Journal of Thermal Analysis, Vol. 52 (1998) 933-943

THE NON-PARAMETRIC KINETICS
A new method for the kinetic study of thermoanalytical data

R. Serra, R. Nomen and J. Sempere

Department of Chemical Engineering, Institut Químic de Sarrià, Universitat Ramon Llull
Via Augusta 390, Barcelona E-08017, Spain

Abstract

The application of the new method non-parametric kinetics for kinetic analysis is discussed. It is shown that this method is able to obtain all the kinetic information needed to reproduce accurately the experimental data. To validate this method a set of numerical simulations of the most commonly used kinetic models has been performed and analysed with the method.

Keywords: kinetics, non-parametric kinetics method

Introduction

The non-parametric kinetics (NPK) method [1] is a new method for the kinetic treatment of non-isothermal thermoanalytical data. The development of the method is based on the classical assumption that the reaction rate can be expressed as a product of two independent functions, $g(\alpha)$ and $f(T)$, as shown in Eq. (1). The first function accounts for the kinetic model, and is a function of the degree of conversion, while the second accounts for the temperature dependence, not necessarily an Arrhenius-type equation.

$$\dot{\alpha} = g(\alpha)f(T) \tag{1}$$

In this method, the reaction rate, $\dot{\alpha}$, is discretised and organised as an $n \times m$ matrix whose rows correspond to different degrees of conversion, from α_1 to α_n, and whose columns correspond to different temperatures, from T_1 to T_m, therefore, the element i, j of matrix **A** is defined by $\mathbf{A}_{ij}=g(\alpha_i)f(T_j)$. Then the functions $g(\alpha)$ and $f(T)$ can also be discretised and expressed as column vectors, named **g** and **f** respectively, whose elements are the discretised values of functions $g(\alpha)$ and $f(T)$:

$$\mathbf{g} = (g(\alpha_1) \quad g(\alpha_2) \quad . \quad . \quad g(\alpha_n))^T \tag{2}$$

1418–2874/98/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

$$\mathbf{f} = (f(T_1) \quad f(T_2) \quad . \quad . \quad f(T_m))^T \tag{3}$$

Subsequently the general expression of the reaction rate, Eq. (1), can be expressed in the form of a matrix product, as shown in Eq. (4):

$$\mathbf{A} = \mathbf{g}\mathbf{f}^T \tag{4}$$

The NPK method uses the Singular Value Decomposition (SVD) [2] to decompose matrix **A** in the two vectors **f** and **g**. The most important feature of this method is its ability to provide a kinetic model that fits the experimental data without any assumption either about the functionality of the reaction rate with the degree of conversion or the temperature.

To simulate the behaviour of the system under any conditions the reaction rate has to be calculated. Classically the reaction rate is calculated as a function of a kinetic model, which includes some parameters, and an Arrhenius equation, that is function of the activation energy and the frequency factor. The NPK method is able to evaluate the reaction rate using the vectors **f** and **g**, because any value of the reaction rate can be expressed as $\dot{\alpha}(\alpha,T)=g(\alpha)f(T)$, where $g(\alpha)$ and $f(T)$ are obtained by interpolation of the elements of **f** and **g** at the required values α and T.

Validation of the method

In order to validate the NPK method, a set of numerical simulations of DSC curves (expressed as reaction rate *vs.* temperature and degree of conversion *vs.* temperature) of several systems characterised by typical values of activation energy (150 kJ mol^{-1}) and frequency factor ($1\cdot10^{16}$ s^{-1}) combined with the kinetic models most commonly used in the literature [3, 4, 5] have been performed. The heating rates used for the simulations are 2, 4, 8 and 16 K min^{-1}. The results of these simulations were used as model experiments and they were analysed using

Table 1 The mathematical expression of the kinetic models

Model	Symbol	Equation, $g(\alpha)$	
Johnson-Mehl-Avrami	JMA(m)	$m(1-\alpha)[-\ln(1-\alpha)]^{1-1/m}$	Eq. (5)
Two-parameter model	SB(n,m)	$\alpha^m(1-\alpha)^n$	Eq. (6)
Two-dimensional diffusion	D2	$[-\ln(1-\alpha)]^{-1}$	Eq. (7)
Jander equation	D3	$3/2(1-\alpha)^{2/3}\left[1-(1-\alpha)^{1/3}\right]^{-1}$	Eq. (8)
Gistling-Brounhstein equation	D4	$3/2\left[(1-\alpha)^{-1/3}-1\right]^{-1}$	Eq. (9)
Reaction order	RO(n)	$(1-\alpha)^n$	Eq. (10)

the NPK method. The mathematical expressions corresponding to the kinetic models used to carry out the simulations are listed in Table 1.

