Journal of Thermal Analysis and Calorimetry, Vol. 56 (1999) 843-849

PROGRESS IN NON-PARAMETRIC KINETICS

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Abstract

The non-parametric kinetics (NPK) method has been recently developed for the kinetic treatment of thermoanalytical data. The most significant feature of this method is its ability to provide information about the reaction kinetics without any assumptions either about the functionality of the reaction rate with the degree of conversion or the temperature. This paper presents the results of the application of the method to adiabatic calorimetry. Some data have been obtained by numerical simulation, but also the thermal decomposition of DTBP, a well known first order reaction, has been studied, being the obtained results in good agreement with literature.

Keywords: adiabatic calorimetry, kinetics, non-parametric kinetics

Introduction

The non-parametric kinetics (NPK) [1, 2] is a recently developed method for the kinetic treatment of thermoanalytical data. This method introduces a new point of view in kinetic analysis. As all the classical methods it is based on the presumption of the validity of the following equation:

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

NPK regards the reaction rate as a surface in a three dimensional space where the axis are the temperature, the degree of conversion and the rate of change of the degree of conversion. This surface, which is continuous, can be discretised and organised as an nxm matrix, where the columns account for the temperature, from T_1 to T_m, while the rows refer to different degrees of conversion, from α_1 to α_n, as can be shown in Eq. (2):

$$\mathbf{A} = \begin{pmatrix} g(\alpha_1)f(T_1) & g(\alpha_1)f(T_2) & g(\alpha_1)f(T_3) & \dots & g(\alpha_1)f(T_m) \\ g(\alpha_2)f(T_1) & g(\alpha_2)f(T_2) & g(\alpha_2)f(T_3) & \dots & g(\alpha_2)f(T_m) \\ \cdot & \cdot & \cdot & \dots & \cdot \\ \cdot & \cdot & \cdot & \dots & \cdot \\ \cdot & \cdot & \cdot & \dots & \cdot \\ g(\alpha_n)f(T_1) & g(\alpha_n)f(T_2) & g(\alpha_n)f(T_3) & \dots & g(\alpha_n)f(T_m) \end{pmatrix} \tag{2}$$

1418–2874/99/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

Matrix **A** can be expressed as the product of two column vectors:

$$\mathbf{A} = \mathbf{u}\mathbf{v}^{\mathrm{T}} \tag{3}$$

$$\mathbf{u} = (g(\alpha_1) \quad g(\alpha_2) \quad g(\alpha_3) \quad \ldots \quad g(\alpha_n))^{\mathrm{T}} \tag{4}$$

$$\mathbf{v} = (f(T_1) \quad f(T_2) \quad f(T_3) \quad \ldots \quad f(T_m))^{\mathrm{T}} \tag{5}$$

where vector **u** contains all the information about the kinetic model and vector **v** about the function $f(T)$.

It is possible to evaluate the reaction rate using only the vectors **u** and **v**, 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 **u** and **v** at the required values of degree of conversion and temperature.

Even though the kinetic parameters, such as activation energy, frequency factor or reaction order, are not necessary to reproduce the system behaviour or to simulate it in different conditions, it is also possible to use the results of the NPK method to obtain model parameters from vector **u** and the activation energy and the frequency factor from vector **v**.

Therefore, applying a procedure that is able to decompose matrix **A** into two vectors as expressed in Equation 3, the vectors **u** and **v** will be obtained and so the reaction kinetics. The NPK method performs this decouplement by using the singular values decomposition (SVD) [3].

It is worth mentioning that the development of the NPK method does not have any limitations in the source of the data, it can be provided by any TA technique that gives reaction rate information as a function of temperature and degree of conversion, for example, DSC or TG, but also another technique which is not commonly used for kinetic analysis: adiabatic calorimetry.

The NPK method has been already tested by using DSC and TG data [1, 2], both experimental and simulated. In this paper, data obtained from adiabatic calorimetry, also simulated and experimental, will be treated with the method in order to obtain kinetic information.

