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A new method for the kinetic study of thermoanalytical data: The non-parametric kinetics method

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Abstract

A new method, called non-parametric kinetics (NPK), for the treatment of non-isothermal thermoanalytical data has been developed. The most significant feature of this method is its ability to provide a kinetic model that fits the experimental data, without any assumptions either about the functionality of the reaction rate with the degree of conversion or the temperature. The thermal decomposition of dibenzoyl peroxide has been studied in order to validate the NPK method, and the results are compared with those of the traditional ones. © 1998 Elsevier Science B.V.

Keywords: DSC; Kinetics; Non-parametric kinetics; Singular value decomposition (SVD)

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1. Introduction

Numerous methods have been developed for the treatment of non-isothermal thermoanalytical data in order to obtain the kinetic parameters that could reproduce the experimental data and predict the behaviour of the system in different conditions.

A general expression for the reaction rate of a simple reaction is:

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

where $g(\alpha)$ symbolises the kinetic model of the process, and $f(T)$ accounts for the temperature dependence of the reaction, expressed usually by an Arrhenius equation.

In this paper, the different methods have been classified according to the basic assumptions made for their derivation. In the simplest methods, an nth-order kinetics is assumed. For the evaluation of the kinetic parameters, a multilinear regression, Eq. (2), or a Freeman–Carroll method, Eq. (3), are often used.

– multilinear regression:

$$\ln\dot{\alpha} = \ln A - \frac{E}{R}\frac{1}{T} + n\ln(1-\alpha) \tag{2}$$

– the Freeman–Carroll method [1]:

$$\frac{\Delta\ln\dot{\alpha}}{\Delta\ln(1-\alpha)} = -\frac{E}{R}\frac{\Delta(1/T)}{\Delta\ln(1-\alpha)} + n \tag{3}$$

All the kinetic parameters in these methods can be evaluated using a single TA curve. Quite frequently, this evaluation leads to meaningless parameters due to a strong ‘kinetic compensation effect’ between the

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parameters E and A [2]. It should be kept in mind that the calculated parameters are apparent, because of the assumption of nth-order behaviour.

A second group of methods uses a set of non-isothermal experiments carried out at different heating rates for the evaluation of kinetic parameters, resulting in more realistic values. In these methods, the activation energy is calculated in a previous stage, thus rendering possible the establishment of the kinetic model that better describes the measured data.

The most popular methods for the determination of activation energies use the maximum point of each TA curve. Widely applied methods of this category are:

– the Kissinger method [3]:

$$\ln\left(\frac{\beta}{T_{\mathrm{p}}^{2}}\right) = \ln\left(-\frac{RA}{E}g'(\alpha_{\mathrm{p}})\right) - \frac{E}{R}\frac{1}{T_{\mathrm{p}}} \tag{4}$$

– the Ozawa method as applied to maximum points [4,5]:

$$\ln(\beta) = C - 1.052\frac{E}{R}\frac{1}{T_{\mathrm{p}}} \tag{5}$$

– the peak heights method [6]:

$$\ln\left(\frac{P}{m}\right) = \ln\left[Cg(\alpha_{\mathrm{p}})\right] - \frac{E}{R}\frac{1}{T_{\mathrm{p}}} \tag{6}$$

A possible alternative is to use isoconversional methods. These methods are based on the simple fact that equal conversion corresponds to the same value of function g(α) and also the integral, $G(\alpha) = \int_0^{\alpha} \partial\alpha/g(\alpha)$, has the same value. Therefore, the general expression of the reaction rate can be manipulated to obtain Eqs. (7)–(9). This process can be repeated for various degrees of conversion, so the isoconversional methods allow to obtain the apparent activation energy as a function of the degree of conversion. Consequently, changes in the reaction mechanism during the reaction can be detected by using isoconversional methods. Some of these methods are:

– the Friedman method [7]:

$$\ln(\dot{\alpha}) = \ln(Ag(\alpha)) - \frac{E}{R}\frac{1}{T_{\alpha}} \tag{7}$$