Simulation of the model JMA

The particular case corresponding to m=2 in Eq. (5) has been studied, the simulations of the reaction rate corresponding to a DSC experiment performed with heating rates of 2, 4, 8 and 16 K min^{-1} are presented in Fig. 1a.

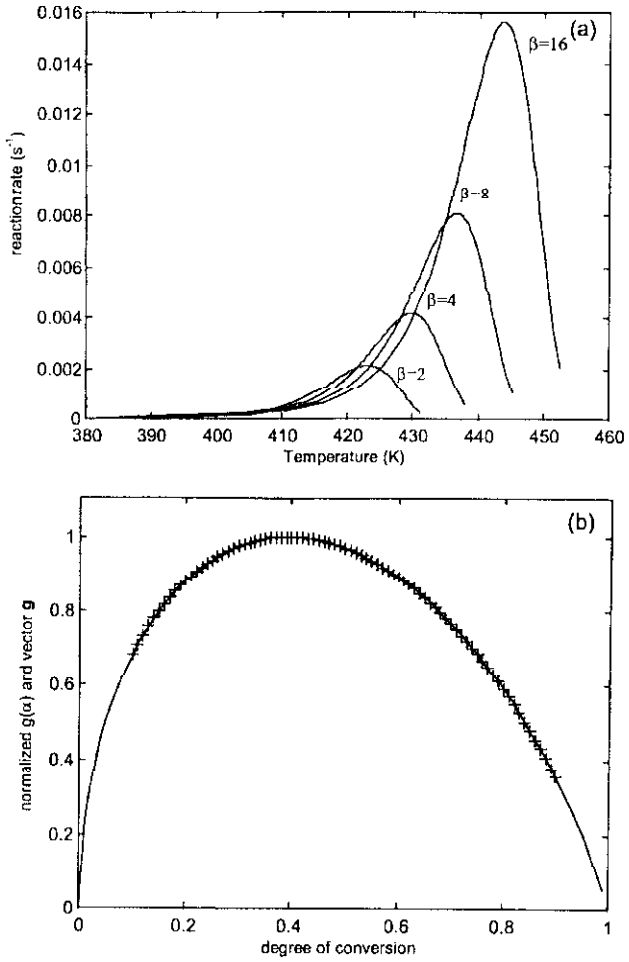

Fig. 1 Simulation of the reaction rate (s^{-1}) *vs.* temperature (K), for the kinetic model JMA(2). Range of simulation 0.03<α<0.99. Heating rates 2, 4, 8 and 16 K min^{-1} (a). Comparison between the obtained vector **g** (+) and the calculated function $g(\alpha)$ (continuous line), Eq. (5) (b)

