), with the degree of conversion ranging from 0.0950 to 0.9587. The rate of reaction ($d\alpha/dT$) was not determined instrumentally (by recording the DTG curve) since this curve may be affected by considerable errors [10, 21]. The required values of $d\alpha/dT$ were determined numerically, by using a curve-fitting method. In order to describe the functional relationship between α and T, a 4th degree polynominal, denoted here as $p(T)$, was used, and the calculations were performed by means of the 'PolynomialFit' package of the Mathematica software system [22]. According to our notation, we may write

$$d\alpha/dT=p'(T) \tag{20}$$

Figure 1 shows the variation in $d\alpha/dT$ with T, as determined by employing Eq. (20).

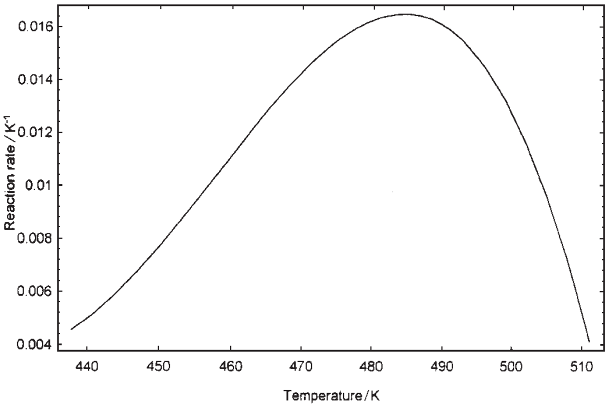

Fig. 1 Plot of $d\alpha/dT$ *vs.* T determined by using Eq. (22) for reacion (I)

The local heating rates can be determined similarly by using the same 'PolynomialFit' package of Mathematica. As already mentioned, functions $s(t)$ and $\varphi(T)$ are approximated by appropriate 4th degree polynomials, which can be inserted into Eqs (4) and (5) in order to obtain $\beta^*(t)$ and $\beta^*(T)$, respectively. On the basis of the acquired experimental data, the calculations performed with the 'PolynomialFit' package reveal the variation in the true heating rate with respect to time and temperature, as illustrated in Figs 2 and 3.

As may be seen from these illustrations, the true heating rate displays a considerable deviation from the constant programmed heating rate of 10 K min^{-1}.

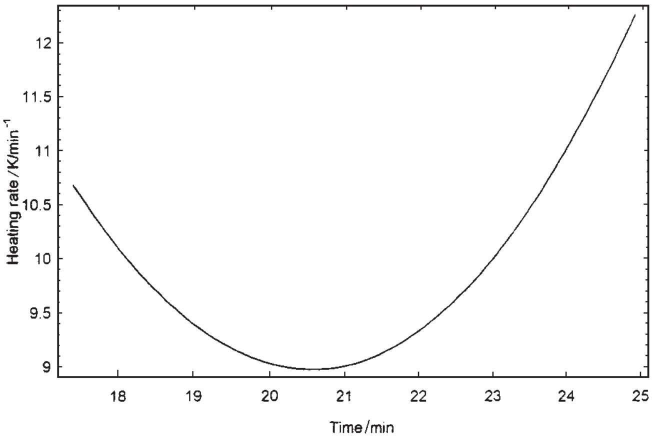

Fig. 2 Plot of β^* *vs.* t for reaction (I)

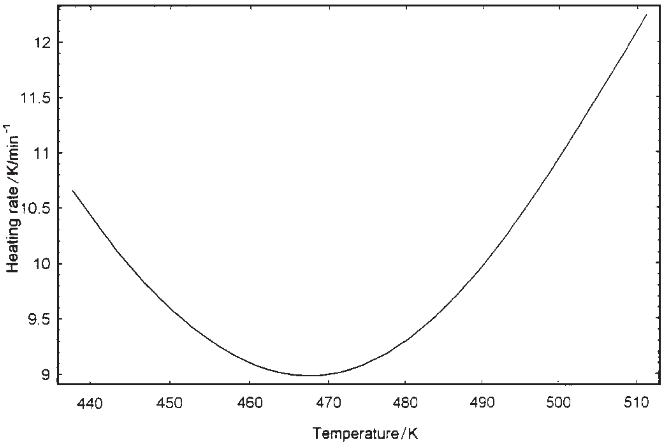

Fig. 3 Plot of β^* *vs.* T for reaction (I)

The most common mechanism functions, $f(\alpha)$, used for applications are listed in Table 1. For the Fn mechanism, not only the usual values of n, e.g. 1, 2 and 3, were considered: non-integer values were also taken into considerations in order to search for the most probable mechanism function.

