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Simulations for evaluation of kinetic methods in differential scanning calorimetry. Part 3 – Peak maximum evolution methods and isoconversional methods

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Abstract

Various peak maximum evolution methods and isoconversional methods are compared, and the specific characteristics of each method are shown, from a mathematical viewpoint and by using simulated data. A convenient way of correcting the activation energy of the Ozawa method is proposed. Isoconversional methods should be preferred to peak maximum evolution methods, especially when an interpolation on the power and/or the temperature is performed.

In the case of a complex mechanism of two parallel reactions, peak maximum evolution methods give only a mean value of the kinetic parameters, while isoconversional methods are useful in describing this complex mechanism. © 1997 Elsevier Science B.V.

Keywords: Activation energy; Complex process; Differential scanning calorimetry; Isoconversional methods; Nonisothermal kinetics; Peak maximum evolution methods; Simulations

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1. Introduction

In our previous studies, theoretical data [1,2] with and without various amounts of random Gaussian errors, have been used to test the validity of single peak methods. This procedure was applied to various multiple linear regression algorithms with one or two kinetic exponents, and to the Achar–Brindley–Sharp, Freeman–Carroll and Ellerstein methods. Simulations were performed according to the results previously obtained for an experimental polymerization of an epoxy–novolac resin, but the procedure can be extended to any set of parameters or mechanisms. The multiple linear regression method with one kinetic exponent gave the best modellings, without leading to unrealistic kinetic parameters (i.e. negative values), such as those obtained with a multiple linear regression method with two kinetic exponents.

Among multiple scans methods (multiheating rate methods), we can distinguish the peak maximum evolution and isoconversional methods. We present in this paper an evaluation of these two kinds of methods, from simulated thermoanalytical curves with, and without additional noise, for a single-step as well as for a complex process. The chief virtue of these methods is to yield the activation energy without knowledge of the conversion function (generalized description) and, in addition, in regard to the isocon-

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versional methods, their possible use for complex reactions.

2. Theoretical

2.1. *Differential equations: Friedman method*

The general equation for the reaction rate is generally written as [3]:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = k(T)f(\alpha) \tag{1}$$

(where $k(T)$ is the Arrhenius rate constant, α the extent of reaction (conversion degree), t the time, T the temperature and $f(\alpha)$ the reaction model). For the differential scanning calorimetry (DSC) data, the extent of reaction is defined as $\alpha_i = H_i/Q$, where H_i is the partial heat of reaction at time i and Q the total heat of reaction. Taking the logarithm of Eq. (1) gives:

$$\ln\left(\frac{\mathrm{d}H}{\mathrm{d}t}\right)_\alpha = \ln[QA_\alpha f(\alpha)] - \frac{E_\alpha}{RT_\alpha} \tag{2}$$

(where R is the gas constant; A_α, E_α, $(\mathrm{d}H/\mathrm{d}t)_\alpha$ and T_α are, respectively, the pre-exponential factor, the activation energy, the heat flux and the temperature at a given conversion degree α). This is the equation upon which Friedman [4] based the differential isoconversional method for calculating activation energies E in the case of a single step reaction and E_α for a multiple step reaction. This equation is established without introducing any approximation, and is not restricted to the use of a linear heating or cooling rate. Using this generalized description, the determination of the activation energy is not influenced by the proper choice of the function describing the mechanism, although this influence has been widely studied [5,6].

From a computational aspect, the method of Friedman requires the determination of the heat flux and of the temperature at a given conversion for various scanning rates. The Friedman plot can be obtained directly from DSC data using Eq. (2), because the heat flux is measured vs. temperature with this technique. Nevertheless, very large errors can be observed if no interpolation is performed. Hence, our computer code has been optimised using simulated data, and a second order polynomial has been retained to fit the variation of the temperature and power at a given conversion degree. This interpolation of the simulated data has been applied to all isoconversional methods, with very similar results to Lagrangian interpolation.

2.2. *Integral equations*

The methods based on the integral form of Eq. (1) are restricted to the use of a linear heating or cooling rate. For nonisothermal conditions, at a constant heating rate $V = \mathrm{d}T/\mathrm{d}t$, Eq. (1) may be rewritten as:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T} = \frac{A}{V}e^{-E/RT}f(\alpha) \tag{3}$$

let us call $g(\alpha) = \int_0^\alpha \frac{\mathrm{d}\alpha}{f(\alpha)}$, then the integral form of Eq. (3) is obtained [7]:

$$g(\alpha) = \frac{AE}{RV}\left[\frac{e^{-x}}{x} - \int_x^\infty \left(\frac{e^{-x}}{x}\right)\mathrm{d}x\right] \tag{4}$$

where $x = E/RT$ is the reduced activation energy at the temperature T. As no exact solution exists for Eq. (4), this equation is generally written as:

$$g(\alpha) = \frac{AE}{RV}p(x) \tag{5}$$

where $p(x)$ is the temperature integral.

2.2.1. *Ozawa–Flynn–Wall method*

Using Doyle's approximation [8]:

$$\ln p(x) \cong -5.3305 - 1.052x \quad (20 \leq x \leq 60)$$

the linear equation of Ozawa–Flynn–Wall can be obtained [9,10]:

$$\ln V \cong \ln\left(\frac{A_\alpha E_\alpha}{R}\right) - \ln g(\alpha) - 5.3305 - 1.052\left(\frac{E_\alpha}{RT_\alpha}\right) \tag{6}$$

The error introduced into the calculation of activation energy by the use of a linear approximation of the logarithm of the temperature integral had already been discussed [11], and corrections proposed [11,12].

We provide a different way of obtaining corrected activation energy values and, in further discussion, this type of calculation will be referred to as the numerical procedure. This simple and powerful method consists in first computing Eq. (6), to obtain an approximate value of E_α at a given conversion. Thus, the mean value of the temperature ($\overline{T_\alpha}$) for the various scanning rates used can be evaluated. The expression for $\ln p'(x)$ is estimated by a numerical integration of the temperature integral (Eqs. (4) and (5)), by using the trapezoidal rule, with a step of 10^{-3}, and for the interval $[x, \infty]$. Therefore, $\ln p'(x)$ values are fitted by a first-order polynomial on the interval $x = E_\alpha(1 \pm 0.2)/(R\overline{T_\alpha})$, for each given conversion, and we will call this method the corrected Ozawa method.