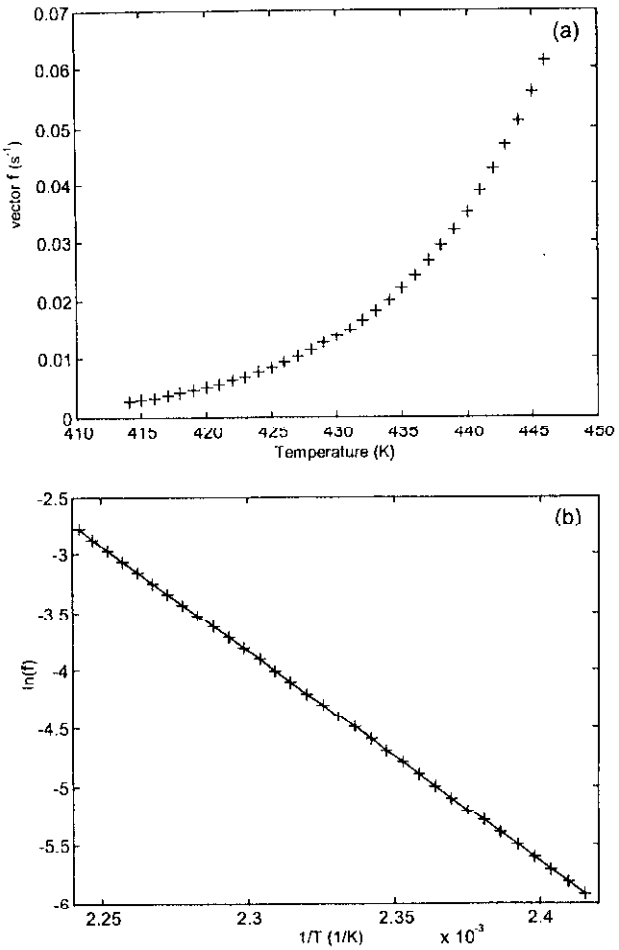

Fig. 2 Graphical representation of the elements of vector **f** in front of the temperature (a). Arrhenius plot of vector **f** (b)

These simulated data are analysed with the NPK method in order to obtain the corresponding vectors **f** and **g** that contain all the kinetic information of the process. Figure 1b shows that the NPK method reproduces the shape of the kinetic model with high accuracy. In Fig. 2a are plotted the elements of vector **f**, which follows an Arrhenius-type functionality, Fig. 2b.

This allows to find the Arrhenius parameters, obtaining a value of activation energy of 150.2 kJ mol^{-1} and the frequency factor of $1.06 \cdot 10^{16}$ s^{-1}, which are in good agreement with those fed to the simulations. The data reconstruction using Eq. (4) is shown in Fig. 3.

There have also been studied the particular cases of JMA corresponding to m=3 and m=4. Figure 4a presents the simulations of the reaction rate for these ki-

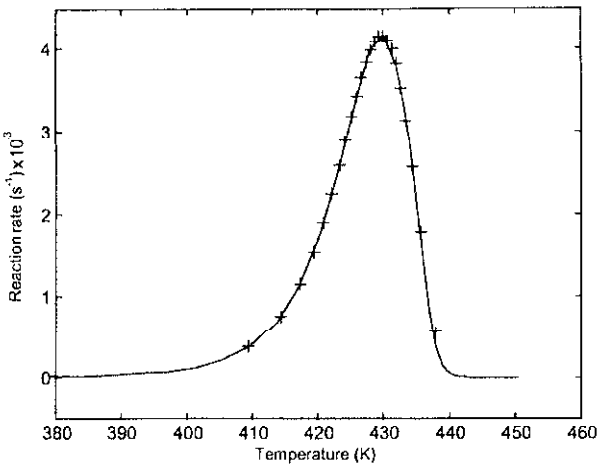

Fig. 3 Data reconstruction: comparison between the simulated data (+) and the reconstructed data (continuous line) using Eq. (4)

netic models for a DSC experiment performed at a heating rate of 2 K min^{-1}. The obtained vectors **g** are presented in Fig. 4b, while the calculated activation energy and frequency factors are shown in Table 2.

Simulation of the model SB

The two-parameter model SB, Eq. (6), has been studied in three different cases, corresponding to (a) n=1, m=1; (b) n=1, m=0.5; (c) n=2, m=1. As an example, the simulations of these kinetic models corresponding to a heating rate of 2 K min^{-1} are shown in Fig. 5a. The analysis of the simulated data with the NPK method provides the shape of the kinetic models, shown in Fig. 5b, and after the rectification of vector **f** using an Arrhenius type equation, the values of the kinetic parameters, presented in Table 3.

Simulation of the models D2, D3 and D4

The simulations of an DSC experiment carried out with a heating rate of 2 K min^{-1} for the kinetic models D2, D3 and D4, Eqs (7)–(9) respectively, are presented in Fig. 6a. The corresponding vectors **g** obtained for each model are plotted in Fig. 6b, where are compared with the theoretical shapes of the mathematical equations. The parameters of the Arrhenius equation are shown in Table 4.

Simulation of the RO model

Four different cases of the RO model have been simulated, corresponding to the cases defined by n=1/2, 2/3, 1 and 2. The simulation of the behaviour of the