The numerical calculations required by minimization of the sum of squares of the residual terms (S_{res}) were performed by using the 'Linear Regression' package of Mathematica [22]. Besides the values of a, b, r, S_{res} and S^2_{xy}, this package provides the appropriate confidence intervals for a and b [11–13, 22]. For all applications, a customary confidence level of 95% was considered.

Table 1 Usual mechanisms from the literature and the corresponding forms of $f(\alpha)$

No.	Mechanism	$f(\alpha)$	Observations
1	Pm Power law	$m\alpha^{(m-1)/m}$	m=1, 2, 3 and 4
2	E1 Exponential law	α	
3	An Avrami-Erofeev	$n(1-\alpha)[-\ln(1-\alpha)]^{(n-1)/n}$	n=3/2, 2, 3, and 4
4	B1 Prout-Tompkins	$\alpha(1-\alpha)$	
5	R2 Contacting surface	$(1-\alpha)^{1/2}$	
6	R3 Contacting volume	$(1-\alpha)^{2/3}$	
7	Fn n^{th} order reaction	$(1-\alpha)^n$	
8	D1 1-D diffusion	$1/(2\alpha)$	
9	D2 2-D diffusion	$[-\ln(1-\alpha)]^{-1}$	
10	D3 3-D diffusion (Jander equation)	$1.5(1-\alpha)^{2/3}[1-(1-\alpha)^{1/3}]^{-1}$	
11	D4 3-D diffusion (Ginstling–Brounshtein equation)	$1.5(1-\alpha)^{1/3}[1-(1-\alpha)^{1/3}]^{-1}$	

The statistical discrimination between the various mechanism functions demonstrated that the most probable mechanism function is Fn, with n=1.002, for the 'classical' method, and n=0.781 for the proposed method. Table 2 presents the results obtained by linear regression.

The kinetic parameters were also evaluated by using the improved integral method of Coats and Redfern (this method utilizes the programmed heating rate, β) [23]. The obtained values of the kinetic parameters are

$$n=0.932 \text{ (Fn model)};\ E=77.630\pm0.244 \text{ (kJ mol}^{-1}\text{)};\ \ln A=14.279\pm0.062 \text{ (s}^{-1}\text{)}.$$

A comparison of these values with those given in Table 2 reveals that the two methods which use the constant programmed heating rate, β, yield closely similar values of the kinetic parameters. On the other hand, as expected, the values calculated by taking into account the deviation of the heating rate programme from a linear one, i.e. by using the true heating rate β^*, differ significantly from them.

In order to evaluate the results obtained, in the following we illustrate the way in which these kinetic parameters describe the experimental data. Figure 4 depicts the experimental (α, t) data points and the α *vs.* t curve generated by inserting the kinetic parameters obtained by the classical differential method into Eq. (7), with $s(t)=0$. Figure 5 shows the same experimental data points and the α *vs.* t curve generated by inserting the kinetic parameters evaluated with the Coats-Redfern method into Eq. (7), also with $s(t)=0$. The α *vs.* t curve generated by inserting the kinetic parameters obtained by the new differential method into Eq. (7), with $s(t)\neq0$, is given in Fig. 6. In a similar way, Figs 7 and 8 exhibit the (α, T) experimental data points and the α *vs.* T curves generated by inserting the kinetic parameters obtained with either the classical differential method or the improved Coats-Redfern method into Eq. (8), with $s(t)=0$, whereas Fig. 9 depicts the same experimental data points and the α *vs.* T curves gen-

Table 2 Values of kinetic parameters and of statistical criteria evaluated by using the classical differential method and the new differential method

Differential method	Mechanism	E/kJ mol^{-1}	ln$A$/s^{-1}	r	S_{xy}^2
Classical; based on Eq. (8)	Fn; n=1.002	82.329±0.580	15.527±0.148	0.99979	$3.5375 \cdot 10^{-4}$
New; based on Eq. (11)	Fn; n=0.781	72.207±0.994	12.741±0.253	0.99920	$1.0388 \cdot 10^{-3}$