Validation of the method

In order to validate the NPK method with adiabatic calorimetry data, a set of numerical simulations of the behaviour of a reaction system under adiabatic conditions has been performed. The systems are characterised by typical values of activation energy (125 kJ mol^{-1}) and frequency factor ($1\cdot10^{15}$ min^{-1}) and an adiabatic increase of temperature of 220 K for $\phi=1$, combined with an nth order reaction or RO(n) model and a Šesták-Berggren or SB(n,m) model, Eqs (6–7).

$$g(\alpha) = (1-\alpha)^{n} \tag{6}$$

$$g(\alpha) = \alpha^{m}(1-\alpha)^{n} \tag{7}$$

The ϕ factor is a very important parameter in adiabatic calorimetry, it expresses the relationship between the amount of heat released by the reaction and the amount of heat accumulated in the sample, as shown in Equation 8:

$$\phi = \frac{m_c c_{pc} + m_s c_{ps}}{m_s c_{ps}} \tag{8}$$

where the subscripts c and s mean can and sample respectively. The ϕ factors used for the simulations are 1.7, 2 and 3. The results of these simulations were used as model experiments and they were analysed by using the NPK method.

Simulation of the RO(n) model

The particular cases corresponding to n=0.5, 1 and 2 have been studied. As an example the results of the simulations corresponding to ϕ=2 are presented in Fig. 1.

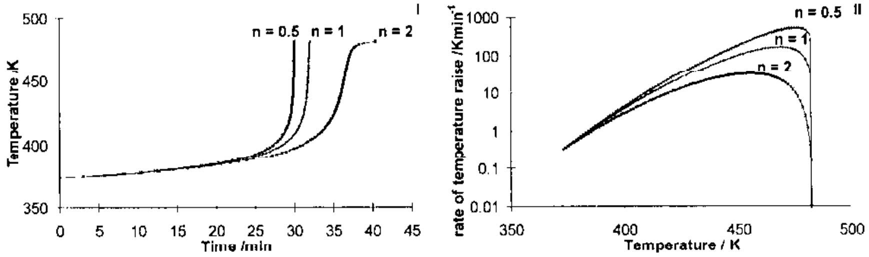

Fig. 1 Kinetic models RO(0.5), RO(1) and RO(2). (I) Simulation of the temperature (K) *vs.* time (min) (solid line). (II) Simulation of the rate of temperature rise (K min^{-1}) *vs.* temperature (K) (solid line). Comparison with the data reconstructed using vectors **u** and **v** (+)

The simulated data are treated by the NPK method giving the two vectors **u** and **v**. Vector **u** is presented in Fig. 2 compared with the shape of the corresponding kinetic model. The original data can be reconstructed with high accuracy (relative error in rate of temperature raise about 0.3%) directly from vectors **u** and **v**, because

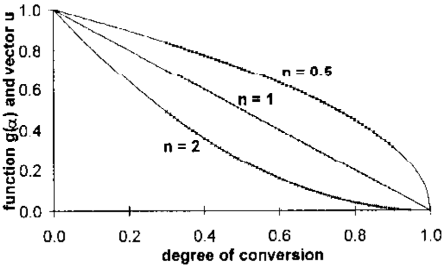

Fig. 2 Comparison between the obtained vectors **u** (+) and the calculated functions $g(\alpha)$ (solid line), Eq. (6)

Table 1 Comparison of the values of the kinetic parameters obtained from vector v with the values used to perform the numerical simulations. Models RO(0.5), RO(1), RO(2)

Model	E/kJ mol^{-1}	Error/%	A/min^{-1}	Error/%
RO(0.5)	125.04	0.03	1.01e+15	1.2
RO(1)	125.04	0.03	1.01e+15	1.2
RO(2)	125.03	0.03	1.01e+15	1.2

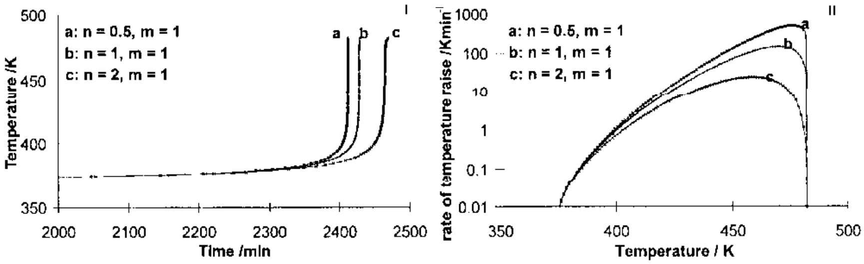

Fig. 3 Kinetic models SB(0.5,1), SB(1,1) and SB(2,1). (I) Simulation of the temperature (K) *vs.* time (min) (solid line). (II) Simulation of the rate of temperature rise (K min^{-1}) *vs.* temperature (K) (solid line). Comparison with the data reconstructed using vectors **u** and **v** (+)

each value of the reaction rate can be calculated as the product of the suitable elements of the vectors: $\dot{\alpha}(\alpha,T)=\mathbf{u}(\alpha)\mathbf{v}(T)$. The data reconstruction carried out following this procedure is also presented in Fig. 1. Moreover, the activation energy and the frequency factor can be also obtained from vector **v**. Their values are shown in Table 1.