– the general Ozawa's isoconversion method:

$$\ln(\beta) = C - 1.052\frac{E}{R}\frac{1}{T_{\alpha}} \tag{8}$$

– the Kissinger–Akahira–Sunose method [8]:

$$\ln\left(\frac{\beta}{T_{\alpha}^{2}}\right) = \ln\left(\frac{RA}{EG(\alpha)}\right) - \frac{E}{R}\frac{1}{T_{\alpha}} \tag{9}$$

Once the activation energy has been determined, it is possible to select the kinetic model which best describes the experimental data. For this choice, either of two different methodologies, described by Málek and Šesták [9], and by J. Málek and M. Criado [10], can be followed. Their main virtues are their simplicity and their sequential application.

The calculation of the activation energy is necessary in all the aforementioned methods for the development of kinetic analysis. The new *non-parametric kinetics* (NPK) method presented in this paper is endowed by its ability to decouple the two functions that the general Eq. (1) employs, i.e. the degree-of-conversion-dependent function $g(\alpha)$ and the temperature-dependent function $f(T)$, without the need of any assumptions about their functionality. The method provides two independent vectors directly from a set of experimental measurements, the first one containing information about $g(\alpha)$ and the second about $f(T)$. Since no assumption about $f(T)$ is made, the method avoids the problem of the exponential temperature integral.

To verify the validity of the new method, the study of the decomposition of dibenzoyl peroxide is performed as an example, and the obtained results are compared with those obtained from traditional methods.

2. Theory

The reaction rate $\dot{\alpha}$ of a simple process, Eq. (1), can be expressed in a three-dimensional space as a surface. The reaction rate of any point of this surface is determined by the corresponding pair of temperature and degree of conversion, and it does not depend on the previous history of the process.

This continuous surface can be discretised and organised as an $(n{\times}m)$ matrix[1], named matrix **A**, whose rows correspond to different degrees of conversion, from α_1–α_n, and whose columns refer to different temperatures, from T_1–T_m. Consequently, the matrix element $A_{i,j}$ expresses the reaction rate at the corresponding pair α_i, T_j, as shown in Eq. (10):

$$\mathbf{A}=\begin{pmatrix} g(\alpha_1)f(T_1) & g(\alpha_1)f(T_2) & g(\alpha_1)f(T_3)\dots g(\alpha_1)f(T_m) \\ g(\alpha_1)f(T_1) & g(\alpha_2)f(T_2) & g(\alpha_2)f(T_3)\dots g(\alpha_2)f(T_m) \\ \vdots & \vdots & \vdots \\ g(\alpha_n)f(T_1) & g(\alpha_n)f(T_2) & g(\alpha_n)f(T_3)\dots g(\alpha_n)f(T_m) \end{pmatrix} \tag{10}$$

Therefore, the general expression for the reaction rate of a single reaction can be written as a matrix product, Eq. (11):

$$\mathbf{A}=\mathbf{g}\cdot\mathbf{f}^T \tag{11}$$

where vectors **g** and **f** are defined as:

$$\mathbf{g}=(g(\alpha_1)g(\alpha_2)g(\alpha_3)\dots g(\alpha_n))^T \tag{12}$$

$$\mathbf{f}=(f(T_1)f(T_2)f(T_3)\dots f(T_m))^T \tag{13}$$

Applying a mathematical procedure capable of decomposing any matrix into a product of vectors as expressed in Eq. (11), two vectors can be obtained, which contain all the kinetic information about the process. The development of a procedure to achieve this decomposition without the need of any assumptions about the functionality of $g(\alpha)$ and $f(T)$ is the most important improvement that the NPK method introduces.