For convenience, the Kissinger and Ozawa methods are often performed using the top of the peak temperature. In fact, the Ozawa method can be applied at a given conversion degree (Eq. (6)). As the conversion degree values are never exactly constant in experimental reactions, we will compare the Ozawa method with the isoconversional method of Ozawa, which we will call Ozawa 50%, and in which α is exactly 50%. Henceforth, the Ozawa method, corrected or not, will be applied as a peak maximum evolution method (Ozawa) and as an isoconversional method.

2.2.2. *Kissinger and Kissinger–Akahira–Sunose methods*

In regard to the given definition of Eq. (1), if the reaction rate is maximum, we can state that:

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right) = 0 \text{ with } \alpha = \alpha(t, T) \text{ and } T = T(t)$$

The plot of $\ln (V/T_p^2)$ vs $1/T_p$ known as the Kissinger method [13] and was initially developed for first-order reactions. In fact, this equation holds for any kinetic model [14]. If the maximum of the reaction rate suits the peak maximum, then we obtain Eq. (7) by differentiating Eq. (1):

$$\ln\left(\frac{V}{T_p^2}\right) = \ln\left(\frac{Q_p A R}{E}\right) - \frac{E}{RT_p} \qquad (7)$$

where $Q_p = -\left[\frac{df(\alpha)}{d\alpha}\right]_{\alpha=\alpha_p}$

Eq. (7) was established without any approximation and holds for any kinetic model, but is only valid for the peak maximum. In this way, the Kissinger method will be applied as a peak maximum evolution method.

On the other hand, the Kissinger–Akahira–Sunose method [15] is valid at any given conversion, but is derived using an approximation for *p(x)*, ($p(x) \cong e^{-x}/x^2$ $(20 \leq x \leq 50)$). Under this assumption, Eq. (8) is obtained as follows:

$$\ln\left(\frac{V}{T_\alpha^2}\right) \cong \ln\left(\frac{A_\alpha R}{E_\alpha}\right) - \ln g(\alpha) - \frac{E_\alpha}{RT_\alpha} \qquad (8)$$

All the isoconversional methods (Friedman, Ozawa, Ozawa corrected and Kissinger–Akahira–Sunose methods) will be applied for $\alpha = 50\%$ and for the overall conversion interval (cf. Section 3.1.3) using the procedure presented above for the Friedman method.

2.3. *The Malek method*

The Malek method [14] allows the calculation of the kinetic exponents *m* and *n* and of the logarithm of the pre-exponential factor (ln *A*), but requires the previous determination of the activation energy by another method. Generally, the Kissinger method is used for this determination, but we can also use the Ozawa or the Friedman methods. The function that best describes the mechanism can be chosen from the shape of the plot of the standardized curve $y(\alpha)$. Only two of the three possible models of this method will be studied here: the reaction-order RO(n) and the Sestak–Berggren (SB) models with two kinetic exponents (also called the autocatalytic model), which are most often used for curing reactions.

2.3.1. *Reaction-order models*

The *f(α)* function of the reaction-order model is expressed as follows:

$$f(\alpha) = (1 - \alpha)^n \qquad (9)$$

(where *n* is the reaction order).The kinetic exponent *n* is obtained by iteration (or dichotomy) of the following equation:

$$\alpha_p \cong 1 - \left[1 + \frac{1-n}{n} x_p \prod(x_p)\right]^{1/(n-1)} \qquad (10)$$

where α_p is the conversion degree at the top of the DSC peak and $\prod(x) = \frac{x}{e^{-x}} p(x)$.Various approximations for *p(x)* were proposed [16]. The approximation derived by Gorbatchev [17] was initially used by

Malek [14] for the reaction-order model of its method:

$$p(x) \cong \frac{e^{-x}}{x(x+2)} \tag{11}$$

Nevertheless, this approximation may be too limited for modelling purpose [18]. When more precision is required, the 4th rational expression of Senum and Yang [19], further used as an approximate expression of the $p(x)$ function obtained by Sestak and Malek [20], should be used:

$$p(x) \cong \frac{e^{-x}}{x}\left(\frac{x^3 + 18x^2 + 88x + 96}{x^4 + 20x^3 + 120x^2 + 240x + 120}\right) \tag{12}$$

The reader should refer to Flynn [21,22] for more precise information on this equation.

In this paper, we will evaluate the accuracy of each of the two ways of computing $p(x)$. For clarification, in the case of the first approximation (Eq. (11)), the method will be called Malek (RO1), while in the second (Eq. (12)), we will call it Malek (RO2).

2.3.2. Sestak–Berggren model

For the Sestak–Berggren model, the $f(\alpha)$ function is expressed as follows:

$$f(\alpha) \equiv \alpha^m(1-\alpha)^n = [\alpha^P(1-\alpha)]^n \tag{13}$$

where m and n are kinetic exponents, $p = m/n$ can be computed using:

$$p = \alpha_M/(1-\alpha_M) \tag{14}$$

where α_M is the maximum of the function $y(\alpha)$. From Eq. (1), we can write:

$$y(\alpha) = \frac{\mathrm{d}H}{\mathrm{d}t}e^{E/RT} = A'f(\alpha) \tag{15}$$

with $A' = QA$. Taking the logarithm of Eq. (15), we obtain:

$$\ln\left[\frac{\mathrm{d}H}{\mathrm{d}t}e^{E/RT}\right] = \ln A' + n\ln[\alpha^p(1-\alpha)] \tag{16}$$

n is determined from the slope of Eq. (16), p from Eq. (14) and the pre-exponential factor A from Eq. (7).

Instead of using approximations, there is evidence that the reaction- order model can be deduced from the plot of $\ln[(\mathrm{d}H/\mathrm{d}t)\exp(E/RT)]$ vs. $\ln[\alpha^p(1-\alpha)]$ of the Sestak–Berggren model. Indeed, since the reaction-order model implies a strictly decreasing function $y(\alpha)$, we find that $\alpha_M = 0$, such that $p = 0$ and, thus, $m = 0$, if $y(\alpha)$ is computed over the entire interval of the reaction. In other words, from a purely mathematical aspect, setting $p = 0$ in Eq. (13), leads to the equation of a reaction-order model (Eq. (9)).

In the following, the Sestak–Berggren model (with m set to zero) will be used as an alternative to the reaction-order models. So, the influence of the error in the preliminary activation energy on the calculated values of the two other kinetic parameters n and $\ln A$, and the influence of the approximations of the reaction-order RO1 and RO2 models, will be shown using simulated data.