Simulation of the SB(n,m) model

In this case, the models SB(0.5,1), SB(1,1) and SB(2,1) have been studied. Figure 3 shows the results of the simulations corresponding to $\phi=2$.

The obtained vectors **u**, which have the same shape that the theoretical models, are shown in Fig. 4, while the comparison of the kinetic parameters E and A are presented in Table 2. In this case, the recalculation of the original data has also been performed directly from vectors **u** and **v**, being the relative error of the calculation of the rate of temperature raise about 0.2%. The results are presented in Fig. 3.

In all the tested cases the application of the NPK method brings the kinetic model with high accuracy and the activation energy with a small error.

Study case

The di-tert-butylperoxid (DTBP) is used as a standard in adiabatic calorimetry, its thermal decomposition is well known and it is often used to check the perfor-mance of an adiabatic calorimeter. In this case DTBP, dissolved 1:4 in mass in toluene, has been chosen to validate the NPK method with experimental adiabatic calorimetry data.

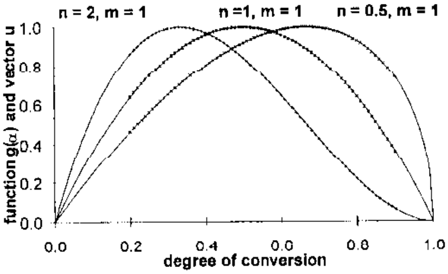

Fig. 4 Comparison between the obtained vectors **u** (+) and the calculated functions $g(\alpha)$ (solid line). Eq. (7)

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

Model	E/kJ mol^{-1}	Error/%	A/min^{-1}	Error/%
SB(0.5,1)	125.10	0.08	1.03e+15	2.9
SB(1,1)	125.10	0.08	1.03e+15	3.0
SB(2,1)	125.10	0.08	1.03e+15	3.0

Table 3 Summary of the experiments carried out

Experiment	Can mass/g	Sample mass/g	ϕ	T_0/ °C	T_f/ °C	K min^{-1}
1	39.8	80.0	1.09	130.0	253.1	759
2	44.8	50.0	1.18	116.9	243.2	385
3	42.6	80.0	1.10	115.3	226.1	103

The experiments have been carried out on the adiabatic calorimeter PHI-TEC II from H.E.L., using thin-walled cans of 100 mL.

It should be pointed out that experiments 1 and 3 have a very similar value of ϕ factor. However, the difference between the initial temperatures produces different temperature *vs.* degree of conversion and rate of temperature raise *vs.* temperature profiles, making possible the analysis using the NPK method.

Figure 5 shows the experimental measurement of temperature *vs.* time and the rate of temperature raise *vs.* temperature.

The study of this data with the NPK method provides the two vectors **u** and **v**, which contain all the kinetic information about the reaction.

Since the relationship between vector **u** and the degree of conversion is a straight line, the kinetic model that better fits the experimental data is a first order reaction [4] as described in literature [5].

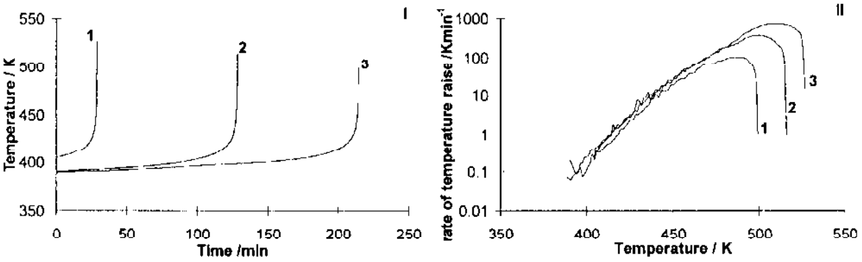

Fig. 5 Experimental measurements of the decomposition of DTBP. (I) Temperature (K) *vs.* time (min). (II) Rate of temperature raise (K min^{-1}) *vs.* temperature (K)