A mathematical algorithm used to perform this decomposition is the singular value decomposition (SVD), which is widely used in chemometrics for principal component analysis (PCA). The SVD algorithm decomposes a matrix **M** of any dimension $(n{\times}m)$, in the product of three matrices as shown in Eq. (14):

$$\mathbf{M}=\mathbf{U}\cdot\mathbf{W}\cdot\mathbf{V}^T \tag{14}$$

where **U** and **V** are orthonormal matrices and W is a diagonal matrix whose elements are the singular values of matrix **M**. The dimensions of these matrices depend on the algorithm, but formally $n{\geq}m$, and **U** is $(n{\times}m)$, **V** is $(m{\times}m)$ and **W** $(m{\times}m)$. If only the first singular value is significant, i.e. if it is much bigger than the rest, then matrix **M** can be expressed as the product of the first column of matrix **U**, called hereinafter vector **u**, the first singular value, called **w**, and the first column of matrix **V**, which is vector **v**:

$$\mathbf{M}=\mathbf{u}\cdot\mathbf{w}\cdot\mathbf{v}^T \tag{15}$$

This latest equation is a generalised expression of Eq. (11), where:

$$\mathbf{u}=x\cdot\mathbf{g} \tag{16}$$

$$\mathbf{v}=y\cdot\mathbf{f} \tag{17}$$

and$1/x\cdot 1/y=\mathbf{w}$. So, applying the SVD to matrix **A**, two matrices **U** and **V** are obtained, whose first col-

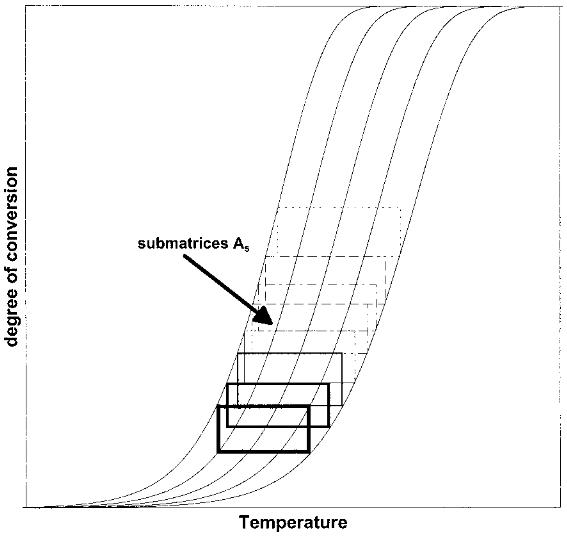

Fig. 1. Definition in an α–T plot of the overlapped submatrices $\mathbf{A}_S$ needed to carry out the NPK method.

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[1] Boldface upper case or lower case letters are used to represent matrices or vectors, respectively. Vectors are treated as columns.

umns, vectors **u** and **v** respectively, are proportional to their corresponding vectors **f** and **g**.

Although, it is not possible to find experimentally all the required elements of matrix **A** for a sufficient range of degrees of conversion and temperatures. However, it is possible to define submatrices of **A**, named $\mathbf{A}_s$, inside the area between the TA curves that will allow the calculation of vectors **u** and **v**, as shown in Fig. 1.

A general expression of these submatrices is shown in Eq. (18):

$$\mathbf{A}_s = \begin{pmatrix} g(\alpha_i)f(T_j) & g(\alpha_i)f(T_{j+1}) & g(\alpha_i)f(T_{j+2})\ldots g(\alpha_i)f(T_{j+k}) \\ g(\alpha_{i+1})f(T_j) & g(\alpha_{i+1})f(T_{j+1}) & g(\alpha_{i+1})f(T_{j+2})\ldots g(\alpha_{i+1})f(T_{j+k}) \\ \vdots & \vdots & \vdots \\ g(\alpha_{i+p})f(T_j) & g(\alpha_{i+p})f(T_{j+1}) & g(\alpha_{i+p})f(T_{j+2})\ldots g(\alpha_{i+p})f(T_{j+k}) \end{pmatrix} \qquad (18)$$

The application of the SVD to this matrix leads to:

$$\mathbf{A}_s = \mu\omega\nu^T \qquad (19)$$

where:

$$\boldsymbol{\mu} = \frac{1}{\chi}\left(u_{(i)}\ u_{(i+1)}\ u_{(i+2)}\ \ldots\ u_{(i+p)}\right)^T \qquad (20)$$

$$\mathbf{v} = \frac{1}{\varphi}\left(v_{(j)}\ v_{(j+1)}\ v_{(j+2)}\ \ldots\ v_{(j+k)}\right)^T \qquad (21)$$

and $\chi\varphi=\omega$.