2.4. Numerical simulations

The generation of the simulated data was previously presented [1]. Simulations without, and with Gaussian noise (mean = 0 and standard deviation = 0.2) on the power were carried out. Evaluation of the kinetic parameters was performed on the artificially created data by using a computer program described elsewhere [3]. Absolute relative errors have been computed by comparing the value obtained with that of reference (the values mentioned are always absolute relative errors); the average of five separate simulations was used to obtain the mean relative errors on the kinetic parameters, in the case of noisy simulated data. For peak maximum evolution methods, the determination of the top of peak temperature was obtained after a linear extrapolation of the baseline.

The kinetic parameters used in the simulations of a single-step process were: scanning rates $V = 1, 2, 4, 5\ \mathrm{K\,min^{-1}}$, heat of the exothermic cure $Q = -77$ J, kinetic order $n = 2$, activation energy E=77 $\mathrm{kJmol^{-1}}$, logarithm of the pre-exponential factor $\ln A = 19$, acquisition time sr = 1s and initial temperature $T_0 = 233.15$ K. These parameters were previously obtained from an experimental polymerization of an epoxy-novolac cured with amine [18]. As a first approximation, it was shown that these parameters accurately model the reaction considered, using a reaction-order model, for the most part of the temperature interval. More information on the complete kinetics of this transformation may be obtained in [23]. Fig. 1 shows the shape of the curves obtained at

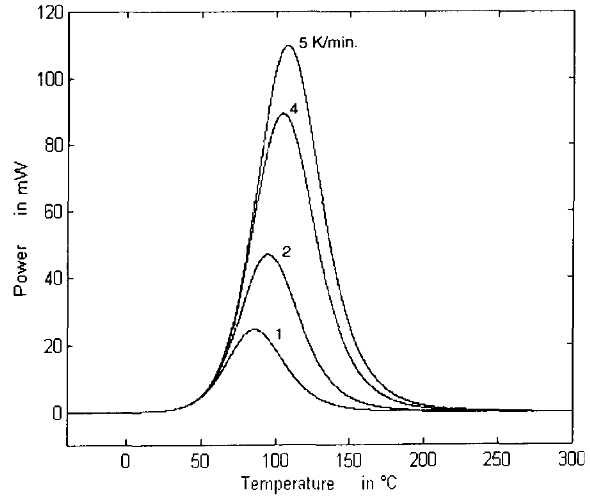

Fig. 1. Thermoanalytical curves of a single-step process (1, 2, 4 and 5 K min^{-1}).

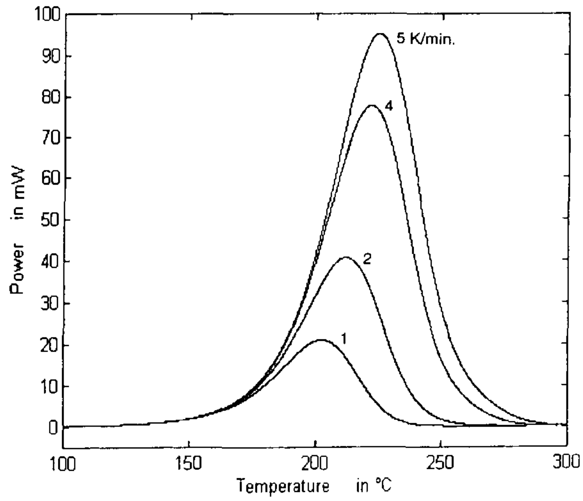

Fig. 2. Thermoanalytical curves of a complex process of two parallel reactions (1, 2, 4 and 5 K min^{-1}).

various scanning rates (1, 2, 4, 5 K min^{-1}) using this model. The temperature interval where the reaction occurs is between 0° and 250°C, which corresponds to a reduced activation energy ($x = E/RT$) between 17.5 and 40.

To test the numerical procedure for a value of $x<20$, we performed the same simulations with $\ln A = 9$. In this case, the temperature interval at 1, 2, 4, 5 K min^{-1} is between 150° and 500°C, which corresponds to $12 < x < 22$.

In a second part, a simple case of complex mechanism of two parallel reactions, governed by a reaction-order model, was simulated. If only the rate of product formation is measured, the mechanism may correspond to the two following kinetic schemes:

$$A \xrightarrow{k_1} C \xleftarrow{k_2} B \text{ or } A \xrightarrow{k_1} B \xrightarrow{k_2} C \ (k_1 \gg k_2)$$

The kinetic parameters were: heat of the exothermic effects $Q_1 = -37.8$ and $Q_2 = -16.2$J; kinetic orders $n_1 = 1.2$, $n_2 = 1$; activation energies $E_1 = 143$ and E_2=74 kJmol^{-1}, logarithms of the pre-exponential factor $\ln A_1 = 29.4$, $\ln A_2 = 11.7$; acquisition time sr = 2s, scanning rates $V = 0.1 - 10\,K\,\text{min}^{-1}$; initial temperature $T_0 = 313.15\,K$. The comparison of the single-step process (Fig. 1) with this complex process (Fig. 2) clearly shows the great dissymmetry of these thermoanalytical curves depending on the contribution of each reaction.

3. Results of numerical simulations

3.1. Single-step mechanism

Various acquisition times were used for the four heating rates studied (Table 1). For the peak maximum evolution methods (Kissinger and Ozawa), no specific difference was observed for the dependence of the relative errors *vs.* the number of points, in comparison with the results already reported for the single peak methods (cf. [1] or Table 1, MLR(n)). The analysis of the relative errors of the isoconversional methods (for $\alpha = 50\%$), clearly shows that a limit is reached for sr = 3s, above this value, relative errors are greatly increased: 3.5-6% for sr = 4 s, 19–22% for sr = 5 s, and finally 115–125% for sr = 10 s. The same conclusion can be drawn for the isoconversional methods applied on a conversion interval of 10–90%. In the following section, the acquisition time of 1 s was used in the simulation of the single-step mechanism.