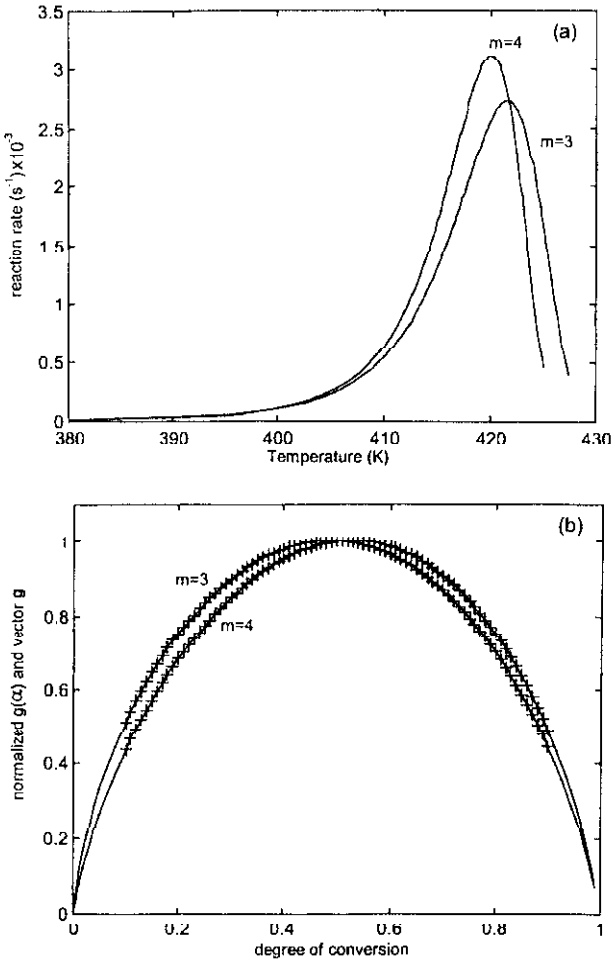

Fig. 4 Simulation of the reaction rate (s^{-1}) *vs.* temperature (K), for the kinetic models JMA with m=3 and m=4. Range of simulation 0.03<α<0.99. Heating rate 2 K min^{-1} (a). Comparison between the obtained vectors **g** (+) and the calculated functions $g(\alpha)$ (continuous line), Eq. (5) (b)

Table 2 Comparison of the values of the kinetic parameters obtained from vector **f** with the values used to perform the numerical simulation

	E/kJ mol^{-1}	Error/%	A/s^{-1}	Error/%
m=3	150.2	0.11	$1.04 \cdot 10^{16}$	4.6
m=4	150.1	0.05	$1.02 \cdot 10^{16}$	2.3

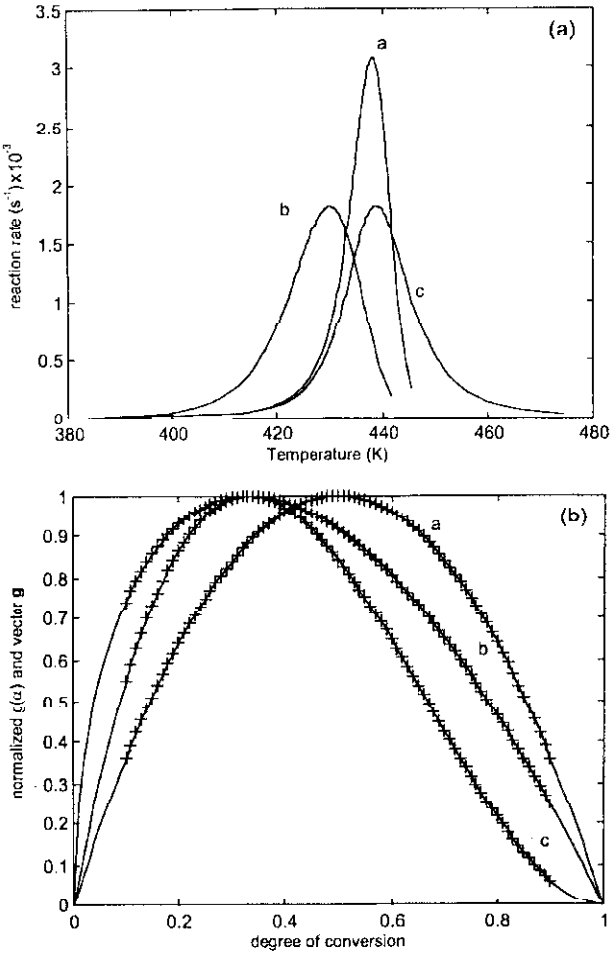

Fig. 5 Simulation of the reaction rate (s^{-1}) *vs.* temperature (K), for the kinetic model SB. Range of simulation $0.03<\alpha<0.99$. Heating rate 2 K min^{-1}. (a) n=1, m=1; (b) n=1, m=0.5; (c) n=2, m=1(a). Comparison between the obtained vectors **g** (+) and the calculated functions $g(\alpha)$ (continuous line), Eq. (6) (b)