In order to calculate the whole vectors **u** and **v**, a sequential process is applied by formulating first q submatrices $\mathbf{A}_s$ of the type of Eq. (18). This process results to q vectors $\boldsymbol{\mu}$ and q vectors **v**. Once these vectors have been calculated, vectors **u** and **v** can be expressed as:

$$\mathbf{u} = \left(\chi_1\boldsymbol{\mu}_1\ \chi_2\boldsymbol{\mu}_2\ \ldots\ \chi_q\boldsymbol{\mu}_q\right)^T \qquad (22)$$

$$\mathbf{v} = \left(\varphi_1\mathbf{v}_1\ \varphi_2\mathbf{v}_2\ \ldots\ \varphi_q\mathbf{v}_q\right)^T \qquad (23)$$

However, because of the normalisation performed by the SVD algorithm, the resulting ω value is different for each matrix $\mathbf{A}_s$. Therefore, the vectors **u** and **v**, defined as in Eqs. (22) and (23), are not continuous. To ensure continuity, each vector μ_i has to be multiplied by a suitable factor ϕ_i and the corresponding vector ν_i has to be divided by the same factor, rendering the product $\boldsymbol{\mu}_i\omega_i\mathbf{v}_i^T$ constant. To obtain these factors, the consecutive pairs of matrices $\mathbf{A}_s$ have to partly overlap each other, as shown in Fig. 1. In this way, continuity is achieved because the shared area of any two consecutive matrices i and i+1 forces the corresponding consecutive vectors $\boldsymbol{\mu}_i$ and $\boldsymbol{\mu}_{i+1}$, and $\mathbf{v}_i$ and $\mathbf{v}_{i+1}$, to share half of their elements, thus allowing the calculation of the appropriate ϕ_i factor. Finally the vectors **u** and **v** can be expressed as:

$$\mathbf{u} = \left(\boldsymbol{\mu}_1\ \phi_2\boldsymbol{\mu}_2\ \ldots\ \phi_q\boldsymbol{\mu}_q\right)^T \qquad (24)$$

$$\mathbf{v} = \left(\omega_1\mathbf{v}_1\ \frac{\omega_2}{\phi_1}\mathbf{v}_2\ \ldots\ \frac{\omega_q}{\phi_q}\mathbf{v}_q\right)^T \qquad (25)$$

where ϕ_1 has been fixed equal to one.

3. Experimental

The decomposition of the dibenzoyl peroxide (DBP) has been studied by dynamic differential scanning calorimetry (DSC) on a DSC30 cell and a TA4000 thermal analysis system of Mettler Toledo. The non-isothermal DSC experiments were carried out with samples of ca. 9 mg, and heating rates of 2, 4, 8 and 16 K min^{-1}, while the isothermal experiment was performed at 110°C with a sample of ca. 7 mg. Stainless steel, 120-µl medium pressure crucibles were used for these measurements.

3.1. Sample preparation

DBP provided by Merck, Lot 51016469, is a white powder which contains 25% of water. This DBP is dissolved 1 : 9 by mass in benzene. The solution obtained has to be dried by means of anhydrous $MgSO_4$ because water modifies the rate of decomposition of DBP. The solution obtained by this way is kept at 4°C until the moment of use (a maximum of few hours).

4. Results and discussion

The results of the DSC measurements are presented in Fig. 2. This data has been studied with all the methods described before in order to obtain the kinetic parameters. These results are compared with the ones obtained with the new NPK method.