3.1.1. Peak maximum evolution methods

Application of the peak maximum evolution methods of Kissinger and Ozawa requires a good constancy of the conversion degree at the top of the peak (α_p) [3]. In this respect, the simulation with noiseless data provides evidence of that quasi-constancy (Table 2), depending on the number of points used (acquisition

Table 1

Relative errors on the activation energy for a single-step mechanism: Peak maximum evolution methods of Kissinger and Ozawa, and isoconversional methods at $\alpha = 50\%$: Kissinger–Akahira–Sunose (KAS), Ozawa 50% (uncorrected), Ozawa 50% corrected (Oc) and Friedman methods, for simulations without noise, with various acquisition times (sr(s))

	Peak maximum evolution methods		Isoconversional methods				Single-scan method
sr	Kissinger	Ozawa	Friedman 50%	KAS	Ozawa 50%	Oc	MLR(n)[a]
1	2.50×10^{-3}	2.93×10^{-2}	1.03×10^{-6}	2.80×10^{-3}	2.42×10^{-2}	8.24×10^{-4}	4.91×10^{-4}
2	1.30×10^{-3}	2.81×10^{-2}	3.06×10^{-6}	2.79×10^{-3}	2.42×10^{-2}	8.29×10^{-4}	9.65×10^{-4}
3	7.12×10^{-3}	3.37×10^{-2}	4.96×10^{-5}	2.73×10^{-3}	2.43×10^{-2}	9.05×10^{-4}	1.44×10^{-3}
4	4.62×10^{-4}	2.65×10^{-2}	3.45×10^{-2}	3.48×10^{-2}	5.98×10^{-2}	3.81×10^{-2}	1.91×10^{-3}
5	1.03×10^{-3}	2.79×10^{-2}	1.92×10^{-1}	2.06×10^{-1}	2.22×10^{-1}	2.08×10^{-1}	2.39×10^{-3}
10	1.03×10^{-2}	3.67×10^{-2}	1.15×10^{0}	1.25×10^{0}	1.17×10^{0}	—	4.77×10^{-3}

[a] Multiple linear regression method MLR(n) at heating rate of 5 K min^{-1}.

Table 2

Top of peak temperatures (T_p) and degrees of conversion (α_p) for simulations (kinetic parameters: E=77 kJmol^{-1}; ln A=19; n=2) without, or with gaussian noise

V (K min^{-1})	No noise		Noise[a] on power	
	T_p (°C)	α_p(%)	T_p (°C)	α_p(%)
1	85.88	46.53	86.95	48.73
2	95.03	46.44	94.80	46.76
4	104.67	46.40	105.07	47.56
5	107.83	46.31	108.33	46.88

[a] Gaussian noise: mean=0, standard deviation=0.2.

time value). Nevertheless, in experimental data, such a constancy is never observed. Results of peak maximum evolution and isoconversional methods at $\alpha = 50\%$ (Kissinger–Akahira–Sunose, Friedman, Ozawa and corrected Ozawa methods) are summarized in Table 3. The dependence of the activation energy value vs. the initial temperature has been examined. Extremely low changes were observed when starting at 233.15 K or below, except for the Friedman 50% method. In this case, the relative error in the activation energy is greatly decreased (from 10^{-1} to 10^{-4}%, as the initial temperature decreased from 273.15 K to 233.15 K). This evidently suggests that the choice of the initial temperature is important. For the other methods, the limited precision due to approximations does not allow this type of observation. The results of the prediction on using the Ozawa and Ozawa 50% methods are the least satisfactory, whereas the use of the corrected Ozawa 50% and the Friedman 50% methods lead to the smallest relative errors. Thus, the corrected Ozawa method gives similar errors compared to the multiple linear regression method, while the Friedman method gives lower errors. The slight variation of the conversion degree at the top of the peak (α_p) affects the activation energy value of the Kissinger method less than does the use of the approximation of the Kissinger–Akahira–Sunose method (at $\alpha = 50\%$). Using the correction of the Doyle approximation, proposed by Flynn [11],

Table 3

Relative errors on the activation energy for a single-step mechanism: Peak maximum evolution methods of Kissinger and Ozawa, and isoconversional methods at $\alpha = 50\%$: Kissinger–Akahira–Sunose (KAS), Ozawa 50% (uncorrected), Ozawa 50% corrected (Oc) and Friedman methods

Noise[a]	T_0[a] (K)	Peak maximum evolution methods		Isoconversional methods			
		Kissinger	Ozawa	KAS	Ozawa	Oc	Friedman
without[b]	273.15	1.69×10^{-3}	2.85×10^{-2}	4.11×10^{-3}	2.30×10^{-2}	4.80×10^{-4}	9.58×10^{-4}
without[c]	233.15	2.50×10^{-3}	2.93×10^{-2}	2.80×10^{-3}	2.42×10^{-2}	8.24×10^{-4}	1.03×10^{-6}
with[d]	233.15	4.45×10^{-2}	5.28×10^{-2}	1.83×10^{-2}	1.81×10^{-2}	1.60×10^{-2}	1.55×10^{-2}

[a] Characteristics of the noise: mean = 0, standard deviation = 0.2; T_0: initial temperature.

For multiple linear regression method MLR(n) at 5 K min^{-1} : [b] RE = 2.20×10^{-3}; [c] RE = 4.91×10^{-4} [1,2]; [d] RE = 2.52×10^{-2}

decreases the error from 2.42 to 0.5% for the Ozawa 50% method. Recent advances in the computer routine render attractive the use of the proposed numerical procedure that gives a relative error of only 0.08%, without requiring the use of a table for corrections.

Results for a reduced activation energy (x), out of range of validity of the Doyle linear approximation ($12 < x < 22$, with $\ln A=9$), have shown that the isoconversional Ozawa methods for $\alpha = 50\%$ and for the conversion interval of 10–90% (RE $\cong$ 6.5%) are also accounted for by the Flynn correction (RE $\cong$ 1.16%) and the numerical procedure (RE $\cong$ 0.5%). In this case, the Friedman 50% method has led to a relative error (RE) of $5.1\ 10^{-7}$ (Friedman 10–90% RE $= 1.5\ 10^{-6}$) in the activation energy, and the Kissinger methods ($\alpha = 50\%$ and 10–90%) have led to a relative error of ~0.66% in the activation energy.