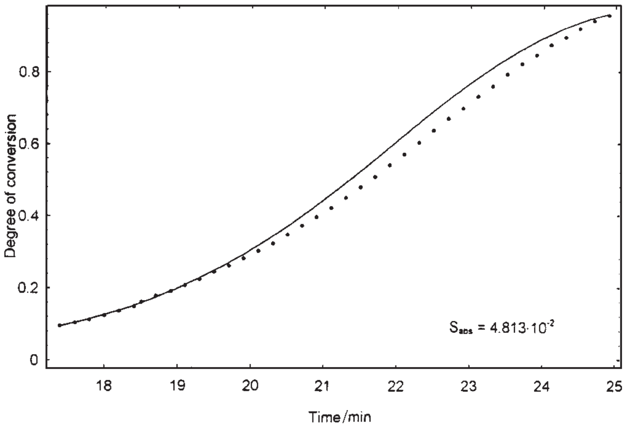

Fig. 4 Experimental (α, *t*) data points (....) and the α *vs. t* curve generated by inserting the kinetic parameters evaluated with the classical differential method into Eq. (7)

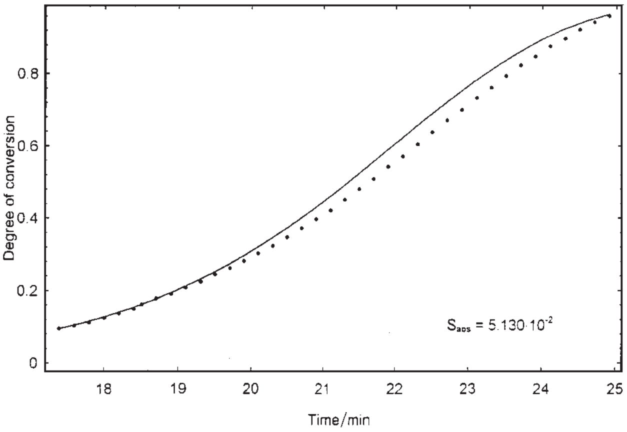

Fig. 5 Experimental (α, *t*) data points (....) and the α *vs. t* curve generated by inserting the kinetic parameters evaluated with the Coats–Redfern method into Eq. (7)

erated by inserting the kinetic parameters obtained with the new differential method into Eq. (8), with $s(t)\neq 0$.

In every case, the α *vs. t* or α *vs. T* curves were generated by solving the corresponding differential equations numerically. This difficult task can be carried out with the 'NDSolve' function of Mathematica [24, 25].

The closeness of the fit can be appreciated qualitatively by using the arithmetic mean of the absolute values of the relative errors (S_{abs}), i.e.

$$S_{abs}=1/N\sum_{i=1}^{N}|(\alpha_{calc,i}-\alpha_{exp,i})/\alpha_{exp,i}| \tag{21}$$

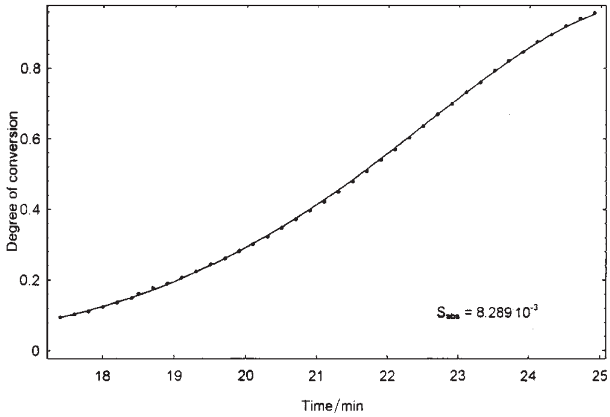

Fig. 6 Experimental (α, *t*) data points (....) and the α *vs.* *t* curve generated by inserting the kinetic parameters evaluated with the new differential method into Eq. (10)

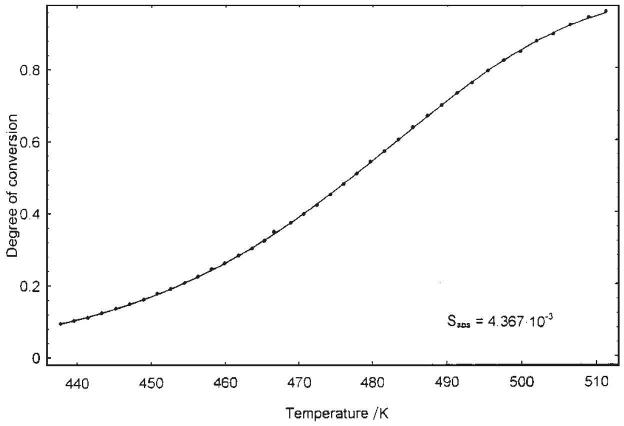

Fig. 7 Experimental (α, *T*) data points (....) and the α *vs.* *T* curve generated by inserting the kinetic parameters evaluated with the classical differential method into Eq. (8)