Table 3 Comparison of the values of the kinetic parameters obtained from vector **f** with the values used to perform the numerical simulation. Models SB(1,1), SB(1,0.5), SB(2,1)

	E/kJ mol^{-1}	Error/%	A/s^{-1}	Error/%
n=1, m=1	150.0	0.03	$9.91 \cdot 10^{15}$	0.9
n=1, m=0.5	150.2	0.11	$1.05 \cdot 10^{16}$	4.8
n=2, m=1	150.1	0.06	$1.03 \cdot 10^{16}$	2.5

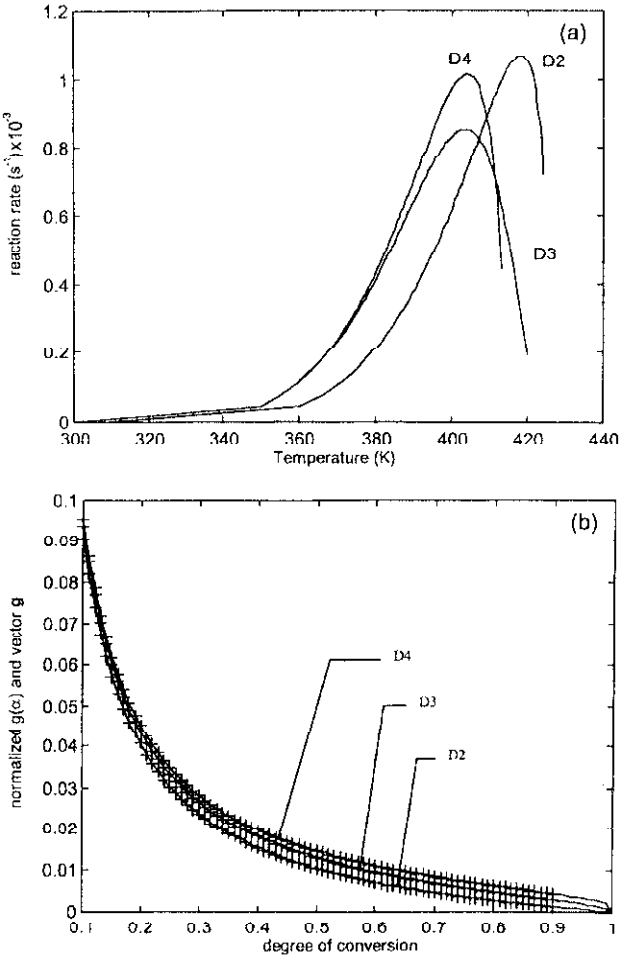

Fig. 6 Simulation of the reaction rate (s^{-1}) *vs.* temperature (K), for the kinetic models D2, D3 and D4. Range of simulation $0.03<\alpha<0.99$. Heating rate 2 K min^{-1} (a). Comparison between the obtained vectors **g** (+) and the calculated functions $g(\alpha)$ (continuous line), Eqs (7)–(9) (b)

Table 4 Comparison of the values of the kinetic parameters obtained from vector **f** with the values used to perform the numerical simulation. Models D2, D3 and D4

	E/kJ mol^{-1}	Error/%	A/s^{-1}	Error/%
D2	150.4	0.26	$1.12 \cdot 10^{16}$	12.0
D3	150.4	0.26	$1.13 \cdot 10^{16}$	12.5
D4	150.4	0.26	$1.12 \cdot 10^{16}$	12.4