4.1. Results from nth-order kinetics methods

The results of multilinear regression, Eq. (2), and those of the linear regression suggested by the Freeman–Carroll method, Eq. (3), using the experimental data in the range of α between 0.2–0.8, are presented in Table 1.

Both sets of results are in good agreement with each other, suggesting that the DBP decomposition is well described by a first-order kinetics, and appear to be in accordance with bibliography [11].

4.2. Results from methods based on maximum points

The application of these methods, Eqs. (4)–(6), results to a straight line from the slope of which is obtained the activation energy. The obtained values for the activation energy are: 119.37±9.36 kJ mol^{-1} using the Kissinger method, 119.98±8.91 kJ mol^{-1} using the Ozawa method, while the result obtained by the peak heights method is 118.97±7.53 kJ mol^{-1}.

The results of the three methods are in good agreement. However, the baseline selected may have a strong influence on the results obtained by the peak heights method, while it has no influence on the other methods. Minor errors in the baseline definition may cause a significant error in the evaluation of the peak height, and consequently, in the activation energy calculated. For this reason, this method is not recommended.

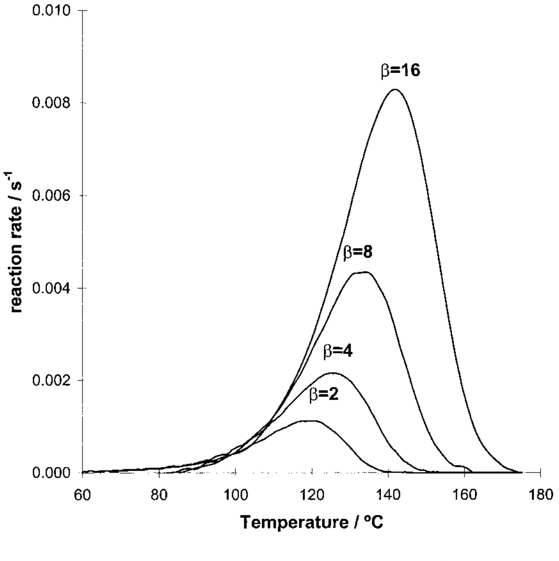

Fig. 2. Experimental curves of the decomposition of DBP. Heating rates: 2, 4, 8, 16 K min^{-1}.

4.3. Results from isoconversional methods

The isoconversional methods allow the calculation of the activation energy for different degrees of conversion. The evolution of the apparent activation energy is shown in Fig. 3 for the three methods. The average values of activation energy are 112.52±2.73 kJ mol^{-1} using the Friedman method, 108.59±2.99 kJ mol^{-1} using the Ozawa's isoconversion method, and 107.60±3.16 kJ mol^{-1} using the Kissinger–Akahira–Sunose method. The methods provide similar values for the activation energy, but they are smaller than those obtained from the methods based only on maximum points.

4.4. The choice of the kinetics

Once activation energy has been found, it is possible to select a kinetic model that describes the experimental data adequately. The application of the Šesták and Málek procedure employs the auxiliary function $Y(\alpha)$, given below:

$$Y(\alpha) = \dot{\alpha} e^{E/RT} \tag{26}$$

As the plot of $Y(\alpha)$ normalised within (0,1) interval, Fig. 4, decreases steadily and linearly, the kinetic model suggested is a first-order reaction.