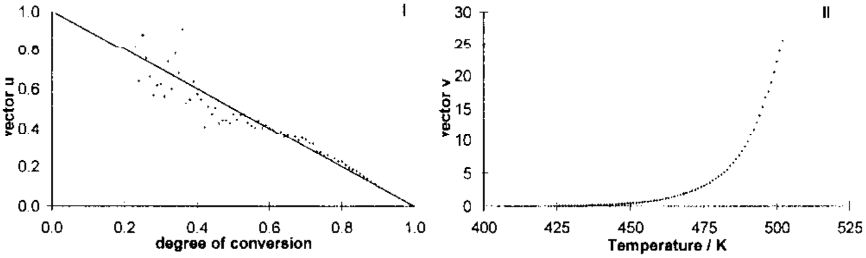

Fig. 6 Result obtained with the NPK method. (I) Vector **u** *vs.* degree of conversion. (II) Vector **v** *vs.* temperature

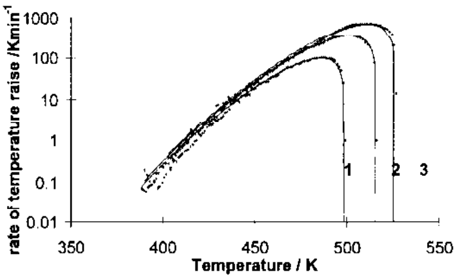

Fig. 7 Thermal decomposition of DTBP: simulation of the rate of temperature raise (K min^{-1}) *vs.* temperature (K) (solid line) and experimental data (+)

On the other hand, fitting an Arrhenius type equation to vector **v** an activation energy of 148.9±0.7 kJ mol^{-1} and a logarithm of the frequency factor of 16.9± 0.2 log$_{10}$(s^{-1}) are obtained. These results are in good agreement with the literature [5] being the relative difference about 6%. These kinetic parameters have been used to recalculate the experimental data. Figure 7 presents the comparison between the experimental and recalculated data (relative error 17%).

Conclusions

The NPK method is able to treat adiabatic calorimetry data without any modification of its basis.

In all tested cases, the NPK method gives with high accuracy the kinetic function that generates the simulated data.

It is worth mentioning the accuracy in the calculation of the activation energy, being the calculation error below 0.1%.

The validity of NPK in adiabatic conditions has been tested by using experimental data of the thermal decomposition of DTBP as a case study. The NPK method provided results that are in good agreement with literature.

Nomenclature

A	Arrhenius frequency factor	$\min^{-1}$ or s^{-1}
$\mathbf{A}$	reaction rate matrix	$\min^{-1}$ or s^{-1}
c_p	specific heat	$J\ g^{-1}\ °C^{-1}$
E	activation energy	$kJ\ mol^{-1}$
$\mathbf{u}$	vector related to degree of conversion dependence, defined in Eq. (4)	
$\mathbf{v}$	vector related to temperature dependence, defined in Eq. (5)	
n	kinetic parameter	
m	kinetic parameter	
m_c	can mass	g
m_s	sample mass	g
T_0	initial temperature of the exotherm	°C
T_f	final temperature of the exotherm	°C

Greek symbols

α	degree of conversion	
$\dot{\alpha}$	reaction rate	s^{-1}
ϕ	phi factor, defined in Eq. (8)	

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One of the authors (R. Serra) would express his gratitude to the 'COMISSIONAT PER A UNIVERSITATS I RECERCA DE LA GENERALITAT DE CATALUNYA' for its pre-PhD grant that has made his participation in this project possible.

References

1 R. Serra, J. Sempere and R. Nomen, Thermochim. Acta, 316 (1998) 37.
2 R. Serra, R. Nomen and J. Sempere, J. Therm. Anal. Cal., 53 (1998) 933.
3 G. H. Golub and C. F. Van Loan, Matrix Computation; The Johns Hopkins University Press, 1989.
4 J. Málek et al., J. Thermal Anal., 38 (1992) 71.
5 D. H. Shaw and H. O. Pritchard, Can. J. Chem., 46 (1986) 2721.