In this expression, α_{exp} is the experimentally determined value of the degree of conversion and α_{calc} is the value of α determined numerically with 'NDSolve'. The smaller the value of S_{abs}, the better the calculated curve fits the experimental data. The values of S_{abs} obtained are given in Figs 4–9.

From these figures, various conclusions may be drawn.

i) The classical non-isothermal equations, i.e. Eqs (7) and (8), with $s(t)=0$, cannot adequately describe the experimental (α, *t*) data, but provide an accurate description of the experimental (α, *T*) data. This is due to the fact that in the classical view we are interested mostly in expressing the functional dependence α *vs.* *T* by taking no account of the real time-temperature dependence, i.e. Eq. (2).

ii) The corrected non-isothermal equations, i.e. Eqs (7) and (8) with $s(t)\neq0$, provide an accurate description of both the experimental (α, t) and (α, T) data.

iii) If the very close values of S_{abs} are taken into account, the experimental (α, T) data are seen to be described with almost the same accuracy by Eq. (8) for either $s(t)=0$ or $s(t)\neq0$.

Finally, the values of the kinetic parameters determined in the present work and the values taken from ref. [4] are presented for comparison in Table 3.

The tabulated data reveal that the methods based on the true heating rate give closely similar values of the kinetic parameters. The three methods that employ the classical constant heating instead of the true heating rate also lead to close values of the kinetic parameters, but they differ from those in the other group.

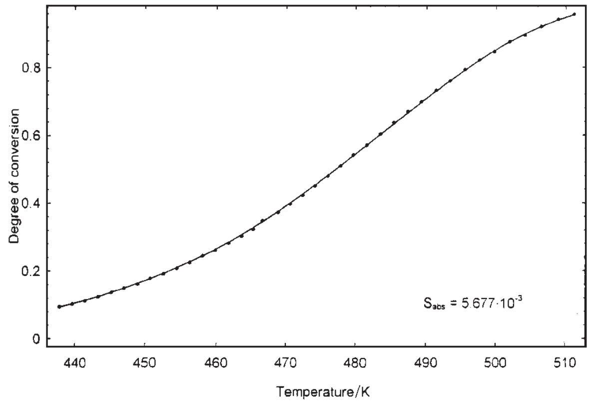

Fig. 8 Experimental (α, T) data points (....) and the α *vs.* T curve generated by inserting the kinetic parameters evaluated with the improved Coats–Redfern method into Eq. (8)

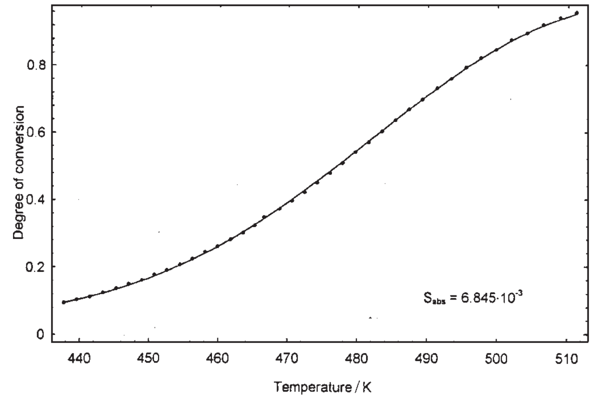

Fig. 9 Experimental (α, T) data points (....) and the α *vs.* T curve generated by inserting the kinetic parameters evaluated with the new differential method into Eq. (11)

Table 3 Kinetic parameters obtained by various methods for reaction (I)

Method	n	E/kJ mol^{-1}	A/s^{-1}	Reference
Classical differential; based on Eq. (8)	1.002	82.329	$5.535 \cdot 10^6$	present work
New differential; based on Eq. (11)	0.781	72.207	$3.413 \cdot 10^5$	present work
Based on Eq. (12); using β	0.981	81.29	$4.25 \cdot 10^6$	[4]
Based on Eq. (12); using β^*	0.741	69.89	$1.85 \cdot 10^5$	[4]
Improved Coats-Redfern	0.932	77.630	$1.589 \cdot 10^6$	present work

Conclusions

1. A new differential method has been presented, which uses local heating rates for the evaluation of non-isothermal kinetic parameters.