An example of conversion degrees and top of peak temperatures obtained for one set with Gaussian random noise is given in Table 2. The relative errors obtained are presented in Table 3. Eq. (7) shows that Kissinger's equation can be exactly demonstrated and that the plot of $\ln V/T_p^2$ vs. $1/T_p$ will be linear if Q_p is constant, that is to say $f(\alpha_p)$ is a constant or varies linearly with α_p. On the other hand, Eqs. (6) and (8) indicate that $g(\alpha)$ should be constant. A plot of $(1-\alpha_p)^n$ vs. the heating rate shows that the condition of linearity is not verified for noisy data, leading to higher average relative errors using the Kissinger method, as compared to the isoconversional methods (although the Kissinger method was more accurate with noiseless data). In the same way, a rapid calculation shows that the constancy of $g(\alpha)$ required by application of Eqs. (6) and (8) is not verified for noisy data. As for the simulations without noise, the Ozawa method leads to the highest relative errors. On the other hand, all the isoconversional methods with $\alpha = 50\%$ give very similar results and improve those obtained with the multiple linear regression method (cf. Table 3 or [1,2]). The lower errors are obtained with the Friedman, then the Ozawa corrected, the Ozawa and the Kissinger–Akahira–Sunose method. As the variation of the conversion degree is generally of same order, or higher for experimental data, isoconversional methods should be preferred to peak maximum evolution methods.

3.1.2. The Malek method

In the usual Malek method, the activation energy is calculated using the Kissinger method. Applied to pure signal and in a kinetic interval of conversion of 10–90% (Table 4), the lowest relative error is observed with the Sestak–Berggren model for the determination of the reaction order, whereas the relative errors observed for the pre-exponential factor are of the same order, whatever the model used. How does the accuracy of the activation energy used in the Malek method influence the error in evaluating the two other kinetic parameters n and $\ln A$? This brings to the fore the problem of minimizing errors in computing the activation energy, the activation energy and the pre-exponential factor being mutually correlated [24,25]. Processing with the activation energy of

Table 4
Single-step mechanism: Relative errors (RE) on the kinetic exponent (n) and on the logarithm of the pre-exponential factor ($\ln A$), for the Malek method with the reaction-order models RO1 and RO2 and the Sestak–Berggren (SB) model

Noise [a]	Model	E from Kissinger [b]		E from Friedman [b]	
		RE(n) [b]	RE($\ln A$) [b]	RE(n) [b]	RE($\ln A$) [b]
without [c]	RO1	5.15×10^{-3}	3.28×10^{-3}	5.57×10^{-3}	5.95×10^{-5}
	RO2	4.98×10^{-3}	3.41×10^{-3}	4.59×10^{-3}	7.11×10^{-5}
	SB	2.13×10^{-3}	3.37×10^{-3}	1.50×10^{-5}	1.11×10^{-5}
with [d]	RO1	3.15×10^{-2}	5.87×10^{-2}	2.93×10^{-2}	8.41×10^{-4}
	RO2	3.78×10^{-2}	5.87×10^{-2}	3.59×10^{-2}	8.74×10^{-4}
	SB	4.33×10^{-2}	5.93×10^{-2}	2.49×10^{-2}	5.89×10^{-4}

[a] Characteristics of the Gaussian noise on power: mean=0 , standard deviation=0.2

[b] n, Kinetic exponent; $\ln A$, logarithm of pre-exponential factor; E, activation energy (kJ mol^{-1}); RE(E) $= 1.69 \times 10^{-3}$ and 9.58×10^{-4} respectively for the Kissinger and Friedman methods for the theorical values E = 77 kJ mol^{-1}; $\ln A=19$; $n=2$
for multiple linear regression method MLR(n) at 5 K min^{-1}:

[c] RE $= 6.50 \times 10^{-5}$ and 3.53×10^{-4}, respectively, for n and $\ln A$, [d] RE $= 4.56 \times 10^{-2}$ and 3.44×10^{-2} for n and $\ln A$.

Friedman, computed at $\alpha = 50\%$, as starting data (improvement of a factor 2000, Table 3), shows that the relative errors in n and ln A are much lower than those obtained with the activation energy of Kissinger (Table 4). The use of the Friedman 50% activation energy and of the Sestak–Berggren model improves the results by a factor 100 for n and 300 for ln A. Extremely low errors (10^{-5}) in the ln A determination were obtained (improvement by a factor 30 compared to the multiple linear regression method). Using the activation energy of Kissinger, the relative errors in n and ln A are of the same order as the relative error in activation energy (i.e. 10^{-3}). Using the activation energy of Friedman computed at $\alpha = 50\%$, the relative errors on n and ln A are also nearly of the same order (i.e. 10^{-5}) as the relative error in activation energy (10^{-6}).

Relative errors in the reaction order n are not affected by the accuracy of the activation energy using the reaction-order models RO1 and RO2 (because of the approximations introduced).

Calculations have also been performed for a reduced activation energy (x), out of range of validity of the Doyle linear approximation ($12 < x < 22$, with ln A=9), using the activation energy of Friedman. Results have shown an increase in the relative errors in the reaction order and in the logarithm of the pre-exponential factor, respectively, of a factor 2 and 3, for the reaction-order models RO1 and RO2. The Sestak–Berggren model has led to a decrease in the relative error on the reaction order by a factor of two and an increase in the relative error in the logarithm of the pre-exponential factor by a factor of six. The Sestak–Berggren model is still the more accurate, with a relative error in the reaction order of 8.09×10^{-6}, while we found ~1% for the two reaction-order models.

Additional Gaussian noise added to the power signal did not modify the shape of the $y(\alpha)$ function, which always indicates a reaction-order model. As for the simulations without noise, the use of the activation energy calculated by the Friedman 50% method and of the Sestak–Berggren model, has led to the best results. The reaction order n and the pre-exponential factor ln A are obtained with an even higher accuracy compared to those obtained by the multiple linear regression method (improvement by a factor 60 for ln A).

3.1.3. Analysis of the entire information of the peak

Because of their validity for any conversion degree, the above-mentioned methods, such as the isoconversional methods, are not restricted to the analysis of the peak evolution at $\alpha = 50\%$, but can also be used for extracting the entire information present in the thermoanalytical curve. In the present case, activation energies have been computed for a conversion degree varying in steps of 2%, from 10 to 90%. Then, evaluation of the methods was performed by computing absolute relative errors for each conversion value, and the mean value over all the interval of conversion retained. Results are presented in Table 5 and Fig. 3.

It is interesting to note that the Friedman method (with interpolation of the data) gives slightly more accurate results for the activation energy than does the multiple linear regression method. On the other hand, if no interpolation is performed, the relative errors observed become much greater even for noiseless data (0.17, 0.14 and 7.9% respectively for the Friedman, the Kissinger–Akahira–Sunose and the Ozawa methods, with $T_0 = 233.15$ K).