Another methodology for kinetic model discrimination has been presented by Málek and Criado. According to this method, the apparent activation energy obtained by the Freeman–Caroll method is compared with the activation energy value calculated independently, e.g. by the Kissinger or Ozawa method. As the reaction order obtained by the Freeman–Carroll method is close to unity, and the ratio $E_{\text{Freeman–Carroll}}/(n_{\text{Freeman–Carroll}}E)$ is also close to unity, the Málek and

Table 1
Results from *n*th-order kinetic methods

Heating rate (K min^{-1})	2	4	8	16	Average
Multilinear regression					
E (kJ mol^{-1})	109.12±0.51	111.11±0.34	119.04±0.57	118.16±0.24	114.36±0.55
log A (log(s^{-1}))	12.04±0.07	12.31±0.05	13.36±0.08	13.23±0.03	12.74±0.08
n	0.92±0.007	0.99±0.005	1.07±0.007	1.09±0.003	1.02±0.007
Freeman–Carroll method					
E (kJ mol^{-1})	116.05±2.67	108.29±2.04	119.46±1.64	114.75±0.97	114.64±2.45
n	1.02±0.05	0.97±0.026	1.07±0.028	1.05±0.017	1.03±0.043

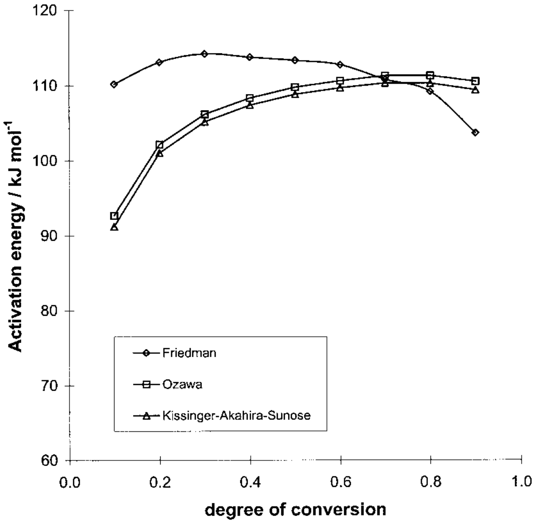

Fig. 3. Evolution of the activation energy calculated by the isoconversion methods.

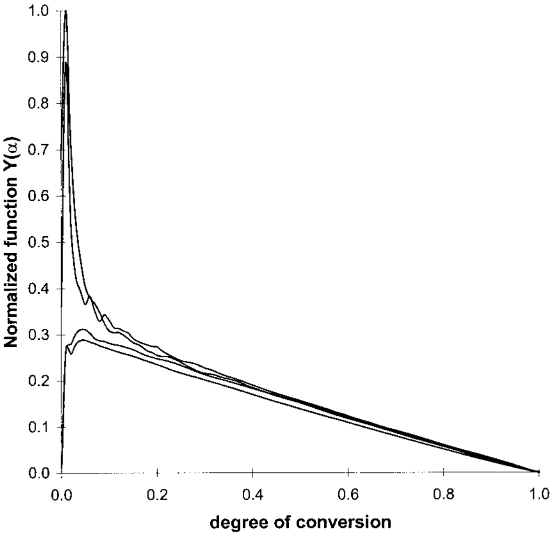

Fig. 4. Evolution of the *Y*(α) function, calculated for the experimental data.

Criado method suggests that the best kinetic model is a first-order reaction.

4.5. Results from the NPK method

The application of the NPK method provides two vectors, **u** and **v**, as described before. These vectors are graphically presented in Figs. 5 and 6.

The elements of vectors **u** and **v** shown in Figs. 5 and 6, have been directly employed for a simulation of the reaction behaviour. The results of this simulation are validated with the experimental data in Fig. 7. The simulation curve obtained from the NPK method reproduces accurately the experimental data. The simulation process takes into account that a concrete value of the reaction rate, $\dot{\alpha}_i(\alpha_i, T_j)$, can be calculated as the product of the corresponding elements of vectors **u** and **v**, $\mathbf{u}(\alpha_i)$ and $\mathbf{v}(T_i)$, respectively, as expressed in Eq. (27). The required values $\mathbf{u}(\alpha_i)$ and $\mathbf{v}(T_i)$ are obtained by interpolation within the obtained elements of vectors **u** and **v**.

$$\dot{\alpha}_i(\alpha_i, T_j) = u(\alpha_i)v(T_j) \tag{27}$$

An isothermal experiment of the DBP decomposition has also been carried out at 110°C. The system behaviour has been simulated accurately with the vectors **u** and **v**. Fig. 8 shows the reaction rate vs. time and the degree-of-conversion vs. time dependences.