2. The results demonstrate that the true heating rate displays a noticeable deviation from the constant value of the programmed heating rate.

3. The kinetic parameters were evaluated by linear regression analysis and, besides the correlation coefficient (r), the residual mean squares (S_{xy}^2) were regarded as a supplementary statistical criterion to determine the most probable mechanism function.

4. Significant differences between the values of the kinetic parameters evaluated by the new method and the values obtained by employing two methods which use constant heating rates were observed for reaction (I).

5. Equation (7) cannot adequately describe the experimental (α, t) data for $s(t)=0$, but provides an accurate description for $s\neq 0$.

6. Equation (8) can adequately describe the experimental (α, T) data for both $s(t)=0$ and $s\neq 0$.

7. The values of the kinetic parameters for the solid-gas decomposition of $[Ni(NH_3)_6]Br_2$ are in good agreement with those obtained previously by the method based on Eq. (10).

* * *

This work was supported in part by the Ministry of Research and Technology under Grant 2003/1996. One of the authors (E. U.) is indebted to the Alexander von Humboldt Foundation (Germany) for the financial support provided for his scientific activity.

References

1 J. H. Flynn and L. A. Wall, J. Res. Natl. Bur. Stand., Sect. A, 70 (1966) 487.
2 J. Šesták, V. Satava and W. W. Wendlandt, Thermochim. Acta, 7 (1973) 447.
3 E. Urbanovici and E. Segal, Thermochim. Acta, 159 (1990) 369.
4 E. Urbanovici and E. Segal, J. Thermal Anal., 40 (1993) 1321.
5 E. Urbanovici and E. Segal, Thermochim. Acta, 221 (1993) 211.
6 E. Urbanovici and E. Segal, Thermochim. Acta, 141 (1989) 9.
7 B. N. Achar, G. W. Brindley and J. H. Sharp, Proc. Int. Clay Conf. Jerusalem, 1 (1966) 67.
8 J. H. Sharp and S. A. Wentworth, Analyt. Chem., 41 (1969) 2060.
9 D. Dollimore, G. R. Heal and B. W. Krupay, Thermochim. Acta, 24 (1978) 293.
10 J. Šesták, Thermophysical properties of solids, Academia, Prague, 1986, Chapter 9.
11 R. L. Wine, Statistics for scientists and engineers, Prentice-Hall, Inc., Englewood Cliffs, N. J., 1964, Chapter 14.
12 G. McPherson, Statistics in scientific investigations – its basis, application, and interpretation, Springer Verlag, New York, 1990, Chapter 18.
13 W. H. Press, S. A. Teukolsky, W. T. Vetterling and B. P. Flannery, Numerical recipes in C – The art of scientific computing, Cambridge University Press, Cambridge, 1992, Chapter 15.
14 D. T. Y. Chen and P. H. Fong, Thermochim. Acta, 18 (1977) 161.

15 D. T. Y. Chen and K.-W. Lai, J. Thermal Anal., 20 (1981) 233.

16 V. Swaminathan, N. S. Madhavan and D. Radhamony, Thermochim. Acta, 43 (1981) 371.

17 S. Boy and K. Böhme, Thermochim. Acta, 46 (1981) 229.

18 S. V. Vyazovkin and A. I. Lesnikovich, J. Thermal Anal., 32 (1987) 249.

19 S. V. Vyazovkin and A. I. Lesnikovich, J. Thermal Anal., 30 (1985) 831.

20 S. V. Vyazovkin and A. I. Lesnikovich, J. Thermal Anal., 18 (1986) 319.

21 P. H. Fong and D. T. Y. Chen, Thermochim. Acta, 18 (1977) 273.

22 P. Boyland et al., Guide to standard Mathematica packages, Wolfram Research, Inc., 1993, Chapter 10 and 11.

23 E. Urbanovici, C. Popescu and E. Segal, Thermochim. Acta, submitted.

24 S. Wolfram, Mathematica – A system for doing mathematics by computer, Addison-Wesley, Reading, Massachusetts, 1991, pp. 696–703.

25 T. B. Bahder, Mathematica for scientists and engineers, Addison-Wesley, Reading, Massachusetts, 1995, pp. 585–592.