For noisy data, the errors obtained are similar to those obtained at $\alpha = 50\%$, with a higher value for the Friedman method. The lower errors are obtained with the Ozawa method, then with the Ozawa corrected, the Kissinger–Akahira–Sunose and the Friedman methods. It is interesting to compare the Friedman method (the only one with no need of approximation and

Table 5
Relative errors on the activation energy for the isoconversional methods (single-step mechanism): Kissinger–Akahira–Sunose (KAS), Ozawa 50% (uncorrected), Ozawa 50% corrected (Oc) and Friedman methods, for the conversion interval 10-90%

Noise	T_0 [a] (K)	KAS	Ozawa	Oc	Friedman
without [b]	273.15	4.77×10^{-3}	2.26×10^{-2}	2.34×10^{-3}	3.42×10^{-3}
without [c]	233.15	2.81×10^{-3}	2.43×10^{-2}	8.48×10^{-4}	1.02×10^{-5}
with [d]	233.15	2.56×10^{-2}	1.89×10^{-2}	2.32×10^{-2}	3.28×10^{-2}

[a] T_0 – initial temperature.
[b, c, and d] cf. Table 3.

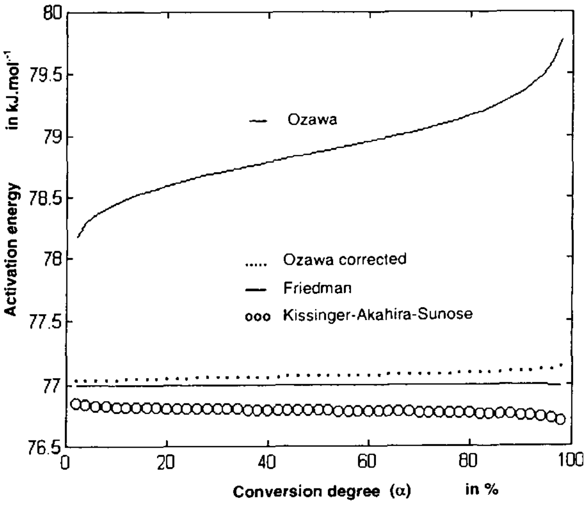

Fig. 3. Activation energies *vs.* conversion degree for the isoconversional methods (Friedman, Ozawa, Ozawa corrected and Kissinger–Akahira–Sunose), for a single-step process (theorical value $E = 77\,\mathrm{kJmol^{-1}}$; $V = 1, 2, 4$ and $5\ \mathrm{K\,min^{-1}}$).

involving the power values) with the other isoconversional methods which use approximations but do not involve the power values. As the amplitude of the simulated power noise used is constant, the peak-to-maximum ratio is obviously much greater at the beginning and end of the signal, leading, with the Friedman method, to greater errors for the edges of the thermoanalytical curve.

4. Complex process of two parallel reaction-order models

4.1. Peak maximum evolution methods

Table 6 gives peak temperatures and degrees of conversion of the complex process shown in Fig. 2, for various heating rates. The great variation of the conversion degree is obvious in such a case (>13%), when a wide range of heating rates was used. A plot of $(1 - \alpha_p)^n$ vs. the heating rate shows that the condition of applicability of Eq. (7) is not valid in the range of heating rates used; nevertheless, if a lower range is chosen (0.1–0.5 or ~1–10 K $\mathrm{min^{-1}}$), as is generally the case for real experiments, this plot should appear as linear. In fact, the plot of $\ln V/T_p^2)$ vs. $1/T_p$ is also linear and does not show the complexity of the reaction studied, so that a straight line is not necessary a proof of the existence of a single-step process. The application of the Kissinger or Ozawa methods shows that the correlation coefficients obtained (−0.99988 and −0.99990, respectively) are always close to one, leading nevertheless to a mean value of the activation energy.

4.2. Information obtained with single-scan methods applied at various scanning rates

The use of a single-scan method and several scanning rates gives more information on the kinetics of the process, in the case of a complex mechanism, than the peak maximum evolution methods or the isoconversional methods applied for $\alpha = 50\%$. The multiple linear regression method that leads to a high increase in the kinetic parameters, while increasing the heating rate (Table 7), shows the existence of several phenomena. Furthermore, the computation of kinetic parameters for the beginning and end of the transformation, in such a case, leads to different values. The Arrhenius plots, presented in Fig. 4 (a) and (b), were obtained with the single-peak method of Achar–Brindley–Sharp [3] (or Borchardt–Daniels) at 5 K $\mathrm{min^{-1}}$, for various values of the kinetic exponent (n). This method gives very similar results with the multiple linear-regression method [1,2], but the kinetic exponent n retained is the one that gives the

Table 6
Peak temperatures (T_p) and degrees of conversion (α_p) obtained with various heating rates used in the simulation of a complex process of two parallel reactions [a], without noise

V/ (K $\mathrm{min^{-1}}$)	0.1	0.3	0.5	1.0	2.0	5.0	10.0
T_p (°C)	174.75	187.08	193.52	202.70	212.20	225.00	235.00
α_p (%)	66.37	63.17	62.04	60.43	58.49	55.35	53.05

[a] Theoretical parameters: $n_1 = 1.2$ and $n_2 = 1$; $E_1 = 143$ and $E_2 = 74\,\mathrm{kJmol^{-1}}$; $\ln A_1 = 29.4$ and $\ln A_2 = 11.7$

Table 7
Kinetic parameters for simulated noiseless data for a complex process of two parallel reactions, using the multiple linear regression method, for the conversion interval 10–90%

V (K min^{-1})	$n^{a,b}$	ln $A^{a,\,b}$	$E^{a,\,b}$	LSM ^{c}
0.1	0.69692	10.80384	75.57976	3.04×10^{-3}
0.3	0.90703	17.58950	98.60711	9.93×10^{-3}
0.5	0.97695	20.03868	107.29275	1.74×10^{-2}
1.0	1.07752	22.79768	117.36907	3.89×10^{-2}
2.0	1.21548	25.26098	126.67011	1.29×10^{-1}
5.0	1.51536	29.02782	141.41117	1.87×10^{0}
10.0	1.92027	33.53551	159.57993	2.31×10^{1}

[a] n – Kinetic exponent; ln A – logarithm of pre-exponential factor; and E – activation energy (kJ mol^{-1}).
[b] Theoretical parameters: $n_1 = 1.2$ and $n_2 = 1$; $E_1 = 143$ and $E_2 = 74$ kJmol^{-1}; $\ln A_1 = 29.4$ and $\ln A_2 = 11.7$.
[c] LSM – fit of the calculated curve with the simulated one (cf. [1] or [2]).

best linearization of the Arrhenius plot (correlation coefficient nearest to one).