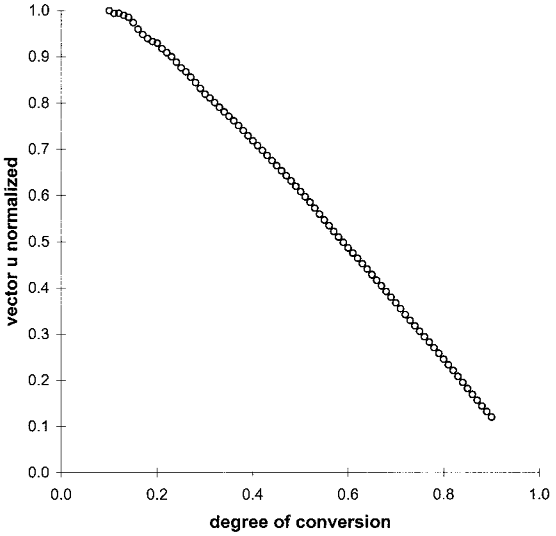

Fig. 5. The vector **u** normalised within (0,1), obtained from the NPK method for the DBP decomposition, against the degree of conversion.

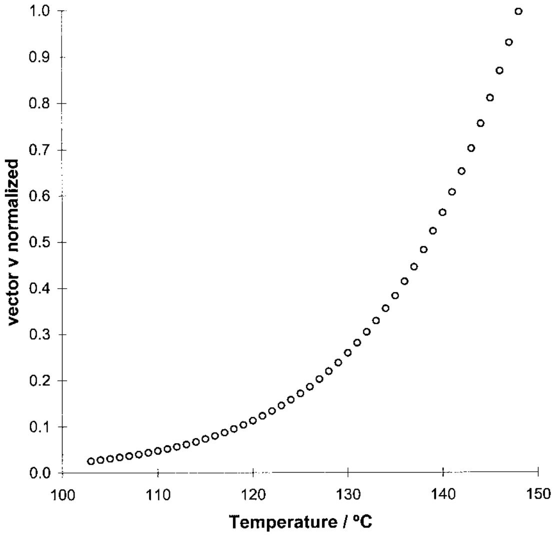

Fig. 6. The vector **v** normalised within (0,1), obtained from the NPK method for the DBP decomposition, against the temperature.

For the calculation of the vectors **u** and **v**, no assumptions were made about the kinetic model or the temperature dependence of the rate constant. However, a kinetic model can be fit to the vector **u**, and an Arrhenius activation energy can be obtained from vector **v**. This allows the calculation of the parameters A, E and n, although these parameters are not necessary to perform a simulation of the

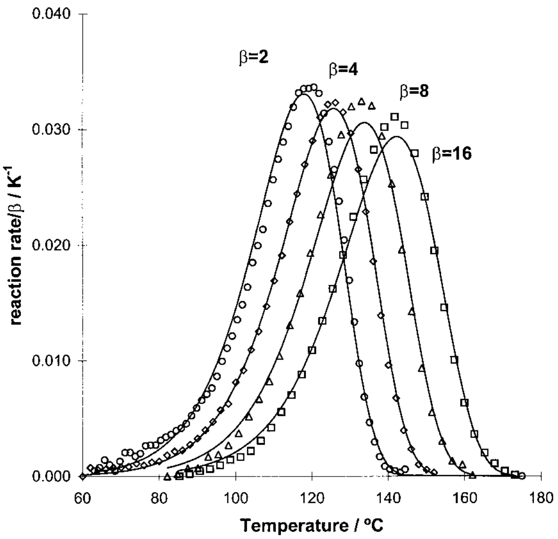

Fig. 7. Experimental (symbols) and simulated (lines) reaction rate-temperature curves using the vectors **u** and **v** obtained using the NPK method. Heating rates: 2, 4, 8 and 16 K min^{-1}.