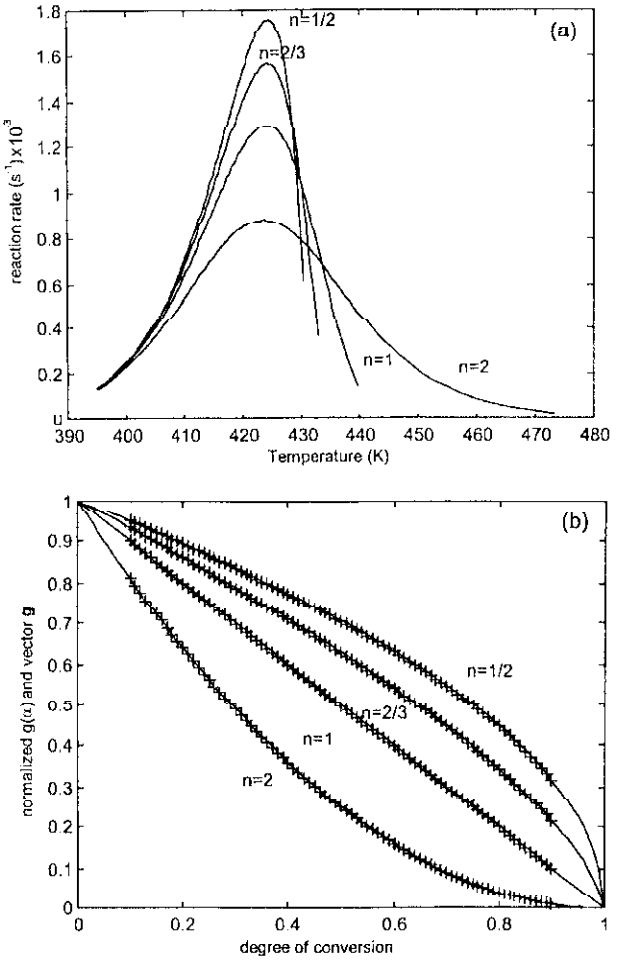

Fig. 7 Simulation of the reaction rate (s^{-1}) *vs.* temperature (K), for the kinetic model RO with n= 1/2, n=2/3, n=1 and n=2. Range of simulation $0.03<\alpha<0.99$. Heating rate 2 K min^{-1} (a). Comparison between the obtained vectors **g** (+) and the calculated functions $g(\alpha)$ (continuous line), Eq. (10) (b)

Table 5 Comparison of the values of the kinetic parameters obtained from vector f with the values used to perform the numerical simulation. Models RO(1/2) , RO(2/3), RO(1), RO(2).

	E/kJ mol^{-1}	Error/%	A/s^{-1}	Error/%
n=1/2	150.3	0.21	$1.09 \cdot 10^{16}$	9.4
n=2/3	150.3	0.21	$1.09 \cdot 10^{16}$	9.3
n=1	150.3	0.23	$1.10 \cdot 10^{16}$	10.0
n=2	150.4	0.29	$1.12 \cdot 10^{16}$	12.2

system during an DSC experiment is presented in Fig. 7a. These simulated data is analysed with the NPK method, which gives the shape of the kinetic models and allows the calculation of the activation energy and the frequency factor. These results are presented in Fig. 7b and Table 5 respectively.

Conclusions

The non-parametric kinetics method is able to obtain both the activation energy and the kinetic model that better fit the thermoanalytical data without any previous assumption.

In all the tested cases, the new NPK method gives with high accuracy the shape of the kinetic equation that generates the simulated data.

It is worth mentioning the accuracy in the calculation of the activation energy, being the calculation error below 0.3 %.

Comparing with the classical methods, like methods described in references [3] and [4], this new method is not restricted to the kinetic equations presented in Table 1, it is open to any other equation.

Another advantage of this method is how it calculates the activation energy. Classical methods calculate it using only few points, usually three or four, corresponding to the maximum of the thermoanalytical curves, however the NPK method uses a larger number of points and a wider range of temperatures. So, the results obtained by this method seem to be applicable in a wider range of situations.

Symbols

A	Arrhenius frequency factor	s^{-1}
$\mathbf{A}$	reaction rate matrix	s^{-1}
E	activation energy	$kJ\,mol^{-1}$
$\mathbf{f}$	vector related to temperature dependence, defined in Eq. (3)	s^{-1}
$\mathbf{g}$	vector related to degree of conversion dependence, defined in Eq. (2)	
n	kinetic parameter	
m	kinetic parameter	
α	degree of conversion	
$\dot{\alpha}$	reaction rate	s^{-1}

* * *

One of the authors (R. Serra) would expreas his gratitude to the 'Comissionat per a Universitats i Recerca de la Generalitat de Catalunya' for its pre-PhD grant that has been made possible his participation in this project.

References

1 R. Serra, J. Sempere and R. Nomen, Thermochim. Acta, in press.
2 G. H. Golub and C. F. Van Loan, Matrix Computation; The Johns Hopkins University Press, 1989.
3 J. Malek and J. M. Criado, Thermochim. Acta, 236 (1994) 187.
4 J. Malek et al., J. Thermal Anal., 38 (1992) 71.
5 J. Llópiz et al., Thermochim. Acta, 256 (1995) 205.