For the interval 10–90%, the best linearization of the Arrhenius plot is obtained for $n = 1.5$ (using a step of 0.1 for n), with a correlation coefficient close to one ($r = -0.9997938$), but Fig. 4a does not show the existence of two phenomena. On the other hand, if the kinetic interval is extended to 1–99%, Fig. 4b clearly shows the existence of several mechanisms, but an unexpected high correlation coefficient value ($r = -0.9991936$) is also observed for the best linearization (for n = 1.4). When a lower heating rate is used (0.1 K min^{-1}), the computation for the beginning and end of the peak, gives parameters nearest to the parameters of each phenomenon (1–30%: $E = 71.58$ kJmol^{-1}, $\ln A = 9.71$, $n = 1$; 70–99%: $E = 141.27$kJmol^{-1}, $\ln A = 29.03$, $n = 1.2$).

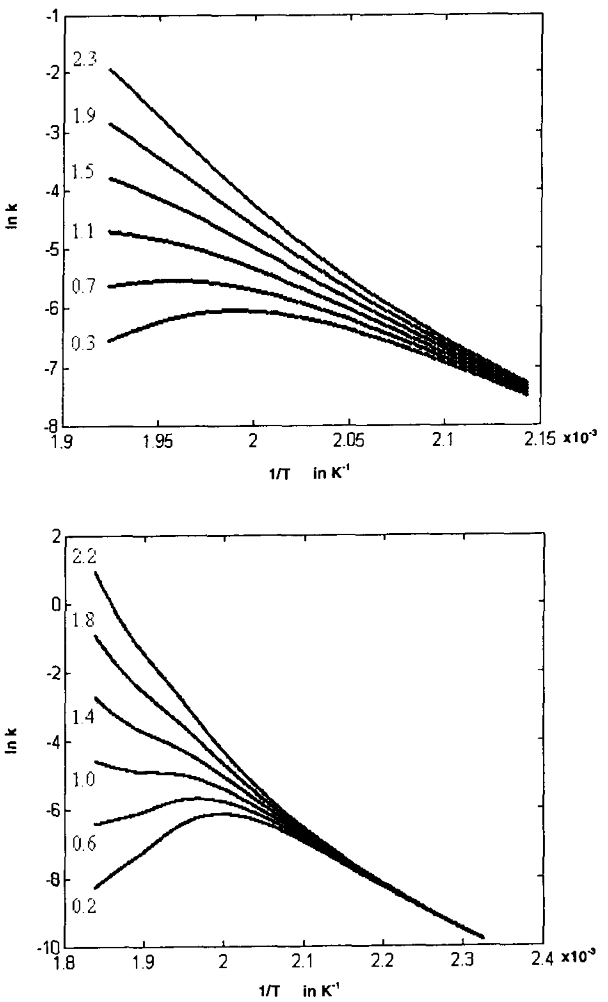

Fig. 4. (a) Arrhenius plots obtained with the Achar–Brindley–Sharp method on the kinetic interval 10–90%, best linearization for $n = 1.5$ (using a step of 0.1 for n), heating rate 5 K min^{-1}.(b) Arrhenius plots obtained with the Achar–Brindley–Sharp method on the kinetic interval 1–99%, best linearization for $n = 1.4$ (using a step of 0.1 for n), heating rate 5 K min^{-1}.

4.3. The Malek method

The Malek method indicates a reaction order model (plot of f(α) vs. α). It is interesting to note that the reaction-order and the Sestak–Berggren models (with $m = 0$) lead here to very different values (Table 8), while this was not the case with a real single reaction-order mechanism. The complexity of the mechanism can only be deduced from the variation of the kinetic order n, in the reaction-order models, but no additional information on the mechanism can be obtained. Only the differences between the results obtained with the reaction-order and the Sestak-Berggren models, supported by different hypotheses, should indicate that a more complex phenomenon is involved. The Sestak–Berggren model (with $m \neq 0$), also led to approximately constant values for the pre-exponential factor and various values of the kinetic exponents m and n. In such a case, the Sestak–Berggren model can be used only for modelling purposes.

Table 8

Kinetic parameters for simulated noiseless data for a complex process of two parallel reactions, using the reaction order (RO1) and (RO2) and the Sestak–Berggren (SB) models of the Malek method (10–90%)

V/(K/min)	Malek RO1		Malek RO2		Malek SB	
	n^a	ln A^a	n^a	ln A^a	n^a	ln A^a
0.1	0.76	27.51	0.76	27.51	1.65	27.70
0.3	0.90	27.57	0.91	27.57	1.41	27.63
0.5	0.96	27.56	0.96	27.56	1.34	27.60
1.0	1.04	27.54	1.04	27.54	1.30	27.55
2.0	1.14	27.51	1.15	27.51	1.32	27.53
5.0	1.33	27.50	1.34	27.50	1.45	27.51
10.0	1.49	27.50	1.50	27.51	1.65	27.52

[a] See footnotes of Table 7, E (Kissinger) =135.57 kJmol.$^{-1}$

4.4. Analysis of the entire information of the peak

The complexity of the process can only be understood when using the isoconversional methods previously presented, or the approach developed by Vyazovkin [26,27]. Fig. 5 shows the dependence of the activation energy upon conversion, obtained using these methods, for the lowest heating rates studied. It is interesting to note that even for ideal simulated data and also with the simulated single-step process, we can observe a difference between the Friedman and other isoconversional methods. This could be explained for the Ozawa and Kissinger–Akahira–Sunose methods, because the reduced activation energy (x) is between 18 and 27, at 0.1 K min^{-1}. Nevertheless, the application of Flynn's correction led to similar results ($E = 121.44$ *kJmol*$^{-1}$, at