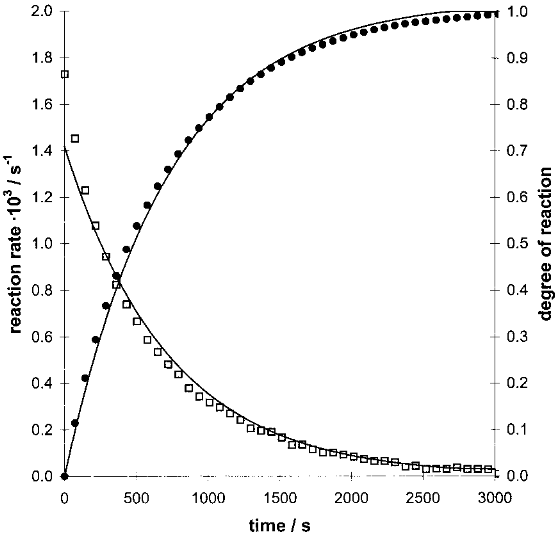

Fig. 8. Reaction rate vs. time (●), experimental and, (———), simulation) and degree-of-conversion vs. time (□), experimental and (———), simulation) for an isothermal measurement performed at 110°C. The simulations have been carried out using the vectors **u** and **v** obtained by the NPK method.

process trough the NPK method. The obtained values are: a reaction order of 0.97±0.004, a frequency factor, expressed as decimal logarithm, 11.93±0.02 log (s^{-1}), and an activation energy of 108.32±0.11 kJ mol^{-1}.

The activation energy calculated by methods based on maximum points has an average value of 119.44±0.51 kJ mol^{-1}. On the other hand, methods where a wider range of data is used, like those of Ozawa or NPK, result to an average value of 108.17±0.51 kJ mol^{-1}. However, all the calculated values are of the same order of magnitude, and there is only a deviation of 9%.

It is worth mentioning that the range of temperature used for the calculation of the activation energy in the NPK method spans 103–148°C, which is significantly larger than the range of temperature used in the methods based on maximum points, which is 120–142°C.

5. Conclusions

The non-parametric kinetics method for the treatment of non-isothermal thermoanalytical data has been developed and verified using experimental measurements.

The results obtained from the NPK method for a simple case are in good agreement with those corresponding to the traditional ones, and the simulation carried out with these results reproduce accurately the experimental data for all the heating rates.

6. Nomenclature

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. (13), s^{-1}
$\mathbf{g}$	vector related to degree of conversion dependence, defined in Eq. (12)
n	order of reaction
m	sample mass, mg
P	peak height, mW
T	temperature, K
$\mathbf{U}$	matrix related to degree of conversion dependence, defined in Eq. (14)
u	vector related to degree of conversion dependence, defined in Eq. (15)
$\mathbf{V}$	matrix related to temperature dependence, defined in Eq. (14), s^{-1}
$\mathbf{v}$	vector related to temperature dependence, defined in Eq. (15), s^{-1}
$\mathbf{W}$	singular values matrix, defined in Eq. (14)
w	singular value, defined in Eq. (15)
x	proportional factor, defined in Eq. (16)
Y	auxiliary function, defined in Eq. (26), s^{-1}
y	proportional factor, defined in Eq. (17)

7. Greek symbols

α	degree of conversion
$\dot{\alpha}$	reaction rate, s^{-1}
β	heating rate, K min^{-1}
$\boldsymbol{\mu}$	vector related to degree-of-conversion dependence, defined in Eq. (20)
$\boldsymbol{\nu}$	vector related to temperature dependence, defined in Eq. (21), s^{-1}
ω	singular value, defined in Eq. (19)
χ	proportional factor, defined in Eq. (20)
φ	proportional factor, defined in Eq. (21)
ϕ	continuity factor

8. Subscripts

p	peak
s	submatrix

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