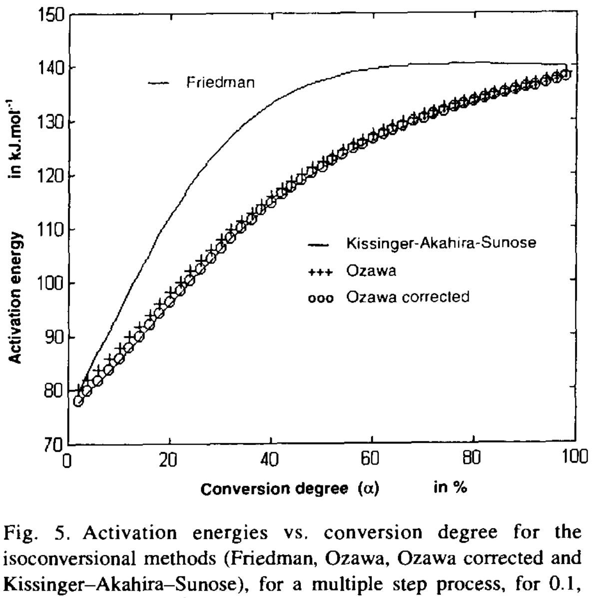

Fig. 5. Activation energies vs. conversion degree for the isoconversional methods (Friedman, Ozawa, Ozawa corrected and Kissinger–Akahira–Sunose), for a multiple step process, for 0.1, 0.3 and 0.5 K min^{-1}.

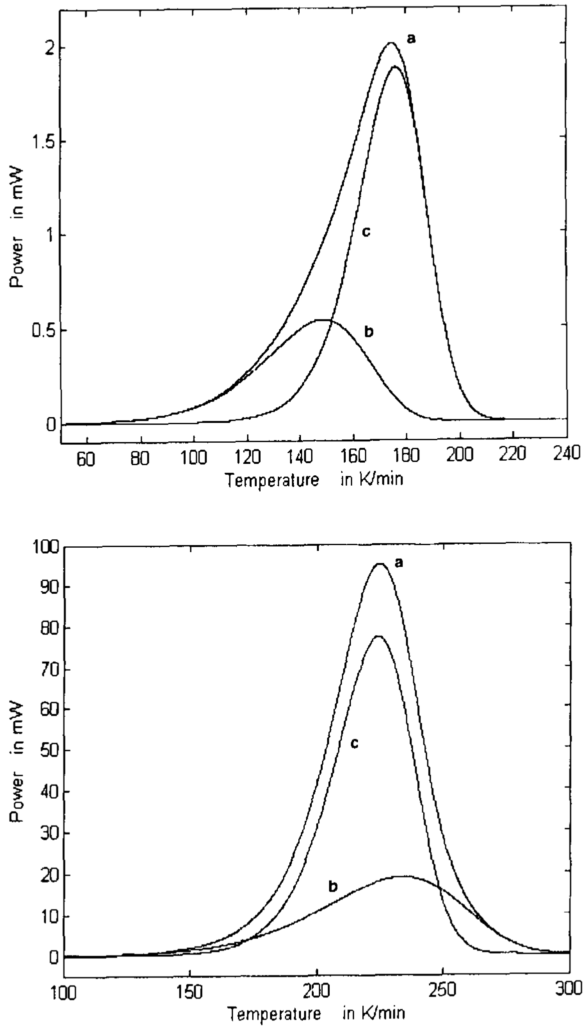

Fig. 6. (a) Thermoanalytical curves of a multiple step process at 0.1 K min^{-1} (a - whole phenomenon b+c, b: $Q_2 = -16.2$ J, $n_2 = 1$, E_2 =74 kJ mol^{-1}, ln A_2 = 11.7; c: $Q_1 = -37.8$ J, $n_1 = 1.2$, E_1 =143 kJmol^{-1}, ln A_1 = 29.4).(b) Thermoanalytical curves of a multiple step process at 5 K min^{-1} (a: whole phenomenon b+c, b: $Q_2 = -16.2$ J, $n_2 = 1$, E_2 =74 kJmol−1 , ln A_2 = 11.7; c: $Q_1 = -37.8$ J, $n_1 = 1.2$, E_1 =143 kJmol^{-1}, ln A_1 = 29.4).

$\alpha = 50\%$), to those found with the proposed correction (Ozawa corrected, Fig. 5), although these last corrections depend on the value of the reduced activation energy.

Furthermore, the extreme values obtained for the activation energy are a good estimate of the values of each phenomenon itself (79.29 and 140.05 kJmol^{-1}, respectively, at $\alpha = 2$ and 98%, with the Friedman method). The separation of the two parallel reactions, evident at the beginning and end of the peak, is only possible if low heating rates are used (Fig. 6(a) and (b)). In such a case, the choice of the heating rate should be make in regard to the degree of overlapping of the two phenomena. In the same way, the concentration ratio of each reactant should be changed for a better separation of the two peaks. As an example, if the concentration of the first reactant is decreased, the corresponding surface of the peak (Fig. 6a, curve b) will be decreased.

5. Conclusion

The fundamental equations of the peak maximum evolution methods (Ozawa and Kissinger) and of the isoconversional methods (Ozawa, Kissinger–Akahira–Sunose and Friedman) have been reviewed, and the use of approximations reported on. The interest of the comparison of the results given by various mathematical treatments based on different hypotheses has been shown. The importance of the conversion degree constancy has been pointed out and our computer code has been optimised using an interpolation on the power and/or on the temperature.

A new method has been proposed for the correction of the Ozawa method. This, and the Friedman method have led to the most accurate results. Using DSC data, the Friedman method can be applied directly, without using approximations and without differentiation of the signal, and gives extremely accurate results. All these methods were stable when a small amount of noise was added on the power.

The Senum and Yang, and Gorbatchev approximations for $p(x)$ were tested without and with Gaussian noise, for the reaction-order model of the Malek method. They provide similar accuracy for the determination of the kinetic parameters. The Sestak–Berggren model of the Malek method can be used for a reaction-order model, if m is set to zero, so that no approximations are needed. Furthermore, a reliable value of the activation energy is essential for the accuracy of the other kinetic parameters.

To show the interest of isoconversional methods, a simple complex mechanism was studied over the entire interval of the reaction. Other complex mechanisms will be studied later. The analysis of the Arrhenius plots of the Achar–Brindley–Sharp method can be used to indicate the existence of several phenomena, and clearly shows the necessity of studying the reaction over the entire interval of temperature (except in the quasi-hypothetic case of a single-step mechanism). This study confirms the value of isoconversional methods for the analysis of the dependence of the activation energy upon conversion for the study of complex mechanisms. Indeed, the peak maximum evolution methods have given only a mean value of the activation energy, while the Malek method has indicated a simple reaction-order model.

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